

Modulating the spin-flip rates and emission energy through ligand design in chromium(III) molecular rubies

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Supporting Information

(51 pages)

Experimental part

Elemental analyses were carried out on a Fisons-Carlo Erba analyser model EA 1108. ¹H Nuclear Magnetic Resonance Spectroscopy (RMN) data were recorded on a 400 MHz BRUKER Nanobay Avance III HD High-Definition spectrometer and the spectra were internally referenced to solvent signals. Cyclic Voltammetry measurements were conducted in a one-compartment three-electrode cell for 0.15 mM analyte solutions in acetonitrile. ⁿBuN₄PF₆ was utilized as the supporting electrolyte with a solution concentration of 0.1 M. Glassy carbon (3 mm diameter) was employed as the working electrode while Pt wire was utilized as the counter electrode and Ag/AgCl (5mM) as reference electrode. Absorption spectra in acetonitrile solution were recorded using a Jasco Cary (Agilent Technologies) spectrometer (quartz cell path length 1 cm or 1 mm, 290-800 nm domain, 2×10⁻⁴ M and 650-800 nm domain, 7.7 mM). Emission and excitation spectra were measured on a UV-VIS-PTI QuantaMaster™ 8000 spectrofluorometer equipped with a Picosecond Photon Detector (230-850nm, PPD-850, HORIBA Scientific) and a continuous Xenon Short Arc Lamp (190-2000nm, USHIO). All the spectra (emission and excitation) were corrected with real-time correction functions. Time Correlated Single Photon Counting (TCSPC) lifetime measurements were performed using a 480 nm or 450 nm flash lamp (1 μs pulse, HORIBA Scientific). Low temperature (77 K) was achieved using liquid quartz transparent Dewar filled with liquid N₂ in the center of which samples were placed. Sample solutions in CH₃CN, were introduced in quartz tube (4 mm interior diameter) and introduced into the sample holder of the Dewar. All emission luminescence quantum yields were measured according to an absolute method which makes use of an integration sphere. Mass spectrometry measurements have been recorded in a Compact Bruker QTOF with UHPLC Elute Ole Bruker. Using the relationship $k_q = 1/[O_2] \cdot (1/\tau_{air} - 1/\tau_{Ar})$, where [O₂] is the oxygen concentration (2.42 mM in CH₃CN at 20 °C), τ_{air} is the ²E/²T₁ lifetime under aerated conditions and τ_{Ar} the respective lifetime under deaerated condition, k_q values for energy transfer from ²E/²T₁ to O₂ could be estimated (see main text). UV-vis transient absorption measurements on the nanosecond timescale were carried out on an LP920-KS instrument from Edinburgh Instruments. A frequency-tripled pulsed Nd:YAG laser (Quantel Q-smart 450, ca. 10 ns pulse width) with a beam expander (BE02-355 from Thorlabs) in the beam path was used for excitation at 355 nm (pulse energy of ~30 mJ) and a frequency-tripled Nd:YAG laser (Quantel Brilliant, ca. 10 ns pulse width) equipped with OPO from Opotek

and a beam expander (GBE02-A from Thorlabs) in the beam path was used for excitation at 450 nm (pulse energy of ~13 mJ). An iCCD camera from Andor was used to detect transient absorption spectra, and single-wavelength kinetics were recorded with a photomultiplier tube (Hamamatsu).

X-Ray Crystallography.

Suitable crystals of **1**, **2** and **3** were mounted on a Bruker D8 Venture diffractometer. Details of the crystals, data collection and refinement parameters are given in Table S1. After data processing (raw data integration, merging of equivalent reflections and absorption correction), the structures were solved by direct or Patterson methods and refined using least squares minimization with the SHELX suite of programs^[S1] integrated in OLEX2.^[S2] Selected bonds and lengths are given in Tables S2 and S3. In **2**, the iodine atom I1 is disordered over two sites and refined with site occupancies of 0.5/0.5. Carbon atoms C1S and C3S, which belong to a diethyl ether solvation molecule, are also disordered. The checkcif file of this structure contains two A-level alerts associated with residual peaks near a triflate counterion which is probably disordered and which we could not model. The CCDC numbers 2266702 (**1**), 2266703 (**2**) and (**3**) 2389781 contain the supplementary crystallographic data for this article. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

Appendix. Experimental section.

Solvents and starting materials

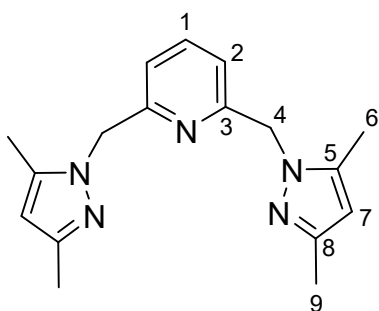
All the chemicals were purchased from commercial suppliers and used without further purification.

Synthesis: Preparation of the ligands and complexes

Synthesis of 2,6-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)pyridine (Mebipzp) and 2,6-bis((4-iodo-3,5-dimethyl-1H-pyrazol-1-yl)methyl)pyridine (IMebipzp) and 2,6-bis(indazol-2-ylmethyl)pyridine (bip).

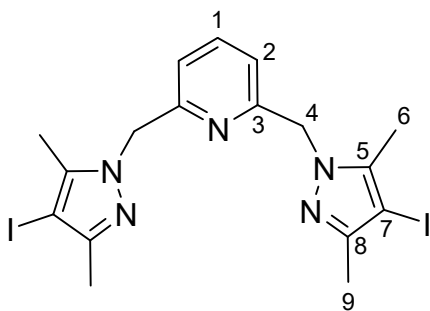
In a 100 mL round-bottom flask containing 20 mL of toluene were added: 0.3050 g of 2,6-bis(chloromethyl)pyridine and 0.3345 g of 3,5-dimethylpyrazole for Mebipzp or 0.3060 of 3,5-dimethyl-4-iodo-pyrazole for IMebipzp. On the other hand, a 40% NaOH solution was prepared, containing 4.8 g of NaOH dissolved in 12 mL of water, and 10 drops of TBAOH were added. This basic solution was added to the pyrazole containing

solution which was subsequently refluxed at 110°C for 24 hours. After this period, the mixture was allowed to cool to room temperature, and a liquid-liquid extraction was performed to separate the organic phase (toluene). The organic phase was washed with 3x10 mL of water. The organic phase was then dried with MgSO₄, filtered, and the solvent was removed under vacuum, resulting in the desired product in the form of a white solid (reaction yield: 90%).



¹H-NMR (400 MHz, CDCl₃, ppm) δ: 7.53-7.49 (t, *J* = 7.8 Hz, 1H), 6.64-6.62 (d, *J* = 7.8 Hz, 2H), 5.87 (s, 2H), 5.30 (s, 4H), 2.30 (s, 6H), 2.19 (s, 6H). ¹³C NMR (CD₃CN) δ = 158.28 (C3), 148.21 (C8), 140.80 (C5), 138.85 (C1), 120.93 (C2), 105.99 (C7), 54.75 (C4), 13.55 (C9), 11.19 (C6).

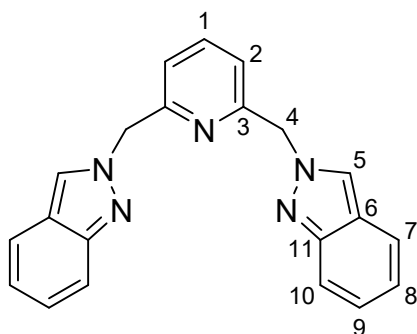
ESI-MS (*m/z*): 296.2 [L+H]⁺.



¹H-NMR (400 MHz, CDCl₃, ppm) δ: 7.55 (t, *J* = 7.8 Hz, 1H), 6.77 (d, *J* = 7.8 Hz 2H), 5.35 (s, 4H), 2.25 (s, 6H), 2.2 (s, 6H). ¹³C NMR (CDCl₃) δ = 156.26 (C3), 149.84 (C8), 141.31 (C5), 138.12 (C1), 119.96 (C2), 63.22 (C7), 55.33 (C4), 13.98 (C6), 11.91 (C9).

ESI-MS (*m/z*): 569.9 [L+Na]⁺.

For the synthesis of 2,6-bis(indazol-2-ylmethyl)pyridine (bip), we use 2,6-bis(bromomethyl)pyridine (0.300 g, 1.132 mmol) instead of 2,6-bis(chloromethyl)pyridine with 1H-indazole (0.267 g, 2.264 mmol). The synthesis procedure is the same as Mebipzp and IMebipzp (reaction yield: 80%).



$^1\text{H-NMR}$ (400 MHz, CDCl_3 , ppm) δ : 8.04 (s, 2H), 7.79 – 7.64 (m, 4H), 7.60 – 7.44 (m, 1H), 7.30 (t, $J = 1.1$, 2H), 7.10 (t, $J = 0.9$, 2H), 6.97 (d, $J = 7.8$, 2H), 5.72 (s, 4H). $^{13}\text{C-NMR}$ (CD_3CN) $\delta = 156.35$ (C11), 149.39, 138.58, 126.89 (C3, C1, C9), 124.82 (C5), 121.92 (C6), 121.50 (C8), 121.19 (C7), 120.98, 117.75 (C2, C10), 58.90 (C4).

ESI-MS (m/z): 362.1 [$\text{L}+\text{Na}$] $^+$.

Synthesis of $[\text{Cr}(\text{Mebipzp})_2](\text{SO}_3\text{CF}_3)_3$ (**1**) and $[\text{Cr}(\text{IMebipzp})_2](\text{SO}_3\text{CF}_3)_3$ (**2**) $[\text{Cr}(\text{bip}^*)_2](\text{SO}_3\text{CF}_3)_3$ (**3**)

In a glovebox 2 mmol of ligand suspended in 10 mL of anhydrous acetonitrile were added dropwise to a solution containing 1 mmol of $\text{Cr}(\text{CF}_3\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$ previously dissolved in 5 mL of anhydrous acetonitrile. The mixture was stirred for 2h at 35°C resulting in a purple solution. Subsequent addition of 1 mmol of AgSO_3CF_3 led to a colour change from purple to orange with the apparition of a grey solid. The mixture was stirred for additional 4 h. The reaction was taken from the glovebox and filtered through a membrane of PTFE of 2 μm . The volume of the orange solution was reduced under vacuum and diethyl ether was added to precipitate the solids which were filtered giving a pale pink solid for **1**, an orange solid for **2** and an orange solid for **3** (reaction yields $>90\%$). Elemental analysis for **1**: $\text{C}_{37}\text{H}_{42}\text{CrF}_9\text{N}_{10}\text{O}_9\text{S}_3\text{P}_3 \cdot 1.8\text{H}_2\text{O}$ %, found: C: 39.75, N: 12.59, H: 3.75; calculated: C: 40.01, N: 12.61, H: 4.02. Elemental analysis for **2**: $\text{C}_{37}\text{H}_{38}\text{CrF}_9\text{I}_4\text{N}_{10}\text{O}_9\text{S}_3\text{P}_3 \cdot \text{H}_2\text{O}$, found %: C: 27.26, N: 8.53, H: 2.49; calculated: C: 27.33, N: 8.61, H: 2.58. Elemental analysis for **3**: $\text{C}_{45}\text{H}_{34}\text{CrF}_9\text{N}_{10}\text{O}_9\text{S}_3 \cdot 0.9 \text{H}_2\text{O}$ %, found: C: 45.13, H: 2.87, N: 11.63; calculated: C: 45.26, H: 3.02, N: 11.73.

Single crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a concentrated acetonitrile solution containing the complexes after 48h.

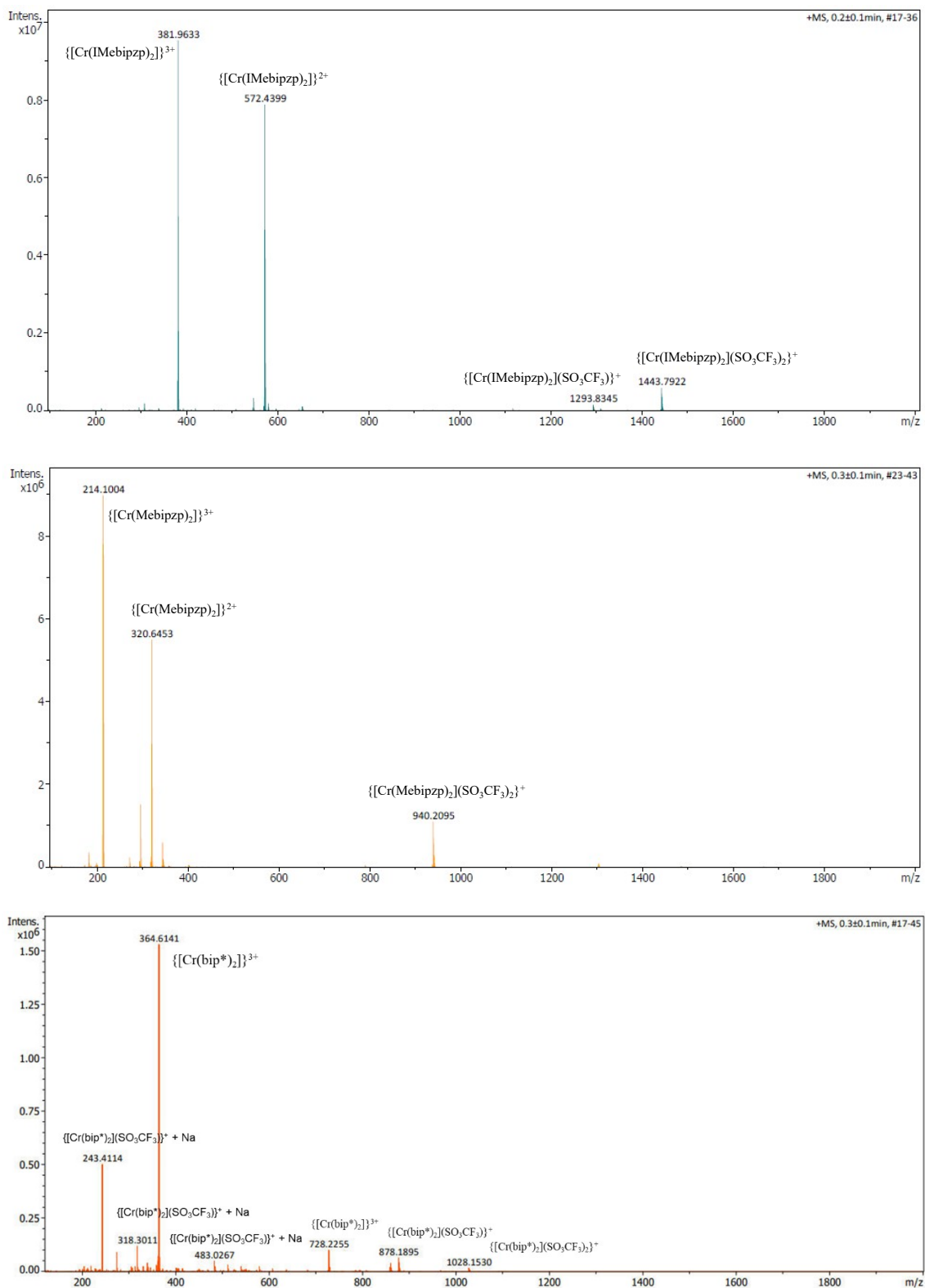


Figure S1. ESI-Mass spectrometry for complex **1** (top), **2** (medium) and **3** (bottom) and their respective assignment.

