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)][PF_6] complexes in which the cyclometallating ligands contain fluoro, sulfane or sulfone groups is 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-butylnitrosyphosphoryl)pyridine (H4), 2-(4-butylnitrosyphosphoryl)pyridine (H5), 2-(4-dodecylsulfonylphenyl)pyridine (H6), 2-(4-dodecylsulfonylphenyl)pyridine (H7). The single crystal structures of H3 and H5 are described. [Ir(C^N)2(bpy)][PF_6] complexes which perform efficiently under bias in LECs.13 The

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-withdrawing 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 coworkers 8 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'-Bu2-bpy)][PF_6] 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.9

Less well explored than the use of fluoro-substituents is the incorporation of SR, SOR and SO_2R electron-withdrawing substituents, either for functionalization of the C^N or N,N ligand.11–13 Among these earlier studies is the use of 1-4-(methylsulfonyl)phenyl)-1H-pyrazole (Hmsppz) as the cyclometallating ligand in a series of green emitting [Ir(msppz)2(N^N)][PF_6] complexes which perform efficiently under bias in LECs.12 The
TOF mass spectra were recorded on Bruker esquire 3000plus.

Cyclometallating ligands may be a viable alternative to the
more commonly employed fluoro-substituted C=N ligands.

We present here a systematic study of the effects of functionalizing the cyclometallating Hppy ligand with increasing 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 fluoro-substituents is rather well understood, ligand H1 was chosen to provide the benchmark complex [Ir(1)(bpy)]2+ to which to relate the properties of the sulfane and sulfene derivatized complexes. The increase in electron-withdrawing properties on changing from SMe and SO2Me in compounds H2 to H3 (Scheme 1) is reflected in the different Hammett parameters (SMe, σ 0.15, S0.00; SO2Me, σ 0.60, 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′-methylsulfonyl-2,2′,6′,2′″-terpyridine), the sulfene 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.

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 Daltonics 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]2 (COD = cycloocta-1,5-diene) and [Ir1(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 aluminum 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-pyrrolidinone (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, H′′′), 7.93 (m, 2H, H′), 7.76–7.67 (overlapping m, 2H, H′′), 7.34 (m, 2H, H′′′), 7.21 (ddd, J = 7.3, 4.8, 1.4 Hz, 1H, H′′′′), 2.53 (s, 3H, HMe). 13C{1H} NMR (126 MHz, CDCl3) δ/ppm 157.0 (CB2), 149.8 (CB6), 139.9 (CA4), 136.9 (CB4), 136.2 (CA1), 127.3 (CA′), 126.5 (CA′′), 122.1 (CB′′′′), 120.2 (CB′′), 15.7 (CMe). IR (solid, 1/cm–1) 3086 (w), 3046 (w), 3002 (w), 2981 (w), 2941 (w), 2892 (w), 1982 (w), 1910 (w), 1767 (w), 1661 (w), 1605 (w), 1591 (w), 1256 (w), 1227 (w), 1190 (m), 1154 (w), 1121 (m), 1098 (m), 1089 (m), 1057 (w), 1008 (m), 988 (m), 969 (m), 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 dissolved in MeOH (35 mL). H2O (30%, 1.20 mL, 1.36 g) was 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 8.75 (ddd, J = 4.7, 1.8, 1.0 Hz, 1H, H′′′), 8.21 (m, 2H, H′′′′), 8.10–7.99 (m, 2H, H′′′′′), 7.87–7.75 (m, 2H, H′′′′′′), 7.34 (ddd, J = 7.0, 4.8, 1.6 Hz, 1H, H′′′′′′), 3.09 (s, 3H, HMe). 13C{1H} NMR (126 MHz, CDCl3) δ/ppm 155.4 (C′′′′′′), 150.2 (C′′′′′), 144.7 (C′′′′), 140.7 (C′′′), 137.3 (C′′′), etc.

