Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information

Scheme S1. Synthetic routes of the pzpy ligand and complexes 1-4.

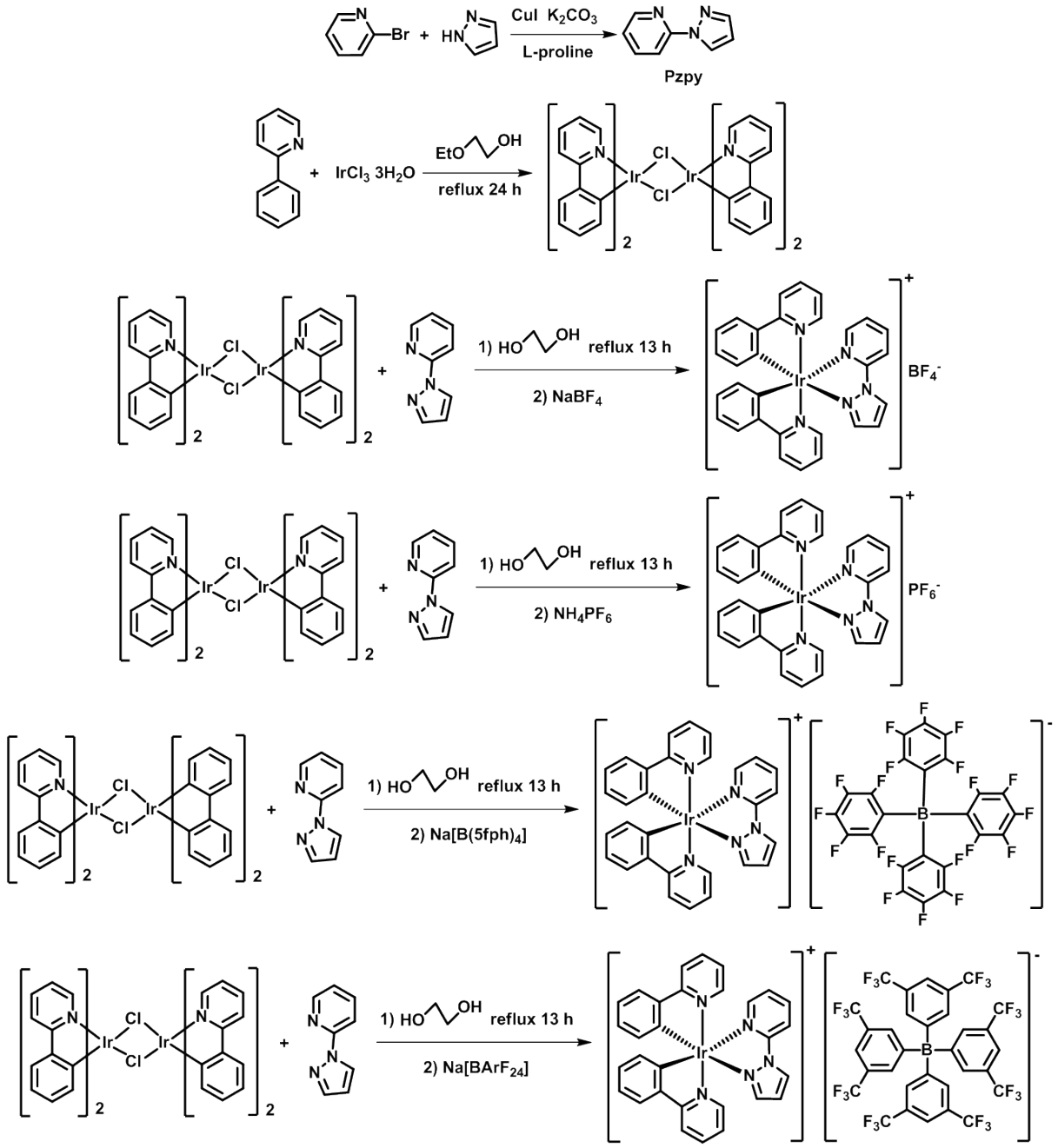


Figure S1. Single crystal structure of complex 1. Here thermal ellipsoids are drawn at 30 % probability. The solvent molecules and hydrogen atoms are omitted for clarity. The unlabeled atoms are carbon atoms.