Table S1. Crystallographic data for complexes **1**, **2** and **3**

| | 1 | 2 |
|---|--|--|
| Empirical formula | C ₄₁ H ₄₈ CrF ₉ N ₁₂ O ₉ S ₃ | C ₄₃ H ₅₁ CrF ₉ L ₄ N ₁₁ O ₁₀ S ₃ |
| Formula weight | 1172.09 | 1708.72 |
| Crystal system | monoclinic | monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>c</i> | <i>P</i> 2 ₁ / <i>n</i> |
| <i>a</i> /Å | 21.2505(15) | 11.8195(5) |
| <i>b</i> /Å | 11.5885(7) | 22.8812(10) |
| <i>c</i> /Å | 20.6086(13) | 22.7016(10) |
| β/° | 92.210(2) | 100.6638(16) |
| Volume/Å ³ | 5071.3(6) | 6033.5(5) |
| <i>Z</i> | 4 | 4 |
| ρ _{calc} /g/cm ³ | 1.535 | 1.881 |
| μ/mm ⁻¹ | 0.447 | 2.428 |
| F(000) | 2412.0 | 3324.0 |
| Crystal size/mm ³ | 0.243 × 0.216 × 0.026 | 0.247 × 0.101 × 0.051 |
| Radiation | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.956 to 56.726 | 3.932 to 56.606 |
| Index ranges | -28 ≤ <i>h</i> ≤ 28, -14 ≤ <i>k</i> ≤ 15, -27 ≤ <i>l</i> ≤ 27 | -15 ≤ <i>h</i> ≤ 15, -30 ≤ <i>k</i> ≤ 30, -28 ≤ <i>l</i> ≤ 30 |
| Reflections collected | 79343 | 92085 |
| Independent reflections | 12613 [R _{int} = 0.0398, R _{sigma} = 0.0284] | 14938 [R _{int} = 0.0548, R _{sigma} = 0.0369] |
| Data/restraints/parameters | 12613/0/686 | 14938/95/772 |
| Goodness-of-fit on F ² | 1.053 | 1.073 |
| Final R indexes [I ≥ 2σ(I)] | R ₁ = 0.0413, wR ₂ = 0.1091 | R ₁ = 0.0611, wR ₂ = 0.1405 |
| Final R indexes [all data] | R ₁ = 0.0500, wR ₂ = 0.1165 | R ₁ = 0.0816, wR ₂ = 0.1539 |
| Largest diff. peak/hole / e Å ⁻³ | 1.26/-0.72 | 3.10/-1.54 |

3

| | |
|--|---|
| Empirical formula | C ₄₅ H ₅₄ CrF ₉ N ₁₀ O ₁₉ S ₃ |
| Formula weight | 1358.16 |
| Temperature/K | 100.00 |
| Crystal system | orthorhombic |
| Space group | <i>Pna</i> 2 ₁ |
| <i>a</i> /Å | 24.8078(9) |
| <i>b</i> /Å | 21.0257(10) |
| <i>c</i> /Å | 11.4987(5) |
| α /° | 90 |
| β /° | 90 |
| γ /° | 90 |
| Volume/Å ³ | 5997.7(4) |
| <i>Z</i> | 4 |
| ρ_{calc} /cm ³ | 1.504 |
| μ /mm ⁻¹ | 0.400 |
| <i>F</i> (000) | 2796.0 |
| Crystal size/mm ³ | 0.246 × 0.221 × 0.216 |
| Radiation | MoK α (λ = 0.71073) |
| 2 Θ range for data collection/° | 3.812 to 50.054 |
| Index ranges | -28 ≤ <i>h</i> ≤ 29, -25 ≤ <i>k</i> ≤ 25, -13 ≤ <i>l</i> ≤ 13 |
| Reflections collected | 49184 |
| Independent reflections | 10588 [<i>R</i> _{int} = 0.0473, <i>R</i> _{sigma} = 0.0293] |
| Data/restraints/parameters | 10588/1284/654 |
| Goodness-of-fit on <i>F</i> ² | 1.687 |
| Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)] | <i>R</i> ₁ = 0.1037, <i>wR</i> ₂ = 0.3308 |
| Final <i>R</i> indexes [all data] | <i>R</i> ₁ = 0.1117, <i>wR</i> ₂ = 0.3517 |
| Largest diff. peak/hole / e Å ⁻³ | 2.19/-1.23 |
| Flack parameter | 0.51(6) |

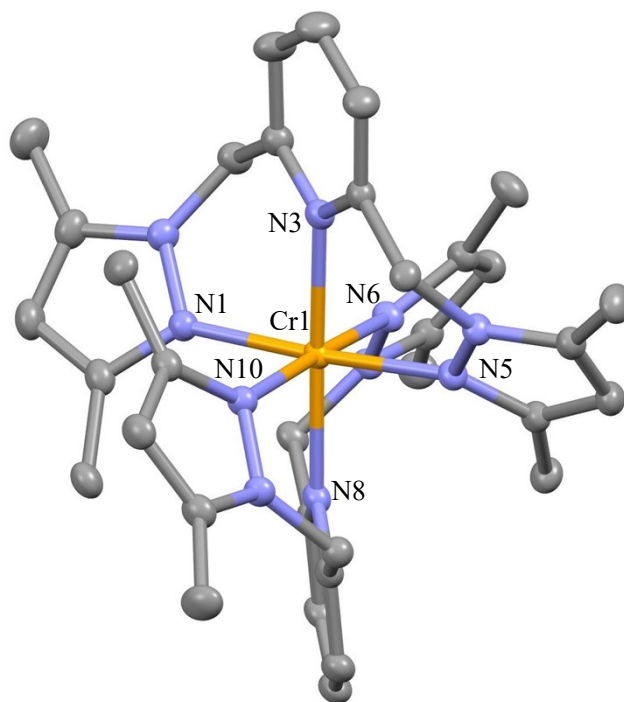


Figure S2. Molecular Structure of 1. Colour codes: Cr (orange), N (blue), C (grey).

Table S2. Selected bond distances (Å) and angles (°) for complex 1

| Bond distances (Å) | | Bond angles (°) | |
|--------------------|------------|-----------------|-----------|
| Cr1-N1 | 2.0527(15) | N1-Cr1-N3 | 88.63(6) |
| Cr1-N3 | 2.0813(14) | N1-Cr1-N5 | 176.25(6) |
| Cr1-N5 | 2.0634(15) | N1-Cr1-N6 | 92.89(6) |
| Cr1-N6 | 2.0550(14) | N1-Cr1-N8 | 93.38(6) |
| Cr1-N8 | 2.0869(14) | N1-Cr1-N10 | 85.80(6) |
| Cr1-N10 | 2.0470(14) | N3-Cr1-N5 | 87.82(6) |
| | | N3-Cr1-N6 | 93.28(6) |
| | | N3-Cr1-N8 | 177.28(6) |
| | | N3-Cr1-N10 | 90.36(6) |
| | | N5-Cr1-N6 | 86.11(6) |
| | | N5-Cr1-N8 | 90.20(6) |
| | | N5-Cr1-N10 | 95.43(6) |
| | | N6-Cr1-N8 | 88.44(6) |
| | | N6-Cr1-N10 | 176.10(6) |
| | | N8-Cr1-N10 | 87.97(6) |

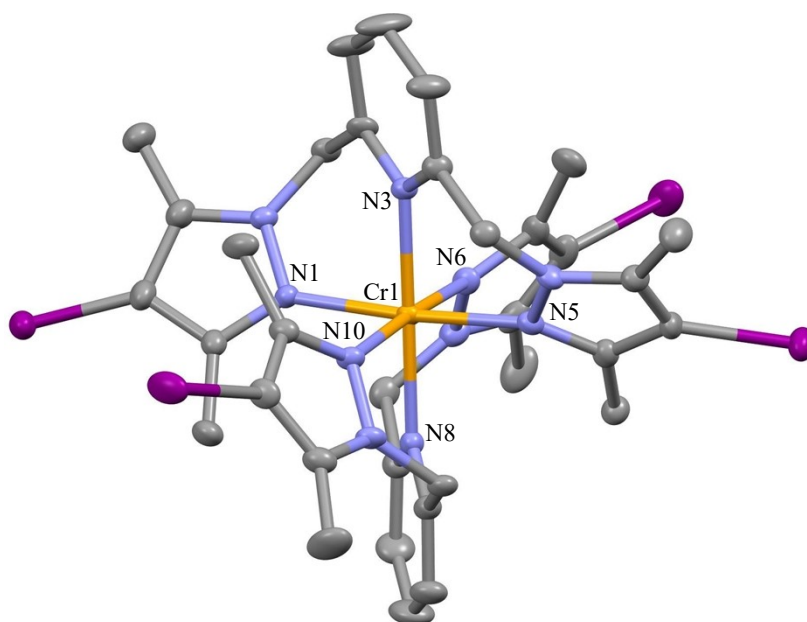


Figure S3. Molecular Structure of **2**. Colour codes: Cr (orange), N (blue), C (grey), I (purple).

Table S3. Selected bond distances (Å) and angles (°) for complex **2**

| Bond distances (Å) | | Bond angles (°) | |
|--------------------|----------|-----------------|------------|
| Cr1-N1 | 2.067(5) | N1-Cr1-N3 | 87.28(18) |
| Cr1-N3 | 2.091(5) | N1-Cr1-N5 | 175.28(19) |
| Cr1-N5 | 2.065(5) | N1-Cr1-N6 | 93.53(19) |
| Cr1-N6 | 2.065(5) | N1-Cr1-N8 | 92.69(18) |
| Cr1-N8 | 2.104(5) | N1-Cr1-N10 | 86.51(19) |
| Cr1-N10 | 2.069(5) | N3-Cr1-N5 | 88.06(18) |
| | | N3-Cr1-N6 | 92.80(19) |
| | | N3-Cr1-N8 | 178.97(19) |
| | | N3-Cr1-N10 | 91.38(18) |
| | | N5-Cr1-N6 | 85.95(19) |
| | | N5-Cr1-N8 | 91.99(18) |
| | | N5-Cr1-N10 | 94.36(19) |
| | | N6-Cr1-N8 | 88.23(19) |
| | | N6-Cr1-N10 | 175.8(2) |
| | | N8-Cr1-N10 | 87.59(18) |

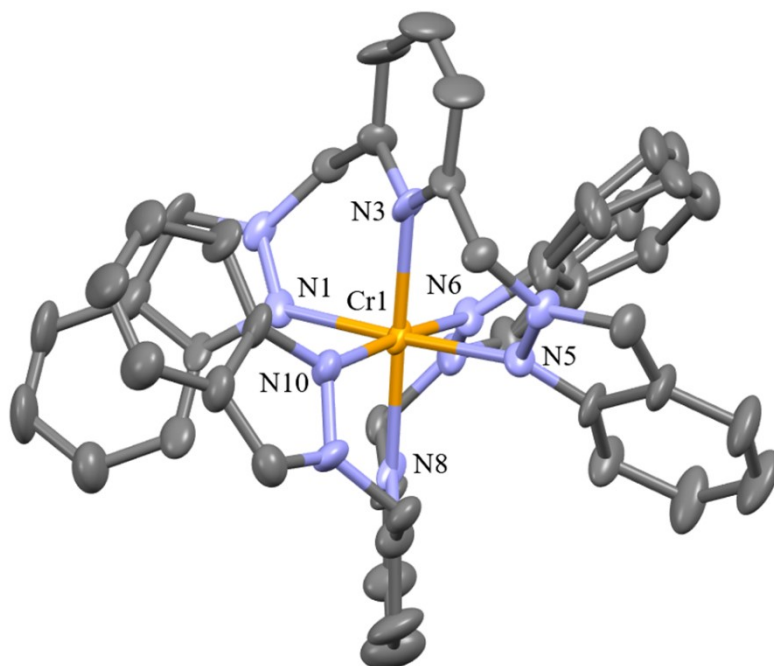


Figure S4. Molecular Structure of **3**. Colour codes: Cr (orange), N (blue), C (grey), I (purple).

Table S4. Selected bond distances (Å) and angles (°) for complex **3**

| Bond distances (Å) | | Bond angles (°) | |
|--------------------|----------|-----------------|----------|
| Cr1-N3 | 2.079(7) | N3-Cr1-N8 | 178.5(2) |
| Cr1-N5 | 2.043(6) | N5-Cr1-N3 | 88.5(3) |
| Cr1-N10 | 2.030(7) | N5-Cr1-N8 | 90.0(2) |
| Cr1-N1 | 2.047(6) | N10-Cr1-N3 | 91.7(3) |
| Cr1-N8 | 2.098(4) | N10-Cr1-N5 | 95.0(3) |
| Cr1-N6 | 1.999(7) | N10-Cr1-N1 | 85.7(2) |
| | | N10-Cr1-N8 | 88.0(3) |
| | | N1-Cr1-N3 | 88.8(3) |
| | | N1-Cr1-N5 | 177.3(3) |
| | | N1-Cr1-N8 | 92.6(2) |
| | | N6-Cr1-N3 | 92.9(3) |
| | | N6-Cr1-N5 | 85.2(2) |
| | | N6-Cr1-N10 | 175.4(3) |
| | | N6-Cr1-N1 | 94.4(3) |
| | | N6-Cr1-N8 | 87.3(3) |

Table S5. SHAPE analysis of the compounds [Cr(bpmp)₂]³⁺, [Cr(btmp)₂]³⁺, 1, 2 and 3

| | JPPY-6 | TPR-6 | OC-6 | PPY-6 | HP-6 |
|--|--------|--------|-------|--------|--------|
| [Cr(bpmp) ₂] ³⁺ | 31.949 | 15.635 | 0.158 | 28.611 | 31.107 |
| [Cr(btmp) ₂] ³⁺ | 32.182 | 15.898 | 0.151 | 28.855 | 30.753 |
| 1 | 31.175 | 14.327 | 0.186 | 27.654 | 31.836 |
| 2 | 31.272 | 14.843 | 0.183 | 27.77 | 31.885 |
| 3 | 31.075 | 14.859 | 0.208 | 27.818 | 31.59 |

JPPY-6 5 C_{5v} Johnson pentagonal pyramid J2

TPR-6 4 D_{3h} Trigonal prism

OC-6 3 O_h Octahedron

PPY-6 2 C_{5v} Pentagonal pyramid

HP-6 1 D_{6h} Hexagon

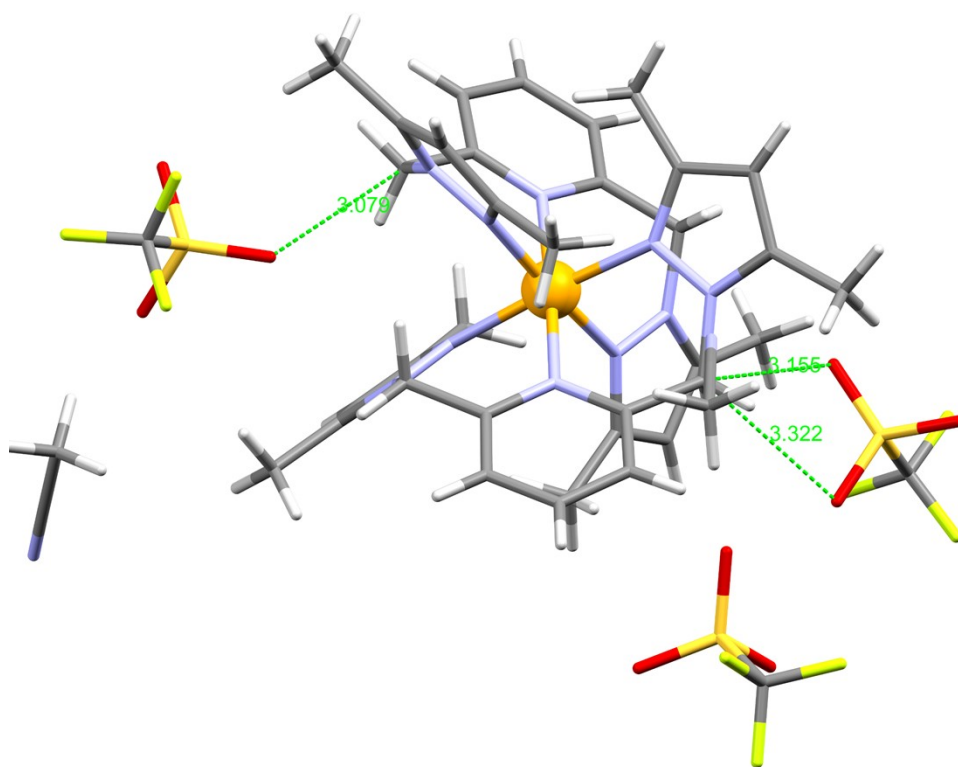


Figure S5. Molecular Structure of **1**. Colour codes: Cr (orange), N (blue), C (grey), H (white), F (green), S (yellow) and O (red).

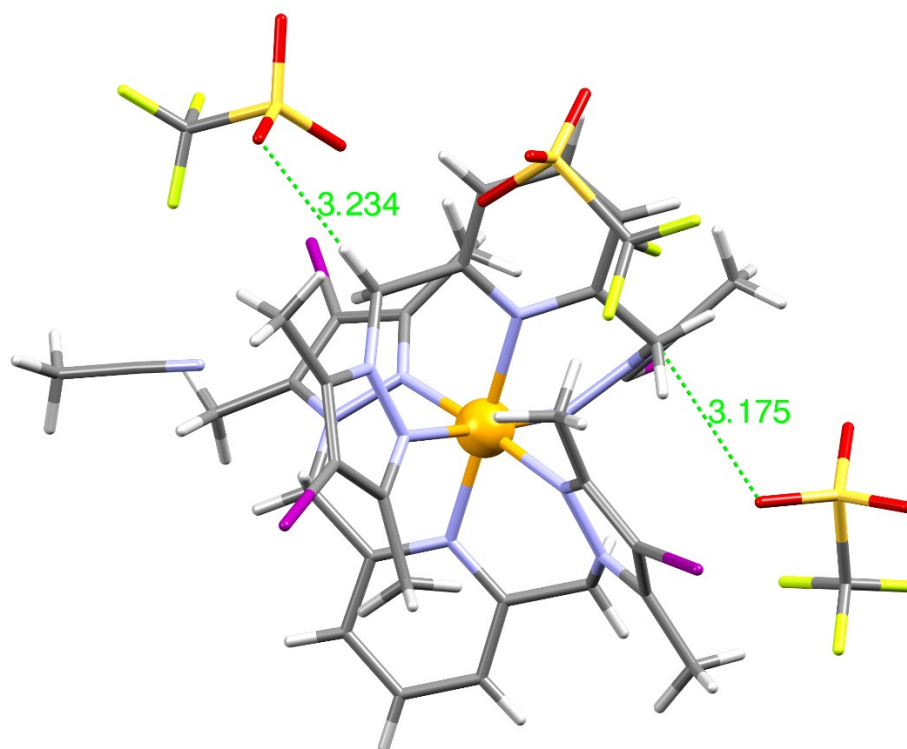


Figure S6. Molecular Structure of **2**. Colour codes: Cr (orange), N (blue), C (grey), H (white), I (purple), F (green), S (yellow) and O (red).

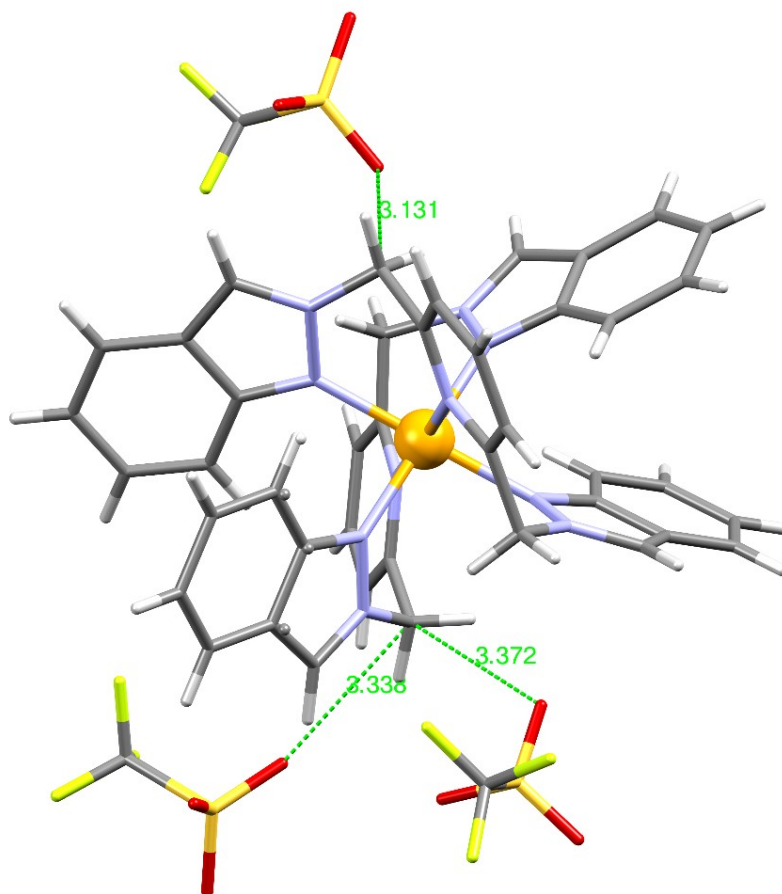


Figure S7. Molecular Structure of **3**. Colour codes: Cr (orange), N (blue), C (grey), H (white), F (green), S (yellow) and O (red).

