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

Rational molecular design of aggregation-induced emission cationic Ir(III) phosphors achieving supersensitive and selective detection of nitroaromatic explosives

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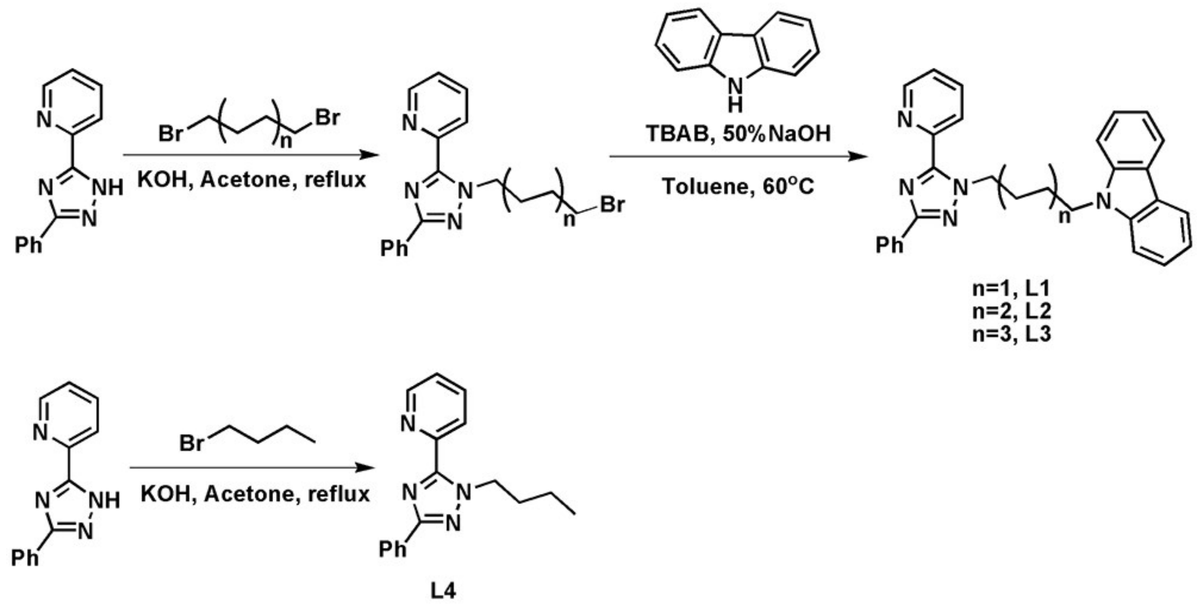


Scheme S1 Synthetic routes of ancillary ligands **L1-L4**.

Characterization of L1.

^{1}H NMR (500 MHz, $CDCl_3$, δ [ppm]): 8.57 (d, J = 4.0 Hz, 1H), 8.32 (d, J = 8.0 Hz, 1H), 8.17–8.18 (m, 2H), 8.08 (d, J = 8.0 Hz, 2H), 7.82–7.85 (m, 1H), 7.42–7.49 (m, 2H), 7.38–7.41 (m, 5H), 7.32–7.34 (m, 1H), 7.19–7.22 (m, 2H), 4.91 (t, J = 7.0 Hz, 2H), 4.37 (t, J = 7.0 Hz, 2H), 2.08–2.11 (m, 2H), 1.96–1.99 (m, 2H).

Characterization of L2.

^{1}H NMR (500 MHz, $CDCl_3$, δ [ppm]): 8.51 (d, J = 4.5 Hz, 1H), 8.28 (d, J = 8.0 Hz, 1H), 8.16–8.17 (m, 2H), 8.09 (d, J = 8.0 Hz, 2H), 7.79–7.82 (m, 1H), 7.35–7.46 (m, 7H), 7.26–7.29 (m, 1H), 7.20–7.25 (m, 2H), 4.82 (t, J = 7.5 Hz, 2H), 4.27 (t, J = 7.0 Hz, 2H), 1.91–1.94 (m, 2H), 1.83–1.86 (m, 2H), 1.40–1.42 (m, 4H).

Characterization of L3.

