

Versatile heteroleptic bis-terdentate Cr(III) chromophores displaying room temperature millisecond excited state lifetimes

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Supporting Information

(31 pages)

Appendix 1. Experimental section.

Solvents and starting materials

2,2':6',2''-terpyridine (tpy) is commercially available. *N,N'*-dimethyl-*N,N''*-dipyridin-2-ylpyridine-2,6-diamine (ddpd),¹⁰ 4'-carbethoxy-2,2':6',2''-terpyridine (tpy-COOEt),²¹ [Cr(tpy)Cl₃],¹⁹ [Cr(ddpd)Cl₃],¹⁷ [Cr(ddpd)₂](BF₄)₃¹⁰ and [Cr(tpy)₂](PF₆)₃¹⁸ were synthesized according to published procedures. Reagent grade acetonitrile (ACN) and chloroform were distilled from CaH₂ when needed. All other chemicals were purchased from commercial suppliers and used without further purification.

Synthesis of heteroleptic complexes.

Method 1: Ligand substitution in trifluoromethane sulfonic acid (Scheme 1).¹⁷

[Cr(tpy)(ddpd)](PF₆)₃. Ligand ddpd (0.1 g, 1.1 eq, 0.343 mmol) was added under N₂ atmosphere into a Schlenk containing a solution of [Cr(tpy)(SO₃CF₃)₃] (0.230 g, 1 eq, 0.312 mmol)¹⁷ in acetonitrile (15 mL). The mixture was heated at 75°C during 4 hours. After cooling down the reaction mixture, solvent was evaporated under reduced pressure. The obtained orange residue was then dissolved in ethanol (1.5 mL) and few drops of a saturated methanol solution of (n-Bu₄)NPF₆ were added. The yellow precipitate was filtered, washed with diethyl ether (2 x 15 mL) and dried under vacuum to give [Cr(tpy)(ddpd)](PF₆)₃ (yield 60%).

Method 2: Ligand substitution in acetonitrile (Schemes 2-3).

[Cr(ddpd)Br₃]. A solution of the ligand ddpd (370 mg, 1.26 mmol) in propan-2-ol (30 mL) was dropwise added into a solution of CrBr₃·6H₂O (520 mg, 1.3 mmol) in 15 mL of the same solvent. The resulting green solution was heated to reflux during 10 h. The mixture was filtered and the green solid was washed with warm ethanol (2 x 10 mL) and diethyl ether (2 x 20 mL). The product was dried under vacuum to obtain an olive drab powder [Cr(ddpd)Br₃] (yield 90%). ESI-MS (CH₃CN) *m/z*: [Cr(ddpd)Br₂]⁺ calc: 502.92, found: 502.9. Slow diffusion of diethyl ether into a concentrated solution of the complex in dimethylformamide led to the formation of green crystals suitable for X-ray diffraction.

[Cr(tpy)Br₃]. A solution of the ligand tpy (293 mg, 1.26 mmol) in propan-2-ol (30 mL) was dropwise added into a solution of CrBr₃·6H₂O (520 mg, 1.3 mmol) in 15 mL of the same solvent. The resulting green solution was refluxed for 10 h. The resulting mixture was filtered and the green solid was washed with warm ethanol (2 x 10 mL) and diethyl ether (2 x 20 mL). The product was dried under vacuum to obtain a dark green powder [Cr(tpy)Br₃] (yield 88%). ESI-MS (CH₃CN) *m/z*: [Cr(tpy)Br₂]⁺ calc: 444.87, found: 444.9.

[Cr(ddpd)(SO₃CF₃)₃]. A mixture of [Cr(ddpd)Br₃] (100 mg, 0.17 mmol) and AgCF₃SO₃ (132 mg, 0.51 mmol) in distilled acetonitrile (4 mL), was heated under microwave irradiation in a sealed cap at 150°C during 0.5 h. After cooling to room temperature, the resulting red solution was filtered to remove the AgBr generated during the reaction. ESI-MS (CH₃CN) *m/z*: [Cr(ddpd)(SO₃CF₃)₂]⁺ calc: 640.99, found: 641. This solution was used directly for the next step.

[Cr(tpy)(SO₃CF₃)₃]. A mixture of [Cr(tpy)Br₃] (0.089 mg, 0.17 mmol) and AgCF₃SO₃ (132 mg, 0.51 mmol) in distilled acetonitrile (4 mL) was heated under microwave irradiation in a sealed cap at 150°C for 0.5 h. After cooling to room temperature, the resulting red solution was filtered in order to remove the AgBr generated during the reaction. ESI-(CH₃CN) *m/z*: [Cr(tpy)(SO₃CF₃)₂]⁺ calc: 582.94, found: 582.8. This solution was used directly for the next step.

[Cr(ddpd)(tpy)](PF₆)₃. A red solution of either [Cr(ddpd)(SO₃CF₃)₃] or [Cr(tpy)(SO₃CF₃)₃] in distilled acetonitrile was loaded into a 5 ml MW vial containing the ligand tpy (42 mg, 0.18 mmol), ddpd (51 mg, 0.18 mmol) respectively. The solution was heated under microwave irradiation for 2h at 75°C. After cooling to room temperature, the solvent was removed under reduced pressure yielding an orange residue. ESI-MS (CH₃CN) *m/z*: [Cr(ddpd)(tpy)](SO₃CF₃)₂⁺ calc: 874.09, found: 874. The orange residue was dissolved in ethanol (2 mL) and few drops of a saturated methanol solution of (*n*-Bu₄)NPF₆ were added. The resulting yellow precipitate was filtered and washed with cold MeOH (1 x 5 mL) and diethyl ether (2 x 15 mL) and finally dried under vacuum to give [Cr(ddpd)(tpy)](PF₆)₃ (yield 45% and 50%, respectively). Slow diffusion of diethyl ether into a concentrated solution of the complex in acetonitrile led to the formation of orange crystals suitable for XRD.

[Cr(ddpd)(tpy-COOEt)](PF₆)₃. A red solution of [Cr(ddpd)(SO₃CF₃)₃] in distilled acetonitrile was loaded into a 5 ml MW vial containing tpy-COOEt (54 mg, 0.18 mmol). The solution was heated under microwave irradiation for 2h at 75°C. After cooling to room temperature, the solvent was removed under reduced pressure yielding an orange residue. ESI-MS (CH₃CN) *m/z*: [Cr(ddpd)(tpy-COOEt)](SO₃CF₃)₂⁺ calc: 945.9, found: 946.0. The orange residue was dissolved in ethanol (2 mL) and few drops of a saturated methanol solution of (*n*-Bu₄)NPF₆ were added. The yellow precipitate was filtered and washed with cold MeOH (1 x 5 mL) and diethyl ether (2 x 15 mL) and finally dried under vacuum to give [Cr(ddpd)(tpy-COOEt)](PF₆)₃ (110 mg, yield 65%) as a fine yellow powder. Slow diffusion of diethyl ether into a concentrated solution of the complex in acetonitrile led to the formation of orange crystals suitable for XRD.

Spectroscopic and analytical measurements.

^1H and ^{13}C NMR spectra were recorded on a *Bruker Avance* 400 MHz spectrometer equipped with a variable temperature unit. Chemical shifts are given in ppm with respect to tetramethylsilane $\text{Si}(\text{CH}_3)_4$. Pneumatically-assisted electrospray (ESI) mass spectra were recorded from 10^{-4} M solutions on an Applied Biosystems API 150EX LC/MS System equipped with a Turbo Ionspray source[®]. Elemental analyses were performed by K. L. Buchwalder from the Microchemical Laboratory of the University of Geneva. Microwave heating was performed in a Biotage initiator plus, producing continuous irradiation at 2.45 GHz. Reaction mixtures were stirred with a magnetic bar during irradiation. Absorption spectra in acetonitrile solution were recorded using a Lambda 1050 Perkin Elmer spectrometer (quartz cell path length 1 cm or 1 mm, 250-800 nm domain, 2×10^{-4} mol/L). Solid-state diffuse reflectance spectra were recorded using UV/Vis/NIR Perkin-Elmer Lambda 900 in reflectance (*R*) mode fitted with an integrating sphere. The pure samples were placed between two 1.0 mm path length quartz cells whose background cell was filled with pure MgO. The signal of pure MgO was used as the baseline. Emission spectra (excitation at 355 nm) and excitation spectra were recorded from frozen solution samples (acetonitrile/propionitrile 6/4 at $C \approx 5 \times 10^{-3}$ mol/L), for powder samples at 77 K or from freeze pump thaw degassed acetonitrile solution ($C \approx 10^{-4}$ mol/L) at 293 K, with a Fluorolog (Horiba Jobin-Yvon), equipped with iHR320, a Xenon lamp 450 Watt Illuminator (FL-1039A/40A) and a water-cooled photo multiplier tube (PMT Hamamatsu R2658 or R928), and corrected for the spectral response of the system. For time-resolved experiments, the decay curves were recorded from previously cited samples at 77K and 293K, with a photomultiplier (Hamamatsu R2658 or R928) and a digital oscilloscope (Tektronix MDO4104C). Pulsed excitation at 355 nm was obtained with the third harmonic of a pulsed Nd:YAG laser (Quantel Qsmart850). Low temperature (77 K) was achieved using liquid quartz transparent Dewar filled with liquid N_2 in the centre of which samples were placed. Microcrystalline samples or acetonitrile/propionitrile (6/4) solutions ($C \approx 5 \times 10^{-3}$ mol/L), were introduced in quartz tube (4 mm interior diameter) introduced in sample holder of the Dewar. The oxygen free decay curve measurements were done at 293 K on acetonitrile solutions of the complex ($C \approx 10^{-4}$ mol/L). The complexes in quartz tube were dissolved in acetonitrile then degassed by freeze pump thaw, and filled with argon. Aerated solutions were prepared by using no-degassed acetonitrile as solvent. All emission quantum yields were measured according to a comparative method using $[\text{Cr}(\text{ddpd})_2]^{3+}$ ($\phi = 12.1$ %, CH_3CN , room temperature, $\lambda_{\text{exc}} =$