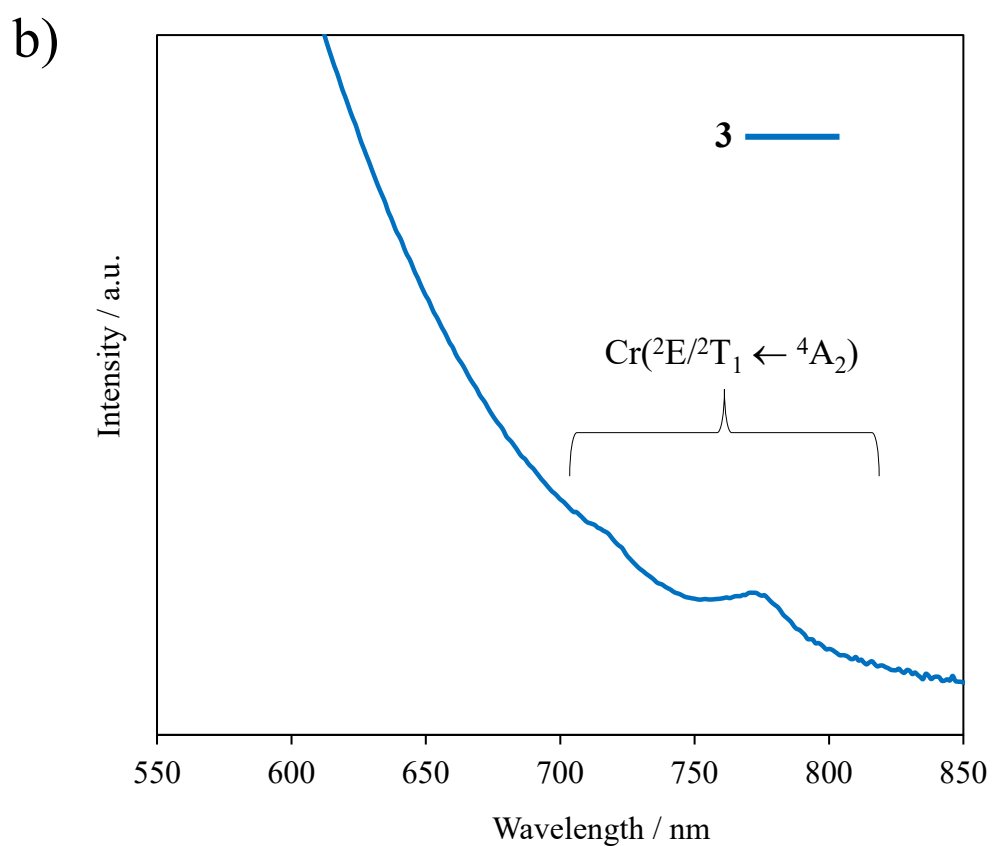
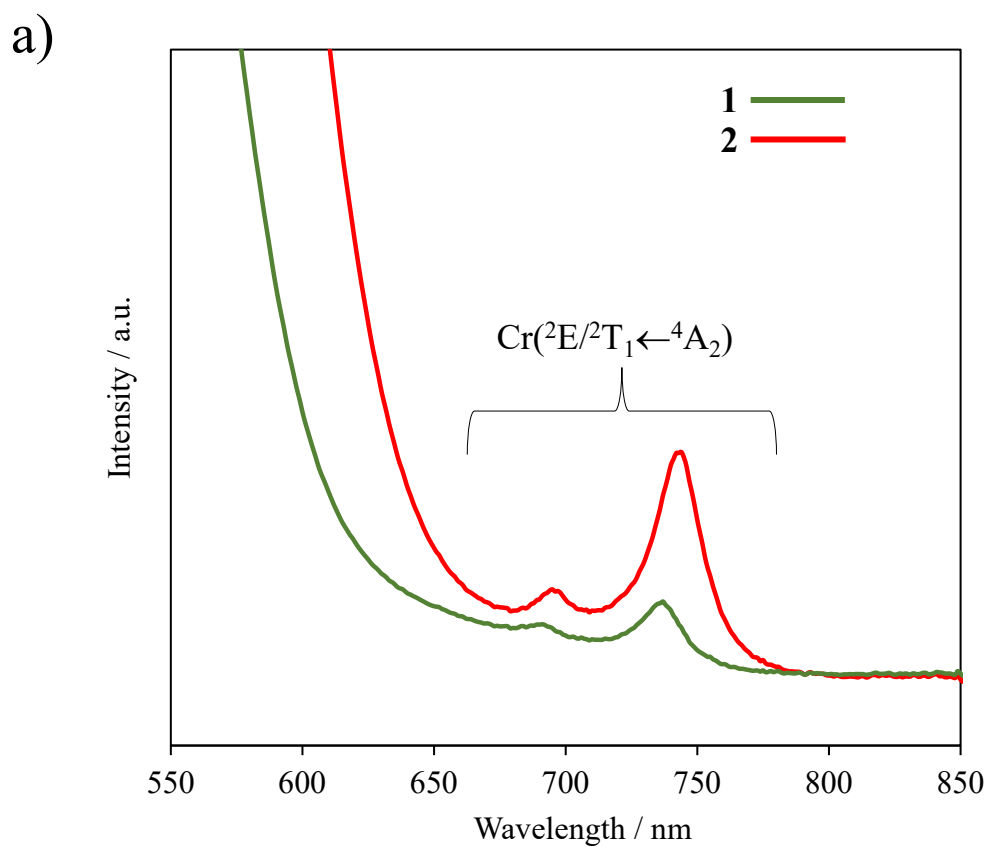


Figure S8. a) Solid state absorption spectra of $[\text{Cr}(\text{Mebipzp})_2]^{3+}$ (**1**) and $[\text{Cr}(\text{IMebipzp})_2]^{3+}$ (**2**), and b) $[\text{Cr}(\text{bip}^*)_2]^{3+}$ (**3**)

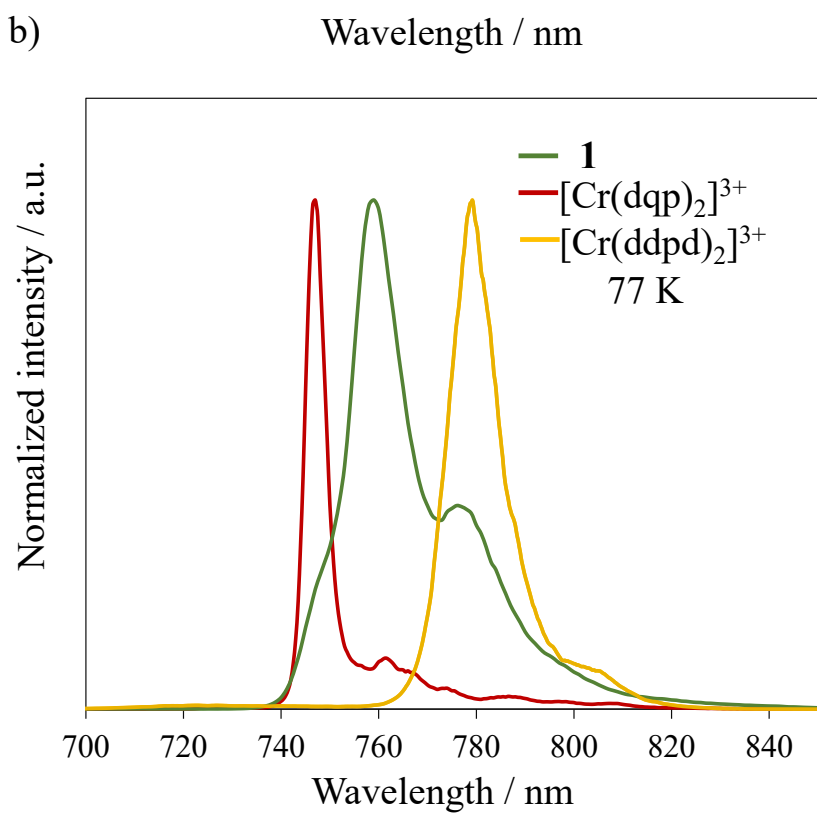
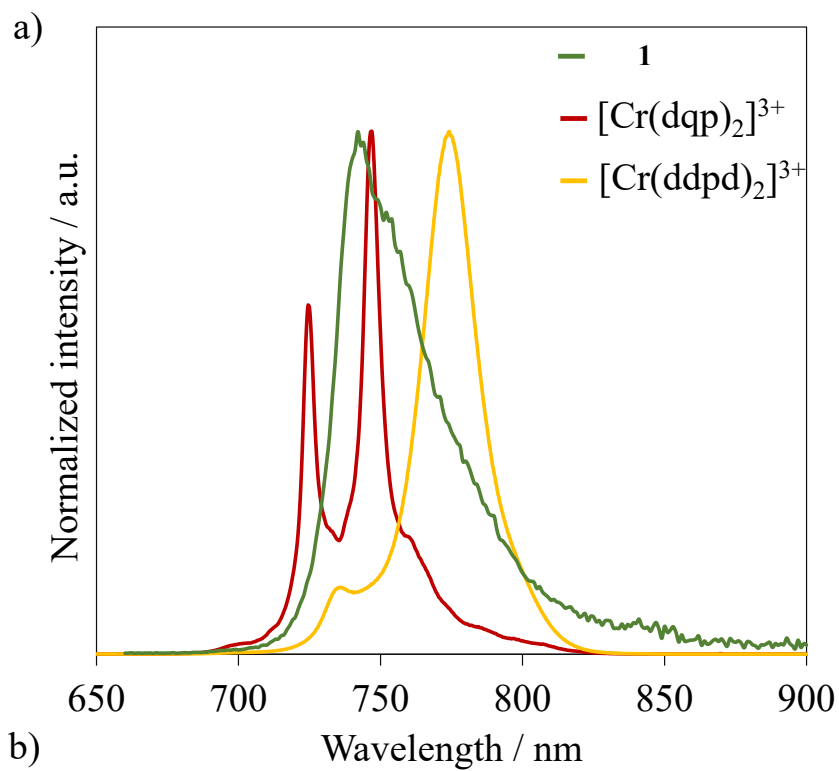


Figure S9. Comparison of emission spectra of 1, [Cr(dqp)₂]³⁺ and [Cr(ddpd)₂]³⁺ at room temperature (a) and 77 K in frozen solution (b).

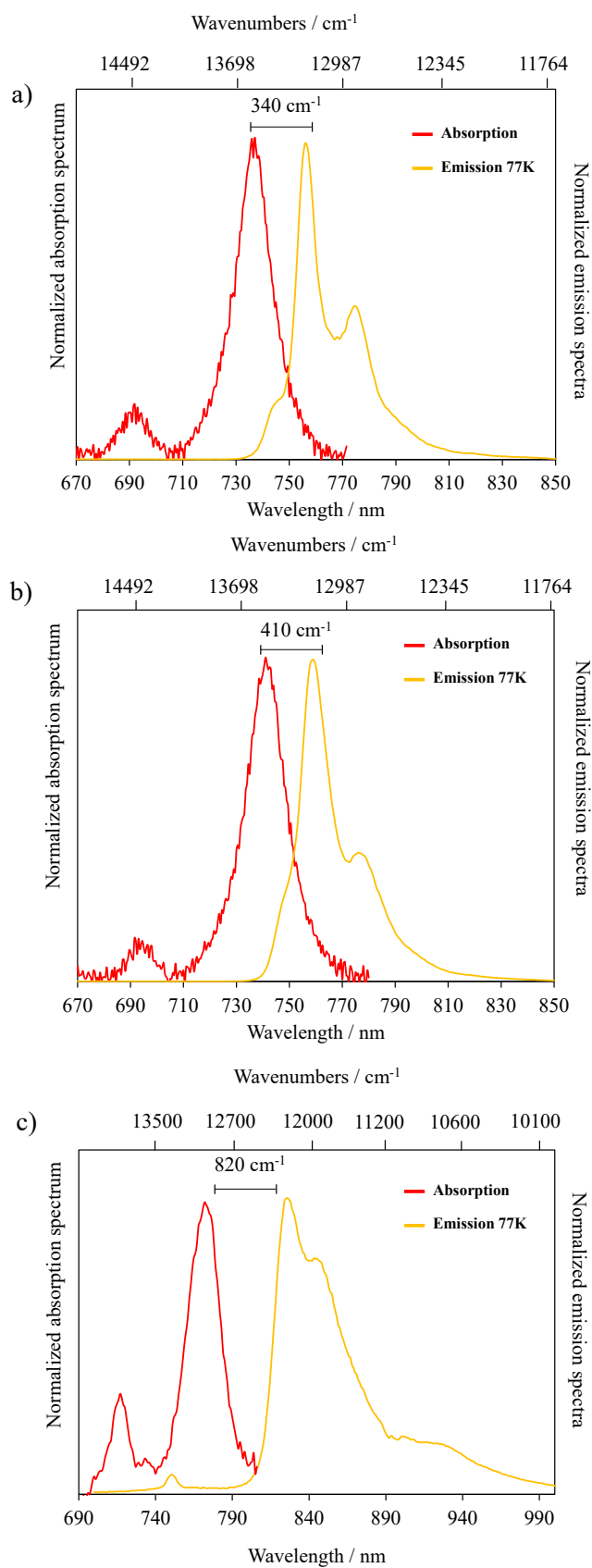


Figure S10. Comparison of absorption and emission spectra at 77 K for complex 1 (a), 2 (b) and 3 (c).

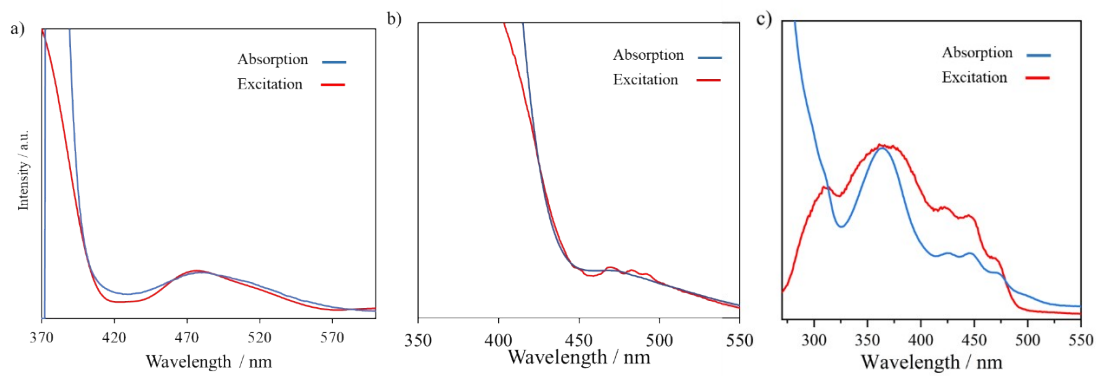


Figure S11. Excitation spectra of **1** (a), **2** (b), upon monitoring $\lambda_{em} = 748$ nm and **3** (c) monitored at $\lambda_{em} = 830$ nm.

