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New, efficient electroluminescent materials based on organometallic Ir complexes†‡

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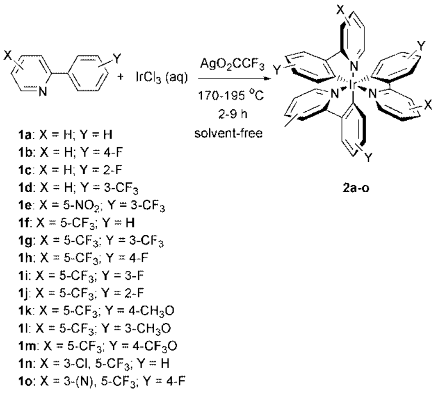
Reaction of $IrCl_3$ with fluorinated 2-arylpyridines in the presence of AgO_2CCF_3 affords *fac*-tris-cyclometalated arylpyridine Ir complexes exhibiting excellent processing and electroluminescent properties which can be fine-tuned *via* systematic control of the nature and position of the substituents on the aromatic rings.

Low cost, lightweight, flexible, ultra-thin flat panel display devices with miserly power consumption are being fabricated using a new generation of materials' chemistry aimed at exploiting the phenomenon of electroluminescence (EL). Molecule-based 'organic' light-emitting diodes (OLEDs) represent a promising approach for just these applications.[1–4] Suitable materials for OLEDs still need to be developed. A key goal of materials' research in this area is achieving very high power efficiency, which translates into enhanced operating lifetimes and longer battery life.

An important breakthrough was reported recently[5] with the use of materials displaying phosphorescence-like EL and having theoretical efficiency four times that of devices based on fluorescence (assuming electron–hole recombination is statistically controlled). Initial reports of electroluminescence from the Ir complex of 2-phenylpyridine ([Ir(ppy)$_3$])[6] doped into a charge-transporting matrix, 4,4′-bis(carbazol-9-yl)biphenyl,[6–8] emphasized its dramatically increased power efficiency, 19 lm W^{-1} (26 cd A^{-1}) with a Mg/Ag cathode.

We now report on the synthesis and characterization of a series of highly efficient LED materials based on fluorinated organometallic iridium compounds.[9] Fluorinated substituents in the aromatic ligand result in markedly reduced concentration-quenching of luminescence, and in excellent volatility which aids device processing.

New tris-cyclometalated arylpyridine complexes were prepared by a novel one-step method [eqn. (1)]. Reaction (1) is run in excess arylpyridine[10] which is easily recovered and reused. Complexes **2a–o** were characterized by elemental analysis, ^1H and ^{19}F NMR data, and cyclic voltammetry (CV). Nearly all of the complexes exhibited fully reversible reduction and oxidation waves (Table 1). Single-crystal X-ray structures were obtained for **2g**, **h**, **j**, and **l**.†§ Only *fac* configuration was observed in all cases,[11] as exemplified by the structure of **2h** (Fig. 1). Importantly, trifluoromethylated complexes **2d–o** sublime more easily than **2a** and thus exhibit processing properties superior to those of [Ir(ppy)$_3$] (Table 1).



(1)

1a: X = H; Y = H
1b: X = H; Y = 4-F
1c: X = H; Y = 2-F
1d: X = H; Y = 3-CF_3
1e: X = 5-NO_2; Y = 3-CF_3
1f: X = 5-CF_3; Y = H
1g: X = 5-CF_3; Y = 3-CF_3
1h: X = 5-CF_3; Y = 4-F
1i: X = 5-CF_3; Y = 3-F
1j: X = 5-CF_3; Y = 2-F
1k: X = 5-CF_3; Y = 4-CH_3O
1l: X = 5-CF_3; Y = 3-CH_3O
1m: X = 5-CF_3; Y = 4-CF_3O
1n: X = 3-Cl, 5-CF_3; Y = H
1o: X = 3-(N), 5-CF_3; Y = 4-F

