Green-emitting iridium(III) complexes containing sulfanyl- or sulfone-functionalized cyclometallating 2-phenylpyridine ligands†

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A series of [Ir(C^N)2(bpy)][PF6] complexes in which the cyclometallating ligands contain fluoro, sulfanyl or sulfone groups are reported. The conjugate acids of the C^N ligands in the complexes are 2-(4-fluorophenyl)pyridine (H1), 2-(4-methylsulfonylphenyl)pyridine (H3), 2-(4-tert-butyldisulfonylphenyl)pyridine (H4), 2-(4-tert-butylsulfonylphenyl)pyridine (H5), 2-(4-tert-dodecysulfonylphenyl)pyridine (H6), and 2-(4-tert-dodecysulfonylphenyl)pyridine (H7). The single crystal structures of H3 and H5 are described. [Ir(C^N)2(bpy)][PF6] with C^N = 1, 3, 4, 5 and 7 were prepared from the appropriate [Ir(C^N)2Cl3] dimer by bpy; the structure of [Ir2(3-tBu2bpy)2-2CH2Cl2 was determined. [Ir62(bpy)][PF6] was prepared by nucleophilic substitution starting from [Ir(12)2(bpy)][PF6]. The [Ir(C^N)2(bpy)][PF6] complexes have been characterized by NMR, IR, absorption and emission spectroscopic and mass spectrometric methods. The single crystal structures of enantiomerically pure Δ-[Ir(12)2(bpy)][PF6] and of rac-4-[Ir(12)2(bpy)][PF6]-Et2O-2CH2Cl2 are described, and the differences in inter-cation packing in the structures compared. [Ir(12)2(bpy)][PF6], [Ir(4-tBu2bpy)][PF6] and [Ir(6)2(bpy)][PF6] (fluoro and sulfane substituents) are yellow emitters (λem between 557 and 577 nm), and the room temperature solution emission spectra are broad. The sulfone derivatives [Ir32(bpy)][PF6], [Ir52(bpy)][PF6] and [Ir72(bpy)][PF6] are green emitters and the emission spectra are structured (λmax = 493 and 523 to 525 nm). High photoluminescence quantum yields (PLQYs) of 64–74% are observed for the sulfone complexes in degassed solutions. The emission lifetimes for the three complexes containing sulfone substituents are an order of magnitude longer (2.33 to 3.36 μs) than the remaining complexes (0.224 to 0.528 μs). Emission spectra of powdered solid samples have also been recorded; the broad emission bands have values of λem in the range 532 to 558 nm, and PLQYs for the powdered compounds are substantially lower (≤23%) than in solution. Trends in the redox potentials for the [Ir(C^N)2(bpy)][PF6] complexes are in accord with the observed emission behaviour.

Introduction

Iridium(III) [Ir(C^N)2(N^N)]+ complexes incorporating cyclometallating (C^N) and N,N-chelating (N^N) ligands offer an adaptable family of emissive ionic materials for use in light-emitting electrochemical cells (LECs).1–4 In [Ir(C^N)2(N^N)]+ cations, the localization of the HOMO and LUMO on the iridium/C^N domain and on the N^N ligands respectively, facilitates manipulation of the HOMO–LUMO separation by judicious choice of ligand substituents. Stabilization of the HOMO has been achieved by introducing electron-donating substituents onto the C^N ligands, and 2-(2,4-difluorophenyl)pyridine (Hdfppy), and to a lesser extent 2-(4-fluorophenyl)pyridine, are regularly employed to achieve blue-shifted emissions in [Ir(C^N)2(N^N)]+ complexes.1,5–7 Bolink, Frey and coworkers8 have shown that the number (one or two) and positions of substitution of fluorine substituents in 2-phenylpyridine (Hppy) have little effect on the photophysical and electrochemical properties of [Ir(C^N)2(4,4′-tBu2-bpy)][PF6] complexes (4,4′-di-tert-butyl-2,2′-bipyridine). However, significantly for application in LECs, increasing the number of fluorine atoms results in shorter lived LECs.

Less well explored than the use of fluoro-substituents is the incorporation of SR, SOR and SO2R electron-withdrawing substituents, either for functionalization of the C=N–13 or N=N ligand.14 Among these earlier studies is the use of 1-(4-methylsulfonyl)phenyl)-1H-pyrazole (HMSSpz) as the cyclometallating ligand in a series of green emitting [Ir(msppz)2(N^N)][PF6] complexes which perform efficiently under bias in LECs.13 The

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TOF mass spectra were recorded on Bruker esquire 3000plus UATR instrument. Electrospray ionization (ESI) and MALDI-photometer, and FT-IR spectra on a Perkin Elmer Spectrum Two.

We present here a systematic study of the effects of functionalizing the cyclometallating Hppy ligand with increasingly electron-withdrawing substituents in the 4-position of the phenyl ring. Our aim was to apply the series of ligands shown in Scheme 1. Since the influence of fluorosubstituents is rather well understood, ligand H1 was chosen to provide the benchmark complex [Ir(Hppy)]2+ to which to relate the properties of the sulfane and sulfone derivatized complexes. The increase in electron-withdrawing properties on changing from Sm and SO2Me in compounds H2 to H3 (Scheme 1) is reflected in the different Hammett parameters (σMe, σSO2Me, σm, 0.60, σp, 0.72), 15–17 and one of us has observed that on going from [Ru(tpy)]2+ to [Ru(4′-MeOStpy)]2+ (tpy = 2,2′,6′,2″-terpyridine, 4′-MeOStpy = 4′-methylenesulfonyl-2,2′,6′,2″-terpyridine), the sulfone unit causes a switch from a non-emissive complex in fluid solution to emissive behaviour in MeCN solution. 18

The pairs of ligands H4/H5 and H6/H7 were selected to investigate the added effects of introducing bulky (butyl) and long-chain (dodecyl) thiol and sulfone substituents.

Scheme 1 Structures of the conjugate acids of the C=N ligands with labelling for NMR spectroscopic assignments.

Achievement of both high luminances and efficiencies under low driving voltages13 suggest that sulfone-functionalized cyclometallating ligands may be a viable alternative to the more commonly employed fluoro-substituted C=N ligands.

Experimental

General

A Biotage Initiator 8 reactor was used for syntheses under microwave conditions.

1H and 13C spectra were recorded at 295 K on a Bruker Avance III-500 spectrometer; chemical shifts are referenced to residual solvent peaks with δ(TMS) = 0 ppm. Solution absorption spectra were recorded on an Agilent 8453 spectrophotometer, and FT-IR spectra on a Perkin Elmer Spectrum Two UATR instrument. Electrospray ionization (ESI) and MALDI-TOF mass spectra were recorded on Bruker esquire 3000plus and Bruker Daltronics Microflex mass spectrometers, respectively. LC-ESI-MS employed a combination of Shimadzu (LC) and Bruker AmaZon X instruments. Electrochemical measurements were carried out using cyclic voltammetry and using a CH Instruments 900B potentiostat with glassy carbon working and platinum auxiliary electrodes; a silver wire was used as a pseudo-reference electrode. Solvent was dry, purified MeCN and 0.1 M [Bu4N][PF6] was used as supporting electrolyte. Cp2Fe was used as internal reference and was added at the end of each experiment.

Solution emission spectra were recorded in MeCN on a Shimadzu 5301PC spectrofluorophotometer. Solution quantum yields were measured using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus_QY. Lifetimes and emission spectra of powdered samples were measured using a Hamamatsu Compact Fluorescence lifetime Spectrometer C11367 Quantaurus-Tau.

Compound H1 was prepared as reported in the literature19 and the spectroscopic properties matched those reported20,21 [Ir2(COD)2Cl2]6 (COD = cycloocta-1,5-diene) and [Ir2(1)Cl]6 were prepared according to literature methods. All solvents were dried before use. Silica and alumina were purchased from Fluka (silica gel 60, 0.040–0.063 mm and activated, neutral aluminium oxide).

