Supplementary Information (SI) for New Journal of Chemistry.

Supporting Information

Dinuclear platinum(II) complexes featuring rigidly linked Pt(*NCN*)X units: the effect of X = SCN^- in favouring low-energy, excimer-like luminescence

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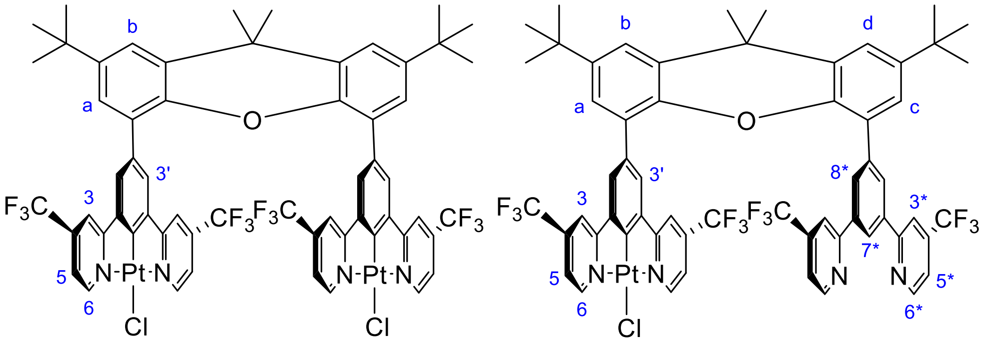
1. Synthesis and characterisation

General

Commercial reagents were used as supplied without further purification. Reactions requiring an inert atmosphere were carried out using Schlenk-line techniques under a nitrogen atmosphere. Thin layer chromatography was performed on F254 silica plates and visualized by UV irradiation at 254 and 365 nm. NMR spectra were recorded on a Bruker Avance-400 spectrometer, a Varian VNMRS-600, or a Varian VNMRS-700. Two-dimensional NMR experiments, including homonuclear correlation spectroscopy (COSY), heteronuclear multiple bond correlation spectroscopy (HMBC) and heteronuclear single quantum coherence spectroscopy (HSQC), were used to facilitate the assignment of signals. Chemical shift values (δ) are reported in parts per million (ppm), coupling constants (J) are reported in Hertz (Hz), and the spectra are referenced to residual solvent peaks: $CDCl_3$ = 7.26 ppm (^{1}H), 77.16 (^{13}C); CD_2Cl_2 = 5.32 ppm (^{1}H), 53.84 (^{13}C). Electrospray ionisation mass spectra (ESI) were recorded using a Waters Acquity TQD Tandem Quadrupole mass spectrometer with either acetonitrile or methanol as the carrier solvent. Atmospheric pressure solids analysis probe (ASAP) ionization mass spectra were obtained using a LCT Premier XE mass spectrometer and an Acquity UPLC from Waters Ltd at 350°C. High-resolution mass spectra were obtained using a Quantum time-of-flight (QTof) mass spectrometer.

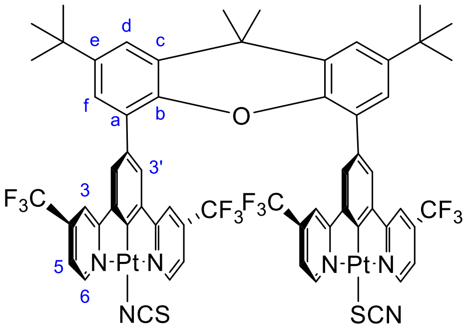
$L^{CF3}(Pt–Cl)_2$ and $HL^{CF3}(Pt–Cl)$



The preparation of the dinuclear complex $L^{CF3}(Pt–Cl)_2$ was carried out by a procedure similar to that previously reported,[1] but in the present case, the mononuclear complex $HL^{CF3}(Pt–Cl)$ was also formed in a significant proportion and isolated by column chromatography. Potassium tetrachloroplatinate(II) (98 mg, 0.237 mmol) was added to a solution of H_2L^{CF3} (50 mg, 0.047 mmol, synthesised as described in our earlier work[1]) in acetic acid (10 mL) in a Schlenk flask and the solution was degassed using three freeze-pump-thaw cycles. The reaction mixture was then heated at reflux (118°C) for 60 h under nitrogen before cooling to room temperature. The crude solid was purified by preparative column chromatography on silica (DCM: MeOH gradient) to yield a mixture of the dinuclear L^{CF3}(Pt–Cl)$_2$ as a yellow-orange solid (6.5 mg, 9%) and the mononuclear product HL^{CF3}Pt–Cl as a yellow solid (23 mg, 38%). Yields for dinuclear complexes of this type in our earlier work were also typically lower than 30%, possibly due to the lower solubility of the mononuclear intermediate and longer reaction times being required, giving more scope for side-reactions to compete.