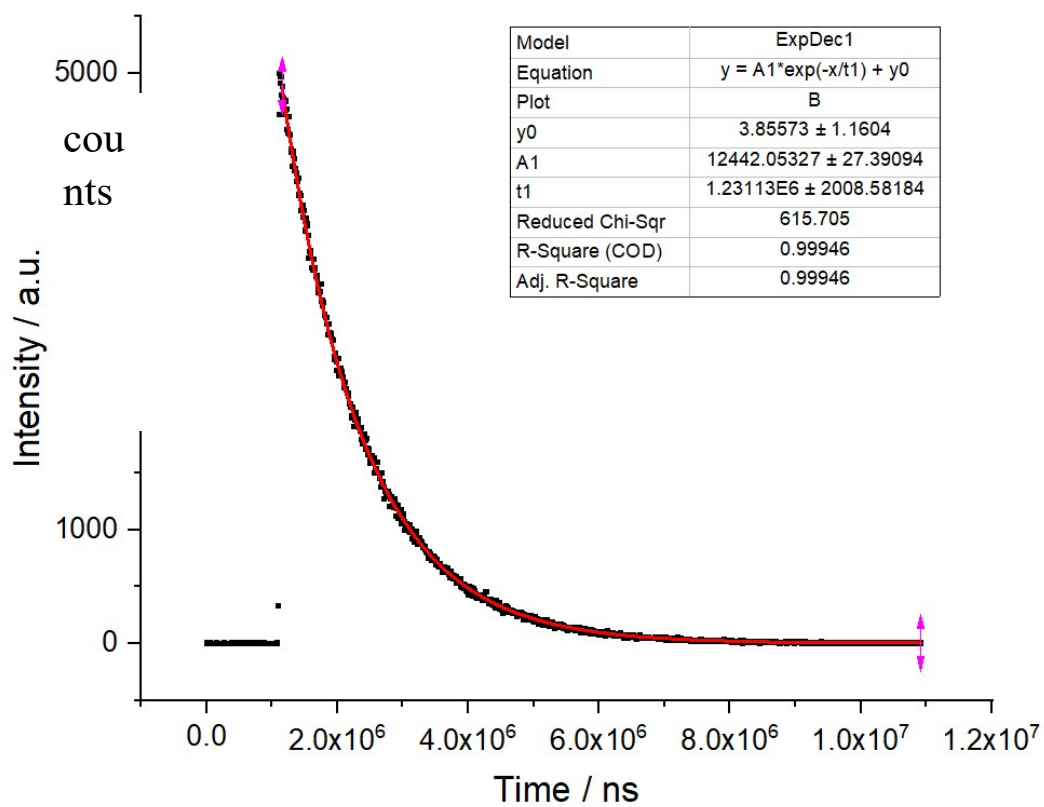


Figure S12. Excited state lifetime and the best fit of the experimental data for the $[\text{Cr}(\text{Mebipzp})_2]^{3+}$ complex ($\lambda_{\text{exc}} = 480 \text{ nm}$) in deaerated acetonitrile solution

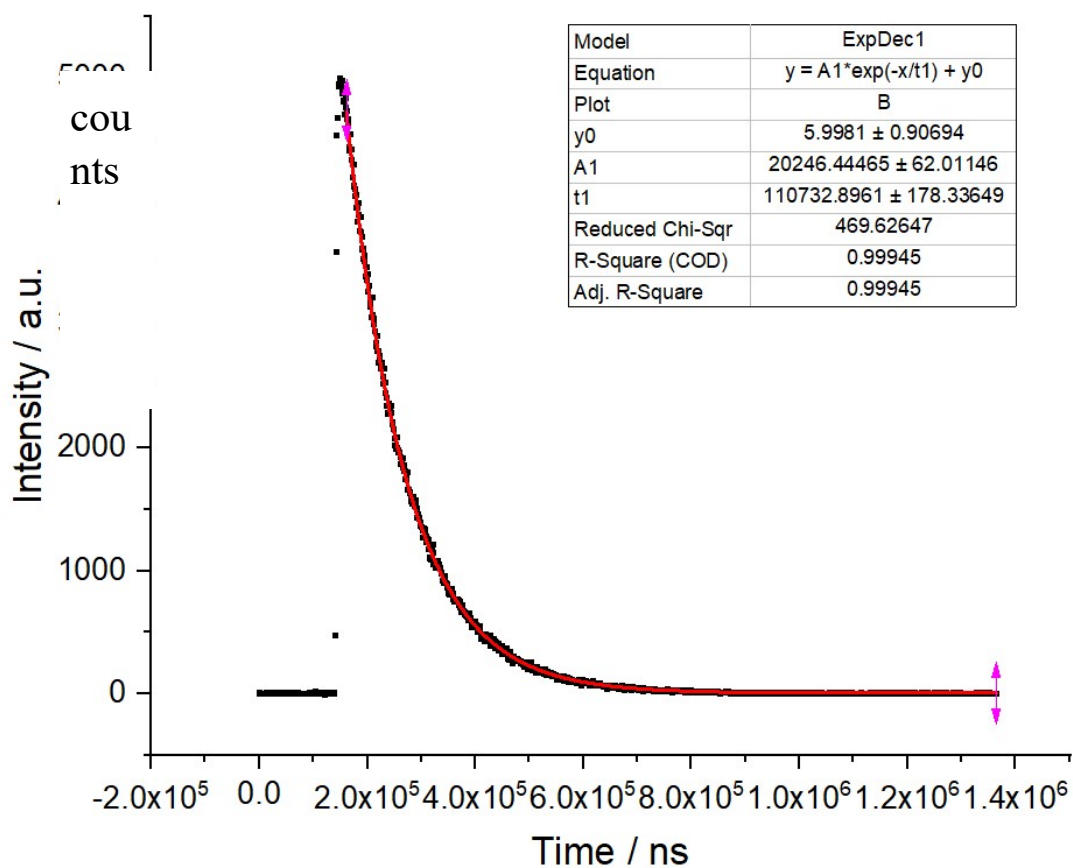


Figure S13. Excited state lifetime and the best fit of the experimental data for the $[\text{Cr}(\text{Mebipzp})_2]^{3+}$ complex ($\lambda_{\text{exc}} = 480 \text{ nm}$) in aerated acetonitrile solution

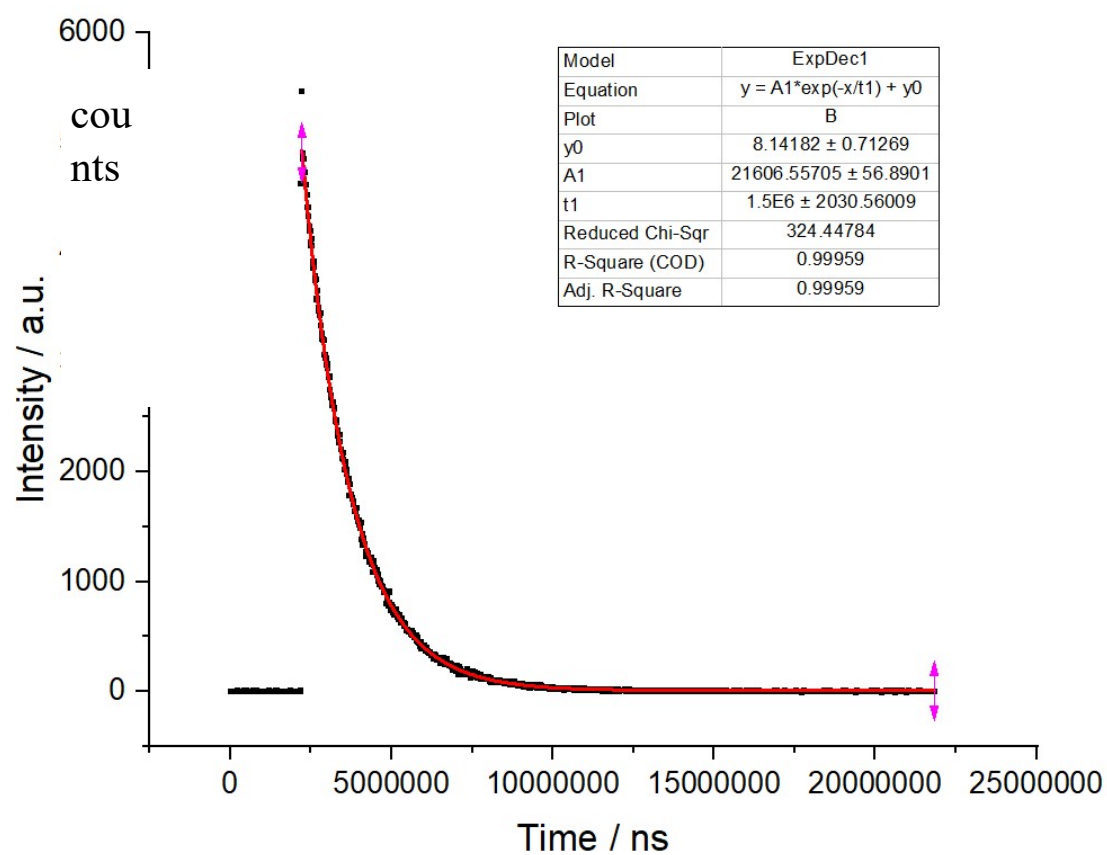


Figure S14. Excited state lifetime and the best fit of the experimental data for the $[\text{Cr}(\text{Mebipzp})_2]^{3+}$ complex ($\lambda_{\text{exc}} = 480 \text{ nm}$) at 77 K in frozen acetonitrile

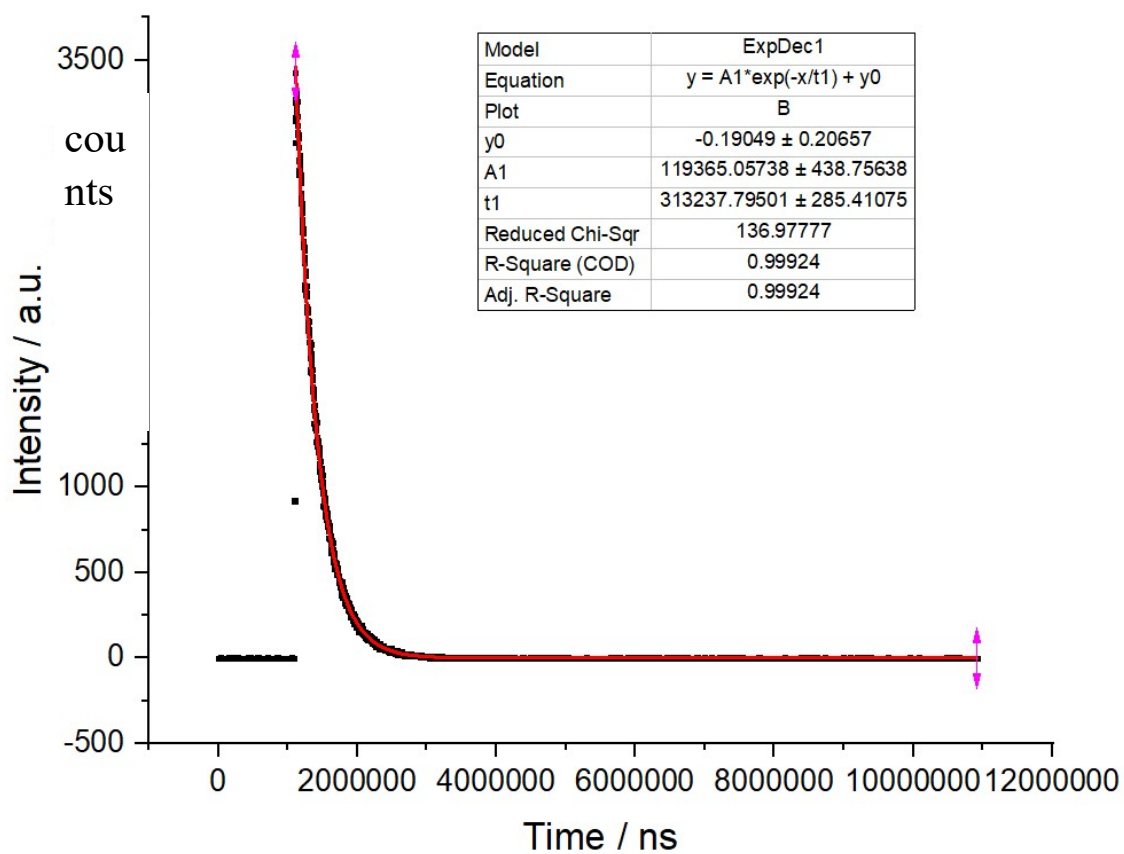


Figure S15. Excited state lifetime and the best fit of the experimental data for the $[\text{Cr}(\text{IMEbipzp})_2]^{3+}$ complex ($\lambda_{\text{exc}} = 480 \text{ nm}$) in deaerated acetonitrile solution

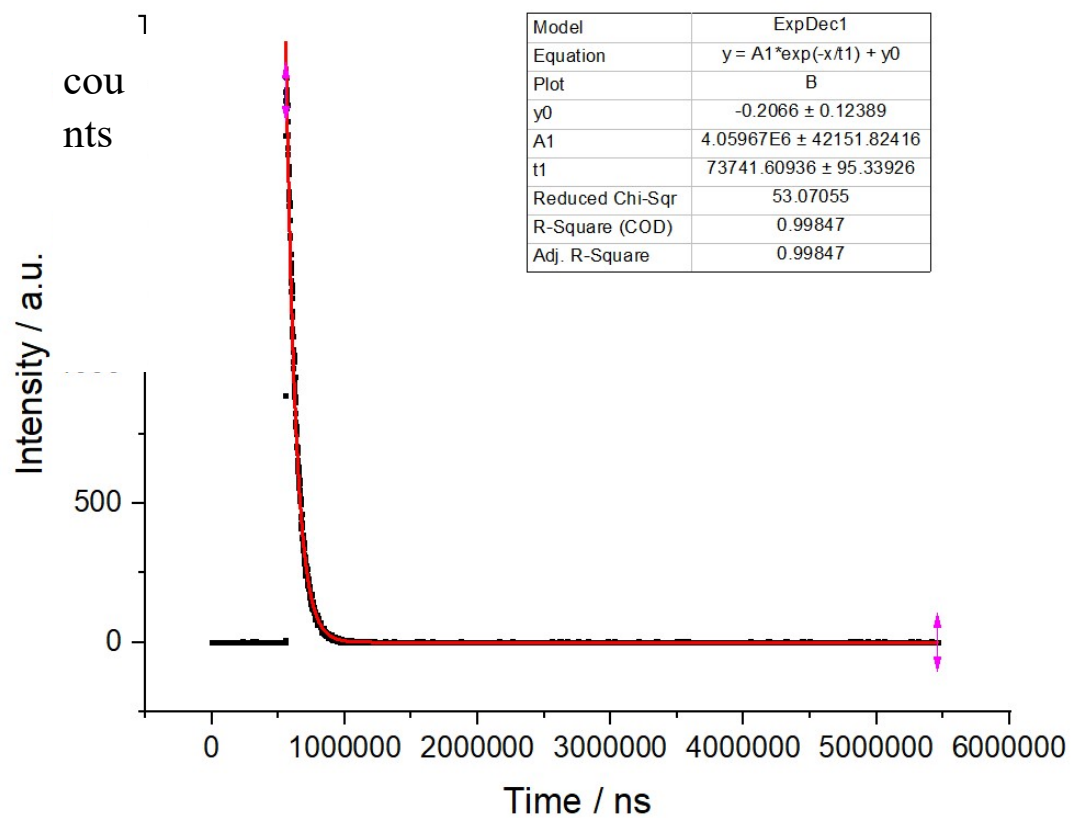


Figure S16. Excited state lifetime and the best fit of the experimental data for the $[\text{Cr}(\text{IMebipzp})_2]^{3+}$ complex ($\lambda_{\text{exc}} = 480 \text{ nm}$) in aerated acetonitrile solution.

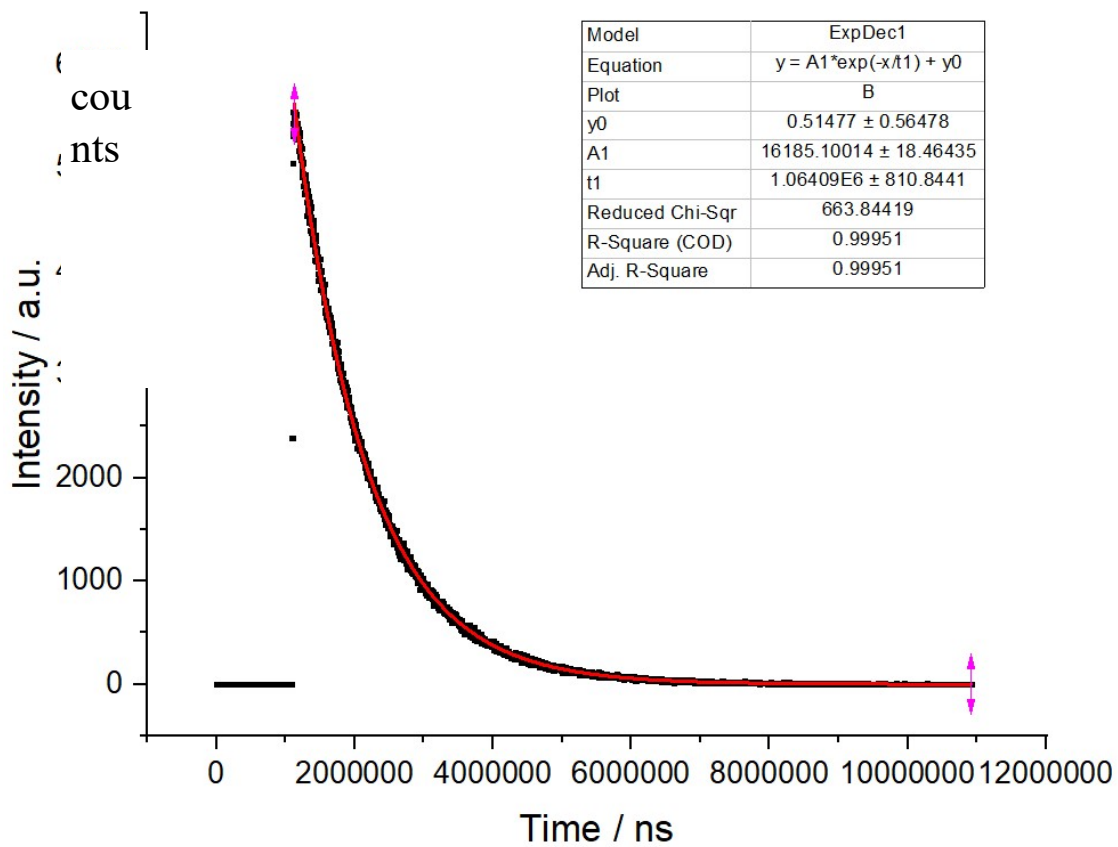


Figure S17. Excited state lifetime and the best fit of the experimental data for the $[\text{Cr}(\text{IMEbipzp})_2]^{3+}$ complex ($\lambda_{\text{exc}} = 480 \text{ nm}$) at 77 K in frozen acetonitrile.