Compound H2. Compound H2 has been previously reported23 but the following procedure gives a higher yield. Compound H1 (617 mg, 3.56 mmol) and an excess of NaSMe (1.06 g, 14.3 mmol) were added to N-methyl-2-pyrrrolidone (NMP) (18 mL) in a microwave vial. The violet reaction mixture was heated at 80 °C for 1 h in a microwave reactor to give a dark brown suspension. This was poured into a mixture of H2O and brine (3:1, 100 mL). The resulting yellow precipitate was separated by filtration, dissolved in CH2Cl2 and dried over Na2SO4. The solvent was removed under reduced pressure to yield H2 as a yellow solid (0.665 g, 3.30 mmol, 92.7%). M.p. 59.5 °C. 1H NMR (500 MHz, CDCl3) δ/ppm 8.67 (ddd, J = 4.9, 1.9, 1.0 Hz, 1H, Hβ2), 7.93 (m, 2H, Hα2), 7.76–7.67 (overlapping m, 2H, Hβ3+β4), 7.34 (m, 2H, Hα3), 7.21 (ddd, J = 7.3, 4.8, 1.4 Hz, 1H, Hβ5), 2.53 (s, 3H, HMe). 13C{1H} NMR (126 MHz, CDCl3) δ/ppm 157.0 (CB2), 149.8 (Cββ), 139.9 (CA4), 136.9 (Cβ4), 136.2 (Cβ1), 127.3 (Cαβ), 126.5 (Cα3), 122.1 (Cβ3), 120.2 (CHβ2), 115.7 (CMe), IR (solid, /cm–1) 3086 (w), 3046 (w), 3002 (w), 2981 (w), 2919 (w), 1982 (w), 1910 (w), 1767 (w), 1661 (w), 1650 (w), 1583 (s), 1569 (s), 1552 (m), 1458 (s), 1431 (s), 1399 (m), 1322 (w), 1296 (w), 1256 (w), 1227 (w), 1190 (m), 1154 (w), 1121 (w), 1098 (m), 1089 (m), 1057 (w), 1008 (m), 988 (m), 969 (w), 958 (m), 884 (w), 830 (m), 772 (s), 738 (s), 725 (m), 708 (m), 675 (w), 636 (w), 616 (w), 569 (w), 544 (w), 484 (m), 461 (m). ESI-MS m/z 202.0 [M + H]+ (calc. 202.1). Found C 71.43, H 5.57, N 6.75; C12H11NS requires C 71.60, H 5.51, N 6.96%.

Compound H3. Compound H2 (1.00 g, 4.97 mmol) and sodium tungstate dihydrate (819 mg, 2.48 mmol) were added and the mixture was stirred overnight at room temperature. The suspension was poured into a mixture of H2O and brine (3:1, 200 mL) and extracted with CH2Cl2 (3 × 100 mL). The combined organic phases were dried over Na2SO4 and the solvent was removed under reduced pressure to yield H3 as a white powder (1.14 g, 4.89 mmol, 98.4%). M.p. 134.5 °C. 1H NMR (500 MHz, CDCl3) δ/ppm 7.75 (m, 2H, HB3+B4), 7.34 (m, 2H, HA3), 7.21 (ddd, J = 7.3, 4.8, 1.0 Hz, 1H, Hβ5), 3.09 (s, 3H, HMe). 13C{1H} NMR (126 MHz, CDCl3) δ/ppm 157.0 (CB2), 149.8 (Cββ), 139.9 (CA4), 136.9 (Cβ4), 136.2 (Cβ1), 127.3 (Cαβ), 126.5 (Cα3), 122.1 (Cβ3), 120.2 (CHβ2), 115.7 (CMe), IR (solid, /cm–1) 3086 (w), 3046 (w), 3002 (w), 2981 (w), 2919 (w), 1982 (w), 1910 (w), 1767 (w), 1661 (w), 1650 (w), 1583 (s), 1569 (s), 1552 (m), 1458 (s), 1431 (s), 1399 (m), 1322 (w), 1296 (w), 1256 (w), 1227 (w), 1190 (m), 1154 (w), 1121 (w), 1098 (m), 1089 (m), 1057 (w), 1008 (m), 988 (m), 969 (w), 958 (m), 884 (w), 830 (m), 772 (s), 738 (s), 725 (m), 708 (m), 675 (w), 636 (w), 616 (w), 569 (w), 544 (w), 484 (m), 461 (m).
128.0 (C\(^{A1}\)), 127.9 (C\(^{A2}\)), 123.5 (C\(^{B5}\)), 121.3 (C\(^{B3}\)), 44.7 (C\(^{Me}\)). IR (solid, \(\nu / \text{cm}^{-1}\)) 3000 (w), 2921 (w), 1586 (m), 1563 (w), 1465 (m), 1435 (m), 1392 (w), 1314 (w), 1292 (s), 1185 (w), 1146 (s), 1087 (m), 1030 (w), 1013 (w), 988 (w), 964 (m), 848 (m), 789 (m), 776 (s), 750 (s), 677 (m), 636 (w), 616 (m), 562 (m), 548 (s), 514 (s). ESI-MS m/z 234.0 [M + H]\(^+\) (calc. 234.1). Found: C 62.03, H 4.95, N 6.29; C\(_12\)H\(_{11}\)NO\(_2\)S requires C 61.78, H 4.75, N 6.00%.

**Compound H4.** NaH (60% suspension in mineral oil, 235 mg, 5.88 mmol) was suspended in DMF (8 ml) under N\(_2\). 2-Methyl-2-propanethiol (0.660 mL, 528 mg, 5.80 mmol) was added leading to gas evolution and a white foam. After the reaction mixture had been stirred for 10 min at room temperature, H1 (501 mg, 2.89 mmol) was added with DMF (2 ml). The mixture was heated at 120 °C for 24 h. The yellow-orange solution was allowed to cool to room temperature and was then poured into water–brine (3:1, 50 ml). The resulting suspension was stirred for 5 min and the precipitate was removed by filtration, washed with H\(_2\)O, dried under vacuum and purified by column chromatography (silica, n-hexane–EtOAc 6:1 by vol. changing to 2:1). H6 was isolated as a white solid (542 mg, 1.52 mmol, 65.8%). M.p. 65.3 °C. 1\(^H\) NMR (500 MHz, CDCl\(_3\)) \(\delta / \text{ppm} 8.67\) (\(\text{ddd}, J = 4.8, 1.8, 1.0 \text{ Hz}, 1\text{H}, \text{H}^{B6}\)), 7.91 (m, 2H, H\(^{B2}\)), 7.78–7.63 (overlapping m, 2H, H\(^{B5}\)), 7.39 (m, 2H, H\(^{B3}\)), 7.21 (\(\text{ddd}, J = 7.2, 4.8, 1.4 \text{ Hz}, 1\text{H}, \text{H}^{B4}\)), 2.97 (m, 2H, H\(^{CH2}\)), 1.68 (m, 2H, 2H\(^{CH2}\)), 1.35–1.12 (overlapping m, 16H, H\(^{CH2}\)), 0.88 (t, \(J = 6.9 \text{ Hz}, 3\text{H}, \text{H}^{CH3}\)). 1\(^{13}\)C{\(^1\)H} NMR (126 MHz, CDCl\(_3\)) \(\delta / \text{ppm} 138.7 (C^{A6}), 136.9 (C^{B6}), 136.7 (C^{A5}), 128.6 (C^{A3}), 127.3 (C^{A4}), 121.1 (C^{B4}), 120.3 (C^{B5}), 33.3 (C^{CH2}), 32.1 (C^{CH3}), 29.8 (2C^{CH2}), 29.7 (2C^{CH2}), 29.5 (2C^{CH2}), 29.3 (2C^{CH2}), 29.2 (2C^{CH2}), 22.8 (2C^{CH2}), 14.3 (C^{CH3}). IR (solid, \(\nu / \text{cm}^{-1}\)) 3059 (w), 2903 (w), 2954 (m), 2917 (s), 2872 (m), 2850 (s), 1545 (s), 1549 (w), 1464 (w), 1433 (s), 1398 (w), 1379 (m), 1297 (m), 1259 (w), 1242 (w), 1191 (w), 1153 (w), 1122 (w), 1100 (m), 1056 (w), 1099 (m), 988 (w), 834 (m), 768 (m), 734 (m), 720 (m), 708 (m), 636 (w), 548 (w), 513 (m), 488 (w), 462 (m). MALDI-TOF MS (no matrix) m/z 355.7 [M\(^+\)] (calc. 355.2). Found C 77.75, H 9.76, N 4.05; C\(_6\)H\(_{12}\)N\(_3\)S requires C 77.69, H 9.35, N 3.94%.