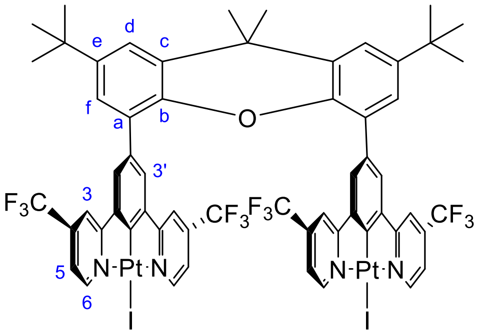
L^{CF3}(Pt–Cl)$_2$: δ_H (700 MHz, CDCl$_3$) 9.53 (4 H, d, J 5.8, {^{195}Pt–^{1}H = 32}, H^{6}), 7.54 (2 H, d, J 2.4, H^{d} or H^{f}), 7.48 (4 H, s, H$^{2'}$), 7.41 (4 H, s, H^{3}), 7.38 (4 H, dd, J 5.8, 1.9, H^{5}), 7.22 (2 H, d, J 2.3, H^{d} or H^{f}), 1.83 (6 H, s, H^{Me}), 1.41 (18 H, s, H$^{t\text{-Bu}}$); δ_C (176 MHz, CDCl$_3$) 167.9 (C^{2}), 161.8 (C$^{4'}$), 154.0 (C^{6}), 146.2 (C^{e}), 144.1 (C^{b}), 139.3 (C$^{1'}$), 129.3 (C^{c}), 128.1 (C^{a}), 126.7 (C$^{2'}$), 125.8 (C^{d} or C^{f}), 123.3 (C^{d} or C^{f}), 119.6 (C^{5}), 115.1 (C^{3}), 34.7 (C^{g}), 34.1 (C$^{t\text{-Bu}}$), 33.7 (C^{Me}); δ_F (376 MHz, CDCl$_3$) –65.5; MS ESI (ES^{+}) *m/z* 1555.7 [M+MeCN]$^{+}$; HRMS ASAP (AP^{+}) *m/z* 1477.8969 [M-Cl]$^{+}$, calc. for [$C_{59}H_{44}ClF_{12}N_4OPt_2$] 1478.2312; Anal. Calc. for $C_{59}H_{44}Cl_2F_{12}N_4OPt_2$: C, 46.8; H, 2.93; N, 3.50 %. Found: C, 46.90; H, 3.10; N, 3.50 %. **HL^{CF3}(Pt–Cl)**: δ H (600 MHz, CDCl$_3$) 9.43 (2 H, d, J 5.9, H^{6}), 8.78 (2 H, d, J 4.9, H^{6*}), 8.56 (1 H, t, J 1.7, H^{7*}), 8.14 (2 H, d, J 1.7, H^{8*}), 7.67 (2 H, dt, J 1.5, 0.7, H^{3*}), 7.56 (2 H, t, J 2.3, H^{b} and H^{d}), 7.39 (2 H, s, H$^{3'}$), 7.36 (2 H, d, J 2.0, H^{3}), 7.33 – 7.28 (3 H, m, H^{c} and H^{5}), 7.23 (1 H, d, J 2.3, H^{a}), 7.10 (2 H, ddd, J 5.0, 1.5, 0.7, H^{5*}), 1.85 (6 H, s, H^{Me}), 1.42 (9 H, s, H$^{t\text{-Bu}}$), 1.40 (9 H, s, H$^{t\text{-Bu}}$); δ C (151 MHz, CDCl$_3$) 168.1 (C^{q}), 156.2 (C^{q}), 152.9 (C^{6}), 150.7 (C^{6*}), 128.9 (C^{8*}), 126.9 (C$^{3'}$), 126.1 (C^{c}), 125.3 (C^{a}), 123.1 (C^{b}), 123.2 (C^{d}), 122.6 (C^{7*}), 118.8 (C^{5}), 117.1 (C^{5*}), 115.0 (C^{3}), 114.6 (C^{3*}), 34.9 (C$^{q\text{-tBu}}$), 34.7 (C$^{q\text{-Me}}$), 33.4 (C^{Me}), 31.6 (C$^{t\text{-Bu}}$); δ_F (376 MHz, CDCl$_3$) −64.60, −65.47; MS ESI (ES^{+}) *m/z* 1248.9 [M-Cl]$^{+}$; HRMS ASAP (AP^{+}) *m/z* 1285.2949 [M]$^{+}$, calc. for [$C_{59}H_{45}ClF_{12}N_4OPt$] 1285.2825; Anal. Calc. for $C_{59}H_{45}ClF_{12}N_4OPt$: C, 55.17; H, 3.53; N, 4.36. Found: C, 54.75; H, 3.58; N, 4.20.

$L^{CF3}(Pt–SCN)_2$



$L^{CF3}(Pt–Cl)_2$ (11 mg, 0.007 mmol) was suspended in acetone (5 mL) in a round-bottom flask. AgOTf (4 mg, 0.016 mmol) was added, and the reaction stirred at RT for 90 min. The precipitated AgCl was removed by centrifugation. KSCN (10 mg, 0.103 mmol) was added to the solution and the mixture stirred at RT for 2 h. The precipitate that formed was isolated by centrifugation and washed successively with water, ethanol and diethyl ether. The solid was extracted into DCM, the resulting solution was centrifuged to remove trace solid, and the solvent was removed under reduced pressure to give the desired product as a red solid (8.6 mg, 79%); δ_H (600 MHz, CD_2Cl_2) 8.97 (4 H, d, J 5.8, H^6), 7.57 (2 H, d, J 2.3, H^d), 7.53-7.45 (4 H, m, $H^{3'}$), 7.41 (8 H, m, H^3 and H^5), 7.25 (2 H, d, J 2.3, H^f), 1.83 (6 H, s, H^{Me}), 1.40 (18 H, s, $H^{t\text{-}Bu}$); δ C (151 MHz, CD_2Cl_2) 127.1 (C^3 or C^5), 125.1 (C^f), 123.4 (C^d), 119.7 (C^3 or C^5), 115.6 ($C^{3'}$), 33.2 (C^{Me}), 31.2 ($C^{t\text{-}Bu}$); δ_F (376 MHz, CD_2Cl_2) –65.6; HRMS (AP^+) *m/z* 1500.2421 $[M\text{-}NCS]^+$, calc. for $[C_{60}H_{44}F_{12}N_5OPt_2S]$ 1500.2430; ν_{max}/cm^{-1} 2074 (SCN/NCS). Only some of the ^{13}C signals could be detected (through HSQC) due to the poor solubility.

