ELECTRONIC SUPPLEMENTARY INFORMATION

Homoleptic tris-cyclometalated platinum(IV) complexes: a new class of long-lived, highly efficient ^{3}LC emitters

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General Considerations and Materials. Unless otherwise noted, preparations were carried out under atmospheric conditions. Synthesis grade solvents were obtained from commercial sources. The compounds $PhICl_2$,[1] **1a–c**,[2-4] and **2a**[5] were prepared following published procedures; compounds **1d** and **2b–d** were not previously described and their preparation and spectroscopic and analytical data are given below. All other reagents were obtained from commercial sources and used without further purification.

Analytical Methods. NMR spectra were recorded on Bruker Avance 200, 300, 400, or 600 spectrometers at 298 K. Chemical shifts are referred to residual signals of non-deuterated solvent. J values are given in Hz. The number of solvation water molecules was calculated from the integral of the ^1H NMR water signal, taking into account the water content of the solvent blank. Elemental analyses were carried out with Carlo Erba 1106 and LECO CHNS-932 microanalyzers.

Preparation of PMMA Thin Films. PMMA thin films supported on quartz slides were prepared by spin-coating technique, using 10-mg/mL solutions of the complexes in MeCN with different emitter/PMMA ratios. The average thickness of the obtained films was about 100 nm.

Photoisomerizations. Photoisomerizations were carried out using a UV-Consulting Peschl photoreactor, model UV-RS-1, equipped with a 150 W medium-pressure mercury immersion UV lamp (TQ 150), a quartz cooling jacket, and a 400 mL reaction vessel with magnetic circulation pump.

Photophysical Characterization. UV-vis absorption spectra were recorded on an Perkin-Elmer Lambda 750S spectrophotometer. Excitation and emission spectra were recorded on a Jobin Yvon Fluorolog 3-22 spectrofluorometer with a 450 W xenon lamp, double-grating monochromators, and a TBX-04 photomultiplier. Solution measurements were carried out in a right angle configuration using 10 mm quartz fluorescence cells or 5 mm quartz NMR tubes. For the low-temperature measurements, a liquid nitrogen Dewar with quartz windows was employed. Solutions of the samples were degassed by bubbling argon for 30 min. Lifetimes were measured using either the Fluorolog's FL-1040 phosphorimeter accessory ($\tau > 10\ \mu s$) or an IBH FluoroHub TCSPC controller and a NanoLED pulse diode excitation ($\tau < 10\ \mu s$); the estimated uncertainty is ±10% or better. Emission quantum yields were measured using a Hamamatsu C11347 Absolute PL Quantum Yield Spectrometer; the estimated uncertainty is ±5% or better.

Electrochemical Characterization. Cyclic voltammograms were registered with a potentiostat/galvanostat AUTOLAB-100 (Echo-Chemie, Utrecht), employing a three-electrode electrochemical cell equipped with a glassy carbon working electrode (Metrohm, 2 mm diameter), a KCl saturated calomel electrode reference (SCE), and a glassy carbon rod counter electrode. The measurements were carried out at 298 K under an argon atmosphere, using degassed 1 mM solutions of the complexes in extra-dry MeCN (Acros Organics) and 0.1 M $(Bu_4N)PF_6$ as the electrolyte. Prior to each experiment, the working electrode was polished with alumina slurry (0.05 mm) and rinsed with water and acetone. The electrodes were activated electrochemically in the background solution by means of several voltammetric cycles at 1 V s^{-1} between –2.2 V and 2.2 V. At the end of each experiment, the reference electrode was checked against the ferrocene/ferricinium redox couple (0.40 V vs SCE in MeCN).[6]

X-ray Structure Determinations. Crystals of *mer*-**3b** and *mer*-**3c**·CH_2Cl_2 suitable for X-ray diffraction studies were obtained by the liquid-liquid diffusion method from CH_2Cl_2/Et_2O or CD_2Cl_2/*n*-pentane, respectively. Numerical details are presented in Table S1. The data were collected on an Bruker SMART APEX CCD diffractometer using monochromated Mo-$K\alpha$ radiation in ω-scan mode for *mer*-**3b** and in ω-scan and φ-scan modes for *mer*-**3c**·CH_2Cl_2. The structures were refined anisotropically on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen).[7] Methyl hydrogens were included as part of rigid idealized methyl groups allowed to rotate but not tip; other hydrogens were included using a riding model. *Special features of refinement:* In both *mer*-**3b** and *mer*-**3c**·CH_2Cl_2, there is a poorly resolved region of residual electron density that could not be adequately modeled and therefore the program SQUEEZE, which is part of the PLATON system, was employed to remove mathematically the effects of the solvent. The void volume per cell was 1031.2 (*mer*-**3b**) or 164 Å^3 (*mer*-**3c**·CH_2Cl_2) with a void electron count per cell of 363 (*mer*-**3b**) or 76 (*mer*-**3c**·CH_2Cl_2); this additional solvent was not taken into account when calculating derived parameters such as the formula weight, because its nature was uncertain. The triflate anion is disordered over two positions, *ca.* 90:10% (*mer*-**3b**) or 73:28% (*mer*-**3c**·CH_2Cl_2). In *mer*-**3c**·CH_2Cl_2, one of the cyclometalated dfppy ligands and the solvent molecule are disordered over two positions, *ca.* 52:48% or 54:46%, respectively.

Table S1. Crystallographic Data for *mer*-**3b** and *mer*-**3c**.

	mer-**3b**	*mer*-**3c**$\cdot CH_2Cl_2$
formula	$C_{37}H_{30}F_3N_3O_3PtS$	$C_{35}H_{20}Cl_2F_9N_3O_3PtS$
fw	848.79	999.59
T (K)	100(2)	100(2)
λ (Å)	0.71073	0.71073
cryst syst	orthorhombic	Triclinic
space group	*Pbca*	$P\bar{1}$
a (Å)	14.0939(12)	10.3618(9)
b (Å)	19.1285(16)	12.3271(11)
c (Å)	26.663(2)	14.6981(12)
α (deg)	90	81.352(2)
β (deg)	90	88.049(2)
γ (deg)	90	80.752(2)
V (Å^3)	7188.3(10)	1831.8(3)
Z	8	2
ρ_{calcd} (Mg m^{-3})	1.569	1.812
μ (mm^{-1})	4.016	4.119
R1[a]	0.0269	0.0355
wR2[b]	0.0609	0.0899

[a] R1 = $\Sigma||F_o|-|F_c||/\Sigma|F_o|$ for reflections with $I > 2\sigma(I)$. [b] wR2 = $[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and a and b are constants set by the program.

Synthesis of [Pt(ppz)(Hppz)Cl] (1d). The following procedure is based on the method described for [Pt(ppy)(Hppy)Cl] (**1a**).[2] K_2PtCl_4 (3.31 g, 7.97 mmol), 1-phenylpyrazole (3 mL, 22.68 mmol) and a degassed 3:1 mixture of 2-ethoxyethanol/water (80 mL) were placed in a Carius tube and heated at 80 °C for 36 h under a N_2 atmosphere. Solvents were removed under reduced pressure, the residue was treated with CH_2Cl_2 (80 mL) and the resulting suspension was filtered through anhydrous $MgSO_4$. The filtrate was concentrated to dryness and the residue was chromatographed on silica gel using a $CHCl_3$/AcOEt mixture (9:1) as the eluent. Complex **1d** was obtained as an off-white solid after evaporation of the solvents. Yield: 2.26 g, 55%. ^1H NMR (400.9 MHz, $CDCl_3$): δ 8.09-8.16 (m, 2 H), 7.89-7.94 (m, 3 H), 7.82 (dd, J = 2.9, 0.7 Hz, 1 H), 7.35-7.44 (m, 3 H), 6.99-7.04 (m, 2 H), 6.78-6.84 (m, 1 H), 6.67 (dd, J = 2.8, 2.4 Hz, 1 H), 6.46 (dd, J = 2.7, 2.3 Hz, 1 H), 6.26 (td with satellites, J_{HH} = 7.5, 0.7 Hz, J_{HPt} = 26 Hz, 1 H). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$): δ 143.9 (CH), 143.2 (C), 140.1 (CH), 138.9 (C), 133.0 (CH), 132.5 (CH), 129.5 (CH), 129.0 (CH), 126.0 (CH), 125.8 (CH), 125.6 (CH), 123.5 (CH), 110.5 (CH), 109.1 (CH), 106.4 (CH). Elemental analysis Calcd for $C_{18}H_{15}ClN_4Pt$: C, 41.75; H, 2.92; N, 10.82; found: C, 41.60; H, 2.67; N, 11.17.

Synthesis of [Pt(tpy)$_2$Cl$_2$] (2b) and [Pt(dfppy)$_2$Cl$_2$] (2c). The following procedure is based on the method described for [Pt(ppy)$_2$Cl$_2$] (**2a**).[5] $PhICl_2$ (480 mg, 1.75 mmol) was added to a solution of **1b** or **1c** (1.58 mmol) in CH_2Cl_2 (90 mL) and the mixture was stirred at room temperature for 1 h. The resulting suspension was concentrated under reduced pressure (20 mL) and Et_2O (tpy derivative) or *n*-pentane (dfppy derivative) (140 mL) was added. The precipitate was filtered off, washed with Et_2O (2 × 5 mL) and vacuum-dried to give **2b**·H_2O or **2c**·0.5H_2O as white solids.

2b·H$_2$O. Yield: 94%. ^1H NMR (400.9 MHz, CD_2Cl_2): δ 9.87 (ddd with satellites, J_{HH} = 6.0, 1.5, 0.6 Hz, J_{HPt} = 14 Hz, 2 H), 8.11 (m, 2 H), 7.97 (m, 2 H), 7.55 (d, J = 7.9 Hz, 2 H), 7.50 (m, 2 H), 6.98 (ddd, J = 7.8, 1.5, 0.6 Hz, 2 H), 5.85 (d with satellites, J_{HH} = 0.7 Hz, J_{HPt} = 16.4 Hz, 2 H), 2.12 (s, 6 H). $^{13}C\{^1H\}$ NMR [100.8 MHz, $(CD_3)_2SO$]: δ 163.3 (C, J_{PtC} = 28 Hz), 148.7 (CH), 141.8 (CH), 141.6 (C), 141.4 (C), 138.0 (C, J_{PtC} = 13 Hz), 126.8 (CH, J_{PtC} = 15 Hz), 126.6 (CH), 125.7 (CH, J_{PtC} = 16 Hz), 124.4 (CH, J_{PtC} = 14 Hz), 121.3 (CH, J_{PtC} = 16 Hz), 21.4 (CH). Elemental analysis Calcd for $C_{24}H_{22}Cl_2N_2OPt$: C, 46.46; H, 3.57; N, 4.52; found: C, 46.66; H, 3.30; N, 4.68.

2c·0.5H_2O. Yield: 90%. ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ 9.91 (dd with satellites, J = 6.0, 1.6 Hz, J_{HPt} = 14.4 Hz, 2 H), 8.37 (m, 2 H), 8.19 (dt, J = 7.9, 1.6 Hz, 2 H), 7.59 (m, 2 H), 6.72 (ddd, J = 12.0, 8.9, 2.4 Hz, 2 H), 5.63 (ddd with satellites, J = 7.7, 2.3, 1.1 Hz, J_{HPt} = 19.6 Hz, 2 H). ^{13}C{^{1}H} NMR [75.5 MHz, $(CD_3)_2SO$]: δ 164.4-157.6 (several multiplets, C), 149.3 (CH), 143.1 (CH), 142.1 (d, J_{CF} = 8 Hz, C), 125.7 (J_{PtC} = 13 Hz, CH), 124.8 (m, CH), 110.3 (m, CH), 102.8 (J_{PtC} = 26 Hz, CH). Elemental analysis Calcd for $C_{22}H_{13}Cl_2F_4N_2O_{0.5}Pt$: C, 40.32; H, 2.00; N, 4.27; found: C, 40.21; H, 1.87; N, 4.35.