**Compound H6.** NaH (60% suspension in mineral oil, 187 mg, 4.67 mmol) was suspended in DMF (6 ml) under N\(_2\). 1-Dodecanethiol (1.14 mL, 956 mg, 4.63 mmol) and then DMF (4 ml) were added and the mixture was stirred for 10 min. H1 (400 mg, 2.31 mmol) was added with DMF (2 ml) and the mixture was heated at 120 °C for 4 h. The yellow mixture was allowed to cool to room temperature and was then poured into water–brine (3:1, 50 ml). The resulting suspension was stirred for 5 min and the precipitate was removed by filtration, washed with H\(_2\)O, dried under vacuum and purified by column chromatography (silica, n-hexane–EtOAc 6:1 by vol. changing to 2:1). H6 was isolated as a white solid (542 mg, 1.52 mmol, 65.8%). M.p. 65.3 °C. 1\(^H\) NMR (500 MHz, CDCl\(_3\)) \(\delta / \text{ppm} 8.67\) (\(\text{ddd}, J = 4.8, 1.8, 1.0 \text{ Hz}, 1\text{H}, \text{H}^{B6}\)), 7.91 (m, 2H, H\(^{B2}\)), 7.78–7.63 (overlapping m, 2H, H\(^{B5}\)), 7.39 (m, 2H, H\(^{B3}\)), 7.21 (\(\text{ddd}, J = 7.2, 4.8, 1.4 \text{ Hz}, 1\text{H}, \text{H}^{B4}\)), 2.97 (m, 2H, H\(^{CH2}\)), 1.68 (m, 2H, 2H\(^{CH2}\)), 1.35–1.12 (overlapping m, 16H, H\(^{CH2}\)), 0.88 (t, \(J = 6.9 \text{ Hz}, 3\text{H}, \text{H}^{CH3}\)).
[Ir(3)(Cl)_3]. [Ir(2(COD)Cl)_2] (285 mg, 0.424 mmol) and H3 (395 mg, 1.69 mol) were suspended in degassed 2-ethoxyethanol and the mixture purged with argon. The suspension was heated at reflux overnight and was then allowed to cool to room temperature. The yellow precipitate was separated by filtration, washed with H2O and EtOH, and dried under vacuum. [Ir(3)(Cl)_3] was isolated as a yellow powder (516 mg, 0.373 mmol, 88.0% crude) and was used without further purification.

1H NMR (500 MHz, CDCl3) δ/ppm 9.21 (dd, J = 5.8, 1.6, 0.7 Hz, 4H, H^A3), 8.06 (ddd, J = 8.4, 1.4, 0.7 Hz, 4H, H^B3), 7.95 (ddd, J = 8.1, 7.5, 1.6 Hz, 4H, H^B5), 7.68 (d, J = 8.2 Hz, 4H, H^A4), 7.36 (dd, J = 8.1, 1.9 Hz, 4H, H^A4), 7.01 (ddd, J = 7.3, 5.7, 1.4 Hz, 4H, H^B5), 6.36 (d, J = 1.9 Hz, 4H, H^B5), 2.75 (s, 12H, H^A6), 1.43 (s, 36H, H^B6). ESI-MS m/z 657.1 [Ir(3)]^+ (calc. 657.1), 698.2 [Ir(3)(MeCN)]^+ (calc. 698.1).

[Ir(4)(Cl)_4]. Compound H4 (401 mg, 1.65 mmol) was dissolved in 2-ethoxyethanol (18 mL) in a vial and the solution was purged with N2. [Ir(2(COD)Cl)_2] (280 mg, 0.417 mmol) was added and the mixture heated at 110 °C for 1.5 h in a microwave reactor. The yellow precipitate was separated by filtration, washed with H2O and EtOH, and dried under vacuum. The mixture was allowed to cool to room temperature for a few min. The resulting suspension was poured into brine (40 mL) and stirred again at room temperature. The precipitate was removed by filtration, washed with H2O, EtOH and Et2O and dried under vacuum. [Ir(4)(Cl)_4] as a yellow powder (216 mg, 0.108 mmol, 84.0% crude) and was used without further purification.

1H NMR (500 MHz, CDCl3) δ/ppm 9.04 (d, J = 5.7, 1.5, 0.6 Hz, 4H, H^B6), 8.04 (pseudo-dt, J = 8.4, 1.0 Hz, 4H, H^B4), 7.94 (pseudo-t, J = 7.8, 1.6 Hz, 4H, H^B5), 7.66 (d, J = 8.2 Hz, 4H, H^A4), 7.31 (dd, J = 8.1, 1.8 Hz, 4H, H^A4), 6.99 (ddd, J = 7.3, 5.7, 1.5 Hz, 4H, H^B5), 6.30 (d, J = 1.8 Hz, 4H, H^A6), 2.74 (m, 8H, H^SO2C), 1.43 (m, 8H, H^B2C2H2Cl^B2), 1.33–1.05 (overlapping m, 72H, H^Me), 0.88 ppm (t, J = 7.0 Hz, 12H, H^Me). [Ir(4)(Cl)_4]^+ (calc. 677.2), 718.3 [Ir(4)(Cl)_4]^+ (calc. 741.1), 782.1 [Ir(4)(Cl)_4]^+ (calc. 82% IrCl3, 99.2 mg, 0.516 mmol) in 743.2 [Ir(3)(Cl)_3]^+ (calc. 741.1), 782.1 [Ir(3)(Cl)_3]^+ (calc. 741.1).
and the mixture was heated at 120 °C in a microwave reactor for 1 h (15 bar). After cooling, an excess of solid NH4PF6 was added to the yellow solution and the resulting suspension was stirred for 15 min at room temperature. The yellow precipitate that formed was separated by filtration, was washed with MeOH and redissolved in CH2Cl2. The solvent was removed under reduced pressure and the product was purified by column chromatography (silica, CH2Cl2 changing to CH2Cl2–4% MeOH). The major fraction was collected and solvent removed under reduced pressure. The residue was suspended in CH2Cl2 and the mixture sonicated and then filtered. [Ir(3)(bpy)][PF6] was isolated as a yellow solid (92.3 mg, 0.0964 mmol, 84.0%). 1H NMR (500 MHz, CD3CN) δ/ppm 8.54 (pseudo-dt, δ = 8.3, 1.1 Hz, 2H, H6E3), 8.23 (pseudo-dt, δ = 8.2, 1.1 Hz, 2H, H6B3), 8.15 (pseudo-tdd, δ = 8.0, 1.6 Hz, 2H, H6B3), 8.02 (d, δ = 8.3 Hz, 2H, H5E3), 7.98 (dd, δ = 8.0, 7.7, 1.5 Hz, 2H, H5B3), 7.95 (dd, δ = 5.4, 1.6, 0.8 Hz, 2H, H6E3), 7.72 (dd, δ = 5.8, 1.5, 0.7 Hz, 2H, H6B3), 7.58 (dd, δ = 8.3, 1.9 Hz, 2H, H5B3), 7.51 (dd, δ = 7.7, 5.5, 1.2 Hz, 2H, H5E3), 7.21 (dd, δ = 7.4, 5.8, 1.4 Hz, 2H, H4E3), 6.70 (d, δ = 1.9 Hz, 2H, H4B3), 2.89 (s, 6H, HMe6). 13C{1H} NMR (126 MHz, CD3CN) δ/ppm 166.2 (CB2), 156.6 (CE2), 151.1 (CB4), 150.9 (CE4), 150.2 (CA5), 142.3 (CA2), 140.7 (CA3), 140.3 (CA4), 134.3 (CA6), 126.31 (CA1), 126.29 (CA3), 125.8 (CE3), 122.6 (CA4), 122.6 (CA3), 144.3 (CE1). IR (solid, ν/cm−1) 2927 (w), 1608 (w), 1575 (w), 1475 (m), 1447 (w), 1430 (w), 1366 (m), 1313 (w), 1294 (m), 1267 (w), 1144 (m), 1137 (m), 1099 (w), 918 (s), 788 (s), 765 (s), 733 (m), 650 (w), 600 (w), 557 (s). UV/Vis (MeCN, 1.0 × 10−5 mol dm−3) ε/μm−1 cm−1 261 (57000), 350 (30500), 415 (48000). Emission (MeCN, 0.99 × 10−5 mol dm−3, λexc = 260 nm): λemmax = 568 nm. ESI-MS m/z 833.5 [M − PF6]− (calc. 833.2). Found C 48.96, H 4.35, N 5.70; C40H44Ir2PF6Ir4NS2 requires C 49.12, H 4.12, N 5.73%.