$L^{CF3}(Pt–I)_2$



This complex was prepared as for the thiocyanate derivative above, starting from $L^{CF3}(Pt–Cl)_2$ (12 mg, 0.008 mmol) and AgOTf (4 mg, 0.016 mmol), but using KI (2 mg, 0.015 mmol) in place of KSCN. The same isolation and purification sequence led to the desired product as an orange solid (13 mg, 98%). δ_H (400 MHz, $CDCl_3$)10.14 (4 H, d, J 5.9, H^6), 7.59 (2 H, d, J 2.3, H^f), 7.54 (4 H, d, J 5.2, H^5), 7.43 (4 H, s, $H^{3'}$), 7.38 (4 H, s, H^3), 7.22 (2 H, s, H^d), 1.86 (6 H, s, H^{Me}), 1.45 (18 H, s, $H^{t\text{-}Bu}$); HRMS (AP$^+$) *m/z* 1569.1752 [M-I]$^+$, calc. for [$C_{59}H_{44}F_{12}IN_4OPt_2$] 1569.1661. The solubility was too poor to obtain a ^{13}C NMR spectrum.

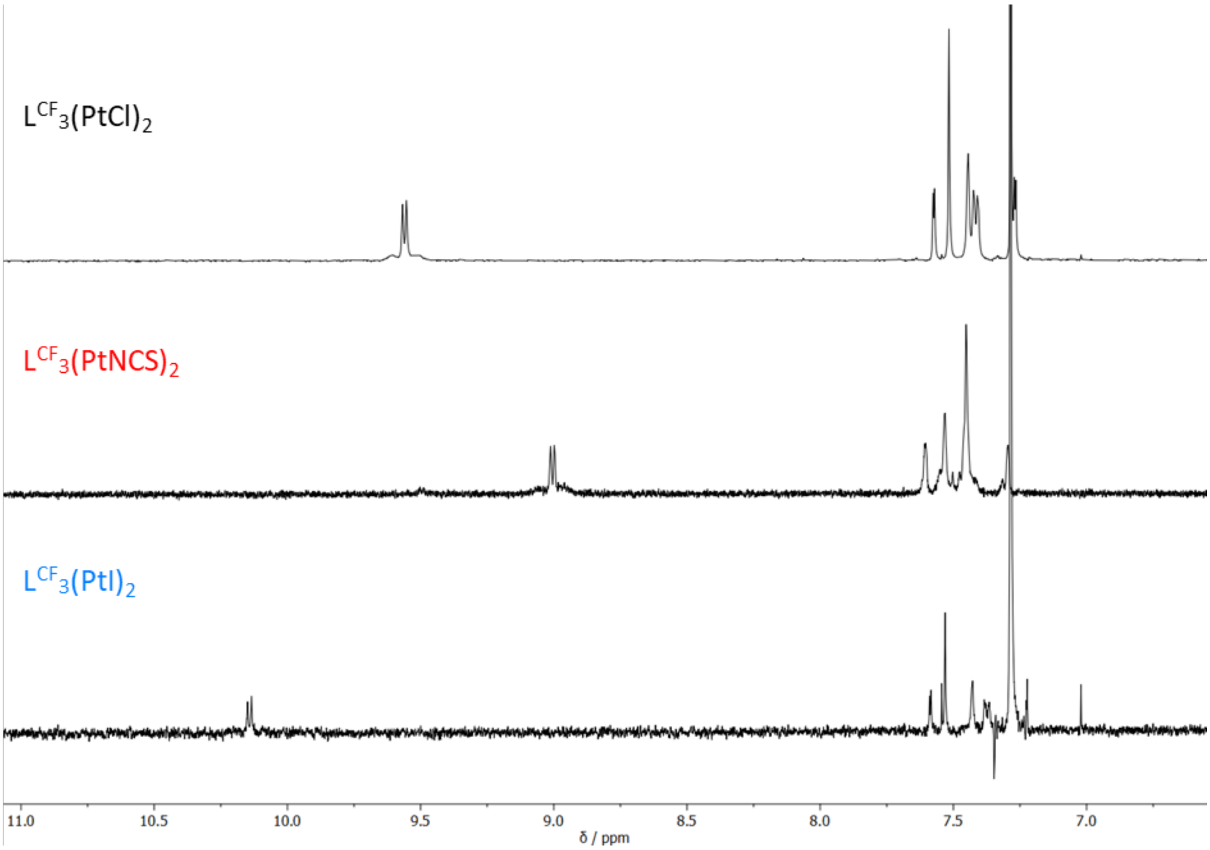


Fig. S1 *^{1}H NMR spectra of $L^{CF3}(Pt\text{–}X)_2$ at room temperature showing the significant shift in the H^6 peak upon ancillary ligand substitution. For X = NCS, the solvent is CD_2Cl_2, as $CDCl_3$ promotes ligand exchange. For X = I, $CDCl_3$ was used, as the solubility in CD_2Cl_2 is low. The spectrum of the X = Cl compound is also in $CDCl_3$.*