Synthesis of [Pt(ppz)$_2$Cl$_2$] (2d). The preparation of this complex had to be carried out at low temperatures to avoid the formation of a mixture of isomeric species. To a solution of **1d** (534 mg, 1.03 mmol) in CH_2Cl_2 (60 mL) at –70 °C was added $PhICl_2$ (315 mg, 1.14 mmol). The mixture was stirred at –50 °C for 1.5 h and then allowed to warm to room temperature. Partial evaporation of the solvent (15 mL) and addition of Et_2O (90 mL) led to the precipitation of a white solid, which was filtered off, washed with Et_2O (2 × 5 mL) and vacuum-dried to give **2d**·0.5H_2O. Yield: 532 mg, 94%. ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ 8.57 (dd with satellites, J_{HH} = 2.4, 0.6 Hz, J_{HPt} = 5.1 Hz, 2 H), 8.28 (dd with satellites, J_{HH} = 2.9, 0.7 Hz, J_{HPt} = 4.5 Hz, 2 H), 7.34 (m, 2 H), 7.17 (dt, J = 7.6, 1.2 Hz, 2 H), 6.85-6.94 (m, 4 H), 6.13 (dd with satellites, J_{HH} = 7.8, 1.2 Hz, J_{HPt} = 17.8 Hz, 2 H). ^{13}C{^{1}H} NMR [50.3 MHz, $(CD_3)_2SO$]: δ 139.0 (J_{PtC} = 18 Hz, CH), 138.2 (C), 130.4 (J_{PtC} = 11 Hz, CH), 128.3 (J_{PtC} = 11 Hz, CH), 127.4 (J_{PtC} = 20 Hz, CH), 126.5 (CH), 125.6 (C), 113.6 (J_{PtC} = 10 Hz, CH), 109.4 (J_{PtC} = 14 Hz, CH). Elemental analysis Calcd for $C_{18}H_{15}Cl_2N_4O_{0.5}Pt$: C, 38.51; H, 2.69; N, 9.98; found: C, 38.58; H, 2.75; N, 9.89.

Synthesis of *mer*-[Pt(ppy)$_3$]OTf (*mer*-3a). A mixture of complex **2a** (191 mg, 0.33 mmol), AgOTf (189 mg, 0.74 mmol), Hppy (0.38 mL, 2.66 mmol) and degassed 1,2-dichloroethane (20 mL) was placed in a Carius tube and stirred at 90 °C under a N_2 atmosphere for 3 days. After cooling to room temperature, CH_2Cl_2 (10 mL) was added and the suspension was filtered trough Celite. In order to remove the 2-phenylpyridinium triflate formed upon metalation of Hppy, the filtrate was stirred vigorously with Na_2CO_3 and then filtered. Partial evaporation of the solution under reduced pressure (5 mL) and addition of Et_2O (30 mL) led to the precipitation of a white solid, which was filtered off, washed with Et_2O (2 × 4 mL) and vacuum-dried to give *mer*-**3a**·0.5H_2O. Yield: 242 mg, 91%. ^{1}H NMR (600.1 MHz, CD_2Cl_2): δ 8.23 (d, J = 8.2 Hz, 1H), 7.96-8.16 (m, 7 H), 7.88-7.94 (m, 2 H), 7.82 (dd, J = 8.0, 1.0 Hz, 1 H), 7.54 (dd with satellites, J_{HH} = 6.1, 0.6 Hz, J_{HPt} = 15.2 Hz, 1 H), 7.10-7.36 (m, 9 H), 6.74

(dd with satellites, J_{HH} = 7.5, 1.0 Hz, J_{HPt} = 10.2 Hz, 1 H), 6.47 (dd with satellites, J_{HH} = 7.5, 0.9 Hz, J_{HPt} = 7.2 Hz, 1 H), 6.18 (dd with satellites, J_{HH} = 7.9, 1.0 Hz, J_{HPt} = 15.2 Hz, 1 H). $^{13}C\{^1H\}$ NMR (100.8 MHz, CD_2Cl_2): δ 167.9 (J_{PtC} = 13 Hz, C), 165.8 (J_{PtC} = 11 Hz, C), 164.3 (C), 162.4 (C), 160.9 (C), 149.9 (J_{PtC} = 9 Hz, CH), 148.7 (CH), 146.1 (CH), 143.9 (C), 143.1 (J_{PtC} = 9 Hz, C), 141.9 (CH), 141.7 (CH), 140.8 (CH), 140.0 (J_{PtC} = 14 Hz, C), 133.7 (J_{PtC} = 14 Hz, CH), 133.0 (J_{PtC} = 11 Hz, CH), 132.8 (J_{PtC} = 20, 16 Hz, CH), 130.5 (J_{PtC} = 12 Hz, CH), 127.0 (J_{PtC} = 15 Hz, CH), 126.8 (J_{PtC} = 8 Hz, CH), 126.5 (J_{PtC} = 8 Hz, CH), 126.1 (J_{PtC} = 15 Hz, CH), 125.8 (CH), 125.6 (J_{PtC} = 6 Hz, CH), 125.4 (J_{PtC} = 8 Hz, CH), 125.2 (J_{PtC} = 14 Hz, CH), 122.3 (J_{PtC} = 16, 6 Hz, CH), 122.0 (J_{PtC} = 17 Hz, CH). Elemental analysis Calcd for $C_{34}H_{25}F_3N_3O_{3.5}PtS$: C, 50.06; H, 3.09; N, 5.15; S, 3.93; found: C, 50.04; H, 2.70; N, 5.12; S, 3.78.

Synthesis of *mer*-[Pt(tpy)$_3$]OTf (*mer*-3b). This complex was obtained as a beige solid following the procedure described for *mer*-**3a**, from **2b** (385 mg, 0.639 mmol), AgOTf (365 mg, 1.42 mmol) and Htpy (0.65 mL, 3.80 mmol). Yield: 434 mg, 80%. ^1H NMR (400.9 MHz, CD_2Cl_2): δ 8.13 (d, J = 8.3 Hz, 1H), 7.93-8.07 (m, 6 H), 7.77-7.87 (m, 3 H), 7.70 (d, J = 7.9 Hz, 1 H), 7.46 (ddd with satellites, J_{HH} = 6.2, 1.3, 0.7 Hz, J_{HPt} = 15.2 Hz, 1 H), 7.22 (ddd, J = 7.5, 5.6, 1.3 Hz, 1 H), 7.07-7.19 (m, 5 H), 6.54 (dd with satellites, J_{HH} = 1.2, 0.5 Hz, J_{HPt} = 10.4 Hz, 1 H), 6.23 (dd with satellites, J_{HH} = 1.1, 0,6 Hz, J_{HPt} = 7.3 Hz, 1 H), 5.94 (dd with satellites, J_{HH} = 1.1, 0.6 Hz, J_{HPt} = 15.5 Hz, 1 H), 2.21 (s, 6 H), 2.17 (s, 3 H). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 167.9 (J_{PtC} = 14 Hz, C), 166.0 (C), 164.4 (C), 162.8 (C), 161.4 (C), 149.8 (J_{PtC} = 9 Hz, CH), 148.5 (CH), 145.8 (CH), 143.9 (C), 143.4 (C), 141.9 (C), 141.6 (CH), 141.4 (CH), 141.1 (C), 140.5 (CH), 140.4 (C), 137.4 (J_{PtC} = 13 Hz, C), 134.4 (J_{PtC} = 15 Hz, CH), 131.2 (CH, J_{PtC} = 12 Hz), 127.6 (CH), 127.5 (J_{PtC} = 15 Hz, CH), 126.7 (CH), 126.6 (J_{PtC} = 8 Hz, CH), 126.4 (J_{PtC} = 8 Hz, CH), 125.9 (J_{PtC} = 15 Hz, CH), 124.9 (J_{PtC} = 7 Hz, CH), 124.7 (CH), 124.4 (J_{PtC} = 15 Hz, CH), 121.9 (J_{PtC} = 15 Hz, CH), 121.8 (CH), 121.6 (J_{PtC} = 17 Hz, CH), 22.1 (CH), 22.0 (CH), 21.9 (CH). Elemental analysis Calcd for $C_{37}H_{32}F_3N_3O_4PtS$: C, 51.27; H, 3.72; N, 4.85; S, 3.70; found: C, 51.39; H, 3.91; N, 4.84; S, 3.70.

Synthesis of *mer*-[Pt(dfppy)$_3$]OTf (*mer*-3c). A mixture of complex **2c** (260 mg, 0.402 mmol), AgOTf (228 mg, 0.887 mmol), Hdfppy (0.49 mL, 3.21 mmol) and degassed *o*-dichlorobenzene (20 mL) was placed in a Carius tube and stirred at 140 °C under a N_2 atmosphere for 4 days. After cooling to room temperature, CH_2Cl_2 (30 mL) was added and the suspension was filtered trough Celite. The filtrate was then stirred vigorously with

Na_2CO_3 and then filtered. Partial evaporation of the solution under reduced pressure (20 mL) and addition of pentane (100 mL) led to the precipitation of a beige solid, which was collected by filtration, recrystallized from CH_2Cl_2/Et_2O and vacuum-dried to give *mer*-**3c**·H_2O as a white solid. Yield: 208 mg, 57%. ^{1}H NMR (400.9 MHz, CD_2Cl_2): δ 8.56 (ddd, *J* = 8.4, 1.9, 0.6 Hz, 1H), 8.40-8.50 (m, 2 H), 8.11-8.21 (m, 3 H), 7.95-8.06 (m, 2 H), 7.54 (dd with satellites, *J* = 6.1, 0.8 Hz, J_{HPt} = 15.2 Hz, 1 H), 7.35-7.45 (m, 2 H), 7.29 (m, 1 H), 6.81-6.94 (m, 3 H), 6.32 (dd with satellites, *J* = 6.8, 2.3 Hz, J_{HPt} = 13.0 Hz, 1 H), 5.93 (dd with satellites, *J* = 6.6, 2.1 Hz, J_{HPt} = 9.5 Hz, 1 H), 5.64 (dd with satellites, *J* = 7.8, 2.0 Hz, J_{HPt} = 18.5 Hz, 1 H). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ 167.4-157.2 (several multiplets, C), 150.0 (CH), 149.1 (CH), 146.7 (CH), 143.2 (CH), 142.9 (CH), 142.3 (CH), 126.6-125-4 (m, CH), 116.1 (m, CH), 113.5 (m, CH), 110.8 (m, CH), 103.8 (J_{PtC} = 27 Hz, CH), 103.7 (J_{PtC} = 26 Hz, CH), 102.9 (J_{PtC} = 26 Hz, CH). Elemental analysis Calcd for $C_{34}H_{18}F_9N_3O_3PtS{\cdot}H_2O$: C, 43.78; H, 2.16; N, 4.51; S, 3.44; found: C, 43.74; H, 1.93; N, 4.41; S, 3.47.