^{1}H NMR (500 MHz, $CDCl_3$, δ [ppm]): 8.57–8.59 (m, 1H), 8.28 (d, J = 8.0 Hz, 1H), 8.16–8.18 (m, 2H), 8.09 (d, J = 8.0 Hz, 2H), 7.77–7.80 (m, 1H), 7.45–7.46 (m, 4H), 7.37–7.44 (m, 3H), 7.24–7.27 (m, 1H), 7.20–7.23 (m, 2H), 4.81 (t, J = 7.5 Hz, 2H), 4.26 (t, J = 7.5 Hz, 2H), 1.84–1.93 (m, 2H), 1.27–1.33 (m, 8H).

Characterization of L4.

^{1}H NMR (500 MHz, $CDCl_3$, δ [ppm]): 8.66–8.68 (m, 1H), 8.30–8.32 (m, 1H), 8.17–8.19 (m, 2H), 7.81–7.85 (m, 1H), 7.43–7.47 (m, 2H), 7.37–7.41 (m, 1H), 7.31–7.34 (m, 1H), 4.84–4.87 (m, 2H), 1.91–1.97 (m, 2H), 1.38–1.42 (m, 2H), 0.94 (t, J = 7.5Hz, 3H).

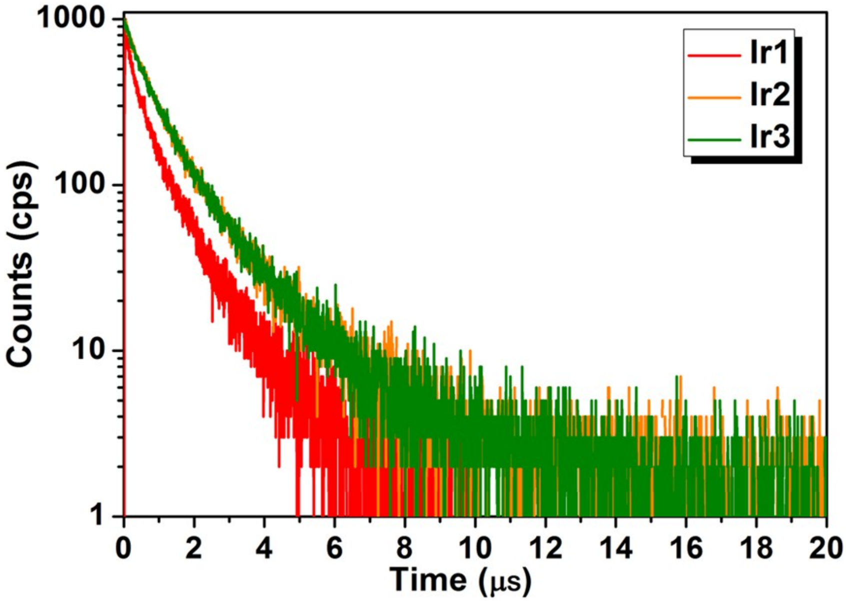


Fig. S1 Excited-state lifetimes in neat films of **Ir1, Ir2** and **Ir3**.

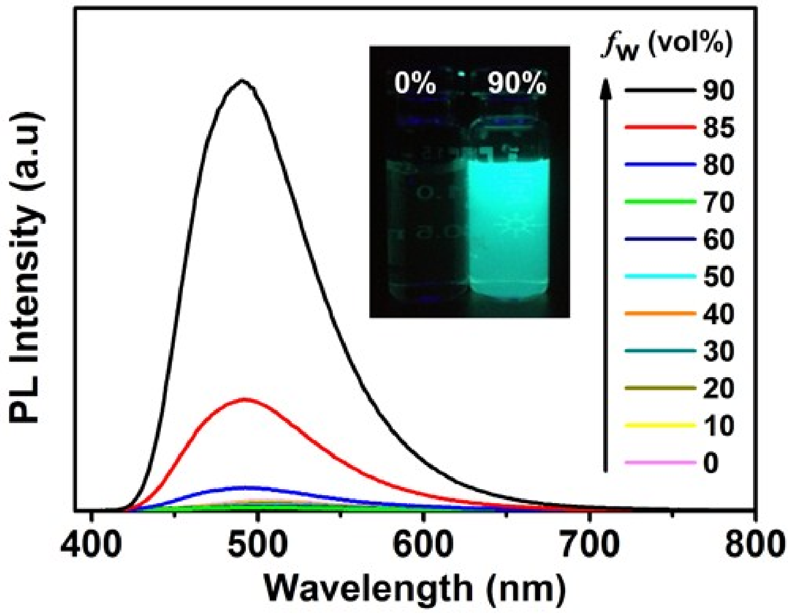


Fig. S2 Emission spectra of **Ir2** in the CH_3CN/H_2O mixtures with different water fractions (0-90%) at room temperature.