Scheme 1 Structures of the conjugate acids of the C=N ligands with labelling for NMR spectroscopic assignments.
Compound H4. NaH (60% suspension in mineral oil, 235 mg, 5.88 mmol) was suspended in DMF (8 mL) under N2. 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. The precipitate was separated by filtration, washed with H2O and dried under vacuum. H4 was isolated as a pale brown solid (704 mg, 2.89 mmol, 100%). M.p. 90.7 °C. 1H NMR (500 MHz, CDCl3) δ/ppm 8.75 (ddd, J = 4.8, 1.9, 1.1 Hz, 1H, HB6), 7.95 (m, 2H, HA3), 7.81–7.87 (overlapping m, 2H, HBr), 7.64 (m, 2H, HAr-B2), 7.26 (m, 1H, HAr-B1), 1.32 (s, 9H, HBr). 13C{1H} NMR (126 MHz, CDCl3) δ/ppm 159.0 (CBr), 149.9 (CBr), 139.8 (CAr-B1), 137.9 (CAr-B2), 137.0 (CAr), 133.9 (CAr), 127.0 (CBr), 122.5 (CBr), 120.8 (CBr), 64.6 (CBr), 31.2 (CBr). IR (solid, ν/cm–1) 1642 (m), 1429 (m), 1393 (w), 1374 (w), 1364 (w), 1284 (w), 1264 (w), 1251 (m), 1211 (w), 1191 (w), 1177 (w), 1150 (w), 1127 (m), 1102 (m), 1089 (w), 988 (m), 844 (s), 780 (s), 748 (s), 725 (m), 682 (w), 633 (m), 618 (w), 579 (w), 560 (m), 520 (m), 491 (m). ESI-MS m/z 244.0 [M + H]+ (calc. 244.1). Found C 77.75, H 9.76, N 3.94%. Compound H5. H5 (501 mg, 2.06 mmol) and sodium tungstate dihydrate (352 mg, 1.07 mmol) were dissolved in MeOH (13 mL). H2O2 (30%, 0.500 mL, 568 mg, 5.80 mmol) was added and the suspension was stirred at room temperature for 20 h. CH2Cl2 (100 mL) was then added and the residue was purified by column chromatography (silica, CH2Cl2 with 1% MeOH). H5 was isolated as a white powder (473 mg, 1.72 mmol, 83.5%). M.p. 174.4 °C. 1H NMR (500 MHz, CDCl3) δ/ppm 8.74 (ddd, J = 4.8, 1.8, 1.0 Hz, 1H, HBr), 7.91 (m, 2H, HAr-B2), 7.78–7.63 (overlapping m, 2H, HBr), 7.39 (m, 2H, HA3), 7.21 (ddd, J = 7.2, 4.8, 1.4 Hz, 1H, HAr-B1), 2.97 (m, 2H, HBr). 13C{1H} NMR (126 MHz, CDCl3) δ/ppm 146.2 (CBr), 137.4 (CBr), 137.3 (CAr-B2), 137.0 (CBr), 128.3 (CBr), 127.4 (CBr), 126.0 (CBr), 122.4 (CBr), 120.3 (CBr), 63.6 (CBr), 31.4 (CBr). IR (solid, ν/cm–1) 1689 (m), 1641 (m), 1591 (w), 1570 (w), 1543 (w), 1521 (m), 1502 (m), 1490 (m), 1485 (m), 1472 (m), 1465 (m), 1447 (m), 1405 (m), 1396 (w), 1386 (w), 1376 (m), 1366 (w), 1354 (m), 1339 (w), 1329 (w), 1285 (w), 1275 (w), 1260 (w), 1250 (w), 1235 (w), 1225 (w), 1215 (w), 1205 (w), 1195 (w), 1185 (m), 1175 (m), 1165 (w), 1151 (w), 1107 (m), 1098 (m), 1059 (w), 1031 (w), 1014 (m), 989 (m), 934 (w), 899 (w), 844 (s), 780 (s), 748 (s), 725 (m), 682 (w), 633 (m), 618 (w), 579 (w), 560 (m), 520 (m), 491 (m). ESI-MS m/z 244.0 [M + H]+ (calc. 244.1). Found C 77.75, H 9.76, N 3.94%.
2-ethoxyethanol (3 mL) and H2O (1 mL) under N2 atmosphere. IrCl3·7H2O (395 mg, 1.69 mmol) was suspended in degassed 2-ethoxyethanol and H2O (1 mL) under N2. The mixture was heated at 110 °C for 1.5 h in a micro-reactor. The precipitate was separated by filtration, washed with H2O and EtOH, and dried under vacuum.

1H NMR (500 MHz, CDCl3) δ/ppm 9.23 (s, 36H, HMe). 13C{1H} NMR (126 MHz, CDCl3) δ/ppm 167.1 (CB2), 151.8 (CCH2), 149.2 (CCH2), 138.0 (CB4), 128.1 (CA6), 124.3 (CB5), 121.0 (CA4), 120.6 (CB3), 44.3 (CMe). ESI-MS m/z 675.1 [Ir3]+ (calc. 675.1), 698.2 [Ir3]+(MeCN)]+ (calc. 698.1).

[Ir4]4+. Compound H4 (401 mg, 1.65 mmol) was dissolved in 2-ethoxyethanol (18 mL) in a vial and the solution was added and the mixture was heated at 110 °C for 1 h in a microwave reactor. The yellow precipitate was separated by filtration, washed with H2O and EtOH and dried under vacuum to yield [Ir4]+Cl3 as a yellow solid (383 mg, 0.295 mmol, 64.5% crude). The compound was used without further purification.

1H NMR (500 MHz, CDCl3) δ/ppm 9.29 (d, J = 5.5, 4H, H4), 7.89 (d, J = 8.0 Hz, 4H, H6), 7.76 (pseudo-dt, J = 7.8, 1.6 Hz, 4H, H4, H6), 7.42 (d, J = 8.0 Hz, 4H, H3A4), 6.92 (ddd, J = 7.9, 1.7 Hz, 4H, H4, H3), 6.78 (ddd, J = 7.3, 5.7, 1.5 Hz, 4H, H4), 5.96 (d, J = 1.6 Hz, 4H, H4), 0.98 (s, 36H, HMe). ESI-MS m/z 677.2 [Ir4]+ (calc. 677.2), 718.3 [Ir4]+(MeCN)]+ (calc. 718.2).

[Ir5]5+. Compound H5 (151 mg, 0.548 mmol, 2.0 eq.) was isolated as a yellow solid (101 mg, 0.0650 mmol, 48%). This was used without further purification.

1H NMR (500 MHz, CDCl3) δ/ppm 9.30 (ddd, J = 5.8, 1.5, 0.6 Hz, 4H, H4), 8.03 (ddd, J = 8.3, 1.3, 0.6 Hz, 4H, H4), 7.93 (td, J = 7.8, 1.5 Hz, 4H, H4), 7.64 (d, J = 8.2 Hz, 4H, H4), 7.30 (ddd, J = 8.1, 1.7 Hz, 4H, H4), 6.98 (ddd, J = 7.3, 5.7, 1.5 Hz, 4H, H4), 6.21 (d, J = 1.8 Hz, 4H, H4), 1.00 (s, 36H, HMe). 13C{1H} NMR (126 MHz, CDCl3) δ/ppm 166.7 (C4), 151.8 (C4), 148.9 (C4), 143.8 (C4), 137.9 (C4), 134.4 (C4), 131.6 (C4), 124.3 (C4), 120.5 (C4), 59.7 (CMe). ESI-MS m/z 742.1 [Ir5]+ (calc. 741.1), 782.1 [Ir5]+(MeCN)]+ (calc. 782.2), 823.1 [Ir5]+(MeCN)]+ (calc. 823.2).