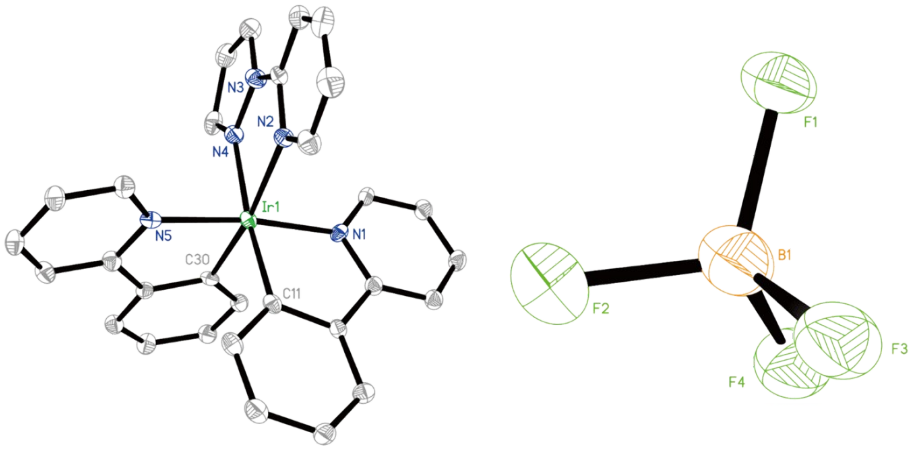


Figure S2. Single crystal structure of complex 2. Here thermal ellipsoids are drawn at 30 % probability. The solvent molecules and hydrogen atoms are omitted for clarity. The unlabeled atoms are carbon atoms.

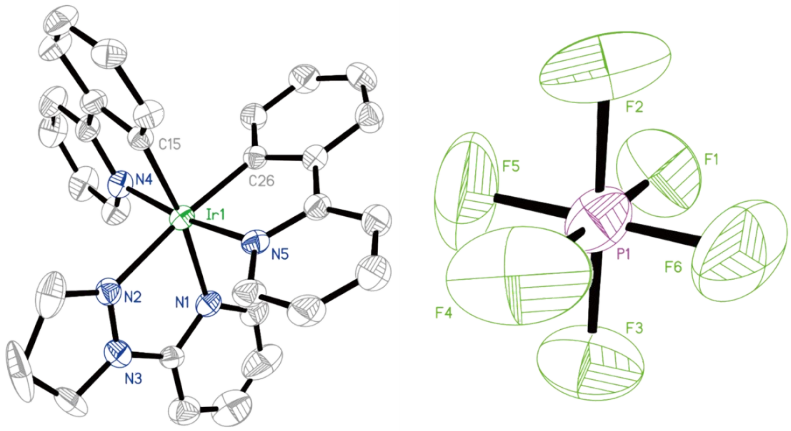


Figure S3. Single crystal structure of complex 3. Here thermal ellipsoids are drawn at 30 % probability. The solvent molecules and hydrogen atoms are omitted for clarity. The unlabeled atoms are carbon atoms.

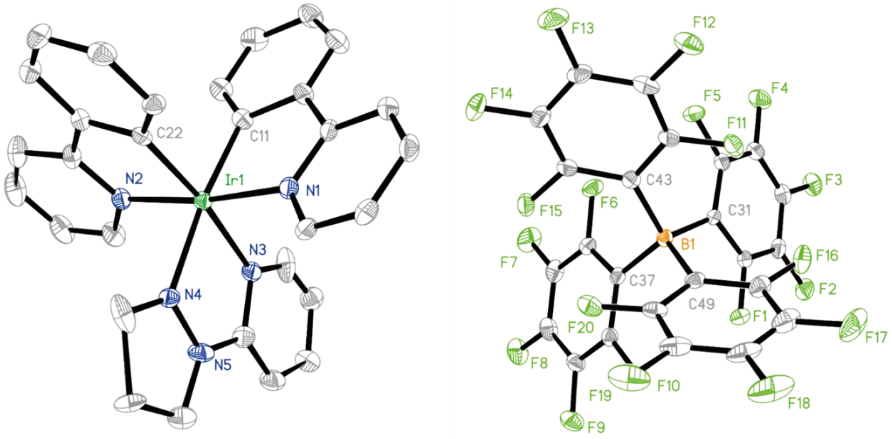


Figure S4. Single crystal structure of complex 4. Here thermal ellipsoids are drawn at 30 % probability. The solvent molecules and hydrogen atoms are omitted for clarity. The unlabeled atoms are carbon atoms.

