Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

SUPPORTING INFORMATION

Ag(I) and Cu(I) cyclic-triimidazole coordination polymers: revealing different deactivation channels for multiple room temperature phosphorescences

Daniele Malpicci,[a] Elena Lucenti,[b] Alessandra Forni,[*b] Daniele Marinotto,[b] Andrea Previtali,[ab] Lucia Carlucci,[a] Pierluigi Mercandelli,[a] Chiara Botta,[c] Stefania Righetto[a] and Elena Cariati*[ab]

[a] *Department of Chemistry, Università degli Studi di Milano and INSTM RU, via Golgi 19, 20133 Milano, Italy.* [b] *Institute of Sciences and Chemical Technologies "Giulio Natta" (SCITEC) of CNR, via Golgi 19, 20133 Milano, Italy.* [c] *Institute of Sciences and Chemical Technologies "Giulio Natta" (SCITEC) of CNR, via Corti 12, 20133 Milano, Italy.*

Table of Contents

1. Experimental details

1.1 General information

All reagents and solvents were purchased from chemical suppliers and used without further purification unless otherwise stated. Triimidazo[1,2-*a*:1',2'-*c*:1'',2''-*e*][1,3,5]triazine (**TT**) [S1], $[Cu(TT)I]_n$ (**1-Cu**) [S2], **TTI** and **TTCo** [S3] have been prepared according to literature procedures.

UV-Visible spectra were collected by a Shimadzu UV3600 spectrophotometer. Absolute photoluminescence quantum yields were measured using a C11347 (Hamamatsu Photonics K.K). Steady state emission and excitation spectra and photoluminescence lifetimes were obtained using both a FLS 980 (Edinburg Instrument Ltd) and a Nanolog (Horiba Scientific) spectrofluorimeter composed of a iH320 spectrograph equipped with a Synapse QExtra charge-coupled device. The steady state measurements were recorded by excitation with a monochromated 450 W Xenon arc lamp and the spectra are corrected for the instrument response. Phosphorescence spectra are obtained with a PPD-850 single photon detector module with time-gated separation by exciting with a pulsed Xe lamp. Photoluminescence lifetime measurements were performed using: Edinburgh Picosecond Pulsed Diode Laser EPL-375, EPLED-300, (Edinburg Instrument Ltd) and microsecond flash Xe-lamp (60W, 0.1÷100 Hz) with data acquisition devices time correlated single-photon counting (TCSPC) and multi-channel scaling (MCS) methods, respectively. Nanolog TCSPC measurements were performed using DeltaTime series DD-300 DeltaDiode and a DD-405L DeltaDiode Laser, with a PPD-850 single photon detector module and are analysed with the instrument software DAS6. Average lifetimes are obtained as $\tau_{av} = \sum \frac{A_i \tau_i^2}{A_i \tau_i}$ from bi-exponential or three-exponential fits. Low temperature measurements are performed in a quartz dewar by immersion of the sample in liquid nitrogen or with a variable temperature liquid nitrogen cryostat Oxford DN1704.

Elemental analyses were carried out at the Microanalytical Laboratory of the University of Milan with a PerkinElmer 2400 instrument.

Solvothermal syntheses were performed in a sealed 20 mL Teflon-lined reactor, heated (5 °C/min rate) in an oven at 120 °C for 36 h and slowly (0.1 °C/min rate) cooled to 35 °C.

1.2 Synthesis of 1D $[Ag(TT)I]_n$ (1-Ag)

AgI (55 mg, 0.234 mmol) is added to a solution of N,N-dimethylformamide (DMF, 5 mL) and KI (20 mg, 0.4 wt%) at 25 °C in the dark. After 15 minutes the resulting transparent solution is transferred into a vial. **TT** (47 mg, 0.238 mmol) dissolved in acetonitrile (CH_3CN, 3 mL) is added to this solution. The vial is kept closed at 25 °C in the dark producing after few days a white powder which is filtered and dried over filter paper.

Alternatively, **TT** (11 mg, 0.056 mmol) dissolved in CH_3CN (2 mL) is added to a vial containing 4 mL of a saturated aqueous solution of AgI in KI. The vial is kept closed at 25 °C in the dark producing after few days needle-shaped crystals suitable for X-ray diffraction analysis.

Anal. Calcd. for $C_9H_6AgIN_6$ (%): C, 25.03; H, 1.17; N, 19.46. Found: C, 25.39; H, 1.29; N, 19.63.

1.3 Synthesis of 3D $[Ag(TT)Cl]_n$ (2-Ag)

In a Teflon beaker, solid AgCl (14 mg, 0.098 mmol) and **TT** (21 mg, 0.106 mmol) are suspended in a CH_3CN/DMF (3 mL/1 mL) solution. The reaction is heated under solvothermal conditions according to the ramp described in the General Information section. An unknown yellow solid is filtered from the reaction mixture. The resulting yellow solution is left for crystallization at 25 °C. Colorless crystals of **2-Ag** start to appear after few weeks.

1.4 Synthesis of 3D $[Ag_3(TT)_4]_n(NO_3)_{3n}\cdot 6nH_2O$ (3-Ag)

A solution of $AgNO_3$ (17 mg, 0.100 mmol) in ethanol (EtOH, 20 mL) is added to a beaker containing **TT** (20 mg, 0.101 mmol) dissolved in dichloromethane (CH_2Cl_2, 20 mL). The resulting mixture is stirred 16 h at 25 °C in the dark to give a white precipitate which is filtered and characterized as $[Ag_3(TT)_4]_n(NO_3)_{3n}\cdot 6nH_2O$ (**3-Ag**) by X-ray powder diffraction (XRPD) and elemental analysis. Slow evaporation of the clear solution left at 25 °C in the dark afforded after few weeks colorless crystals of **3-Ag** suitable for single crystal X-ray diffraction analysis.

The same crystalline product can be obtained in a vial by slow diffusion of $AgNO_3$ (9.3 mg, 0.055 mmol) dissolved in ethanol (EtOH, 10 mL) into a dichloromethane solution (CH_2Cl_2, 10 mL) of **TT** (10 mg, 0.051 mmol). The vial is kept closed at 25 °C in the dark.

Anal. Calcd. for $C_{37}H_{39}Ag_3N_{27}O_{15}$ (%): C, 31.18; H, 2.76; N, 26.53. Found: C, 30.71; H, 2.87; N, 25.86.

1.5 Crystal Structure Analysis

Single-crystal X-ray diffraction data for the coordination networks **1-Ag**–**3-Ag** were collected at 150 K on a Bruker APEX II CCD area detector diffractometer, using graphite-monochromated Mo *K*α radiation (λ = 0.71073 Å). A full sphere of reciprocal space was scanned by 0.5° ω steps, collecting 2160 frames in six different regions of the reciprocal space. After

integration, an empirical absorption correction was made on the basis of the symmetry-equivalent reflection intensities measured [S4].

The structures were solved by direct methods (SIR 2014 [S5]) and subsequent Fourier synthesis; they were refined by full-matrix least-squares on F^2 (SHELX 2014 [S6]) using all reflections. Weights were assigned to individual observations according to the formula $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$; a and b were chosen to give a flat analysis of variance in terms of F_o^2. Anisotropic parameters were assigned to all non-hydrogen atoms. All the hydrogen atoms were clearly visible in difference-Fourier maps (except those of the disordered water molecules in **3-Ag**); however, they were eventually placed in idealized position and refined riding on their parent atom with an isotropic displacement parameter 1.2 times that of the pertinent parent atom.

In the structure of **3-Ag** the nitrate anion is disordered over the Wyckoff position 16*c* (site symmetry 3). One of the oxygen atoms lies on the threefold axis while the nitrogen atom and the other independent oxygen atom lay outside the axis, generating three images of the anion equally occupied. The overall site occupancy of the nitrate anion has been fixed in order to grant the electroneutrality of the structure. In the same structure, the oxygen atom of the water molecule shows a markedly prolate atomic displacement ellipsoid because of the large volume (32 Å^3) of the cavity occupied. Any attempt to refine the water molecule as disordered over more than one position leads only to negligible improvements on the *R* factors at the expense of a significant increase of the number of refined parameters, and has been therefore discarded. The water content is in agreement with the results of elemental and thermogravimetric analyses.

The final difference electron density map showed no features of chemical significance, with the largest peaks lying close to the silver atoms.

Crystal data, data collection and refinement details of the structural analyses are summarized in Table S1, while a selection of geometric parameters for the three coordination networks are collected in Tables S2–S4. CCDC 2041933–2041935 contain the supplementary crystallographic data for **1-Ag**–**3-Ag**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

1.6 Computational details

Computational studies have been performed on discrete models of the **1÷3-Ag** coordination polymers and the Cu analogues **1-Cu** and **2-Cu** by using the Gaussian 16 suite of programs [S7]. The geometries of the 1-M and 2-M (M = Ag, Cu) model compounds have been optimized with proper constraints (see below) at the ωB97X/def2-TZVP and ωB97X/6-311++G(d,p) levels of theory for the Ag and the Cu compounds, respectively, starting from the X-ray fragments extracted from the respective crystal structures. The def2-TZVP basis set [S8] and the all-electron basis set for iodine were downloaded from the Basis Set Exchange site [S9], with the exponents of the s and p diffuse functions taken from the literature [S10]. The ωB97X functional [S11] has been chosen in view of its optimal performance in treating the geometrical and electronic features of **TT** derivatives [S12], including π-π interactions that play an important role in the photophysics of the present structures. In particular, it was previously verified [S12a] that other largely used functionals such as PBE0 are not able to provide stable π-π stacked dimeric units of **TT**. On the other side, geometry optimization of **3-Ag** (lacking π-π interactions in its crystal structure) was performed by adopting the PBE0 functional owing to the strong tendency of the four **TT** units of the complex to collapse into dimeric pairs during optimization if the ωB97X functional is used. The same def2-TZVP basis set as adopted for **1-Ag** and **2-Ag** has been chosen. TDDFT calculations were performed for all compounds at the ωB97X/def2-TZVP (Ag) and ωB97X/6-311++G(d,p) (Cu) levels of theory. QTAIM analysis has been performed by the AIMAll program [S13]

2. Crystal structures

Table S1. Crystal data, data collection and refinement details for the silver coordination networks **1-Ag**, **2-Ag**, and **3-Ag**.

	[Ag(TT)I]$_n$ (**1-Ag**)	[Ag(TT)Cl]$_n$ (**2-Ag**)	[Ag$_3$(TT)$_4$]$_n$(NO$_3$)$_{3n}$·6nH$_2$O (**3-Ag**)
Crystal data			
Chemical formula	$C_9H_6AgIN_6$	$C_9H_6AgClN_6$	$C_{36}H_{24}Ag_3N_{24}(NO_3)_3\cdot 6H_2O$ = $C_{36}H_{36}Ag_3N_{27}O_{15}$
M_r	432.97	341.52	1410.53
Crystal system	monoclinic	cubic	cubic
Space group	$P2_1/c$ (No. 14)	$Pa\bar{3}$ (No. 205)	$I\bar{4}3d$ (No. 220)
Temperature [K]	150(2)	150(2)	150(2)
a [Å]	13.858(2)	12.7192(4)	17.2491(7)
b [Å]	4.7312(7)	12.7192(4)	17.2491(7)
c [Å]	17.303(3)	12.7192(4)	17.2491(7)
α [°]	90	90	90
β [°]	105.388(2)	90	90
γ [°]	90	90	90
V [Å^3]	1093.8(3)	2057.69(19)	5132.2(6)
Z	4	8	4
μ(MoKα) [mm^{-1}]	4.650	2.202	1.226
Crystal size [mm]	0.305 × 0.045 × 0.030	0.125 × 0.125 × 0.070	0.200 × 0.200 × 0.160
Data collection			
T_{min}, T_{max}	0.331, 0.934	0.804, 0.857	0.742, 0.828
No. of measured reflections	12349	48142	36683
No. of independent reflections	3516	1220	1422
No. of observed reflections [$I > 2\sigma(I)$]	2515	1118	1361
R_{int}	0.0478	0.0215	0.0625
R_σ	0.0456	0.0056	0.0205
$(\sin\theta/\lambda)_{max}$ [Å^{-1}]	0.743	0.752	0.737
Refinement			
$R[F^2 > 2\sigma(F^2)]$	0.0343	0.0160	0.0326
$wR(F^2)$	0.0692	0.0435	0.0822
S	0.962	1.053	1.319
No. of reflections	3516	1220	1422
No. of parameters	154	52	75
No. of restraints	0	0	5
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.145, –1.211	0.488, –0.428	0.517, –0.342

Table S2. Bond distances [Å] and angles [°] for the coordination network $[Ag(TT)I]_n$ (**1-Ag**)

Ag1–N1	2.319(3)	N1–Ag1–I1	123.34(10)	C4–C5–N4	105.1(3)
Ag1–I1	2.8084(5)	N1–Ag1–I1^{i}	102.71(7)	N5–C6–N6	113.6(3)
Ag1–I1^{i}	2.8682(5)	N1–Ag1–I1^{ii}	94.77(7)	N5–C6–N4	128.9(3)
Ag1–I1^{ii}	2.9221(5)	N1–Ag1···Ag1^{i}	132.62(7)	N6–C6–N4	117.5(3)
Ag1···Ag1^{i}	3.1591(5)	N1–Ag1···Ag1^{ii}	123.67(7)	C8–C7–N5	112.3(3)
C1–C2	1.354(5)	I1–Ag1–I1^{i}	113.568(12)	C7–C8–N6	105.2(3)
C1–N1	1.400(4)	I1–Ag1–I1^{ii}	111.927(12)	N1–C9–N2	112.8(3)
C2–N2	1.391(4)	I1^{i}–Ag1–I1^{ii}	109.584(16)	N1–C9–N6	129.9(3)
C3–N3	1.299(4)	Ag1^{i}···Ag1···Ag1^{ii}	96.975(18)	N2–C9–N6	117.3(3)
C3–N4	1.371(4)	Ag1^{i}···Ag1–I1	58.284(13)	C9–N1–C1	104.1(3)
C3–N2	1.391(4)	Ag1^{i}···Ag1–I1^{i}	55.288(10)	C9–N1–Ag1	135.1(2)
C4–C5	1.353(5)	Ag1^{i}···Ag1–I1^{ii}	130.801(16)	C1–N1–Ag1	119.4(2)
C4–N3	1.393(5)	Ag1^{ii}···Ag1–I1	57.090(13)	C9–N2–C3	123.3(3)
C5–N4	1.389(4)	Ag1^{ii}···Ag1–I1^{i}	130.428(16)	C9–N2–C2	106.6(3)
C6–N5	1.297(4)	Ag1^{ii}···Ag1–I1^{ii}	54.840(11)	C3–N2–C2	130.0(3)
C6–N6	1.374(4)	Ag1–I1–Ag1^{ii}	67.621(9)	C3–N3–C4	103.1(3)
C6–N4	1.382(4)	Ag1–I1–Ag1^{i}	66.875(9)	C3–N4–C6	123.1(3)
C7–C8	1.344(5)	Ag1^{ii}–I1–Ag1^{i}	109.584(16)	C3–N4–C5	105.5(3)
C7–N5	1.386(4)	C2–C1–N1	111.5(3)	C6–N4–C5	131.3(3)
C8–N6	1.392(4)	C1–C2–N2	105.0(3)	C6–N5–C7	103.6(3)
C9–N1	1.305(4)	N3–C3–N4	114.1(3)	C9–N6–C6	122.3(3)
C9–N2	1.368(4)	N3–C3–N2	129.4(3)	C6–N6–C8	105.3(3)
C9–N6	1.384(4)	N4–C3–N2	116.4(3)	C9–N6–C8	132.3(3)
		C5–C4–N3	112.2(3)		

Superscripts i–ii indicate atoms generated by the following symmetry operations: (i) *–x*, *y* + ½, *–z* + ½ and (ii) *–x*, *y* – ½, *–z* + ½.

Table S3. Bond distances [Å] and angles [°] for the silver coordination network [Ag(TT)Cl]n (**2-Ag**)

Ag1–N1	2.3544(10)	N1–Ag1–Cl1	117.31(2)	C2–N2–C3^{ii}	131.01(10)
Ag1–Cl1	2.4562(5)	N1–Ag1–N1^{i}	100.62(3)	C3–N2–C3^{ii}	122.25(10)
N1–C1	1.3956(15)	Ag1–N1–C1	119.43(7)	N1–C3–N2	112.95(10)
N1–C3	1.3035(14)	Ag1–N1–C3	134.03(8)	N1–C3–N2^{iii}	129.47(10)
C1–C2	1.3596(16)	C1–N1–C3	104.17(9)	N2–C3–N2^{iii}	117.56(10)
C2–N2	1.3930(14)	N1–C1–C2	111.54(10)		
N2–C3	1.3700(13)	C1–C2–N2	104.83(10)		
N2–C3^{ii}	1.3833(13)	C2–N2–C3	106.51(9)		

Superscripts i–iii indicate atoms generated by the following symmetry operations: (i) *z*, *x*, *y*; (ii) *–y* + 1, *z* + ½, *–x* + ½ and (iii) *z* – ½, *–x* + 1, *y* – ½.

Table S4. Bond distances [Å] and angles [°] for the coordination network $[Ag_3(TT)_4]_n(NO_3)_{3n}\cdot 6nH_2O$ (**3-Ag**)

Ag1–N1	2.308(4)	N1–Ag1–N1^{i}	124.7(2)	C2–N2–C3	106.2(4)
N1–C1	1.386(6)	N1–Ag1–N1^{ii}	102.45(9)	C2–N2–C3^{iii}	131.7(4)
N1–C3	1.304(6)	Ag1–N1–C1	119.2(3)	C3–N2–C3^{iii}	122.1(4)
C1–C2	1.358(7)	Ag1–N1–C3	134.3(3)	N1–C3–N2	112.3(4)
C2–N2	1.394(6)	C1–N1–C3	105.3(4)	N1–C3–N2^{iv}	129.7(4)
N2–C3	1.370(5)	N1–C1–C2	110.7(4)	N2–C3–N2^{iv}	117.9(4)
N2–C3^{iii}	1.373(5)	C1–C2–N2	105.5(4)		

Superscripts i–iv indicate atoms generated by the following symmetry operations: (i) $-x + 1, -y + ½, z$; (ii) $y + ¼, -x + ¾, -z + ¼$; (iii) $-y + 1, z + ½, -x + ½$ and (iv) $-z + ½, -x, y - ½$.

3. Photophysical Studies

3.1 1D Coordination Polymer $[Ag(TT)I]_n$ (1-Ag)

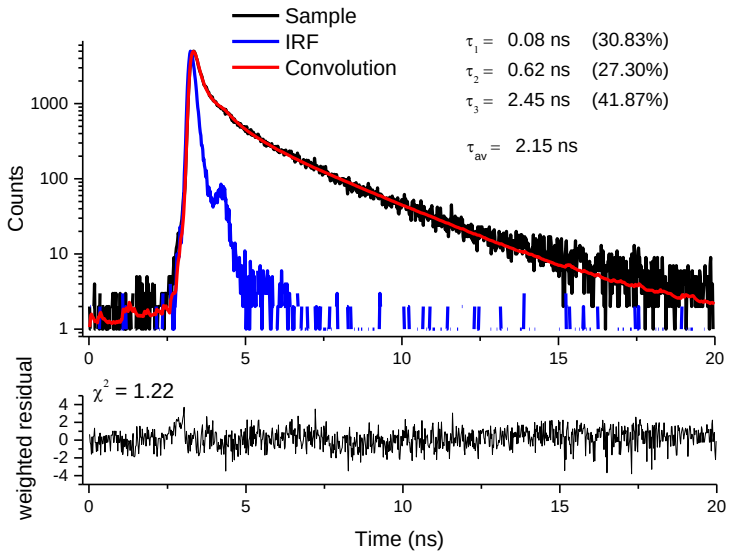


Figure S1. Lifetime measurement (λ_{exc}=374nm , λ_{em}=400 nm) of **1-Ag** at 298 K. τ_{av} = 2.15 ns

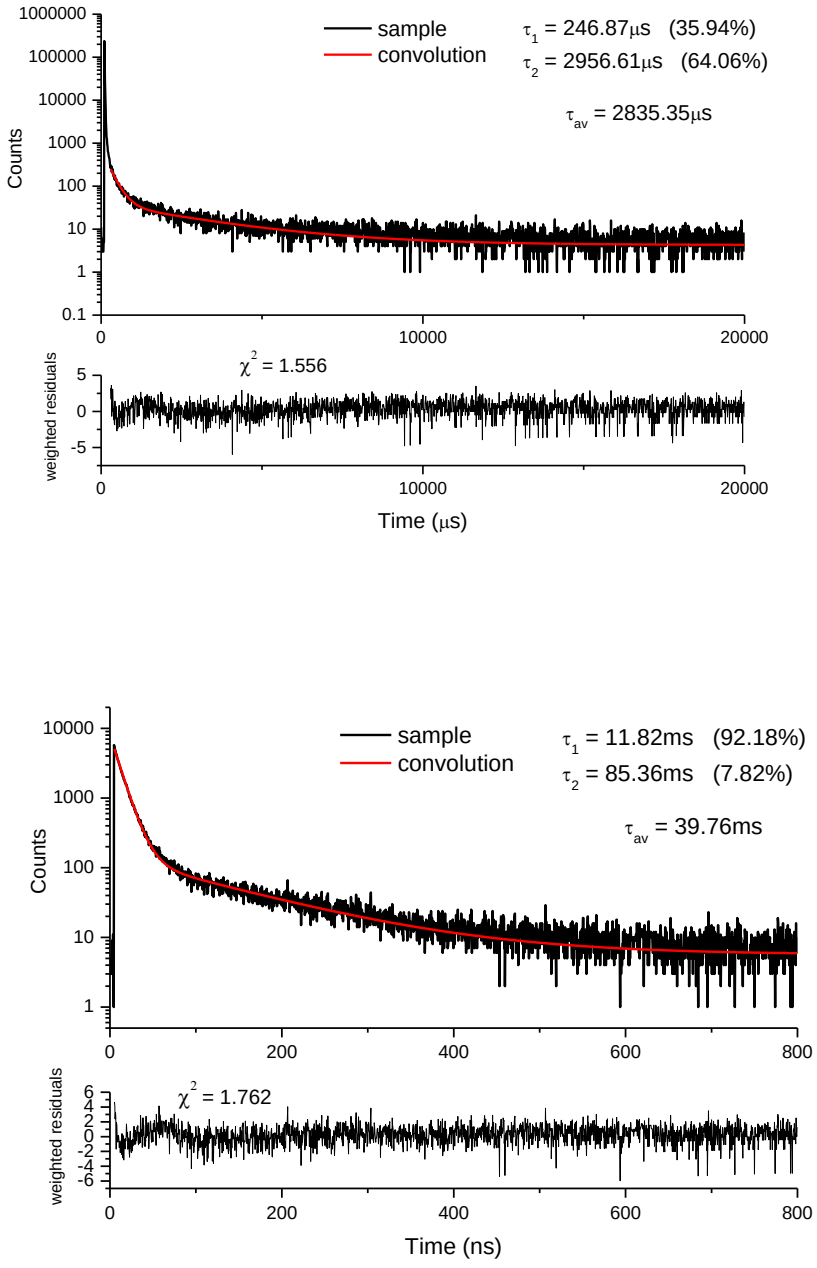


Figure S2. Lifetime measurement of **1-Ag** at 298 K. Upper panel: λ_{exc}=374nm, λ_{em}=449nm, τ_{av} = 2835.35 μs. Lower panel: λ_{exc}=374nm, λ_{em}=530nm, τ_{av} = 39.76 ms

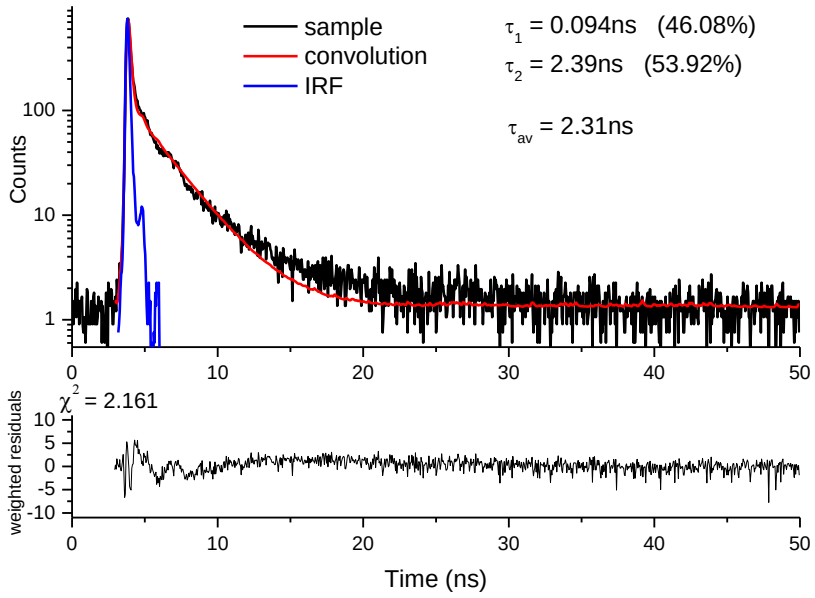


Figure S3. Lifetime measurement (λ_{exc}=374nm, λ_{em}=424nm) of **1-Ag** at 77 K. τ_{av} = 2.31 ns.