435nm) as reference.^{A1-10} Molar concentration were adjusted to 1×10^{-6} M for all complexes to ensure $A < 0.1$ at 435 nm.

X-Ray Crystallography.

Summary of crystal data, intensity measurements and structure refinements for compounds **1** to **3** were collected in Tables S2, S5 and S8 (ESI). The crystals were mounted on MiTeGen cryoloops with protection oil. X-ray data collections were performed with an Agilent SuperNova Dual diffractometer equipped with a CCD Atlas detector (Cu[K α] radiation) or a Rigaku synergy S equipped with an hyPIX detector (we thank Fraser White and the Rigaku team for assistance during data collection). The structures were solved in SHELXT by using dual space methods.^{A1-1} Full-matrix least-square refinements on F^2 were performed with SHELXL^{A1-2} within the Olex2 program.^{A1-3} CCDC 1868830-1868832 contain the supplementary crystallographic data. The cif files can be obtained free of charge on www.ccdc.cam.ac.uk.

References

- A1-1 G. M. Sheldrick, *Acta Cryst. A*, 2015, **71**, 3–8.
- A1-2 G. M. Sheldrick, *Acta Cryst. Sect. C*, 2015, **71**, 3–8.
- A1-3 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J Appl. Cryst.*, 2009, **42**, 339–341.

Table S1. Elemental analyses found for homoleptic and heteroleptic Cr(III) complexes.^a

Compound	Found C, H, N (%)	Calculated C, H, N (%)	Molecular Formula	MW /g.mol ⁻¹
[Cr(ddpd)Br ₃] $\cdot$ 0.5H ₂ O	34.45, 3.14, 11.40	34.49, 3.06, 11.83	C ₁₇ H ₁₇ N ₅ Br ₃ Cr $\cdot$ 0.5H ₂ O	592.1
[Cr(tpy)Br ₃] $\cdot$ 2H ₂ O	32.91, 2.61, 7.52	32.11, 2.69, 7.49	C ₁₅ H ₁₁ N ₃ Br ₃ Cr $\cdot$ 2H ₂ O	561
[Cr(tpy)(ddpd)](PF ₆) ₃ $\cdot$ H ₂ O (method 1)	37.52, 3.00, 10.83	37.33, 2.94, 10.88	C ₃₂ H ₂₈ CrF ₁₈ N ₈ P ₃ $\cdot$ 1H ₂ O	1029.5
[Cr(ddpd)(tpy)](PF ₆) ₃ $\cdot$ 2H ₂ O (method 2)	36.47, 3.18, 10.86	36.69, 3.08, 10.70	C ₃₂ H ₂₈ CrF ₁₈ N ₈ P ₃ $\cdot$ 2H ₂ O	1047.5
[Cr(ddpd)(tpy-COOEt)](PF ₆) ₂ (SO ₃ CF ₃) $\cdot$ 4H ₂ O	36.93, 3.23, 9.72	37.28, 3.48, 9.66	C ₃₅ H ₃₂ CrF ₁₈ N ₈ O ₈ P ₃ $\cdot$ 4H ₂ O	1159.7
[Cr(ddpd) ₂](BF ₄) ₃ $\cdot$ 1.5H ₂ O	43.86, 4.11, 15.10	43.77, 4.00, 15.01	C ₃₄ H ₃₄ B ₄ CrF ₁₂ N ₁₀ $\cdot$ 1.5H ₂ O	932.9
[Cr(tpy) ₂](PF ₆) ₃	37.74, 2.31, 8.83	37.79, 2.33, 8.81	C ₃₀ H ₂₂ CrF ₁₈ N ₆ P ₃ F ₁₈	953.4

^a The nature of the solvent molecules are deduced from IR spectroscopies and the solvent contents were obtained by multi-linear least-square fits of the experimental %C, % H, %N data.

Table S2. Crystal data and structure refinement for [Cr(ddpd)(tpy)](PF₆)₃ (**1**).

CCDC	1868830	
Empirical formula	C ₃₆ H ₃₄ Cr F ₁₈ N ₁₀ P ₃	
Formula weight	1093.64	
Temperature	180.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	Pna2 ₁	
Unit cell dimensions	a = 20.0625(3) Å	α = 90°
	b = 16.1756(3) Å	β = 90°
	c = 13.5227(2) Å	γ = 90°
Volume	4388.40(12) Å ³	
Z	4	
Density (calculated)	1.655 Mg/m ³	
Absorption coefficient	4.274 mm ⁻¹	
F(000)	2204	
Crystal size	0.208 x 0.141 x 0.103 mm ³	
Theta range for data collection	3.510 to 78.171°.	
Index ranges	-22 ≤ h ≤ 25, -18 ≤ k ≤ 20, -14 ≤ l ≤ 17	
Reflections collected	24416	
Independent reflections	7452 [R(int) = 0.0258]	
Completeness to theta = 67.684°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.993 and 0.641	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7452 / 1 / 618	
Goodness-of-fit on F ²	1.018	
Final R indices [I > 2σ(I)]	R1 = 0.0484, wR2 = 0.1191	
R indices (all data)	R1 = 0.0499, wR2 = 0.1204	
Absolute structure parameter	0.003(8)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.515 and -0.953 e.Å ⁻³	

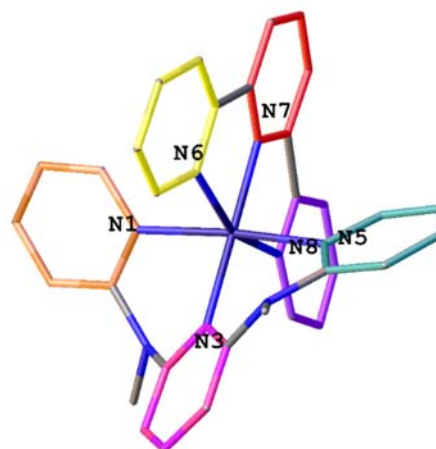
Table S3 Selected bond distances (Å), bond angles (°) in [Cr(ddpd)(tpy)](PF₆)₃ (**1**).

Atom	Atom	Length/Å
Cr1	N6	2.074(4)
Cr1	N7	1.987(4)
Cr1	N8	2.081(4)
Cr1	N5	2.060(4)
Cr1	N3	2.038(4)
Cr1	N1	2.064(4)

Atom	Atom	Atom	Angle/°
N6	Cr1	N8	156.69(16)
N7	Cr1	N6	78.21(16)
N7	Cr1	N8	78.50(16)
N7	Cr1	N5	91.66(17)
N7	Cr1	N3	177.81(17)
N7	Cr1	N1	93.88(17)
N5	Cr1	N6	90.59(16)
N5	Cr1	N8	91.08(15)
N5	Cr1	N1	174.19(16)
N3	Cr1	N6	99.79(15)
N3	Cr1	N8	103.51(15)
N3	Cr1	N5	87.45(16)
N3	Cr1	N1	86.95(16)
N1	Cr1	N6	88.86(16)
N1	Cr1	N8	91.71(16)

Table S4. Interplanar angles (°) in [Cr(ddpd)(tpy)](PF₆)₃ (**1**).