Synthesis of *mer*-[Pt(ppz)$_3$]OTf (*mer*-3d). A mixture of complex **2d** (305 mg, 0.55 mmol), Ag(OTf) (315 mg, 1.23 mmol), Hppz (0.44 mL, 3.33 mmol) and degassed 1,2-dichloroethane (40 mL) was placed in a Carius tube and stirred at 90 °C under a N_2 atmosphere for 3 days. After cooling to room temperature, MeCN (10 mL) was added and the suspension was filtered trough Celite. The filtrate was then stirred vigorously with Na_2CO_3 and then filtered. Partial evaporation of the solution under reduced pressure (10 mL) and addition of Et_2O (90 mL) led to the precipitation of a colorless solid, which was collected by filtration and extracted with dichloromethane (60 mL) in a Soxhlet for 24 h. Partial evaporation of the solution under reduced pressure (5 mL) and addition of Et_2O (30 mL) led to the precipitation of a white solid, which was filtered off and vacuum-dried to give *mer*-**3d**·1.5H_2O. Yield: 252 mg, 59%. ^{1}H NMR (400.9 MHz, CD_3CN): δ 8.55-8.50 (m, 3 H), 7.71 (dd, *J* = 8.1, 0.7 Hz, 1 H), 7.66 (dd, *J* = 7.3, 0.7 Hz, 1 H), 7.61 (m, 1 H), 7.36-7.30 (m, 4 H), 7.23-7.03 (m, 5 H), 6.80-6.72 (m, 2 H), 6.70-6.62 (m, 3 H), 6.20 (dd with satellites, *J* = 7.8, 1.1 Hz, J_{HPt} = 17.5 Hz, 1 H). ^{13}C{^{1}H} NMR (100.8 MHz, CD_3CN): δ 144.1 (J_{PtC} = 9 Hz, C), 142.6 (C), 142.1 (J_{PtC} = 9 Hz, CH), 140.9 (J_{PtC} = 23 Hz, CH), 140.3 (C), 139.9 (C), 139.7 (C), 138.7 (J_{PtC} = 18 Hz, CH), 135.7 (J_{PtC} = 12 Hz, CH), 133.6 (J_{PtC} = 8 Hz, CH), 131.8 (J_{PtC} = 10 Hz, CH), 131.4 (CH), 130.6 (J_{PtC} = 11 Hz, CH), 129.7 (J_{PtC} = 10 Hz, CH), 129.5 (CH), 129.4 (J_{PtC} = 22 Hz, CH), 129.3 (J_{PtC} = 14 Hz, CH), 128.5 (CH), 128.3 (CH), 127.7 (CH), 124.9 (C), 115.4 (J_{PtC} = 6 Hz, CH), 115.1 (J_{PtC} = 11 Hz, CH), 114.7 (J_{PtC} = 6 Hz, CH), 111.1 (J_{PtC} = 16 Hz, CH), 110.7 (J_{PtC}

= 14 Hz, CH), 110.6 (J_{PtC} = 5 Hz, CH). Elemental analysis Calcd for $C_{37}H_{33}F_3N_3O_{4.5}PtS$: C, 42.00; H, 3.02; N, 10.50; S, 4.00; found: C, 42.00; H, 2.87; N, 10.33; S, 4.21.

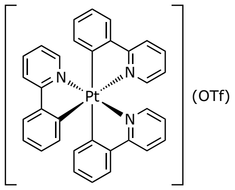
Synthesis of *fac*-[Pt(C^N)$_3$]OTf [C^N = ppy (*fac*-3a), tpy (*fac*-3b), dfppy (*fac*-3c), ppz (*fac*-3d)]. A degassed solution of the corresponding *mer* isomer (0.20–0.50 mmol) in MeCN (350 mL) was irradiated in a UV photoreactor for 2 (**3a–c**) or 1 (**3d**) h. The solvent was evaporated under reduced pressure and the remaining residue was chromatographed on silica gel using a $CHCl_3$/MeOH mixture (4:1) as the eluent. The complexes were isolated as off-white solids after evaporation of the solvents.

***fac*-3a.** Yield: 28%. ^{1}H NMR (400.9 MHz, CD_3CN): δ 8.28 (dt, J = 8.1, 0.9 Hz, 1 H), 8.12 (m, 1 H), 7.95 (m, 1 H), 7.72 (m, 1 H), 7.37-7.28 (m, 2 H), 7.09 (m, 1 H), 6.57 (dd with satellites, J = 7.7, 0.9 Hz, J_{HPt} = 22.8 Hz, 1 H). ^{13}C{^{1}H} NMR (75.5 MHz, CD_3CN): δ 163.3 (C), 148.3 (CH), 142.7 (CH), 142.6 (C), 133.6 (J_{PtC} = 29 Hz, CH), 132.8 (J_{PtC} = 25 Hz, CH), 129.5 (C), 127.5 (CH), 127.4 (J_{PtC} = 16 Hz, CH), 126.7 (J_{PtC} = 5 Hz, CH), 123.0 (J_{PtC} = 7 Hz, CH). Elemental analysis Calcd for $C_{34}H_{24}F_3N_3O_3PtS$: C, 50.62; H, 3.00; N, 5.21; S, 3.97; found: C, 50.41; H, 2.98; N, 5.26; S, 3.85.

***fac*-3b·0.5H$_2$O.** Yield: 27%. ^{1}H NMR (400.9 MHz, CD_3CN): δ 8.21 (ddd, J = 8.3, 0.8, 0.9 Hz, 1 H), 8.08 (m, 1 H), 7.82 (dt, J = 8.0, 2.1 Hz, 1 H), 7.64 (m, 1 H), 7.28 (m, 1 H), 7.13 (m, 1 H), 6.42 (d with satellites, J = 0.9 Hz, J_{HPt} = 23.1 Hz, 1 H), 2,13 (s, 3 H). ^{13}C{^{1}H} NMR (100.8 MHz, CD_3CN): δ 163.4 (J_{PtC} = 24 Hz, C), 148.0 (CH), 144.1 (J_{PtC} = 29 Hz, CH), 142.9 (C), 142.4 (CH), 140.0 (C), 133.4 (J_{PtC} = 25 Hz, CH), 128.1 (CH), 127.2 (J_{PtC} = 16 Hz, CH), 126.0 (J_{PtC} = 5 Hz, CH), 122.5 (J_{PtC} = 7 Hz, CH), 22.1 (CH). Elemental analysis Calcd for $C_{37}H_{31}F_3N_3O_{3.5}PtS$: C, 51.81; H, 3.64; N, 4.90; S, 3.74; found: C, 51.82; H, 3.92; N, 5.09; S, 3.60.

***fac*-3c.** Yield: 26%. ^{1}H NMR (400.9 MHz, CD_3CN): δ 8.50 (m, 1 H), 8.19 (m, 1 H), 7.71 (m, 1 H), 7.41 (m, 1 H), 7.00 (ddd, J = 12.7, 9.0, 2.4 Hz, 1 H), 6.22 (ddd with satellites, J = 8.1, 2.4, 0.8 Hz, J_{HPt} = 26.3 Hz, 1 H). ^{13}C{^{1}H} NMR (100.8 MHz, CD_3CN): δ 157.2-166.1 (several multiplets, C), 148.8 (CH), 143.8 (d, J_{CF} = 8 Hz, C), 143.6 (CH), 142.4 (CH), 127.1-126.7 (m, CH), 116.2 (m, CH), 104.2 (J_{PtC} = 27 Hz, CH). Elemental analysis Calcd for $C_{34}H_{18}F_9N_3O_3PtS$: C, 44.65; H, 1.98; N, 4.59; S, 3.51; found: C, 44.37; H, 2.16; N, 4.44; S, 3.43.

***fac*-3d·H_2O.** Yield: 43%. ^1H NMR (400.9 MHz, CD_3CN): δ 8.51 (m, 1 H), 7.62 (ddt, J = 8.1, 3.8, 1.1 Hz, 1 H), 7.41 (m, 1 H), 7.35 (m, 1H), 7.01 (ttd, J = 7.6, 4.5, 1.3 Hz, 1 H), 6.73 (m, 1 H), 6.55 (dd with satellites, J = 7.7, 1.3 Hz, J_{HPt} = 24.5 Hz, 1 H). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_3CN): δ 141.2 (J_{PtC} = 8 Hz, CH), 140.5 (C), 133.5 (J_{PtC} = 18 Hz, CH), 129.4 (J_{PtC} = 29 Hz, CH), 128.4 (J_{PtC} = 20 Hz, CH), 132.3 (C), 115.7 (J_{PtC} = 11 Hz, CH), 110.5 (CH). Elemental analysis Calcd for $C_{37}H_{32}F_3N_3O_4PtS$: C, 42.48; H, 2.93; N, 10.62; S, 4.05; found: C, 42.49; H, 2.87; N, 10.60; S, 3.90.



mer-3a

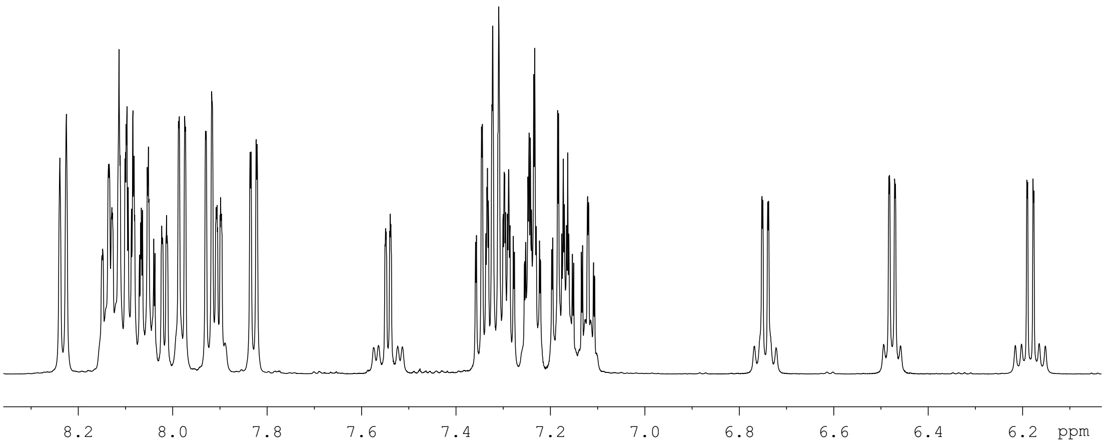


Figure S1. ^{1}H NMR spectrum of *mer*-**3a** (600.1 MHz, CD_2Cl_2).

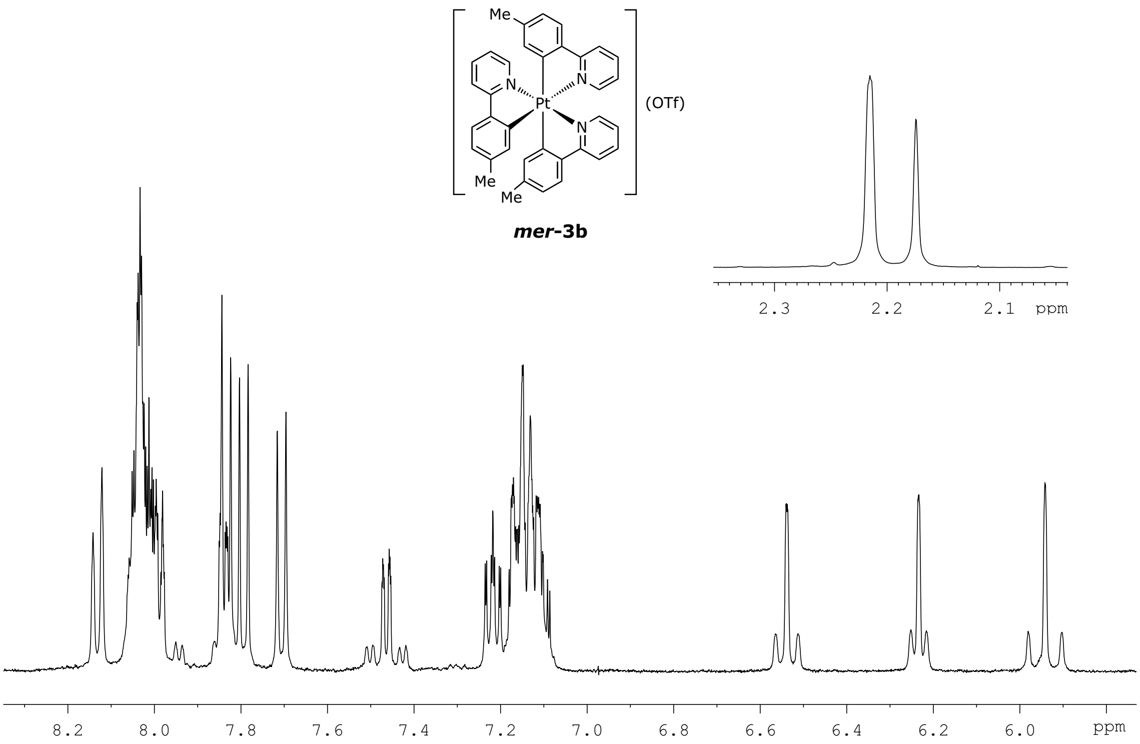
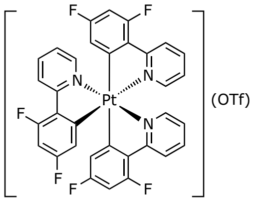


Figure S2. ^{1}H NMR spectrum of *mer*-**3b** (400.9 MHz, CD_2Cl_2).