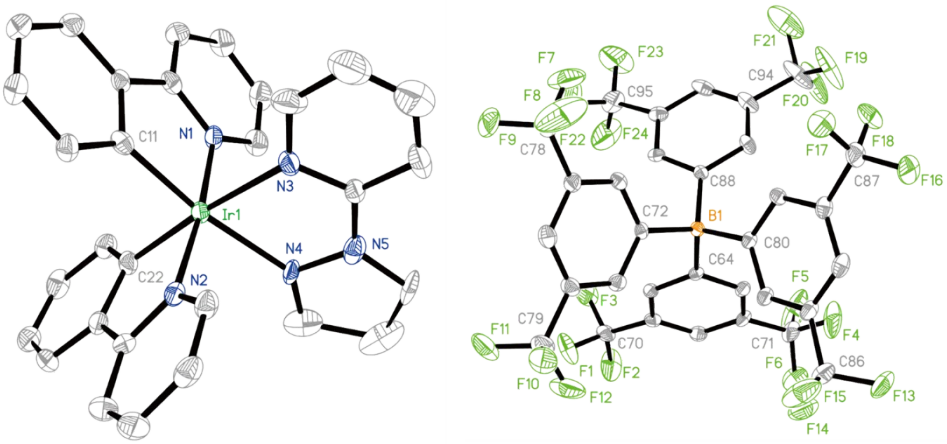


Figure S5. Absorption spectra of complexes 1-4 in acetonitrile solution (1×10^{-5} M).

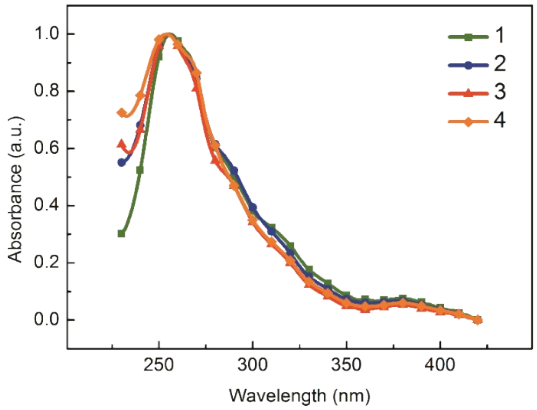


Figure S6. Molecular orbital surfaces of the coordinated iridium(III) cation, $[Ir(ppy)_2(pzpy)]^+$. (a) HOMO orbital, (b) LUMO orbital. All the MO surfaces correspond to an isocontour value of $|\psi| = 0.025$.

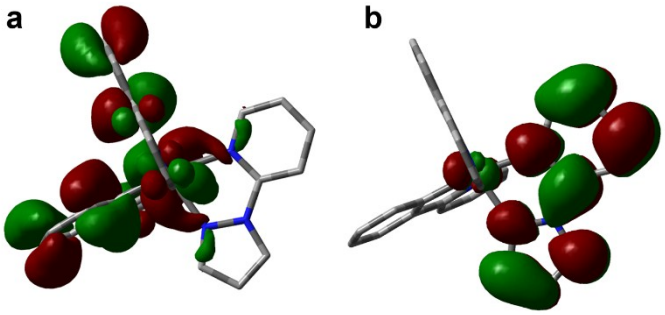


Figure S7. (a) *J-V* and (b) *L-V* characteristics of solution-processed OLEDs with a structure of ITO/ PEDOT: PSS (60 nm)/ PVK: OXD-7: *x* wt. % Complex 1 (85 nm)/ Cs_2CO_3 (2.3 nm)/ Al (150 nm), *x* = 2, 3, 5, 10, 15 or 20. (c) PL spectra of the light-emitting layer, and (d) EL spectra of devices.