	Py1	N1 C1 C2 C3 C4 C5
	Py2	N3 C7 C8 C9 C10 C11
	Py3	N5 C17 C16 C15 C14 C13
	Py4	N6 C18 C19 C20 C21 C22
	Py5	N7 C23 C24 C25 C26 C27
	Py6	N8 C28 C29 C30 C31 C32



		RMSD (Å)
P1	N1 C1 C2 C3 C4 C5	0.012
P2	N3 C7 C8 C9 C10 C11	0.008
P3	N5 C17 C16 C15 C14 C13	0.014
P4	N6 C18 C19 C20 C21 C22	0.014
P5	N7 C23 C24 C25 C26 C27	0.004
P6	N8 C28 C29 C30 C31 C32	0.011

RMSD: Root mean square deviation between the atoms and the plane

	Py1	Py2	Py3	Py4	Py5	Py6
Py1		51.0	75.8	86.5	94.3	97.7
Py2			38.5	125.0	130.3	125.5
Py3				107.0	107.0	98.3
Py4					8.6	16.3
Py5						10.0

The error is typically $\pm 0.1^\circ$.

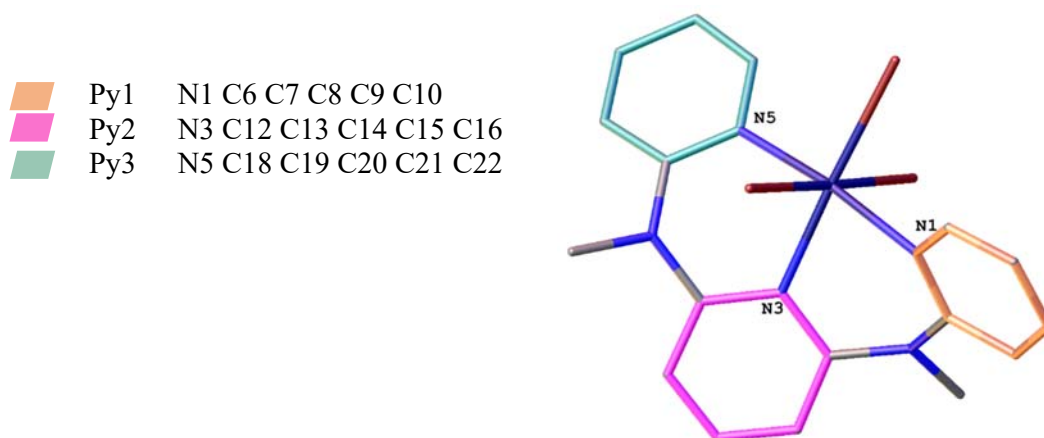
Table S5. Crystal data and structure refinement for [Cr(ddpd)Br₃] (**2**).

CCDC	1868831	
Empirical formula	C ₁₇ H ₁₇ Br ₃ Cr N ₅	
Formula weight	583.08	
Temperature	180.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 1 2 ₁ /n 1	
Unit cell dimensions	a = 9.35425(14) Å	α = 90°
	b = 15.1963(2) Å	β = 95.8596(13)°
	c = 13.72684(18) Å	γ = 90°
Volume	1941.08(5) Å ³	
Z	4	
Density (calculated)	1.995 Mg/m ³	
Absorption coefficient	12.180 mm ⁻¹	
F(000)	1132	
Crystal size	0.268 x 0.218 x 0.15 mm ³	
Theta range for data collection	4.353 to 70.471°.	
Index ranges	-11 ≤ h ≤ 8, -18 ≤ k ≤ 18, -16 ≤ l ≤ 16	
Reflections collected	17654	
Independent reflections	3696 [R(int) = 0.0380]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.538 and 0.154	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3696 / 0 / 237	
Goodness-of-fit on F ²	1.038	
Final R indices [I > 2σ(I)]	R ₁ = 0.0367, wR ₂ = 0.1182	
R indices (all data)	R ₁ = 0.0399, wR ₂ = 0.1247	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.368 and -0.758 e.Å ⁻³	

Table S6 Selected bond distances (Å), bond angles (°) in [Cr(ddpd)Br₃] (**2**).

Atom	Atom	Length/Å
Br1	Cr1	2.5062(5)
Br2	Cr1	2.4784(6)
Br3	Cr1	2.4852(5)
Cr1	N1	2.063(3)
Cr1	N3	2.074(3)
Cr1	N5	2.077(3)

Atom	Atom	Atom	Angle/°
Br2	Cr1	Br1	88.85(2)
Br2	Cr1	Br3	89.92(2)
Br3	Cr1	Br1	178.62(3)
N1	Cr1	Br1	91.46(8)
N1	Cr1	Br2	90.88(8)
N1	Cr1	Br3	89.17(7)
N1	Cr1	N3	86.30(12)
N1	Cr1	N5	173.06(12)
N3	Cr1	Br1	91.01(8)
N3	Cr1	Br2	177.17(9)
N3	Cr1	Br3	90.26(7)
N3	Cr1	N5	86.83(13)
N5	Cr1	Br1	87.69(8)
N5	Cr1	Br2	95.98(9)
N5	Cr1	Br3	91.84(8)

Table S7. Interplanar angles (°) in [Cr(ddpd)Br₃] (**2**).

RMSD: Root mean square deviation between the atoms and the plane

		RMSD (Å)
Py1	N1 C6 C7 C8 C9 C10	0.013
Py2	N3 C12 C13 C14 C15 C16	0.010
Py3	N5 C18 C19 C20 C21 C22	0.006

	Py1	Py2	Py3
Py1		133.25	105.6
Py2			46.9

The error is typically $\pm 0.1^\circ$.

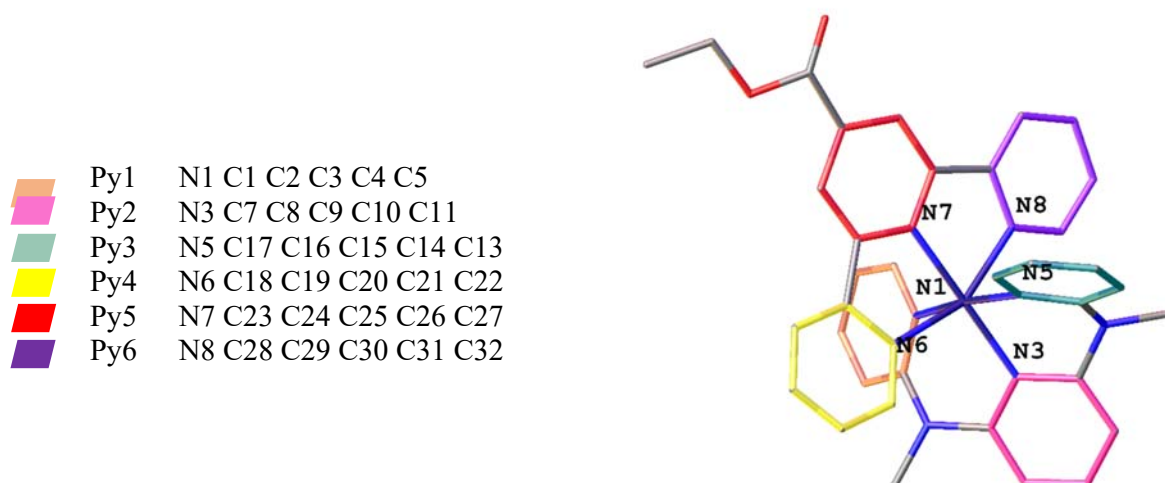
Table S8. Crystal data and structure refinement for [Cr(ddpd)(tpy-COOEt)](PF₆)₂(SO₃CF₃)·3CH₃CN (**3**)

CCDC	1868832	
Empirical formula	C ₄₂ H ₄₁ Cr F ₁₅ N ₁₁ O ₅ P ₂ S	
Formula weight	1210.86	
Temperature	180.01(10) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.9089(6) Å	α = 74.089(5)°
	b = 12.6435(8) Å	β = 75.790(5)°
	c = 19.9341(10) Å	γ = 69.487(6)°
Volume	2666.0(3) Å ³	
Z	2	
Density (calculated)	1.508 Mg/m ³	
Absorption coefficient	3.655 mm ⁻¹	
F(000)	1230	
Crystal size	0.463 x 0.231 x 0.023 mm ³	
Theta range for data collection	3.816 to 68.915°.	
Index ranges	-14 ≤ h ≤ 13, -15 ≤ k ≤ 14, -19 ≤ l ≤ 23	
Reflections collected	20526	
Independent reflections	9722 [R(int) = 0.0334]	
Completeness to theta = 67.684°	99.6 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.241	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9722 / 485 / 805	
Goodness-of-fit on F ²	1.041	
Final R indices [I > 2σ(I)]	R1 = 0.0556, wR2 = 0.1555	
R indices (all data)	R1 = 0.0686, wR2 = 0.1695	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.955 and -0.438 e.Å ⁻³	

Table S9 Selected bond distances (Å), bond angles (°) in [Cr(ddpd)(tpy-COOEt)](PF₆)₂(SO₃CF₃)·3CH₃CN (**3**)

Atom	Atom	Length/Å
Cr1	N1	2.043(2)
Cr1	N3	2.030(2)
Cr1	N5	2.057(2)
Cr1	N6	2.075(3)
Cr1	N7	2.006(2)
Cr1	N8	2.064(3)

Atom	Atom	Atom	Angle/°
N1	Cr1	N5	173.80(9)
N1	Cr1	N6	91.54(10)
N1	Cr1	N8	90.98(10)
N3	Cr1	N1	86.43(10)
N3	Cr1	N5	87.42(10)
N3	Cr1	N6	100.96(10)
N3	Cr1	N8	103.07(10)
N5	Cr1	N6	90.33(10)
N5	Cr1	N8	89.71(10)
N7	Cr1	N1	94.12(10)
N7	Cr1	N3	179.03(10)
N7	Cr1	N5	92.04(10)
N7	Cr1	N6	78.24(11)
N7	Cr1	N8	77.72(11)
N8	Cr1	N6	155.95(10)

Table S10. Interplanar angles (°) in [Cr(ddpd)(tpy-COOEt)](PF₆)₂(SO₃CF₃)·3CH₃CN (**3**).