***mer*-3c**

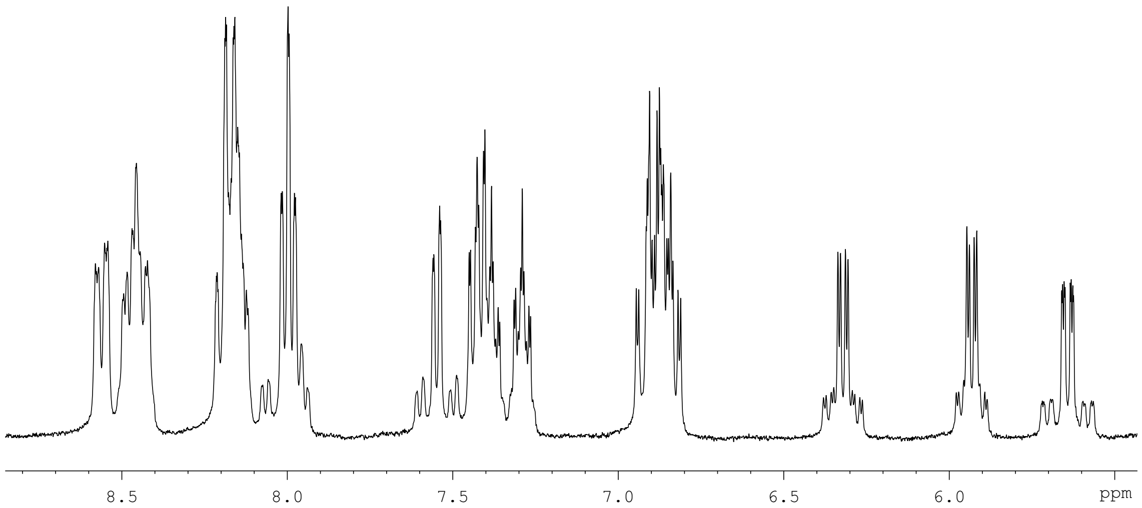
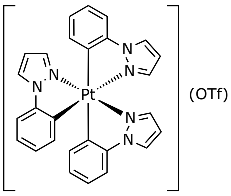


Figure S3. ^{1}H NMR spectrum of *mer*-**3c** (300.1 MHz, CD_2Cl_2).



***mer*-3d**

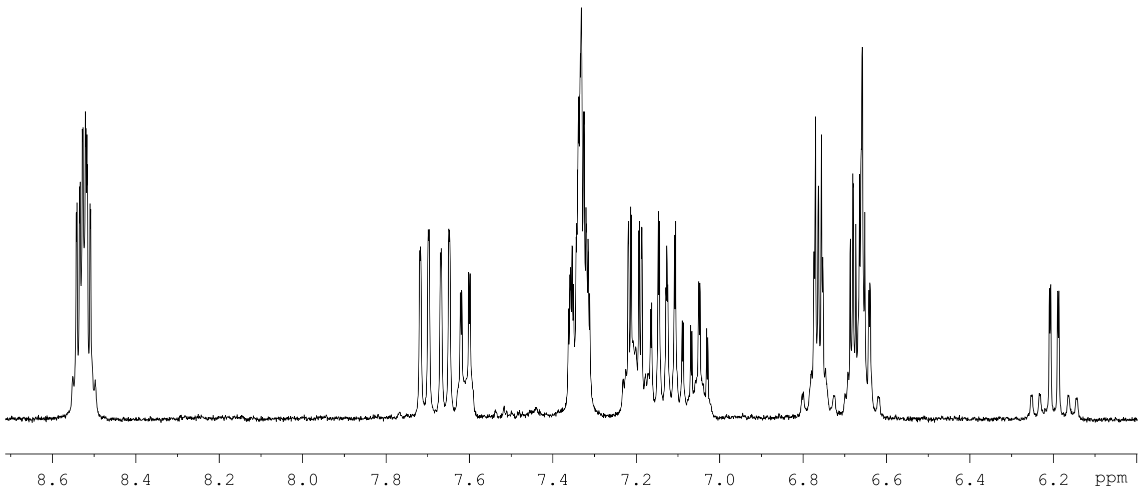
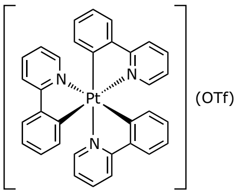


Figure S4. ^{1}H NMR spectrum of *mer*-**3d** (400.9 MHz, CD_3CN).



***fac*-3a**

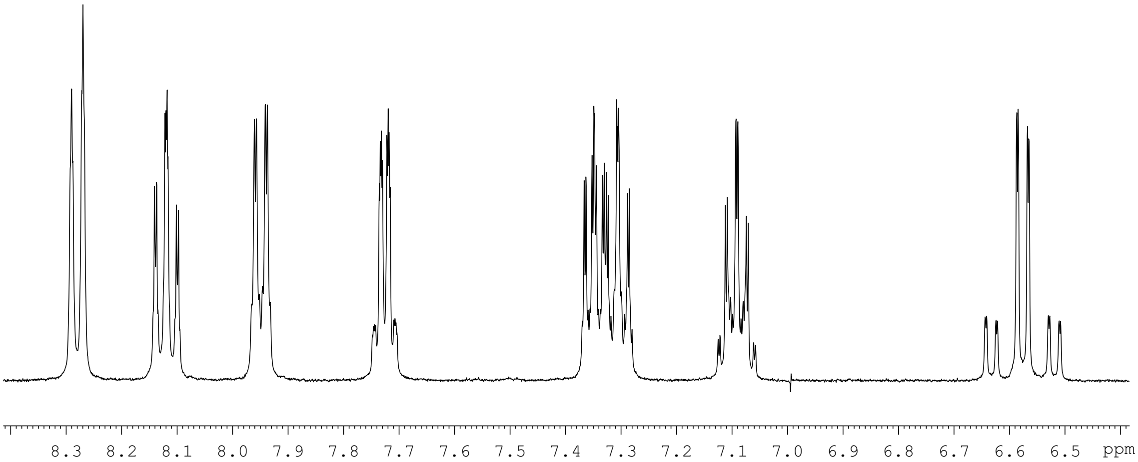
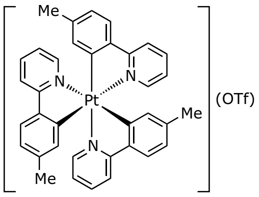
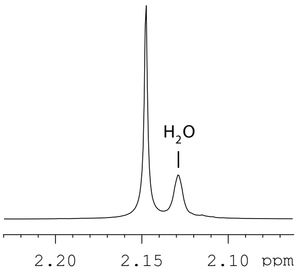


Figure S5. ^{1}H NMR spectrum of *fac*-**3a** (400.9 MHz, CD_3CN).



***fac*-3b**



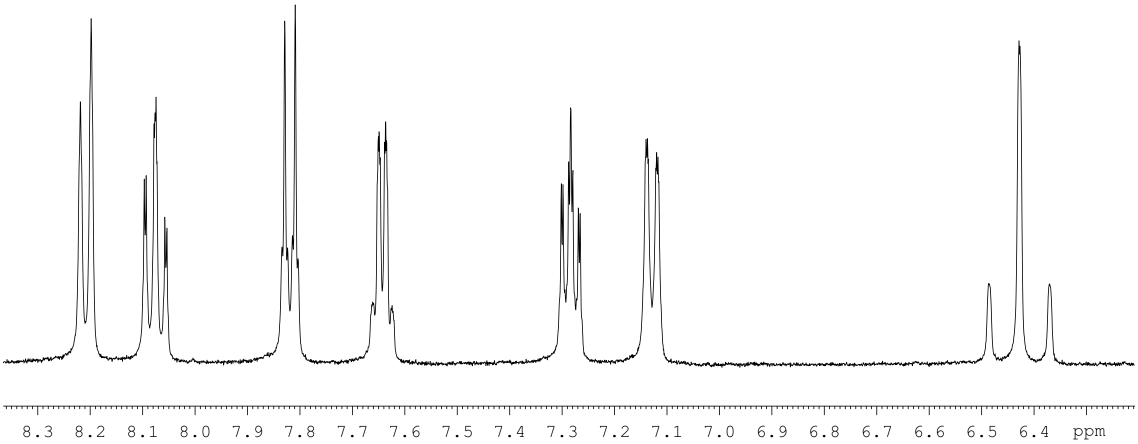
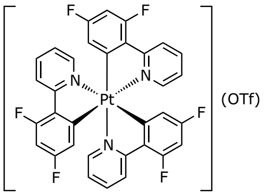


Figure S6. ^{1}H NMR spectrum of *fac*-**3b** (400.9 MHz, CD_3CN).



***fac*-3c**

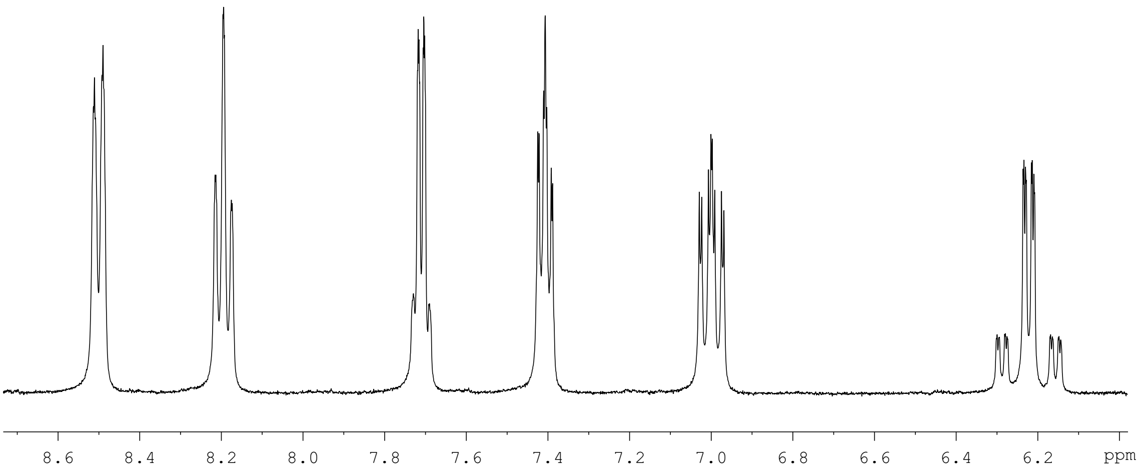
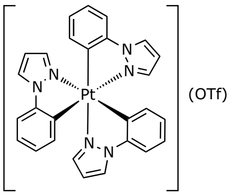


Figure S7. ^{1}H NMR spectrum of *fac*-**3c** (400.9 MHz, CD_3CN).