[Ir7]7+. Compound H7 (151 mg, 0.548 mmol, 2.0 eq.) was isolated as a yellow solid (101 mg, 0.0650 mmol, 48%). This was used without further purification.

1H NMR (500 MHz, CDCl3) δ/ppm 9.30 (ddd, J = 5.8, 1.5, 0.6 Hz, 4H, H4), 8.03 (ddd, J = 8.3, 1.3, 0.6 Hz, 4H, H4), 7.93 (td, J = 7.8, 1.5 Hz, 4H, H4), 7.64 (d, J = 8.2 Hz, 4H, H4), 7.30 (ddd, J = 8.1, 1.7 Hz, 4H, H4), 6.98 (ddd, J = 7.3, 5.7, 1.5 Hz, 4H, H4), 6.21 (d, J = 1.8 Hz, 4H, H4), 1.00 (s, 36H, HMe). 13C{1H} NMR (126 MHz, CDCl3) δ/ppm 166.7 (C4), 151.8 (C4), 148.9 (C4), 143.8 (C4), 137.9 (C4), 134.4 (C4), 131.6 (C4), 124.3 (C4), 120.5 (C4), 59.7 (CMe). ESI-MS m/z 742.1 [Ir5]+ (calc. 741.1), 782.1 [Ir5]+(MeCN)]+ (calc. 782.2), 823.1 [Ir5]+(MeCN)]+ (calc. 823.2).

[Ir3]3+. Compound [Ir3]+Cl3 (280 mg, 0.417 mmol) was added and the mixture was heated at reflux overnight and then allowed to cool to room temperature. After filtration, an excess of solid NH4PF6 was added to the filtrate and the mixture was stirred for 1 h at room temperature. The yellow precipitate was separated by filtration, washed with H2O and redissolved in CH2Cl2. The solution was dried over Na2SO4 and the solvent removed under reduced pressure. The yellow residue was purified by column chromatography (silica, CH2Cl2 changing to CH2Cl2–2% MeOH). [Ir3]+(bpyp)[PF6] was isolated as a yellow solid (405 mg, 0.483 mmol, 79.8%). 1H NMR (500 MHz, CDCl3) δ/ppm 8.35 (pseudo-dt, J = 8.3, 1.0 Hz, 2H, H3), 8.14 (pseudo-t, J = 8.0, 1.6 Hz, 2H, H4), 8.01 (m, 4H, H3, H4, H5, H6), 7.85 (m, 4H, H3, H4, H5, H6), 7.57 (ddd, J = 5.8, 1.5, 0.8 Hz, 2H, H4), 7.51 (ddd, J = 7.7, 5.5, 1.2 Hz, 2H, H5), 7.04 (ddd, J = 7.3, 5.8, 1.4 Hz, 2H, H6), 6.81 (m, 2H, H4), 5.89 (dd, JHF = 9.6 Hz, JHH = 2.6 Hz, 2H, H6). 13C{1H} NMR (126 MHz, CDCl3) δ/ppm 167.1 (C2), 164.6 (d, JCH = 253 Hz, C3), 156.6 (C2), 154.3 (d, JCB = 5.8 Hz, C1), 151.8 (C2), 150.1 (C2), 141.4 (d, JCF = 2.1 Hz, C3), 140.5 (C2), 139.8 (C2), 129.4 (C2), 128.1 (d, JCF = 9.4 Hz, C3), 125.7 (C2), 124.5 (C2), 121.0 (C2), 118.3 (d, JCF = 17.7 Hz, C3), 110.5 (d, J = 23.3 Hz, C4), 9.00 (d, J = 253 Hz, C3), 95.36 (d, JCF = 253 Hz, C3), 86.75 (d, JCF = 253 Hz, C3), 73.0 (m, 2H, H4), 57.6 (m, 2H, H4), 55.6 (s). UV/Vis (MeCN, 1.1 × 10−5 mol dm−3) λem/nm (ε/dm3 mol−1 cm−1) 260 (62000), 295 sh (33000), 310 sh (2000), 395 sh (4300). Emission (MeCN, 1.1 × 10−5 mol dm−3, λexc = 269 nm) λmax = 557 nm. ESI-MS m/z 693.2 [M − PF6]− (calc. 693.1). Found C 45.95, H 2.84, N 6.74; C36H22F8IrN4P requires C 45.88, H 2.65, N 6.69%.
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, 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%). 1H NMR (500 MHz, CD3CN) δ/ppm 8.54 (pseudo-dt, J = 8.3, 1.1 Hz, 2H, H^E3), 8.23 (pseudo-dt, J = 8.2, 1.1 Hz, 2H, H^E^B3), 8.15 (pseudo-t, J = 8.0, 1.6 Hz, 2H, H^E^B^B3), 8.02 (d, J = 8.3 Hz, 2H, H^A^B4), 7.98 (dd, J = 8.0, 7.7, 1.5 Hz, 2H, H^B^B4), 7.95 (dd, J = 5.4, 1.6, 0.8 Hz, 2H, H^E^B^6), 7.72 (dd, J = 5.8, 1.5, 0.7 Hz, 2H, H^E^B^6), 7.58 (dd, J = 8.3, 1.9 Hz, 2H, H^E^A^B^6), 7.51 (dd, J = 7.7, 5.5, 1.2 Hz, 2H, H^E^A^A^6), 7.21 (dd, J = 7.4, 5.8, 1.4 Hz, 2H, H^A^B^A^6), 6.70 (d, J = 1.9 Hz, 2H, H^A^A^6), 2.89 (s, 6H, H^Me^B^6), 1^C(1H) NMR (126 MHz, CD3CN) δ/ppm 166.2 (C^B^2), 156.6 (C^E^2), 152.0 (C^E^6), 151.2 (C^A^4), 150.9 (C^E^4), 150.2 (C^A^6), 142.3 (C^A^2), 140.7 (C^A^3), 140.3 (C^B^6), 129.6 (C^E^E^6), 126.31 (C^A^3), 126.29 (C^E^B^6), 125.8 (C^E^E^3), 122.6 (C^A^A^4), 122.6 (C^B^3), 44.3 (C^Me^B^6). IR (solid, v/cm^−1) 2927 (w), 1608 (w), 1475 (m), 1447 (w), 1430 (w), 1375 (w), 1294 (m), 1267 (w), 1144 (s), 1091 (m), 1062 (m), 1030 (w), 957 (m), 892 (w), 838 (s), 808 (m), 782 (m), 753 (s), 733 (m), 699 (m), 666 (m), 651 (w), 650 (w), 592 (w), 557 (s), 546 (s), 524 (m), 497 (s). UV/Vis (MeCN, 1.0 × 10^−5 mol dm^−3) λ/nm (ε/dm^3 mol^−1 cm^−1) 256 (38000), 300 sh (30000), 350 sh (7500), 390 (49000), 425 sh (3200). Emission (MeCN, 1.0 × 10^−5 mol dm^−3, λ_ex = 262 nm) λ_max = 493, 525 nm. ESI-MS (m/z) 813.1 [M – PF6]^+ (calc. 813.1). Found C 71.4, H 3.3, N 5.9; C_{40}H_{40}F_{6}IrN_{4}O_{4}PS_{2}H_{2}O requires C 41.84, H 3.10, N 5.74%.