		RMSD (Å)
Py1	N1 C1 C2 C3 C4 C5	0.011
Py2	N3 C7 C8 C9 C10 C11	0.014
Py3	N5 C17 C16 C15 C14 C13	0.014
Py4	N6 C18 C19 C20 C21 C22	0.013
Py5	N7 C23 C24 C25 C26 C27	0.007
Py6	N8 C28 C29 C30 C31 C32	0.014

RMSD: Root mean square deviation between the atoms and the plane.

	Py1	Py2	Py3	Py4	Py5	Py6
Py1		136.8	102.9	97.19	97.14	89.4
Py2			53.2	53.1	46.6	52.7
Py3				89	76.6	76.0
Py4					12.7	17.0
Py5						8.0

The error is typically $\pm 0.1^\circ$.

Table S11. Absorption spectra recorded for $[\text{Cr}(\text{tpy})_2](\text{PF}_6)_3$, $[\text{Cr}(\text{ddpd})_2](\text{BF}_4)_3 \cdot 1.5\text{H}_2\text{O}$, $[\text{Cr}(\text{ddpd})(\text{tpy})](\text{PF}_6)_3 \cdot 2\text{H}_2\text{O}$, $[\text{Cr}(\text{ddpd})(\text{tpy}-\text{COOEt})](\text{PF}_6)_2(\text{SO}_3\text{CF}_3) \cdot 4\text{H}_2\text{O}$ in CH_3CN ($2 \cdot 10^{-4} \text{ M}$; 250-650 nm) and in the solid state (650-850 nm) at 293 K.

Compound	λ (nm)	ν (cm^{-1})	ε ($\text{M}^{-1} \text{ cm}^{-1}$)	Assignments ^a
$[\text{Cr}(\text{ddpd})(\text{tpy})]^{3+}$	273	36630	19417	$\pi^* \leftarrow \pi$
	289	34602	18734	$\pi^* \leftarrow \pi$
	314	31847	16922	$\pi^* \leftarrow \pi$
	344	29069	13525	$\pi^* \leftarrow \pi$
	363	27548	12539	$\pi^* \leftarrow \pi$
	410	24390	1600	LMCT
	438	22831	1625	LMCT
	470	21276	1117	LMCT
	497	20120	<i>b</i>	$^4\text{T}_2 \leftarrow ^4\text{A}_2$
	698	14327	<i>b</i>	$^2\text{T}_1 \leftarrow ^4\text{A}_2$
	730	13699	<i>b</i>	$^2\text{T}_1 \leftarrow ^4\text{A}_2$
	758	13192	<i>b</i>	$^2\text{E} \leftarrow ^4\text{A}_2$
$[\text{Cr}(\text{ddpd})(\text{tpy}-\text{COOEt})]^{3+}$	277	36101	23123	$\pi^* \leftarrow \pi$
	291	34364	20925	$\pi^* \leftarrow \pi$
	318	31446	13224	$\pi^* \leftarrow \pi$
	356	28090	11300	$\pi^* \leftarrow \pi$
	372	26882	11154	$\pi^* \leftarrow \pi$
	427	23419	1605	LMCT
	449	22272	1758	LMCT
	486	20576	1020	LMCT
	490	20408	<i>b</i>	$^4\text{T}_2 \leftarrow ^4\text{A}_2$
	700	14285	<i>b</i>	$^2\text{T}_1 \leftarrow ^4\text{A}_2$
	712	14044	<i>b</i>	$^2\text{T}_1 \leftarrow ^4\text{A}_2$
	735	13605	<i>b</i>	$^2\text{T}_1 \leftarrow ^4\text{A}_2$
	760	13157	<i>b</i>	$^2\text{E} \leftarrow ^4\text{A}_2$

$[\text{Cr}(\text{tpy})_2]^{3+}$	265	37736	36102	$\pi^* \leftarrow \pi$
	282 (sh)	35461	26458	$\pi^* \leftarrow \pi$
	290	34483	21698	$\pi^* \leftarrow \pi$
	315	31746	13020	$\pi^* \leftarrow \pi$
	325	30769	14735	$\pi^* \leftarrow \pi$
	350	28571	20253	$\pi^* \leftarrow \pi$
	365	27397	23288	$\pi^* \leftarrow \pi$
	421	23752	2335	LMCT
	442	22624	2492	LMCT
	474	21097	1537	LMCT
	525	19047	100	LMCT
	530 ¹⁸	18867	<i>b</i>	$^4\text{T}_2 \leftarrow ^4\text{A}_2$
	715	13986	<i>b</i>	$^2\text{T}_1 \leftarrow ^4\text{A}_2$
	730	13698	<i>b</i>	$^2\text{T}_1 \leftarrow ^4\text{A}_2$
	773	12936	<i>b</i>	$^2\text{E} \leftarrow ^4\text{A}_2$
$[\text{Cr}(\text{dppd})_2]^{3+}$	301	33223	28608	$\pi^* \leftarrow \pi$
	316 (sh)	31646	24960	$\pi^* \leftarrow \pi$
	341	29326	14421	$\pi^* \leftarrow \pi$
	437	22783	3936	LMCT
	439 ¹⁰	22883	<i>b</i>	$^4\text{T}_2 \leftarrow ^4\text{A}_2$
	697	14347	<i>b</i>	$^2\text{T}_1 \leftarrow ^4\text{A}_2$
	738	13550	<i>b</i>	$^2\text{T}_1 \leftarrow ^4\text{A}_2$
	775	12903	<i>b</i>	$^2\text{E} \leftarrow ^4\text{A}_2$

^a Octahedral point groups (O , O_h) are assumed for the $[\text{CrN}_6]$ chromophores, see main text. ^b Recorded in the solid state.

Table S12. Emission spectra recorded for $[\text{Cr}(\text{tpy})_2](\text{PF}_6)_3$, $[\text{Cr}(\text{ddpd})_2](\text{BF}_4)_3 \cdot 1.5\text{H}_2\text{O}$, $[\text{Cr}(\text{ddpd})(\text{tpy})](\text{PF}_6)_3 \cdot 2\text{H}_2\text{O}$, $[\text{Cr}(\text{ddpd})(\text{tpy}-\text{COOEt})](\text{PF}_6)_2(\text{SO}_3\text{CF}_3) \cdot 4\text{H}_2\text{O}$ in CH_3CN (10^{-4}M ; $\lambda_{\text{exc}} = 355\text{ nm}$).

Compound	λ_{max} (77 K)	Assignment	λ_{max} (293 K)	Assignment
$[\text{Cr}(\text{ddpd})(\text{tpy})]^{3+}$	754	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=0))$	711	$\text{Cr}(^2\text{T}_1 \rightarrow ^4\text{A}_2)$
	770	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=1))$	771	$\text{Cr}(^2\text{E} \rightarrow ^4\text{A}_2)$
	796	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=2))$		
$[\text{Cr}(\text{ddpd})(\text{tpy}-\text{COOEt})]^{3+}$			711	$\text{Cr}(^2\text{T}_1 \rightarrow ^4\text{A}_2)$
	761	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=0))$	736	$\text{Cr}(^2\text{T}_1 \rightarrow ^4\text{A}_2)$
	796	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=1))$	774	$\text{Cr}(^2\text{E} \rightarrow ^4\text{A}_2)$
$[\text{Cr}(\text{ddpd})_2]^{3+}$	778	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=0))$	736	$\text{Cr}(^2\text{T}_1 \rightarrow ^4\text{A}_2)$
	804	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=1))$	774	$\text{Cr}(^2\text{E} \rightarrow ^4\text{A}_2)$
$[\text{Cr}(\text{tpy})_2]^{3+}$	771	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=0))$		
	782	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=1))$	711	$\text{Cr}(^2\text{T}_1 \rightarrow ^4\text{A}_2)$
	788	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=2))$	771	$\text{C}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=2))$
	796	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=3))$		

Table S13. Emission spectra recorded for $[\text{Cr}(\text{tpy})_2](\text{PF}_6)_3$, $[\text{Cr}(\text{ddpd})_2](\text{BF}_4)_3 \cdot 1.5\text{H}_2\text{O}$, $[\text{Cr}(\text{ddpd})(\text{tpy})](\text{PF}_6)_3 \cdot 2\text{H}_2\text{O}$, $[\text{Cr}(\text{ddpd})(\text{tpy}-\text{COOEt})](\text{PF}_6)_2(\text{SO}_3\text{CF}_3) \cdot 4\text{H}_2\text{O}$ in the solid state ($\lambda_{\text{exc}} = 355 \text{ nm}$).