***fac*-3d**

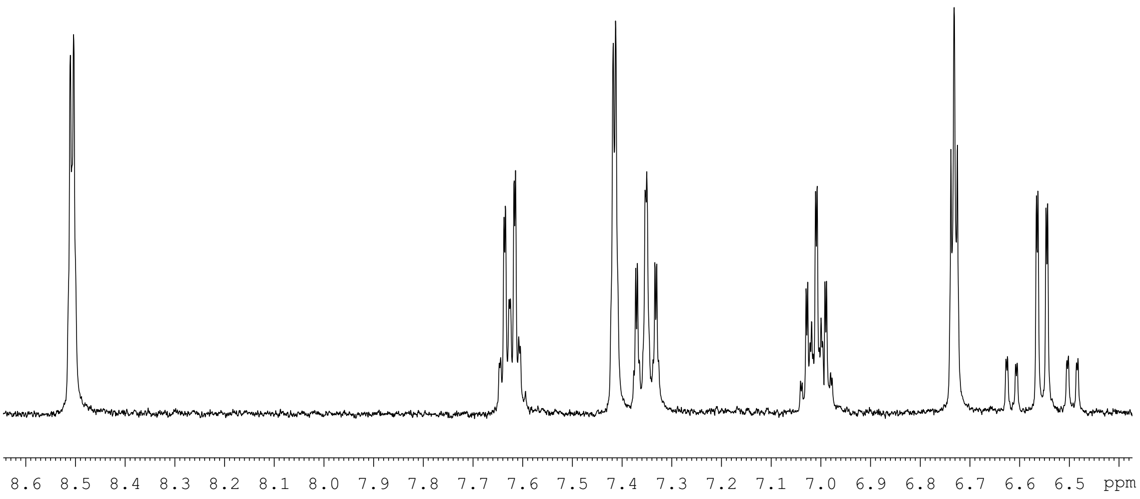


Figure S8. ^{1}H NMR spectrum of *fac*-**3d** (400.9 MHz, CD_3CN).

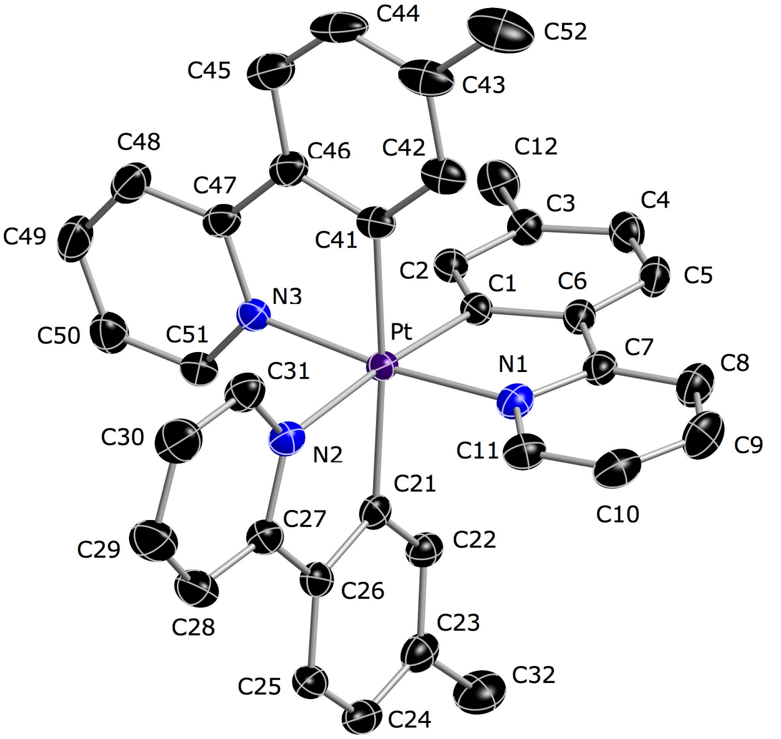


Table S2. Selected bond distances (Å) and angles (deg) for the cation of compound *mer*-**3b**.

Pt-C(1)	2.005(2)	C(1)-Pt-N(1)	81.46(10)
Pt-N(1)	2.027(2)	N(3)-Pt-C(41)	80.68(10)
Pt-N(3)	2.033(2)	C(21)-Pt-N(2)	78.98(10)
Pt-C(41)	2.064(3)		
Pt-C(21)	2.081(3)		
Pt-N(2)	2.138(2)		

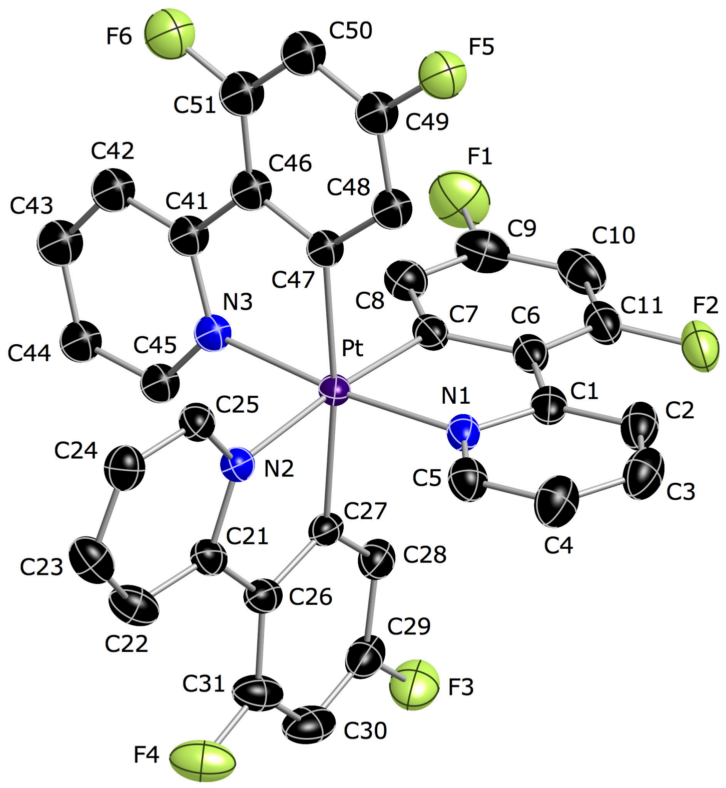
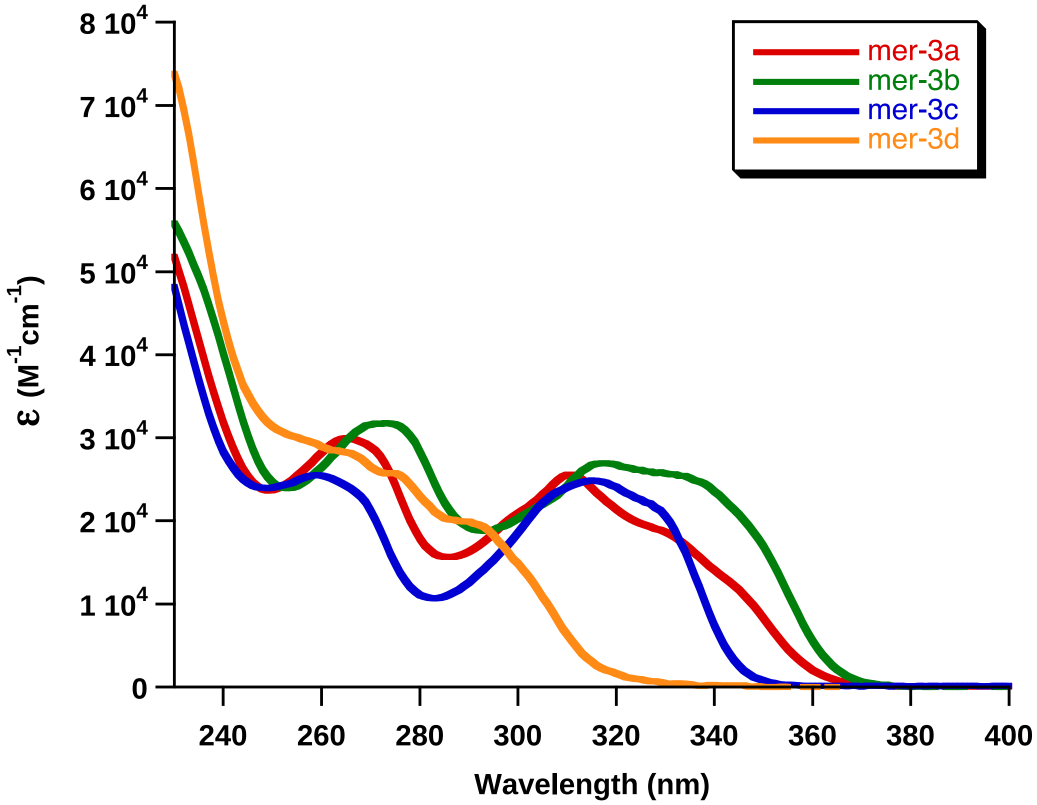


Table S3. Selected bond distances (Å) and angles (deg) for the cation of compound *mer*-**3c**.

Pt-C(7)	2.002(4)	C(7)-Pt-N(1)	81.09(17)
Pt-N(1)	2.026(4)	C(47)-Pt-N(3)	78.4(5)
Pt-C(47)	2.058(11)	C(27)-Pt-N(2)	79.14(16)
Pt-N(3)	2.072(11)		
Pt-C(27)	2.082(4)		
Pt-N(2)	2.116(4)		



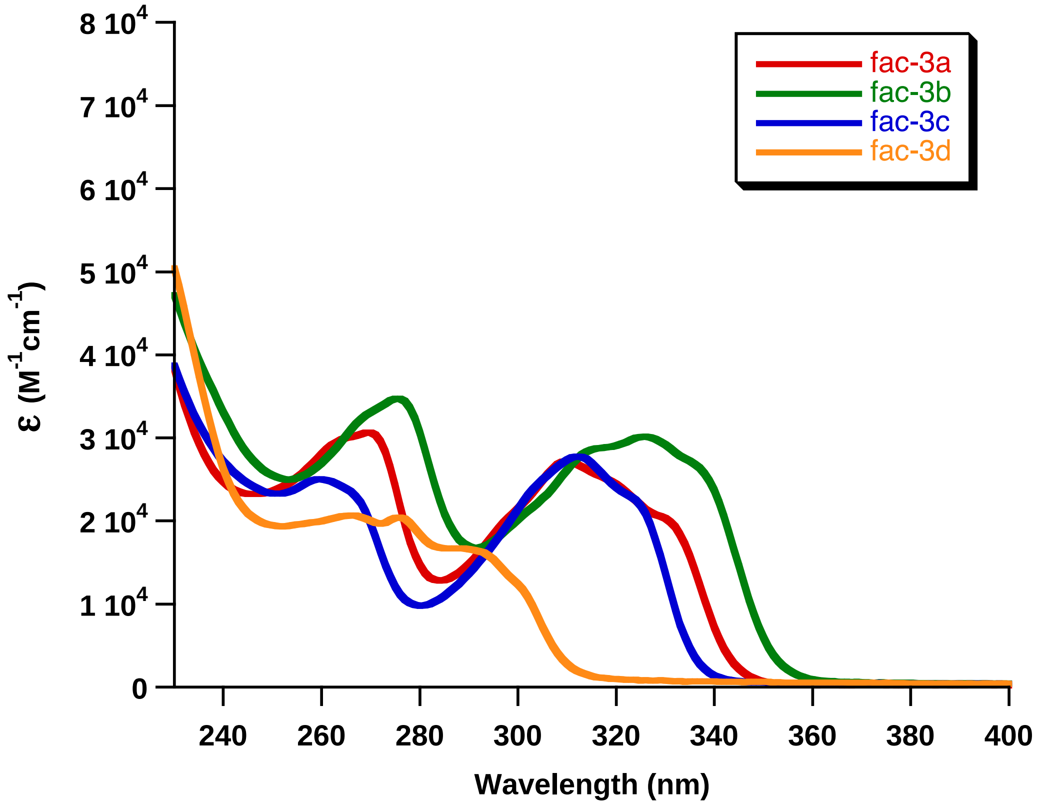


Figure S9. Absorption spectra of *mer*/*fac*-**3a–d** in CH_2Cl_2 solution (*ca.* 5 × 10^{-5} M) at 298 K.