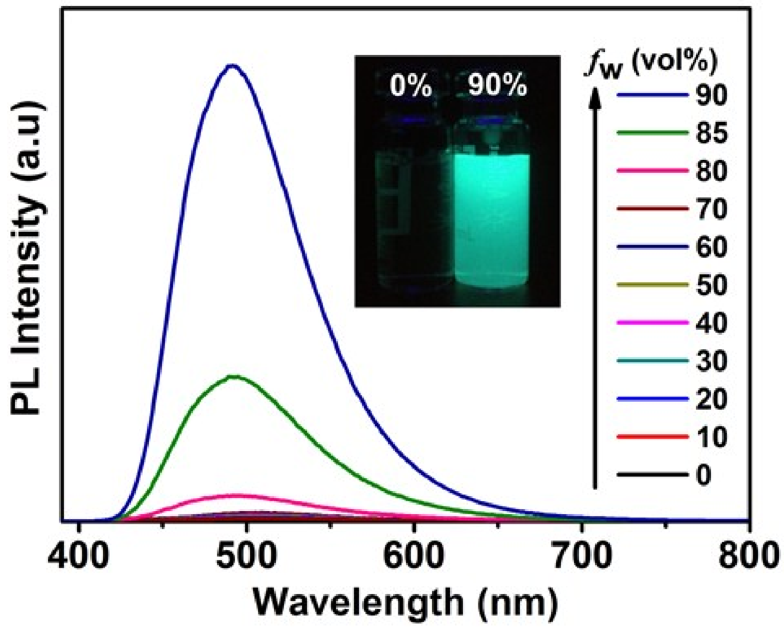


Fig. S3 Emission spectra of **Ir3** in the CH_3CN/H_2O mixtures with different water fractions (0-90%) at room temperature.

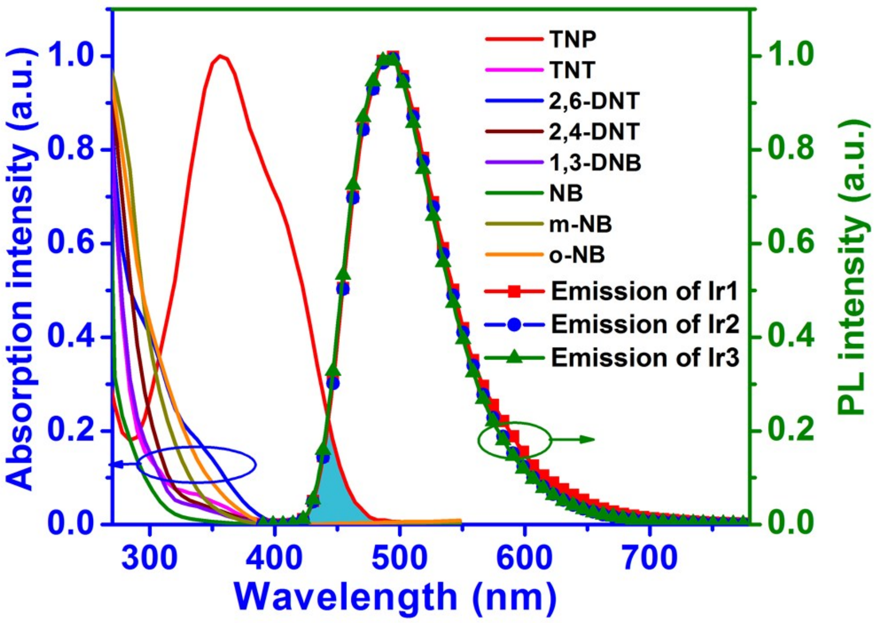
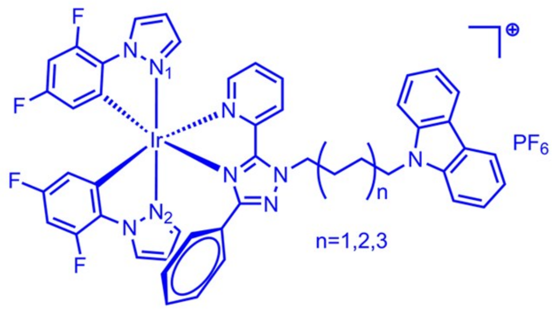