[Ir(4)(bpy)][PF6]. [Ir(4)(bpy)]Cl2 (101 mg, 0.0650 mmol) and bpy (43.4 mg, 0.284 mmol) were suspended in MeOH (10 mL) and the mixture was heated at reflux for 14 h. The solution was left to cool to room temperature, and an excess of solid NH4PF6 was then added followed by enough H2O to precipitate the product. The resulting suspension was stirred for 30 min. The yellow precipitate was separated by filtration, washed with H2O and redissolved in CH2Cl2. After removal of the solvent under reduced pressure, the residue was purified by column chromatography (silica, CH2Cl2 changing to CH2Cl2–2% MeOH). [Ir(5)(bpy)][PF6] was isolated as a yellow solid (119 mg, 0.1414 mmol, 87.7%). 1H NMR (500 MHz, CD3CN) δ/ppm 8.58 (dd, δ = 8.2, 1.1 Hz, 2H, H6E3), 8.22 (d, δ = 8.0, 1.5 Hz, 2H, H6B3), 8.09 (m, 2H, H6E3), 8.02–7.93 (overlapping m, 4H, H5E3−H5B3), 7.71 (m, 2H, H4E3), 7.31 (dd, δ = 6.9, 5.5, 1.2 Hz, 2H, H5E3), 7.45 (dd, δ = 8.2, 1.8 Hz, 2H, H4E3), 7.20 (dd, δ = 7.4, 5.8, 1.4 Hz, 2H, H4B3), 6.50 (d, d = 1.8 Hz, 2H, H4B3), 0.93 (s, 18H, H8Bu). 13C{1H} NMR (126 MHz, CD3CN, 295 K) δ/ppm 166.2 (CB2), 156.9 (CE2), 152.9 (CE5), 150.9 (CB5), 142.4 (CA5), 140.5 (CA6), 132.2 (CA1), 126.3 (CA3), 125.9 (CA4), 125.4 (CA2), 122.5 (CA1), 60.3 (CA4), 23.5 (CE1). IR (solid, ν/cm−1) 2927 (w), 1607 (w), 1575 (w), 1475 (m), 1440 (s), 1380 (w), 1337 (w), 1285 (m), 1193 (w), 1082 (m), 836 (s), 806 (m), 781 (m), 764 (m), 710 (m), 672 (m), 658 (m), 648 (m), 585 (m), 569 (m), 556 (s), 492 (m). UV/Vis (MeCN, 0.99 × 10−5 mol dm−3) ε/μm−1 cm−1 257 (59000), 295 sh (35000), 391 (47000), 420 sh (3400 dm3 mol−1 cm−1). Emission (MeCN, 0.99 × 10−5 mol dm−3, λexc = 262 nm): εmax = 493, 525 nm. ESI-MS m/z 970 (calc. 970). [Ir(6)(bpy)][PF6]. 1-Dodecanethiol (0.060 mL, 50.4 mg, 0.249 mmol) was added to a suspension of NaH (60% in mineral oil, 10.0 mg, 0.250 mmol) in DMF (2 mL) under N2. The mixture was stirred at room temperature for 10 min. [Ir(6)(bpy)][PF6] (53.0 mg, 0.0633 mmol) was added to the reaction mixture; this was heated at 120 °C for 1.5 h. The dark brown mixture was allowed to cool to room temperature and was then poured into a mixture of H2O and brine (3 : 1 by vol.,
20 mL). The resulting suspension was stirred for 30 min at room temperature. The brown-yellow precipitate was separated by filtration and was washed with H2O. The solid was redissolved in CH2Cl2 and the solution dried over Na2SO4. Solvent was removed in vacuo and the product was purified by column chromatography (silica, CH2Cl2 changing to CH2Cl2-2% MeOH). [Ir(6)2(bpyp)][PF6] was isolated as an orange solid (56.1 mg, 0.0467 mmol, 73.8%). 1H NMR (500 MHz, CD2CN) δ/ppm 8.54 (pseudo-dt, J = 8.3, 1.0 Hz, 2H, H3), 8.13 (pseudo-t, J = 7.9, 1.6 Hz, 2H, H4), 8.06 (m, 2H, H6), 8.00 (pseudo-dt, J = 8.4, 1.1 Hz, 2H, H8), 7.83 (m, 2H, H4), 7.68 (d, J = 8.3 Hz, 2H, H5), 7.58 (pseudo-dt, J = 5.9, 1.1 Hz, 2H, H2), 7.53 (dd, J = 7.7, 5.4, 1.2 Hz, 2H, H1), 7.00 (dd, J = 7.3, 5.8, 1.4 Hz, 2H, H7), 6.94 (dd, J = 8.2, 1.9 Hz, 2H, H4), 6.69 (d, J = 1.9 Hz, 2H, H8), 2.63 (m, 4H, HSCCH2), 1.40 (m, 4H, HSCCH2), 1.35–1.16 (m, 36H, H2CH2), 0.89 (t, J = 7.0 Hz, 6H, H3CH2), 12C{1H} NMR (126 MHz, CD3CN) δ/ppm 168.0 (C=O), 156.7 (C2), 151.8 (C=O), 150.1 (C=O), 141.6 (C=O), 141.5 (C=O), 140.3 (C=O), 139.4 (C=O), 129.4 (C=O), 128.7 (C=O), 126.1 (C2), 125.6 (C2), 123.9 (C2), 122.0 (C=O), 120.5 (C=O), 32.6 (C=CH2), 32.0 (C=CH2), 30.3 (C=CH2), 30.2 (C=CH2), 30.1 (C=CH2), 29.9 (C=CH2), 29.7 (C=CH2), 29.4 (C=CH2), 23.4 (C=CH2), 14.4 (C=CH2). IR (solid, ν/cm−1) 2922 (m), 2852 (m), 1606 (m), 1567 (m), 1537 (w), 1472 (m), 1446 (m), 1423 (m), 1373 (w), 1315 (w), 1261 (w), 1244 (w), 1164 (w), 1095 (m), 1062 (w), 1030 (w), 876 (w), 835 (s), 791 (m), 769 (s), 732 (m), 650 (w), 639 (w), 556 (s), 520 (w). UV/Vis (MeCN, 0.99 × 10−5 mol dm−3, λmax = 262 nm) 251 nm (ε = 25 000), 310 nm (ε = 25 000), 350 nm (ε = 7900), 390 nm (ε = 5000), 420 nm (ε = 3700 dm3 mol−1 cm−1). Emission (MeCN, 1.0 × 10−5 mol dm−3, λexc = 225 nm) λmax = 493, 524 nm. ESI-MS m/z 1121.6 [M − PF6]+ (calc. 1121.5). Found C 53.38, H 5.73, N 4.42%. 