Table S4. Electronic absorption data for compounds *mer/fac*-**3a–d** in CH_2Cl_2 solution (*ca.* 5 × 10^{-5} M) at 298 K

compd	**λ_{max}/nm ($\varepsilon \times 10^{-3}$/$M^{-1}$ cm^{-1})**
mer-**3a**	267 (29.7), 310 (25.6), 330 (18.6), 342 (13.2, sh)
fac-**3a**	270 (30.6), 309 (27.2), 320 (24.4), 330 (20.3, sh)
mer-**3b**	272 (31.7), 317 (26.9), 336 (24.9), 348 (18.6, sh)
fac-**3b**	276 (34.7), 316 (28.7), 326 (30.2), 336 (26.8, sh)
mer-**3c**	260 (25.4), 314 (24.7), 327 (22.0, sh)
fac-**3c**	260 (25.0), 312 (27.7), 323 (22.9, sh)
mer-**3d**	266 (28.1), 275 (25.8), 292 (19.5)
fac-**3d**	266 (20.6), 275 (20.4), 293 (16.2)

Table S5. Emission Data for Compounds *mer*-**3a–d** in PrCN glasses at 77 K and in CH_2Cl_2 solution at 298 K

compd	**emission at 77 K**		**emission at 298 K**[a]
	λ_{em}/nm[b]	**τ/µs**	**λ_{em}/nm**[b]
mer-**3a**	*446*, 479, 506	362	447, *477*, 505(sh)
mer-**3b**	*452*, 485, 512	404	454, *484*, 513(sh)
mer-**3c**	*435*, 466, 490	511	440, *467*, 495(sh)
mer-**3d**	399, *416*, 441, 465	533, 61.6	-

[a] See comments on page 22. [b]The most intense peak is italicized.

Table S6. Emission data for compounds *fac*-**3a–d** in PrCN glasses at 77 K and in CH_2Cl_2 solution at 298 K

compd	**emission at 77 K**		**emission at 298 K**	
	λ_{em} / nm[a]	**τ / µs**	**λ_{em} / nm**[a]	**τ / µs**
fac-**3a**	*443*, 475, 500	412	*446*, 477, 504(sh)	215
fac-**3b**	*449*, 482, 508	482	*454*, 484, 511(sh)	248
fac-**3c**	*432*, 463, 487	635	436, *465*, 493(sh)	319
fac-**3d**	*393*, 418, 437	1040	402, *424*, 445(sh)	3.44

[a]The most intense peak is italicized.

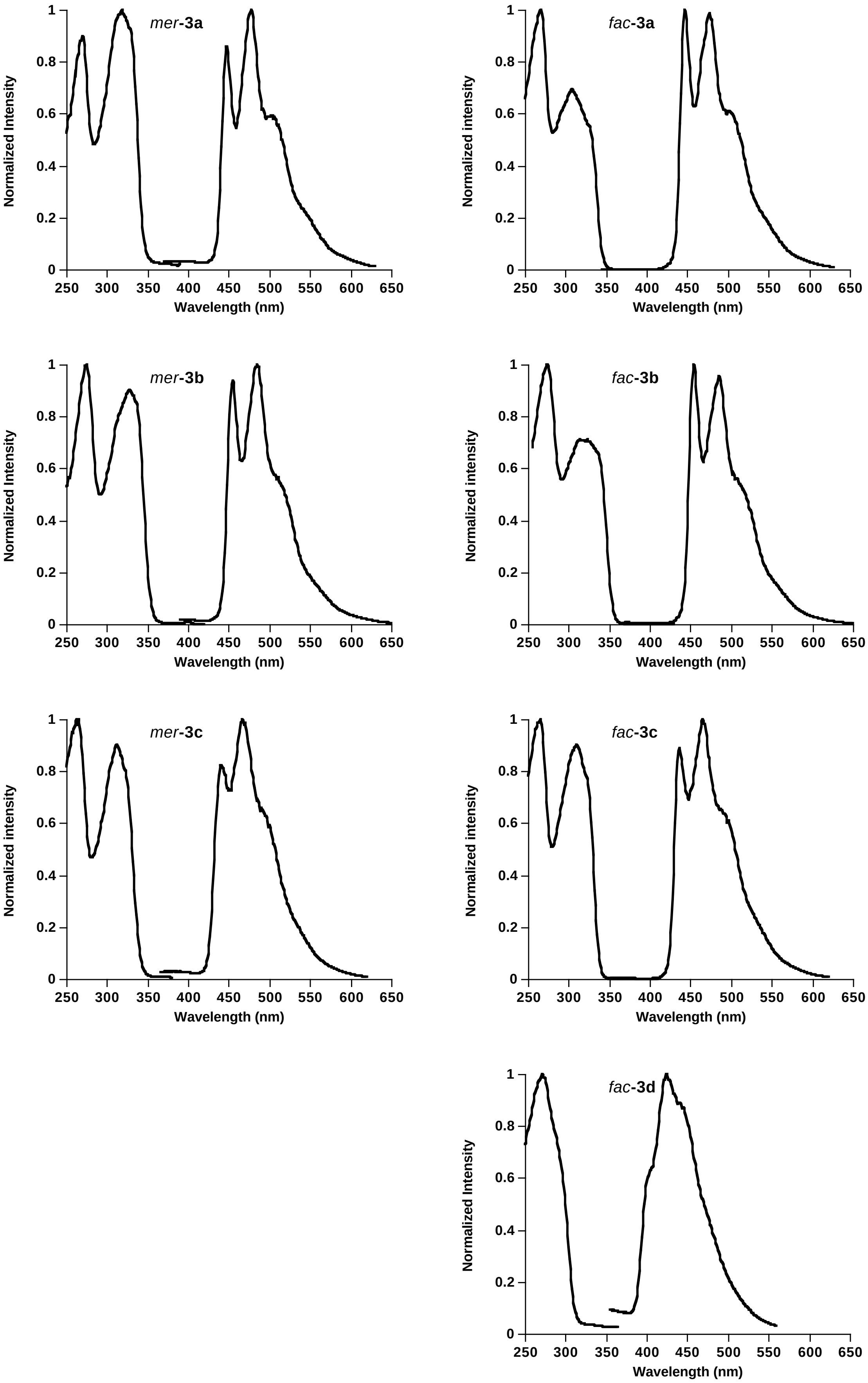


Figure S10. Excitation and emission spectra of *mer*-**3a–c** and *fac*-**3a–d** at 298 K in CH_2Cl_2.

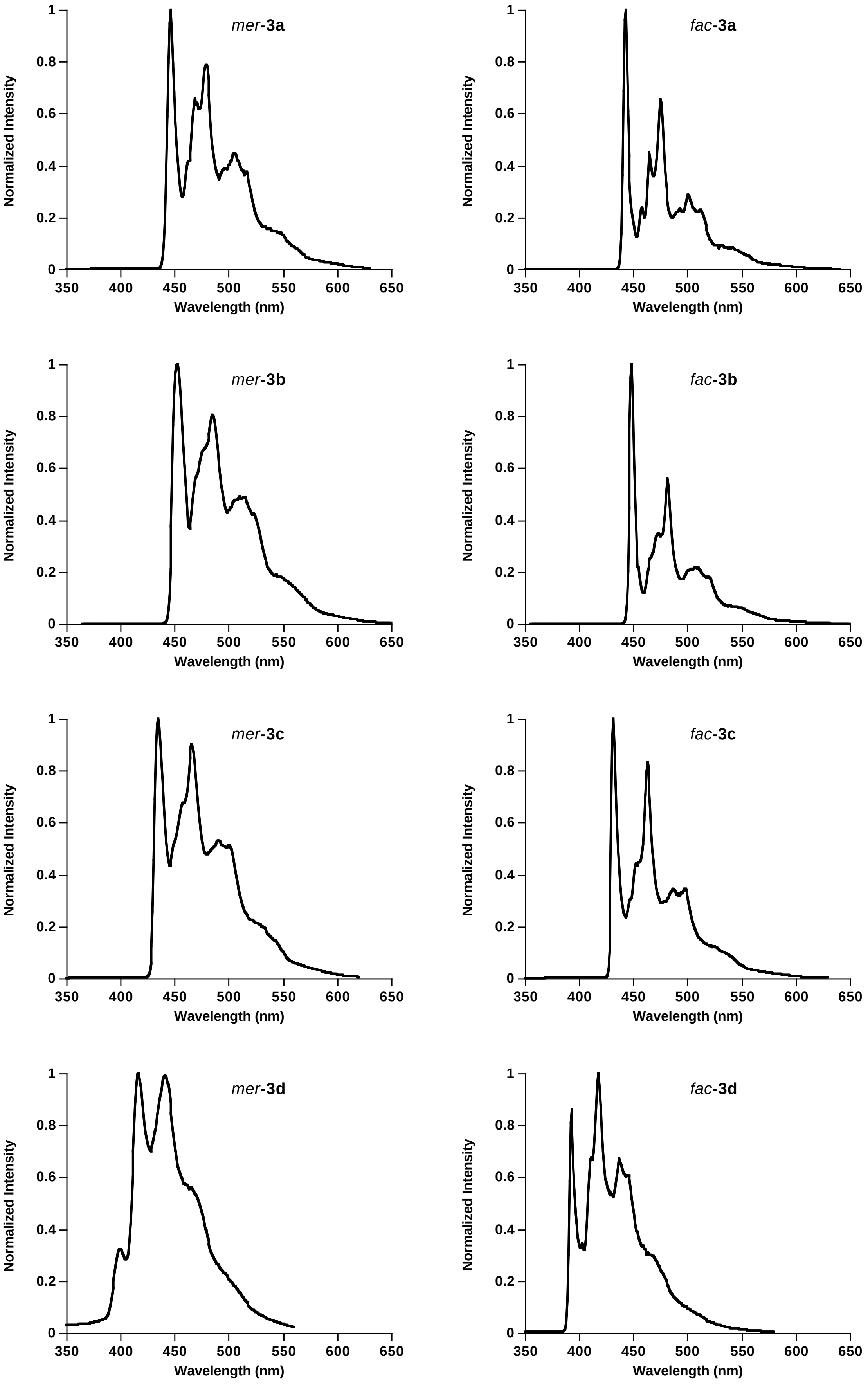


Figure S11. Emission spectra of *mer*- and *fac*-**3a–d** at 77 K in PrCN.

Comments on the emission data of the meridional isomers. We have measured the emission spectra of a solution of *mer*-**3a** in deaerated CH_2Cl_2 (*ca.* 5 × 10^{-5} M) at 298 K after different times of continued excitation at 330 nm, using the xenon lamp of our spectrofluorometer as the excitation source and a slit width of 2 nm. The results are shown in Figure S12. After only 5 min of irradiation, the emission intensity doubled, which can only be attributed to partial isomerization to the much more intensely emissive *fac* isomer.

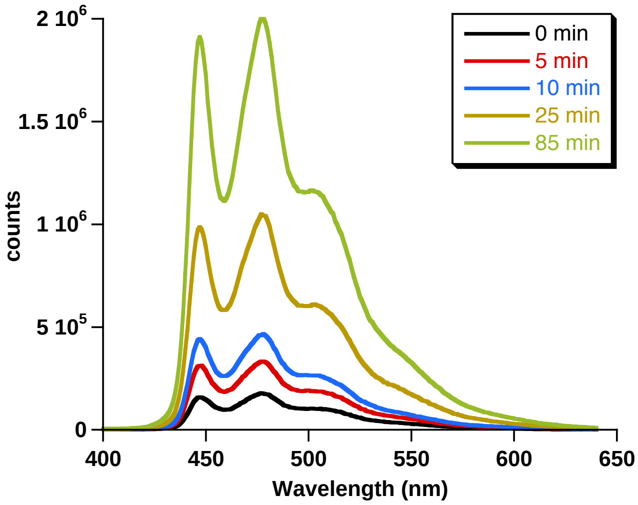


Figure S12. Emission spectra of a solution of *mer*-**3a** in deaerated CH_2Cl_2 (*ca.* 5 × 10^{-5} M) at 298 K after different times of continued excitation at 330 nm.

