Supplementary Information

Emission enhancement in a luminescent polychlorinated diphenylpyridylmethyl radical through coordination to silver(I)

Takuto Mibu,*[ab] Ryota Matsuoka,[ab] Masanari Nagasaka,[a] and Tetsuro Kusamoto*[abcd]

[a]Institute for Molecular Science, Okazaki, Aichi 444-8585, Japan

[b]Division of Frontier Materials Science, Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

[c]Spintronics Research Network Division, Institute for Open and Transdisciplinary Research Initiatives, Osaka University, Toyonaka, Osaka 560-8531, Japan

[d]FOREST, JST, Honcho 4-1-8, Kawaguchi, Saitama 332-0012, Japan

*Corresponding Authors. Email: t-mibu@sagami.or.jp; kusamoto.tetsuro.es@osaka-u.ac.jp

Table of Contents

X-ray crystallographic analyses

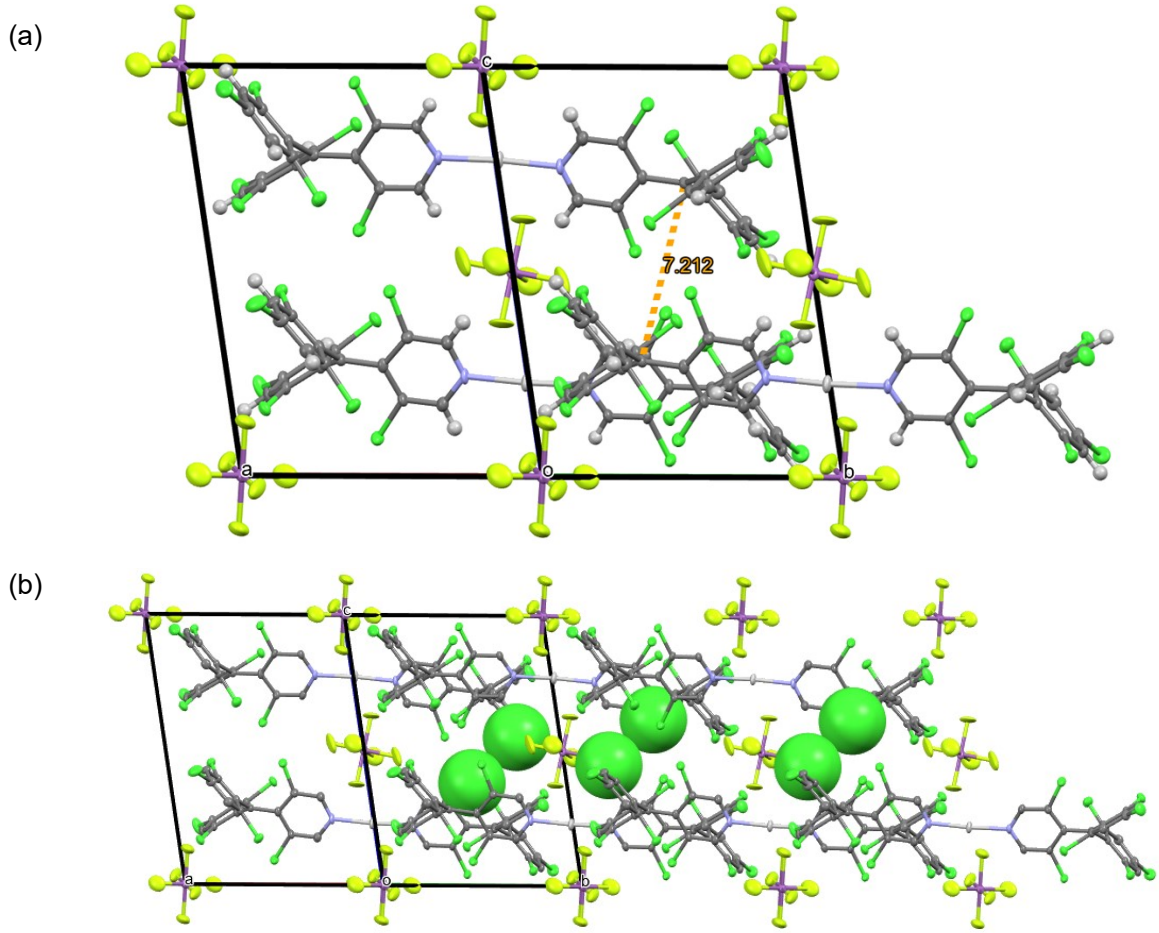


Figure S1. The crystal structure of $[Ag(PyBTM)_2](SbF_6)$ showing (a) the shortest intermolecular distance between the radical carbon centers (C6···C24, 7.212 Å) and (b) Cl···Cl atomic contact (3.402 Å). The atoms are shown in an ellipsoidal model (50% probability) except some of the chlorine atoms in (b), which are shown in a space-fill model. Hydrogen atoms are omitted in (b) for clarity. C, dark gray; N, blue; F, yellow green; Cl, light green; Sb, purple; Ag, light gray; H, white.