[Ir(4)(bpy)][PF6]. [Ir(4)(bpy)Cl] (144 mg, 0.101 mmol) and bpy (44.3 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, 0.114 mmol, 87.7%). 1H NMR (500 MHz, CD3CN) δ/ppm 8.58 (dd, J = 8.2, 1.1 Hz, 2H, H^E^3), 8.22 (d, J = 8.0 Hz, 2H, H^E^6), 8.17 (pseudo-t, J = 8.0, 1.5 Hz, 2H, H^E^6), 8.09 (m, 2H, H^E^B^6), 8.02–7.93 (overlapping m, 4H, H^A^3+B^4), 7.71 (m, 2H, H^E^B^6), 7.51 (ddd, J = 6.9, 5.5, 1.2 Hz, 2H, H^E^6), 7.45 (dd, J = 8.2, 1.8 Hz, 2H, H^E^6), 7.20 (ddd, J = 7.4, 5.8, 1.4 Hz, 2H, H^E^B^6), 6.50 (d, J = 1.8 Hz, 2H, H^A^A^6), 0.93 (s, 18H, H^t^Bu). 1^C(1H) NMR (126 MHz, CD3CN, 295 K) δ/ppm 166.2 (C^B^2), 156.6 (C^E^2), 152.0 (C^E^6), 150.9 (C^B^6), 150.6 (C^A^A^4), 150.1 (C^A^6), 142.0 (C^E^4), 140.4 (C^A^2), 135.9 (C^A^3), 133.2 (C^A^6), 126.3 (C^A^2), 126.3 (C^A^4), 125.5 (C^A^3), 122.5 (C^A^6), 60.3 (C^A^B^6), 23.5 (C^t^Bu). IR (solid, v/cm^−1) 2979 (w), 1755 (w), 1475 (m), 1448 (w), 1430 (w), 1373 (w), 1285 (m), 1193 (w), 1129 (s), 1082 (m), 836 (s), 806 (m), 781 (m), 764 (m), 730 (w), 710 (m), 672 (m), 658 (m), 648 (m), 585 (w), 569 (m), 556 (s), 492 (m), UV/Vis (MeCN, 0.99 × 10^−5 mol dm^−3) λ/nm (ε/dm^3 mol^−1 cm^−1) 257 (59000), 295 sh (35000), 391 (47000), 420 sh (3400 dm^3 mol^−1 cm^−1). Emission (MeCN, 0.99 × 10^−5 mol dm^−3, λ_ex = 262 nm) λ_max = 493, 523 nm. ESI-MS (m/z) 897.2 [M – PF6]^+ (calc. 897.2). Found C 45.1, H 4.05, N 5.56; C_{40}H_{40}F_{6}IrN_{4}O_{4}PS_{2}H_{2}O requires C 45.32, H 3.99, N 5.29%.

[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(1)(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 redisolving 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(bpy)][PF6] was isolated as an orange solid (56.1 mg, 0.0467 mmol, 73.8%). 1H NMR (500 MHz, CD3CN) δ/ppm 8.54 (pseudo-t, J = 8.3, 1.0 Hz, Hβ3), 8.15 (pseudo-td, J = 7.9, 1.6 Hz, 2H, Hβ4), 8.06 (m, 2H, Hβ6), 8.00 (pseudo-t, J = 8.4, 1.1 Hz, 2H, Hβ3), 7.83 (m, 2H, Hβ4), 7.68 (d, J = 8.3 Hz, 2H, Hβ4), 7.58 (pseudo-td, J = 5.9, 1.1 Hz, 2H, Hβ6), 7.53 (dd, J = 7.7, 5.4, 1.2 Hz, 2H, Hβ5), 7.00 (ddd, J = 7.3, 5.8, 1.4 Hz, 2H, Hα5), 6.94 (dd, J = 8.2, 1.9 Hz, 2H, Hα4), 6.09 (d, J = 1.9 Hz, 2H, Hβ6), 2.63 (m, 4H, SCH2), 1.40 (m, 4H, HSCCH2), 1.35–1.16 (m, 36H, HCH2), 0.89 (t, J = 7.0 Hz, 6H, HCH3). 13C{1H} NMR (126 MHz, CD3CN) δ/ppm 168.0 (C B2), 156.7 (C E2), 151.8 (C A4), 150.1 (C A6), 141.6 (C A2), 141.5 (C A5), 140.3 (C E3), 139.4 (C A1), 129.4 (C A5), 128.7 (C A6), 126.1 (C A3), 125.6 (C E3), 123.9 (C A2), 122.0 (C A4), 120.5 (C B3), 32.6 (C CH2), 30.0 (C CH2), 29.7 (C CH2), 29.0 (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), 1388 (w), 1358 (m), 1308 (w), 1167 (m), 1147 (m), 1072 (m), 1058 (m), 926 (m), 849 (m), 756 (w), 684 (w), 652 (w), 582 (w), 556 (s), 500 (m). UV/Vis (MeCN, 1.0 × 10⁻⁵ mol dm⁻³) λmax = 556 (s), 500 (m), 310 sh (25 000), 350 sh (7900), 390 (5000), 420 sh (3700 dm⁻³ mol⁻¹ cm⁻¹). Emission (McCN, 1.0 × 10⁻⁵ mol dm⁻³, λexc = 262 nm) λmax = 493, 524 nm. ESI-MS m/z 1126 [M – PF6]⁺ (calc. 1121.5). Found C 53.38, H 5.57, N 4.72; C56H72F6IrN4O4PS2 requires C 53.11, H 5.73, N 4.42%.