2. Crystallography

The X-ray single crystal data have been collected at temperature 120.0(2)K using MoKα radiation (λ =0.71073Å) on a Bruker D8Venture (Photon III MM C14 CPAD detector, IμS-III-microsource, focusing mirrors) 3-circle diffractometer equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostat. The structure was solved by direct method and refined by full-matrix least squares on F^2 for all data using Olex2[2] and SHELXTL software.[3] All non-disordered non-hydrogen atoms were refined in anisotropic approximation, hydrogen atoms were placed in calculated positions and refined in riding mode. Disordered atoms were refined with fixed SOF=0.5. Crystal data and parameters of refinement are listed in Table 1 below. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication CCDC-2370430.

Table S1 Crystal data and structure refinement parameters for L^{CF3}(Pt–SCN)$_2$.

Empirical formula	$C_{68.5}H_{61.5}F_{12}N_{8.5}O_{3.5}Pt_2S_2$
Durham crystallography ref.	21srv388
Formula weight	1742.06
Temperature/K	120.0
Crystal system	monoclinic
Space group	Pc
a/Å	14.9657(3)
b/Å	16.2514(4)
c/Å	27.9021(6)
α/°	90
β/°	103.4175(8)
γ/°	90
Volume/Å^3	6600.9(3)
Z	4
ρ_{calc}g/cm^3	1.753
μ/mm^{-1}	4.387
F(000)	3424.0
Crystal size/mm^3	0.07 × 0.03 × 0.006
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.796 to 54.998
Index ranges	$-19 \leq h \leq 19$, $-21 \leq k \leq 21$, $-36 \leq l \leq 36$
Reflections collected	136379
Independent reflections	30186 [R_{int} = 0.0661, R_{sigma} = 0.0623]
Data/restraints/parameters	30186/324/1718
Goodness-of-fit on F^2	1.031

3. Photophysical details and additional spectra

Equipment and methods

UV-visible absorption spectra were recorded on a Biotek Instruments Uvikon XS spectrometer operated with LabPower software. Emission spectra were acquired on a Jobin Yvon Fluoromax-2 spectrometer equipped with a Hamamatsu R928 photomultiplier tube. All samples were contained within 1 cm pathlength quartz cuvettes modified for connection to a vacuum line. Degassing was achieved by at least three freeze-pump-thaw cycles whilst connected to the vacuum manifold: final vapour pressure at 77 K was $< 5 \times 10^{-2}$ mbar. Emission was recorded at 90° to the excitation source, and spectra were corrected after acquisition for dark count and for the spectral response of the detector. The quantum yields were determined relative to an aqueous solution of $[\mathrm{Ru(bpy)_3}]\mathrm{Cl_3}$, for which $\Phi_{\mathrm{lum}} = 0.04$.[4] Emission spectra at 77 K were recorded in 4 mm diameter tubes held within a liquid-nitrogen-cooled quartz Dewar, using the same spectrometer. The luminescence lifetimes τ in solution at 295 K were measured by time-correlated single-photon counting, for $\tau < 10$ μs, using an EPL405 pulsed-diode laser as excitation source (405 nm excitation, pulse length of 60 ps, repetition rate 20 kHz, or faster for shorter lifetimes). The emission was detected at 90° to the excitation source, after passage through a monochromator, using an R928 PMT thermoelectrically cooled to –20°C.

The solid-state samples were prepared by drop-casting on to sapphire substrates from $\mathrm{CH_2Cl_2}$ solution. The substrates were pre-washed in concentrated nitric acid if required. After neutralisation in water, they were cleaned using analytical-grade acetone and Kimtech wipes. Deposition of the neat film was carried out directly from a stock solution of 0.5 mg/mL for $\mathrm{L^{CF3}(Pt–SCN)_2}$ and 0.1 mg/mL for $\mathrm{L^{CF3}(Pt–I)_2}$ and $\mathrm{L^{CF3}(Pt–Cl)_2}$. The PMMA polymer solution was made up at 100 mg/mL concentration and mixed with the stock solutions of the compounds to create 0.1, 1 and 10 wt % films of the compound by mass in the polymer. These were then also drop-cast onto sapphire substrates. The UV-Vis absorption spectra of the films were measured on a Shimadzu UV-3600 double beam spectrophotometer with a second sapphire substrate as a blank reference. The photoluminescence spectra and the quantum yields in the films were measured using an integrating sphere, in conjunction with an Ocean Optics QePro spectrometer with an embedded CCD detector that spans the range 350–1000 nm, following excitation at 365 nm with an Ocean Optics LLS-LED.