Compound	λ_{max} (77 K)	Assignment	λ_{max} (293 K)	Assignment
$[\text{Cr}(\text{ddpd})(\text{tpy})]^{3+}$	757	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=0))$	713	$\text{Cr}(^2\text{T}_1 \rightarrow ^4\text{A}_2)$
	772	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=1))$	733	$\text{Cr}(^2\text{T}_1 \rightarrow ^4\text{A}_2)$
	784	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=2))$	758	$\text{Cr}(^2\text{T}_1 \rightarrow ^4\text{A}_2)$
	800	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=3))$	776	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=0))$
$[\text{Cr}(\text{ddpd})(\text{tpy}-\text{COOEt})]^{3+}$			713	$\text{Cr}(^2\text{T}_1 \rightarrow ^4\text{A}_2)$
	765	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=0))$	733	$\text{Cr}(^2\text{T}_1 \rightarrow ^4\text{A}_2)$
	781	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=1))$	762	$\text{Cr}(^2\text{T}_1 \rightarrow ^4\text{A}_2)$
			776	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=0))$
$[\text{Cr}(\text{ddpd})_2]^{3+}$	781	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=0))$	736	$\text{Cr}(^2\text{T}_1 \rightarrow ^4\text{A}_2)$
	801	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=1))$	774	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=0))$
$[\text{Cr}(\text{tpy})_2]^{3+}$	772	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=0))$	771	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=0))$
	784	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=1))$	784	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=1))$
	800	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=2))$	798	$\text{Cr}(^2\text{E}(\nu=0) \rightarrow ^4\text{A}_2(\nu=2))$

Table S14. Energies of the Cr(4A_2), Cr(2T_1) and Cr(2E) levels and ligand field Δ and Racah parameters B and C computed with eqs 1-3 for [Cr(tpy) $_2$](PF $_6$) $_3$, [Cr(ddpd) $_2$](BF $_4$) $_3 \cdot 1.5H_2O$ [Cr(ddpd)(tpy)](PF $_6$) $_3 \cdot 2H_2O$, [Cr(ddpd)(tpy-COOEt)](PF $_6$) $_2$ (SO $_3$ CF $_3$) $\cdot 4H_2O$ in the solid state at 293 K. ^a

Compound	Δ/cm^{-1}	B/cm^{-1}	C/cm^{-1}	Δ/B	C/B	$^2E/\text{cm}^{-1}$	$^2T_1/\text{cm}^{-1}$	$^4T_2/\text{cm}^{-1}$	$^2T_2/\text{cm}^{-1}{}^b$	$^4T_1/\text{cm}^{-1}{}^b$
[Cr(ddpd)(tpy)] $^{3+}$	20121	791	2531	25	3.2	13192	14013	20121	19089	28083
[Cr(ddpd)(tpy-COOEt)] $^{3+}$	20408	798	2553	26	3.2	13157	13977	20408	19099	28368
[Cr(ddpd) $_2$] $^{3+}$	22883	763	2442	30	3.2	12903	13949	22883	19176	30823
[Cr(tpy) $_2$] $^{3+}$	18750	790	2512	26	3.2	12936	13842	18750	18589	26640

^a The energy of Cr(2T_1) is taken as the average of its split components (see text). ^b Computed using $E(^2T_2) = 15B + 5C - 176(B^2/\Delta)$ and $E(^4T_1) = 1.5\Delta + 7.5B - 0.5\sqrt{225B^2 + \Delta^2 - 18\Delta B}$.¹⁸

Table S15. Cr(²E) excited-state lifetimes and global luminescent quantum yields determined for heteroleptic [Cr(ddpd)(tpy)]³⁺, [Cr(ddpd)(tpy-COOEt)]³⁺ and homoleptic [Cr(ddpd)₂]³⁺ and [Cr(tpy)₂]³⁺ in solution.

Compounds	$\tau_{77\text{ K}}/\mu\text{s}$ ^a	$\tau_{293\text{ K}}/\mu\text{s}$ ^b	$\tau_{293\text{ K}}/\mu\text{s}$ ^c	$\phi_{293\text{ K}}/\%$ ^b	$\phi_{293\text{ K}}/\%$ ^c
[Cr(ddpd)(tpy)] ³⁺	1060(10)	1002(10)	40(10)	0.06	0.014
[Cr(ddpd)(tpy-COOEt)] ³⁺	1070(10)	980(10)	40(10)	0.14	0.018
[Cr(ddpd) ₂] ³⁺	1300(15)	975(10)	30(10)	12.1 ^d	0.855
[Cr(tpy) ₂] ³⁺	670(10)	< 2	< 2	< 0.001 ^e	-

^a measurement in acetonitrile/propionitrile (6/4) solution (10⁻⁴ mol/L). ^b measurement in freeze-pump-thaw degassed acetonitrile solution (10⁻⁴ mol/L). ^c Measurements in aerated acetonitrile solution (10⁻⁴ mol/L). ^d Literature reference value.¹⁰ ^e value obtained in water.^{25,26}

Table S16. Cr(²E) excited-state lifetimes determined for [Cr(tpy)₂](PF₆)₃, [Cr(ddpd)₂](BF₄)₃·1.5H₂O [Cr(ddpd)(tpy)](PF₆)₃·2H₂O, [Cr(ddpd)(tpyCOOEt)](PF₆)₂(SO₃CF₃)·4H₂O in the solid state at 77 K.

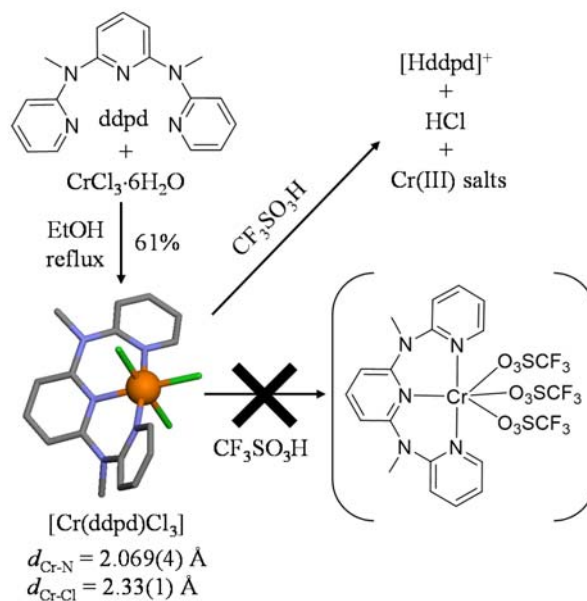
Compounds	$\tau_1/\mu\text{s}$	$\tau_2/\mu\text{s}$	$A1$	$A2$
[Cr(ddpd)(tpy)] ³⁺	390	110	0.00217 (55%)	0.00177 (45%)
[Cr(ddpd)(tpy-COOEt)] ³⁺	30	267	0.00285 (62%)	0.00173 (38%)
[Cr(ddpd) ₂] ³⁺	86	492	0.00239 (55%)	0.00197 (45%)
[Cr(tpy) ₂] ³⁺	< 2	20	0.01254 (59%)	0.00864 (41%)

Intensity decay curves were fitted with the following equation: $I = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} + y_0$