Crystal Data for $C_{36}H_{12}AgCl_{16}F_6N_2Sb$ (M =1383.31 g/mol): triclinic, space group P-1 (no. 2), a = 11.6295(2) Å, b = 14.5514(3) Å, c = 15.1131(3) Å, α = 110.462(2)°, β = 92.463(2)°, γ = 106.895(2)°, V = 2262.72(8) Å^3, Z = 2, T = 123 K, μ(Mo Kα) = 0.723 mm^{-1}, D_{calc} = 2.030 g/cm^3, 31369 reflections measured (5.046° ≤ 2θ ≤ 54.968°), 10365 unique (R_{int} = 0.0333, R_{sigma} = 0.0416) which were used in all calculations. The final R_1 was 0.0309 (I > 2σ(I)) and wR_2 was 0.0415 (all data). The goodness-of-fit on F_2 was 1.073.

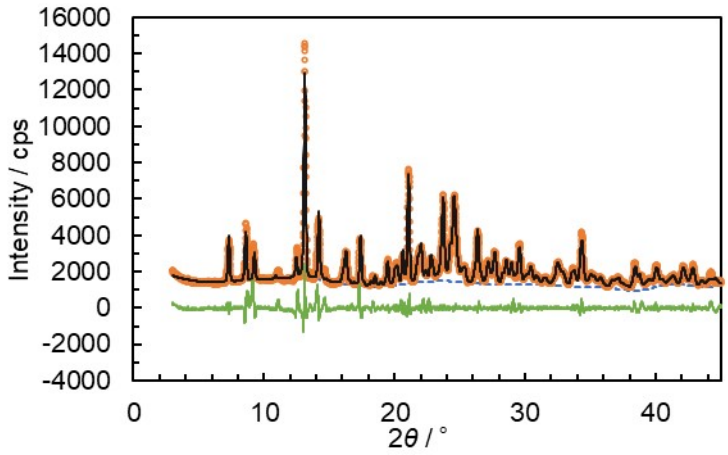


Figure S2. Observed (orange dots) and simulated (black line) powder X-ray diffraction profile of $[Ag(PyBTM)_2](SbF_6)$. The bottom green curve represents the difference plot on the same intensity scale. The experimental PXRD pattern measured at room temperature was analyzed by whole-powder-pattern decomposition methods (Pawley method): a = 11.592(2) Å, b = 14.401(3) Å, c = 15.098(3) Å, α = 109.535(7)°, β = 92.843(6)°, γ = 106.930(5)°, V = 2241.920 Å^3, R_{wp} = 0.0838, R_p = 0.0533, S = 2.9706, χ^2 = 8.8246.

Magnetic properties

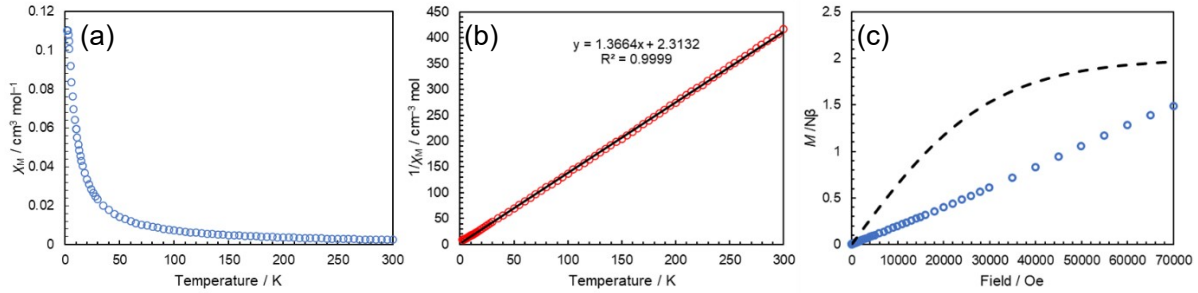


Figure S3. Temperature-dependent (a) magnetic susceptibility χ_M and (b) $1/\chi_M$ plots of $[Ag(PyBTM)_2](SbF_6)$ (H = 10000 Oe). The black line in (b) represents the Curie-Weiss fit. (c) Field-dependent magnetization plot of $[Ag(PyBTM)_2](SbF_6)$ (T = 2.0 K). The black dashed line represents the Brillouin function for non-interacting two S = 1/2 spins.