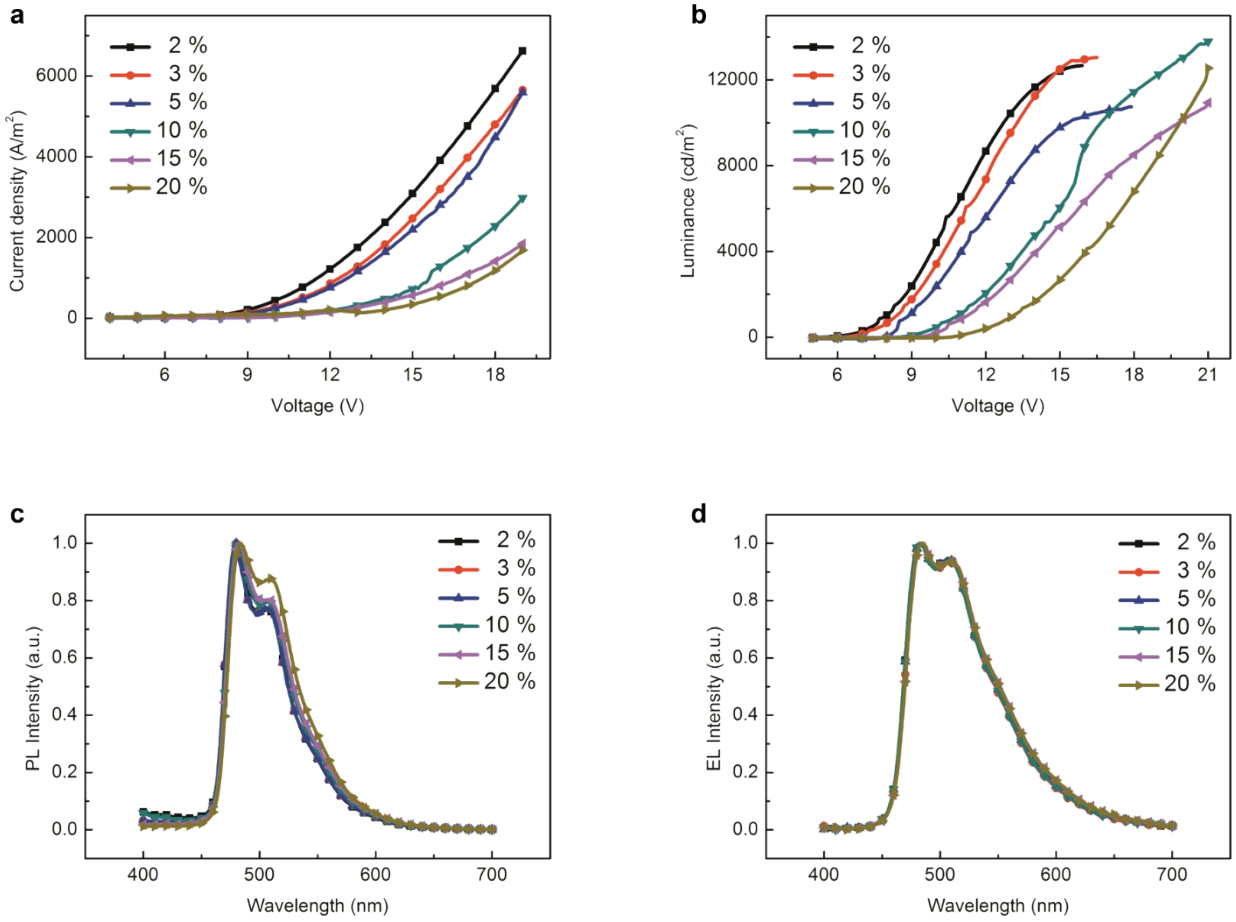
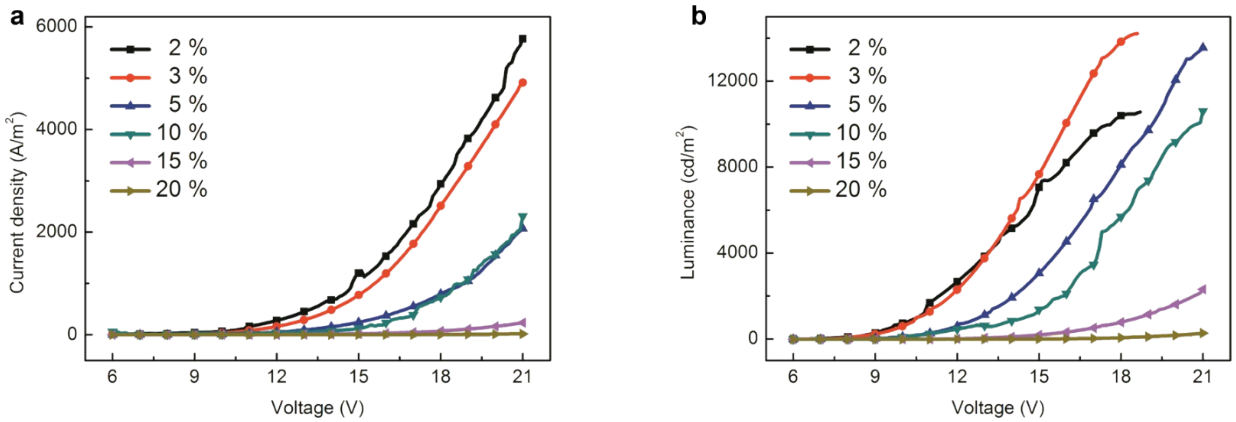