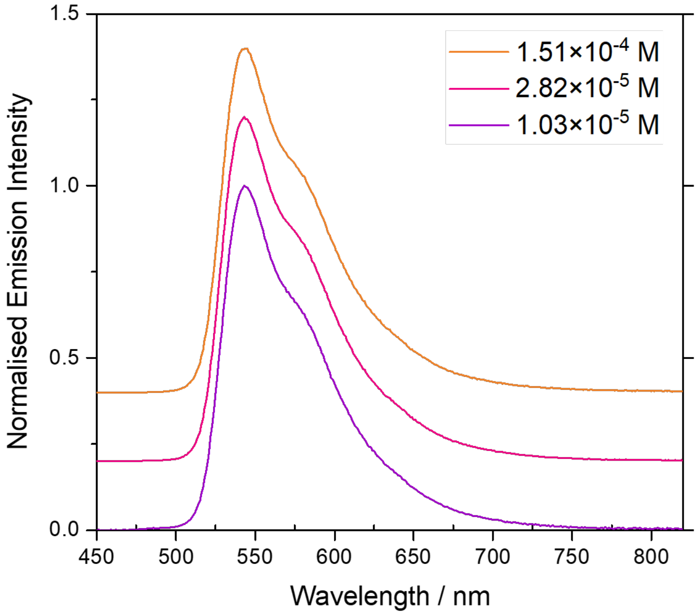


Fig. S2 *Normalised emission spectra of HL^{CF3}(Pt–Cl) at the indicated concentrations in CH_2Cl_2 at 295 K; the spectra are offset vertically for clarity.*

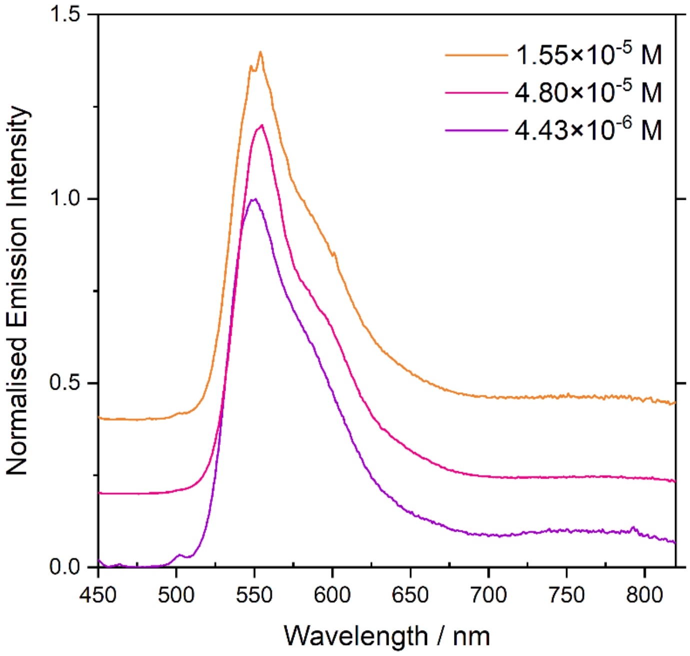
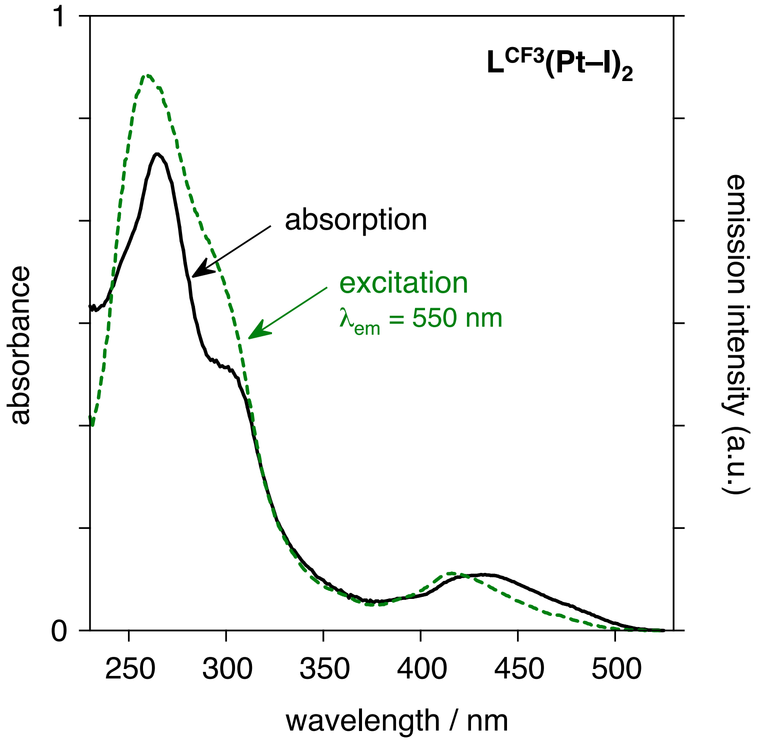


Fig. S3 *Normalised emission spectra of L^{CF3}(Pt–I)$_2$ at the indicated concentrations in CH_2Cl_2 at 295 K; the spectra are offset vertically for clarity.*