Concentration-dependent absorption of $[Ag(PyBTM)_2](SbF_6)$ in solution

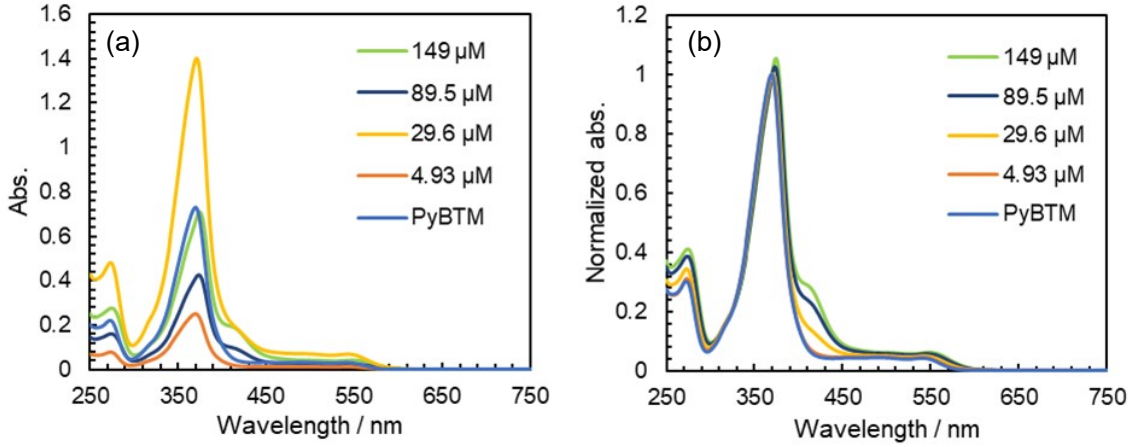


Figure S4. (a) Concentration-dependent absorption spectra of $[Ag(PyBTM)_2](SbF_6)$ in dichloromethane with the absorption spectrum of PyBTM (30 μM) in the same solvent. 149 μM and 89.5 μM solution were measured using a 1 mm pathlength cell and the others were measured using a 10 mm pathlength cell. (b) Normalized spectra of (a).

Titration experiments

Experimental procedure

0.78 mg of PyBTM was dissolved in CH_2Cl_2 and diluted to 50 mL in a volumetric flask to prepare 30 μM stock solution of PyBTM (**stock solution A**). 3.10 mg of $AgSbF_6$ was dissolved in **stock solution A** and diluted to 25 mL in a volumetric flask to prepare a 361 μM stock solution of $AgSbF_6$ containing 30 μM PyBTM (**stock solution B**). In a UV cell (pathlength = 10 mm), 3.0 mL of **stock solution A** was placed, and 0.05–0.20 mL each of **stock solution B** was titrated into the solution at the constant concentrations of PyBTM. UV-vis absorption measurements were performed during the titration. The absorption spectral change during the titration is shown in Figure 2a. The association constant *K* was determined by the least square fitting of the 1:1 binding model using the TitrationFit Software (Figure S5).[1]