Figure S8. (a) *J-V* and (b) *L-V* characteristics of solution-processed OLEDs with a structure of ITO/ PEDOT: PSS (60 nm)/ PVK: OXD-7: *x* wt. % Complex 2 (85 nm)/ Cs_2CO_3 (2.3 nm)/ Al (150 nm), *x* = 2, 3, 5, 10, 15 or 20. (c) PL spectra of the light-emitting layer, and (d) EL spectra of devices.



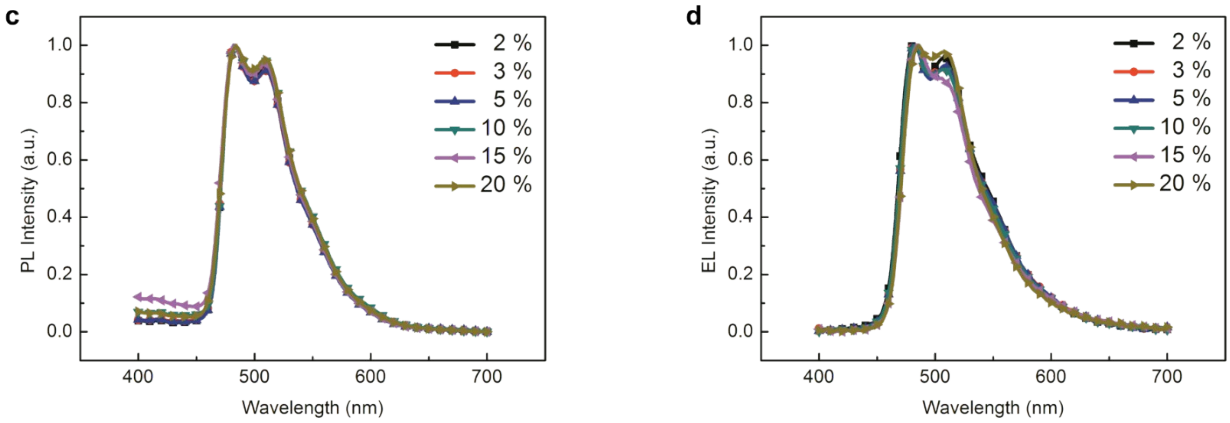


Figure S9. (a) *J*-*V* and (b) *L*-*V* characteristics of solution-processed OLEDs with a structure of ITO/ PEDOT: PSS (60 nm)/ PVK: OXD-7: *x* wt. % Complex 3 (85 nm)/ Cs_2CO_3 (2.3 nm)/ Al (150 nm), *x* = 2, 3, 5, 10, 15 or 20. (c) PL spectra of the light-emitting layer, and (d) EL spectra of devices.