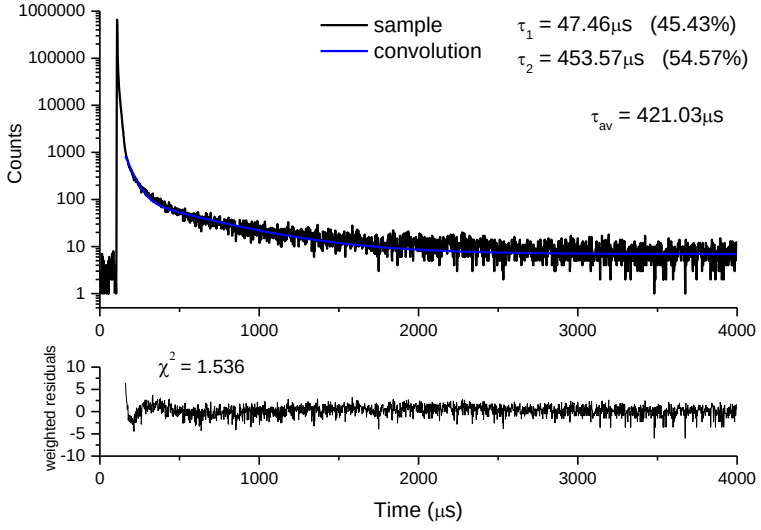


Figure S4. Lifetime measurement (λ_{exc}=374nm, λ_{em}=449nm) of **1-Ag** at 77 K. τ_{av} = 421.03 μs.

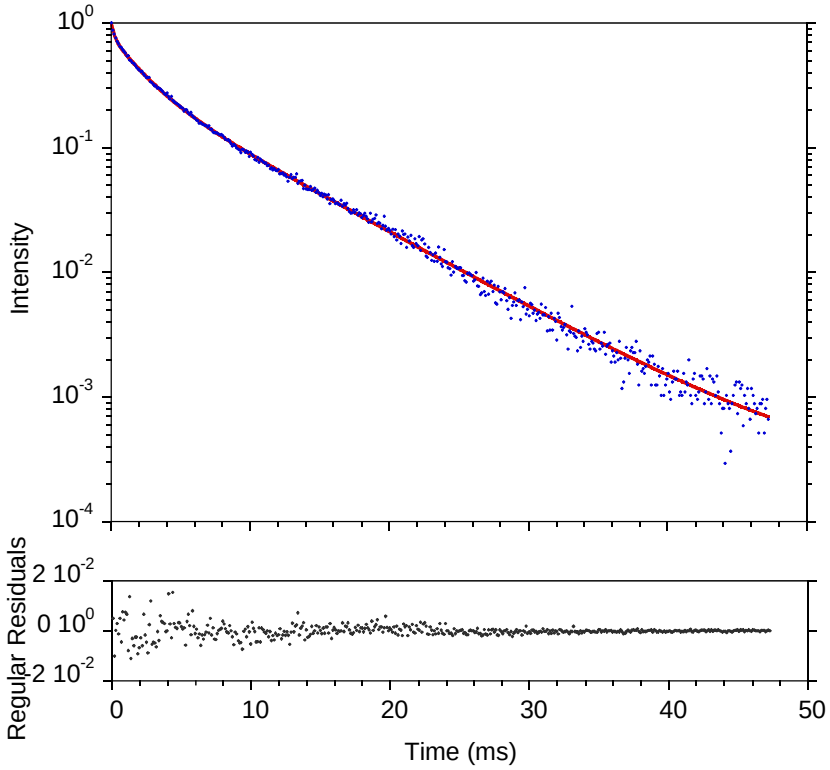


Figure S5. Lifetime measurement (λ_{exc} = 360nm, λ_{em}= 449nm) of **1-Ag** at 77 K. τ_{av} =5.67ms; τ_1 = 7.13 ms (A_1 = 32.52%); τ_2 = 2.08 ms (A_2 = 41.10%); τ_3 = 0.21 ms (A_3 = 26.37%); Adj. R-Square 0.99967

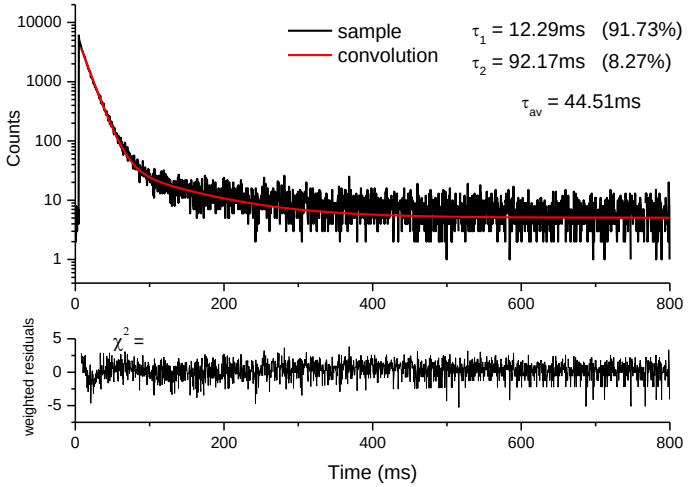


Figure S6. Lifetime measurement (λ_{exc}=374nm, λ_{em}=530nm) of **1-Ag** at 77 K. τ_{av} = 44.51 ms.

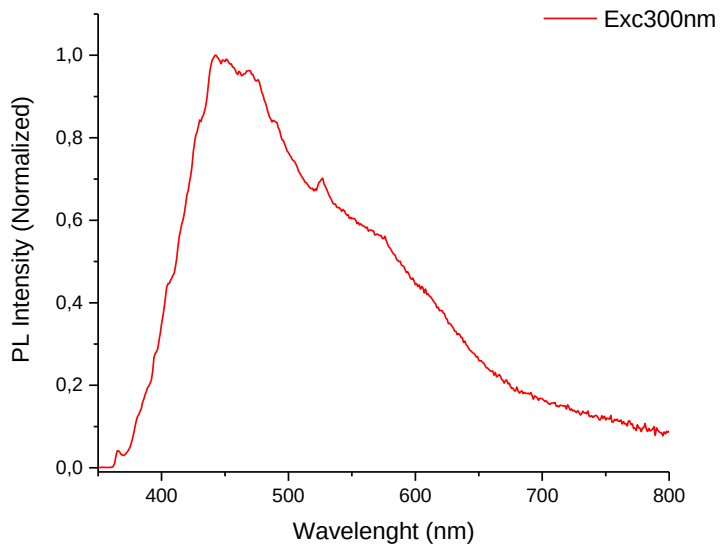


Figure S7. Normalized emission spectrum of **1-Ag** at 77 K, λ_{exc}=300nm

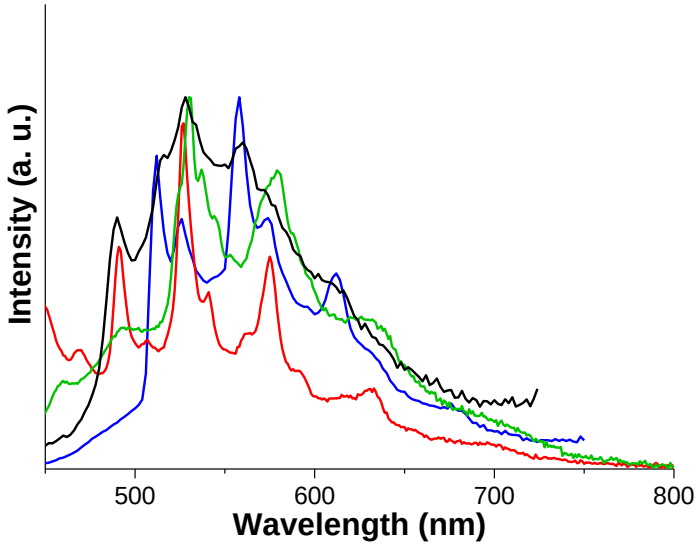


Figure S8. Comparison of the normalized emission band associated with **TT** organization in H-aggregates in crystals of **1-Ag** (red line); **1-Cu** (green line); **TTI** (blue line) and **TTCo** (black line).

3.2 1D Coordination Polymer $[Cu(TT)I]_n$ (1-Cu)

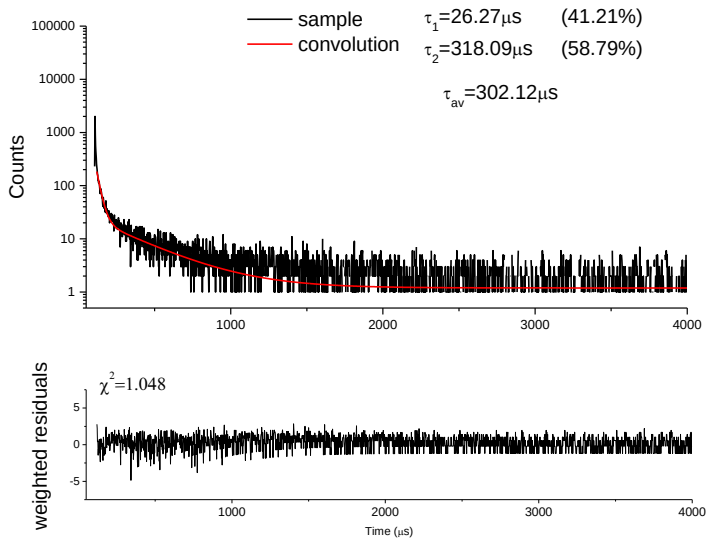


Figure S9. Lifetime measurement (λ_{exc}=390nm, λ_{em}=530nm) of **1-Cu** at 298 K. τ_{av} = 302.12 μs

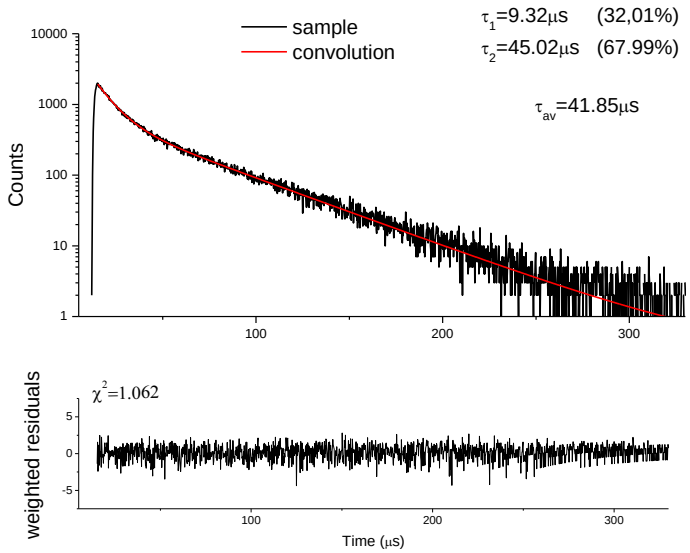


Figure S10. Lifetime measurement (λ_{exc}=300nm, λ_{em}=550nm) of **1-Cu** at 77 K. τ_{av} = 41.85 μs

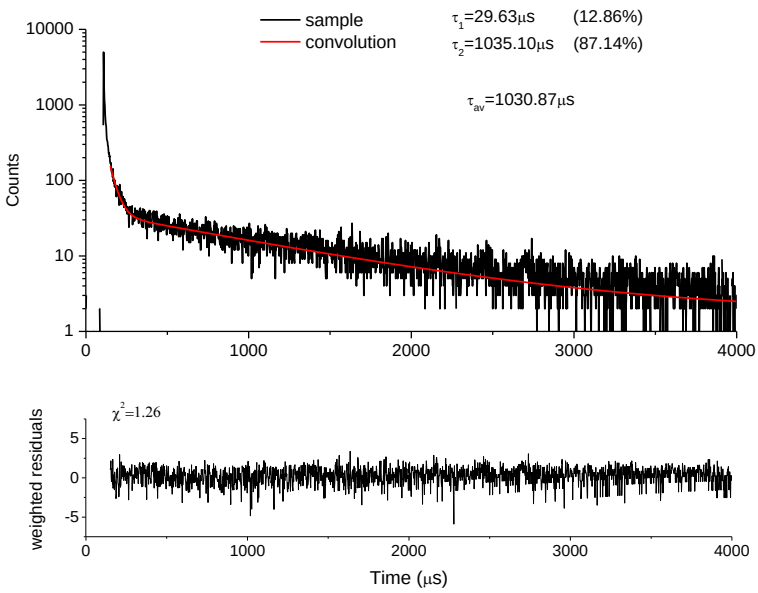


Figure S11. Lifetime measurement (λ_{exc}=390nm, λ_{em}=530nm) of **1-Cu** at 77 K. τ_{av} = 1030.87 μs

3.3. 3D Coordination Polymer [Ag(TT)Cl]$_n$ (2-Ag)

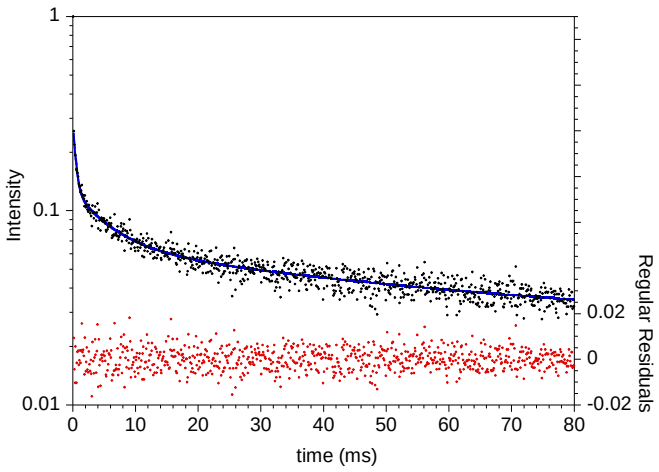


Figure S12. Phosphorescence decays of **2-Ag** (λ_{exc}=360nm; λ_{em}=565nm, black points) at room temperature. Three exponential fit (solid line): τ_{av}=47.7ms (0.47104ms (0.62), 5.55881 ms (0.23), 55.648ms (0.15), Adj. R-Square 0.95313).

3.4. 3D Coordination Polymer [Cu(TT)Cl]$_n$ (2-Cu)

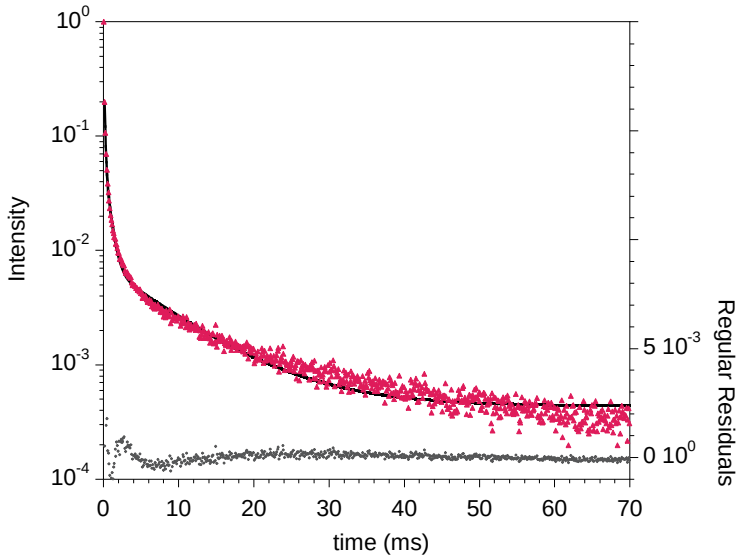


Figure S13. Phosphorescence decays of **2-Cu** (λ_{exc}=360nm; λ_{em}=570nm, red triangles) at room temperature. Three exponential fit (solid line): τ_{av}=3.56ms (0.11482ms (0.89), 0.67398 ms (0.10), 8.9524ms (0.01), Adj. R-Square 0.99933).

3.5 3D Coordination Polymer $[Ag_3(TT)_4]_n(NO_3)_{3n}\cdot 6nH_2O$ (3-Ag)

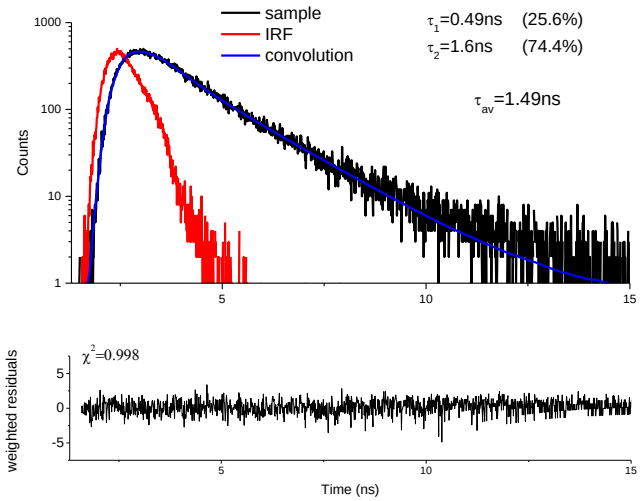


Figure S14. Lifetime measurement (λ_{exc}=300nm, λ_{em}=410nm) of **3-Ag** at 298 K. τ_{av} = 1.49 ns.

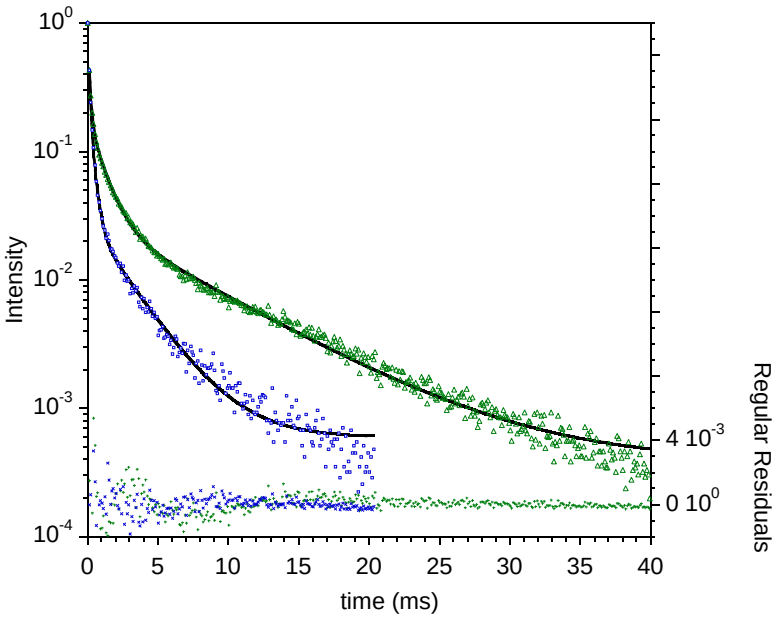


Figure S15. Phosphorescence decays of **3-Ag** (λ_{exc}=300nm; λ_{em}=520nm, green points; λ_{em}=620nm, blue points) at room temperature. Three exponential fits (solid lines): λ_{em}=520nm, τ_{av}=3.41ms (0.1322ms (0.81), 1.022 ms (0.16), 7.029ms (0.03), Adj. R-Square 0.99954). λ_{em}=620nm, τ_{av}=1.04ms (2.648ms (0.03), 0.10686 ms (0.72), 0.32194ms (0.25) Adj. R-Square 0,99971).

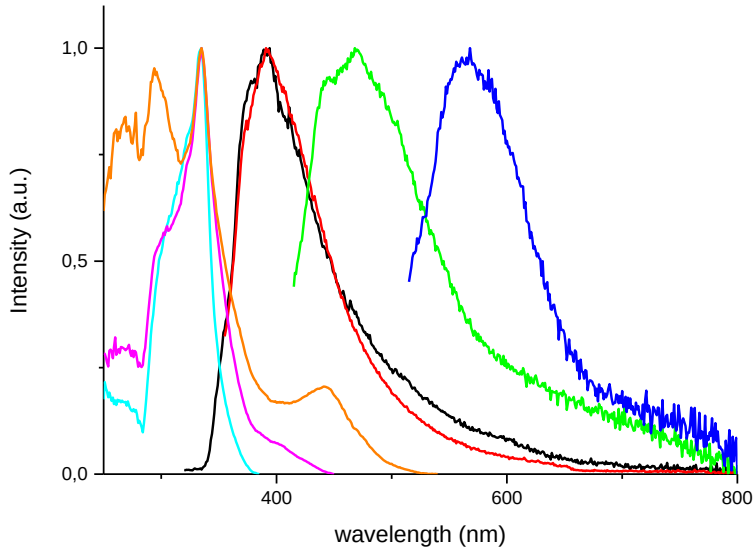


Figure S16. Normalized Emission spectra: λ_{exc}=300nm (black line), λ_{exc}=334nm (red line), λ_{exc}=400nm (green line), λ_{exc}=500nm (blue line) and excitation spectra λ_{em}=400nm (cyan line), λ_{em}=469nm (pink line), λ_{em}=563nm (orange line) of **3-Ag** at 77 K.

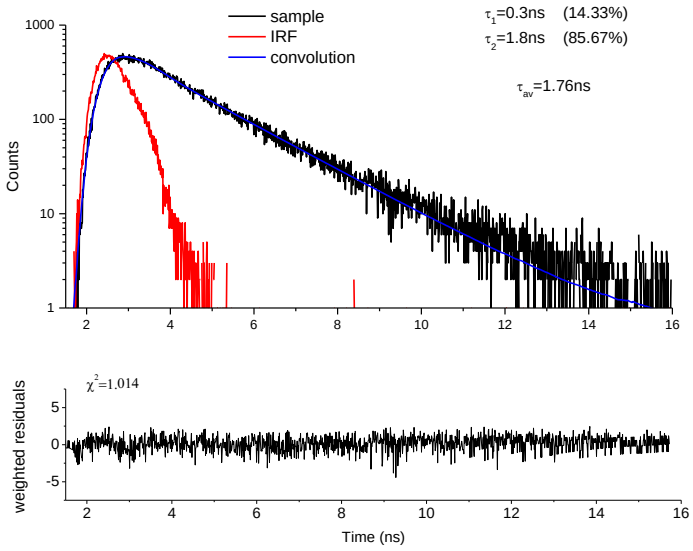


Figure S17. Lifetime measurement (λ_{exc}=300nm, λ_{em}=392nm) of **3-Ag** at 77 K. τ_{av} = 1.76 ns.

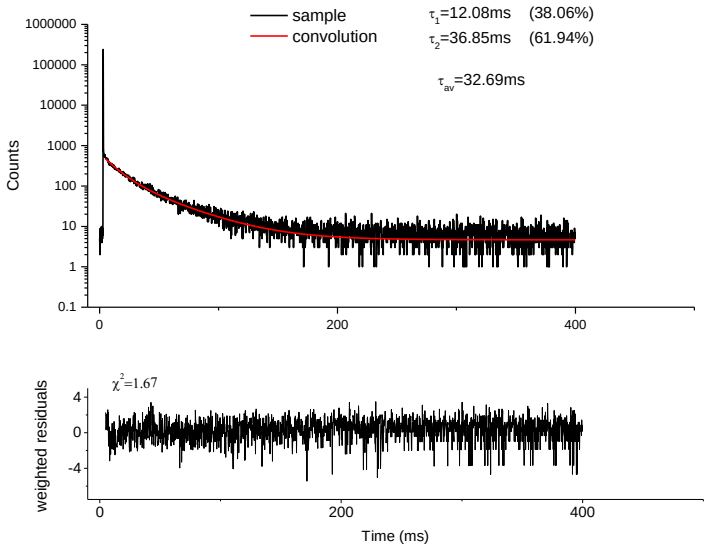


Figure S18. Lifetime measurement (λ_{exc}=334nm, λ_{em}=448nm) of **3-Ag** at 77 K. τ_{av} = 32.69 ms.

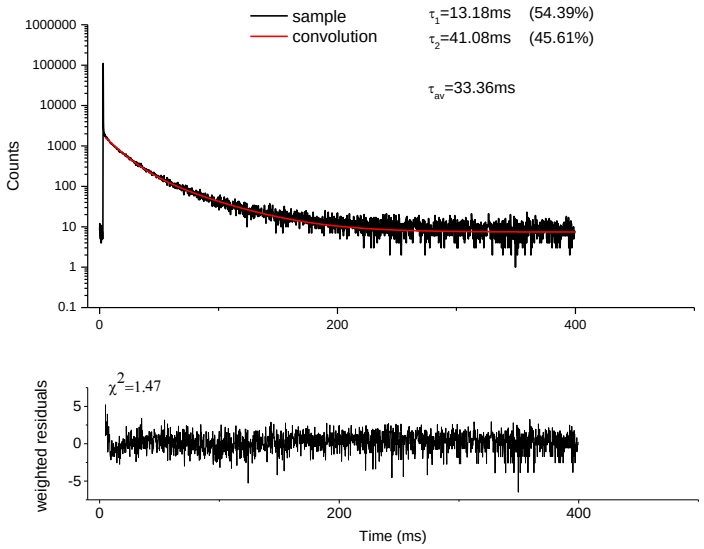


Figure S19. Lifetime measurement (λ_{exc}=334nm, λ_{em}=563nm) of **3-Ag** at 77 K. τ_{av} = 33.36 ms.

4. Theoretical studies

4.1. 1-Ag, 1-Cu

To simulate the 1D $[M(TT)I]_n$ (M = Ag, Cu) stair-step polymeric structures **1-Ag** and **1-Cu**, the $[M(TT)I]_4$ discrete model (see Fig. S20), including two **TT** ligands on either sides of the stair, has been chosen in order to properly describe the π-π interactions between the aromatic moieties, in addition to the metal-ligand and the metal-iodine bonds. Geometry optimization has been performed by freezing angles and torsions to preserve the correct coordination geometry around the metal ions. The optimized distances are generally rather close to the experimental values, though the symmetry of the infinite polymeric chain is lost owing to major boundary effects. In particular, the interplanar distances between adjacent **TT** ligands are equal to 3.213, 3.169 Å (M = Ag) and 3.228, 3.083 Å (M = Cu), to be compared with the X-ray values of 3.1726(19) (**1-Ag**) and 3.1730(6) Å (**1-Cu**), respectively. The distances between triazinic centroids are equal to 4.735, 4.693 Å (Ag) and 4.537, 4.451 Å (Cu), close to the experimental values of 4.731(2) (**1-Ag**) and 4.5090(13) Å (**1-Cu**), respectively. The M–I bond lengths within a step are slightly shorter for the steps external to the chain with respect to the internal ones, varying from 2.75 to 2.91 Å (Ag) and from 2.56 to 2.65 Å (Cu), to be compared with the X-ray distances of 2.8084(5) (**1-Ag**) and 2.611 Å (**1-Cu**), and the M···M separations are 3.19, 3.24 (Ag) and 3.16, 3.24 Å (Cu), in good agreement with the X-ray values (3.1591(5) for **1-Ag** and 3.248 Å for **1-Cu**). Finally, the M–N bond lengths, 2.35-2.38 Å (Ag) and 2.05-2.10 Å (Cu), are only slightly longer than the experimental values, 2.319(3) (**1-Ag**) and 2.028 Å (**1-Cu**).