Experimental Section

Crystallography

Data were collected on a Bruker-Nonius KappaAPEX diffractometer with data reduction, solution and refinement using the programs APEX234 and SHELXL97.25 ORTEP-type diagrams and structure analysis used Mercury v. 3.0.26,27 Crystallographic data are given in Table 1.

Results and discussion

Ligand synthesis and characterization

The fluoro compound H1 is a convenient precursor to each of H2, H4 and H6. The thiomethyl group in H2 is readily introduced by reaction of H1 with Na2Me in NMP under microwave conditions. The 93% yield of H2 is superior to the 10% obtained using the reported Ullmann coupling of 2-bromopyridine and 4-bromothianisole.23 The synthesis of H4 was adapted from that reported for the formation of 2(4-butyliophenyl)pyridine,28 and H6 was prepared in a similar manner. For each, the appropriate thiol was treated with NaOH in DMF to generate the corresponding thiolate to displace the fluoro group from H1. Of the oxidation strategies tried for conversion of the thiolates to corresponding sulfones, use of Na2WO4–H2O229 proved to be the most efficient.

Compounds H2–H8 were characterized by routine spectroscopic methods, mass spectrometry and elemental analysis. The base peak in the electrospray mass spectrum of H2, H3, H4, H5 and H7 corresponded to the [M + H]+ with the isotopic distribution matching that calculated in each case. For H6, a parent ion (m/z 355.7) was observed in the MALDI-TOF mass spectrum, but no [M + H]+ ion was detected in the ESI-MS.1H and 13C NMR spectra were assigned using 2D methods (COSY, HSQC and HMBC) and were consistent with the structures shown in Scheme 1.

Single crystals of H3 were grown by overlaying a CHCl3 solution with hexanes, and of H5 by overlaying a CH2Cl2 solution with hexanes. The structures are shown in Fig. 1 and 2. Both compounds crystallize in the monoclinic space group C2/c. Detailed analyses of the structures of a range of aryli alkyl sulfones30,31 and diaryl sulfones30,31 illustrate the formation both intra- and intermolecular CH···O hydrogen bonds. In H3, the O1···S1−C9−C10 and O2···S1−C9−C8 torsion angles are −25.0(1) and 28.2(1)°, respectively, leading to intramolecular O1···H10a and O2···H8a contacts of 2.60 and 2.64 Å. In H5, the corresponding angles (O1···S1−C9−C8 and O2···S1−C9−C10)
Table 1  Crystallographic data

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Fig. 1 ORTEP representation of the structure of H3 (ellipsoids plotted at 40% probability level). Selected bond lengths and angles: S1–O2 = 1.4411(9), S1–O1 = 1.4434(10), S1–C12 = 1.7569(14), S1–C9 = 1.7575(11) Å; S2–O1 = 1.1819(6), O2–S1–C12 = 108.03(7), O1–S1–C12 = 108.11(6), O2–S1–C9 = 109.20(6), O1–S1–C9 = 108.45(6), C12–S1–C9 = 103.93(6)°.

Fig. 2 ORTEP representation of the structure of H5 (ellipsoids plotted at 40% probability level). Selected bond distances and angles: S1–O2 = 1.4378(12), S1–O1 = 1.4402(12), S1–C12 = 1.8190(16), S1–C9 = 1.7727(15) Å; S2–S1–O1 = 118.85(8), S2–S1–C9 = 107.48(7), O1–S1–C9 = 107.03(7), O2–S1–C12 = 108.05(8), O1–S1–C12 = 107.50(8), C9–S1–C12 = 107.46(7)°.

are −23.1(1) and 24.6(1)° with O1···H8a and O2···H10a separations of 2.57 and 2.64 Å. The dihedral angles between the phenyl and pyridine rings are 17.7° in H3, and 37.7° in H5. This marked difference is associated with face-to-face π-stacking of phenyl and pyridine rings in H3 (but not in H5). Centrosymmetric pairs of H3 molecules interact through a slipped arrangement of aromatic rings (Fig. 3a) with an intercentroid distance of 3.81 Å. The sulfone group engages in hydrogen-bonded contacts to the methyl groups of two adjacent molecules and the pyridine ring CH of a third molecule. In contrast, a primary packing interaction in H5 involves CHphenyl···O sulfone contacts resulting in the formation of ribbons of hydrogen-bonded molecules (Fig. 3b). The butyl groups protrude along one side of the ribbon, and pairs of adjacent ribbons associate through short CHbutyl···Npyridine contacts (2.73 Å) giving an extended domain of butyl units sandwiched between aromatic domains (Fig. 3c).

Synthesis and characterization of [Ir2(C=N)2Cl2] dimers

Complexes in the [Irppy]3(N=N) family are usually synthesized by reaction between the N=N ligand and the chlorido-bridged dimer [Ir2(ppy)3Cl2]. Typically, this dimer is prepared from the reaction of IrCl3-nH2O with Hppy, 3,3,4. Although [Ir2(1),Cl2] (prepared by the latter method) has previously been described, 6 the remaining chlorido-bridged precursors to the target complexes [Ir2(C=N)2(ppy)] with C=N = 2 to 7 have not, to the best of our knowledge, been previously reported.

The reaction of IrCl3-nH2O with sulfones H5 and H7 proceeded smoothly under reflux in a mixture of 2-ethoxyethanol and water (Scheme 2). The compounds [Ir2(5),Cl2] and...
[Ir2(7)Cl4] were isolated as yellow solids. The 1H and 13C NMR spectra of the complexes showed negligible impurities and the compounds were used in the next step (see the next section) without purification. The NMR spectra were assigned using routine 2D methods and were in accord with the structures shown in Scheme 2. For a MeOH solution of [Ir2(5)Cl4], the second most intense peak in the electrospray mass spectrum came at m/z 741.2 and as assigned to the [Ir(5)Cl]⁺ ion. The base peak at m/z 782.1 and a lower intensity peak at m/z 583.1 arose from [Ir(5)(MeCN)]⁺ and [Ir(5)(MeCN)]⁺, respectively; we assume that the MeCN arises from the eluent in the LC column of the LC-ESI-MS. The isotope distributions for each peak matched the calculated patterns. MALDI-TOF mass spectrometry proved more amenable to observing a mass spectrum of [Ir2(7)Cl4], with the base peak at m/z 965.9 corresponding to [Ir7]⁺.

Attempts to prepare the dimers [Ir2(C–N)3Cl4] with C–N = 2, 3 or 4 from reactions of H2, H3 or H4 with IrCl3·H2O were unsuccessful. We therefore adopted an alternative strategy which involves the reaction of the conjugate acid of the cyclo-metalling ligand with [Ir2(COD)2Cl4]. Unfortunately, reaction of H2 with [Ir2(COD)2Cl4] gave an insoluble solid which could not be characterized, and attempts to prepare and isolate [Ir2(2)Cl4] were abandoned. We note that the latter insoluble material reacted with bpy in MeOH to give a mixture of products rather than a salt of the desired [Ir2(bpy)]⁺.