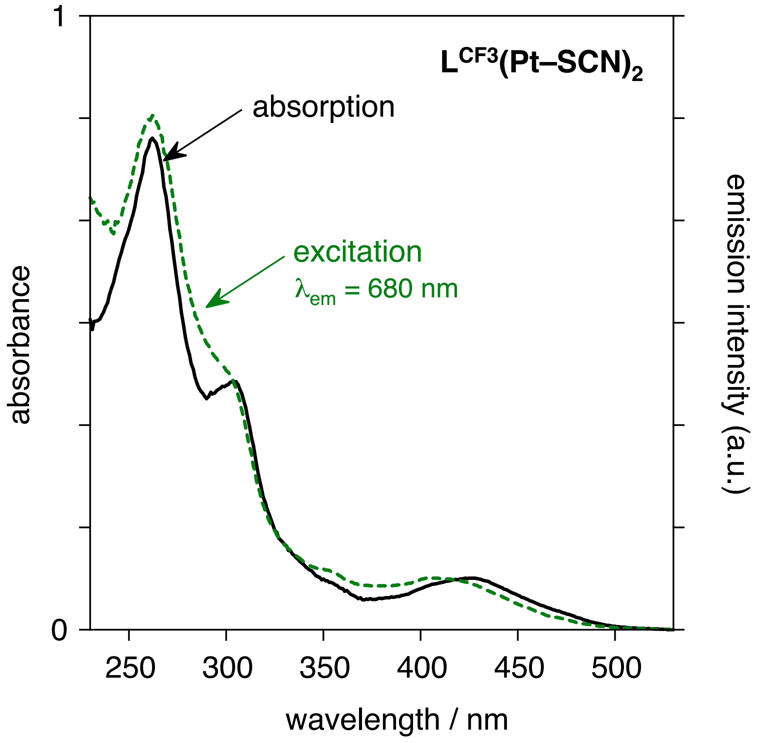


Fig. S4 *Overlay of the absorption spectra (solid black lines) and the excitation spectra recorded at the* λ_{em} *values indicated (dashed green lines) of* $L^{CF3}(Pt–I)_2$ *(top) and* $L^{CF3}(Pt-SCN)_2$ *(bottom) in* CH_2Cl_2 *solution at 295 K.*

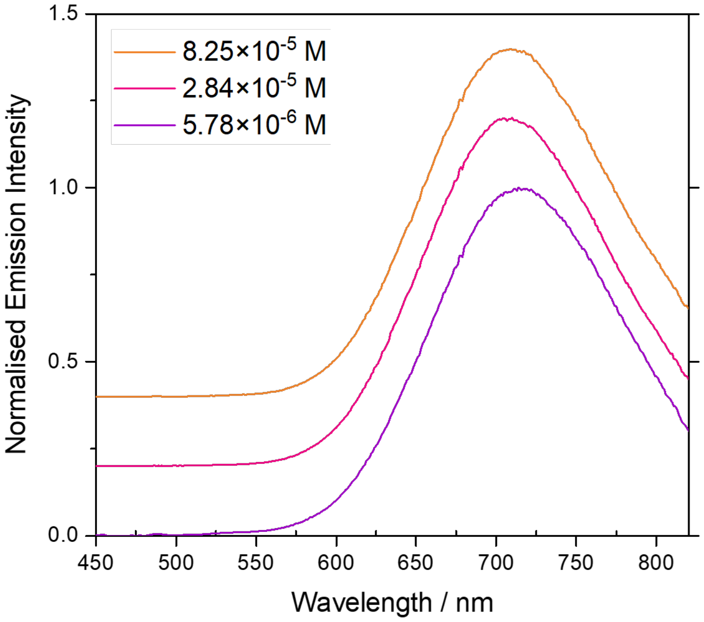


Fig. S5 *Normalised emission spectra of* L^{CF3}*(Pt–SCN)*$_2$ *at the indicated concentrations in* CH_2Cl_2 *at 295 K; the spectra are offset vertically for clarity.*

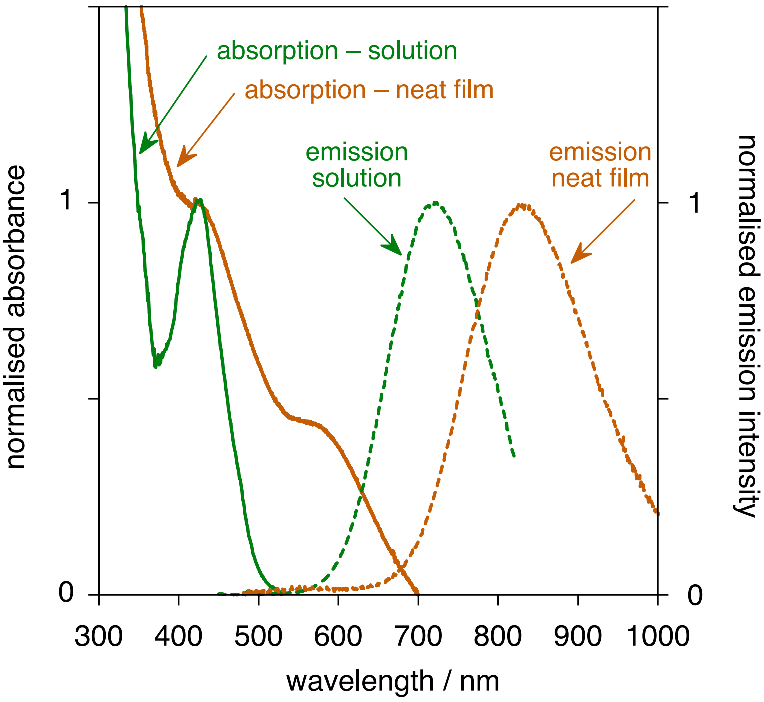


Fig. S6 *Absorption and emission spectra of* L^{CF3}*(Pt–SCN)*$_2$ *in neat films (solid and dashed orange lines respectively) at 295 K, with the corresponding spectra in* CH_2Cl_2 *shown overlaid for comparison (green lines, normalised y scale).*