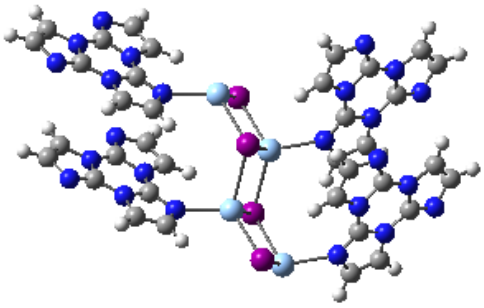


Figure S20. Tetrameric model compound of **1-Ag**, $[Ag(TT)I]_4$.

The nature of bonding and non-bonding interactions involved in $[Ag(TT)I]_4$ and $[Cu(TT)I]_4$ has been explored by means of the QTAIM approach. The topological properties computed at selected bond critical points and ring critical points are reported in Table S2, while in Figure S21 are reported the molecular graphs. Looking at the bcp properties of the M–N bonds, it emerges a larger shared-shell character for the Cu compound with respect to the Ag compound. This is evidenced especially by the H_{bcp}/ρ_{bcp} and $|V_{bcp}|/G_{bcp}$ ratios and by the electron Delocalization Index (i.e., average number of electrons shared between M and N), which are larger for the former than for the latter compound.

Table S5. Selected bond distances and bcp and rcp properties (electron density, ρ_{bcp}, Laplacian of electron density, $\nabla^2\rho_{bcp}$, potential, kinetic and total energy density, V_{bcp}, G_{bcp} and H_{bcp}, respectively, and delocalization index, DI) for $[Ag(TT)I]_4$ and $[Cu(TT)I]_4$ model compounds.

	r (Å)	ρ_{bcp} (e/Å^3)	$\nabla^2\rho_{bcp}$ (e/Å^3)	H_{bcp}/ρ_{bcp}	$\|V_{bcp}\|/G_{bcp}$	DI(A,B)
Ag–N[a]	2.35-2.38	0.327-0.352	4.75-5.18	-0.084 – -0.091	1.076-1.082	0.353-0.391
Cu–N[a]	2.05-2.10	0.448-0.506	7.11-8.36	-0.169 – -0.174	1.131-1.132	0.426-0.470
<Ag–N>[a,b]	2.374	0.334	4.87	-0.086	1.08	0.368
<Cu–N>[a,b]	2.072	0.480	7.75	-0.171	1.13	0.452
Ag···Ag	3.19, 3.24	no bcp				
Cu···Cu	3.16, 3.24	no bcp				
Ag–I–Ag–I[c]		0.104-0.113				
Cu–I–Cu–I[c]		0.091-0.109				

[a]Bond critical point; [b]Averages on the bcp properties of the four M–N bonds of the tetrameric models; [c]Ring critical point.

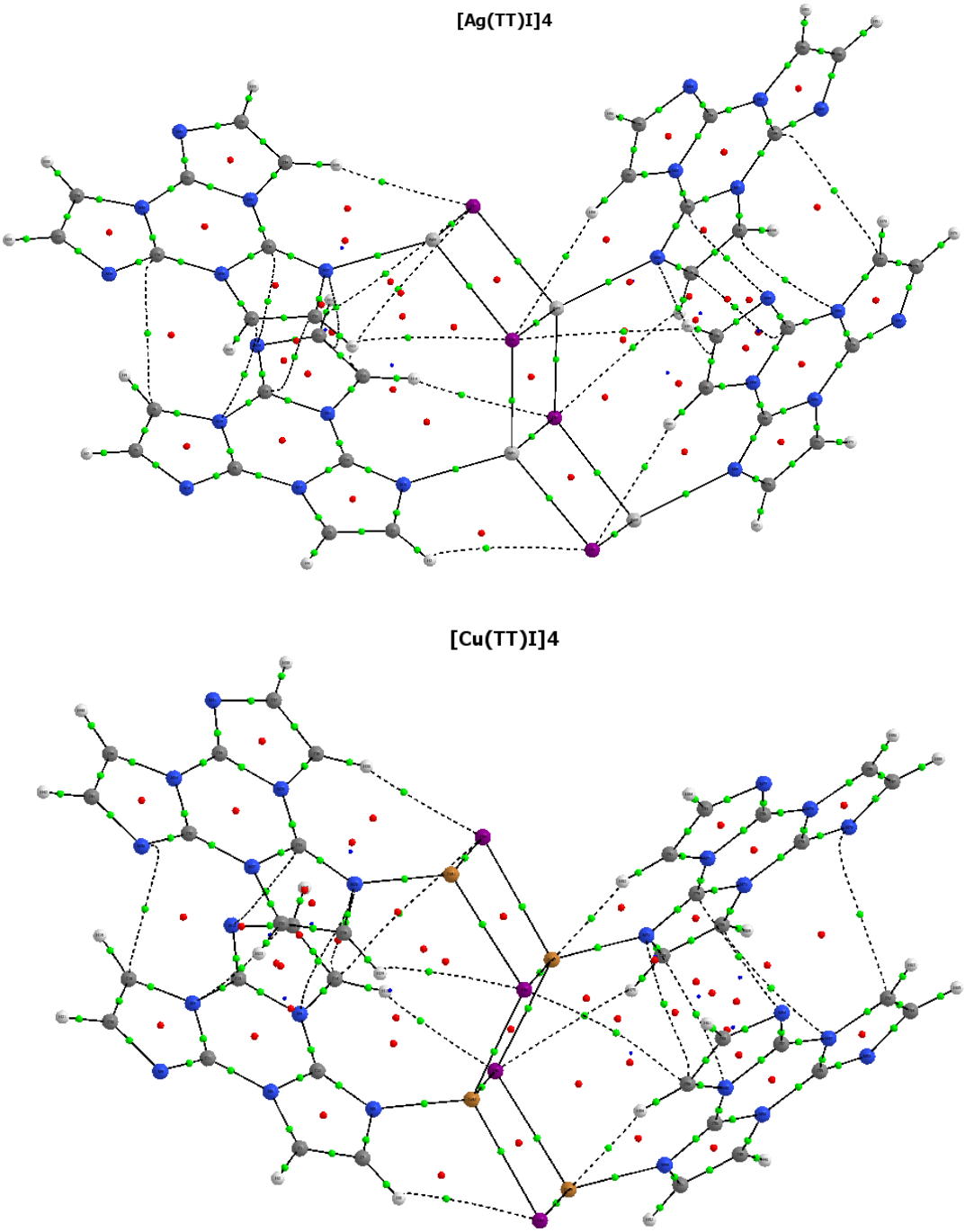


Figure S21. Molecular graphs of $[Ag(TT)I]_4$ (top) and $[Cu(TT)I]_4$ (bottom) with bond paths, bond critical points (green circles) and ring critical points (red circles).

The results of DFT/TDDFT calculations on model compounds $[Ag(TT)I]_4$ and $[Cu(TT)I]_4$ are reported in Figures S22 (simulated absorption spectra), S23 (scheme of excited states), S24, S25 (Plots of the MOs mainly involved in the lowest energy transitions) and Tables S6, S7 (Gaussian16 output of the $S_0 \rightarrow S_n$ and $T_0 \rightarrow T_n$ transitions).

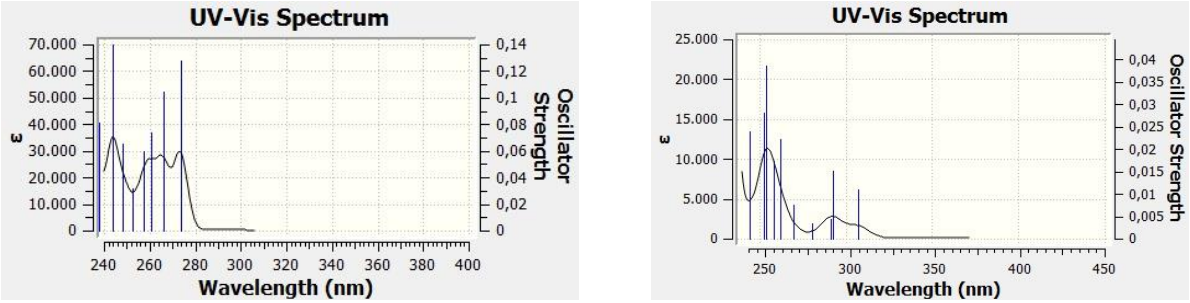


Figure S22. Simulated absorption spectra of model compounds $[Ag(TT)I]_4$ (at ωB97X/def2-TZVP level. left) and $[Cu(TT)I]_4$ (at ωB97X/6-311++G(d,p) level, right), resulting from convolution of the excitation energies with 0.06 eV ($[Ag(TT)I]_4$) and 0.1 eV ($[Cu(TT)I]_4$) of half-bandwidth.

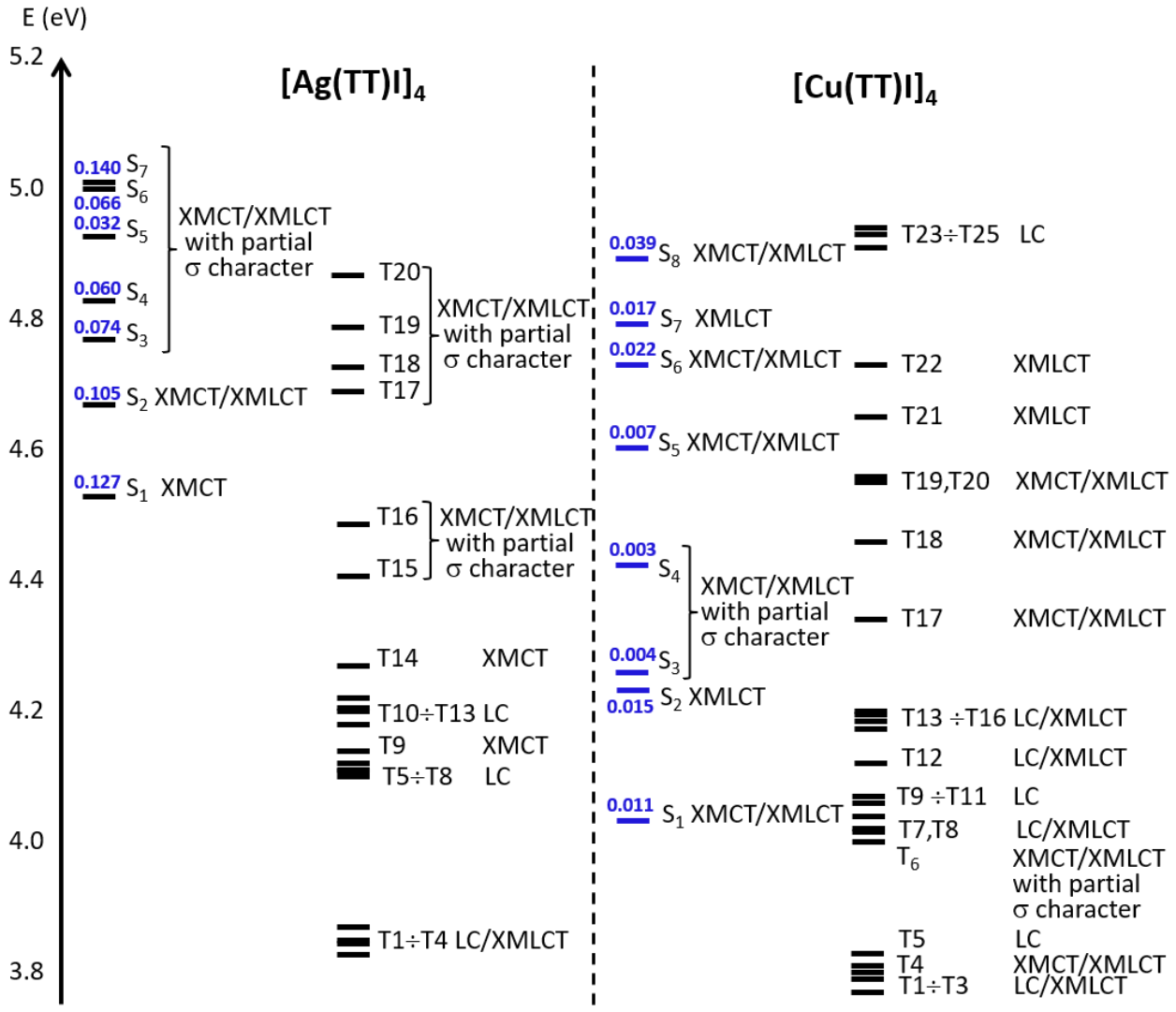
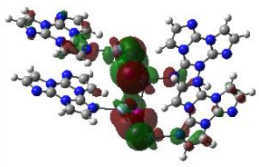
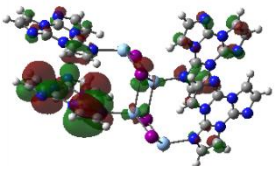


Figure S23. Scheme of singlet and triplet electronic levels with oscillator strengths for singlet states (in blue) and character for model compounds $[Ag(TT)I]_4$ (at ωB97X/def2-TZVP level, left) and $[Cu(TT)I]_4$ (at ωB97X/6-311++G(d,p) level, right).

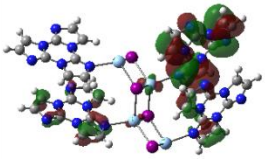
$[Ag(TT)I]_4$: HOMOs



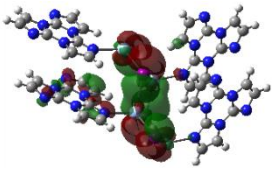
MO = 272 (HOMO-20)



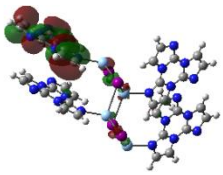
273 (HOMO-19)



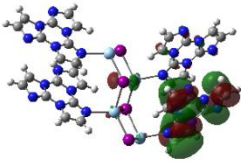
274 (HOMO-18)



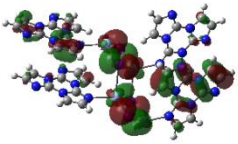
275 (HOMO-17)



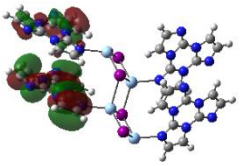
276 (HOMO-16)



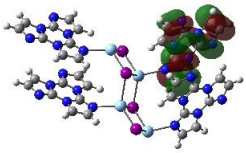
277 (HOMO-15)



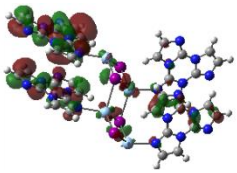
278 (HOMO-14)



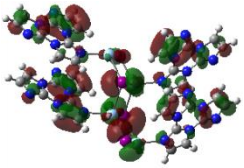
279 (HOMO-13)



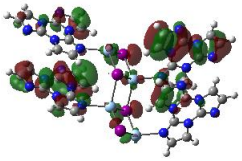
280 (HOMO-12)



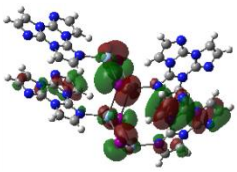
281 (HOMO-11)



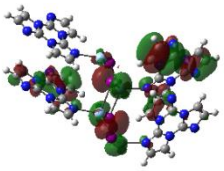
282 (HOMO-10)



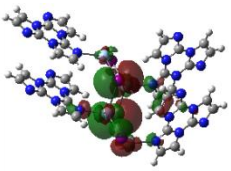
283 (HOMO-9)



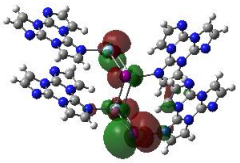
284 (HOMO-8)



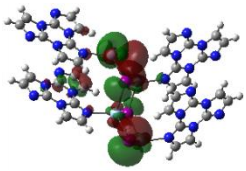
285 (HOMO-7)



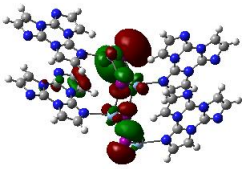
286 (HOMO-6)



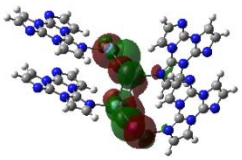
287 (HOMO-5)



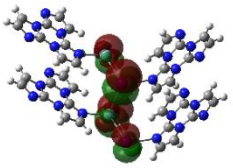
288 (HOMO-4)



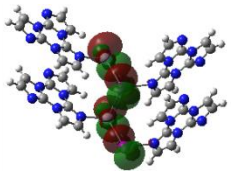
289 (HOMO-3)



290 (HOMO-2)

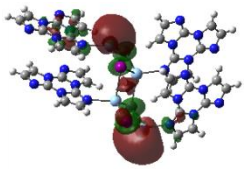


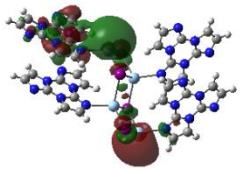
291 (HOMO-1)

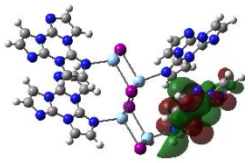


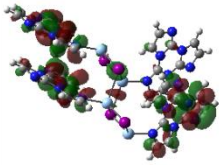
292 (HOMO)

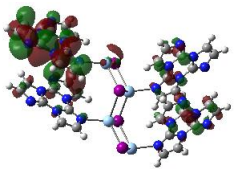
[Ag(TT)I]$_4$: LUMOs

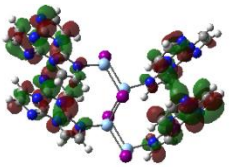

MO = 293 (LUMO)

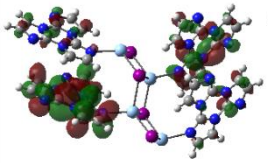

294 (LUMO+1)

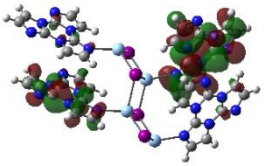

295 (LUMO+2)

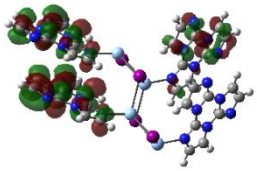

296 (LUMO+3)


297 (LUMO+4)


298 (LUMO+5)


299 (LUMO+6)


300 (LUMO+7)


301 (LUMO+8)

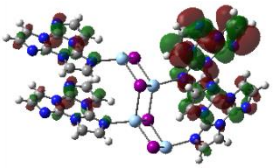
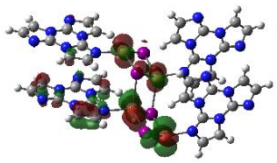
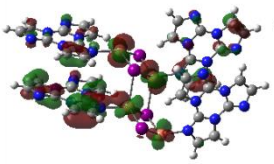
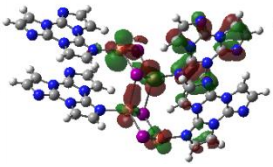

302 (LUMO+9)

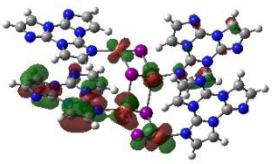
Figure S24. Plots of the ωB97X/def2-TZVP MOs mainly involved in the lowest energy transitions of [Ag(TT)I]$_4$ (Isosurfaces value 0.02).

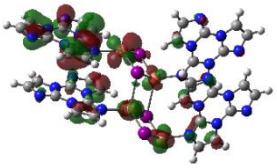
[Cu(TT)I]$_4$: HOMOs

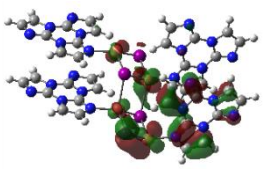

MO = 340 (HOMO-28)

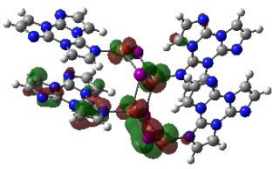

341 (HOMO-27)

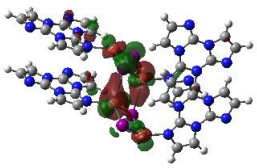

342 (HOMO-26)

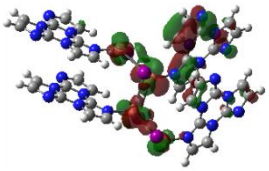

343 (HOMO-25)


344 (HOMO-24)

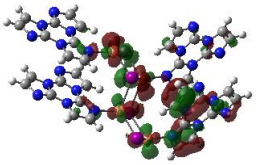

345 (HOMO-23)


346 (HOMO-22)

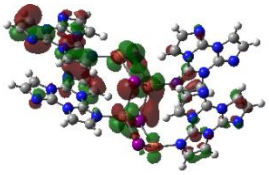

347 (HOMO-21)



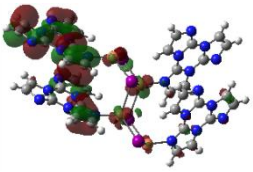
348 (HOMO-20)



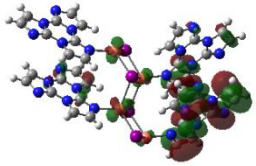
349 (HOMO-19)



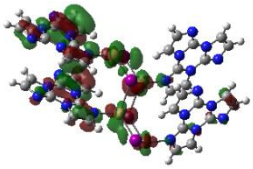
350 (HOMO-18)



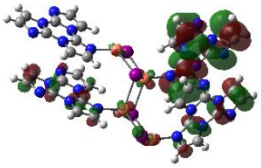
351 (HOMO-17)



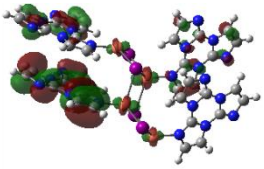
352 (HOMO-16)



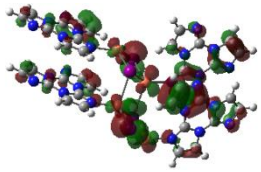
353 (HOMO-15)



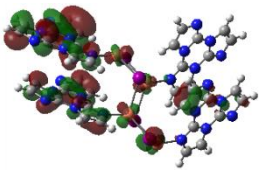
354 (HOMO-14)



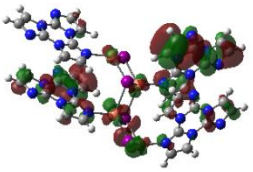
355 (HOMO-13)



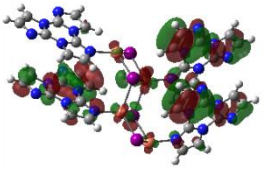
356 (HOMO-12)



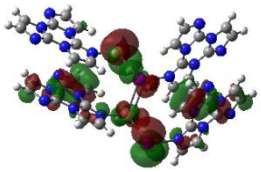
357 (HOMO-11)



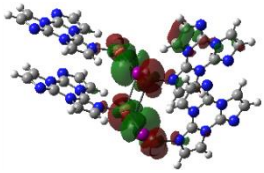
358 (HOMO-10)



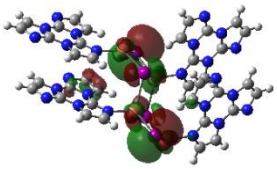
359 (HOMO-9)



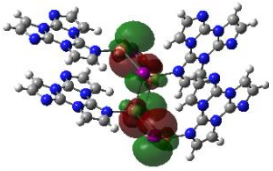
360 (HOMO-8)



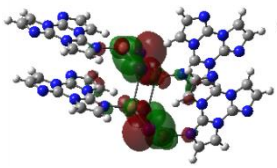
361 (HOMO-7)



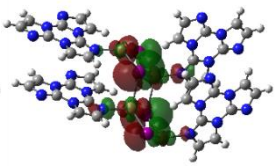
362 (HOMO-6)



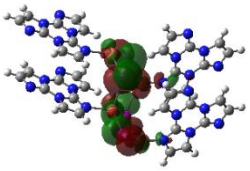
363 (HOMO-5)



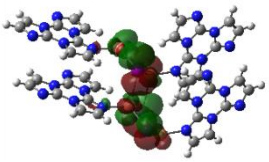
364 (HOMO-4)



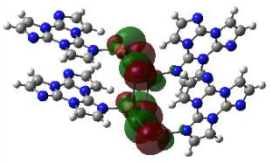
365 (HOMO-3)



366 (HOMO-2)

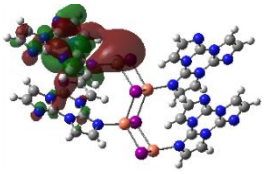


367 (HOMO-1)

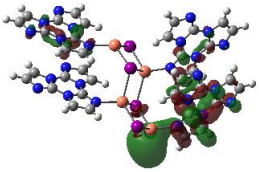


368 (HOMO)

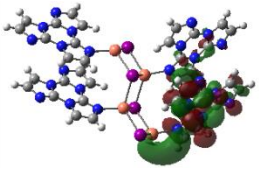
[Cu(TT)I]$_4$: LUMOs



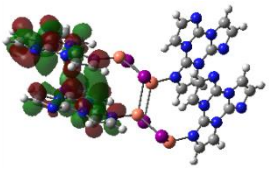
MO = 369 (LUMO)



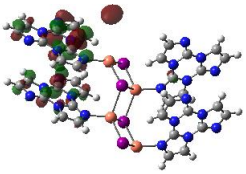
370 (LUMO+1)



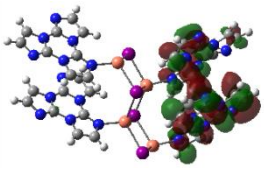
371 (LUMO+2)



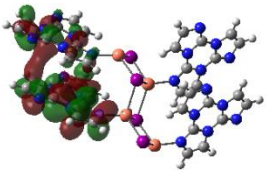
372 (LUMO+3)



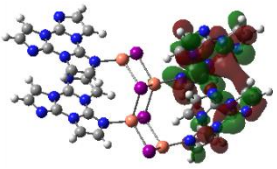
373 (LUMO+4)



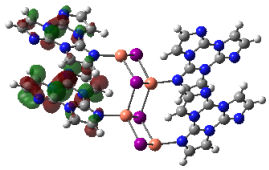
374 (LUMO+5)



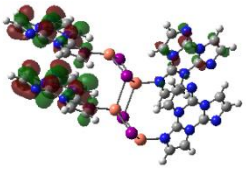
375 (LUMO+6)



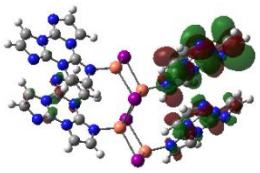
376 (LUMO+7)



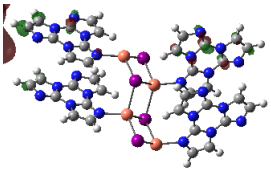
377 (LUMO+8)



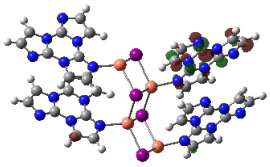
378 (LUMO+9)



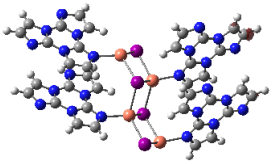
379 (LUMO+10)



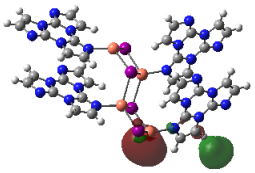
380 (LUMO+11)



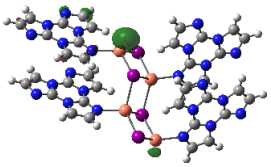
381 (LUMO+12)



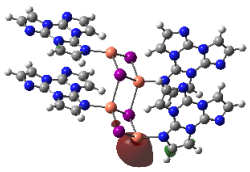
382 (LUMO+13)



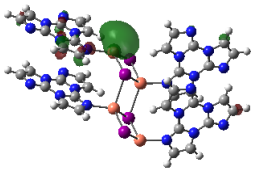
383 (LUMO+14)



384 (LUMO+15)



385 (LUMO+16)



386 (LUMO+17)

Figure S25. Plots of the ωB97X/6-311++G(d,p) MOs mainly involved in the lowest energy transitions of [Cu(TT)I]$_4$ (Isosurfaces value 0.02).