The reaction of [Ir2(COD)2Cl4] with H3 and H4 (Scheme 2) yielded [Ir2(3)Cl4] and [Ir2(4)Cl4] as yellow powders in good yields. As judged by 1H NMR spectroscopy, the crude products were pure enough to be used directly in the next step (see the next section). The solution 1H and 13C NMR spectra of [Ir2(3)Cl4] were assigned by COSY, HMQC and HMBC methods and were in accord with the structures in Scheme 2. In contrast, [Ir2(4)Cl4] is poorly soluble in most common organic solvents. The 1H NMR spectrum was assigned using a COSY spectrum and by comparison with those of the other dimers, but the 1D 13C NMR spectra of [Ir2(3)Cl4] showed peaks at m/z 657.1 and 698.2 assigned to [Ir(3)Cl]⁺ and [Ir(3)(MeCN)]⁺, respectively; (the origin of the MeCN is explained above). Analogous peaks were observed in the ESI mass spectrum of [Ir2(4)Cl4].

The synthesis of [Ir2(6)Cl4] could not be achieved by the reaction of [Ir2(COD)2Cl4] with H6, and unreacted ligand was recovered from the reaction mixture after 22 hours reflux in 2-ethoxyethanol. Despite the widespread synthetic use of [Ir2(C–N)4Cl4] dimers, X-ray diffraction data for this family of complexes in which C–N is (or is derived from) a 2-phenylpyridine ligand remains sparse. A search of the Cambridge Structural Database26 (CSD, v. 5.34 with November 2012, and February and May 2103 updates) using Conquest v. 1.3526 generated only nine hits,17–44 including the structures of the enantiomerically pure Δ,Δ- and Δ,Δ-forms42 of [Ir2(ppy)4Cl4] as well as that of the centrosymmetric Δ,Δ-form.41 In addition, we have recently
reported the structure of \([\text{Ir}_2(\text{dfppz})_2(\mu\text{-Cl})_2] \text{CH}_2\text{Cl}_2\) (Hdpfpz = 1-(2,4-difluorophenyl)-1H-pyrazole). Single crystals of \([\text{Ir}_2(\text{C}^\text{N})_2]_2\text{CH}_2\text{Cl}_2\) were grown from a \text{CH}_2\text{Cl}_2 solution of the complex overlaid with \text{Et}_2\text{O}. The structure of the dimer is shown in Fig. 4; each iridium atom is in an octahedral environment. The complex crystallizes in the orthorhombic space group \text{Pbca} and the asymmetric unit contains the \(\Lambda,\Lambda\)-enantionic form with both the \(\Lambda,\Lambda\)- and \(\Delta,\Delta\)-forms present in the lattice. As in other \([\text{Ir}_2(\text{C}^\text{N})_4]\) dimers and in mononuclear \([\text{Ir}(\text{C}^\text{N})_2(\text{N}^\text{N})]^{+}\) cations, the two cyclometallated ligands are arranged with the \(\text{N}\)-donors \text{trans} to di sulfone contact. 

**Fig. 4** ORTEP representation of \([\text{Ir}_2(\text{C}^\text{N})_2]_2\text{Cl}_2\) (ellipsoids plotted at 30% probability level and H atoms omitted). Important bond parameters: \(\text{Ir}1–\text{C19} = 1.984(8), \text{Ir}1–\text{C7} = 1.988(8), \text{Ir}1–\text{N1} = 2.050(7), \text{Ir}1–\text{N2} = 2.057(7), \text{Ir}1–\text{C11} = 2.486(2), \text{Ir}1–\text{C21} = 2.512(2), \text{Ir}2–\text{C43} = 1.995(8), \text{Ir}2–\text{C31} = 2.015(9), \text{Ir}2–\text{N4} = 2.043(7), \text{Ir}2–\text{N3} = 2.053(7), \text{Ir}2–\text{C2} = 2.503(2), \text{Ir}2–\text{C21} = 2.504(2), \text{S1}–\text{O3} = 1.404(9), \text{S1}–\text{O4} = 1.441(8), \text{S1}–\text{C21} = 1.778(9), \text{S1}–\text{C24} = 1.786(10), \text{O1}–\text{S2} = 1.422(8), \text{O2}–\text{S2} = 1.439(7) \text{Å}; \text{C11}–\text{Ir1}–\text{C12} = 84.46(7), \text{C12}–\text{Ir1}–\text{C11} = 84.30(6), \text{C19}–\text{Ir1}–\text{N1} = 80.2(3), \text{C7}–\text{Ir1}–\text{N2} = 80.9(3), \text{C31}–\text{Ir2}–\text{N3} = 80.7(3), \text{O3}–\text{S3}–\text{O4} = 117.5(5), \text{O1}–\text{S2}–\text{O2} = 117.0(5), \text{O6}–\text{S3}–\text{O5} = 117.9(5), \text{O7}–\text{S4}–\text{O8} = 117.16(9).**

**Synthesis and characterization of \([\text{Ir}(\text{C}^\text{N})_2(\text{bpy})]^{+}\) complexes**

Synthesis of the \([\text{Ir}(\text{C}^\text{N})_2(\text{bpy})]^{+}\) complexes was initially approached using the established methodology of treating the appropriate \([\text{Ir}_2(\text{C}^\text{N})_4]\) dimer with two equivalents of bpy. This method was successful in five out of six cases (Scheme 3a). \([\text{Ir}(1\text{bpy})]^{+}\), \([\text{Ir}(3\text{bpy})]^{+}\), \([\text{Ir}(4\text{bpy})]^{+}\) and \([\text{Ir}(5\text{bpy})]^{+}\) were isolated in yields ranging from 70.3 to 87.7%. Purification of \([\text{Ir}(4\text{bpy})]^{+}\) required a series of chromatographic and precipitation steps (see Experimental section), but a high yield was still obtained. Purification of \([\text{Ir}(7\text{bpy})]^{+}\) also required two chromatography columns and the final yield was only 30.0%; unreacted dimer was not recovered and the side products were not identified. Since the dimer \([\text{Ir}_2(6\text{Cl})_4]\) could not be prepared (see above), we adopted a nucleophilic substitution approach to prepare \([\text{Ir}6(\text{bpy})]^{+}\) from \([\text{Ir}(1\text{bpy})]^{+}\) (Scheme 3b).

The fluoro-derivative was treated with 1-dodecanethiol in the presence of sodium hydride and, after workup, \([\text{Ir}(6\text{Cl})]^{+}\) was obtained in 73.8% yield. We have recently demonstrated that the presence of small amounts of chloride ion can have significant negative impact on the performance of materials in LECs, and all new compounds were shown to exhibit no changes in their \(^1\text{H}\) NMR spectra upon the addition of \([^\text{Bu}_4\text{N}]^+\).46