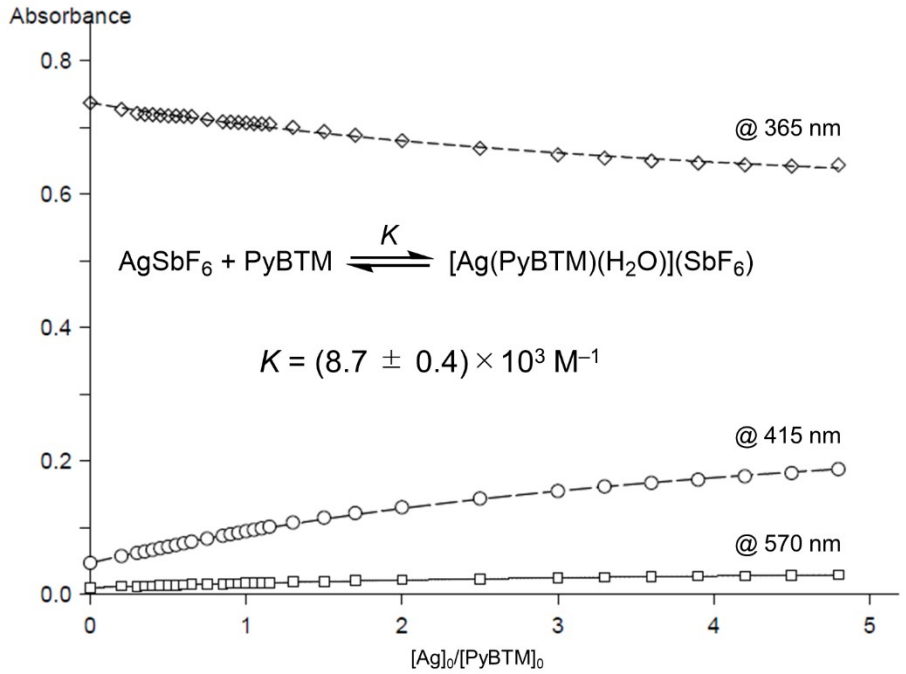


Figure S5. Changes in the absorbance of PyBTM (30 μM in CH_2Cl_2) at 365, 415, and 570 nm upon the addition of $AgSbF_6$ (0–4.8 equiv.) at room temperature. The solid and dashed lines show the least squares fitting to determine the association constant *K* based on the equation shown in the figure.