### Crystallography

Data were collected on a Bruker-Nonius KappaAPEX diffractometer with data reduction, solution and refinement using the programs APEX224 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 treatment of H1 with NaSmE in NMP under micro-wave 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 NaH 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–H2O220 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 557.7) 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, HMQC 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 aryl–alkyl sulfones29 and diaryl sulfones30,31 illustrate the formation both intra- and intermolecular CH…O–S hydrogen bonds. In H3, the O1–S1–C9–C10 and O2–S1–C9–C8 torsion angles are −25°(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...C10–C9–C8–C7)
### Table 1  Crystallographic data

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<th>Compound</th>
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<th>H5</th>
<th>[Ir2(3,4Cl2)2CH2Cl2]</th>
<th>Δ-[Ir(1)3(bpy)][PF6]</th>
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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; O2–S1–O1 = 118.19(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 = 1.7772(15) Å; O2–S1–O1 = 118.85(8), O2–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)°.

In contrast, a primary packing interaction in H5 involves CHphenyl⋯O sulfone contacts resulting in the formation of hydrogen-bonded contacts in 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(CN2Cl2] dimers**

Complexes in the [Ir(ppy)2(N2N)] family are usually synthesized by reaction between the N2N ligand and the chlorido-bridged dimer [Ir2(ppy)2Cl2]. Typically, this dimer is prepared from the reaction of IrCl3·nH2O with Hppy,3,4 Although [Ir2(1)3Cl2] (prepared by the latter method) has previously been described,6 the remaining chlorido-bridged precursors to the target complexes [Ir2(CN2Cl2)] 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...
[Ir$_2$(7)$_4$Cl$_4$] were isolated as yellow solids. The $^1$H and $^{13}$C 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 [Ir$_2$(5)$_4$Cl$_2$], the second most intense peak in the electrospray mass spectrum came at m/z 741.2 and as assigned to the [Ir(5)$_2$]$^+$ ion. The base peak at m/z 782.1 and a lower intensity peak at m/z 823.1 arose from [Ir(5)$_2$(MeCN)]$^+$ and [Ir(5)$_2$(MeCN)$_2$]$^+$, 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 [Ir$_2$(7)$_4$Cl$_4$], with the base peak at m/z 965.9 corresponding to [Ir(7)$_2$]$^+$.

Attempts to prepare the dimers [Ir$_2$(C$^N$)$_4$Cl$_2$] with C$^N$ = 2, 3 or 4 from reactions of H$_2$, H$_3$ or H$_4$ with IrCl$_3$·H$_2$O were unsuccessful. We therefore adopted an alternative strategy which involves the reaction of the conjugate acid of the cyclobutadiene with [Ir$_2$(COD)$_2$Cl$_2$]. Unfortunately, reaction of H$_2$ with [Ir$_2$(COD)$_2$Cl$_2$] gave an insoluble solid which could not be characterized, and attempts to prepare and isolate [Ir$_2$(2)$_4$Cl$_2$] 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 [Ir(2)$_2$(bpy)]$^+$.

The reaction of [Ir$_2$(COD)$_2$Cl$_2$] with H$_3$ and H$_4$ (Scheme 2) yielded [Ir$_2$(3)$_4$Cl$_2$] and [Ir$_2$(4)$_4$Cl$_2$] as yellow powders in good yields. As judged by $^1$H NMR spectroscopy, the crude products were pure enough to be used directly in the next step (see the next section). The solution $^1$H and $^{13}$C NMR spectra of [Ir$_2$(3)$_4$Cl$_2$] were assigned by COSY, HMQC and HMBC methods and were in accord with the structures in Scheme 2. In contrast, [Ir$_2$(4)$_4$Cl$_2$] is poorly soluble in most common organic solvents. The $^1$H NMR spectrum was assigned using a COSY spectrum and by comparison with those of the other dimers, but the 2D $^{13}$C NMR spectra of [Ir$_2$(3)$_4$Cl$_2$] showed peaks at m/z 657.1 and 698.2 assigned to [Ir(3)$_2$]$^+$ and [Ir(3)$_2$(MeCN)]$^+$, respectively; (the origin of the MeCN is explained above). Analogous peaks were observed in the ESI mass spectrum of [Ir$_2$(4)$_4$Cl$_2$].

The synthesis of [Ir$_2$(6)$_4$Cl$_2$] could not be achieved by the reaction of [Ir$_2$(COD)$_2$Cl$_2$] with H$_6$, and unreacted ligand was recovered from the reaction mixture after 22 hours reflux in 2-ethoxyethanol.