The base peak in the electrospray mass spectrum of each \([\text{Ir}(\text{C}^\text{N})_2(\text{bpy})]^{+}\) complex consisted of a peak envelope corresponding to \([\text{M}–\text{PF}_6]^–\) exhibiting the characteristic isotopic distribution for iridium. The \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra of each complex were consistent with a \(\Delta,\Delta\)-symmetric cation. Fig. 5 shows the \(^1\text{H}\) NMR spectrum of \([\text{Ir}(5\text{bpy})]^{+}\) as a representative example. Signals in the \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra were assigned using a combination of COSY, HMQC and HMBC methods. The \(^1\text{H}\) NMR signal for the \(\text{b}^4\text{yl} \) group in \([\text{Ir}(\text{bpy})]^{+}\) appears at \(\delta 1.00\) ppm and shifts to lower frequency (\(\delta 0.93\) ppm) in the analogous sulfone derivative \([\text{Ir}(\text{bpy})]^{+}\). The \(^{13}\text{C}\) NMR resonance for the primary carbon atom in the \(\text{b}^4\text{yl} \) group shifts from \(\delta 31.1\) to 23.5 ppm on going from \([\text{Ir}(\text{4bpy})]^{+}\) to \([\text{Ir}(5\text{bpy})]^{+}\), while the \(S\)-attached \(^{13}\text{C}\) nucleus resonates at \(\delta 46.8\) and 60.3 ppm, respectively, in the sulfane and sulfone complexes. In \([\text{Ir}(6\text{bpy})]^{+}\) and \([\text{Ir}(7\text{bpy})]^{+}\), the \(\text{SCH}_2\) unit is characterized by signals at \(\delta(^1\text{H}) 2.63\) ppm and \(\delta(^{13}\text{C}) 32.0\) ppm in the sulfane and \(\delta(^1\text{H}) 2.87\) ppm and \(\delta(^{13}\text{C}) 56.3\) ppm in the sulfone. Across the series of \([\text{Ir}(\text{C}^\text{N})_2(\text{bpy})]^{+}\) complexes, the only proton signal to be noticeably affected is that assigned to \(\text{H}^\text{66}\) (see Scheme 3) since only this bpy proton is directed towards the substituted phenyl ring. As expected, signals arising from the phenyl-ring protons (\(\text{H}^\text{A1}, \text{H}^\text{A4}\) and \(\text{H}^\text{A6}\)) undergo the most significant changes in chemical shift. For each pair of sulfane and sulfone complexes, signals for \(\text{H}^\text{A3}\), \(\text{H}^\text{A4}\) and \(\text{H}^\text{A6}\) all move to higher frequency (\(\Delta \delta\) is in the range 0.20 and 0.56 ppm). Signals for protons \(\text{H}^\text{A6}\) and \(\text{H}^\text{A4}\) is disordered and has been modelled over two sites of fractional occupancies 0.62 and 0.38.

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undergo the largest shifts to lower frequency in the fluoro-derivative, appearing at $\delta$ 5.89 and 6.81 ppm, respectively.

Single-crystal data were collected for $\text{[Ir}^1(\text{bpy})_2\text{][PF}_6]$ (crystals being grown from MeCN or CH$_2$Cl$_2$ solutions of the complex overlaid with Et$_2$O, respectively) and fortuitously resulted in the determination of the structures of $\Delta\text{-[Ir}^1(\text{bpy})_2\text{][PF}_6]$ and $\text{rac-4-[Ir}^1(\text{bpy})_2\text{][PF}_6]$-Et$_2$O·2CH$_2$Cl$_2$.

Enantiomerically pure $\Delta\text{-[Ir}^1(\text{bpy})_2\text{][PF}_6]$ crystallizes in the trigonal space group $P3_121$ and Fig. 6 shows the structure of the $\Delta\text{-[Ir}^1(\text{bpy})_2\text{]}^+$ cation. The octahedral environment of Ir1 with trans-arrangement of the N donors (N3 and N4) of the cyclo-metallating ligands is as expected, and bond parameters (see Fig. 6 caption) are typical. We note that the packing interactions are predominantly CH⋯F contacts involving the F atoms of both the [PF$_6$]$^-$ anions and the fluorophenyl rings. There are no π-stacking interactions between arene rings of adjacent cations. This is in contrast to those observed in rac-[Ir1(2(bpy)]$\text{[PF}_6]$ described below.
lies partly over the pyridine π of a bpy ligand; the rings are slipped such that the F atom trident distances are 2.59 and 3.03 Å. Face-to-face Δ between crystallographically independent \((bpy)\]^+ cations extend beyond the single pair in the asymmetric unit. Extensive CH···F contacts contribute to the crystal packing. The CH$_2$Cl$_2$ solvent molecule is ordered, and the Et$_2$O molecule is half occupancy.

### Photophysical properties

The solution electronic absorption spectra of \([Ir(C^N)_2(bpy)][PF_6]\) \(C^N = 1, 3–7\) are shown in Fig. 9. All are dominated by intense high-energy bands which we assign to ligand-centred (LC), spin-allowed π*←π or π*←n transitions. The origin of the lower intensity and broader spectrum of \([Ir(6)_2(bpy)][PF_6]\) is not readily interpreted, but reproducibility with different batches of compound was confirmed. All spectra extend into the visible region, consistent with the yellow colour of the compounds \([Ir(C^N)_2(bpy)][PF_6]\) \(C^N = 1, 3–5, 7\) and orange colour of \([Ir(6)_2(bpy)][PF_6]\). Absorptions at wavelengths in the approximate range 350 to 450 nm are attributed to low intensity\(^1\)MLCT and \(^1\)LLCT bands.

Excitation of MeCN solutions of the complexes with λ$_{\text{exc}}$ varying between 269 and 300 for \([Ir(1)_2(bpy)][PF_6]\), and between 252 and 400 nm for the other complexes results in the emission spectra shown in Fig. 10. The spectra are invariant of chosen values of λ$_{\text{exc}}$ in the above ranges with the exception of the appearance of the relevant harmonic band. The complexes \([Ir(1)_2(bpy)][PF_6]\, \[Ir(4)_2(bpy)][PF_6]\, \[Ir(6)_2(bpy)][PF_6]\) \((i.e.\) fluoro and sulfone substituents on the C^N ligands) are yellow emitters and the emission bands are broad and featureless. In contrast, \([Ir(3)_2(bpy)][PF_6]\, \[Ir(5)_2(bpy)][PF_6]\) and \([Ir(7)_2(bpy)][PF_6]\) are green emitters and the emission spectra exhibit vibrational structure. The emitting state of \([Ir(C^N)_2(N^N)][PF_6]\) is the lowest energy triplet state which may contain contributions from \(^3\)MLCT, \(^3\)LC and \(^3\)LLCT states.\(^1\) Significant charge-transfer contributions lead to broad emission bands, but when the CT contributions are small, structured emissions are observed as is the case for the sulfone-containing complexes \([Ir(3)_2(bpy)][PF_6]\, \[Ir(5)_2(bpy)][PF_6]\) and \([Ir(7)_2(bpy)][PF_6]\). Table 2 summarizes the room temperature solution photophysical properties of the complexes. Compared...
Replacement of F by the introduction of the electron-withdrawing fluoro-groups. 

Table 2

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{\text{exc}}$/nm</th>
<th>$\lambda_{\text{em}}$/nm</th>
<th>$\tau_{1/2}$/μs</th>
<th>PLQY/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(ppy)$_2$(bpy)][PF$_6$]</td>
<td>269</td>
<td>557</td>
<td>0.224</td>
<td>36</td>
</tr>
<tr>
<td>[Ir(ppy)$_2$(bpy)][PF$_6$]</td>
<td>262</td>
<td>493, 525</td>
<td>2.33</td>
<td>74</td>
</tr>
<tr>
<td>[Ir(ppy)$_2$(bpy)][PF$_6$]</td>
<td>260</td>
<td>568</td>
<td>0.528</td>
<td>24</td>
</tr>
<tr>
<td>[Ir(ppy)$_2$(bpy)][PF$_6$]</td>
<td>262</td>
<td>493, 523</td>
<td>3.36</td>
<td>64</td>
</tr>
<tr>
<td>[Ir(ppy)$_2$(bpy)][PF$_6$]</td>
<td>252</td>
<td>577</td>
<td>0.369</td>
<td>15</td>
</tr>
<tr>
<td>[Ir(ppy)$_2$(bpy)][PF$_6$]</td>
<td>262</td>
<td>493, 524</td>
<td>3.21</td>
<td>64</td>
</tr>
</tbody>
</table>