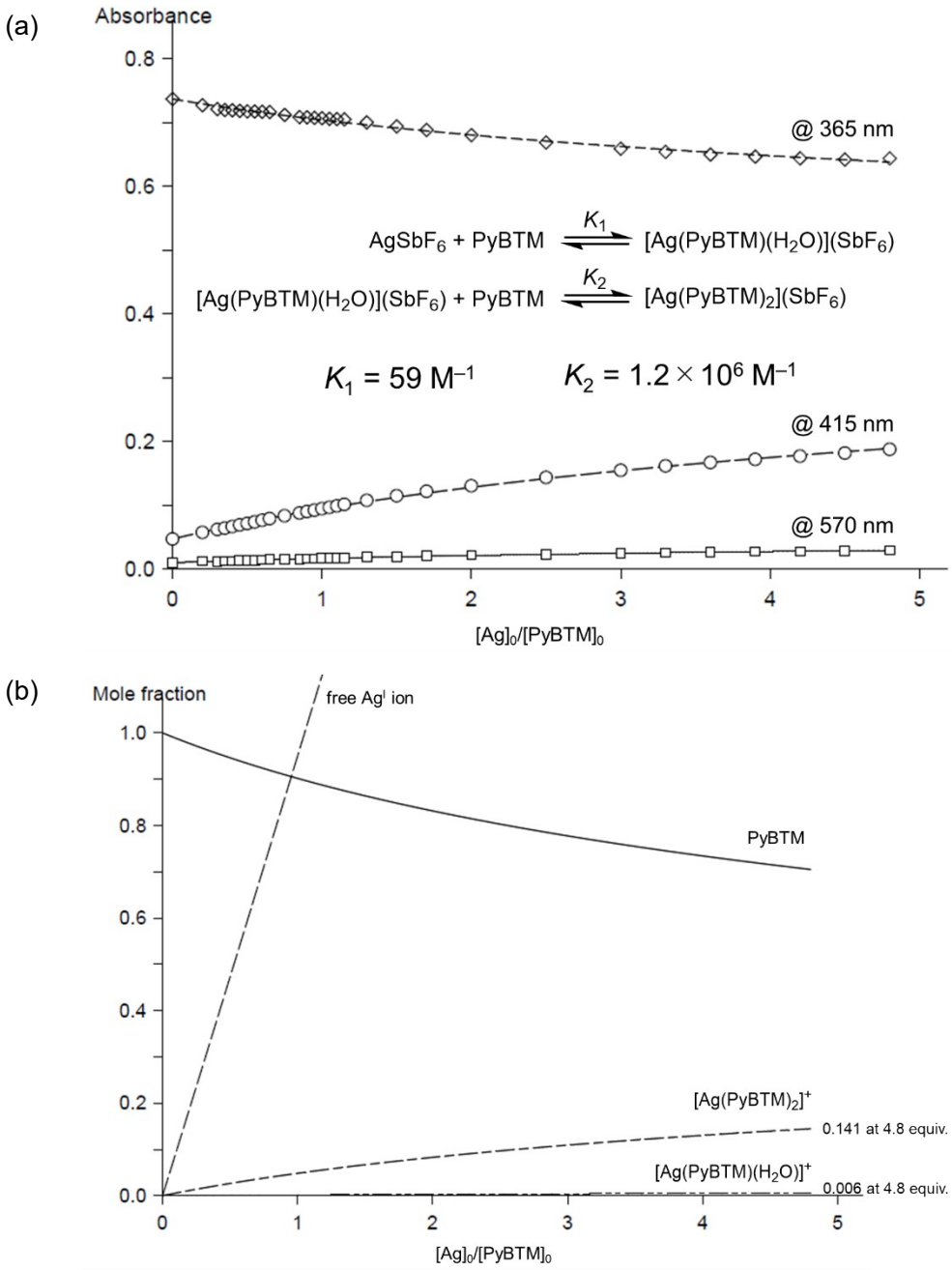


Figure S6. (a) One of the least squares fitting results of the titration data in Figure S5 based on the stepwise coordination equilibrium to give $[Ag(PyBTM)(H_2O)]^+$ (**1b**$^+$) and $[Ag(PyBTM)_2]^+$ (**1a**$^+$) (the equations are shown in the figure). (b) The simulated mole fractions of PyBTM, free Ag^I ion, **1a**$^+$, and **1b**$^+$ based on the equilibrium constants shown in (a).

The least squares fitting based on the stepwise coordination equilibrium did not converge to a single solution. However, we were able to simulate the mole fractions of the coordination products for each of the fitting solutions obtained. The simulations suggested that K_2 must be several orders of magnitude higher than K_1 for the exclusive formation of **1a**$^+$ (i.e., the mole fraction of **1b**$^+$ below 1%) during the titration. Such a K_2 much larger than K_1 is unrealistic in this molecular system. We therefore concluded that this stepwise model is unsuitable.

Soft X-ray absorption spectroscopy

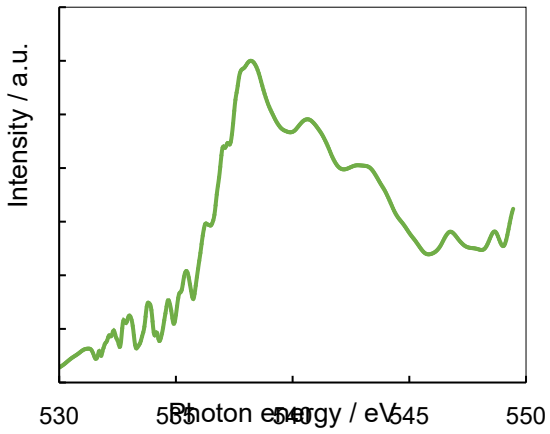
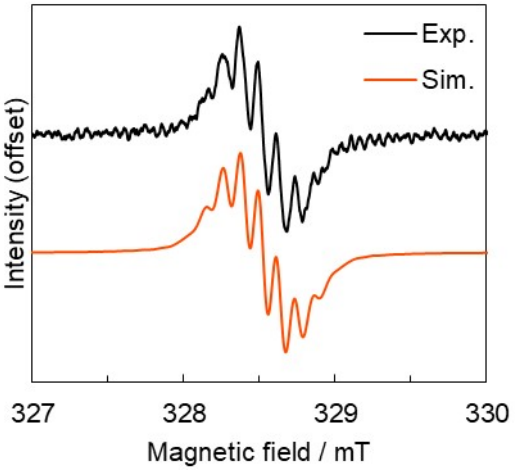


Figure S7. The oxygen *K*-edge X-ray absorption spectrum of $AgSbF_6$ (21.3 mM) in CH_2Cl_2 at room temperature. No distinct pre-edge peak was observed.