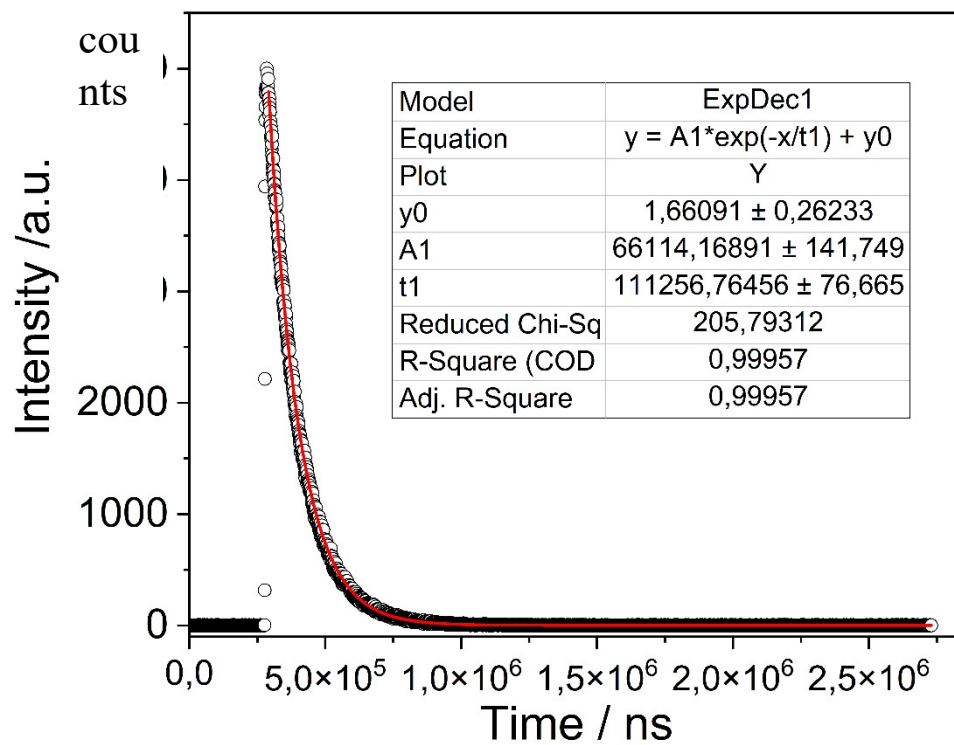


Figure S18. Excited state lifetime and the best fit of the experimental data for the $[\text{Cr}(\text{bip}^*)_2]^{3+}$ complex ($\lambda_{\text{exc}} = 450 \text{ nm}$) in deaerated acetonitrile solution at room temperature.

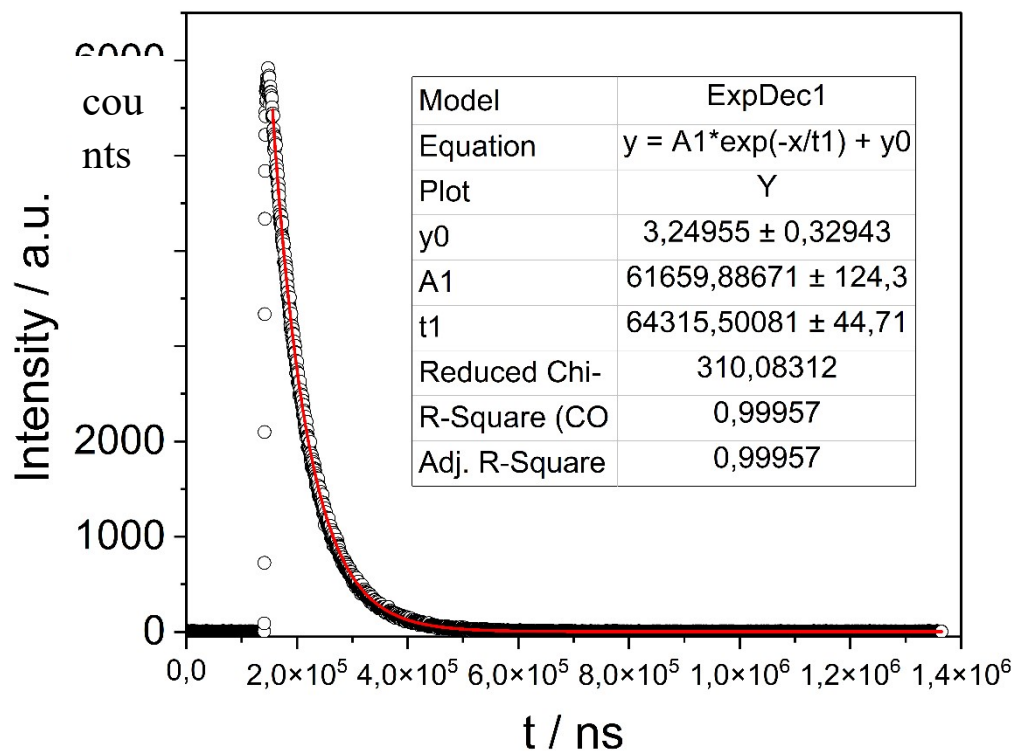


Figure S19. Excited state lifetime and the best fit of the experimental data for the $[\text{Cr}(\text{bip}^*)_2]^{3+}$ complex ($\lambda_{\text{exc}} = 450 \text{ nm}$) in aerated acetonitrile solution at room temperature.

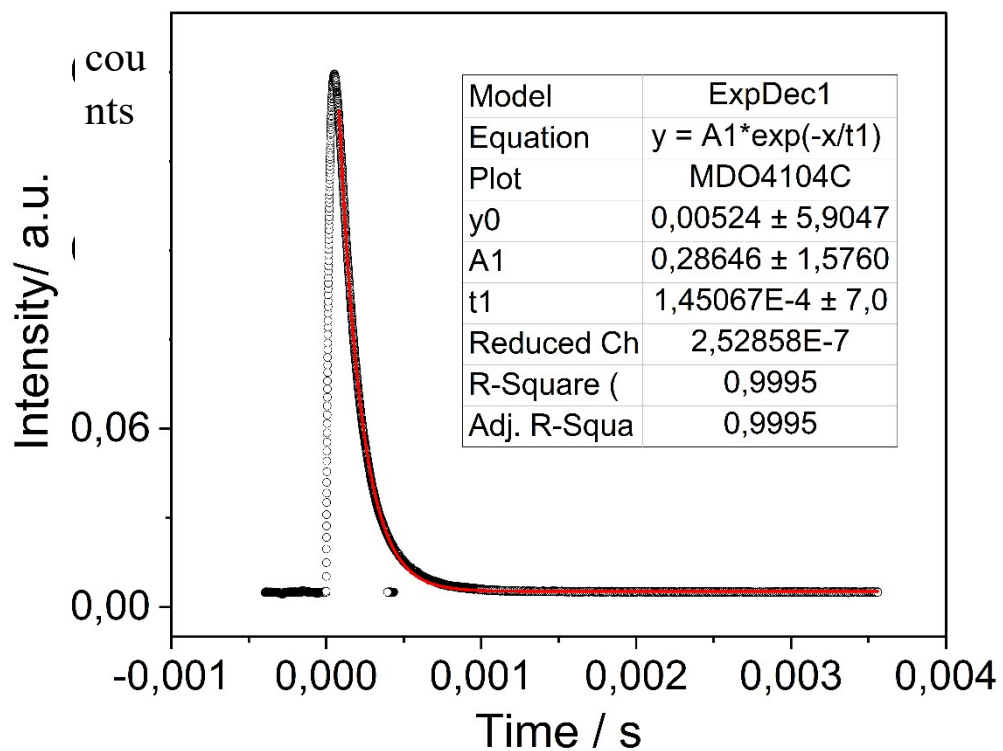


Figure S20. Excited state lifetime and the best fit of the experimental data for the $[\text{Cr}(\text{bip}^*)]^{3+}$ complex ($\lambda_{\text{exc}} = 450 \text{ nm}$) at 77 K in frozen acetonitrile.

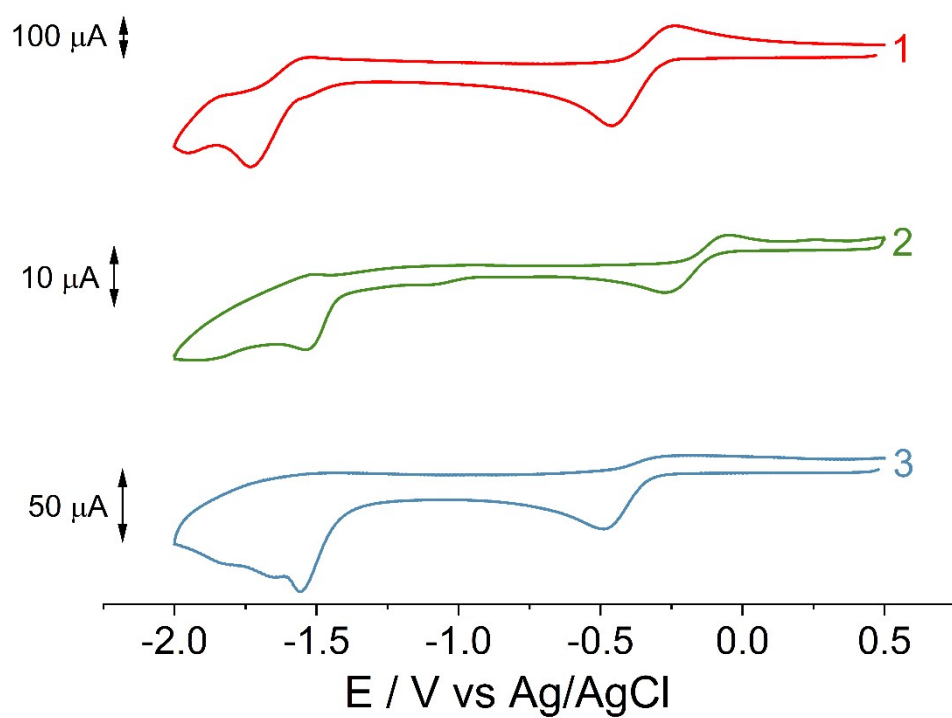


Figure S21. CV diagrams of 1 - 3 in CH_3CN containing 0.1 M $TBAPF_6$.

Theoretical studies

The Orca^[S3] (version 5.0.3) and Gaussian 16^[S4] (revision A.03) software packages were used to investigate the structural and electronic properties of the studied complexes. Starting from the X-ray diffraction structures, the ground, 4A_2 state, structure of the two complexes were obtained from DFT optimizations using the unrestricted version of the Becke three-parameters exchange function in combination with the Lee-Yang-Parr correlation functional (UB3LYP). The Ahlrichs' polarized valence triple- ζ basis set def2-TZVPP was used for these optimizations. The D3 version of Grimme's dispersion with Becke-Johnson damping (GD3BJ) was applied. Solvent effects were included via the Conductor-like Polarizable Continuum Model (CPCM) as implemented in Orca 5.0.3 with the dielectric constant of acetonitrile. Optimized geometries were confirmed to be stationary points by analysis of their vibrational frequencies. Tight convergence criteria were selected for the optimization step. The resolution of identity approach for the Coulomb term in combination with the chain-of-spheres approximation for the exchange term (RIJCOSX) was applied. The zero-order relativistic approximation (ZORA) was used to describe relativistic effects. Spin density information was extracted from the optimized geometries.

Ab initio ligand field (AILF) analysis was performed over the optimized geometries using Orca version 5.0.3. The complete-active-space self-consistent field method (CASSCF) together with the fully internally contracted N-electron valence perturbation theory to second order (FIC-NEVPT2) was used, selecting only the 3d orbitals as active space (CASSCF(3,5)/FIC-NEVPT2) and using the def2-TZVPP basis set in combination with the RI-JK approximation (def2/JK as auxiliary base). 10 quartet and 40 doublet roots were computed for the AILF analysis.

To accurately model the ligand field, CASSCF together with FIC-NEVPT2 was used. Dominant bonding/antibonding orbitals formed between ligand and chromium and a second d shell were considered, creating an active space of 7 electrons and 12 orbitals (CASSCF(7,12)/FIC-NEVPT2). 10 quartet and 9 doublet roots were computed to calculate the energies of the excited states.

The 50 lowest energetic transitions were calculated by TD-DFT as implemented in Gaussian 16, using the unrestricted version of the Coulomb-attenuated B3LYP functional (UCAM-B3LYP), selecting the def2-TZVPP basis set and considering solvent effects. Electronic transitions were corrected by -0.3 eV to better fit experimental results. Charge transfer numbers were computed using TheoDORÉ 2.4.^[S5] Electron density difference maps (EDDMs) were obtained using GaussSum,^[S6] and visualized using UCSF Chimera (isoval=0.002).^[S7]

Optimized Geometries

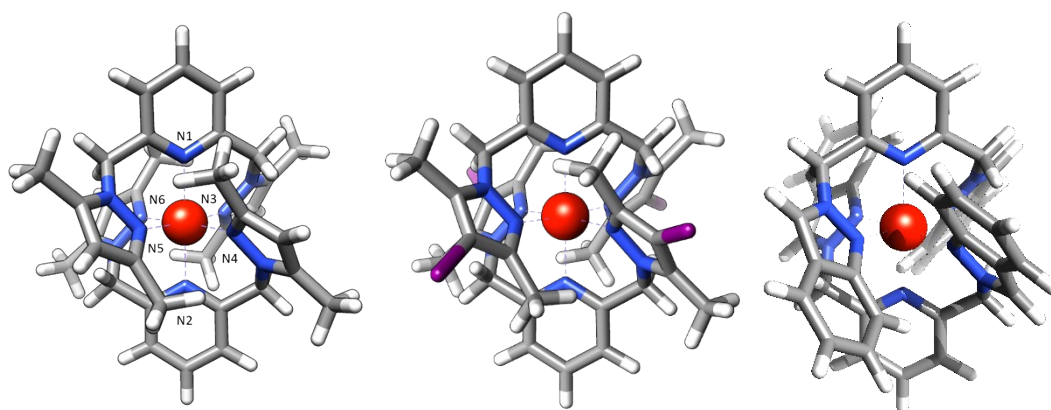


Figure S22. DFT optimized geometries of the quartet ground state of **1**(left), **2** (middle) and **3** (right). Spin density at the Cr center: 3.162171, 3.143759 and 3.111739 (respectively).

Table S6. Bond lengths (Å) and angles (°) of **1** and **2** from XRD measurements and DFT calculations. and CASSCF(7,12)/FIC-NEVPT2 results of **1**, **2** and **3**. Energies in cm⁻¹.

| | 3 | | 2 | | 1 | |
|----------|----------|--------|----------|--------|----------|--------|
| | XRD | DFT | XRD | DFT | XRD | DFT |
| Cr-N1 | 2.0777 | 2.1313 | 2.1040 | 2.1169 | 2.0868 | 2.1137 |
| Cr-N2 | 2.0976 | 2.1314 | 2.0910 | 2.1168 | 2.0812 | 2.1136 |
| Cr-N3 | 1.9976 | 2.0572 | 2.0687 | 2.0819 | 2.0471 | 2.0764 |
| Cr-N4 | 2.0433 | 2.0564 | 2.0656 | 2.0788 | 2.0634 | 2.0765 |
| Cr-N5 | 2.0293 | 2.0564 | 2.0650 | 2.0837 | 2.0550 | 2.0765 |
| Cr-N6 | 2.0470 | 2.0572 | 2.0677 | 2.0802 | 2.0527 | 2.0764 |
| N1-Cr-N2 | 178.48 | 179.84 | 178.97 | 179.96 | 177.28 | 179.99 |
| N1-Cr-N3 | 92.93 | 87.14 | 87.60 | 87.72 | 87.97 | 88.24 |
| N1-Cr-N4 | 88.83 | 92.67 | 91.98 | 92.20 | 90.20 | 91.75 |
| N1-Cr-N5 | 91.69 | 87.22 | 88.24 | 87.92 | 88.44 | 88.24 |
| N1-Cr-N6 | 88.52 | 92.97 | 92.70 | 92.29 | 93.39 | 91.76 |
| N2-Cr-N3 | 87.31 | 92.97 | 91.37 | 92.32 | 90.36 | 91.75 |
| N2-Cr-N4 | 92.65 | 87.21 | 88.03 | 87.81 | 87.82 | 88.25 |
| N2-Cr-N5 | 88.07 | 92.67 | 92.79 | 92.04 | 93.29 | 91.77 |
| N2-Cr-N6 | 90.00 | 87.15 | 87.30 | 87.70 | 88.63 | 88.24 |
| N3-Cr-N4 | 94.41 | 94.20 | 94.32 | 93.64 | 95.43 | 93.72 |
| N3-Cr-N5 | 175.38 | 174.36 | 175.83 | 175.65 | 176.10 | 176.48 |
| N3-Cr-N6 | 85.15 | 86.05 | 86.55 | 86.48 | 85.80 | 86.39 |
| N4-Cr-N5 | 85.65 | 86.10 | 85.98 | 86.50 | 86.11 | 86.40 |
| N4-Cr-N6 | 177.29 | 174.36 | 175.27 | 175.51 | 176.25 | 176.49 |
| N5-Cr-N6 | 95.00 | 94.20 | 93.49 | 93.72 | 92.89 | 93.70 |

| | ² E (1) | ² E (2) | ² T ₁ (1) | ² T ₁ (2) | ² T ₁ (3) | ² T ₂ (1) | ² T ₂ (2) | ² T ₂ (3) | ⁴ T ₂ (1) | ⁴ T ₂ (2) | ⁴ T ₂ (3) |
|----------|--------------------|--------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 1 | 15557 | 16110 | 15247 | 15314 | 16019 | 23553 | 23700 | 23976 | 21386 | 21410 | 22690 |
| 2 | 15558 | 16104 | 15230 | 15377 | 16033 | 23490 | 23699 | 23924 | 21205 | 21244 | 22522 |
| 3 | 15342 | 15916 | 14741 | 14933 | 15722 | 23268 | 23410 | 23909 | 20486 | 21446 | 22129 |

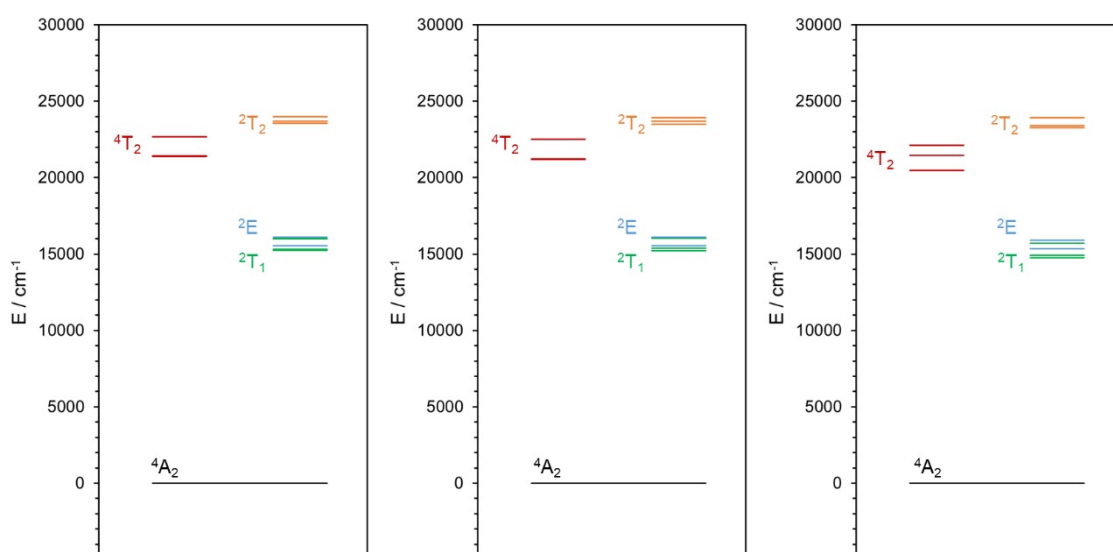


Figure S23. Schematic representation of the energy levels for the calculated (CASSCF(7,12)/FIC-NEVPT2) excited states of **1** (left), **2** (middle) and **3** (right).