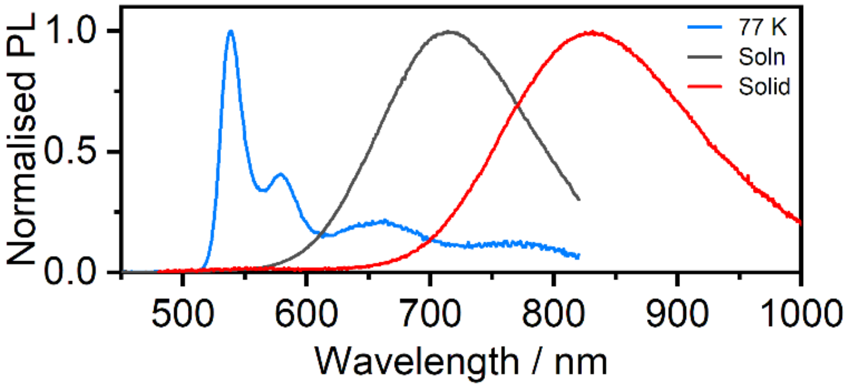


Fig. S7 *Overlay of the emission spectra of* $L^{CF}{}_3(Pt\text{–}SCN)_2$ *in* CH_2Cl_2 *solution at 295 K (black), at 77 K in EPA (blue), and in neat film (red) (EPA = diethyl ether / isopentane / ethanol, 2:2:1 v/v).*

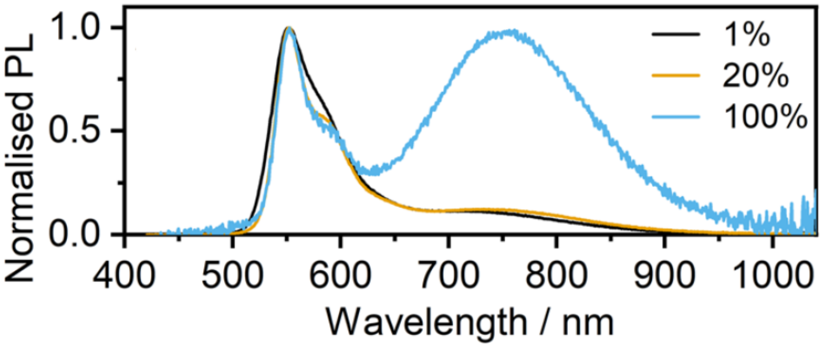


Fig. S8 *Emission spectra of* $L^{CF3}(Pt\text{–}Cl)_2$ *in polystyrene film at the concentrations shown, as reported in our earlier study,[1] reproduced here to facilitate comparison with the thiocyanate and iodo derivatives.*

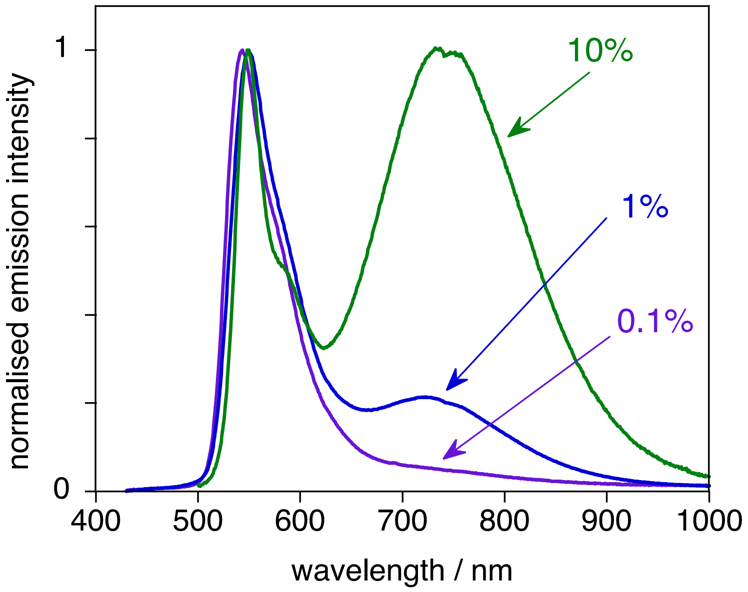


Fig. S9 *Emission spectra of* L^{CF3}*(Pt–Cl)*$_2$ *in PMMA film at the concentrations shown, corresponding to those for* L^{CF3}*(Pt–SCN)*$_2$ *in PMMA, shown in Fig. 5 in the same colours.*