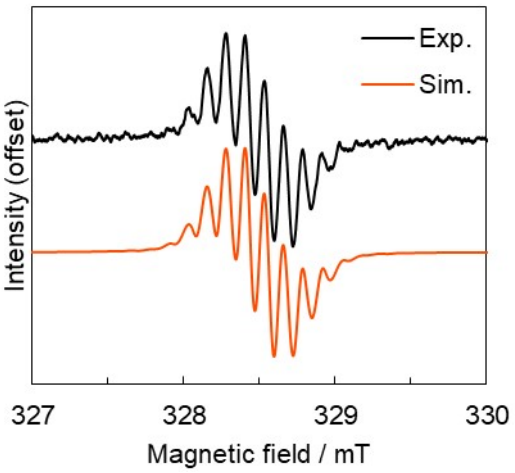
ESR spectroscopy



Simulation parameters
g(isotropic) = 2.0041
Line width = 0.091 mT (Lorentzian)

Hyperfine coupling constants (hfccs)
^{1}H (6 atoms): 3.37 MHz
^{14}N (1 atom): 2.97 MHz
^{13}C (1 atom): 36.0 MHz

Figure S8. Measured (black) and simulated (orange) ESR spectra of PyBTM (30 μM) in CH_2Cl_2 at 175 K. The fitting parameters are described in the right box.



Simulation parameters
g(isotropic) = 2.0040
Line width = 0.063 mT (Lorentzian)

Hyperfine coupling constants (hfccs)
^{1}H (6 atoms): 3.82 MHz
^{14}N (1 atom): 3.07 MHz
^{13}C (1 atom): 35.4 MHz
^{107}Ag/^{109}Ag (1 atom): 2.60 MHz

Figure S9. Measured (black) and simulated (orange) ESR spectra of **soln_99** containing 30 μM of **1b**$^{+}$ at 175 K. The fitting parameters are described in the right box.

Excitation spectroscopy

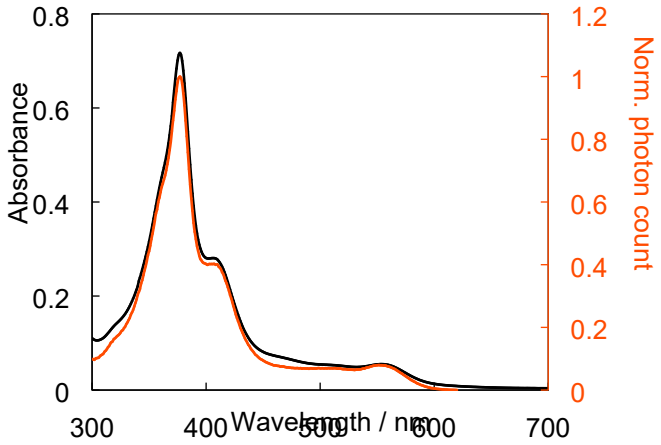


Figure S10. Absorption (black) and excitation (orange, λ_{em} = 670 nm) spectra of **Soln_99** containing 30 μM of **1b**$^{+}$.

DFT and TD-DFT calculations

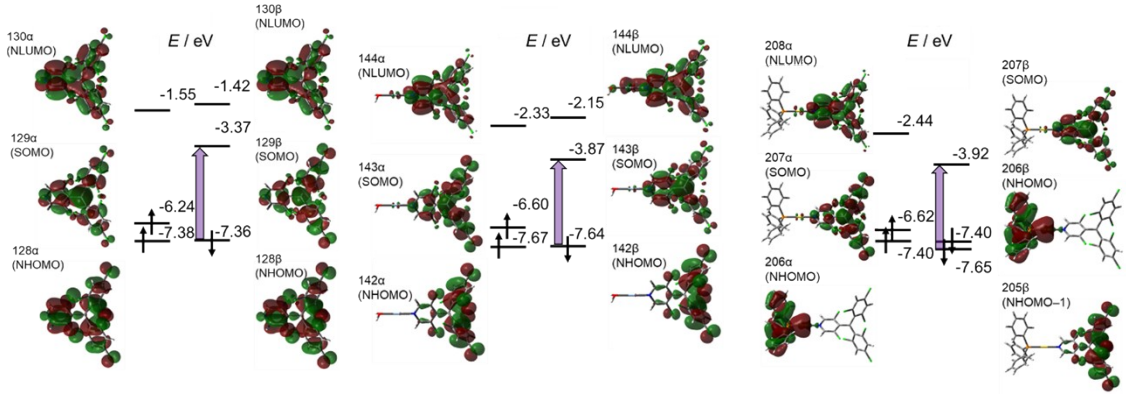


Figure S11. Frontier molecular orbitals of PyBTM, [Ag(PyBTM)(H_2O)]$^{+}$ and [Au(PyBTM)(PPh_3)]$^{+}$ calculated using DFT (UM06/SDD(Ag or Au);6-31G(d)(H, C, N, Cl, and O or P)). The effect of the solvent (dichloromethane) was treated with the polarizable continuum model (PCM). The purple arrows indicate a major component of the lowest energy transition for each compound.