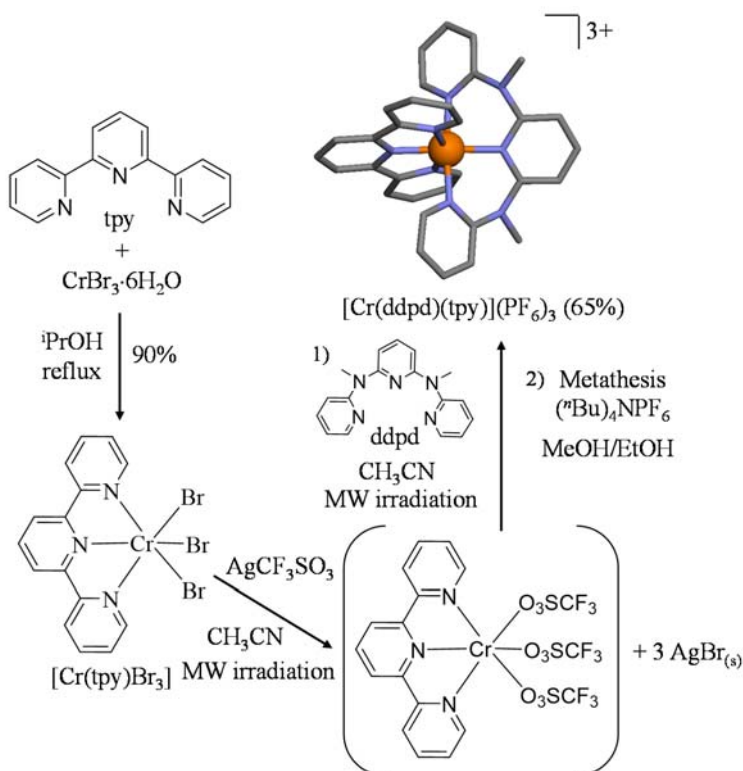
Table S17. Cr(²E) excited-state lifetimes determined for [Cr(tpy)₂](PF₆)₃, [Cr(ddpd)₂](BF₄)₃·1.5H₂O [Cr(ddpd)(tpy)](PF₆)₃·2H₂O, [Cr(ddpd)(tpyCOOEt)](PF₆)₂(SO₃CF₃)·4H₂O in the solid state at 293 K.

Compounds	$\tau_1/\mu\text{s}$	$\tau_2/\mu\text{s}$	$A1$	$A2$
[Cr(ddpd)(tpy)] ³⁺	< 2	< 2	0.26184 (73%)	0.09413 (27%)
[Cr(ddpd)(tpy-COOEt)] ³⁺	< 2	< 2	0.01289 (30%)	0.02954 (70%)
[Cr(ddpd) ₂] ³⁺	211	30	0.00529 (44%)	0.00669 (56%)
[Cr(tpy) ₂] ³⁺	< 2	< 2	0.00969 (34%)	0.01871 (66%)

Intensity decay curves were fitted with the following equation: $I = Ae^{-\frac{t}{\tau_1}} + A_2e^{-\frac{t}{\tau_2}} + y_0$



Scheme S1 Reactivity of $[\text{Cr}(\text{ddpd})\text{Cl}_3](\text{PF}_6)_3$. The crystal structure of $[\text{Cr}(\text{ddpd})\text{Cl}_3]$ is shown.¹⁸ Color code: gray = C, blue = N, green = Cl and orange = Cr. Hydrogens atoms have been omitted for clarity.



Scheme S2 Synthesis and structure of heteroleptic $[\text{Cr}(\text{ddpd})(\text{tpy})](\text{PF}_6)_3$ (**1**). Color code: gray = C, blue = N, red = O, and orange = Cr. Hydrogens atoms and counter anions have been omitted for clarity.

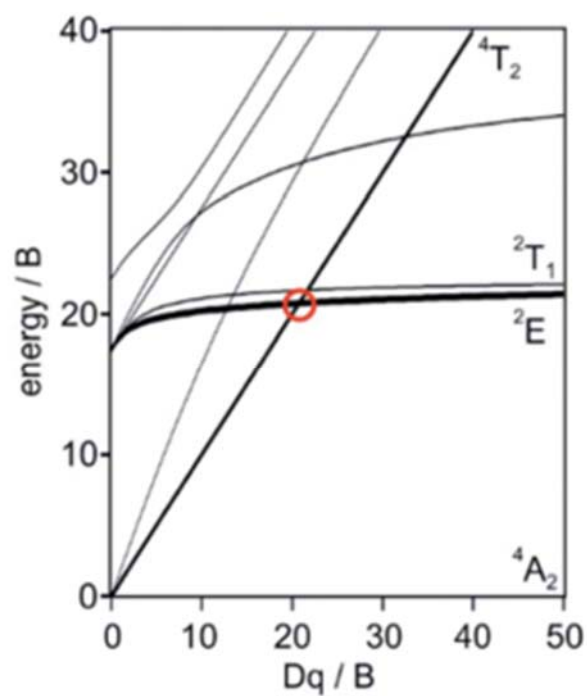


Figure S1. Tanabe-Sugano diagram for the d^3 electron configuration.

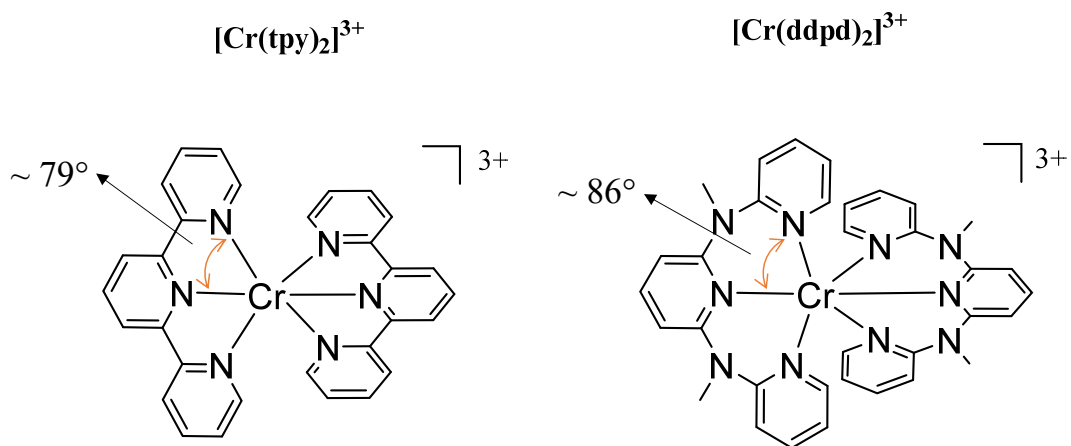


Figure S2. Bis-terdentate pseudo-octahedral Cr(III) complexes $[\text{Cr}(\text{ddpd})_2]^{3+}$ (right) and, $[\text{Cr}(\text{tpy})_2]^{3+}$ (left) highlighting average N-Cr-N chelate angles.

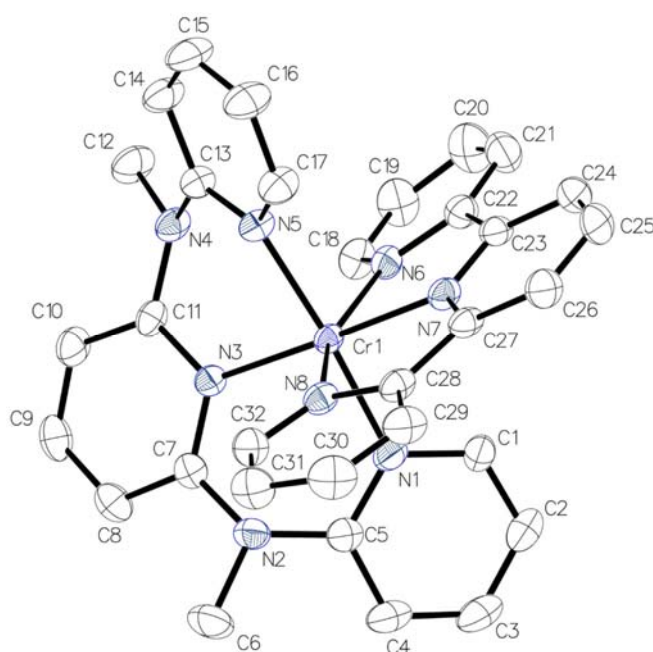


Figure S3 ORTEP view of [Cr(tpy)(ddpd)](PF₆)₃ (**1**) with numbering scheme. Thermal ellipsoids are drawn at 50% probability level. Counter ions and H atoms are omitted for clarity.