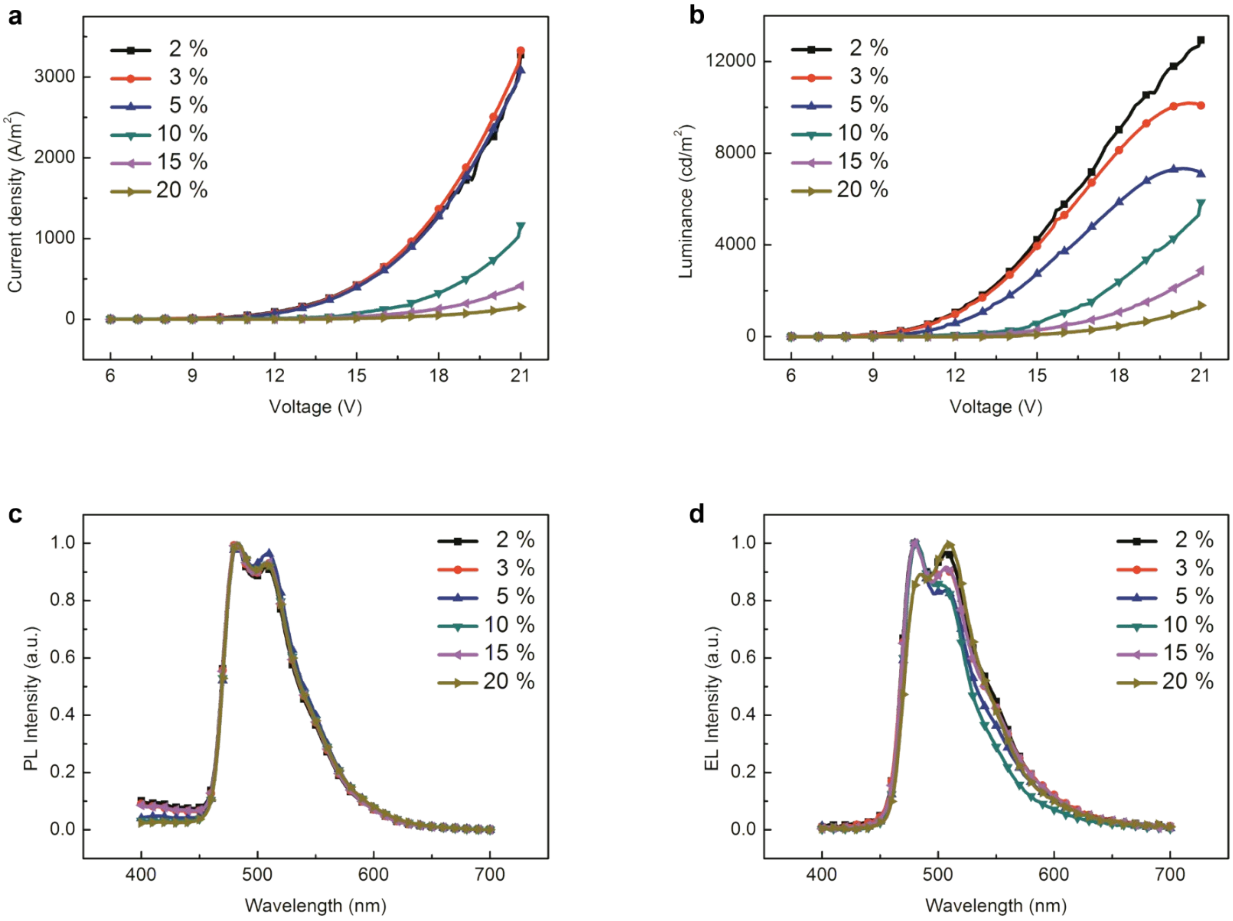


Figure S10. (a) *J-V* and (b) *L-V* characteristics of solution-processed OLEDs with a structure of ITO/ PEDOT: PSS (60 nm)/ PVK: OXD-7: *x* wt. % Complex 4 (85 nm)/ Cs_2CO_3 (2.3 nm)/ Al (150 nm), *x* = 2, 3, 5, 10, 15 or 20. (c) PL spectra of the light-emitting layer, and (d) EL spectra of devices.