Table S7. Orbitals used in the CASSCF(7,12)/FIC-NEVPT2 calculations for **1** (isoval=0.04).

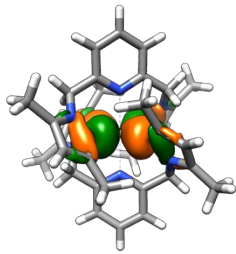
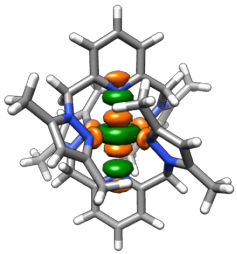
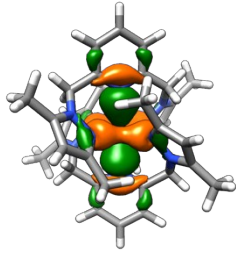
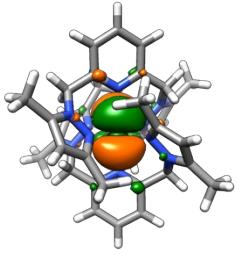
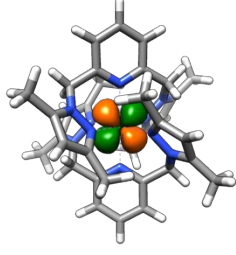
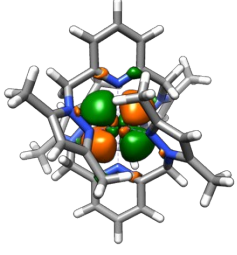
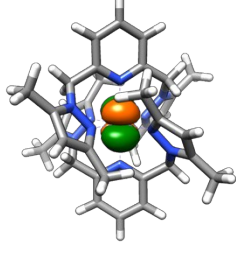
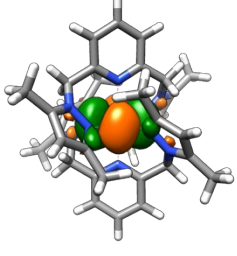
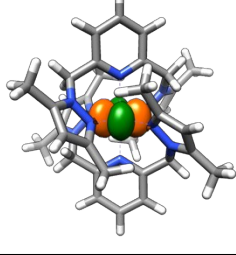
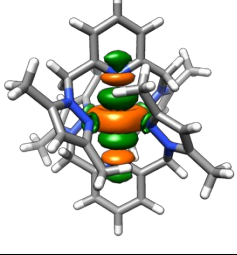
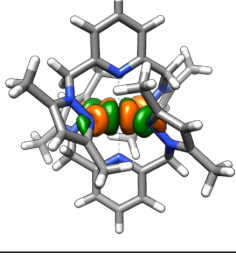
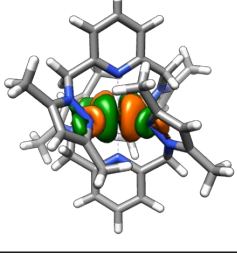
| # | E (hartrees) | Orbital | # | Energy | Orbital |
|-----|-----------------|---|-----|-----------|---|
| 165 | -0.877399 |  | 171 | -0.205190 |  |
| 166 | -0.867665 |  | 172 | 0.730059 |  |
| 167 | -0.421046 |  | 173 | 0.753275 |  |
| 168 | -0.411074 |  | 174 | 0.755171 |  |
| 169 | -0.403576 |  | 175 | 1.365514 |  |
| 170 | -0.199660 |  | 176 | 1.405373 |  |

Table S8. Orbitals used in the CASSCF(7,12)/FIC-NEVPT2 calculations for **2** (isoval=0.04).

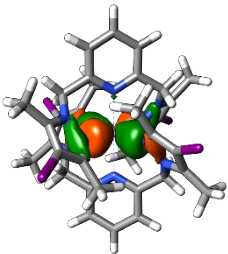
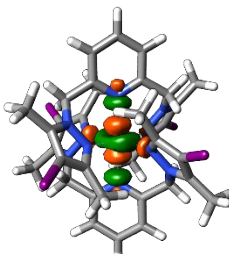
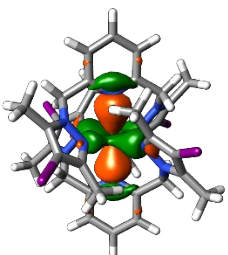
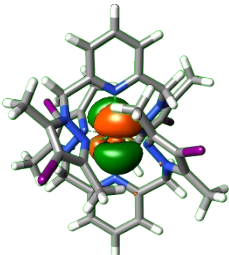
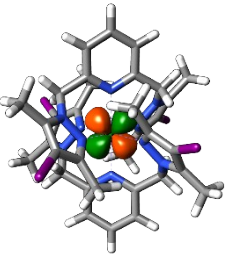
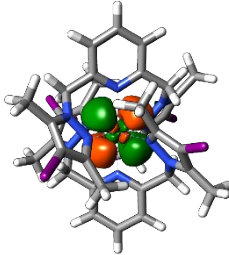
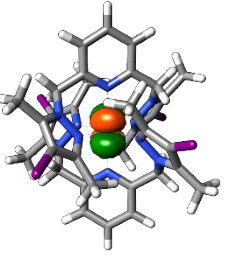
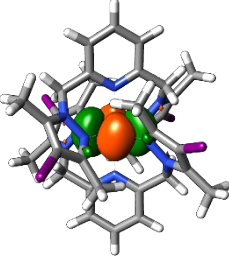
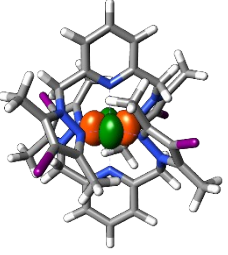
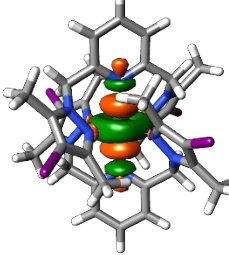
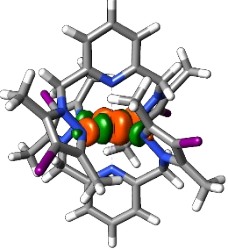
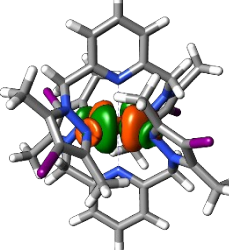
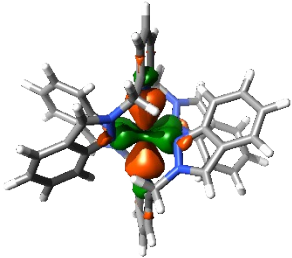
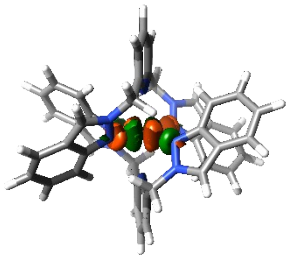
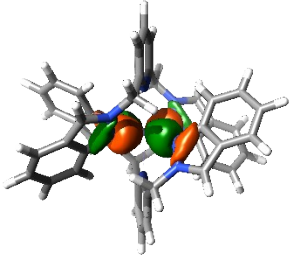
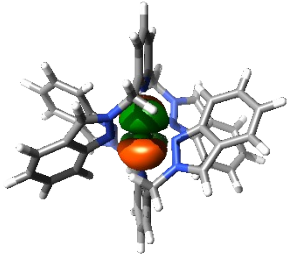
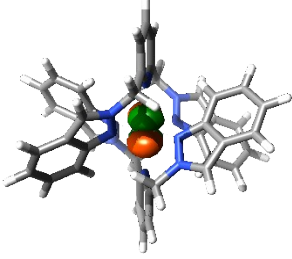
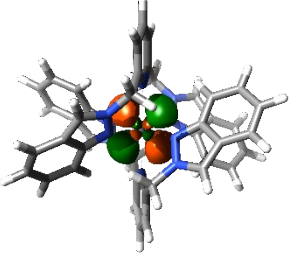
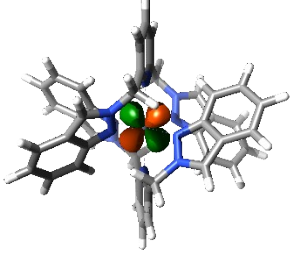
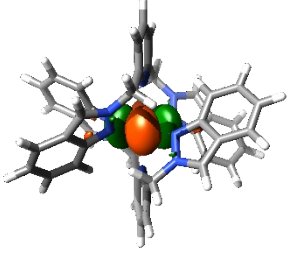
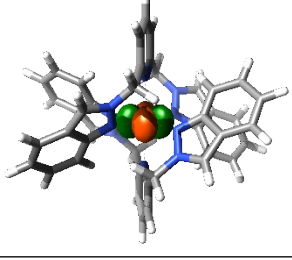
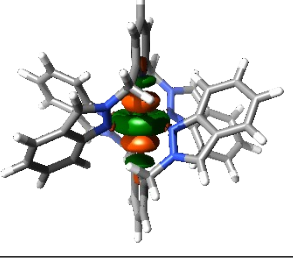
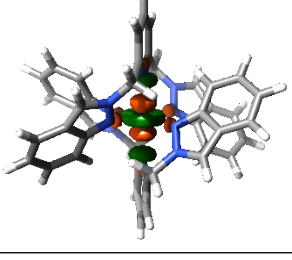
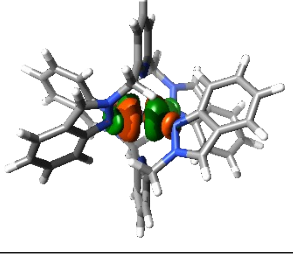
| # | E (hartrees) | Orbital | # | Energy | Orbital |
|-----|-----------------|---|-----|-----------|---|
| 213 | -0.876005 |  | 219 | -0.209919 |  |
| 214 | -0.868147 |  | 220 | 0.728399 |  |
| 215 | -0.424772 |  | 221 | 0.750394 |  |
| 216 | -0.414683 |  | 222 | 0.749667 |  |
| 217 | -0.408243 |  | 223 | 1.356002 |  |
| 218 | -0.205755 |  | 224 | 1.387980 |  |

Table S9. Orbitals used in the CASSCF(7,12)/FIC-NEVPT2 calculations for **3** (isoval=0.04).

| # | Energy (Hartrees) | Orbital | # | Energy (Hartrees) | Orbital |
|-----|-------------------|---|-----|-------------------|---|
| 185 | -0.856996 |  | 191 | -0.180911 |  |
| 186 | -0.871802 |  | 192 | 0.758509 |  |
| 187 | -0.407756 |  | 193 | 0.741001 |  |
| 188 | -0.396342 |  | 194 | 0.771543 |  |
| 189 | -0.389943 |  | 195 | 1.355980 |  |
| 190 | -0.195714 |  | 196 | 1.427039 |  |

Electronic transitions

Table S10. Calculated 100 lowest electronic transitions for compound **1**, their energies (in nm) and oscillatory strength (in cgs units).

| Transition number | Wavelength / nm | Osc. Strength / cgs | Transition number | Wavelength / nm | Osc. Strength / cgs |
|-------------------|-----------------|---------------------|-------------------|-----------------|---------------------|
| 1 | 460.7 | 0.000081863 | 41 | 282.9 | 0.000889228 |
| 2 | 448.7 | 0.000259487 | 42 | 282.5 | 0.000001299 |
| 3 | 425.0 | 0.000862935 | 43 | 282.3 | 0.003932199 |
| 4 | 407.0 | 0.000000016 | 44 | 281.3 | 0.020161778 |
| 5 | 363.2 | 0.001127841 | 45 | 280.8 | 0.011463406 |
| 6 | 361.3 | 0.027948874 | 46 | 280.6 | 0.005825521 |
| 7 | 348.1 | 0.000892393 | 47 | 279.8 | 0.001363765 |
| 8 | 343.5 | 0.001190661 | 48 | 277.5 | 0.000000091 |
| 9 | 336.5 | 0.005098185 | 49 | 276.6 | 0.013389699 |
| 10 | 336.3 | 0.000031111 | 50 | 276.2 | 0.000003607 |
| 11 | 336.2 | 0.005176938 | 51 | 274.6 | 0.000279987 |
| 12 | 335.7 | 0.000647932 | 52 | 274.3 | 0.010322406 |
| 13 | 333.6 | 0.013829627 | 53 | 274.3 | 0.000059324 |
| 14 | 324.5 | 0.003391283 | 54 | 273.5 | 0.000000048 |
| 15 | 323.0 | 0.000000132 | 55 | 272.4 | 0.000259427 |
| 16 | 319.1 | 0.002116681 | 56 | 272.1 | 0.002594494 |
| 17 | 317.6 | 0.003542893 | 57 | 271.4 | 0.002749908 |
| 18 | 317.3 | 0.018891410 | 58 | 270.3 | 0.000273288 |
| 19 | 316.1 | 0.000000628 | 59 | 269.9 | 0.002898735 |
| 20 | 314.2 | 0.012021121 | 60 | 269.3 | 0.001554501 |
| 21 | 314.1 | 0.046859758 | 61 | 269.0 | 0.000000184 |
| 22 | 311.3 | 0.000650194 | 62 | 268.2 | 0.009999719 |
| 23 | 310.2 | 0.003400632 | 63 | 267.9 | 0.000057385 |
| 24 | 308.1 | 0.000001021 | 64 | 267.8 | 0.005520642 |
| 25 | 306.8 | 0.020748280 | 65 | 266.5 | 0.002296036 |
| 26 | 306.4 | 0.010516683 | 66 | 265.6 | 0.000000645 |
| 27 | 305.2 | 0.009946552 | 67 | 265.0 | 0.001347851 |
| 28 | 304.9 | 0.040115754 | 68 | 264.6 | 0.027537825 |
| 29 | 303.1 | 0.000000020 | 69 | 264.2 | 0.000065921 |
| 30 | 299.7 | 0.000435332 | 70 | 264.2 | 0.016717507 |
| 31 | 297.4 | 0.000000526 | 71 | 264.0 | 0.000027847 |
| 32 | 294.8 | 0.004628151 | 72 | 263.6 | 0.000074037 |
| 33 | 290.9 | 0.000381853 | 73 | 263.4 | 0.000129992 |
| 34 | 290.5 | 0.003349217 | 74 | 263.2 | 0.006593176 |
| 35 | 289.6 | 0.000000011 | 75 | 262.1 | 0.013083716 |
| 36 | 286.1 | 0.002487443 | 76 | 261.9 | 0.000908007 |
| 37 | 286.1 | 0.000000104 | 77 | 261.6 | 0.000000686 |
| 38 | 285.4 | 0.005353684 | 78 | 261.2 | 0.002838866 |
| 39 | 284.7 | 0.004214731 | 79 | 259.2 | 0.000000491 |
| 40 | 284.0 | 0.007086297 | 80 | 257.0 | 0.009056044 |

| Transition number | Wavelength / nm | Osc. Strength / cgs | Transition number | Wavelength / nm | Osc. Strength / cgs |
|-------------------|-----------------|---------------------|-------------------|-----------------|---------------------|
| 81 | 257.0 | 0.011461363 | 91 | 243.5 | 0.000600390 |
| 82 | 255.2 | 0.004128707 | 92 | 242.9 | 0.003617675 |
| 83 | 254.6 | 0.000000128 | 93 | 240.0 | 0.000758261 |
| 84 | 253.2 | 0.003872623 | 94 | 239.9 | 0.000000715 |
| 85 | 251.8 | 0.000000031 | 95 | 239.4 | 0.000397302 |
| 86 | 251.5 | 0.006550820 | 96 | 239.2 | 0.000000018 |
| 87 | 251.1 | 0.007999773 | 97 | 238.9 | 0.022079010 |
| 88 | 250.6 | 0.000770306 | 98 | 238.5 | 0.000542087 |
| 89 | 250.2 | 0.001993544 | 99 | 238.4 | 0.000000170 |
| 90 | 250.2 | 0.000038909 | 100 | 238.1 | 0.008775422 |

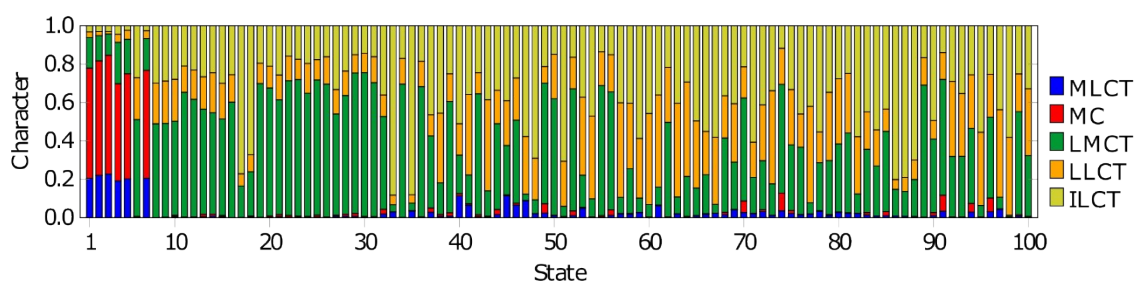


Figure S24. TD-DFT charge transfer numbers of **1** defined from 0 to 1 of the first 50 electronic transitions.