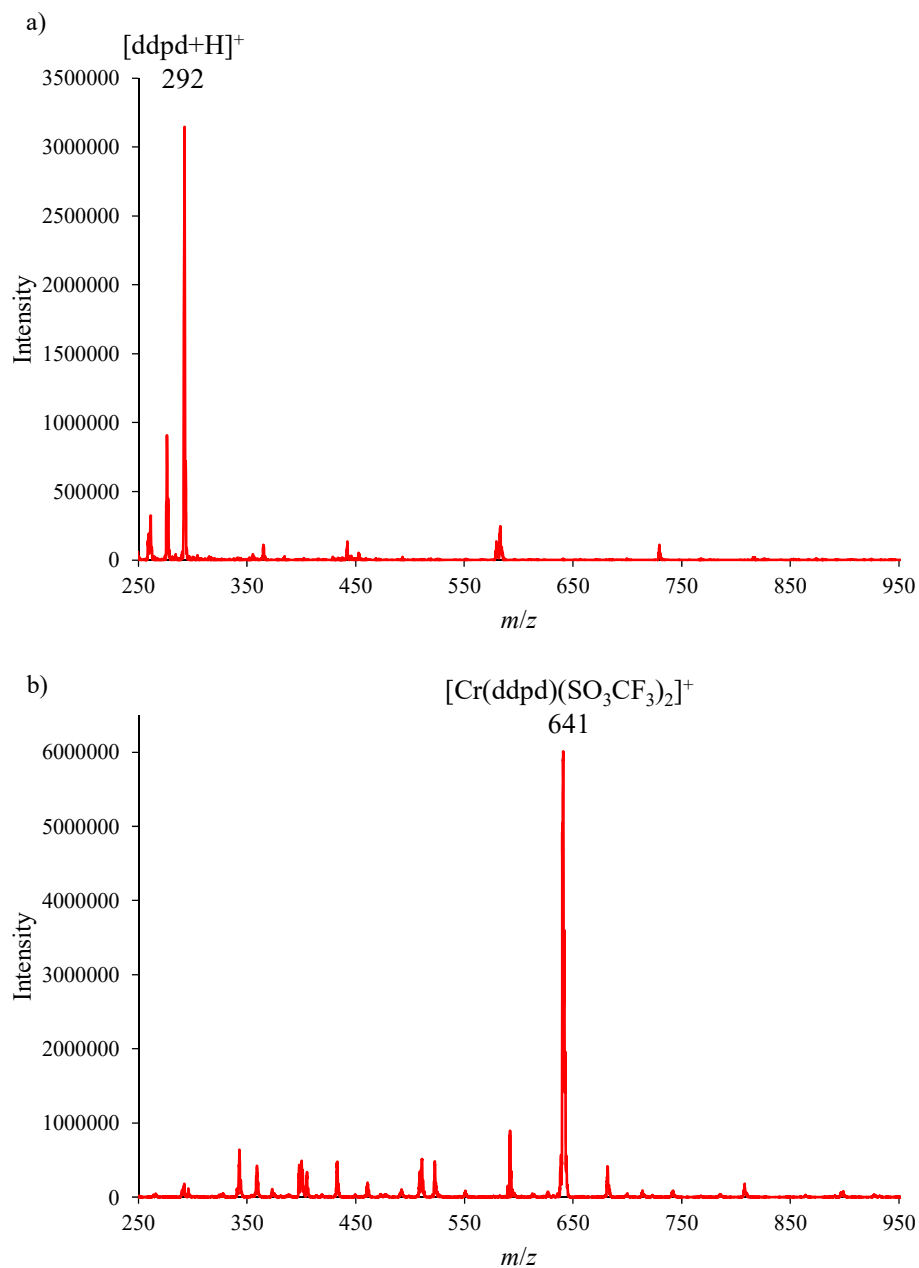


Figure S4 ESI-MS spectra recorded upon reaction of a) $[\text{Cr}(\text{ddpd})\text{Cl}_3]$ with $\text{CF}_3\text{SO}_3\text{H}$ and b) $[\text{Cr}(\text{ddpd})\text{Br}_3]$ with AgCF_3SO_3 .

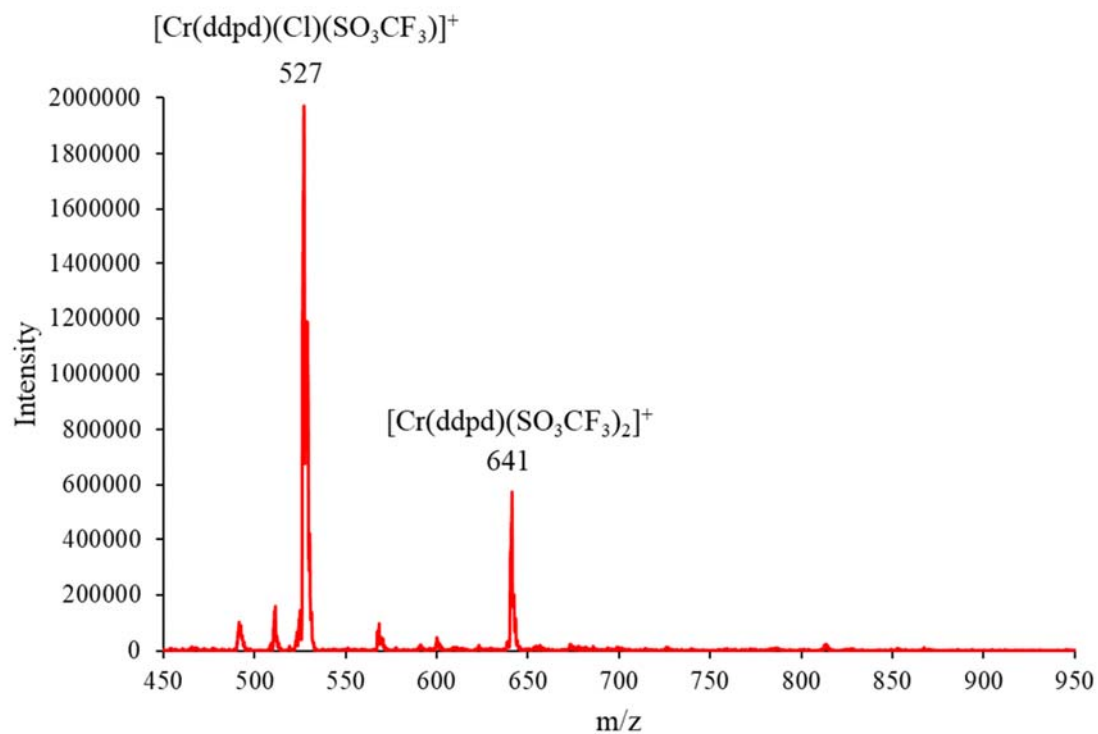


Figure S5 ESI-MS spectra recorded upon reaction of $[\text{Cr}(\text{ddpd})\text{Cl}_3]$ with AgCF_3SO_3 .

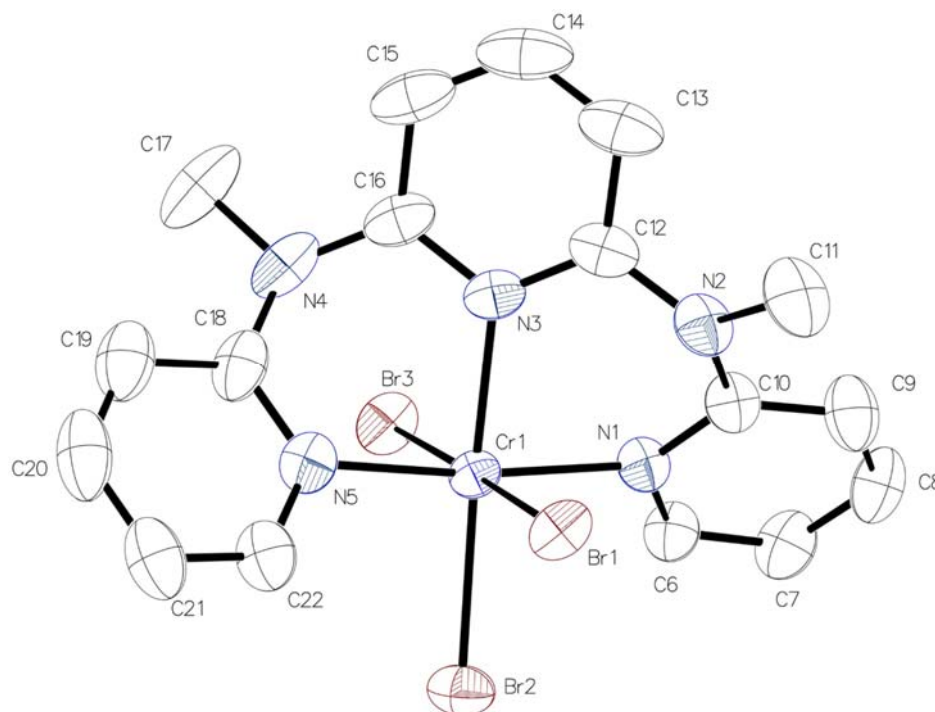


Figure S6 ORTEP view of $[\text{Cr}(\text{tpy})\text{Br}_3]$ (2) with numbering scheme. Thermal ellipsoids are drawn at 50% probability level. H atoms are omitted for clarity.