Table S6. First TD-ωB97X/def2-TZVP $S_0 \rightarrow S_n$ and $T_0 \rightarrow T_n$ transitions computed for the optimized geometry of $[Ag(TT)I]_4$.

Singlets:

```
Excited State   1:      Singlet-A      4.5326 eV  273.54 nm  f=0.1274  <S**2>=0.000
     290 -> 293       -0.29536
     290 -> 294       -0.25764
     292 -> 293        0.40815
     292 -> 294        0.23580

 Excited State   2:      Singlet-A      4.6615 eV  265.97 nm  f=0.1046  <S**2>=0.000
     290 -> 293       -0.28652
     290 -> 294        0.16850
     291 -> 293       -0.10771
     292 -> 293       -0.27900
     292 -> 294        0.35119
     292 -> 296       -0.13051
     292 -> 297       -0.11634

 Excited State   3:      Singlet-A      4.7565 eV  260.66 nm  f=0.0739  <S**2>=0.000
     286 -> 293        0.12916
     286 -> 294        0.11063
     287 -> 293        0.38717
     287 -> 294        0.28041
     290 -> 294       -0.10694
     291 -> 293       -0.27546
     291 -> 294       -0.15628
     292 -> 293        0.12200

 Excited State   4:      Singlet-A      4.8212 eV  257.17 nm  f=0.0599  <S**2>=0.000
     287 -> 293       -0.10406
     288 -> 293        0.25566
     288 -> 294       -0.23671
     289 -> 293        0.21377
     289 -> 294       -0.21300
     291 -> 293       -0.22367
     291 -> 294        0.18753

 Excited State   5:      Singlet-A      4.9067 eV  252.68 nm  f=0.0321  <S**2>=0.000
     284 -> 293        0.14346
     284 -> 294        0.10553
     286 -> 293       -0.16108
     286 -> 294       -0.15820
     287 -> 293        0.14649
     287 -> 294        0.15265
     288 -> 293        0.35589
     288 -> 294        0.18314
     289 -> 293       -0.23219
     291 -> 293        0.15423
     291 -> 294        0.10394

 Excited State   6:      Singlet-A      4.9937 eV  248.28 nm  f=0.0658  <S**2>=0.000
     287 -> 293        0.20070
     289 -> 293        0.30757
     289 -> 294       -0.27348
     289 -> 296        0.11509
     289 -> 297        0.12376
     289 -> 304        0.10846
     290 -> 294        0.10596
     291 -> 293        0.21666

 Excited State   7:      Singlet-A      5.0891 eV  243.63 nm  f=0.1397  <S**2>=0.000
     286 -> 293        0.39834
     286 -> 296        0.11132
     286 -> 303        0.18811
     288 -> 294       -0.10482
     290 -> 294        0.11232
     291 -> 293        0.19636
     291 -> 303        0.13012
     292 -> 303        0.22670

 Excited State   8:      Singlet-A      5.2131 eV  237.83 nm  f=0.0815  <S**2>=0.000
     278 -> 293        0.17708
     284 -> 293        0.10922
     288 -> 294        0.14408
     290 -> 304        0.11486
     291 -> 293       -0.25200
     291 -> 296       -0.14357
```

```
     291 -> 303       -0.25204
     292 -> 293        0.13187
     292 -> 296        0.14070
     292 -> 303        0.30077

 Excited State   9:      Singlet-A      5.3205 eV  233.03 nm  f=0.0049  <S**2>=0.000
     272 -> 294        0.10219
     275 -> 293       -0.11939
     278 -> 294        0.10630
     282 -> 293        0.24307
     283 -> 293        0.10639
     284 -> 293       -0.13953
     285 -> 293        0.23596
     286 -> 294        0.19845
     291 -> 294        0.16969
     292 -> 303       -0.12984

 Excited State  10:      Singlet-A      5.3262 eV  232.78 nm  f=0.0139  <S**2>=0.000
     277 -> 295        0.38704
     278 -> 296       -0.12437
     278 -> 298       -0.13417
     281 -> 298       -0.10147
     282 -> 298        0.10850
     284 -> 295        0.14521
     284 -> 296        0.17544
     284 -> 298        0.18657
```

Triplets:

```
Excited State   1:      Triplet-A      3.8293 eV  323.78 nm  f=0.0000  <S**2>=2.000
     277 -> 295        0.26814
     278 -> 296       -0.12064
     278 -> 298       -0.13934
     282 -> 298        0.10061
     283 -> 295       -0.10919
     284 -> 295        0.23524
     284 -> 296        0.13498
     284 -> 298        0.17610
     284 -> 302       -0.10479

 Excited State   2:      Triplet-A      3.8478 eV  322.22 nm  f=0.0000  <S**2>=2.000
     276 -> 297        0.21015
     279 -> 296        0.11215
     279 -> 301       -0.13618
     281 -> 294        0.16837
     281 -> 296        0.17159
     281 -> 298       -0.19495
     281 -> 299       -0.11523
     281 -> 301       -0.13222
     282 -> 301       -0.12540
     283 -> 301        0.15228

 Excited State   3:      Triplet-A      3.8539 eV  321.71 nm  f=0.0000  <S**2>=2.000
     279 -> 299       -0.24022
     279 -> 300       -0.14002
     281 -> 301       -0.21599
     282 -> 296        0.11167
     282 -> 298       -0.10531
     283 -> 296       -0.17086
     283 -> 298        0.18268
     283 -> 301       -0.15012
     285 -> 296       -0.10633
     285 -> 298        0.11301
     285 -> 301       -0.11285

 Excited State   4:      Triplet-A      3.8690 eV  320.46 nm  f=0.0000  <S**2>=2.000
     280 -> 299       -0.12638
     280 -> 300        0.25507
     280 -> 302        0.10775
     282 -> 302        0.14254
     283 -> 298        0.12192
     283 -> 302        0.21699
     285 -> 297        0.10779
     285 -> 298       -0.14708
     285 -> 301       -0.11592
     285 -> 302       -0.25795

 Excited State   5:      Triplet-A      4.1040 eV  302.10 nm  f=0.0000  <S**2>=2.000
```

```
    277 -> 295        0.21563
    277 -> 296       -0.23047
    277 -> 297        0.10428
    277 -> 298       -0.22324
    277 -> 299        0.10354
    277 -> 302        0.11403
    278 -> 295        0.15994
    284 -> 295       -0.12468

Excited State   6:      Triplet-A      4.1138 eV  301.39 nm  f=0.0000  <S**2>=2.000
    273 -> 296       -0.10878
    273 -> 298        0.12518
    273 -> 301       -0.12833
    276 -> 297       -0.19919
    279 -> 299       -0.25405
    279 -> 300       -0.15779
    279 -> 301        0.15080
    281 -> 299        0.10882
    282 -> 301       -0.10767

Excited State   7:      Triplet-A      4.1221 eV  300.78 nm  f=0.0000  <S**2>=2.000
    273 -> 301       -0.10702
    276 -> 294        0.11506
    276 -> 296        0.11676
    276 -> 297        0.33173
    278 -> 297       -0.11373
    279 -> 299       -0.13331
    279 -> 301        0.15332
    281 -> 306        0.11007

Excited State   8:      Triplet-A      4.1280 eV  300.35 nm  f=0.0000  <S**2>=2.000
    274 -> 302       -0.18511
    280 -> 299        0.16561
    280 -> 300       -0.35634
    280 -> 301       -0.11305
    280 -> 302       -0.19164
    285 -> 302       -0.11740

Excited State   9:      Triplet-A      4.1410 eV  299.41 nm  f=0.0000  <S**2>=2.000
    290 -> 293       -0.27763
    290 -> 294       -0.26320
    291 -> 293       -0.11189
    292 -> 293        0.40902
    292 -> 294        0.18371

Excited State  10:      Triplet-A      4.1836 eV  296.35 nm  f=0.0000  <S**2>=2.000
    273 -> 299       -0.25366
    273 -> 300       -0.14548
    273 -> 301        0.10250
    279 -> 296       -0.15396
    279 -> 298        0.15349
    279 -> 299       -0.14492
    279 -> 301       -0.12224
    279 -> 307       -0.14296
    281 -> 301        0.10882
    283 -> 299       -0.13888
    283 -> 301        0.10356

Excited State  11:      Triplet-A      4.2013 eV  295.11 nm  f=0.0000  <S**2>=2.000
    270 -> 295       -0.19114
    271 -> 295        0.23331
    277 -> 295       -0.29561
    277 -> 305       -0.15982
    277 -> 307       -0.10653
    284 -> 295       -0.10634

Excited State  12:      Triplet-A      4.2131 eV  294.28 nm  f=0.0000  <S**2>=2.000
    274 -> 299        0.13795
    274 -> 300       -0.27474
    280 -> 298       -0.13223
    280 -> 302       -0.21757
    280 -> 308        0.19171
    282 -> 300       -0.11279
    283 -> 300       -0.12394
    285 -> 300        0.15857

Excited State  13:      Triplet-A      4.2236 eV  293.55 nm  f=0.0000  <S**2>=2.000
    269 -> 297       -0.15263
```

```
    270 -> 297        0.18057
    271 -> 297        0.15481
    276 -> 294        0.12600
    276 -> 296        0.12704
    276 -> 298       -0.13318
    276 -> 301       -0.13594
    276 -> 306        0.19926
    281 -> 297        0.20937
    282 -> 297        0.10582

Excited State  14:      Triplet-A      4.2700 eV  290.36 nm  f=0.0000  <S**2>=2.000
    288 -> 293       -0.13671
    290 -> 293       -0.29376
    290 -> 294        0.12553
    292 -> 293       -0.23149
    292 -> 294        0.31132
    292 -> 296       -0.13996
    292 -> 297       -0.11090

Excited State  15:      Triplet-A      4.3959 eV  282.04 nm  f=0.0000  <S**2>=2.000
    286 -> 293        0.17014
    286 -> 294        0.12154
    287 -> 293        0.31046
    287 -> 294        0.25557
    291 -> 293       -0.30601
    291 -> 294       -0.14088
    292 -> 293       -0.11375

Excited State  16:      Triplet-A      4.4838 eV  276.52 nm  f=0.0000  <S**2>=2.000
    287 -> 293        0.16146
    288 -> 293       -0.22403
    288 -> 294        0.21408
    289 -> 293       -0.13469
    289 -> 294        0.11811
    290 -> 293        0.10020
    291 -> 293        0.20217
    291 -> 294       -0.20124
    291 -> 296        0.10371
    292 -> 294       -0.10462

Excited State  17:      Triplet-A      4.6848 eV  264.65 nm  f=0.0000  <S**2>=2.000
    284 -> 293        0.11020
    287 -> 293        0.24067
    287 -> 294        0.20076
    288 -> 293        0.31635
    288 -> 294        0.13258
    289 -> 293       -0.15282
    289 -> 294       -0.13907
    291 -> 293        0.19492
    291 -> 303        0.14244

Excited State  18:      Triplet-A      4.7167 eV  262.86 nm  f=0.0000  <S**2>=2.000
    278 -> 293       -0.11135
    284 -> 293       -0.11334
    286 -> 293        0.19873
    288 -> 294       -0.19216
    289 -> 293        0.19008
    291 -> 293        0.20919
    291 -> 296        0.18425
    291 -> 303        0.37087

Excited State  19:      Triplet-A      4.7822 eV  259.26 nm  f=0.0000  <S**2>=2.000
    286 -> 293       -0.11794
    287 -> 293        0.14634
    287 -> 294       -0.11012
    289 -> 293        0.32443
    289 -> 294       -0.29433
    289 -> 296        0.12483
    289 -> 297        0.13435
    289 -> 304        0.11597
    291 -> 303       -0.11860

Excited State  20:      Triplet-A      4.8647 eV  254.87 nm  f=0.0000  <S**2>=2.000
    278 -> 293        0.11187
    286 -> 293        0.26547
    286 -> 303        0.15105
    290 -> 294        0.14962
    290 -> 304        0.13382
```

```
     292 -> 293        0.11395
     292 -> 296        0.15828
     292 -> 303        0.38636
```

Table S7. First TD-ωB97X/6-311++G(d,p) $S_0 \rightarrow S_n$ and $T_0 \rightarrow T_n$ transitions computed for the optimized geometry of $[Cu(TT)I]_4$.

```
Singlets:

Excited State   1:      Singlet-A      4.0385 eV  307.01 nm  f=0.0109  <S**2>=0.000
     366 -> 370        0.19515
     366 -> 371        0.12027
     366 -> 383       -0.16744
     366 -> 385       -0.12479
     368 -> 370        0.20325
     368 -> 371        0.12385
     368 -> 383       -0.17253
     368 -> 385       -0.13018

 Excited State   2:      Singlet-A      4.2393 eV  292.46 nm  f=0.0152  <S**2>=0.000
     349 -> 369        0.12407
     361 -> 369        0.12702
     366 -> 369       -0.17398
     367 -> 369        0.20183
     367 -> 386       -0.10714
     368 -> 369        0.23296
     368 -> 386       -0.12012

 Excited State   3:      Singlet-A      4.2588 eV  291.13 nm  f=0.0043  <S**2>=0.000
     364 -> 370       -0.18461
     364 -> 371       -0.12601
     364 -> 383        0.16278
     364 -> 385        0.11918
     365 -> 370       -0.12602
     365 -> 383        0.11030

 Excited State   4:      Singlet-A      4.4184 eV  280.61 nm  f=0.0034  <S**2>=0.000
     364 -> 369        0.24714
     364 -> 386       -0.13397
     364 -> 390       -0.10334
     365 -> 369       -0.19547
     365 -> 386        0.10496
     368 -> 369       -0.12234

 Excited State   5:      Singlet-A      4.5995 eV  269.56 nm  f=0.0075  <S**2>=0.000
     345 -> 370        0.13117
     345 -> 383       -0.12171
     362 -> 370        0.13266
     362 -> 383       -0.11490
     363 -> 370        0.17083
     363 -> 371        0.10877
     363 -> 383       -0.14467
     363 -> 385       -0.10424

 Excited State   6:      Singlet-A      4.7308 eV  262.08 nm  f=0.0223  <S**2>=0.000
     343 -> 370       -0.13655
     343 -> 383        0.12651
     346 -> 370        0.11888
     346 -> 383       -0.10857
     349 -> 370       -0.11858
     349 -> 383        0.10413

 Excited State   7:      Singlet-A      4.7939 eV  258.63 nm  f=0.0174  <S**2>=0.000
     335 -> 369        0.10133
     336 -> 369       -0.11191
     342 -> 369       -0.11001
     344 -> 369        0.12343
     362 -> 369       -0.19986
     362 -> 386        0.11342
     363 -> 369        0.19565
     363 -> 386       -0.10687

 Excited State   8:      Singlet-A      4.8812 eV  254.00 nm  f=0.0387  <S**2>=0.000
     338 -> 370        0.14997
     338 -> 383       -0.14017
     338 -> 385       -0.10686
     340 -> 370       -0.14274
     340 -> 383        0.13206
```

```
     345 -> 370        0.16277
     345 -> 371        0.10649
     345 -> 383       -0.14863
     345 -> 385       -0.11269
     346 -> 370       -0.12811
     346 -> 383        0.11688

 Excited State   9:      Singlet-A      4.9008 eV  252.99 nm  f=0.0282  <S**2>=0.000
     333 -> 369       -0.10280
     339 -> 369        0.10157
     342 -> 369        0.12432
     344 -> 369        0.14294
     346 -> 369        0.10396
     347 -> 369        0.10860
     357 -> 369        0.11657
     367 -> 369        0.14685

Triplets:

Excited State   1:      Triplet-A      3.7725 eV  328.65 nm  f=0.0000  <S**2>=2.000
     349 -> 371       -0.12414
     349 -> 374        0.10744
     352 -> 371       -0.11782
     352 -> 374       -0.11660
     352 -> 376       -0.11124
     356 -> 371       -0.13966
     356 -> 374        0.15399
     358 -> 374       -0.11021
     359 -> 371        0.15530
     359 -> 374       -0.19296
     359 -> 379        0.10259
     360 -> 371        0.12164
     360 -> 374       -0.16941

 Excited State   2:      Triplet-A      3.7905 eV  327.09 nm  f=0.0000  <S**2>=2.000
     353 -> 372       -0.10658
     355 -> 375       -0.23405
     357 -> 375       -0.12739
     358 -> 372       -0.12884
     358 -> 378        0.12655
     359 -> 372       -0.15260
     359 -> 377       -0.11243
     359 -> 378        0.14849
     360 -> 372        0.13936
     360 -> 377        0.10098
     360 -> 378       -0.13322

 Excited State   3:      Triplet-A      3.8036 eV  325.97 nm  f=0.0000  <S**2>=2.000
     351 -> 369        0.14103
     351 -> 372        0.11961
     351 -> 375       -0.11164
     353 -> 369       -0.18437
     355 -> 369       -0.13172
     356 -> 369       -0.11196
     357 -> 369        0.23351
     357 -> 372       -0.21356
     357 -> 373       -0.15658
     357 -> 378       -0.16448

 Excited State   4:      Triplet-A      3.8097 eV  325.44 nm  f=0.0000  <S**2>=2.000
     366 -> 370        0.18425
     366 -> 371        0.11298
     366 -> 383       -0.16314
     366 -> 385       -0.12259
     368 -> 370        0.19084
     368 -> 371        0.11733
     368 -> 383       -0.16598
     368 -> 385       -0.12453

Excited State   5:      Triplet-A      3.8288 eV  323.82 nm  f=0.0000  <S**2>=2.000
     354 -> 376        0.22179
     358 -> 374        0.19161
     358 -> 379        0.24108
     359 -> 374       -0.17505
     359 -> 379       -0.19645

 Excited State   6:      Triplet-A      4.0017 eV  309.83 nm  f=0.0000  <S**2>=2.000
     364 -> 370       -0.18371
```

```
     364 -> 371       -0.11608
     364 -> 383        0.16416
     364 -> 385        0.12271
     365 -> 370       -0.11744
     365 -> 383        0.10512

 Excited State   7:      Triplet-A      4.0236 eV  308.14 nm  f=0.0000  <S**2>=2.000
     352 -> 374        0.20405
     352 -> 376        0.13510
     366 -> 369       -0.10438
     367 -> 369        0.11964
     368 -> 369        0.13854

 Excited State   8:      Triplet-A      4.0244 eV  308.08 nm  f=0.0000  <S**2>=2.000
     352 -> 374       -0.19865
     352 -> 376       -0.13016
     366 -> 369       -0.11325
     367 -> 369        0.12313
     368 -> 369        0.14599

 Excited State   9:      Triplet-A      4.0305 eV  307.61 nm  f=0.0000  <S**2>=2.000
     355 -> 375        0.23425
     355 -> 377       -0.12680
     355 -> 378        0.14028
     357 -> 378        0.10886
     359 -> 375       -0.10535
     360 -> 375        0.10613

 Excited State  10:      Triplet-A      4.0593 eV  305.43 nm  f=0.0000  <S**2>=2.000
     350 -> 372       -0.17124
     350 -> 375        0.10177
     351 -> 369       -0.13821
     351 -> 372       -0.22672
     351 -> 375        0.19149
     351 -> 378       -0.10563
     355 -> 378        0.10809
     357 -> 369        0.17261

 Excited State  11:      Triplet-A      4.0732 eV  304.39 nm  f=0.0000  <S**2>=2.000
     352 -> 376        0.10478
     354 -> 376       -0.21838
     354 -> 379       -0.27856
     356 -> 376       -0.11995
     358 -> 376       -0.13136
     359 -> 376        0.10836

Excited State  12:      Triplet-A      4.1308 eV  300.15 nm  f=0.0000  <S**2>=2.000
     340 -> 375        0.10210
     341 -> 375       -0.15297
     343 -> 375       -0.16587
     346 -> 375       -0.12132
     351 -> 372       -0.11462
     351 -> 375       -0.11216
     355 -> 372       -0.18890
     355 -> 375       -0.20481
     355 -> 402       -0.12455
     358 -> 375       -0.10578
     359 -> 375       -0.10487

 Excited State  13:      Triplet-A      4.1673 eV  297.52 nm  f=0.0000  <S**2>=2.000
     344 -> 369       -0.13926
     351 -> 369       -0.17790
     364 -> 369        0.18130
     364 -> 386       -0.10589
     365 -> 369       -0.13129

 Excited State  14:      Triplet-A      4.1834 eV  296.37 nm  f=0.0000  <S**2>=2.000
     337 -> 376        0.14278
     338 -> 376       -0.10051
     339 -> 376       -0.10584
     342 -> 376        0.12547
     354 -> 374       -0.11831
     354 -> 376        0.16249
     354 -> 401        0.11342
     358 -> 376       -0.12803
     358 -> 379       -0.12717

 Excited State  15:      Triplet-A      4.1884 eV  296.02 nm  f=0.0000  <S**2>=2.000
```

```
     336 -> 371       -0.10627
     337 -> 371        0.13293
     339 -> 371        0.11132
     345 -> 370       -0.10964
     345 -> 371        0.16038
     349 -> 371       -0.10061
     352 -> 370        0.13844
     352 -> 371       -0.19721
     352 -> 395        0.10820

 Excited State  16:      Triplet-A      4.1962 eV  295.47 nm  f=0.0000  <S**2>=2.000
     336 -> 369        0.11980
     344 -> 369        0.12894
     350 -> 369        0.10755
     351 -> 369        0.14293
     351 -> 373       -0.10022
     353 -> 369       -0.13770
     357 -> 372        0.12278
     364 -> 369        0.14640
     365 -> 369       -0.11494

Excited State  17:      Triplet-A      4.3507 eV  284.97 nm  f=0.0000  <S**2>=2.000
     345 -> 370        0.11031
     345 -> 383       -0.10504
     362 -> 370        0.11926
     362 -> 383       -0.10687
     363 -> 370        0.16708
     363 -> 371        0.11099
     363 -> 383       -0.14833
     363 -> 385       -0.10902

 Excited State  18:      Triplet-A      4.4625 eV  277.84 nm  f=0.0000  <S**2>=2.000
     340 -> 370       -0.11615
     340 -> 383        0.11036
     343 -> 370       -0.12532
     343 -> 383        0.11897
     349 -> 370       -0.11098
     349 -> 383        0.10369

 Excited State  19:      Triplet-A      4.5514 eV  272.41 nm  f=0.0000  <S**2>=2.000
     338 -> 370        0.13845
     338 -> 383       -0.13248
     338 -> 385       -0.10188
     340 -> 370       -0.12315
     340 -> 383        0.11704
     345 -> 370        0.17580
     345 -> 371        0.11465
     345 -> 383       -0.16579
     345 -> 385       -0.12654
     346 -> 370       -0.13366
     346 -> 383        0.12560

 Excited State  20:      Triplet-A      4.5623 eV  271.76 nm  f=0.0000  <S**2>=2.000
     335 -> 369       -0.10772
     336 -> 369        0.11387
     362 -> 369        0.17624
     362 -> 386       -0.10565
     363 -> 369       -0.18229
     363 -> 386        0.10857

 Excited State  21:      Triplet-A      4.6509 eV  266.58 nm  f=0.0000  <S**2>=2.000
     333 -> 369       -0.10349
     339 -> 369        0.10270
     342 -> 369        0.12044
     344 -> 369        0.14076
     346 -> 369        0.10804
     347 -> 369        0.10783
     367 -> 369        0.13066

Excited State  22:      Triplet-A      4.7346 eV  261.87 nm  f=0.0000  <S**2>=2.000
     335 -> 369       -0.10231
     339 -> 369       -0.10091
     340 -> 369        0.10383
     341 -> 369        0.12132
     342 -> 369       -0.15186
     344 -> 369        0.15156
     350 -> 369       -0.11282
```

```
Excited State  23:      Triplet-A      4.9100 eV  252.51 nm  f=0.0000  <S**2>=2.000
    350 -> 369         0.15998
    351 -> 369         0.26149
    351 -> 372        -0.14114
    351 -> 373        -0.12574
    351 -> 378        -0.12303
    357 -> 369        -0.14105

Excited State  24:      Triplet-A      4.9334 eV  251.31 nm  f=0.0000  <S**2>=2.000
    355 -> 372         0.22037
    355 -> 375         0.10893
    355 -> 378        -0.11875
    358 -> 375        -0.14308
    359 -> 375        -0.17428
    360 -> 375         0.16604

Excited State  25:      Triplet-A      4.9377 eV  251.10 nm  f=0.0000  <S**2>=2.000
    349 -> 374        -0.12007
    352 -> 370        -0.14162
    352 -> 371         0.22766
    352 -> 374        -0.16893
    354 -> 371         0.12533
    356 -> 374        -0.11715
    359 -> 371         0.11052
    359 -> 374         0.11250
    360 -> 371         0.12275

Excited State  26:      Triplet-A      4.9769 eV  249.12 nm  f=0.0000  <S**2>=2.000
    345 -> 374         0.13383
    352 -> 395         0.12409
    368 -> 370         0.13683
    368 -> 371        -0.12301

Excited State  27:      Triplet-A      4.9847 eV  248.73 nm  f=0.0000  <S**2>=2.000
    354 -> 401        -0.10859
    366 -> 370        -0.10889
    366 -> 376        -0.12268
    368 -> 374        -0.10607
    368 -> 376         0.12322

Excited State  28:      Triplet-A      4.9946 eV  248.24 nm  f=0.0000  <S**2>=2.000
    354 -> 374        -0.19002
    354 -> 376         0.14947
    354 -> 379        -0.19408
    358 -> 376         0.17365
    358 -> 379         0.10319
    359 -> 376        -0.14039
```

4.2. **2-Ag**, **2-Cu** and **3-Ag**

In the case of the 3D $[M(TT)Cl]_n$ (M =Ag, Cu) and $[Ag_3(TT)_4]_n(NO_3)_{3n}\cdot 6nH_2O$ polymeric structures, the $M(TT)_3Cl$ and the $Ag(TT)_4^+$ models, respectively, have been adopted (see Figure S26). For these systems geometry optimizations have been performed without constraints, starting from the X-ray structures. In $M(TT)_3Cl$ optimized complexes, the M–N and M–Cl bonds measure 2.426, 2.448 Å (M=Ag) and 2.168, 2.274 Å (M=Cu), respectively, to be compared with the X-ray values 2.3544(10), 2.4562(5) Å (**2-Ag**) and 2.130, 2.257 Å (**2-Cu**). In $Ag(TT)_4^+$ complex, the Ag–N bond measures 2.346-2.363 Å, to be compared with the X-ray value 2.308(4) Å.