In addition, the excitation spectrum of a CH_2Cl_2 solution of *mer*-**3a** at 298 K in is more similar to the absorption spectrum of *fac*-**3a** than to that of *mer*-**3a**, suggesting that most of the emission arises from small amounts of the *fac* isomer (Figure S13).

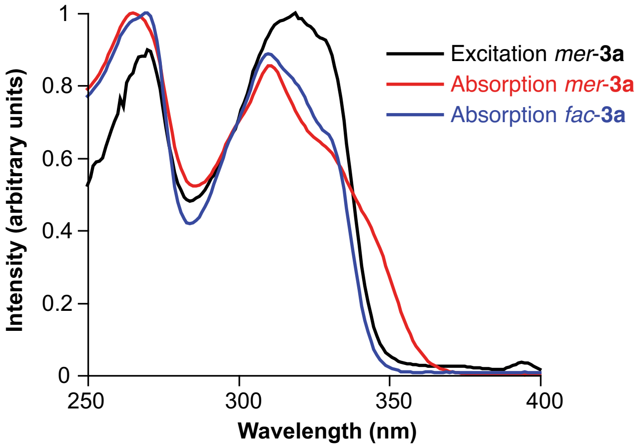


Figure S13. Comparison of the excitation spectrum of a solution of *mer*-**3a** with the absorption spectra of *mer*- and *fac*-**3a** in CH_2Cl_2 (*ca.* 5 × 10^{-5} M) at 298 K.

Quantum yield measurements for CH_2Cl_2 solutions of *mer*-**3a-d** at 298 K gave values below 0.01, but in view of the facts mentioned above, we consider that the data are not reliable. For the same reasons, the measured lifetimes cannot be ascribed to a single isomer.

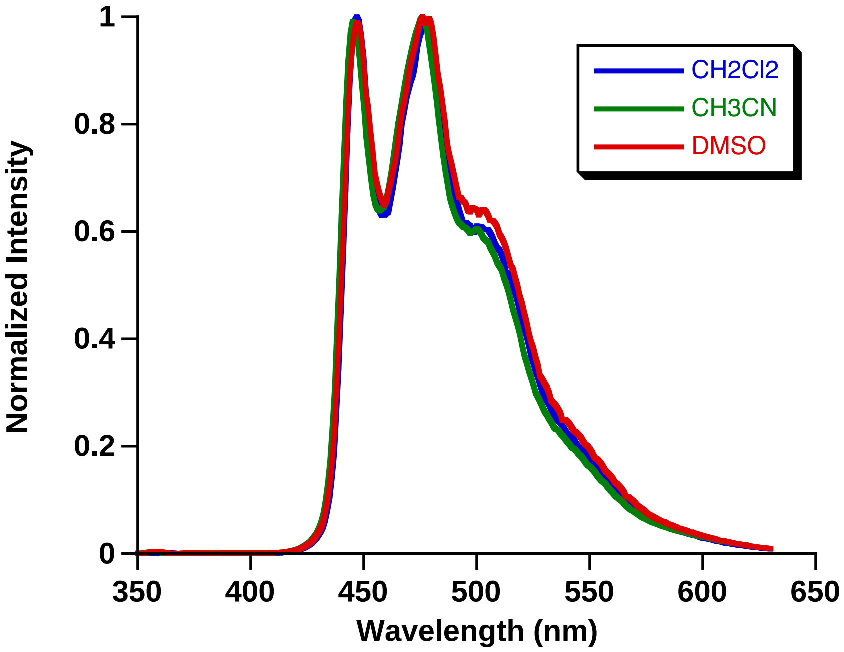


Figure S14. Emission spectra of *fac*-**3a** in deaerated CH_2Cl_2, MeCN and DMSO at 298 K.

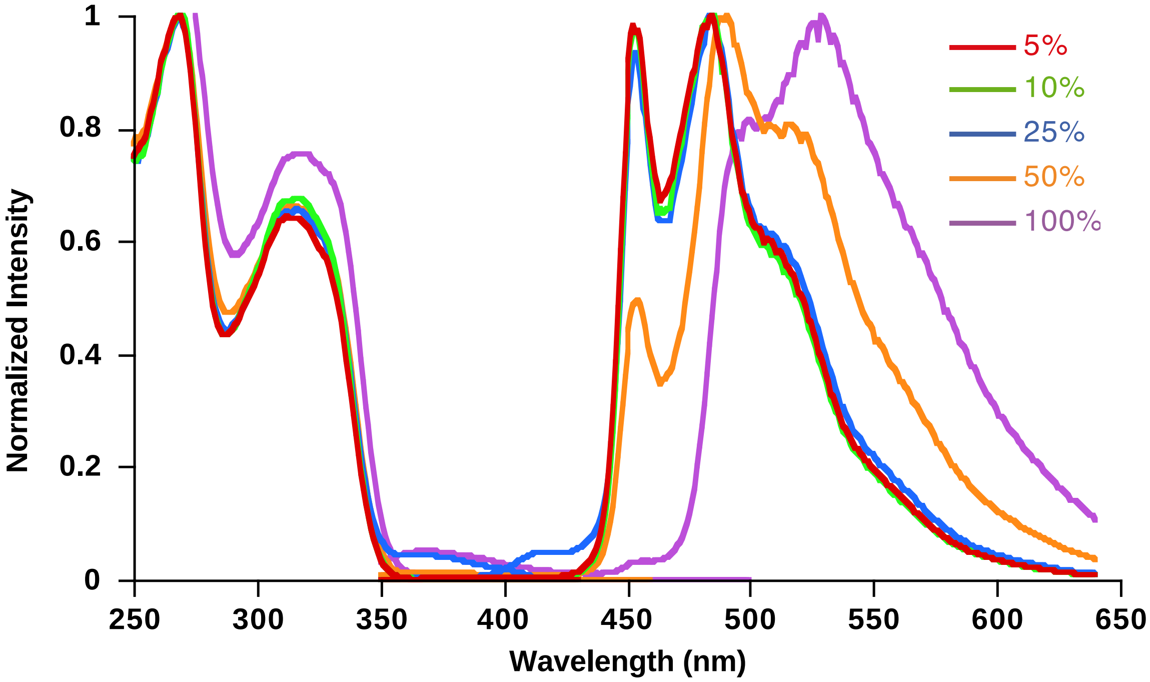


Figure S15. Excitation (left) and emission (right) spectra of *fac*-**3b** in PMMA thin films at variable concentrations (wt%) and as neat film.

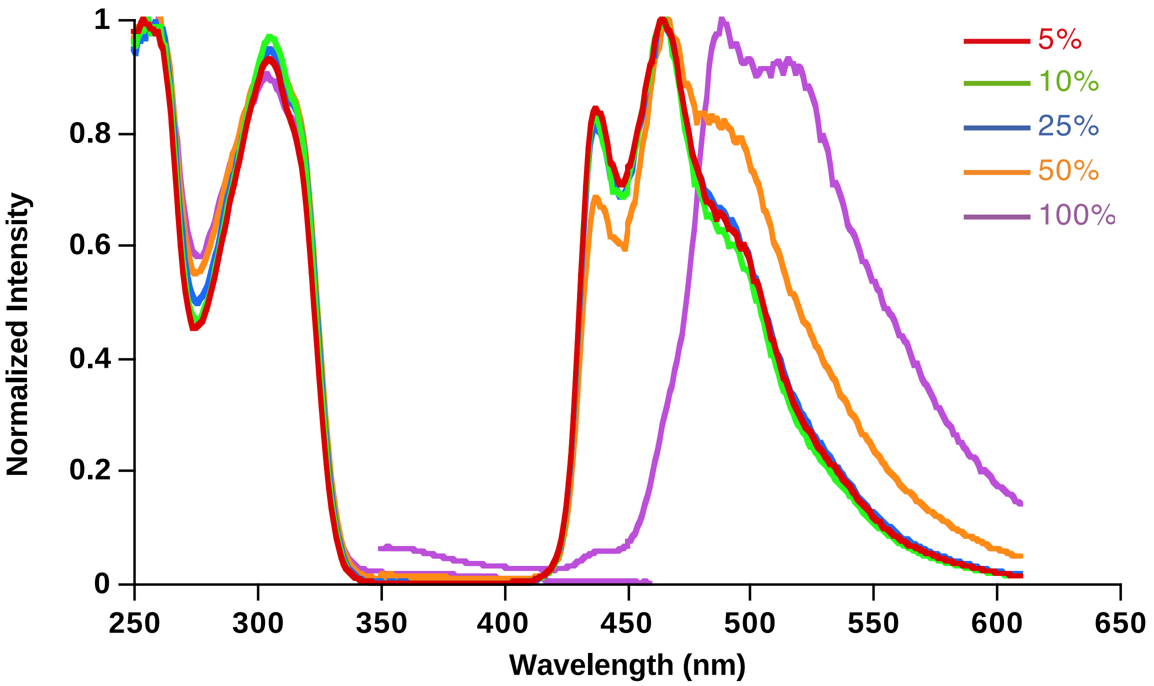


Figure S16. Excitation (left) and emission (right) spectra of *fac*-**3c** in PMMA thin films at variable concentrations (wt%) and as neat film.

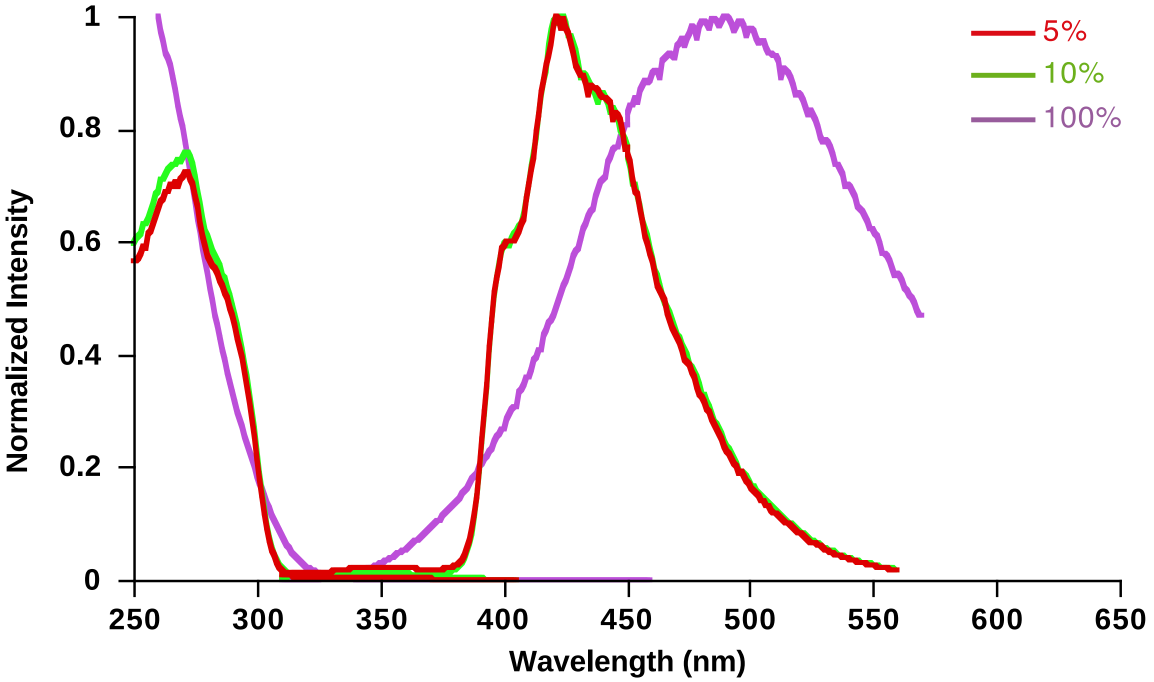


Figure S17. Excitation (left) and emission (right) spectra of *fac*-**3d** in PMMA thin films at variable concentrations (wt%) and as neat film. Concentrations higher than 10% could not be achieved because of the low solubility of this complex.