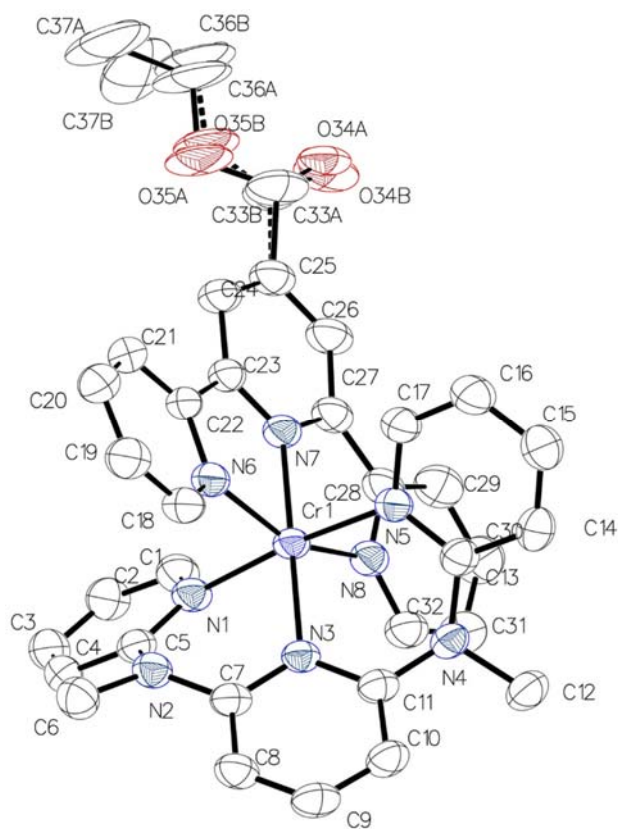


Figure S7 ORTEP view of $[\text{Cr}(\text{ddpd})(\text{tpy-COOEt})](\text{PF}_6)_2(\text{CF}_3\text{SO}_3) \cdot 3\text{CH}_3\text{CN}$ (**3**) with numbering scheme. Thermal ellipsoids are drawn at 50% probability level. Counter ions, solvent molecules and H atoms are omitted for clarity.

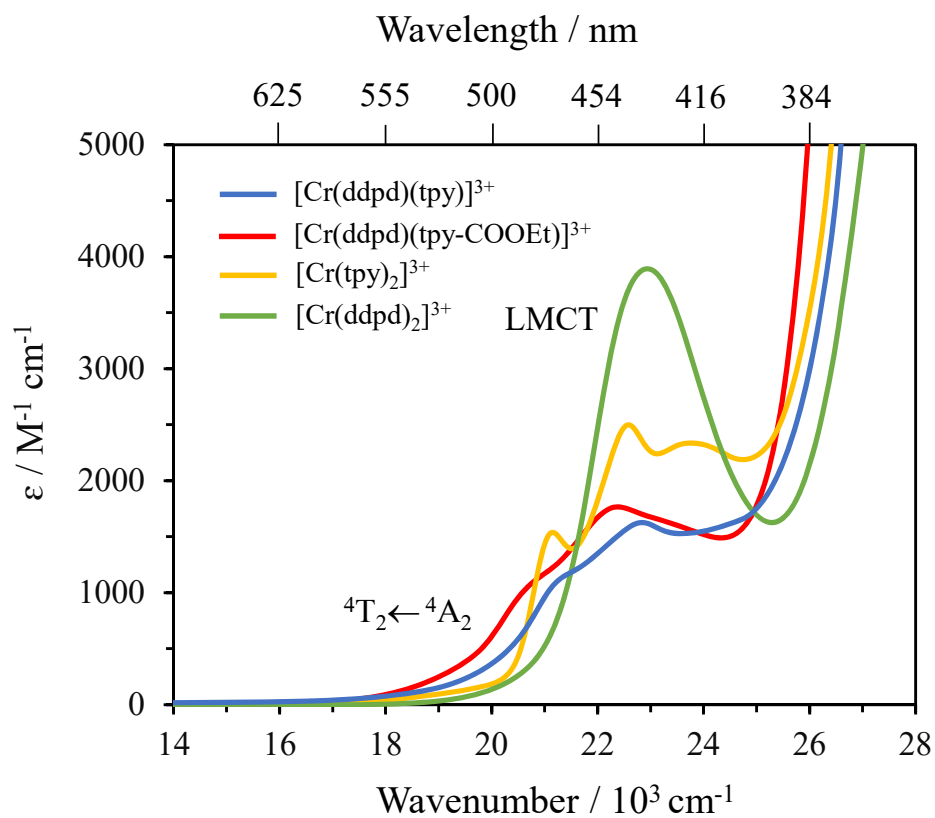


Figure S8. Zoom of the absorption spectra of heteroleptic $[\text{Cr}(\text{ddpd})(\text{tpy})]^{3+}$ (blue trace), $[\text{Cr}(\text{ddpd})(\text{tpy-COOEt})]^{3+}$ (red trace) and homoleptic $[\text{Cr}(\text{tpy})_2]^{3+}$ (yellow trace) and $[\text{Cr}(\text{ddpd})_2]^{3+}$ (green trace) recorded in acetonitrile solution ($2 \cdot 10^{-4}$ M) at 293 K

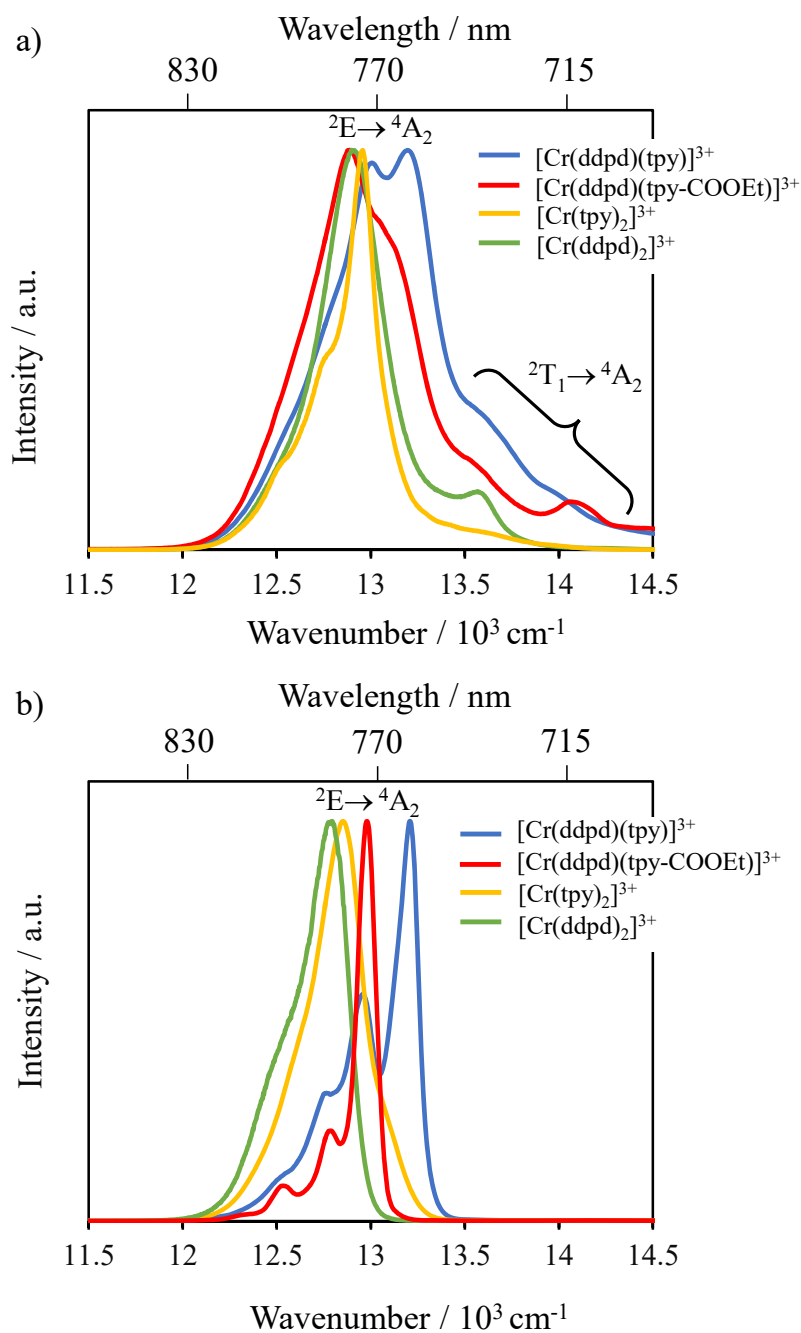


Figure S9. Emission spectra ($\lambda_{\text{exc}} = 355 \text{ nm}$) of heteroleptic $[\text{Cr}(\text{ddpd})(\text{tpy})]^{3+}$ (blue trace), $[\text{Cr}(\text{ddpd})(\text{tpy-COOEt})]^{3+}$ (red trace) and homoleptic $[\text{Cr}(\text{tpy})_2]^{3+}$ (yellow trace) and $[\text{Cr}(\text{ddpd})_2]^{3+}$ (green trace) recorded in the solid state at a) 293K and b) 77 K.