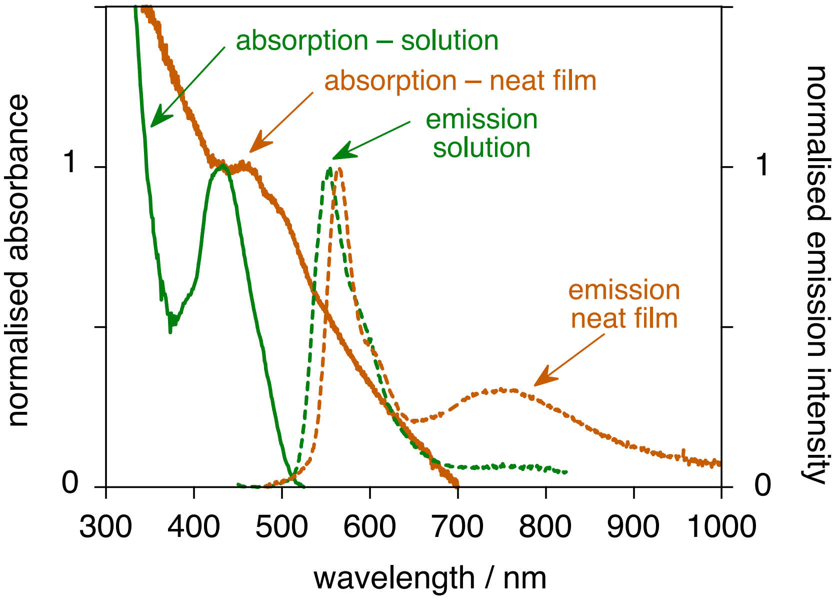


Fig. S10 *Absorption and emission spectra of* L^{CF3}*(Pt–I)*$_2$ *in neat films (solid and dashed orange lines respectively) at 295 K, with corresponding spectra in* CH_2Cl_2 *shown overlaid for comparison (green lines). The absorption spectrum in film is shown on an expanded scale to highlight the weak low-energy tail, which may be due to weak ground-state interactions.*

Table S2 Comparison of the photophysical properties in solution and in neat films.

Complex	**Dilute CH_2Cl_2 solutions**		**Neat films**	
	λ_{max} / nm *** = excimer**	**Φ_{PL} [a]**	**λ_{max} / nm** *** = excimer**	**Φ_{PL} [a]**
$L^{CF3}(Pt–Cl)_2$	542, 582, 762*	0.12	553, 593sh, 753*	0.04
$L^{CF3}(Pt–SCN)_2$	714*	0.11	831*	0.05
$L^{CF}(Pt–I)_2$	551, 584	0.01	565, 755*	0.02

a The estimated uncertainty on photoluminescence quantum yields is ± 20% or better.

Table S3 Decay times of the luminescence of $L^{CF3}(Pt–SCN)_2$ in neat and PMMA-doped films.

Complex	**Doping %**	**Lifetime / ns [a, b]** * denotes excimer
$L^{CF3}(Pt–SCN)_2$	0.1%	6300, 330*
	1%	6200, 210*
	10%	240*
	100 % (neat)	150*

a λ_{ex} = 405 nm. *b* The estimated uncertainty in τ is ±10%; the values for the excimer at 1% and 10% loading are thus not significantly different.

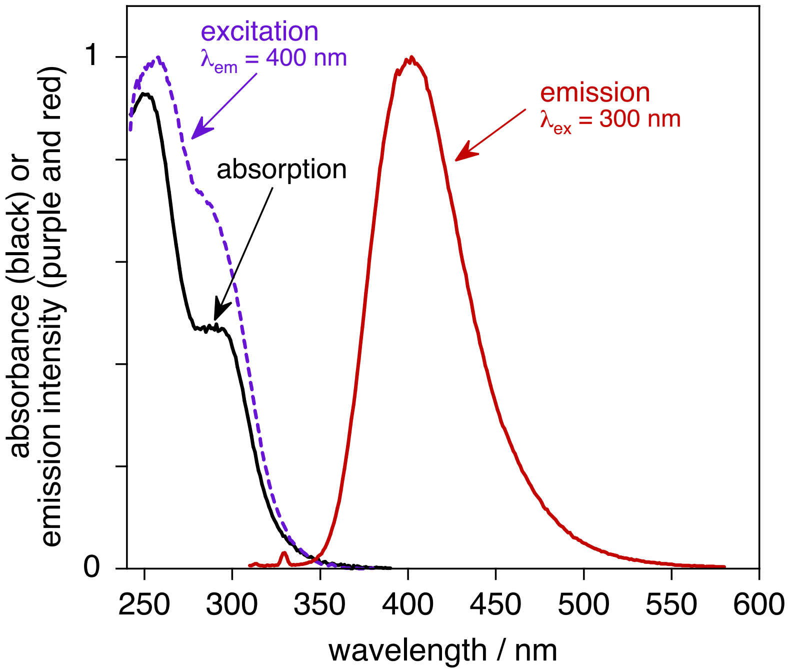


Fig. S11 *Absorption (black line), excitation (dashed purple line) and emission spectra (red line) of the proligand* H_2L^{CF3} *in* CH_2Cl_2 *at 295 K.*

References

1. P. Pander, M. T. Walden, R. J. Salthouse, A. Sil, D. S. Yufit, F. B. Dias and J. A. G. Williams, *J. Mater. Chem. C*, 2023, **11**, 15335–15346.
2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. *Appl. Cryst.* 2009, **42**, 339–341.
3. G.M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112–122.
4. K. Suzuki, A. Kobayashi, S. Kaneko, K. Takehira, T. Yoshihara, H. Ishida, Y. Shiina, S. Oishi and S. Tobita, *Phys. Chem. Chem. Phys.* 2009, **11**, 9850–9860.