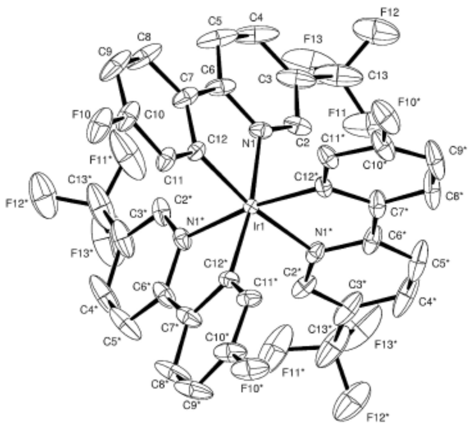


Fig. 1 An ORTEP drawing of **2h**

OLED devices were fabricated with **2a–o** by the thermal evaporation technique, and characterized by measuring current–voltage (*I–V*) curves, EL radiance *vs.* voltage, and EL spectra *vs.* voltage. A typical five-layer device employed ITO (indium doped tin oxide) as the anode, bis[4-(*N*,*N*-diethylamino)-2-methylphenyl](4-methylphenyl)methane (MPMP) as the hole transport material, **2a–o** as the luminescent material, 4,7-diphenyl-1,10-phenanthroline (DPA) or 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (DDPA) as the electron transport material, and Al as the cathode (Table 1).

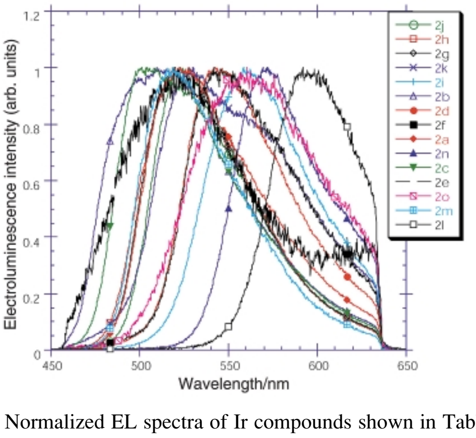


Fig. 2 Normalized EL spectra of Ir compounds shown in Table 1.

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† Electronic supplementary information (ESI) available: details of the crystallographic studies, electrochemical measurements and device configuration. See http://www.rsc.org/suppdata/cc/b1/b103490c/

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Table 1 Electroluminescent, thermal and electrochemical properties of **2a–o**

Emitter	Yield[a] (%)	Device configuration[b]	LED peak efficiency/[c] cd A^{-1}	LED peak radiance/ cd m^{-2}	$\lambda_{em\ max}$/ nm	TGA[d]/ °C	$E_{\frac{1}{2}}$ (Red)[e]/V	$E_{\frac{1}{2}}$ (Ox)[f]/V
2a	25	MPMP (523 Å), **2a** (402 Å), DDPA (406 Å), Al (742 Å), ITO-2	3.8	570	522	425	−2.77; −2.95; −3.19	0.26
2b	26	MPMP (643 Å), **2b** (409 Å), DDPA (112 Å), AlQ (361 Å), Al (737 Å), ITO-1	1.9	800	514	453	−2.74	0.48
2c	44	MPMP (603 Å), **2c** (415 Å), DDPA (111 Å), AlQ (303 Å), Al (732 Å), ITO-1	3.8	1150	506, 526	417	−2.64; −2.83; −3.12	0.46
2d[g]	14	MPMP (539 Å), **2d** (430 Å), DDPA (109 Å), AlQ (318 Å), Al (725 Å), ITO-1	2	1200	517	382	−2.56; −2.78; −2.99	0.62
2e[g]	16	MPMP (525 Å), **2e** (406 Å), DDPA (106 Å), AlQ (341 Å), Al (762 Å), ITO-1	0.013	7.6	521, ⩾630	392	−1.30; −1.46	Irrev. Ox.[h]
2f	60	MPMP (547 Å), **2f** (412 Å), DDPA (105 Å), AlQ (300 Å), Al (730 Å), ITO-1	4	400	545	383	−2.31	0.55
2g[g]	40	MPMP (553 Å), **2g** (417 Å), DDPA (439 Å), Al (714 Å), ITO-1	9.5	1500	525	345	−2.06; −2.37	0.91
2h	82	MPMP (508 Å), **2h** (428 Å), DPA (461 Å), Al (731 Å), ITO-2	20	4800	525	370	−2.24	0.77
2i[i]	52	MPMP (545 Å), **2i** (462 Å), DDPA (111 Å), AlQ (319 Å), Al (741 Å), ITO-1	2.2	514	560	305	−2.17	0.67
2j	49	MPMP (551 Å), **2j** (465 Å), DDPA (106 Å), AlQ (313 Å), Al (730 Å), ITO-1	2.1	340	525	336	−2.16	0.76
2k	9	MPMP (570 Å), **2k** (441 Å), DDPA (107 Å), AlQ (339 Å), Al (742 Å), ITO-1	1.8	175	530, 563	372	−2.47	0.52
2l[g]	22	MPMP (504 Å), **2l** (417 Å), DPA (407 Å), Al(744 Å), ITO-2	1.4	360	595	384	−2.29	0.33; 0.51; 0.69[j]
2m	72	MPMP (520 Å), **2m** (405 Å), DDPA (410 Å), AlQ (730 Å), ITO-1	5	400	520	315	−2.16; −2.53	0.84
2n	8	MPMP (532 Å), **2n** (457 Å), DDPA (108 Å), AlQ (306 Å), Al (730 Å), ITO-1	3.3	190	575	280	−1.56[k]	0.68
2o	14	MPMP (553 Å), **2o** (417 Å), DDPA (439 Å), Al (714 Å), ITO-1	9.5	1500	525	376	−1.91; −2.27	0.89