Despite the widespread synthetic use of [Ir$_2$(C$^N$)$_4$Cl$_2$] 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 Database$^{26}$ (CSD, v. 5.34 with November 2012, and February and May 2103 updates) using Conquest v. 1.35$^{26}$ generated only nine hits,$^{37-44}$ including the structures of the enantiomERICALLY pure $\Lambda,\Lambda$- and $\Delta,\Delta$-forms$^{42}$ of [Ir$_2$(ppy)$_4$Cl$_2$] as well as that of the centrosymmetric $\Delta,\Lambda$-form.$^{41}$ In addition, we have recently
is disordered and has been modelled over two sites of fractional occupancies 0.62 and 0.38.

Synthesis and characterization of [Ir(C=N)₂(bpy)][PF₆] complexes

Synthesis of the [Ir(C=N)₂(bpy)][PF₆] complexes was initially approached using the established methodology³² of treating the appropriate [Ir₃(C=N)₃Cl₂] dimer with two equivalents of bpy. This method was successful in five out of six cases (Scheme 3a). [Ir(1)₃(bpy)][PF₆], [Ir(3)₃(bpy)][PF₆], [Ir(4)₃(bpy)][PF₆] and [Ir(5)₃(bpy)][PF₆] were isolated in yields ranging from 70.3 to 87.7%. Purification of [Ir(4)₃(bpy)][PF₆] required a series of chromatographic and precipitation steps (see Experimental section), but a high yield was still obtained. Purification of [Ir(7)₃(bpy)][PF₆] 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 [Ir₃(6)Cl₂] could not be prepared (see above), we adopted a nucleophilic substitution approach to prepare [Ir(6)₃(bpy)][PF₆] from [Ir(1)₃(bpy)][PF₆] (Scheme 3b). The fluoro-derivative was treated with 1-dodecanethiol in the presence of sodium hydride and, after workup, [Ir(6)₃(bpy)][PF₆] 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 ¹H NMR spectra upon the addition of [¹⁴Bu₄N][PF₆].⁴⁶

The base peak in the electrospray mass spectrum of each [Ir(C=N)₂(bpy)][PF₆] complex consisted of a peak envelope corresponding to [M – PF₆]⁺ exhibiting the characteristic isotopic distribution for iridium. The ¹H and ¹³C NMR spectra of each complex were consistent with a C₂-symmetric cation. Fig. 5 shows the ¹H NMR spectrum of [Ir(5)₃(bpy)][PF₆] as a representative example. Signals in the ¹H and ¹³C NMR spectra were assigned using a combination of COSY, HMQC and HMBC methods. The ¹H NMR signal for the ²butyl group in [Ir(4)₃(bpy)][PF₆] appears at δ 1.00 ppm and shifts to lower frequency (δ 0.93 ppm) in the analogous sulfone derivative [Ir(5)₃(bpy)][PF₆]. The ¹³C NMR resonance for the primary carbon atom in the ²butyl group shifts from δ 31.1 to 23.5 ppm on going from [Ir(4)₃(bpy)][PF₆] to [Ir(5)₃(bpy)][PF₆], while the S-attached ¹³C nucleus resonates at δ 46.8 and 60.3 ppm, respectively, in the sulfane and sulfone complexes. In [Ir(6)₃(bpy)][PF₆] and [Ir(7)₃(bpy)][PF₆], the CH₂ unit is characterized by signals at δ(¹H) 2.63 ppm and δ(¹³C) 32.0 ppm in the sulfane and δ(¹H) 2.87 ppm and δ(¹³C) 56.3 ppm in the sulfone. Across the series of [Ir(C=N)₂(bpy)][PF₆] complexes, the only bpy-proton signal to be noticeably affected is that assigned to H⁶⁶ (see Scheme 3) since only this bpy proton is directed towards the substituted phenyl ring. As expected, signals arising from the phenyl-ring protons (H⁴³, H⁴⁴ and H⁶⁶) undergo the most significant changes in chemical shift. For each pair of sulfane and sulfone complexes, signals for H⁴³, H⁴⁴ and H⁶⁶ all move to higher frequency (Δδ is in the range 0.20 and 0.56 ppm). Signals for protons H⁶⁶ and H⁴⁴...
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 $\text{[Ir(}1\text{]}_2\text{(bpy)}\text{][PF}_6\text{]}$ (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 $\Delta$-$\text{[Ir(}1\text{]}_2\text{(bpy)}\text{][PF}_6\text{]}$ and $\text{rac-4-[Ir(}1\text{]}_2\text{(bpy)}\text{][PF}_6\text{]}$-$\text{Et}_2\text{O}$-$2\text{CH}_2\text{Cl}_2$.

Enantiomerically pure $\Delta$-$\text{[Ir(}1\text{]}_2\text{(bpy)}\text{][PF}_6\text{]}$ crystallizes in the trigonal space group $P3_121$ and Fig. 6 shows the structure of the $\Delta$-$\text{[Ir(}1\text{]}_2\text{(bpy)}\text{]}^+$ cation. The octahedral environment of Ir1 with trans-arrangement of the N donors (N1 and N2) 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-$\text{[Ir(}1\text{]}_2\text{(bpy)}\text{][PF}_6\text{]}$ described below.
lies partly over the pyridine π of a bpy ligand; the rings are slipped such that the F atom contact is between a fluorophenyl ring and one pyridine ring.

The asymmetric unit. Extensive CH⋯F contacts contribute to the crystal packing. The CH2Cl2 solvent molecule is ordered, and the Et2O molecule is half occupancy.

**Photophysical properties**

The solution electronic absorption spectra of [Ir(C^N)2(bpy)][PF6] [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)][PF6] 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)][PF6] [C^N = 1, 3–5, 7] and orange colour of [Ir(6)2(bpy)][PF6]. Absorptions at wavelengths in the approximate range 350 to 450 nm are attributed to low intensity 1MLCT and 1LLCT bands.