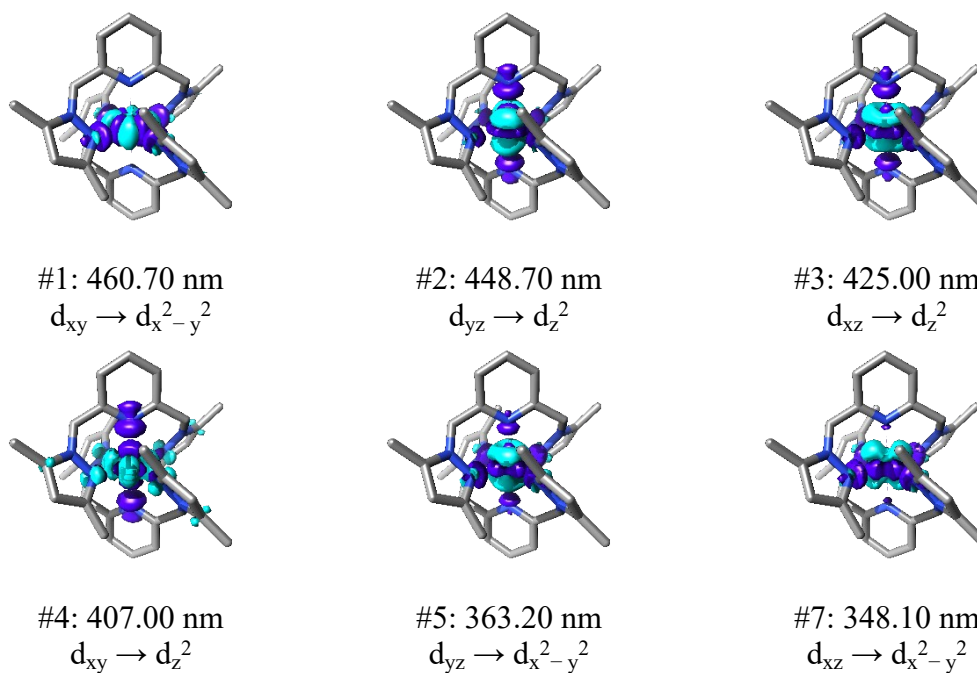


Figure S25. Electron density difference maps (EDDM) of the six MC electronic transitions calculated for **1** (isoval 0.002). Blue: density loss; Purple: density gain.

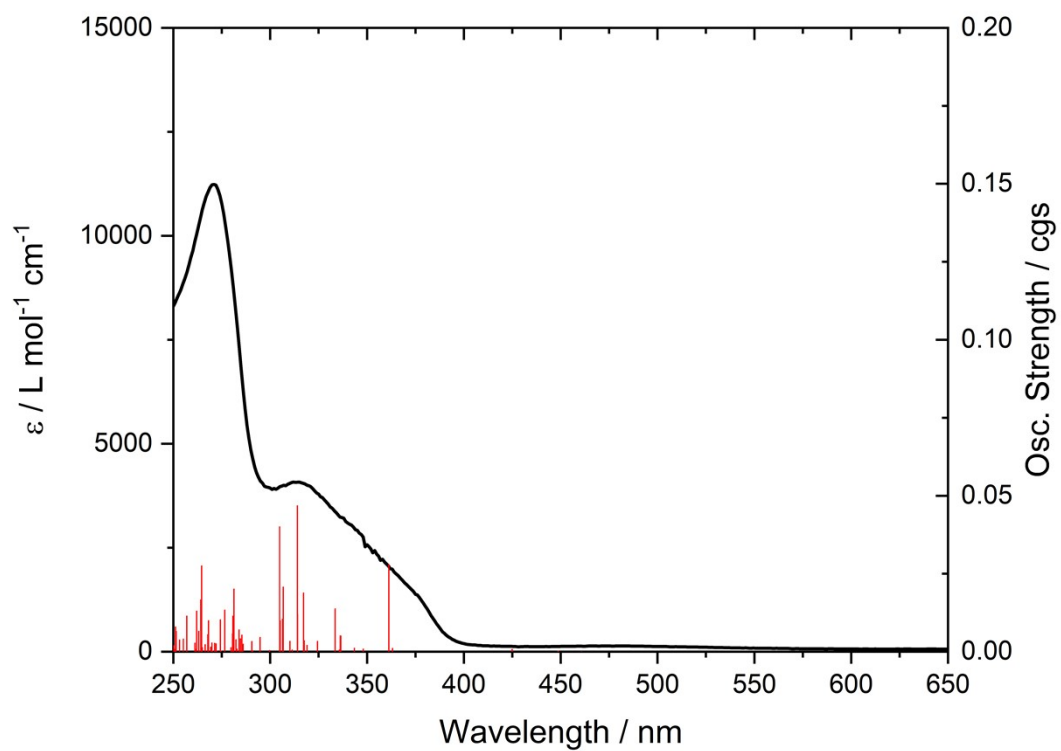


Figure S26. Experimental UV-Vis spectrum of compound **1** in acetonitrile and calculated oscillatory strength of the calculated electronic transitions.

Table S7. Calculated 100 lowest electronic transitions for compound **2**, their energies (in nm) and oscillatory strength (in cgs units).

| Transition number | Wavelength / nm | Osc. Strength / cgs | Transition number | Wavelength / nm | Osc. Strength / cgs |
|-------------------|-----------------|---------------------|-------------------|-----------------|---------------------|
| 1 | 473.10 | 0.000108964 | 41 | 318.20 | 0.000263198 |
| 2 | 456.50 | 0.000452785 | 42 | 316.90 | 0.008250000 |
| 3 | 433.60 | 0.002120000 | 43 | 316.30 | 0.058120000 |
| 4 | 421.70 | 0.016060000 | 44 | 315.80 | 0.000985345 |
| 5 | 418.80 | 0.000068200 | 45 | 315.10 | 0.000107209 |
| 6 | 418.20 | 0.001340000 | 46 | 314.90 | 0.000030102 |
| 7 | 417.20 | 0.000016529 | 47 | 314.80 | 0.000192036 |
| 8 | 412.10 | 0.016820000 | 48 | 314.10 | 0.000598102 |
| 9 | 393.00 | 0.004440000 | 49 | 313.70 | 0.000030902 |
| 10 | 391.50 | 0.035680000 | 50 | 313.30 | 0.000015566 |
| 11 | 390.50 | 0.028460000 | 51 | 313.20 | 0.000275754 |
| 12 | 385.40 | 0.001030000 | 52 | 312.20 | 0.031220000 |
| 13 | 384.30 | 0.000661078 | 53 | 310.60 | 0.000008509 |
| 14 | 383.20 | 0.000032186 | 54 | 309.30 | 0.000037478 |
| 15 | 381.90 | 0.000000908 | 55 | 306.80 | 0.000039574 |
| 16 | 381.10 | 0.001170000 | 56 | 306.70 | 0.000757662 |
| 17 | 377.20 | 0.006460000 | 57 | 306.60 | 0.000260772 |
| 18 | 368.10 | 0.000055521 | 58 | 306.20 | 0.001170000 |
| 19 | 361.70 | 0.038660000 | 59 | 305.60 | 0.000515571 |
| 20 | 359.20 | 0.001340000 | 60 | 301.60 | 0.000104348 |
| 21 | 354.00 | 0.000060078 | 61 | 301.40 | 0.000234251 |
| 22 | 353.70 | 0.001060000 | 62 | 301.10 | 0.000031909 |
| 23 | 352.50 | 0.000393966 | 63 | 300.80 | 0.000012235 |
| 24 | 344.60 | 0.000040619 | 64 | 300.10 | 0.000014117 |
| 25 | 339.60 | 0.013930000 | 65 | 300.00 | 0.000349261 |
| 26 | 338.40 | 0.000355893 | 66 | 299.80 | 0.000059690 |
| 27 | 338.10 | 0.000377016 | 67 | 299.50 | 0.000052418 |
| 28 | 336.00 | 0.000003415 | 68 | 296.90 | 0.003600000 |
| 29 | 334.50 | 0.000046120 | 69 | 293.00 | 0.000007392 |
| 30 | 330.80 | 0.000196906 | 70 | 291.60 | 0.000393282 |
| 31 | 326.80 | 0.006340000 | 71 | 290.50 | 0.000752906 |
| 32 | 326.30 | 0.000424654 | 72 | 289.90 | 0.000006983 |
| 33 | 325.00 | 0.008490000 | 73 | 289.60 | 0.000008326 |
| 34 | 323.10 | 0.000030904 | 74 | 289.10 | 0.001010000 |
| 35 | 322.90 | 0.002350000 | 75 | 287.70 | 0.000320723 |
| 36 | 322.00 | 0.002180000 | 76 | 287.00 | 0.000187108 |
| 37 | 321.30 | 0.000376841 | 77 | 285.60 | 0.017430000 |
| 38 | 319.40 | 0.001310000 | 78 | 284.90 | 0.017870000 |
| 39 | 318.60 | 0.000213804 | 79 | 284.10 | 0.019970000 |
| 40 | 318.40 | 0.000317286 | 80 | 283.30 | 0.005930000 |

| Transition number | Wavelength / nm | Osc. Strength / cgs | Transition number | Wavelength / nm | Osc. Strength / cgs |
|-------------------|-----------------|---------------------|-------------------|-----------------|---------------------|
| 81 | 283.00 | 0.000121244 | 91 | 277.10 | 0.000200959 |
| 82 | 282.90 | 0.000757880 | 92 | 277.10 | 0.000194927 |
| 83 | 282.90 | 0.000597674 | 93 | 276.70 | 0.003830000 |
| 84 | 282.50 | 0.000952859 | 94 | 276.40 | 0.010510000 |
| 85 | 282.30 | 0.000178893 | 95 | 275.60 | 0.001890000 |
| 86 | 282.30 | 0.001010000 | 96 | 275.40 | 0.002880000 |
| 87 | 278.60 | 0.011260000 | 97 | 275.30 | 0.001330000 |
| 88 | 278.30 | 0.000042284 | 98 | 274.60 | 0.001930000 |
| 89 | 278.00 | 0.001410000 | 99 | 273.80 | 0.009130000 |
| 90 | 277.80 | 0.000243845 | 100 | 269.70 | 0.031430000 |

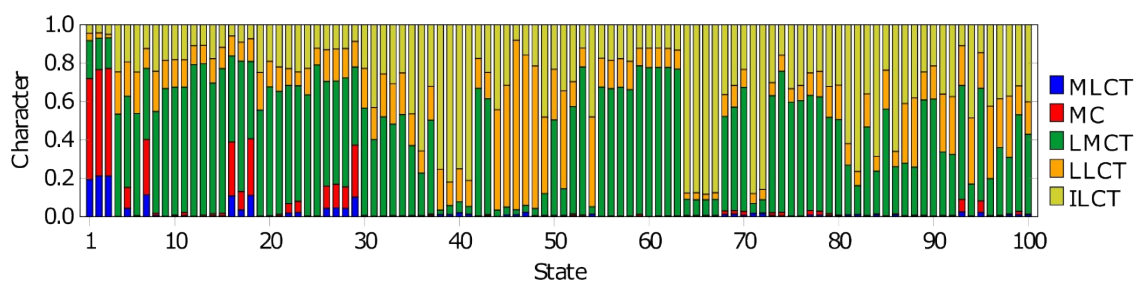


Figure S27. TD-DFT charge transfer numbers of **2** defined from 0 to 1 of the first 100 electronic transitions.

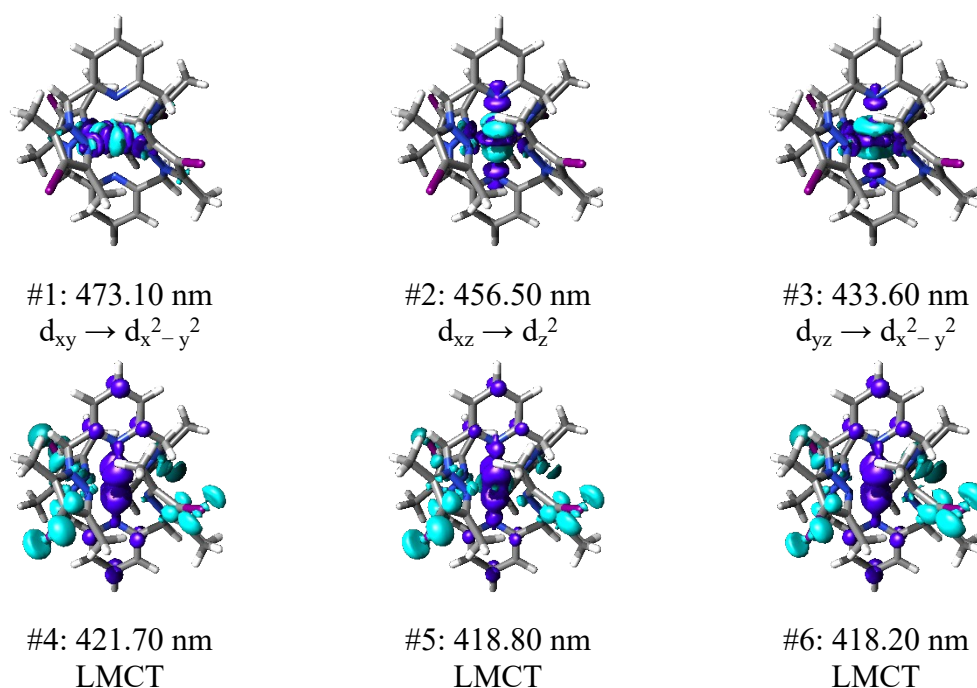


Figure S28. Electron density difference maps (EDDM) of the first six electronic transitions calculated for **2** (isoval 0.002). Blue: density loss; Purple: density gain.

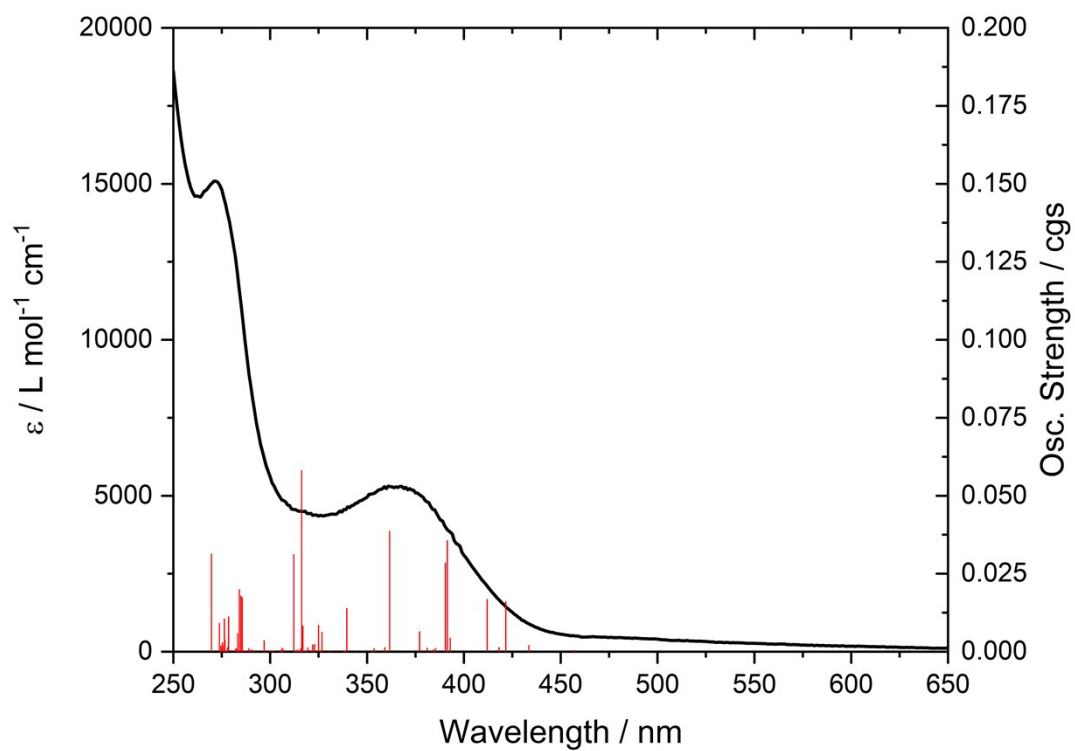


Figure S29. Experimental UV-Vis spectrum of compound **2** in acetonitrile and calculated oscillatory strength of the calculated electronic transitions. a) Full view; b) Zoom view.