The results of DFT/TDDFT calculations on $M(TT)_3Cl$ are reported in Figures S27 (scheme of excited states), S28, S29 (Plots of the MOs mainly involved in the lowest energy transitions) and Tables S8, S9 (Gaussian16 output of the $S_0 \rightarrow S_n$ and $T_0 \rightarrow T_n$ transitions), while those on $Ag(TT)_4^+$ are reported in Figures S30 (scheme of excited states), S31 (Plot of the MOs mainly involved in the lowest energy transitions) and Table S10 (Gaussian16 output of the $S_0 \rightarrow S_n$ and $T_0 \rightarrow T_n$ transitions).

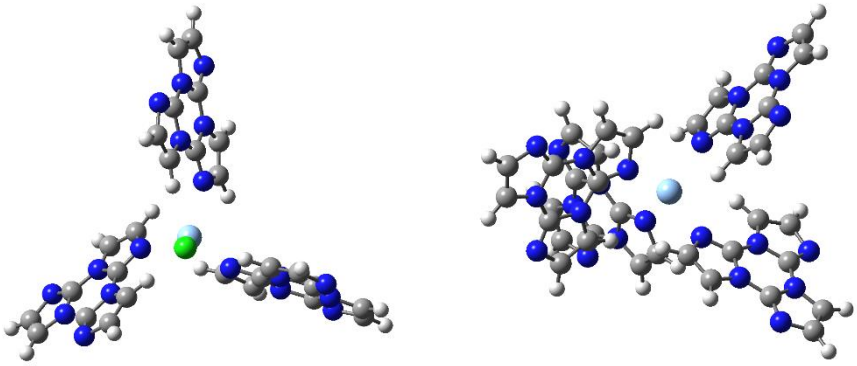


Figure S26. Discrete model compounds of **2-Ag**, $Ag(TT)_3Cl$ (left), and **3-Ag**, $Ag(TT)_4^+$ (right).

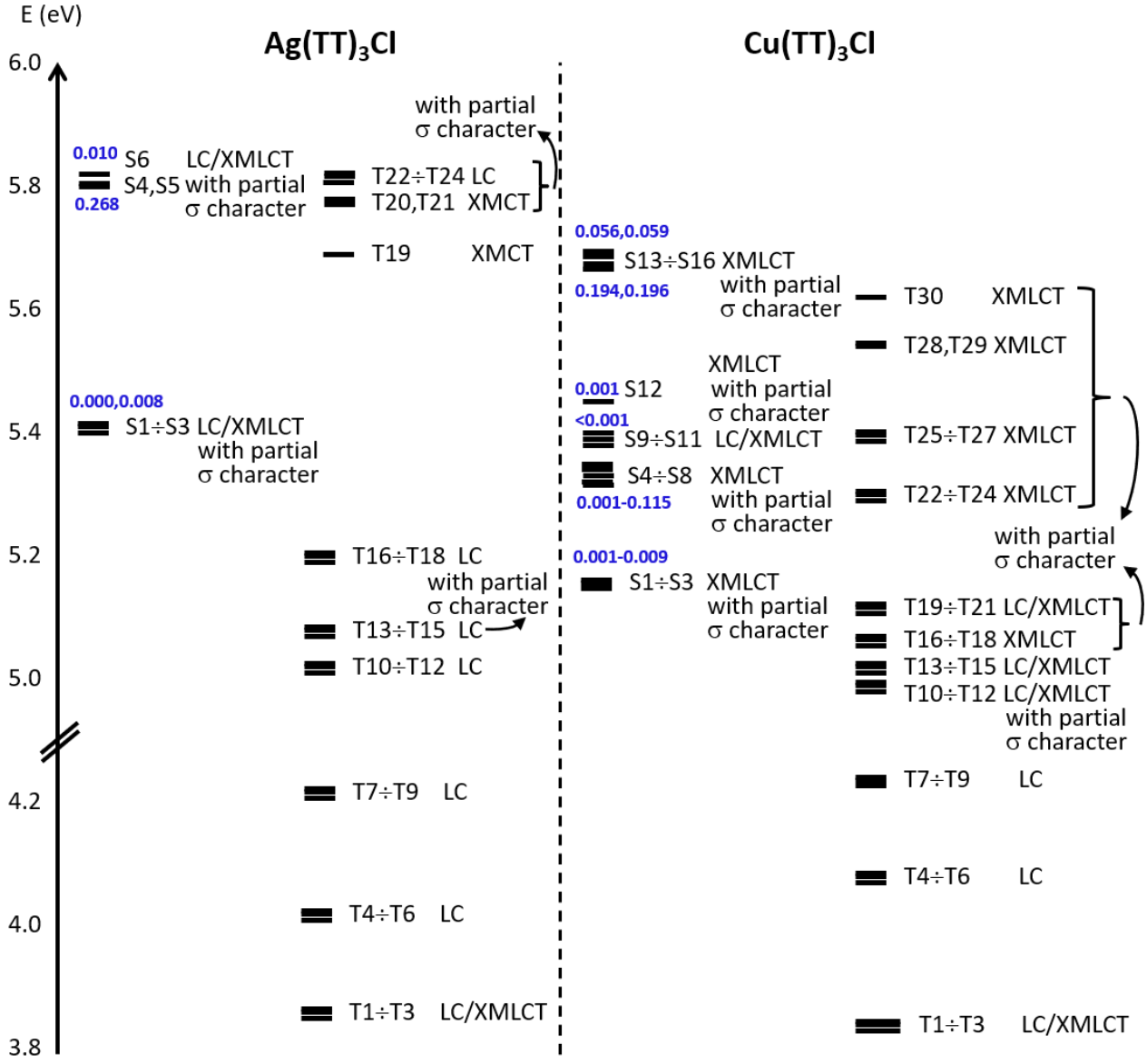
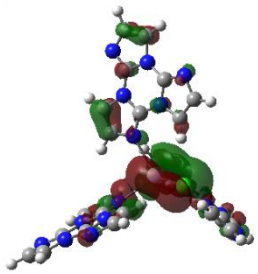
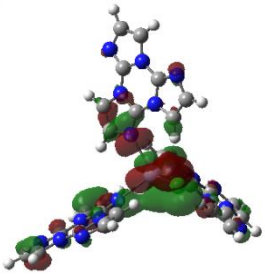


Figure S27. Scheme of singlet and triplet electronic levels with oscillator strengths (for singlet states, in blue) and character for model compounds $Ag(TT)_3Cl$ (at ωB97X/def2-TZVP level, left) and $Cu(TT)_3Cl$ (at ωB97X/6-311++G(d,p) level, right).

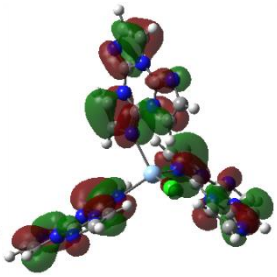
$Ag(TT)_3Cl$: HOMOs



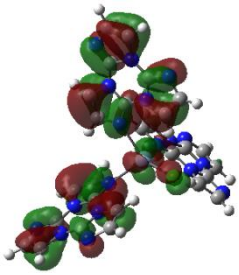
MO = 158 (HOMO-13)



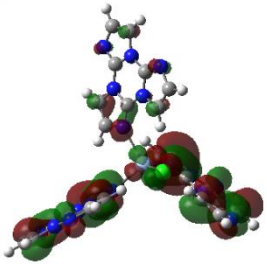
159 (HOMO-12)



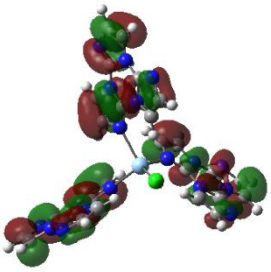
160 (HOMO-11)



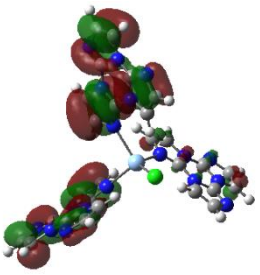
161 (HOMO-10)



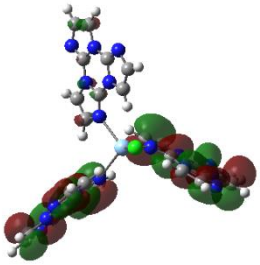
162 (HOMO-9)



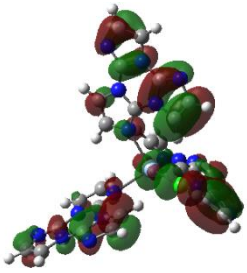
163 (HOMO-8)



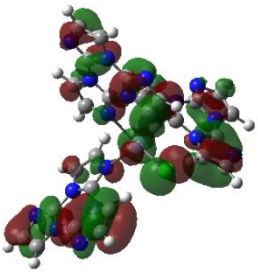
164 (HOMO-7)



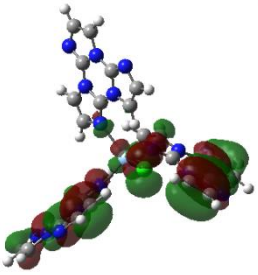
165 (HOMO-6)



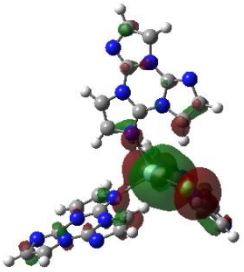
166 (HOMO-5)



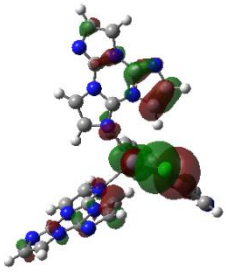
167 (HOMO-4)



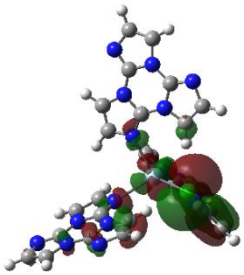
168 (HOMO-3)



169 (HOMO-2)

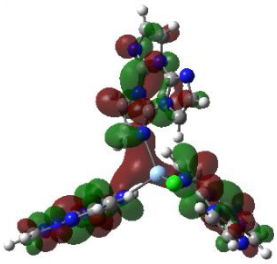


170 (HOMO-1)

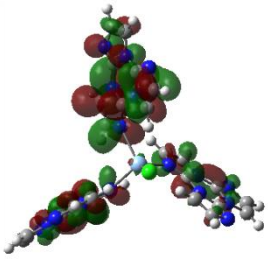


171 (HOMO)

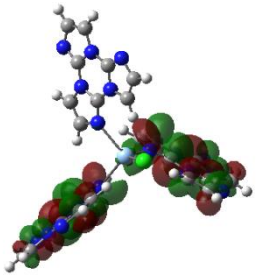
$Ag(TT)_3Cl$: LUMOs



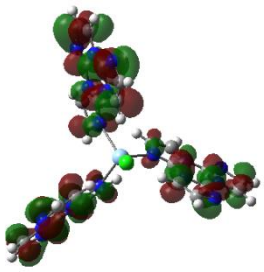
MO = 172 (LUMO)



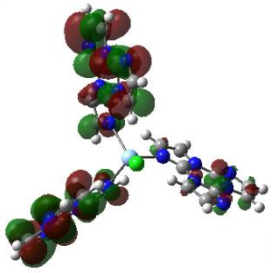
173 (LUMO+1)



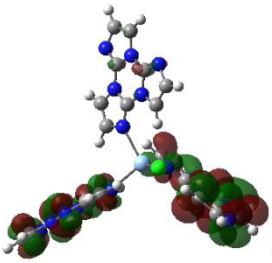
174 (LUMO+2)



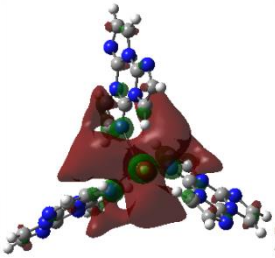
175 (LUMO+3)



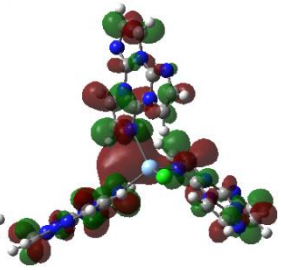
176 (LUMO+4)



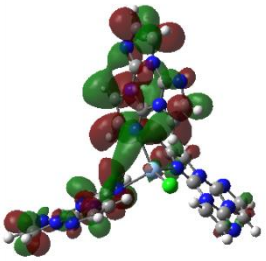
177 (LUMO+5)



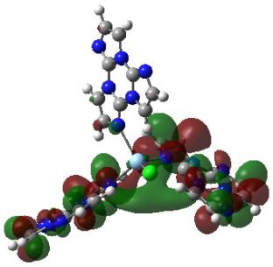
178 (LUMO+6)



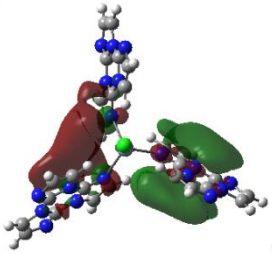
179 (LUMO+7)



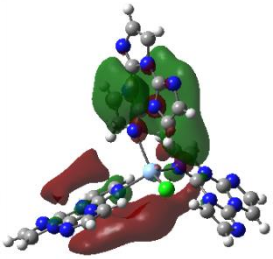
180 (LUMO+8)



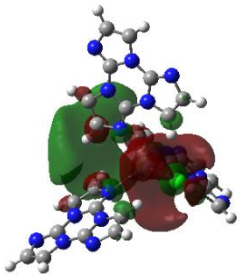
181 (LUMO+9)



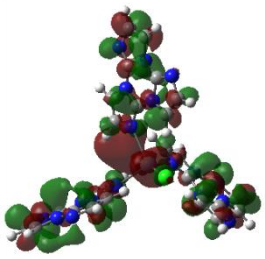
182 (LUMO+10)



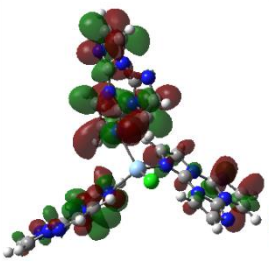
183 (LUMO+11)



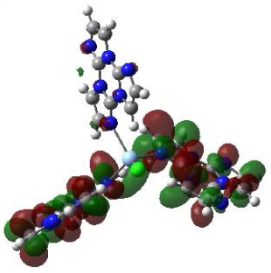
184 (LUMO+12)



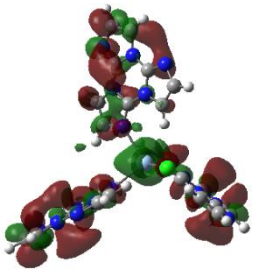
185 (LUMO+13)



186 (LUMO+14)



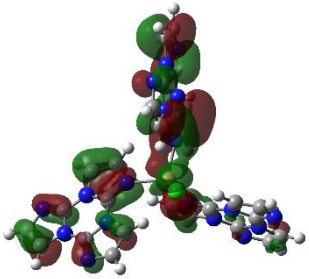
187 (LUMO+15)



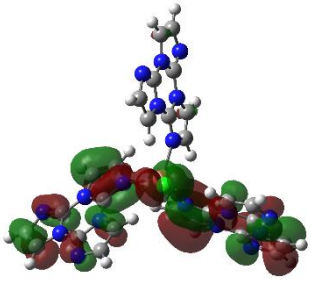
188 (LUMO+16)

Figure S28. Plots of the ωB97X/def2-TZVP MOs mainly involved in the lowest energy transitions of $Ag(TT)_3Cl$ (Isosurfaces value 0.02).

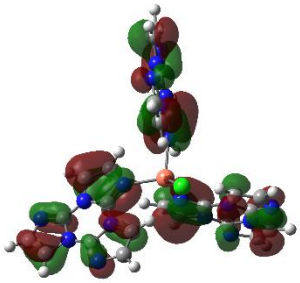
$Cu(TT)_3Cl$: HOMOs



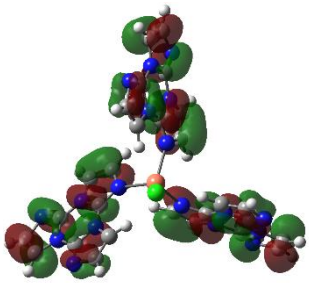
MO = 161 (HOMO-13)



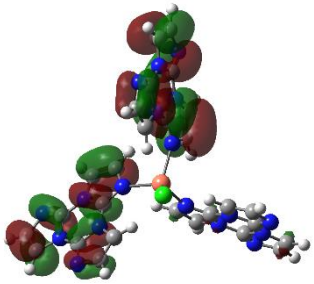
162 (HOMO-12)



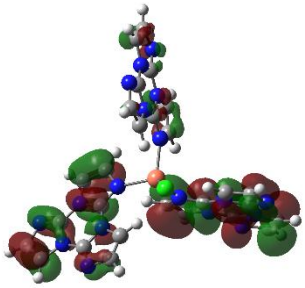
163 (HOMO-11)



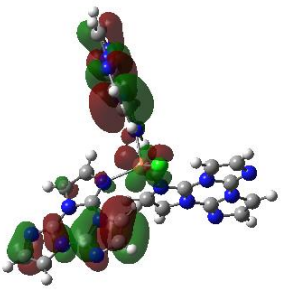
166 (HOMO-10)



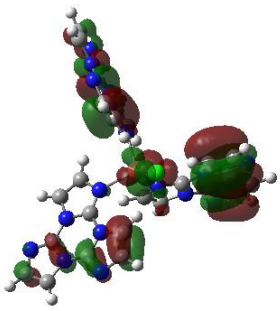
167 (HOMO-9)



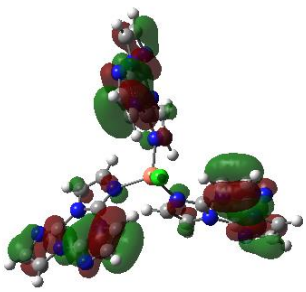
168 (HOMO-8)



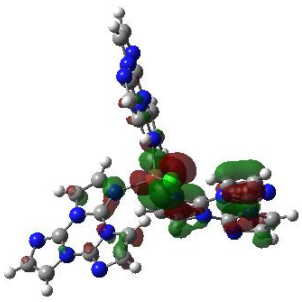
169 (HOMO-7)



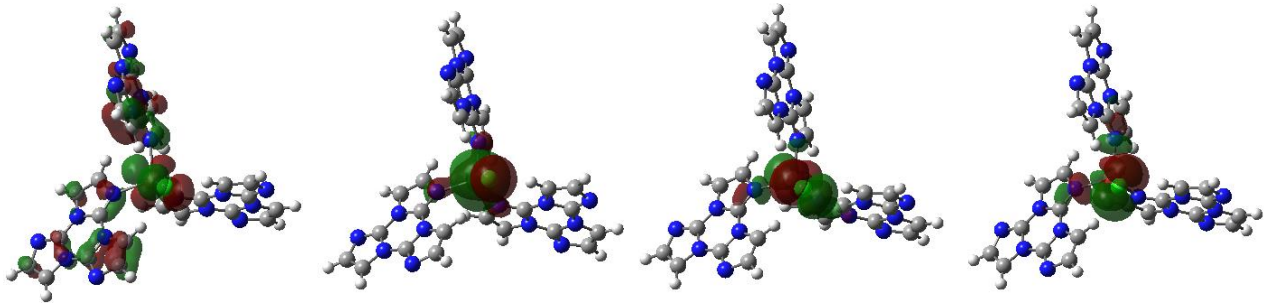
170 (HOMO-6)



171 (HOMO-5)

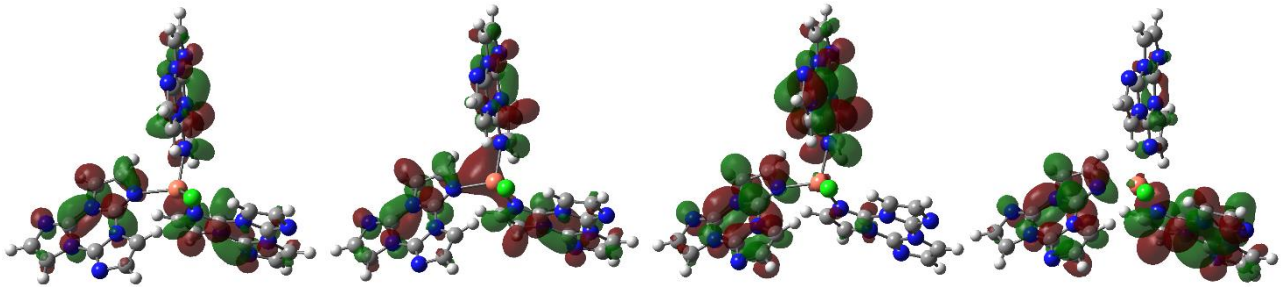


172 (HOMO-4)

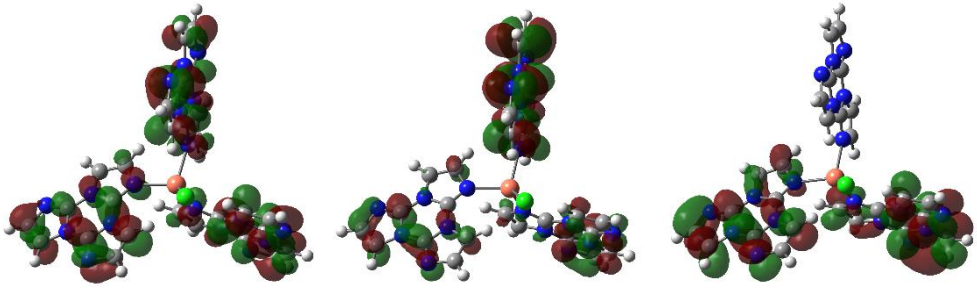


173 (HOMO-3) 174 (HOMO-2) 175 (HOMO-1) 176 (HOMO)

$Cu(TT)_3Cl$: LUMOs



MO = 177 (LUMO) 178 (LUMO+1) 179 (LUMO+2) 180 (LUMO+3)



181 (LUMO+4) 182 (LUMO+5) 183 (LUMO+6)

Figure S29. Plots of the ωB97X/6-311++G(d,p) MOs mainly involved in the lowest energy transitions of $Cu(TT)_3Cl$ (Isosurfaces value 0.02).

Table S8. First TD-ωB97X/def2-TZVP $S_0 \rightarrow S_n$ and $T_0 \rightarrow T_n$ transitions computed for the optimized geometry of $Ag(TT)_3Cl$.