$^{a} \lambda_{\text{exc}} = 280$ nm for complexes with 3, 5 and 7; 340 nm for complexes with 1, 4 and 6.

to the parent complex [Ir(ppy)$_2$(bpy)][PF$_6$] which emits at 585 nm (de-aerated MeCN, 298 K),$^{31}$ [Ir(ppy)$_2$(bpy)][PF$_6$] shows an emission at 557 nm, consistent with a lowering of the energy of the HOMO and widening of the HOMO–LUMO gap upon the introduction of the electron-withdrawing fluoro-groups. Replacement of F by 1BuS on going from [Ir(1)$_2$(bpy)][PF$_6$] to [Ir(4)$_2$(bpy)][PF$_6$] results in an 11 nm red-shift in the emission, and a change from 1-butyl to 1-dodecyl sulfane gives a further 9 nm red-shift. Both sulfane complexes are blue-shifted with respect to [Ir(ppy)$_2$(bpy)][PF$_6$]. The three sulfane complexes exhibit almost identical solution emission spectra (Fig. 10 and Table 2) with $\lambda_{\text{em}}$ blue-shifted by 92 nm with respect to [Ir(ppy)$_2$(bpy)][PF$_6$]. The photoluminescence quantum yields (PLQY) and lifetimes ($\tau_{1/2}$) of the solution-state emissions should be compared with values of 14% and 0.43 μs measured for [Ir(ppy)$_2$(bpy)][PF$_6$] under analogous room temperature conditions.$^{31}$ Substantial enhancement of the PLQY is observed for the most electron-withdrawing (F and SO$_2$R) substituents (Table 2). The value of 74% for [Ir(ppy)$_2$(bpy)][PF$_6$] (SO$_3$Me substituents) is particularly high, and it appears that increasing the steric bulk of the alkyl substituent may be detrimental to the PLQY value. We note that if solution samples are not de-aerated, the PLQY values are dramatically reduced to values of between 2.6% for [Ir(6)$_2$(bpy)][PF$_6$] and 5.5% for [Ir(5)$_2$(bpy)][PF$_6$], consistent with strong quenching of the phosphorescence by oxygen.

The emission lifetimes for the six complexes in de-aerated MeCN were measured under argon and are given in Table 2. The longest lived emission (3.3 μs) is for [Ir(5)$_2$(bpy)][PF$_6$]; in general, the complexes in which the cyclometallated ligand bears a sulfane substituent exhibit lifetimes that are an order of magnitude longer than those containing fluoro or sulfane group.

Table 3

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{\text{em}}$/nm</th>
<th>$\lambda_{\text{em}}$ (for PLQY)/nm</th>
<th>PLQY/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(1)$_2$(bpy)][PF$_6$]</td>
<td>547</td>
<td>269</td>
<td>23</td>
</tr>
<tr>
<td>[Ir(3)$_2$(bpy)][PF$_6$]</td>
<td>532</td>
<td>262</td>
<td>6.6</td>
</tr>
<tr>
<td>[Ir(4)$_2$(bpy)][PF$_6$]</td>
<td>553</td>
<td>260</td>
<td>4.9</td>
</tr>
<tr>
<td>[Ir(5)$_2$(bpy)][PF$_6$]</td>
<td>535</td>
<td>262</td>
<td>15</td>
</tr>
<tr>
<td>[Ir(6)$_2$(bpy)][PF$_6$]</td>
<td>558</td>
<td>252</td>
<td>2.6</td>
</tr>
<tr>
<td>[Ir(7)$_2$(bpy)][PF$_6$]</td>
<td>537</td>
<td>262</td>
<td>4.2</td>
</tr>
</tbody>
</table>

$^a \lambda_{\text{exc}} = 405$ nm.
Table 4  Cyclic voltammetric data with respect to Fe/CFe⁺ in MeCN solutions with [Bu₄N][PF₆] as supporting electrolyte, and a scan rate of 0.1 V s⁻¹ (ir = irreversible; qr = quasi-reversible)

<table>
<thead>
<tr>
<th>Complex</th>
<th>E°/V</th>
<th>E½/ν</th>
<th>ΔE½/ν</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(1)₃(bpy)][PF₆]</td>
<td>+1.07²qr</td>
<td>−1.74, −2.41³ir, −2.54</td>
<td>2.81³</td>
</tr>
<tr>
<td>[Ir(3)₃(bpy)][PF₆]</td>
<td>+1.18</td>
<td>−1.72, −2.16, −2.06³ir</td>
<td>2.90</td>
</tr>
<tr>
<td>[Ir(4)₃(bpy)][PF₆]</td>
<td>+1.04³ir</td>
<td>−1.75, −2.48³ir, −2.57³ir</td>
<td>2.79</td>
</tr>
<tr>
<td>[Ir(5)₃(bpy)][PF₆]</td>
<td>+1.19</td>
<td>−1.73, −2.18, −2.43³ir</td>
<td>2.92</td>
</tr>
<tr>
<td>[Ir(6)₃(bpy)][PF₆]</td>
<td>+0.82³ir</td>
<td>−1.76, −2.53³ir</td>
<td>2.79</td>
</tr>
<tr>
<td>[Ir(7)₃(bpy)][PF₆]</td>
<td>+1.25</td>
<td>−1.71, −2.16, −2.39³ir</td>
<td>2.96</td>
</tr>
</tbody>
</table>

Electrochemistry

Each of the [Ir(C=N)₃(bpy)][PF₆] complexes (C=N = 1, 3–7) is electrochemically active, and cyclic voltammetric data are given in Table 4. Unless stated otherwise, the electrochemical processes are reversible or near-reversible. Each fluoro or sulfone derivative (C=N = 1, 3, 5, 7) exhibits an iridium-based reversible or quasi-reversible oxidation process at more positive potential than [Ir(pppy)₃(bpy)][PF₆] (E°/V vs internal Fe/CFe⁺).¹³ consistent with the introduction of strongly electron-withdrawing substituents on the cyclometallated ligands. Compounds [Ir(4)₃(bpy)][PF₆] and [Ir(6)₃(bpy)][PF₆] also undergo irreversible oxidations at +1.04 and +0.82 V, respectively, which we have not investigated in detail. Two or three ligand-based reductions are observed for each complex, and the E½ potentials in Table 4 compare with −1.77 and −2.60 V for [Ir(pppy)₃(bpy)][PF₆].³¹ The LUMO is localized on the bpy ligand,¹³ and the values of the reduction potentials are consistent with the processes being bpy-based, being little affected by the electronic changes made to the C=N ligand across the series of compounds.

The electrochemical band gaps, ΔE½ (Table 4) are all larger than the 2.61 V in [Ir(pppy)₃(bpy)][PF₆],¹³ consistent with the lowering of the HOMO upon introducing electron-withdrawing substituents into the C=N domain. As expected, the largest band gaps are observed for the sulfone derivatives (C=N = 3, 5, 7). The trends in Table 4 parallel those observed in the solution emission spectra (Table 2). The slightly smaller values of ΔE½ on going from fluoro to sulfane derivatives are consistent with the observed red-shift in emission maxima, while the increase in ΔE½ on going to sulfones [Ir(C=N)₃(bpy)][PF₆] (C=N = 3, 5, 7) corresponds to the blue-shift in the emissions compared to those of [Ir(C=N)₃(bpy)][PF₆] (C=N = 1, 4, 6).

Conclusions

We have prepared a series of [Ir(C=N)₃(bpy)][PF₆] complexes in which the cyclometallating ligands contain electron-withdrawing fluoro, sulfane or sulfone groups. The well-established synthetic route of treatment of a [Ir₂(C=N)₄Cl₂] dimer with the bpy ligand,¹ and the values of the reduction potentials are consistent with the processes being bpy-based, being little affected by the electronic changes made to the C=N ligand across the series of compounds.

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Notes and references