Table S7. Quantum Yields of *fac*-**3a–d** in PMMA thin films at different concentrations and as neat films under N_2 at 298 K.

Compound	**Concentration (wt%)**	**$\Phi(N_2)$**
***fac*-3a**	5%	0.46
	10%	0.46
	25%	0.31
	50%	0.05
	100% (neat film)	0.01
***fac*-3b**	5%	0.61
	10%	0.54
	25%	0.41
	50%	0.09
	100% (neat film)	0.03
***fac*-3c**	5%	0.49
	10%	0.47
	25%	0.32
	50%	0.08
	100% (neat film)	0.02
***fac*-3d**	5%	0.16
	10%	0.13
	100% (neat film)	<0.01

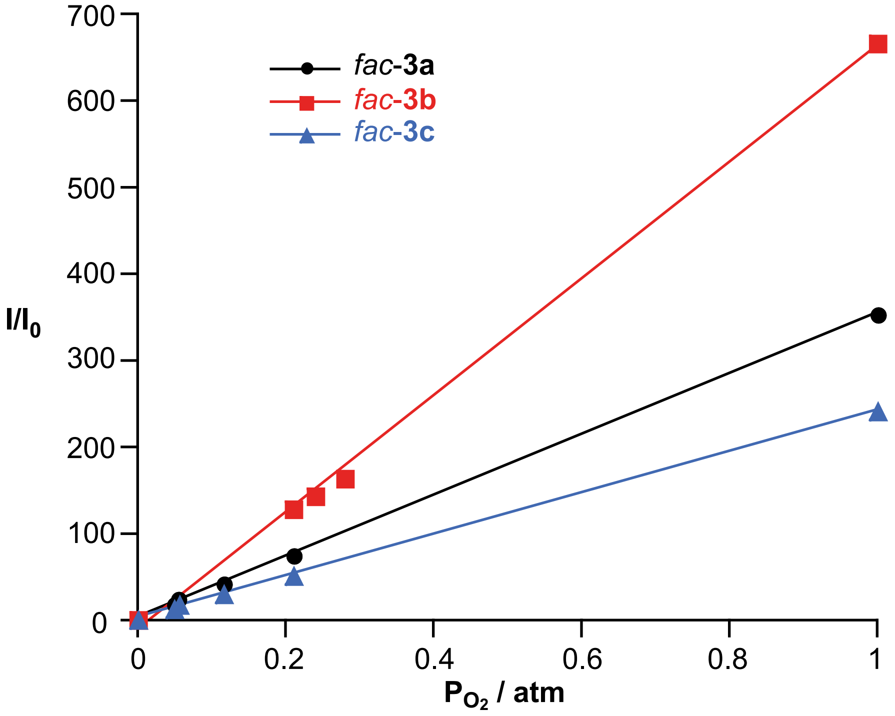


Figure S18. Stern-Volmer plots for the phosphorescence quenching of *fac*-**3a-c** by molecular oxygen in CH_2Cl_2 solution at 298 K.

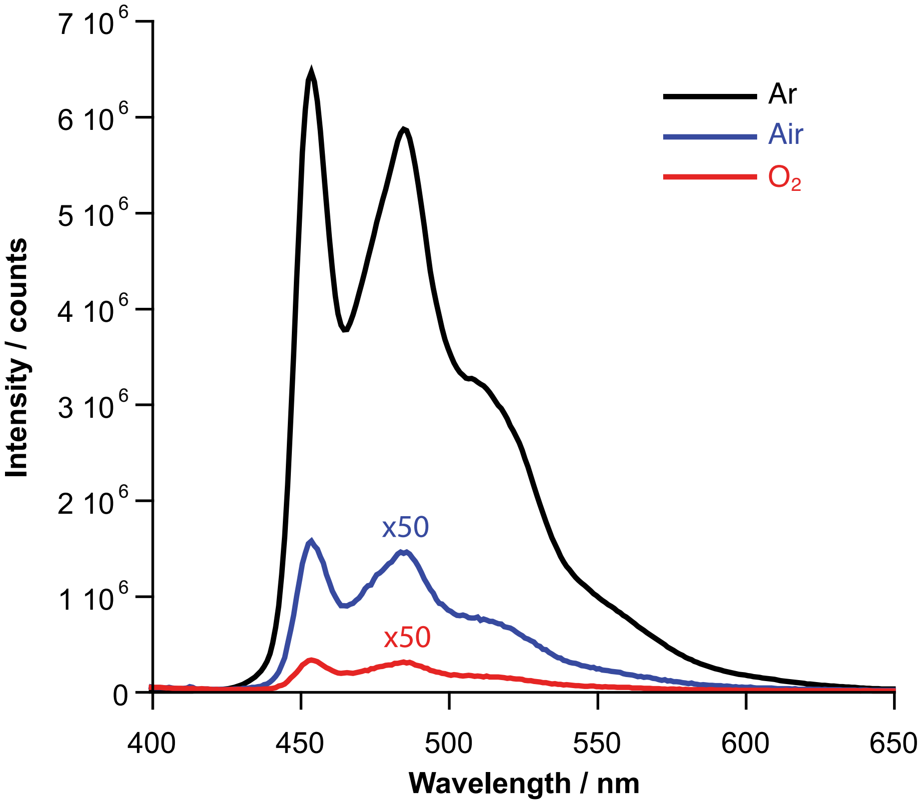


Figure S19. Comparison of the emission intensities of *fac*-**3b** in CH_2Cl_2 solutions saturated with argon, air or oxygen at 298 K.

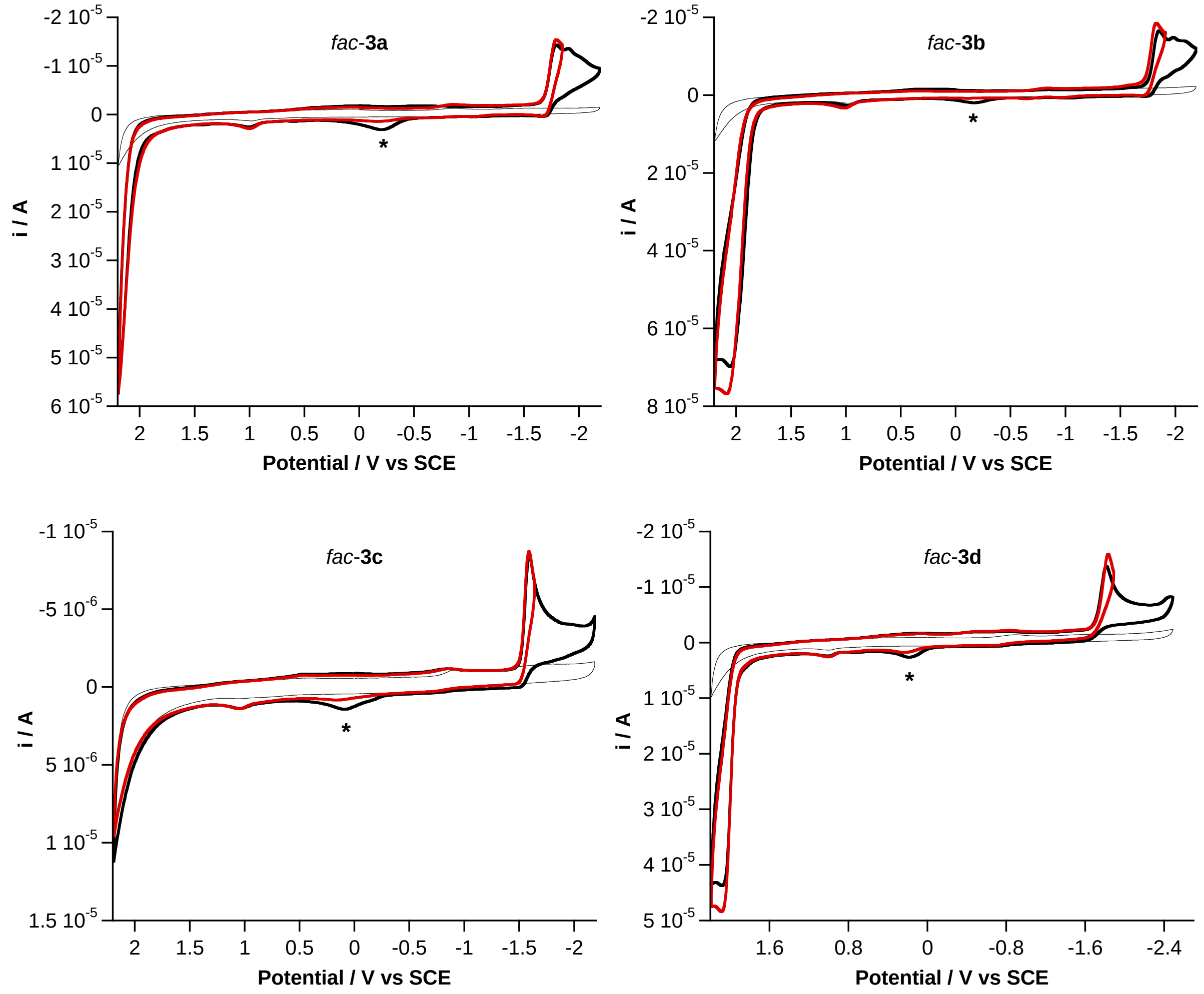


Figure S20. Cyclic voltammograms of *fac*-**3a-d** in MeCN at 100 mV s^{-1}. The thin line is the solvent blank.

Further comments on the electrochemical characterization. All redox processes remained irreversible at high scan rates (up to 5 V s^{-1}). The intensity of the oxidation wave observed between –0.20 and –0.15 V (marked with an asterisk in Figure S20) decreases if the limit of the scanned cathodic region is set immediately after the first reduction peak, which confirms that it is the return wave of the irreversible reduction processes.

HOMO/LUMO energy estimations for *fac*-3a–d from electrochemical data. When possible, the HOMO/LUMO energies were estimated from the onset values of the oxidation and reduction waves referenced against Fc$^+$/Fc (0.40 V vs SCE in MeCN), using a formal potential of 5.1 eV for the Fc$^+$/Fc couple in the Fermi scale:[8]

$$\mathrm{E_{HOMO}} = -(E_{onset,\ ox} + 5.1 - 0.4)\ \mathrm{eV};\ \mathrm{E_{LUMO}} = -(E_{onset,\ red} + 5.1 - 0.4)\ \mathrm{eV}$$

Table S8. HOMO/LUMO energy estimations for *fac*-**3a–d**.

Complex	**$E_{onset,\ ox}$/V^a**	**$E_{onset,\ red}$/V^a**	**$\mathrm{E_{HOMO}}$ /eV**	**$\mathrm{E_{LUMO}}$/eV**	**$\Delta\mathrm{E_{HOMO\text{-}LUMO}}$/eV**
fac-**3a**	–^{b}	–1.69	–	–2.71	–
fac-**3b**	1.83	–1.73	–6.53	–2.97	3.56
fac-**3c**	–^{b}	–1.51	–	–3.19	–
fac-**3d**	1.93	–1.71	–6.63	–2.99	3.64

[a] vs SCE. [b] Oxidation outside solvent window.

For *fac*-**3b**, the estimated HOMO-LUMO energy gap of 3.56 eV (348 nm) approximately matches the lowest-energy electronic absorption (3.69 eV, 336 nm), which is consistent with ligand-localized frontier orbitals. In contrast, for *fac*-**3d**, the estimated HOMO-LUMO gap of 3.64 eV (340 nm) is significantly lower than the observed lowest-energy absorption (4.19 eV, 293 nm); since the HOMO energy is similar to that found for *fac*-**3b**, this suggests that the LUMO is not localized on the ligand.

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