Singlets:

```
Excited State   1:      Singlet-A      5.4066 eV  229.32 nm  f=0.0083  <S**2>=0.000
     163 -> 173       -0.24365
     164 -> 172       -0.23516
     164 -> 173       -0.17898
     165 -> 172       -0.12451
     165 -> 174        0.18025
     166 -> 175       -0.12192
     166 -> 176        0.24997
     166 -> 177        0.11634
     167 -> 175       -0.24310
     168 -> 177       -0.19198
     170 -> 175        0.11605

 Excited State   2:      Singlet-A      5.4068 eV  229.31 nm  f=0.0083  <S**2>=0.000
     163 -> 174        0.23820
     164 -> 172       -0.12606
     164 -> 174       -0.18314
     165 -> 172        0.23358
     165 -> 173       -0.18085
     166 -> 176        0.13561
     166 -> 177       -0.16010
     167 -> 175       -0.11515
     167 -> 177        0.21540
     168 -> 175        0.21702
     168 -> 176        0.18842

 Excited State   3:      Singlet-A      5.4142 eV  229.00 nm  f=0.0000  <S**2>=0.000
     163 -> 172        0.26539
     164 -> 173        0.25739
     165 -> 174        0.26047
     166 -> 175        0.26418
     167 -> 176       -0.24215
     168 -> 177       -0.24505
     169 -> 175       -0.10068
     170 -> 176        0.11660
     171 -> 177        0.11766

 Excited State   4:      Singlet-A      5.8026 eV  213.67 nm  f=0.2680  <S**2>=0.000
     163 -> 173       -0.11269
     164 -> 175       -0.11911
     166 -> 173        0.37150
     167 -> 172        0.28985
     167 -> 173        0.12392
     168 -> 174       -0.22490
     169 -> 173       -0.15255
     170 -> 172       -0.13101
     170 -> 173       -0.10233
     171 -> 174        0.10235

 Excited State   5:      Singlet-A      5.8028 eV  213.66 nm  f=0.2683  <S**2>=0.000
     163 -> 174       -0.10935
     165 -> 175       -0.10120
     166 -> 174        0.24147
     167 -> 174       -0.29978
     168 -> 172        0.30069
     168 -> 173       -0.21771
     169 -> 174       -0.15071
     170 -> 174        0.10350
     171 -> 172       -0.12929
     171 -> 173        0.10307

 Excited State   6:      Singlet-A      5.8284 eV  212.72 nm  f=0.0104  <S**2>=0.000
     163 -> 175       -0.15003
     164 -> 176        0.13030
     165 -> 177        0.13090
     166 -> 172        0.30239
     167 -> 173        0.30049
     168 -> 174        0.31279
     169 -> 172       -0.13842
     170 -> 173       -0.15329
     171 -> 174       -0.15371

 Excited State   7:      Singlet-A      6.0300 eV  205.61 nm  f=0.6092  <S**2>=0.000
     163 -> 173        0.14925
```

```
     163 -> 176        0.18453
     163 -> 177        0.11490
     164 -> 172        0.18840
     164 -> 173        0.12009
     164 -> 175       -0.15462
     164 -> 176        0.12879
     165 -> 172        0.15727
     165 -> 174       -0.12529
     165 -> 177       -0.15730
     166 -> 176        0.17808
     166 -> 177        0.12490
     167 -> 175       -0.14283
     168 -> 177       -0.16150

 Excited State   8:      Singlet-A      6.0301 eV  205.61 nm  f=0.6075  <S**2>=0.000
     161 -> 175       -0.10134
     163 -> 174        0.14765
     163 -> 176       -0.12187
     163 -> 177        0.18074
     164 -> 172       -0.15902
     164 -> 174       -0.12475
     164 -> 177       -0.14269
     165 -> 172        0.18795
     165 -> 173       -0.12310
     165 -> 175       -0.11405
     165 -> 176       -0.16147
     166 -> 176       -0.15756
     166 -> 177        0.11309
     167 -> 175        0.11231
     167 -> 177       -0.16616
     168 -> 175       -0.12882
     168 -> 176       -0.14211

 Excited State   9:      Singlet-A      6.0573 eV  204.68 nm  f=0.2063  <S**2>=0.000
     159 -> 178       -0.11423
     160 -> 173        0.15729
     161 -> 172       -0.13919
     163 -> 176        0.13881
     164 -> 175       -0.17169
     165 -> 176        0.10706
     168 -> 178        0.15618
     171 -> 178        0.28944
     171 -> 184        0.18322

 Excited State  10:      Singlet-A      6.0582 eV  204.65 nm  f=0.2084  <S**2>=0.000
     158 -> 178        0.11406
     160 -> 174       -0.15631
     162 -> 172       -0.13849
     163 -> 177       -0.13628
     165 -> 175        0.14354
     165 -> 177        0.12202
     167 -> 178        0.15054
     170 -> 178        0.28879
     170 -> 184        0.18278
```

Triplets:

```
Excited State   1:      Triplet-A      3.8608 eV  321.13 nm  f=0.0000  <S**2>=2.000
     163 -> 172        0.16006
     164 -> 173        0.15789
     164 -> 176        0.10768
     165 -> 174        0.11043
     166 -> 173        0.10397
     166 -> 175        0.30244
     166 -> 176       -0.10174
     167 -> 173        0.17434
     167 -> 176       -0.22275
     168 -> 174        0.13857
     168 -> 177       -0.18822
     169 -> 175       -0.10681
     170 -> 176        0.11898

 Excited State   2:      Triplet-A      3.8611 eV  321.11 nm  f=0.0000  <S**2>=2.000
     163 -> 173        0.13088
     164 -> 172        0.13625
     165 -> 174       -0.13250
     166 -> 173        0.16721
```

```
    166 -> 176       -0.20912
    166 -> 177       -0.12497
    167 -> 175        0.24311
    168 -> 174       -0.16775
    168 -> 175        0.10774
    168 -> 177        0.23702
    170 -> 175       -0.11243
    171 -> 177       -0.11081

Excited State   3:      Triplet-A      3.8612 eV  321.10 nm  f=0.0000  <S**2>=2.000
    163 -> 174        0.13300
    164 -> 174       -0.10469
    165 -> 172        0.14021
    166 -> 174        0.12035
    166 -> 176        0.13520
    166 -> 177       -0.14403
    167 -> 174       -0.15858
    167 -> 175       -0.13765
    167 -> 176       -0.12675
    167 -> 177        0.18824
    168 -> 173       -0.11579
    168 -> 175        0.21736
    168 -> 176        0.18114

Excited State   4:      Triplet-A      4.1075 eV  301.85 nm  f=0.0000  <S**2>=2.000
    160 -> 175       -0.14242
    161 -> 176       -0.13221
    162 -> 177        0.10645
    163 -> 172        0.23742
    163 -> 175       -0.13499
    164 -> 173        0.21664
    164 -> 176        0.21685
    165 -> 174        0.14502
    165 -> 177        0.15895
    166 -> 175       -0.11744

Excited State   5:      Triplet-A      4.1077 eV  301.84 nm  f=0.0000  <S**2>=2.000
    161 -> 175        0.11403
    162 -> 177       -0.12920
    163 -> 173        0.16850
    163 -> 176        0.16381
    163 -> 177        0.11766
    164 -> 172        0.19719
    164 -> 175       -0.11512
    165 -> 172        0.15263
    165 -> 174       -0.18392
    165 -> 177       -0.19942

Excited State   6:      Triplet-A      4.1078 eV  301.83 nm  f=0.0000  <S**2>=2.000
    162 -> 175        0.10142
    163 -> 174       -0.17118
    163 -> 176        0.11516
    163 -> 177       -0.16318
    164 -> 172        0.14208
    164 -> 174        0.14716
    164 -> 177        0.13487
    165 -> 172       -0.20446
    165 -> 173        0.12456
    165 -> 176        0.15048

Excited State   7:      Triplet-A      4.2075 eV  294.67 nm  f=0.0000  <S**2>=2.000
    160 -> 172       -0.23662
    161 -> 173        0.18896
    162 -> 174       -0.17691
    163 -> 172        0.10224
    163 -> 175        0.15810
    163 -> 179        0.13245
    164 -> 173        0.13170
    164 -> 176       -0.12837
    164 -> 180       -0.15024
    165 -> 174        0.12366
    165 -> 177       -0.13058
    165 -> 181       -0.14252
    166 -> 172        0.12086
    167 -> 173        0.11230
    168 -> 174        0.10640

Excited State   8:      Triplet-A      4.2079 eV  294.65 nm  f=0.0000  <S**2>=2.000
```

```
    160 -> 173        0.18069
    160 -> 174        0.10537
    161 -> 172       -0.15427
    161 -> 173       -0.12633
    162 -> 172        0.15284
    162 -> 174       -0.14252
    163 -> 173       -0.10662
    163 -> 180        0.11646
    164 -> 175       -0.13154
    164 -> 179       -0.10323
    165 -> 177       -0.10950
    165 -> 181       -0.11163
    167 -> 172       -0.11739

Excited State   9:      Triplet-A      4.2080 eV  294.64 nm  f=0.0000  <S**2>=2.000
    160 -> 173       -0.10450
    160 -> 174        0.17848
    161 -> 172        0.15185
    161 -> 174        0.14029
    162 -> 172        0.15239
    162 -> 173       -0.12631
    163 -> 174       -0.10399
    163 -> 181        0.11331
    164 -> 175        0.10940
    164 -> 181       -0.10645
    165 -> 175       -0.10848
    165 -> 176       -0.10523
    165 -> 179       -0.10168
    165 -> 180       -0.10127
    168 -> 172       -0.11984

Excited State  10:      Triplet-A      5.0247 eV  246.75 nm  f=0.0000  <S**2>=2.000
    160 -> 179        0.10018
    160 -> 180       -0.10347
    161 -> 180        0.15353
    163 -> 173        0.13985
    163 -> 175        0.16889
    164 -> 173        0.22429
    164 -> 175        0.17570
    164 -> 176       -0.15868
    164 -> 186        0.11716
    166 -> 172       -0.15059
    166 -> 173       -0.14066
    166 -> 176       -0.11815
    167 -> 173       -0.12039
    167 -> 176       -0.11274

Excited State  11:      Triplet-A      5.0249 eV  246.74 nm  f=0.0000  <S**2>=2.000
    162 -> 181       -0.16049
    163 -> 173       -0.10054
    163 -> 174       -0.10470
    163 -> 175        0.11297
    163 -> 177        0.11600
    164 -> 175       -0.10174
    165 -> 174        0.23037
    165 -> 175       -0.11393
    165 -> 177       -0.20472
    165 -> 187       -0.11514
    167 -> 172        0.11565
    168 -> 172        0.10323
    168 -> 174       -0.15480
    168 -> 177       -0.15665

Excited State  12:      Triplet-A      5.0249 eV  246.74 nm  f=0.0000  <S**2>=2.000
    160 -> 181        0.11646
    163 -> 174       -0.15479
    163 -> 176       -0.10821
    163 -> 177        0.10788
    164 -> 174        0.13907
    164 -> 175        0.11413
    165 -> 173        0.12207
    165 -> 175       -0.15557
    165 -> 176       -0.12833
    167 -> 174       -0.12396
    167 -> 177       -0.10102
    168 -> 172        0.13472

Excited State  13:      Triplet-A      5.0732 eV  244.39 nm  f=0.0000  <S**2>=2.000
```

```
    160 -> 175        0.17395
    161 -> 176        0.17983
    162 -> 177       -0.16592
    163 -> 179        0.13603
    164 -> 180       -0.13363
    165 -> 181       -0.11585
    166 -> 172       -0.14851
    166 -> 179        0.13208
    166 -> 191       -0.10872
    167 -> 173       -0.13252
    167 -> 176       -0.10989
    167 -> 180       -0.12429
    168 -> 174       -0.12014
    168 -> 177       -0.10504
    168 -> 181       -0.11480

Excited State  14:      Triplet-A      5.0738 eV  244.36 nm  f=0.0000  <S**2>=2.000
    160 -> 176        0.14191
    160 -> 177        0.11279
    161 -> 175        0.13941
    162 -> 175       -0.10038
    162 -> 177       -0.15267
    163 -> 180        0.10675
    164 -> 179       -0.11026
    165 -> 181       -0.10348
    166 -> 173        0.13539
    166 -> 176        0.12049
    166 -> 180        0.12145
    167 -> 172        0.11833
    167 -> 179       -0.11561
    168 -> 174       -0.11176
    168 -> 177       -0.10127
    168 -> 181       -0.10883

Excited State  15:      Triplet-A      5.0740 eV  244.35 nm  f=0.0000  <S**2>=2.000
    160 -> 176       -0.11364
    160 -> 177        0.13920
    161 -> 175       -0.11560
    161 -> 177        0.11122
    162 -> 175       -0.11042
    162 -> 176       -0.13351
    163 -> 181        0.10532
    165 -> 179       -0.11020
    167 -> 174       -0.12339
    167 -> 177       -0.10138
    167 -> 181       -0.11331
    168 -> 172        0.11849
    168 -> 179       -0.11603

Excited State  16:      Triplet-A      5.2036 eV  238.26 nm  f=0.0000  <S**2>=2.000
    160 -> 172        0.18056
    160 -> 175        0.11846
    161 -> 173       -0.21371
    162 -> 174        0.20650
    163 -> 172        0.13523
    163 -> 179        0.10436
    164 -> 173        0.10413
    164 -> 180       -0.13036
    165 -> 174        0.10068
    165 -> 181       -0.12619

Excited State  17:      Triplet-A      5.2048 eV  238.21 nm  f=0.0000  <S**2>=2.000
    160 -> 173       -0.21526
    161 -> 172        0.18207
    161 -> 173        0.11202
    161 -> 175        0.11456
    162 -> 174        0.12172
    163 -> 173       -0.10206
    163 -> 180        0.12768
    164 -> 172       -0.13623
    164 -> 179       -0.10894
    166 -> 180       -0.10646

Excited State  18:      Triplet-A      5.2048 eV  238.21 nm  f=0.0000  <S**2>=2.000
    160 -> 174        0.21361
    161 -> 174        0.11779
    162 -> 172        0.18025
    162 -> 173       -0.11910
```

```
    162 -> 175        0.10530
    163 -> 181       -0.12409
    165 -> 172        0.13532
    165 -> 179        0.10857

Excited State  19:      Triplet-A      5.7071 eV  217.25 nm  f=0.0000  <S**2>=2.000
    166 -> 178        0.14720
    166 -> 184        0.10366
    169 -> 178        0.45092
    169 -> 184        0.31129
    169 -> 185        0.14793
    169 -> 188       -0.14070

Excited State  20:      Triplet-A      5.7734 eV  214.75 nm  f=0.0000  <S**2>=2.000
    159 -> 178       -0.17118
    168 -> 178        0.18554
    168 -> 184        0.12298
    170 -> 178       -0.16019
    170 -> 184       -0.11526
    171 -> 178        0.32803
    171 -> 184        0.22905
    171 -> 185        0.10466

Excited State  21:      Triplet-A      5.7747 eV  214.70 nm  f=0.0000  <S**2>=2.000
    158 -> 178       -0.17021
    167 -> 178       -0.17662
    167 -> 184       -0.11743
    170 -> 178       -0.32521
    170 -> 184       -0.22722
    170 -> 185       -0.10358
    171 -> 178       -0.15833
    171 -> 184       -0.11423

Excited State  22:      Triplet-A      5.7982 eV  213.83 nm  f=0.0000  <S**2>=2.000
    145 -> 177        0.10917
    160 -> 179       -0.11521
    161 -> 180       -0.11801
    162 -> 181        0.11861
    163 -> 185        0.10541
    164 -> 186       -0.11184
    165 -> 187        0.11168
    166 -> 172       -0.14084
    166 -> 191        0.16164
    167 -> 173       -0.12668
    168 -> 174       -0.13162
    168 -> 195        0.10287

Excited State  23:      Triplet-A      5.8003 eV  213.75 nm  f=0.0000  <S**2>=2.000
    143 -> 175       -0.10761
    143 -> 176        0.11619
    160 -> 180        0.11610
    161 -> 179        0.10028
    163 -> 186       -0.11080
    166 -> 173       -0.14436
    166 -> 186       -0.10021
    166 -> 194        0.11757
    167 -> 172       -0.13717
    167 -> 191        0.14650
    171 -> 178        0.12745

Excited State  24:      Triplet-A      5.8005 eV  213.75 nm  f=0.0000  <S**2>=2.000
    145 -> 177       -0.13197
    160 -> 181        0.11444
    163 -> 187        0.10712
    167 -> 174        0.11625
    168 -> 172       -0.13990
    168 -> 191        0.15025
    170 -> 178       -0.13378

Excited State  25:      Triplet-A      6.1489 eV  201.64 nm  f=0.0000  <S**2>=2.000
    160 -> 172       -0.12882
    161 -> 173        0.15046
    162 -> 174       -0.14190
    163 -> 175       -0.16042
    164 -> 176        0.15746
    165 -> 177        0.14810
    166 -> 172       -0.13208
    167 -> 180        0.12367
```

```
     168 -> 181        0.12142

 Excited State  26:      Triplet-A      6.1499 eV  201.60 nm  f=0.0000  <S**2>=2.000
     160 -> 173        0.11859
     161 -> 172       -0.14340
     163 -> 176       -0.14940
     164 -> 175        0.16906
     165 -> 176       -0.10173
     166 -> 173        0.12303
     166 -> 180       -0.12863

 Excited State  27:      Triplet-A      6.1500 eV  201.60 nm  f=0.0000  <S**2>=2.000
     160 -> 174       -0.11731
     162 -> 172       -0.14212
     163 -> 177        0.14499
     165 -> 175       -0.13660
     165 -> 177       -0.12285
     168 -> 172       -0.10139

 Excited State  28:      Triplet-A      6.2082 eV  199.71 nm  f=0.0000  <S**2>=2.000
     137 -> 172       -0.10017
     158 -> 174        0.21301
     159 -> 173        0.22074
     167 -> 174        0.13911
     168 -> 173       -0.15262
     169 -> 172        0.12886
     170 -> 173        0.14184
     170 -> 174        0.21476
     171 -> 173       -0.22566
     171 -> 174        0.13721

 Excited State  29:      Triplet-A      6.2268 eV  199.11 nm  f=0.0000  <S**2>=2.000
     137 -> 173        0.13414
     158 -> 174        0.13265
     159 -> 172       -0.14628
     159 -> 173       -0.12671
     159 -> 175       -0.10748
     168 -> 172        0.12369
     168 -> 174        0.10507
     169 -> 173       -0.19159
     170 -> 173       -0.18106
     171 -> 172        0.17652
     171 -> 174        0.18572
     171 -> 175        0.11184

 Excited State  30:      Triplet-A      6.2271 eV  199.10 nm  f=0.0000  <S**2>=2.000
     158 -> 172       -0.14408
     158 -> 173        0.12971
     159 -> 174        0.13132
     167 -> 172       -0.11798
     167 -> 174        0.12374
     168 -> 173        0.10665
     169 -> 174       -0.19070
     170 -> 172       -0.17401
     170 -> 174        0.19156
     171 -> 173        0.17926
```

Table S9. First TD-ωB97X/def2-TZVP $S_0 \rightarrow S_n$ and $T_0 \rightarrow T_n$ transitions computed for the optimized geometry of $Cu(TT)_3Cl$.

Singlets:

```
Excited State   1:      Singlet-A      5.1537 eV  240.57 nm  f=0.0008  <S**2>=0.000
     175 -> 180       -0.38006
     176 -> 179        0.46147
     176 -> 182       -0.11715

 Excited State   2:      Singlet-A      5.1726 eV  239.70 nm  f=0.0093  <S**2>=0.000
     175 -> 179       -0.29541
     175 -> 180       -0.13104
     176 -> 177       -0.28790
     176 -> 178       -0.23596
     176 -> 180        0.30377
     176 -> 181        0.22257

 Excited State   3:      Singlet-A      5.1747 eV  239.59 nm  f=0.0094  <S**2>=0.000
     175 -> 177        0.28447
```

```
    175 -> 178        0.23214
    175 -> 179       -0.12504
    175 -> 180        0.34666
    175 -> 181       -0.21957
    176 -> 179        0.25442
    176 -> 180        0.10397

Excited State   4:      Singlet-A      5.3251 eV  232.83 nm  f=0.1155  <S**2>=0.000
    174 -> 179        0.44458
    174 -> 182       -0.13309
    175 -> 177       -0.18090
    175 -> 178       -0.15253
    175 -> 180        0.17441
    175 -> 181        0.14190
    176 -> 179        0.16858

Excited State   5:      Singlet-A      5.3271 eV  232.74 nm  f=0.1080  <S**2>=0.000
    172 -> 181       -0.10216
    174 -> 180        0.32826
    174 -> 183       -0.10108
    175 -> 179        0.22281
    176 -> 177       -0.22723
    176 -> 178       -0.18911
    176 -> 180       -0.20238
    176 -> 181        0.17634

Excited State   6:      Singlet-A      5.3319 eV  232.53 nm  f=0.0043  <S**2>=0.000
    174 -> 179        0.41671
    174 -> 182       -0.11021
    175 -> 177        0.21915
    175 -> 178        0.17625
    175 -> 179        0.11266
    175 -> 180       -0.18543
    175 -> 181       -0.16452
    176 -> 179       -0.18603

Excited State   7:      Singlet-A      5.3350 eV  232.40 nm  f=0.0122  <S**2>=0.000
    174 -> 180        0.51358
    174 -> 183       -0.14001
    174 -> 203       -0.10858
    175 -> 179       -0.16693
    176 -> 177        0.16677
    176 -> 178        0.13187
    176 -> 180        0.10962
    176 -> 181       -0.12289

Excited State   8:      Singlet-A      5.3450 eV  231.96 nm  f=0.0009  <S**2>=0.000
    167 -> 179        0.12773
    168 -> 180        0.13770
    170 -> 183       -0.10652
    171 -> 181        0.15645
    174 -> 177        0.19060
    174 -> 178        0.15793
    175 -> 179        0.30209
    176 -> 180        0.34523
    176 -> 183       -0.11117

Excited State   9:      Singlet-A      5.3832 eV  230.32 nm  f=0.0005  <S**2>=0.000
    166 -> 179       -0.17299
    166 -> 180       -0.15159
    167 -> 177        0.13604
    167 -> 178        0.12809
    167 -> 180       -0.16579
    168 -> 177        0.11923
    168 -> 178        0.11262
    168 -> 179       -0.16472
    169 -> 181       -0.19384
    169 -> 183        0.14761
    170 -> 182        0.14964
    171 -> 182        0.12621
    171 -> 183        0.21167
    173 -> 181       -0.11184
    175 -> 177       -0.11189
    175 -> 180        0.11382
    176 -> 179        0.11007

Excited State  10:      Singlet-A      5.3834 eV  230.31 nm  f=0.0005  <S**2>=0.000
    166 -> 179        0.15185
```

```
    166 -> 180       -0.17023
    167 -> 177       -0.11811
    167 -> 178       -0.11197
    167 -> 179       -0.17063
    168 -> 177        0.13540
    168 -> 178        0.12702
    168 -> 180        0.16309
    169 -> 182        0.15121
    170 -> 181       -0.19212
    170 -> 183       -0.14477
    171 -> 182       -0.21090
    171 -> 183        0.12864
    172 -> 181        0.11046
    175 -> 179        0.11530
    176 -> 177       -0.11177
    176 -> 180       -0.11266

Excited State  11:      Singlet-A      5.3966 eV  229.75 nm  f=0.0006  <S**2>=0.000
    166 -> 177        0.15599
    166 -> 178        0.14544
    167 -> 179       -0.21081
    168 -> 180       -0.21596
    169 -> 182        0.14687
    170 -> 183        0.15128
    171 -> 181       -0.21271
    172 -> 183       -0.11370
    173 -> 182        0.11102
    175 -> 179        0.23692
    176 -> 180        0.24556

Excited State  12:      Singlet-A      5.4542 eV  227.32 nm  f=0.0012  <S**2>=0.000
    174 -> 177        0.38086
    174 -> 178        0.32738
    174 -> 181       -0.31774
    175 -> 179       -0.15992
    176 -> 180       -0.16048

Excited State  13:      Singlet-A      5.6692 eV  218.70 nm  f=0.1962  <S**2>=0.000
    171 -> 179       -0.15779
    172 -> 179        0.21308
    173 -> 177        0.20224
    173 -> 178        0.16818
    173 -> 180       -0.21051
    176 -> 177        0.17265
    176 -> 181        0.18495
    176 -> 195       -0.15299
    176 -> 204        0.11062
    176 -> 208       -0.14213

Excited State  14:      Singlet-A      5.6711 eV  218.63 nm  f=0.1942  <S**2>=0.000
    171 -> 180        0.15846
    172 -> 177        0.20017
    172 -> 178        0.16558
    172 -> 180        0.20429
    173 -> 179        0.22156
    175 -> 177        0.17100
    175 -> 181        0.18535
    175 -> 195       -0.15291
    175 -> 204        0.11036
    175 -> 208       -0.14155

Excited State  15:      Singlet-A      5.6920 eV  217.82 nm  f=0.0591  <S**2>=0.000
    171 -> 179        0.14100
    172 -> 179       -0.17274
    173 -> 177       -0.18054
    173 -> 178       -0.15275
    173 -> 180        0.17082
    173 -> 181        0.10020
    176 -> 177        0.24150
    176 -> 181        0.23479
    176 -> 195       -0.18629
    176 -> 204        0.12240
    176 -> 208       -0.14567

Excited State  16:      Singlet-A      5.6941 eV  217.74 nm  f=0.0563  <S**2>=0.000
    171 -> 180       -0.14479
    172 -> 177       -0.18154
    172 -> 178       -0.15310
```

```
     172 -> 180       -0.16642
     172 -> 181        0.10055
     173 -> 179       -0.17533
     175 -> 177        0.24111
     175 -> 181        0.23684
     175 -> 195       -0.18710
     175 -> 204        0.12267
     175 -> 208       -0.14555

 Excited State  17:      Singlet-A      5.7430 eV  215.89 nm  f=0.0310  <S**2>=0.000
     169 -> 179       -0.13796
     170 -> 180       -0.14398
     171 -> 177        0.20467
     171 -> 178        0.18463
     172 -> 180        0.36159
     173 -> 179       -0.35344
     174 -> 181        0.10208

 Excited State  18:      Singlet-A      5.8074 eV  213.49 nm  f=0.0113  <S**2>=0.000
     172 -> 180       -0.10504
     173 -> 179        0.10974
     174 -> 177        0.31793
     174 -> 181        0.32512
     174 -> 187        0.10171
     174 -> 195       -0.24526
     174 -> 198        0.11368
     174 -> 204        0.14525
     174 -> 208       -0.16049
     174 -> 238       -0.10576

 Excited State  19:      Singlet-A      5.8268 eV  212.78 nm  f=0.0020  <S**2>=0.000
     169 -> 180       -0.11785
     170 -> 179        0.13346
     172 -> 179        0.40912
     172 -> 182       -0.11307
     173 -> 180        0.37954
     173 -> 183       -0.10392

 Excited State  20:      Singlet-A      5.8451 eV  212.12 nm  f=0.0233  <S**2>=0.000
     169 -> 179       -0.10639
     170 -> 180        0.10223
     172 -> 177       -0.19252
     172 -> 178       -0.17106
     172 -> 180        0.20762
     173 -> 179        0.20595
     176 -> 178        0.23048
     176 -> 181        0.23273
     176 -> 198        0.21593
     176 -> 208        0.12650
```