Abstracted results of TD-DFT calculations

PyBTM (UM06/6-31g(d), SCRF (solvent = CH_2Cl_2)), ground state

129A is SOMO.

Excited State 1: 2.293-A 2.6232 eV 472.65 nm f=0.0279 <S**2>=1.065

129A ->131A	0.27006
124B ->131B	-0.12247
125B ->129B	-0.18764
126B ->129B	0.27461
128B ->129B	0.83775

Excited State 2: 2.357-A 2.7635 eV 448.64 nm f=0.0077 <S**2>=1.139

128A ->131A	0.13862
129A ->130A	0.29903
129A ->137A	0.10477
122B ->130B	0.10455
124B ->129B	0.59189
127B ->129B	0.62443
128B ->131B	-0.11870

Excited State 3: 2.218-A 2.8863 eV 429.57 nm f=0.0141 <S**2>=0.979

129A ->131A	0.13155
125B ->129B	-0.20667
126B ->129B	0.84131
128B ->129B	-0.40186
128B ->130B	-0.11938

Excited State 4: 2.196-A 2.9961 eV 413.82 nm f=0.0022 <S**2>=0.956

129A ->130A	-0.18181
124B ->129B	-0.58259
127B ->129B	0.73643

Excited State 5: 2.139-A 3.0018 eV 413.03 nm f=0.0078 <S**2>=0.894

129A ->131A	-0.10334
129A ->132A	-0.11919
125B ->129B	0.89885
126B ->129B	0.31856
127B ->131B	0.11253
128B ->129B	0.15642

$[Ag(PyBTM)(H_2O)]^+$ (UM06/ SDD(Ag), 6-31G(d)(H, C, N, Cl, O), SCRF (solvent = CH_2Cl_2)), ground state 143A is SOMO.

Excited State 1:	2.201-A	2.4798 eV	499.98 nm	f=0.0441	<S**2>=0.961	
143A ->146A	-0.10163					
143A ->147A	-0.17548					
140B ->143B	0.18898					
142B ->143B	0.91278					
142B ->144B	-0.11559					
Excited State 2:	2.248-A	2.6305 eV	471.34 nm	f=0.0074	<S**2>=1.014	
143A ->144A	0.26229					
143A ->155A	-0.10008					
136B ->143B	0.12803					
139B ->143B	0.60101					
141B ->143B	0.66306					
Excited State 3:	2.115-A	2.7884 eV	444.64 nm	f=0.0093	<S**2>=0.868	
139B ->143B	0.18644					
140B ->143B	0.89839					
141B ->143B	-0.23574					
142B ->143B	-0.22026					
Excited State 4:	2.157-A	2.7924 eV	444.01 nm	f=0.0036	<S**2>=0.913	
143A ->144A	-0.21496					
139B ->143B	-0.56419					
140B ->143B	0.30568					
141B ->143B	0.68249					
Excited State 5:	2.331-A	3.0093 eV	412.01 nm	f=0.0284	<S**2>=1.108	
139A ->144A	-0.16887					
143A ->144A	0.28462					
143A ->146A	-0.14111					
136B ->143B	0.11718					
138B ->143B	0.87022					
138B ->144B	0.14566					
139B ->143B	-0.14953					
Excited State 6:	2.248-A	3.0106 eV	411.83 nm	f=0.1132	<S**2>=1.013	

138A ->144A 0.17553
139A ->146A 0.10690
143A ->144A 0.71486
136B ->143B 0.31700
138B ->143B -0.34278
139B ->143B -0.36720