Table S7. Calculated 100 lowest electronic transitions for compound **3**, their energies (in nm) and oscillatory strength (in cgs units).

| Transition number | Wavelength / nm | Osc. Strength / cgs | Transition number | Wavelength / nm | Osc. Strength / cgs |
|-------------------|-----------------|---------------------|-------------------|-----------------|---------------------|
| 1 | 480.90 | 0.000502828 | 41 | 327.40 | 0.000419571 |
| 2 | 469.50 | 0.000072148 | 42 | 324.10 | 0.000002021 |
| 3 | 452.60 | 0.000002317 | 43 | 322.10 | 0.000448382 |
| 4 | 449.10 | 0.042220000 | 44 | 321.10 | 0.000000117 |
| 5 | 443.40 | 0.034090000 | 45 | 320.20 | 0.010290000 |
| 6 | 438.00 | 0.001590000 | 46 | 315.20 | 0.005560000 |
| 7 | 424.10 | 0.000000218 | 47 | 312.70 | 0.002310000 |
| 8 | 423.60 | 0.019750000 | 48 | 311.50 | 0.000901356 |
| 9 | 418.40 | 0.000014488 | 49 | 309.80 | 0.000005275 |
| 10 | 414.30 | 0.010280000 | 50 | 309.20 | 0.000060072 |
| 11 | 404.00 | 0.000000630 | 51 | 306.60 | 0.002170000 |
| 12 | 398.80 | 0.000001024 | 52 | 306.30 | 0.002850000 |
| 13 | 394.80 | 0.006230000 | 53 | 305.70 | 0.000376664 |
| 14 | 385.70 | 0.000451373 | 54 | 305.10 | 0.000948934 |
| 15 | 384.80 | 0.000019833 | 55 | 304.80 | 0.000618534 |
| 16 | 383.60 | 0.011100000 | 56 | 304.20 | 0.011410000 |
| 17 | 376.20 | 0.001330000 | 57 | 299.00 | 0.000338436 |
| 18 | 375.60 | 0.097690000 | 58 | 297.70 | 0.000262351 |
| 19 | 373.30 | 0.073920000 | 59 | 297.50 | 0.009260000 |
| 20 | 363.50 | 0.088430000 | 60 | 297.00 | 0.052430000 |
| 21 | 360.70 | 0.005600000 | 61 | 296.70 | 0.001060000 |
| 22 | 359.80 | 0.001540000 | 62 | 295.50 | 0.001140000 |
| 23 | 353.50 | 0.000003055 | 63 | 295.40 | 0.000032476 |
| 24 | 347.20 | 0.014470000 | 64 | 294.60 | 0.000262728 |
| 25 | 345.40 | 0.004540000 | 65 | 294.40 | 0.000066425 |
| 26 | 341.80 | 0.000007731 | 66 | 294.30 | 0.000439374 |
| 27 | 341.20 | 0.003760000 | 67 | 294.20 | 0.000348638 |
| 28 | 340.30 | 0.001190000 | 68 | 293.80 | 0.000009963 |
| 29 | 338.70 | 0.000026103 | 69 | 293.20 | 0.003590000 |
| 30 | 337.40 | 0.000305482 | 70 | 291.50 | 0.000000426 |
| 31 | 336.60 | 0.000129417 | 71 | 291.00 | 0.000000251 |
| 32 | 334.70 | 0.004950000 | 72 | 291.00 | 0.004640000 |
| 33 | 334.20 | 0.001630000 | 73 | 290.50 | 0.004660000 |
| 34 | 334.20 | 0.000095017 | 74 | 289.40 | 0.000539907 |
| 35 | 332.40 | 0.015170000 | 75 | 289.30 | 0.000158726 |
| 36 | 331.20 | 0.000176195 | 76 | 289.30 | 0.000105146 |
| 37 | 330.70 | 0.001130000 | 77 | 289.10 | 0.000002374 |
| 38 | 330.40 | 0.000588991 | 78 | 288.70 | 0.001650000 |
| 39 | 329.40 | 0.001860000 | 79 | 288.20 | 0.003640000 |
| 40 | 327.50 | 0.002100000 | 80 | 286.50 | 0.003540000 |

| Transition number | Wavelength / nm | Osc. Strength / cgs | Transition number | Wavelength / nm | Osc. Strength / cgs |
|-------------------|-----------------|---------------------|-------------------|-----------------|---------------------|
| 81 | 286.20 | 0.004070000 | 91 | 280.50 | 0.074520000 |
| 82 | 285.80 | 0.000378163 | 92 | 278.10 | 0.004930000 |
| 83 | 283.90 | 0.000553583 | 93 | 277.80 | 0.003430000 |
| 84 | 283.70 | 0.010230000 | 94 | 276.40 | 0.000233219 |
| 85 | 283.30 | 0.004560000 | 95 | 276.20 | 0.000844896 |
| 86 | 282.90 | 0.000234102 | 96 | 275.60 | 0.000359979 |
| 87 | 281.90 | 0.006860000 | 97 | 275.30 | 0.000024417 |
| 88 | 280.90 | 0.000001937 | 98 | 274.40 | 0.000685888 |
| 89 | 280.70 | 0.070110000 | 99 | 274.40 | 0.014700000 |
| 90 | 280.50 | 0.034560000 | 100 | 273.90 | 0.000135663 |

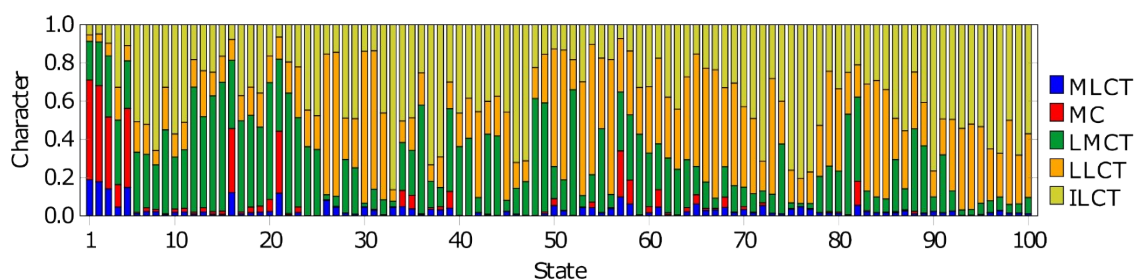


Figure S30. TD-DFT charge transfer numbers of **3** defined from 0 to 1 of the first 100 electronic transitions.

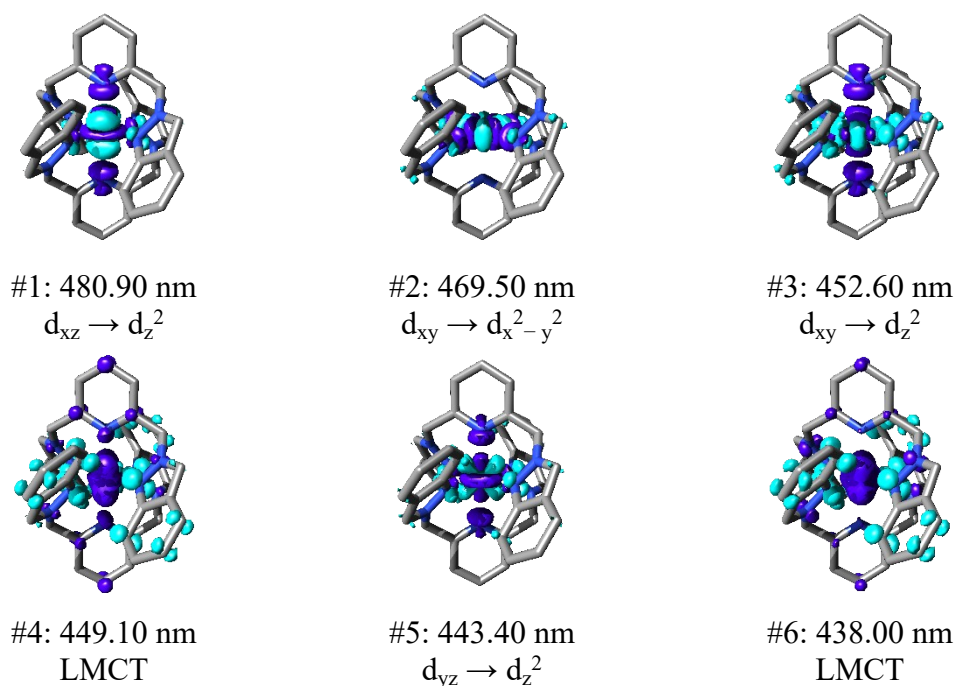


Figure S31. Electron density difference maps (EDDM) of the first six electronic transitions calculated for **3** (isoval 0.002). Blue: density loss; Purple: density gain.

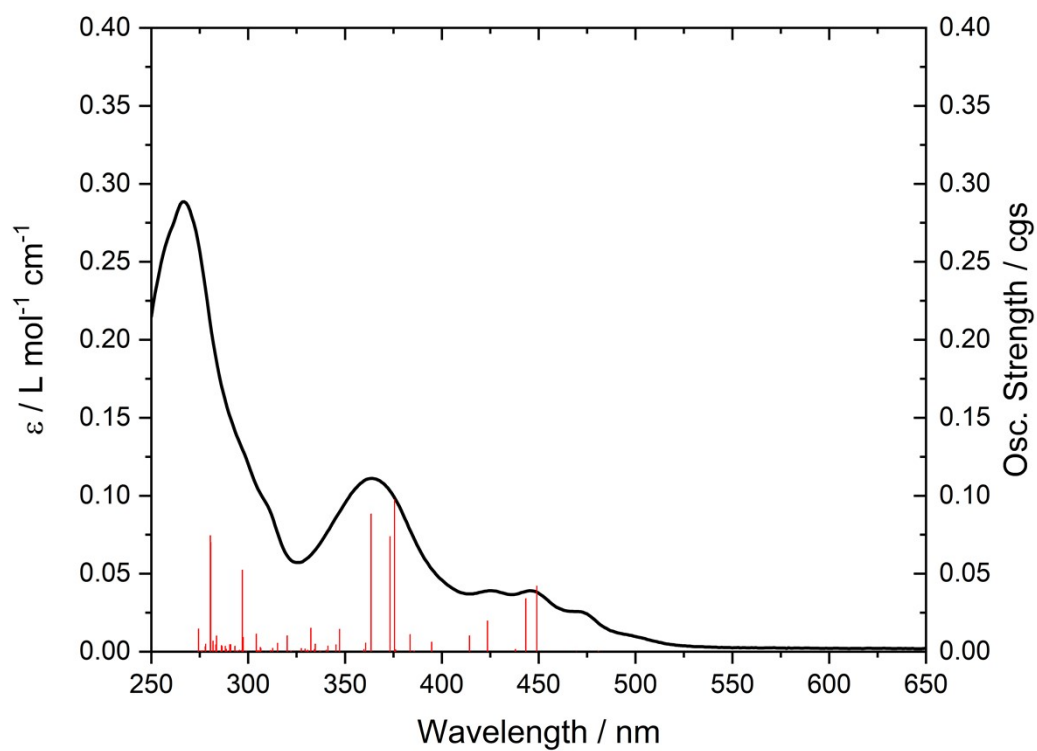


Figure S32. Experimental UV-Vis spectrum of compound **3** in acetonitrile and calculated oscillatory strength of the calculated electronic transitions. a) Full view; b) Zoom view.

Geometries

1

| | | | |
|----|-------------------|-------------------|-------------------|
| Cr | 0.00030435029453 | -0.00017921823173 | -0.00049039987500 |
| N | -2.33690501176889 | 1.07453338641386 | 1.54343861201445 |
| N | 1.42021167754291 | 0.06641599046485 | -1.51406696974597 |
| N | 1.42009516649813 | -0.05722678341546 | 1.51370684643270 |
| N | 2.33652506414530 | -1.07103247340930 | 1.54761055108532 |
| N | -1.41905175054907 | -0.07040328779766 | -1.51430386441064 |
| N | 2.33061672107800 | 1.08568819930022 | -1.54682149288553 |
| N | -2.32947040999390 | -1.08972189779818 | -1.54509724965039 |
| N | -0.00647124177198 | 2.11345029297479 | -0.00295235841621 |
| N | 0.00761741825178 | -2.11383361537157 | 0.00184572279727 |
| N | -1.42036804250698 | 0.06072034091955 | 1.51274332120682 |
| C | -1.60109726134686 | -0.64270531968421 | 2.65426867191383 |
| C | 1.59954384398627 | 0.64853842038052 | 2.65398965361242 |
| C | 2.63618670704127 | -0.05499484214087 | -3.38803305902396 |
| H | 3.01234560254262 | -0.38916785164203 | -4.33860568049301 |
| C | -1.17284506599860 | 4.18157141273865 | 0.26108791883780 |
| H | -2.10188352231432 | 4.68766473434493 | 0.47601195629188 |
| C | 1.14653909533677 | -2.79687123507452 | 0.25138153063932 |
| C | -2.42757082910356 | 2.04425946984976 | 0.47137228721253 |
| H | -3.20353732131943 | 2.74859879817172 | 0.74450134500887 |
| H | -2.74683381802563 | 1.54738902558661 | -0.44152987828438 |
| C | -2.63537593970796 | -0.06414620564550 | 3.38707700600673 |
| H | -3.00958258512013 | -0.39876062706591 | 4.33826301050327 |
| C | 1.12811020607375 | 2.80393628545001 | -0.25186764848613 |
| C | 2.42841050279070 | -2.04296016020391 | 0.47769556764389 |
| H | 3.20432323354385 | -2.74650573711252 | 0.75300571907730 |
| H | 2.74834719876172 | -1.54792093511288 | -0.43595884483670 |
| C | -1.60448252879049 | 0.63245104493416 | -2.65542307916467 |
| C | 3.08335560452259 | -1.02221077250337 | 2.66870787752026 |
| C | -2.41372481780895 | -2.06066483566597 | -0.47361040587721 |
| H | -3.18479294777447 | -2.77014405618854 | -0.74732000990819 |
| H | -2.73659810859847 | -1.56657667380639 | 0.43951704182228 |
| C | 1.60483290615673 | -0.63783268619559 | -2.65447341808929 |
| C | -1.14529147768609 | 2.79735117639127 | 0.24462675956393 |
| C | 2.41508781490573 | 2.05842100232835 | -0.47700576711007 |
| H | 3.18653784044103 | 2.76707063657466 | -0.75177688404985 |
| H | 2.73749100429962 | 1.56577946553665 | 0.43707522117763 |
| C | -1.12651324294178 | -2.80522137800358 | -0.24670917483573 |
| C | -3.08466142870465 | 1.02831940756000 | 2.66403371607060 |
| C | 1.14704169436231 | 4.18827962576077 | -0.27097099963382 |
| H | 2.07284330717151 | 4.69988337379384 | -0.48684483230121 |
| C | 3.07901592847109 | 1.04145230787862 | -2.66707550235465 |
| C | -2.63539264039187 | 0.04785043812918 | -3.38820359985458 |
| H | -3.01195016547075 | 0.38059298864902 | -4.33912100789813 |
| C | -0.01509668298371 | 4.89187155024801 | -0.00559337657824 |
| H | -0.01844962864345 | 5.97260050973459 | -0.00658961847157 |

| | | | |
|---|-------------------|-------------------|-------------------|
| C | -0.84166577166289 | 1.84806404540798 | -3.05193483338164 |
| H | -1.09753546491073 | 2.70368148526904 | -2.42849422984877 |
| H | -1.10013745211576 | 2.09956828565903 | -4.07759567343375 |
| H | 0.23234353022277 | 1.70021304787845 | -3.00153810038465 |
| C | 0.84071967412469 | -1.85301431950943 | -3.04978865826255 |
| H | 1.09623720950150 | -2.70846300007124 | -2.42600484237624 |
| H | 1.09840853256206 | -2.10538391490192 | -4.07543884751156 |
| H | -0.23315847115887 | -1.70425186635333 | -2.99892797746669 |
| C | 1.17465998439909 | -4.18105705575511 | 0.27013581616154 |
| H | 2.10376392455681 | -4.68638733927216 | 0.48657282259070 |
| C | -3.07779486728827 | -1.04762593798348 | -2.66548896540726 |
| C | 2.63336656369166 | 0.07183520010900 | 3.38889797664904 |
| H | 3.00654600335131 | 0.40846329963011 | 4.33977602594454 |
| C | 0.82812466232199 | 1.85955972838741 | 3.04793193642062 |
| H | 1.07819617953989 | 2.71573588119078 | 2.42294794202702 |
| H | 1.08443766921371 | 2.11480084021218 | 4.07321450813818 |
| H | -0.24481833936402 | 1.70410974432391 | 2.99748179265814 |
| C | -0.83047442932573 | -1.85326121977666 | 3.05120271578389 |
| H | -1.07919490427022 | -2.71021311758443 | 2.42675526851216 |
| H | -1.08876680821094 | -2.10725336109809 | 4.07629149351362 |
| H | 0.24254985698938 | -1.69772082748106 | 3.00260908087383 |
| C | -4.15867218930084 | 2.00706719884704 | 2.97213904174765 |
| H | -3.76866259207043 | 3.02557964592842 | 2.99496859781053 |
| H | -4.58482705899344 | 1.77714883239494 | 3.94507912657256 |
| H | -4.95392655953992 | 1.96684366053135 | 2.22628635747401 |
| C | -1.14482294160243 | -4.18959623400191 | -0.26361810773028 |
| H | -2.07025438961482 | -4.70196811187958 | -0.47925272566163 |
| C | 4.14726498837911 | 2.02590912703745 | -2.97701487095687 |
| H | 3.75153381591643 | 3.04218814698547 | -3.00058703249598 |
| H | 4.57398858562554 | 1.79736847431706 | -3.95002900219650 |
| H | 4.94331034701031 | 1.99088842486725 | -2.23173832924206 |
| C | 4.15703044325350 | -2.00027853291341 | 2.98008786754460 |
| H | 3.76708196333500 | -3.01878291376500 | 3.00430733632825 |
| H | 4.58183735630819 | -1.76846747636099 | 3.95316959618664 |
| H | 4.95331063981987 | -1.96138121243364 | 2.23525806866097 |
| C | 0.01743142371726 | -4.89227035862705 | 0.00370314931439 |
| H | 0.02124591192511 | -5.97299789588840 | 0.00441042443470 |
| C | -4.14592155500946 | -2.03278340108520 | -2.97364641042079 |
| H | -3.74987829862428 | -3.04896293543716 | -2.99625375815370 |
| H | -4.57329168299908 | -1.80554861102460 | -3.94668229586976 |
| H | -4.94152290859922 | -1.99713971781796 | -2.22792849875097 |

2

| | | | |
|----|-------------------|-------------------|-------------------|
| I | 12.58196104507405 | 3.36399154591363 | 7.24531204989903 |
| I | 2.93564970014811 | 10.68078108987436 | 4.38389425417440 |
| I | 3.61493688681225 | 7.97824043210413 | 10.49047994459432 |
| Cr | 8.02182188157902 | 7.47593898995100 | 6.09193121485771 |
| I | 12.94404849298149 | 7.83352871509917 | 2.26333023871842 |
| N | 9.94533602215487 | 6.51007087022082 | 8.18730404998615 |

| | | | |
|---|-------------------|-------------------|------------------|
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