Excitation of MeCN solutions of the complexes with λ_{exc} varying between 269 and 300 for [Ir(1)3(bpy)][PF6], 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_{exc} in the above ranges with the exception of the appearance of the relevant harmonic band. The complexes [Ir(1)3(bpy)][PF6], [Ir(4)3(bpy)][PF6] and [Ir(6)3(bpy)][PF6] (i.e. fluoro and sulfane substituents on the C^N ligands) are yellow emitters and the emission bands are broad and featureless. In contrast, [Ir(3)3(bpy)][PF6], [Ir(5)3(bpy)][PF6] and [Ir(7)3(bpy)][PF6] are green emitters and the emission spectra exhibit vibrational structure. The emitting state of [Ir(C^N)3(N^N)]+ is the lowest energy triplet state which may contain contributions from 1MLCT, 3LC and 3LLCT states. 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)3(bpy)][PF6], [Ir(5)3(bpy)][PF6] and [Ir(7)3(bpy)][PF6]. Table 2 summarizes the room temperature solution photophysical properties of the complexes. Compared

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**Fig. 7** Face-to-face/edge-to-face embrace between the two independent Δ and Λ-[Ir(1)3(bpy)]+ cations in rac-4[[Ir(1)3(bpy)][PF6]]·Et2O·2CH2Cl2: (a) space-filling, and (b) showing relative orientations of the fluorophenyl and pyridine rings involved in the face-to-face interaction and CH⋯π contacts (red hashed lines).

**Fig. 8** Chain of alternating Δ- (red) and Λ- (blue) [Ir(1)3(bpy)]+ cations in rac-4[[Ir(1)3(bpy)][PF6]]·Et2O·2CH2Cl2.

**Fig. 9** Absorption spectra of MeCN solutions of [Ir(C^N)2(bpy)][PF6] for C^N = 1, 3, 4, 5, 6 and 7. See experimental section for concentrations.
Replacement of F by the introduction of the electron-withdrawing fluoro-groups. 

\[ \text{Ir(ppy)2(bpy)[PF6]} \] under analogous room temperature conditions. Excitation wavelengths: 300 nm (with 1) and 400 nm (with 3, 4, 5, 6 and 7). * = Harmonic at 600 nm.

Table 2: Solution photophysical properties of \([\text{Ir(C}^\text{N})_2(\text{bpy})]\)[PF6] (C^N = 1, 3–7). PLQY measured in de-aerated MeCN; lifetimes measured in de-aerated MeCN under argon atmosphere

| Complex                  | \(\lambda_{\text{exc}}/\text{nm}\) | \(\lambda_{\text{max}}/\text{nm}\) | \(\tau_{1/2}/\mu\text{s}\) | PLQY/\% \\|-------------------------|------------------|------------------|------------------|--------|  \\\| [Ir(1)_2(ppy)][PF_6]   | 269              | 557              | 0.224            | 36     |  \\\| [Ir(3)_2(ppy)][PF_6]   | 262              | 493, 525         | 2.33             | 74     |  \\\| [Ir(4)_2(ppy)][PF_6]   | 260              | 568              | 0.528            | 24     |  \\\| [Ir(5)_2(ppy)][PF_6]   | 262              | 493, 523         | 3.36             | 64     |  \\\| [Ir(6)_2(ppy)][PF_6]   | 252              | 577              | 0.369            | 15     |  \\\| [Ir(7)_2(ppy)][PF_6]   | 262              | 493, 524         | 3.21             | 64     |  \\\| & \(\lambda_{\text{exc}} = 280 \text{ nm for complexes with 3, 5 and 7; 340 nm for complexes with 1, 4 and 6.}

Fig. 10: Solution emission spectra of \([\text{Ir(C}^\text{N})_2(\text{bpy})]\)[PF6] for C^N = 1, 3, 4, 5, 6 and 7 (298 K, MeCN). See experimental section for solution concentrations. Excitation wavelengths: 300 nm (with 1) and 400 nm (with 3, 4, 5, 6 and 7). * = Harmonic at 600 nm.

Table 3: Solid-state photophysical properties of \([\text{Ir(C}^\text{N})_2(\text{bpy})]\)[PF6] (C^N = 1, 3–7)

| Complex                  | \(\lambda_{\text{max}}^a/\text{nm}\) | \(\lambda_{\text{exc}}^a/\text{nm}\) | PLQY/\% \\|-------------------------|------------------|------------------|--------|  \\\| [Ir(1)_2(ppy)][PF_6]   | 547              | 269              | 23     |  \\\| [Ir(3)_2(ppy)][PF_6]   | 532              | 262              | 6.6    |  \\\| [Ir(4)_2(ppy)][PF_6]   | 553              | 260              | 4.9    |  \\\| [Ir(5)_2(ppy)][PF_6]   | 535              | 262              | 15     |  \\\| [Ir(6)_2(ppy)][PF_6]   | 558              | 252              | 2.6    |  \\\| [Ir(7)_2(ppy)][PF_6]   | 537              | 262              | 4.2    |  \\\| & \(\lambda_{\text{exc}} = 405 \text{ nm.}

The longest lived emission (3.36 \mu s) is for [Ir(5)_2(ppy)][PF_6]; in general, the complexes in which the cyclometallated ligand bears a sulfone substituent exhibit lifetimes that are an order of magnitude longer than those containing fluoro or sulfane group.

Fig. 11: Solid-state emission spectra of \([\text{Ir(C}^\text{N})_2(\text{bpy})]\)[PF6] for C^N = 1 and 3–7. Excitation wavelengths: see Table 3.