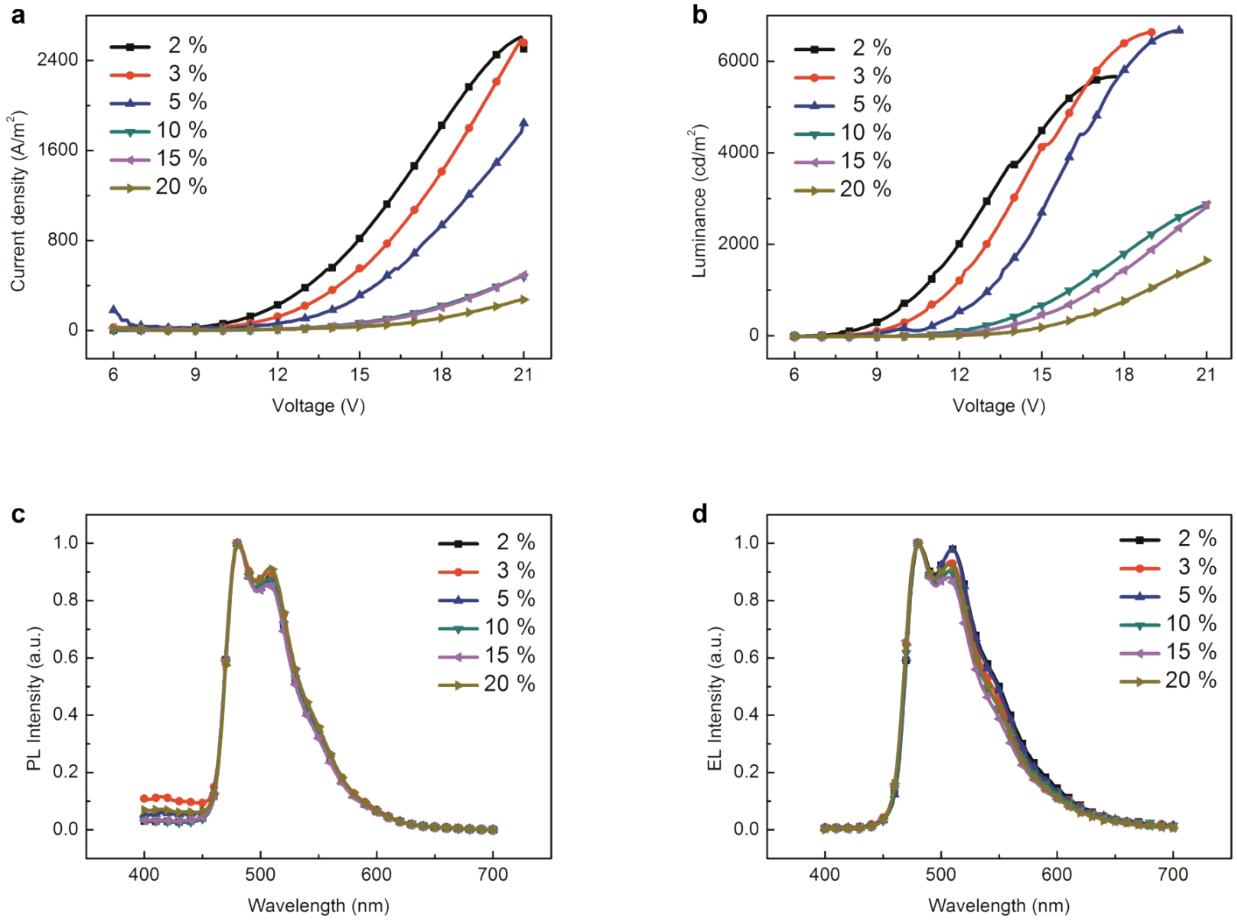


Table S1. Summary of reported performance of selected OLEDs based on ionic transition metal complexes (iTMCs).