[a] Most yields are not optimized. [b] See ESI† for details. [c] LED device efficiency is dependent on the ITO substrate used and emitter purity; **2a** and **2h** received more purification effort. [d] At point of 50% weight loss (1 atm, N_2, 10 °C min^{-1}). [e] In THF, *vs.* Cp_2Fe/Cp_2Fe^+. Only fully reversible 2nd and 3rd reduction waves are listed. [f] In CH_2Cl_2, *vs.* Cp_2Fe/Cp_2Fe^+. [g] Substituent on the Ph ring *para* to Ir. [h] No return wave observed. [i] Mixture of isomers containing F *ortho* or *para* to Ir. [j] Multiple oxidation waves were only observed for **2l**; the second and third waves are tentatively assigned to ligand-based redox processes. [k] E_{pc}.

Most complexes **2a–o** show good EL efficiency on the order of a few cd A^{-1} (Table 1). A non-optimized device based on **2h** with an Al cathode yields a peak radiance of *ca.* 4800 cd m^{-2} and a peak external efficiency of 20 cd A^{-1} (*ca.* 16 lm W^{-1}). Improvement in the device is expected with a low work function cathode (*e.g.*, Mg/Ag or LiF/Mg) and further optimization.

Forrest and coworkers[6] used [Ir(ppy)$_3$] as a 6% dopant in a charge-transporting host, in order to achieve highest efficiency. This is presumably due to the self-quenching effect in pure **2a**.[6] Measuring the relative luminescence quantum yield of **2h** *vs.* **2a** in the form of a solid state thin film under N_2 showed that the photoluminescence efficiency of pure **2h** was 10 times that of **2a**. Preliminary studies demonstrated comparable photoluminescence quantum yields of *ca.* 0.5–0.6 for **2a** and **2h** in toluene solution. The marked reduction of the self-quenching effect for some of the fluorinated iridium complexes (compare **2a** with **2b–d**, **f–o** in Table 1) obviates the need to dope them into a host material.

By changing the substituents and their position, the peak wavelength of the LED can be tuned from *ca.* 500 to 595 nm (Fig. 2). The peak wavelength is sensitive not only to the nature but also to the position of the substituent. Thus, **2l** with a MeO group *para* to Ir exhibits yellow–orange EL at 595 nm, whereas its *meta* isomer **2k** is green electroluminescent (530 and 565 nm). With fluorine *meta* to Ir (**2h** and **2j**) EL is at 525 nm, while the *ortho*/*para* isomers (**2i**) show EL at 560 nm. These changes are likely due to the strong π-donating effect of both F and MeO.[12] The F and MeO groups may π-interact with either Ir (**2i**, **2l**) or the pyridine ring (**2h**, **2j**, **2k**), leading to destabilization of the HOMO (Ir) and stabilization of the LUMO (Py). These findings raise the exciting possibility of color tuning all the way from blue to red *via* systematic control of the nature and position of the substituents. If material efficiencies can be maintained as this tuning occurs (as intimated by unoptimized results in Table 1) then these materials will provide a unique platform for full color display devices of the future.

Notes and references

§ CCDC reference numbers 161821–161824. See http://www.rsc.org/suppdata/cc/b1/b103490c/ for crystallographic data in CIF or other electronic format.

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