Table 3: Solid-state photophysical properties of \([\text{Ir(C}^\text{N})_2(\text{bpy})]\)[PF6] (C^N = 1, 3–7)

| Complex                  | \(\lambda_{\text{max}}^a/\text{nm}\) | \(\lambda_{\text{exc}}^a/\text{nm}\) | PLQY/\% \\|-------------------------|------------------|------------------|--------|  \\\| [Ir(1)_2(ppy)][PF_6]   | 547              | 269              | 23     |  \\\| [Ir(3)_2(ppy)][PF_6]   | 532              | 262              | 6.6    |  \\\| [Ir(4)_2(ppy)][PF_6]   | 553              | 260              | 4.9    |  \\\| [Ir(5)_2(ppy)][PF_6]   | 535              | 262              | 15     |  \\\| [Ir(6)_2(ppy)][PF_6]   | 558              | 252              | 2.6    |  \\\| [Ir(7)_2(ppy)][PF_6]   | 537              | 262              | 4.2    |  \\\| & \(\lambda_{\text{exc}} = 405 \text{ nm.}

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 (3.36 \mu s) is for [Ir(5)_2(ppy)][PF_6]; in general, the complexes in which the cyclometallated ligand bears a sulfone substituent exhibit lifetimes that are an order of magnitude longer than those containing fluoro or sulfane group.

Fig. 11 illustrates the emission spectra of powdered samples of the complexes and emission maxima and PLQY values are given in Table 3. All emission bands are broad and featureless. For the complexes containing the sulfane- or fluoro-substituted C^N ligands (4, 6 or 1), a blue shift in the emission is observed on going from solution to the solid state. For [Ir(3)_2(ppy)][PF_6], [Ir(5)_2(ppy)][PF_6] and [Ir(7)_2(ppy)][PF_6], the solid-state emission maximum is red-shifted to \(\approx 535 \text{ nm.}

With the exception of [Ir(1)_2(ppy)][PF_6] for which the solid-state PLQY is 23% \(\lambda_{\text{exc}} = 269 \text{ nm}, PLQYs for powdered samples are significantly lower than those obtained in de-aerated solution (compare Tables 2 and 3).
Electrochemistry

Each of the [Ir(C^N)_2(bpy)][PF_6] 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(ppy)_2(bpy)][PF_6] (E^ox_1/2 = +0.84 V versus internal Fe/C)31, consistent with the introduction of strongly electron-withdrawing substituents on the cyclometallating ligands. Compounds [Ir(4f)_2(bpy)][PF_6] and [Ir(6f)_2(bpy)][PF_6] 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 E^red_1/2 potentials in Table 4 compare with –1.77 and –2.60 V for [Ir(ppy)_2(bpy)][PF_6].31 The LUMO is localized on 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.

The electrochemical band gaps, ΔE1/2 (Table 4) are all larger than the 2.61 V in [Ir(ppy)_2(bpy)][PF_6]31 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 ΔE1/2 on going from fluoro to sulfane derivatives are consistent with the observed red-shift in emission maxima, while the increase in ΔE1/2 on going to sulfones [Ir(C^N)_2(bpy)][PF_6] (C^N = 3, 5, 7) corresponds to the blue-shift in the emissions compared to those of [Ir(C^N)_2(bpy)][PF_6] (C^N = 1, 4, 6).

Conclusions

We have prepared a series of [Ir(C^N)_2(bpy)][PF_6] complexes in which the cyclometallating ligands contain electron-withdrawing fluoro, sulfane or sulfone groups. The well-established synthetic route of treatment of a [Ir(C^N)_2Cl_2] dimer with the bpy proved appropriate for the preparation of [Ir(C^N)_2(bpy)][PF_6] with C^N = 1, 3, 4, 5 and 7. However, [Ir(6f)_2(bpy)][PF_6] was prepared by nucleophilic substitution starting from fluoro-
derivative [Ir(1f)_2(bpy)][PF_6] since attempts to prepare the dimer [Ir_2(6f)_2Cl_2] were unsuccessful.

The new complexes have been fully characterized by spectroscopic and mass spectrometric methods. The single crystal structures of Δ[Ir(1f)_2(bpy)][PF_6] and of rac-4[[Ir(1f)_2(bpy)]- [PF_6]-Et_2O-2CH_2Cl_2 have been elucidated, along with the structures of the free ligands H3 and H5, and of the dimer [Ir_2(3f)_2Cl_2-2CH_2Cl_2. The solution absorption spectra of the complexes are dominated by ligand-centred transitions, with a tail into the visible arising from low intensity 1MLCT and 1LLCT bands. The room temperature, solution emission spectra of [Ir(1f)_2(bpy)][PF_6], [Ir(4f)_2(bpy)][PF_6] and [Ir(6f)_2(bpy)][PF_6] (fluoro and sulfane substituents) are broad and featureless, consistent with substantial CT contributions to the lowest energy triplet (emitting) state. These complexes are all yellow emitters with λ_{em} max between 557 and 577 nm. In contrast, incorporation of the sulfone substituents into the cyclometallating ligands results in [Ir(3f)_2(bpy)][PF_6], [Ir(5f)_2(bpy)][PF_6] and [Ir(7f)_2(bpy)][PF_6] being green emitters which exhibit structured emissions (λ_{em} max = 493 and 523 to 525 nm), consistent with only minor CT contributions to the lowest energy triplet state. The solution PLQYs of the sulfone complexes are 74% for [Ir(3f)_2(bpy)][PF_6] and 64% for both [Ir(5f)_2(bpy)][PF_6] and [Ir(7f)_2(bpy)][PF_6] but for powdered solid samples, these are significantly lower (≤15%). The emission lifetimes for the complexes containing sulfone substituents in the C^N ligands (3, 5 and 7) are an order of magnitude longer (2.33 to 3.36 μs) than the complexes in which the C^N ligand carries a fluoro or sulfane unit (0.224 to 0.528 μs). We are currently screening [Ir(3f)_2(bpy)][PF_6], [Ir(5f)_2(bpy)][PF_6] and [Ir(7f)_2(bpy)][PF_6] and related complexes in device configuration in LECs.

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Notes and references