iTMCs dopant	Max *CE* (cd A^{-1}) (*EQE*)[e]	Max *L* (cd m^{-2})[f]	EL (nm)[g]	*CIE* (*x, y*)[h]	Reference
$[Ir(ppy)_2(pzpy)]BF_4$	14.8 (5.8 %)	12.5×10^3	482, 508 (sh)	(0.23, 0.48)	This work
$[Ir(ppy)_2(pzpy)]PF_6$	17.1 (6.8 %)	14.2×10^3	482, 508 (sh)	(0.21, 0.48)	This work
$[Ir(ppy)_2(pzpy)][B(5fph)_4]$	13.6 (5.4 %)	10.2×10^3	480, 506 (sh)	(0.21, 0.46)	This work
$[Ir(ppy)_2(pzpy)][BArF_{24}]$	12.4 (4.9 %)	5.7×10^3	480, 508 (sh)	(0.21, 0.48)	This work
$[Ir(dfppy)_2(pzpy)]PF_6$	2.4	995	458	(0.16, 0.28)	20
$[Ir(dfppy)_2(dppmmi)]PF_6$[a]	3.4	730	478	(0.20, 0.38)	26
$[Ir(dfppy)_2(pyim)]PF_6$	0.6 (0.3 %)	890	484	(0.21, 0.38)	21
$[Ir(ppy)_2(dppmmi)]PF_6$[a]	3.8	1.1×10^3	498	(0.24, 0.48)	26
$[Ir(dfppy)_2(bpy)]PF_6$	12.0	17.8×10^3	517	(0.29, 0.58)	22
$[Ir(dfppy)_2(pybi)]PF_6$	0.5 (0.2 %)	730	516, 548	(0.37, 0.57)	21
$[Ir(ppy)_2(pyim)]PF_6$	4.1 (1.3 %)	11.5×10^3	528	(0.35, 0.56)	21
$[Ir(ppy)_2(bpy)]PF_6$	12.5 (1.48 %)	Not mentioned	560	Not mentioned	18
$[Ir(L)_2(N^N)]PF_6$[b]	19.72 (6.48 %)	15.6×10^3	565	(0.44, 0.47)	19
$[Ir(ppy)_2(pybi)]PF_6$	1.2 (0.4 %)	3.6×10^3	566	(0.47, 0.52)	21
$[Ir(ppy)_2(qlbi)]PF_6$	0.4 (0.3 %)	1.1×10^3	618	(0.62, 0.38)	21
$[Ir(npy)_2(c\text{-}phen)]PF_6$[a]	10.0 (7.1 %)	3.2×10^3	618	(0.57, 0.40)	24
$[Ir(npy)_2(o\text{-}phen)]PF_6$[a]	9.1 (6.5 %)	2.3×10^3	620	(0.57, 0.40)	24
$[Cu(dnbp)(DPEphos)]BF_4$[a]	11.0	1.5×10^3	519	Not mentioned	36
$[Cu(phen)(DPEphos)]BF_4$[a]	2.6	1.7×10^3	555	Not mentioned	36
Os-salt-1[c]	(0.48 %)	1430	611	Not mentioned	37
Os-salt-2[d]	1.9 (2.2 %)	870	637	Not mentioned	37

[a] In OLEDs with hole blocking layers. [b] In OLEDs fabricated by vacuum evaporation deposition. [c] short for [Os(II)(4,7-bis(*p*-methoxyphenyl)-1,10-phenanthroline)$_2$(*cis*-1,2-bis(diphenylphosphino)ethylene)](tosylate)$_2$; [d] short for [Os(II)(4,7-bis(4-naphth-2-ylphenyl)-1,10-phenanthroline)$_2$(*cis*-1,2-vinylenebis(diphenylarsine))]$(PF_6)_2$. [e] *CE*, current efficiency; *EQE*, external quantum efficiency. [f] *L*, luminance. [g] *EL*, electroluminescence wavelength. [h] *CIE*, Commission Internationale de l'Elairage.