Excited State 7: 2.843-A 3.2134 eV 385.84 nm f=0.0777 <S**2>=1.770
136A ->144A -0.11115
138A ->144A 0.20951
139A ->146A 0.18477
140A ->147A -0.12688
140A ->148A 0.11500
141A ->149A -0.14322
142A ->147A 0.16232
143A ->144A -0.34830
143A ->155A 0.13343
136B ->143B 0.61395
136B ->144B 0.11248
138B ->146B 0.22725
139B ->143B 0.18142
139B ->144B 0.14943
140B ->147B -0.11298
140B ->148B 0.10761
141B ->149B 0.12886
142B ->147B -0.15004

Excited State 8: 2.910-A 3.2995 eV 375.76 nm f=0.1195 <S**2>=1.867
140A ->149A 0.22321
141A ->148A -0.23288
142A ->144A -0.18892
142A ->155A 0.13342
143A ->145A -0.11697
143A ->146A 0.32097
143A ->147A 0.51829
138B ->143B 0.15875
139B ->147B -0.17873
140B ->143B 0.16105
140B ->149B 0.19568

141B ->147B -0.11836
141B ->148B 0.18769
142B ->143B 0.29190
142B ->144B 0.19165
142B ->156B 0.13123

Excited State 9: 2.360-A 3.6086 eV 343.58 nm f=0.0110 <S**2>=1.142
140A ->148A -0.10035
141A ->149A 0.11060
143A ->144A -0.12308
137B ->143B 0.89828
137B ->144B 0.18814
141B ->149B -0.10163

Excited State 10: 2.985-A 3.6145 eV 343.02 nm f=0.0191 <S**2>=1.977
140A ->147A -0.14845
140A ->148A 0.26313
141A ->149A -0.29245
142A ->146A 0.15237
142A ->147A 0.14982
142A ->148A 0.14555
143A ->144A 0.33417
136B ->143B -0.31680
137B ->143B 0.32845
138B ->146B -0.12739
139B ->143B 0.20367
139B ->144B 0.12880
139B ->156B 0.10387
140B ->147B -0.15267
140B ->148B 0.24976
141B ->149B 0.26997
142B ->146B 0.13184
142B ->147B -0.18490
142B ->148B -0.13690

Excited State 11: 2.219-A 3.7378 eV 331.70 nm f=0.0081 <S**2>=0.980
138A ->146A 0.14533
139A ->144A -0.12593
143A ->145A 0.18530

143A ->146A 0.84173
143A ->147A -0.39720

Excited State 12: 3.115-A 3.8205 eV 324.53 nm f=0.0051 <S**2>=2.176
139A ->146A -0.49756
139A ->147A 0.21813
139A ->148A 0.12789
136B ->143B 0.51601
136B ->144B -0.11068
138B ->146B -0.51250
138B ->147B -0.14776
138B ->148B -0.12954

$[Au(PyBTM)(PPh_3)]^+$ (UM06/ SDD(Au), 6-31G(d)(H, C, N, Cl, P), SCRF (solvent = CH_2Cl_2)), ground state 207A is SOMO.

Excited State 1:	2.187-A	2.4530 eV	505.43 nm	f=0.0448	<S**2>=0.946
207A ->210A	0.15708				
201B ->207B	-0.19264				
205B ->207B	0.91597				
205B ->208B	0.12992				

Excited State 2:	2.231-A	2.6039 eV	476.14 nm	f=0.0089	<S**2>=0.995
207A ->208A	0.25911				
194B ->207B	0.13074				
199B ->207B	0.58254				
204B ->207B	0.67964				

Excited State 3:	2.106-A	2.7520 eV	450.52 nm	f=0.0098	<S**2>=0.858
201B ->207B	0.94897				
205B ->207B	0.23180				

Excited State 4:	2.163-A	2.7591 eV	449.37 nm	f=0.0023	<S**2>=0.920
207A ->208A	-0.25521				
199B ->207B	-0.59841				
204B ->207B	0.69659				

Excited State 5:	2.180-A	2.9511 eV	420.13 nm	f=0.1901	<S**2>=0.939
196A ->208A	-0.14875				
207A ->208A	0.80341				
194B ->207B	0.27674				
199B ->207B	-0.41347				

Excited State 6:	2.129-A	2.9967 eV	413.73 nm	f=0.0005	<S**2>=0.883
195B ->207B	-0.10945				
196B ->207B	0.12600				
206B ->207B	0.98070				

References

1. S. Akine, *TitrationFit*, *ver 1.1.0, for analysis of titration data in host-guest chemistry*, **2013**. http://chem.s.kanazawa-u.ac.jp/coord/titrationfit_e.html.