Triplets:

```
Excited State   1:      Triplet-A      3.8338 eV  323.40 nm  f=0.0000  <S**2>=2.000
     166 -> 179        0.10838
     167 -> 179       -0.13610
     167 -> 182       -0.11513
     169 -> 179       -0.15740
     169 -> 181        0.18139
     169 -> 182        0.21423
     170 -> 179        0.11316
     170 -> 181       -0.11726
     170 -> 182       -0.12859
     171 -> 179        0.15501
     171 -> 181       -0.16882
     171 -> 182       -0.20057
     173 -> 179       -0.10765
     173 -> 181        0.10197
     173 -> 182        0.11250

 Excited State   2:      Triplet-A      3.8342 eV  323.37 nm  f=0.0000  <S**2>=2.000
     169 -> 179        0.12456
     169 -> 180        0.12559
     169 -> 181        0.18740
     169 -> 182       -0.10840
     169 -> 183       -0.18631
     170 -> 181        0.13219
     171 -> 179        0.10197
     171 -> 180        0.13732
```

```
    171 -> 181        0.14226
    171 -> 183       -0.19847

Excited State   3:      Triplet-A      3.8343 eV  323.36 nm  f=0.0000  <S**2>=2.000
    168 -> 180       -0.15992
    168 -> 183       -0.10924
    170 -> 180       -0.19567
    170 -> 181        0.19035
    170 -> 182       -0.11683
    170 -> 183        0.22965
    171 -> 180        0.13501
    171 -> 181       -0.19869
    171 -> 182        0.11548
    171 -> 183       -0.14753
    172 -> 180        0.12366
    172 -> 181       -0.10065
    172 -> 183       -0.11806

Excited State   4:      Triplet-A      4.0849 eV  303.52 nm  f=0.0000  <S**2>=2.000
    162 -> 181       -0.12312
    163 -> 183       -0.11928
    166 -> 180       -0.17623
    166 -> 183       -0.20199
    167 -> 183       -0.11789
    168 -> 177        0.18722
    168 -> 178        0.19448
    168 -> 180        0.10595
    168 -> 181        0.10081
    168 -> 182       -0.12091
    170 -> 181        0.10977
    171 -> 180        0.10901

Excited State   5:      Triplet-A      4.0850 eV  303.51 nm  f=0.0000  <S**2>=2.000
    161 -> 181        0.12381
    163 -> 182        0.11796
    166 -> 179        0.17860
    166 -> 182        0.20317
    167 -> 177       -0.18737
    167 -> 178       -0.19500
    167 -> 180        0.10019
    167 -> 181       -0.10266
    167 -> 182       -0.11446
    168 -> 179        0.10043
    168 -> 183        0.12252
    169 -> 181       -0.11036
    171 -> 179       -0.10748

Excited State   6:      Triplet-A      4.0874 eV  303.34 nm  f=0.0000  <S**2>=2.000
    161 -> 182       -0.11546
    162 -> 183       -0.11207
    163 -> 181       -0.14039
    166 -> 177       -0.17833
    166 -> 178       -0.18743
    166 -> 181       -0.11744
    167 -> 179        0.19247
    167 -> 182        0.19837
    168 -> 180        0.18504
    168 -> 183        0.19153
    169 -> 179       -0.10116
    171 -> 181       -0.10999

Excited State   7:      Triplet-A      4.1713 eV  297.23 nm  f=0.0000  <S**2>=2.000
    161 -> 179        0.10932
    162 -> 177       -0.14423
    162 -> 178       -0.14585
    162 -> 180       -0.11194
    163 -> 180       -0.20141
    166 -> 180        0.11033
    166 -> 183       -0.11257
    168 -> 181        0.15421

Excited State   8:      Triplet-A      4.1714 eV  297.22 nm  f=0.0000  <S**2>=2.000
    161 -> 177       -0.14426
    161 -> 178       -0.14632
    161 -> 180        0.11121
    162 -> 179        0.11364
    163 -> 179       -0.19816
    166 -> 179        0.11104
```

```
    166 -> 182       -0.11439
    167 -> 181        0.15544
    167 -> 198       -0.10031

Excited State   9:      Triplet-A      4.1741 eV  297.03 nm  f=0.0000  <S**2>=2.000
    161 -> 179        0.18098
    161 -> 182        0.10334
    162 -> 180        0.18043
    162 -> 183        0.10357
    163 -> 177        0.17428
    163 -> 178        0.17371
    166 -> 181        0.15592
    167 -> 179        0.13329
    167 -> 182       -0.12115
    168 -> 180        0.13322
    168 -> 183       -0.12091
    172 -> 180       -0.11668
    173 -> 179        0.11804

Excited State  10:      Triplet-A      4.9756 eV  249.18 nm  f=0.0000  <S**2>=2.000
    161 -> 182        0.12052
    162 -> 183        0.10743
    163 -> 181        0.16008
    166 -> 198       -0.11432
    167 -> 202       -0.11357
    168 -> 203        0.10097
    173 -> 179       -0.10589
    175 -> 180       -0.22611
    176 -> 179        0.25940

Excited State  11:      Triplet-A      4.9886 eV  248.54 nm  f=0.0000  <S**2>=2.000
    161 -> 181       -0.13272
    163 -> 182       -0.13514
    167 -> 181       -0.13612
    167 -> 198       -0.12520
    174 -> 179       -0.13684
    175 -> 179       -0.11489
    175 -> 180       -0.13793
    176 -> 177       -0.11429
    176 -> 179       -0.11250
    176 -> 180        0.10540
    176 -> 181        0.12924

Excited State  12:      Triplet-A      4.9896 eV  248.48 nm  f=0.0000  <S**2>=2.000
    162 -> 181       -0.13165
    163 -> 183       -0.13637
    168 -> 181       -0.13684
    168 -> 198       -0.12503
    174 -> 180       -0.13615
    175 -> 177        0.11374
    175 -> 179       -0.12343
    175 -> 180        0.11972
    175 -> 181       -0.12844
    176 -> 180        0.12946

Excited State  13:      Triplet-A      5.0049 eV  247.73 nm  f=0.0000  <S**2>=2.000
    166 -> 181        0.17166
    167 -> 179        0.18545
    167 -> 182       -0.10558
    168 -> 180        0.17756
    168 -> 183       -0.10326
    169 -> 179       -0.13510
    169 -> 182       -0.12103
    170 -> 180       -0.12774
    170 -> 183       -0.11333
    171 -> 177        0.15426
    171 -> 178        0.15824
    172 -> 180        0.12016
    173 -> 179       -0.12879
    174 -> 177        0.11316

Excited State  14:      Triplet-A      5.0068 eV  247.63 nm  f=0.0000  <S**2>=2.000
    166 -> 179       -0.15945
    167 -> 180       -0.11510
    167 -> 181       -0.15537
    168 -> 179       -0.11388
    169 -> 177       -0.12031
    169 -> 178       -0.12598
```

```
    171 -> 179        0.17118
    171 -> 182        0.13064
    173 -> 177       -0.11700
    173 -> 178       -0.11248
    174 -> 179        0.14063

Excited State  15:      Triplet-A      5.0070 eV  247.62 nm  f=0.0000  <S**2>=2.000
    166 -> 180       -0.15690
    167 -> 179       -0.10743
    168 -> 180        0.12381
    168 -> 181       -0.15390
    170 -> 177       -0.12006
    170 -> 178       -0.12542
    170 -> 180       -0.10106
    171 -> 180        0.17305
    171 -> 183        0.13224
    172 -> 177        0.11669
    172 -> 178        0.11194
    174 -> 180        0.13977

Excited State  16:      Triplet-A      5.0621 eV  244.92 nm  f=0.0000  <S**2>=2.000
    166 -> 179       -0.10598
    175 -> 179        0.19411
    176 -> 177        0.19652
    176 -> 178        0.16687
    176 -> 179        0.25642
    176 -> 180       -0.16132
    176 -> 181       -0.15286

Excited State  17:      Triplet-A      5.0630 eV  244.89 nm  f=0.0000  <S**2>=2.000
    166 -> 180        0.10053
    175 -> 177        0.18032
    175 -> 178        0.15249
    175 -> 179       -0.15224
    175 -> 181       -0.13821
    176 -> 179        0.27328
    176 -> 180        0.19242

Excited State  18:      Triplet-A      5.0661 eV  244.73 nm  f=0.0000  <S**2>=2.000
    162 -> 183        0.10554
    168 -> 180       -0.13691
    175 -> 177        0.10007
    175 -> 180        0.39490
    176 -> 179       -0.15200

Excited State  19:      Triplet-A      5.1078 eV  242.73 nm  f=0.0000  <S**2>=2.000
    161 -> 179       -0.12015
    162 -> 180       -0.10248
    167 -> 179        0.10192
    169 -> 179        0.12106
    169 -> 182        0.10613
    170 -> 180        0.10314
    174 -> 177        0.17198
    174 -> 178        0.14144
    174 -> 181       -0.13841
    175 -> 180        0.11838
    176 -> 179       -0.13900

Excited State  20:      Triplet-A      5.1127 eV  242.50 nm  f=0.0000  <S**2>=2.000
    163 -> 179       -0.11904
    171 -> 182       -0.11542
    174 -> 179        0.26568
    175 -> 179       -0.11052
    176 -> 180        0.12225

Excited State  21:      Triplet-A      5.1137 eV  242.46 nm  f=0.0000  <S**2>=2.000
    163 -> 180       -0.12102
    171 -> 183       -0.11532
    174 -> 180        0.26210
    175 -> 180        0.14419
    176 -> 179        0.10406

Excited State  22:      Triplet-A      5.2914 eV  234.31 nm  f=0.0000  <S**2>=2.000
    174 -> 177       -0.14176
    174 -> 178       -0.12571
    174 -> 181        0.12137
    175 -> 179       -0.41740
    175 -> 182        0.12515
```

```
    176 -> 180       -0.37789
    176 -> 183        0.11230

Excited State  23:      Triplet-A      5.3096 eV  233.51 nm  f=0.0000  <S**2>=2.000
    174 -> 179        0.26011
    175 -> 177        0.29429
    175 -> 178        0.24666
    175 -> 179        0.11828
    175 -> 180       -0.21106
    175 -> 181       -0.21682
    176 -> 179       -0.20810
    176 -> 180       -0.14272

Excited State  24:      Triplet-A      5.3110 eV  233.45 nm  f=0.0000  <S**2>=2.000
    174 -> 180       -0.25623
    175 -> 179        0.18469
    175 -> 180        0.12731
    176 -> 177       -0.29479
    176 -> 178       -0.24650
    176 -> 179        0.12881
    176 -> 180       -0.24254
    176 -> 181        0.21596

Excited State  25:      Triplet-A      5.3881 eV  230.11 nm  f=0.0000  <S**2>=2.000
    163 -> 179        0.13047
    174 -> 179        0.41537
    174 -> 182       -0.12735
    174 -> 202        0.10376
    175 -> 177       -0.14157
    175 -> 178       -0.10588
    175 -> 180        0.11926
    176 -> 179        0.11134

Excited State  26:      Triplet-A      5.3906 eV  230.00 nm  f=0.0000  <S**2>=2.000
    163 -> 180       -0.13034
    174 -> 180       -0.41745
    174 -> 183        0.12728
    174 -> 203        0.10382
    175 -> 179       -0.12251
    176 -> 177        0.13418
    176 -> 178        0.10001
    176 -> 180        0.10214

Excited State  27:      Triplet-A      5.3996 eV  229.62 nm  f=0.0000  <S**2>=2.000
    162 -> 180        0.10200
    172 -> 180       -0.10684
    174 -> 177        0.33292
    174 -> 178        0.26130
    174 -> 181       -0.23967
    176 -> 180       -0.10613

Excited State  28:      Triplet-A      5.5252 eV  224.40 nm  f=0.0000  <S**2>=2.000
    176 -> 177        0.24008
    176 -> 181        0.17524
    176 -> 187        0.12664
    176 -> 195       -0.18905
    176 -> 201        0.13921
    176 -> 204        0.16859
    176 -> 205        0.14169
    176 -> 208       -0.24549
    176 -> 225       -0.11976
    176 -> 229       -0.11219
    176 -> 232       -0.14480
    176 -> 233        0.15037
    176 -> 238       -0.17959
    176 -> 241        0.11102
    176 -> 245       -0.12148
    176 -> 268        0.13455

Excited State  29:      Triplet-A      5.5272 eV  224.32 nm  f=0.0000  <S**2>=2.000
    175 -> 177        0.23957
    175 -> 181        0.17572
    175 -> 187        0.12658
    175 -> 195       -0.18943
    175 -> 201        0.13929
    175 -> 204        0.16868
    175 -> 205        0.14174
    175 -> 208       -0.24574
```

```
     175 -> 225       -0.11971
     175 -> 229       -0.11235
     175 -> 232       -0.14506
     175 -> 233        0.15044
     175 -> 238       -0.17956
     175 -> 241        0.11112
     175 -> 245       -0.12147
     175 -> 268        0.13471

 Excited State  30:      Triplet-A      5.6170 eV  220.73 nm  f=0.0000  <S**2>=2.000
     174 -> 177        0.23932
     174 -> 181        0.19158
     174 -> 187        0.12781
     174 -> 195       -0.19682
     174 -> 201        0.14024
     174 -> 204        0.17056
     174 -> 205        0.14149
     174 -> 208       -0.24311
     174 -> 225       -0.12066
     174 -> 229       -0.11117
     174 -> 232       -0.14487
     174 -> 233        0.14928
     174 -> 238       -0.17933
     174 -> 241        0.10951
     174 -> 245       -0.12102
     174 -> 268        0.13303
```

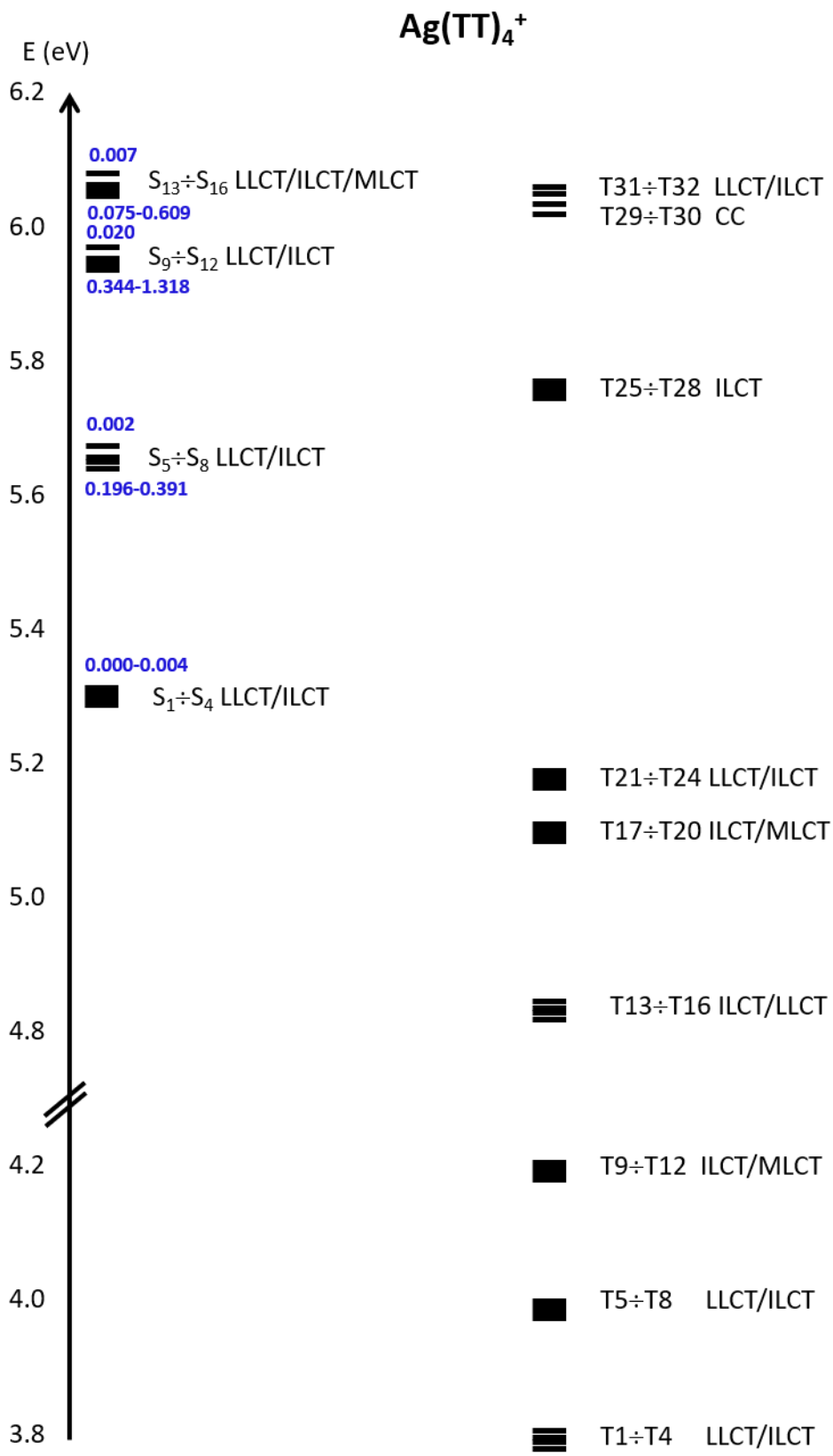
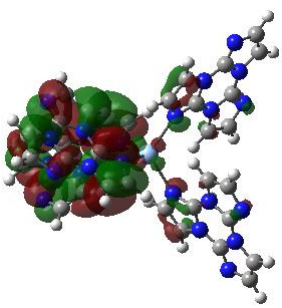
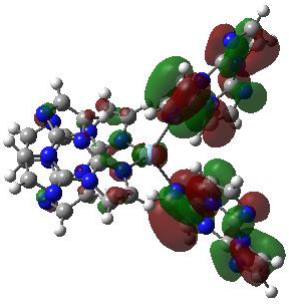


Figure S30. Scheme of singlet and triplet electronic levels with oscillator strengths (for singlet states, in blue) and character for model compound $Ag(TT)_4^+$ at ωB97X/def2-TZVP level of theory.

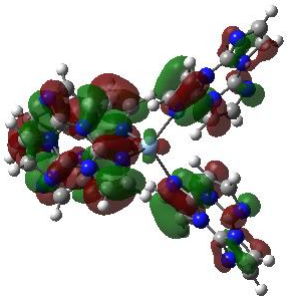
$Ag(TT)_4$: HOMOs



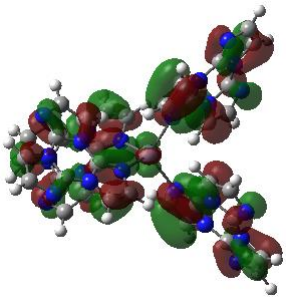
MO = 202 (HOMO-11)



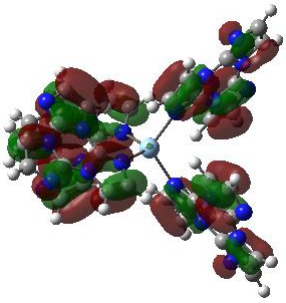
203 (HOMO-10)



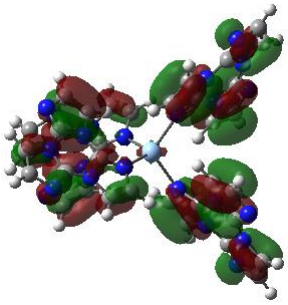
204 (HOMO-9)



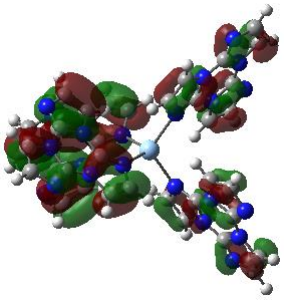
205 (HOMO-8)



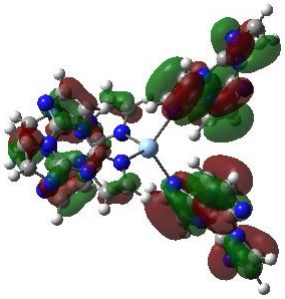
206 (HOMO-7)



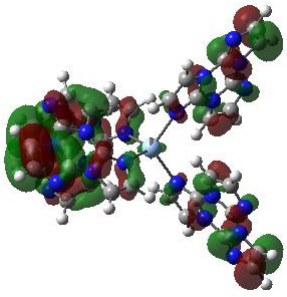
207 (HOMO-6)



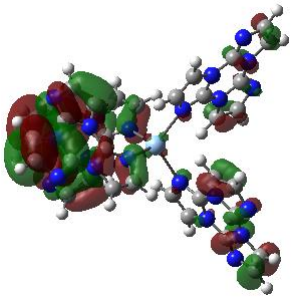
208 (HOMO-5)



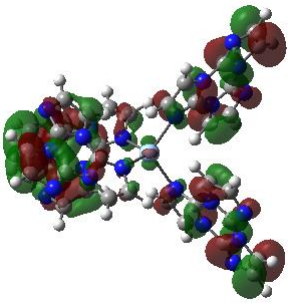
209 (HOMO-4)



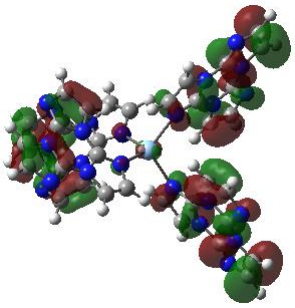
210 (HOMO-3)



211 (HOMO-2)

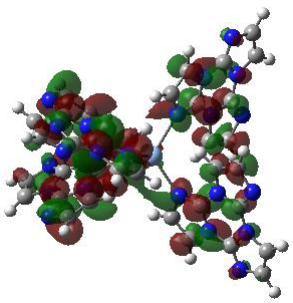


212 (HOMO-1)

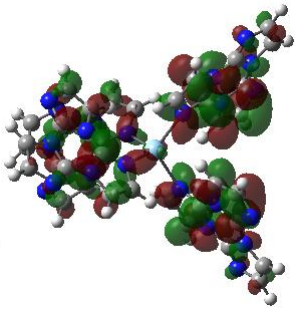


213 (HOMO)

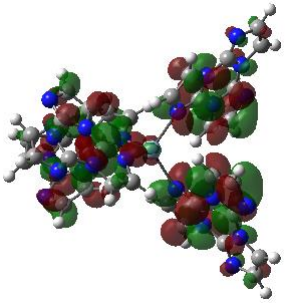
$Ag(TT)_4$: LUMOs



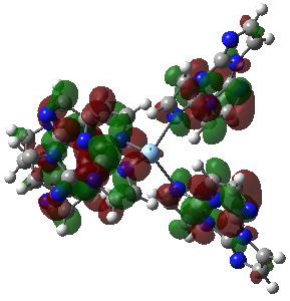
MO = 214 (LUMO)



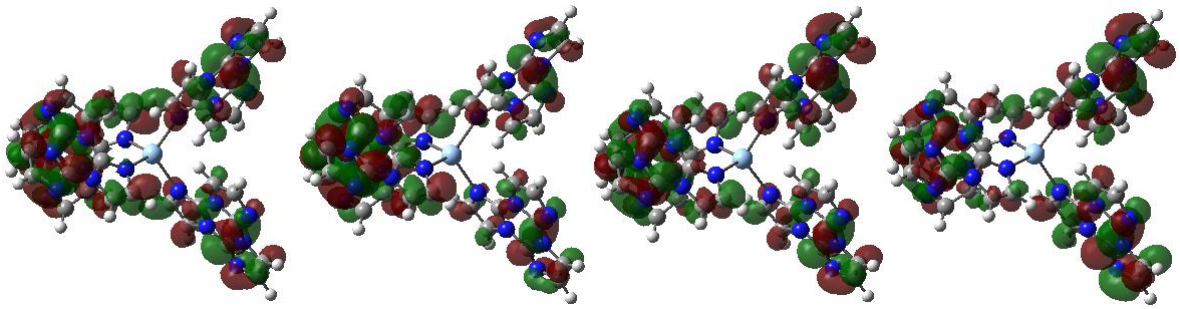
215 (LUMO+1)



216 (LUMO+2)



217 (LUMO+3)



218 (LUMO+4) 219 (LUMO+5) 220 (LUMO+6) 221 (LUMO+7)

Figure S31. Plots of the ωB97X/def2-TZVP MOs mainly involved in the lowest energy transitions of $Ag(TT)_4^+$ (Isosurfaces value 0.02).

Table S10. First TD-ωB97X/def2-TZVP $S_0 \rightarrow S_n$ and $T_0 \rightarrow T_n$ transitions computed for the optimized geometry of $Ag(TT)_4^+$.

Singlets:

```
Excited State   1:      Singlet-A      5.2985 eV  234.00 nm  f=0.0000  <S**2>=0.000
     206 -> 216        0.23112
     206 -> 217        0.11532
     207 -> 217        0.22663
     208 -> 214        0.18378
     208 -> 215        0.22464
     209 -> 214        0.21158
     210 -> 220       -0.21759
     211 -> 219        0.17561
     211 -> 221       -0.19034
     212 -> 218        0.21373
     213 -> 219       -0.17306

 Excited State   2:      Singlet-A      5.3026 eV  233.82 nm  f=0.0036  <S**2>=0.000
     206 -> 217        0.21956
     207 -> 216        0.25860
     208 -> 214        0.21778
     209 -> 215        0.27808
     210 -> 218        0.20725
     211 -> 219        0.18008
     212 -> 220       -0.22059
     213 -> 221        0.24685

 Excited State   3:      Singlet-A      5.3054 eV  233.70 nm  f=0.0029  <S**2>=0.000
     206 -> 214        0.13372
     206 -> 215       -0.16999
     207 -> 214       -0.15673
     207 -> 215        0.24633
     208 -> 216       -0.11921
     208 -> 217        0.11617
     209 -> 216        0.25407
     209 -> 217       -0.19744
     210 -> 219        0.11380
     210 -> 221        0.15247
     212 -> 219       -0.11687
     212 -> 221       -0.20492
     213 -> 218        0.19316
     213 -> 220        0.20756

 Excited State   4:      Singlet-A      5.3073 eV  233.61 nm  f=0.0019  <S**2>=0.000
     206 -> 214        0.23433
     206 -> 215        0.16773
     207 -> 214        0.19288
     207 -> 215        0.11106
     208 -> 216        0.21342
     208 -> 217        0.23766
     209 -> 217        0.14007
     210 -> 219        0.19108
     210 -> 221       -0.13455
     211 -> 218        0.20271
     211 -> 220       -0.19827
     212 -> 219        0.16875
     213 -> 218       -0.11096

 Excited State   5:      Singlet-A      5.6429 eV  219.72 nm  f=0.1963  <S**2>=0.000
```

```
    210 -> 214        0.31095
    210 -> 215        0.16098
    211 -> 216        0.23968
    211 -> 217        0.33015
    212 -> 214        0.20395
    212 -> 215        0.20454
    213 -> 216       -0.17593
    213 -> 217       -0.10820

Excited State   6:      Singlet-A      5.6452 eV  219.63 nm  f=0.2647  <S**2>=0.000
    210 -> 214       -0.11417
    210 -> 215        0.25661
    211 -> 216        0.18942
    212 -> 214        0.23966
    212 -> 215       -0.26017
    213 -> 216        0.29841
    213 -> 217       -0.27785

Excited State   7:      Singlet-A      5.6632 eV  218.93 nm  f=0.3908  <S**2>=0.000
    210 -> 216        0.30239
    211 -> 214        0.15420
    211 -> 215        0.27585
    212 -> 217        0.30368
    213 -> 214       -0.29026
    213 -> 215        0.17393

Excited State   8:      Singlet-A      5.6879 eV  217.98 nm  f=0.0022  <S**2>=0.000
    206 -> 218       -0.11797
    207 -> 220        0.11951
    208 -> 219       -0.13034
    209 -> 221        0.12589
    210 -> 217        0.29237
    211 -> 214        0.31325
    212 -> 216        0.30024
    213 -> 215       -0.29560

Excited State   9:      Singlet-A      5.9362 eV  208.86 nm  f=0.3445  <S**2>=0.000
    206 -> 214        0.14988
    206 -> 219       -0.14420
    206 -> 221        0.16754
    207 -> 215        0.11022
    207 -> 219       -0.18245
    208 -> 217        0.12466
    208 -> 218       -0.16851
    208 -> 220        0.22691
    209 -> 216        0.11966
    209 -> 218       -0.18228
    210 -> 219       -0.21752
    211 -> 218       -0.17792
    211 -> 220        0.10806
    212 -> 221        0.17953
    213 -> 220       -0.12142

Excited State  10:      Singlet-A      5.9441 eV  208.58 nm  f=1.3181  <S**2>=0.000
    206 -> 217       -0.14678
    206 -> 220       -0.15045
    207 -> 216       -0.16606
    207 -> 218        0.15138
    208 -> 214       -0.14861
    208 -> 221       -0.18807
    209 -> 215       -0.16132
    209 -> 219        0.18515
    210 -> 218        0.22141
    211 -> 219        0.16883
    212 -> 220       -0.21692
    213 -> 221        0.19627

Excited State  11:      Singlet-A      5.9467 eV  208.49 nm  f=0.4917  <S**2>=0.000
    206 -> 215        0.11907
    206 -> 219       -0.16574
    207 -> 214        0.10828
    207 -> 221        0.22300
    208 -> 216        0.11693
    208 -> 218       -0.19788
    209 -> 217        0.14253
    209 -> 218        0.12721
    209 -> 220        0.23366
    210 -> 221        0.19184
```

```
    211 -> 220        0.11606
    212 -> 219       -0.17537
    212 -> 221       -0.12403
    213 -> 218        0.16488
    213 -> 220        0.12172

Excited State  12:      Singlet-A      5.9687 eV  207.72 nm  f=0.0202  <S**2>=0.000
    202 -> 214       -0.14997
    203 -> 215        0.14239
    204 -> 217       -0.15629
    205 -> 216        0.15540
    206 -> 216       -0.18476
    207 -> 217       -0.17108
    208 -> 214       -0.11525
    208 -> 215       -0.15973
    209 -> 214       -0.16458
    210 -> 220       -0.21858
    211 -> 219        0.14397
    211 -> 221       -0.18594
    212 -> 218        0.22487
    213 -> 219       -0.17640
    213 -> 221       -0.10578

Excited State  13:      Singlet-A      6.0464 eV  205.05 nm  f=0.0753  <S**2>=0.000
    202 -> 214        0.12641
    202 -> 215        0.15920
    203 -> 214       -0.16774
    203 -> 215        0.13239
    204 -> 216        0.20502
    205 -> 217       -0.20185
    206 -> 220       -0.22663
    207 -> 218        0.25585
    208 -> 219        0.10912
    208 -> 221       -0.18507
    209 -> 219        0.18952
    209 -> 221        0.12323

Excited State  14:      Singlet-A      6.0524 eV  204.85 nm  f=0.5693  <S**2>=0.000
    202 -> 216       -0.19584
    202 -> 217       -0.16689
    203 -> 217        0.13593
    204 -> 214       -0.14860
    204 -> 215       -0.19456
    205 -> 214        0.21172
    206 -> 219       -0.14733
    206 -> 221        0.15414
    207 -> 219       -0.17478
    208 -> 217       -0.10126
    208 -> 218       -0.14669
    208 -> 220        0.18649
    209 -> 218       -0.15762
    211 -> 218        0.14543
    213 -> 220        0.12834

Excited State  15:      Singlet-A      6.0595 eV  204.61 nm  f=0.6095  <S**2>=0.000
    202 -> 217       -0.14315
    203 -> 216        0.22904
    203 -> 217       -0.13137
    204 -> 214       -0.19109
    205 -> 215        0.24162
    206 -> 219       -0.13192
    207 -> 214       -0.10115
    207 -> 221        0.19681
    208 -> 218       -0.13417
    209 -> 218        0.15522
    209 -> 220        0.18404
    211 -> 220       -0.13145
    213 -> 218       -0.14636

Excited State  16:      Singlet-A      6.0918 eV  203.53 nm  f=0.0069  <S**2>=0.000
    202 -> 214        0.16404
    203 -> 215       -0.15758
    204 -> 217        0.16424
    205 -> 216       -0.17102
    206 -> 218        0.26071
    207 -> 220       -0.24824
    208 -> 219        0.26621
    209 -> 221       -0.25508
```

Triplets:

```
Excited State   1:      Triplet-A      3.7593 eV  329.81 nm  f=0.0000  <S**2>=2.000
     206 -> 216        0.16821
     207 -> 216       -0.15727
     207 -> 217        0.18792
     208 -> 215        0.12974
     209 -> 214        0.16616
     209 -> 215       -0.19243
     210 -> 220       -0.16136
     211 -> 221       -0.12897
     212 -> 218        0.17674
     212 -> 220        0.12973
     213 -> 215        0.13974
     213 -> 219       -0.17100
     213 -> 221       -0.19951

 Excited State   2:      Triplet-A      3.7595 eV  329.79 nm  f=0.0000  <S**2>=2.000
     206 -> 215       -0.15161
     207 -> 214       -0.14151
     207 -> 215        0.19806
     209 -> 216        0.19741
     209 -> 217       -0.16987
     210 -> 221        0.15593
     212 -> 219       -0.13335
     212 -> 221       -0.18594
     213 -> 216       -0.12609
     213 -> 217        0.12186
     213 -> 218        0.17476
     213 -> 220        0.18337

 Excited State   3:      Triplet-A      3.7630 eV  329.48 nm  f=0.0000  <S**2>=2.000
     206 -> 216        0.11503
     206 -> 217        0.20492
     207 -> 216        0.15321
     207 -> 217        0.10216
     208 -> 214        0.21995
     208 -> 215        0.11924
     209 -> 215        0.11816
     210 -> 218        0.19558
     210 -> 220       -0.12744
     211 -> 214       -0.12193
     211 -> 219        0.23133
     211 -> 221       -0.12577
     212 -> 218        0.10373
     212 -> 220       -0.16090
     213 -> 214        0.10475
     213 -> 221        0.11635

 Excited State   4:      Triplet-A      3.7649 eV  329.32 nm  f=0.0000  <S**2>=2.000
     206 -> 214        0.20235
     206 -> 215        0.12869
     207 -> 214        0.14914
     207 -> 215        0.10736
     208 -> 216        0.15839
     208 -> 217        0.19721
     210 -> 219        0.19310
     210 -> 221       -0.12599
     211 -> 218        0.20721
     211 -> 220       -0.18184
     212 -> 219        0.15464
     212 -> 221       -0.11417

 Excited State   5:      Triplet-A      3.9824 eV  311.33 nm  f=0.0000  <S**2>=2.000
     205 -> 221       -0.10061
     206 -> 221       -0.12277
     207 -> 219        0.11412
     207 -> 221        0.15034
     208 -> 220       -0.11819
     209 -> 218        0.16092
     209 -> 220        0.15492
     210 -> 221        0.12655
     212 -> 221       -0.16440
     213 -> 216        0.11921
     213 -> 218        0.13024
     213 -> 220        0.14406
```

```
Excited State   6:      Triplet-A      3.9826 eV  311.31 nm  f=0.0000  <S**2>=2.000
    203 -> 221       -0.11747
    206 -> 220       -0.12443
    207 -> 218        0.14897
    207 -> 220        0.10940
    208 -> 221       -0.15007
    209 -> 219        0.15008
    209 -> 221        0.16707
    210 -> 218        0.12717
    212 -> 218       -0.10766
    212 -> 220       -0.15395
    213 -> 214       -0.11672
    213 -> 215        0.11630
    213 -> 221        0.16889

Excited State   7:      Triplet-A      3.9851 eV  311.12 nm  f=0.0000  <S**2>=2.000
    206 -> 218        0.11621
    206 -> 219        0.11832
    208 -> 218        0.13302
    208 -> 219        0.13477
    208 -> 220       -0.10910
    210 -> 219        0.11524
    210 -> 220       -0.10958
    211 -> 214        0.10009
    211 -> 217        0.10394
    211 -> 219        0.10806

Excited State   8:      Triplet-A      3.9853 eV  311.10 nm  f=0.0000  <S**2>=2.000
    206 -> 218       -0.11714
    206 -> 219        0.10642
    208 -> 218        0.12928
    208 -> 219       -0.15258
    208 -> 220       -0.10658
    210 -> 220        0.10419
    211 -> 219       -0.10485

Excited State   9:      Triplet-A      4.1975 eV  295.37 nm  f=0.0000  <S**2>=2.000
    202 -> 216        0.16498
    202 -> 217        0.16294
    203 -> 217       -0.11654
    204 -> 214        0.12499
    204 -> 215        0.17753
    204 -> 219        0.10087
    205 -> 214       -0.16993
    206 -> 214        0.14885
    207 -> 215        0.12628
    208 -> 217        0.17330
    209 -> 216        0.11454

Excited State  10:      Triplet-A      4.1982 eV  295.33 nm  f=0.0000  <S**2>=2.000
    202 -> 217       -0.11541
    203 -> 216        0.17624
    203 -> 217       -0.10317
    203 -> 218        0.11374
    204 -> 214       -0.15077
    205 -> 215        0.19245
    206 -> 215       -0.12813
    207 -> 214       -0.12593
    207 -> 221        0.10341
    208 -> 216       -0.11432
    209 -> 217       -0.12724
    209 -> 220        0.10169

Excited State  11:      Triplet-A      4.1984 eV  295.31 nm  f=0.0000  <S**2>=2.000
    202 -> 215        0.14632
    203 -> 214       -0.15042
    203 -> 215        0.11034
    204 -> 216        0.16975
    205 -> 217       -0.16907
    206 -> 217        0.13024
    207 -> 216        0.13354
    207 -> 218        0.12271
    208 -> 214        0.14628
    209 -> 215        0.15444

Excited State  12:      Triplet-A      4.1994 eV  295.24 nm  f=0.0000  <S**2>=2.000
    202 -> 214       -0.18511
    203 -> 215        0.17223
```

```
    204 -> 217       -0.19386
    205 -> 216        0.17904
    205 -> 218        0.10578
    206 -> 216       -0.13054
    206 -> 218       -0.12116
    207 -> 217       -0.13103
    207 -> 220        0.11127
    208 -> 215       -0.15253
    209 -> 214       -0.14211

Excited State  13:      Triplet-A      4.8214 eV  257.15 nm  f=0.0000  <S**2>=2.000
    203 -> 228       -0.11873
    207 -> 216       -0.10087
    209 -> 215       -0.13248
    209 -> 221        0.10359
    210 -> 216       -0.11320
    210 -> 217        0.10733
    212 -> 216        0.15876
    212 -> 217       -0.11977
    213 -> 214        0.12322
    213 -> 215       -0.18118

Excited State  14:      Triplet-A      4.8217 eV  257.14 nm  f=0.0000  <S**2>=2.000
    203 -> 218        0.10025
    205 -> 228       -0.10127
    207 -> 215       -0.10007
    209 -> 216       -0.13744
    209 -> 217        0.11523
    210 -> 215       -0.12543
    212 -> 214       -0.11276
    212 -> 215        0.16000
    213 -> 216       -0.17161
    213 -> 217        0.13118

Excited State  15:      Triplet-A      4.8232 eV  257.06 nm  f=0.0000  <S**2>=2.000
    202 -> 229        0.11696
    208 -> 214       -0.13591
    210 -> 216       -0.12628
    210 -> 217       -0.14120
    211 -> 214       -0.16752
    211 -> 215       -0.12981
    212 -> 217       -0.11769

Excited State  16:      Triplet-A      4.8239 eV  257.02 nm  f=0.0000  <S**2>=2.000
    202 -> 218       -0.10251
    202 -> 227        0.10015
    204 -> 229       -0.10468
    208 -> 216        0.11155
    208 -> 217        0.11319
    208 -> 218       -0.11138
    210 -> 214        0.15184
    210 -> 215        0.10397
    211 -> 216        0.13441
    211 -> 217        0.15218
    212 -> 214        0.13671

Excited State  17:      Triplet-A      5.0934 eV  243.42 nm  f=0.0000  <S**2>=2.000
    202 -> 214       -0.12171
    202 -> 219        0.10177
    210 -> 217        0.11565
    211 -> 214        0.14196

Excited State  18:      Triplet-A      5.0938 eV  243.40 nm  f=0.0000  <S**2>=2.000
    202 -> 218        0.10722
    204 -> 219        0.10269
    206 -> 229        0.10240
    208 -> 227       -0.12380
    211 -> 216        0.11512
    211 -> 217        0.11704
    212 -> 214        0.10410

Excited State  19:      Triplet-A      5.0957 eV  243.31 nm  f=0.0000  <S**2>=2.000
    203 -> 216       -0.13852
    203 -> 217        0.10301
    205 -> 215       -0.12596
    205 -> 219        0.10136
    207 -> 229       -0.10673
    209 -> 227        0.12992
```

```
    210 -> 214       -0.10400
    212 -> 215       -0.13308
    213 -> 216        0.15087
    213 -> 218        0.12537

Excited State  20:      Triplet-A      5.0958 eV  243.31 nm  f=0.0000  <S**2>=2.000
    203 -> 215       -0.12815
    203 -> 221        0.12384
    204 -> 216       -0.10097
    205 -> 217        0.11388
    209 -> 228       -0.12557
    210 -> 216        0.11011
    212 -> 217        0.10517
    212 -> 220       -0.10628
    213 -> 214       -0.13042
    213 -> 215        0.13590
    213 -> 221        0.12657

Excited State  21:      Triplet-A      5.1654 eV  240.03 nm  f=0.0000  <S**2>=2.000
    202 -> 216        0.12811
    202 -> 217        0.15003
    204 -> 214        0.13204
    204 -> 215        0.10463
    205 -> 214       -0.10823
    206 -> 219       -0.14959
    206 -> 221        0.11456
    207 -> 219       -0.12534
    208 -> 218       -0.11722
    208 -> 220        0.13715
    211 -> 224        0.10968
    211 -> 227        0.11180

Excited State  22:      Triplet-A      5.1663 eV  239.99 nm  f=0.0000  <S**2>=2.000
    203 -> 216        0.14676
    203 -> 217       -0.10737
    205 -> 215        0.13976
    206 -> 221        0.11104
    207 -> 221       -0.16509
    209 -> 218       -0.12412
    209 -> 220       -0.14461
    213 -> 224        0.11858
    213 -> 227       -0.11356

Excited State  23:      Triplet-A      5.1665 eV  239.98 nm  f=0.0000  <S**2>=2.000
    202 -> 214        0.15728
    204 -> 217        0.14619
    205 -> 216       -0.11152
    206 -> 218       -0.13520
    207 -> 220        0.13006
    208 -> 219       -0.16734
    210 -> 227        0.10829

Excited State  24:      Triplet-A      5.1676 eV  239.93 nm  f=0.0000  <S**2>=2.000
    203 -> 214       -0.12356
    203 -> 215        0.13831
    204 -> 216        0.11752
    205 -> 216        0.10285
    205 -> 217       -0.12160
    206 -> 220        0.12814
    207 -> 218       -0.13996
    207 -> 220       -0.10220
    208 -> 221        0.10808
    209 -> 219       -0.12554
    209 -> 221       -0.14805
    212 -> 227        0.11092
    213 -> 229        0.11456

Excited State  25:      Triplet-A      5.7542 eV  215.47 nm  f=0.0000  <S**2>=2.000
    211 -> 239        0.11963
    211 -> 243       -0.11071

Excited State  26:      Triplet-A      5.7545 eV  215.46 nm  f=0.0000  <S**2>=2.000
    208 -> 237        0.10293
    211 -> 243        0.11647

Excited State  27:      Triplet-A      5.7552 eV  215.43 nm  f=0.0000  <S**2>=2.000
    182 -> 221        0.10751
    204 -> 229       -0.10182
```

```
    206 -> 237        0.10254
    207 -> 235       -0.11387
    209 -> 231       -0.12259
    210 -> 243        0.12649
    212 -> 215       -0.10590
    212 -> 241       -0.14977
    213 -> 216        0.11304
    213 -> 239        0.11840

Excited State  28:      Triplet-A      5.7563 eV  215.39 nm  f=0.0000  <S**2>=2.000
    183 -> 221        0.10982
    203 -> 229        0.10483
    205 -> 227       -0.10575
    206 -> 231       -0.10029
    209 -> 232       -0.10424
    209 -> 235        0.12563
    213 -> 215       -0.10463
    213 -> 241       -0.15444
    213 -> 243       -0.10058

Excited State  29:      Triplet-A      6.0228 eV  205.86 nm  f=0.0000  <S**2>=2.000
    201 -> 222       -0.35075
    201 -> 230        0.20481

Excited State  30:      Triplet-A      6.0368 eV  205.38 nm  f=0.0000  <S**2>=2.000
    200 -> 222        0.30115
    200 -> 230       -0.17995
    208 -> 214        0.10771
    210 -> 218       -0.10699
    211 -> 219       -0.10844

Excited State  31:      Triplet-A      6.0513 eV  204.89 nm  f=0.0000  <S**2>=2.000
    203 -> 215        0.14048
    205 -> 216        0.13277
    209 -> 214        0.10534
    212 -> 218       -0.11791
    213 -> 219        0.10056
    213 -> 221        0.10297

Excited State  32:      Triplet-A      6.0518 eV  204.87 nm  f=0.0000  <S**2>=2.000
    202 -> 217       -0.11816
    204 -> 214       -0.13576
    205 -> 215        0.11810
    206 -> 215        0.10466
    207 -> 214        0.11577
    208 -> 216        0.11538
    210 -> 221        0.10055
    210 -> 229       -0.10027
    211 -> 220        0.11028
    211 -> 227        0.11563
    211 -> 240        0.10521
    212 -> 219       -0.11060
    213 -> 218        0.11625

Excited State  33:      Triplet-A      6.0836 eV  203.80 nm  f=0.0000  <S**2>=2.000
    200 -> 222       -0.41164
    200 -> 230        0.24084
    205 -> 222        0.12294

Excited State  34:      Triplet-A      6.0874 eV  203.67 nm  f=0.0000  <S**2>=2.000
    201 -> 222        0.38424
    201 -> 230       -0.22440
```

5. References

[S1] Schubert, D. M.; Natan, D. T.; Wilson, D. C.; Hardcastle, K. I. Facile Synthesis and Structures of Cyclic Triimidazole and Its Boric Acid Adduct. *Cryst. Growth Des.* 2011, **11**, 843-850

[S2] Lucenti, E.; Cariati, E.; Previtali, A.; Marinotto, D.; Forni, A.; Bold, V.; Kravtsov, V. C.; Fonari, M. S.; Galli, S.; Carlucci, L., Versatility of Cyclic Triimidazole to Assemble 1D, 2D, and 3D Cu(I) Halide Coordination Networks. *Cryst. Growth Des.* 2019, **19**, 1567-1575.

[S3] Lucenti, E.; Forni, A.; Botta, C.; Giannini, C.; Malpicci, D.; Marinotto, D.; Previtali, A.; Righetto, S.; Cariati, E., Intrinsic and Extrinsic Heavy-Atom Effects on the Multifaceted Emissive Behavior of Cyclic Triimidazole. *Chem. Eur. J.* 2019, **25**, 2452-2456.

[S4] SADABS 2012. Area detector absorption correction. Bruker AXS Inc., Madison, Wisconsin, USA.

[S5] Burla, M. C.; Caliandro, R.; Carrozzini, B.; Cascarano, G. L.; Cuocci, C.; Giacovazzo, C.; Mallamo, M.; Mazzone A.; Polidori, G. Crystal structure determination and refinement via SIR2014. *J. Appl. Cryst.* 2015, **48**, 306–309.

[S6] Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr., Sect. C: Struct. Chem.* 2015, **71**, 3–8.

[S7] Gaussian 16, Revision A.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

[S8] (a) Andrae, D., Häußermann, U., Dolg, M., Stoll, H., Preuß, H., Energy-adjusted ab initio pseudopotentials for the second and third row transition elements, *Theor. Chim. Acta* 1990, **77**, 123-141; (b) Peterson, K. A., Figgen, D., Goll, E., Stoll, H., Dolg, M., Systematically convergent basis sets with relativistic pseudopotentials. II. Small-core pseudopotentials and correlation consistent basis sets for the post-d group 16-18 elements, *J. Chem. Phys.* 2003, **119**, 11113-11123; (c) Weigend, F., Ahlrichs, R., Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, *Phys. Chem. Chem. Phys.* 2005, **7**, 3297.

[S9] (a) Pritchard, B. P., Altarawy, D., Didier, B., Gibsom, T. D., Windus, T. L., A New Basis Set Exchange: An Open, Up-to-date Resource for the Molecular Sciences Community, J. Chem. Inf. Model., 59, 4814-4820 (2019); (b) Feller, D., The role of databases in support of computational chemistry calculations, J. Comput. Chem., 17, 1571-1586 (1996); (c) Schuchardt, K. L., Didier, B. T., Elsethagen, T., Sun, L., Gurumoorthi, V., Chase, J., Li, J., Windus, T. L., Basis Set Exchange: A Community Database for Computational Sciences, J. Chem. Inf. Model., 47, 1045-1052 (2007).

[S10] Glukhovtsev, M. N.; Pross, A.; McGrath, M. P.; Radom, L. Extension of Gaussian-2 (G2) Theory to Bromine- and Iodine Containing Molecules: Use of Effective Core Potentials. *J. Chem. Phys.* 1995, **103**, 1878−1885.

[S11] Chai, J.D.; Head-Gordon, M. Systematic optimization of long-range corrected hybrid density functionals. *J. Chem. Phys*. 2008, **128**, 084106.

[S12] (a) Lucenti, E.; Forni, A.; Botta, C.; Carlucci, L.; Giannini, C.; Marinotto, D.; Previtali, A.; Righetto, S.; Cariati, E., H-Aggregates Granting Crystallization-Induced Emissive Behavior and Ultralong Phosphorescence from a Pure Organic Molecule. *J. Phys. Chem. Lett.* 2017, **8,** 1894-1898. (b) Lucenti, E.; Forni, A.; Botta, C.; Carlucci, L.; Giannini, C.; Marinotto, D.; Pavanello, A.; Previtali, A.; Righetto, S.; Cariati, E., Cyclic Triimidazole Derivatives: Intriguing Examples of Multiple Emissions and Ultralong Phosphorescence at Room Temperature. *Angew. Chem. Int. Ed.* 2017, **56**, 16302-16307. (c) Lucenti, E.; Forni, A.; Botta, C.; Carlucci, L.; Colombo, A.; Giannini, C.; Marinotto, D.; Previtali, A.; Righetto, S.; Cariati, E., The Effect of Bromo Substituents on the Multifaceted Emissive and Crystal-Packing Features of Cyclic Triimidazole Derivatives. *ChemPhotoChem* 2018, **2**, 801-805. (d) Previtali, A.; Lucenti, E.; Forni, A.; Mauri, L.; Botta, C.; Giannini, C.; Malpicci, D.; Marinotto, D.; Righetto, S.; Cariati, E., Solid State Room Temperature Dual Phosphorescence from 3-(2-Fluoropyridin-4-yl)triimidazo[1,2-*a*:1′,2′-*c*:1″,2″-*e*][1,3,5]triazine. *Molecules* 2019, **24**, 2552. (e) Lucenti, E.; Forni, A.; Previtali, A.; Marinotto, D.; Malpicci, D.; Righetto, S.; Giannini, C.; Virgili, T.; Kabacinski, P.; Ganzer, L.; Giovanella, U.; Botta, C.; Cariati, E., Unravelling the intricate photophysical behavior of 3-(pyridin-2-yl)triimidazotriazine AIE and RTP polymorphs. *Chem. Sci.* 2020, **11**, 7599-7608.

[S13] Keith, T. A. AIMAll, Version 17.11.14, Professional; TK Gristmill Software: Overland Park, KS, 2017, http://aim.tkgristmill.com.