Fig. S4 Absorption spectra of selected explosives and emission spectra of **Ir1, Ir2** and **Ir3** in CH_3CN/H_2O (v/v = 1 : 9) mixtures.



In ^{3}MC state	Bond lengths (Å)	
	Ir-N1	Ir-N2
Ir1	2.4940	2.1608
Ir2	2.4939	2.1613
Ir3	2.4941	2.1610

Fig. S5 Calculated geometric parameters for ^{3}MC of **Ir1, Ir2** and **Ir3**.

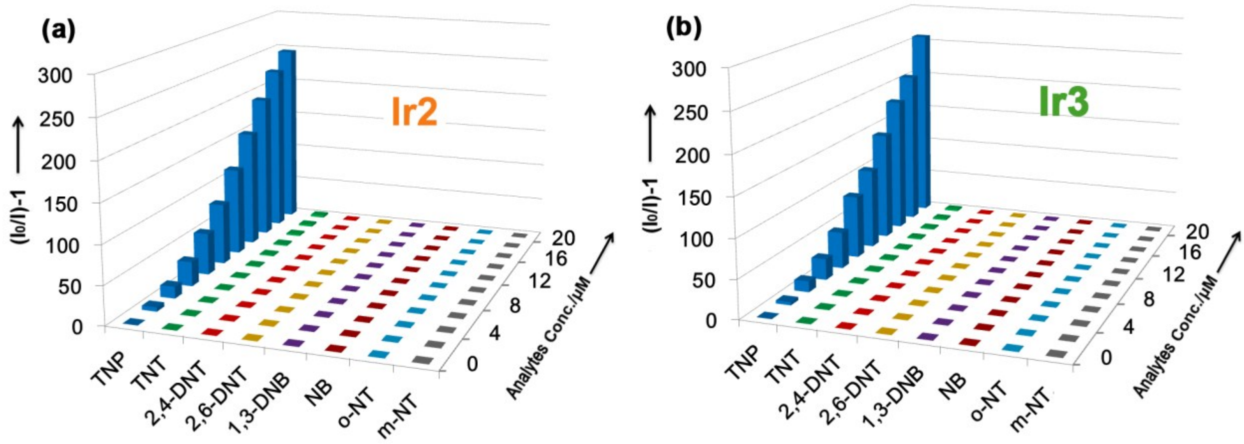


Fig. S6 Stern–Volmer plots of analytes for **Ir2** and **Ir3** in CH_3CN/H_2O (v/v = 1 : 9) mixtures.

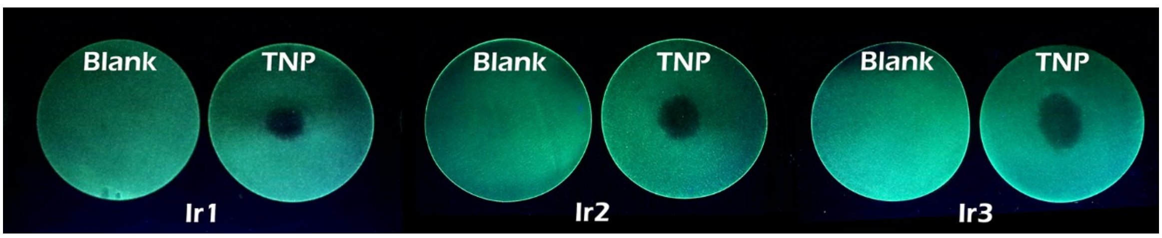


Fig. S7. Luminescent photographs of filter papers impregnated by **Ir1–Ir3** against 2 ppm TNP.

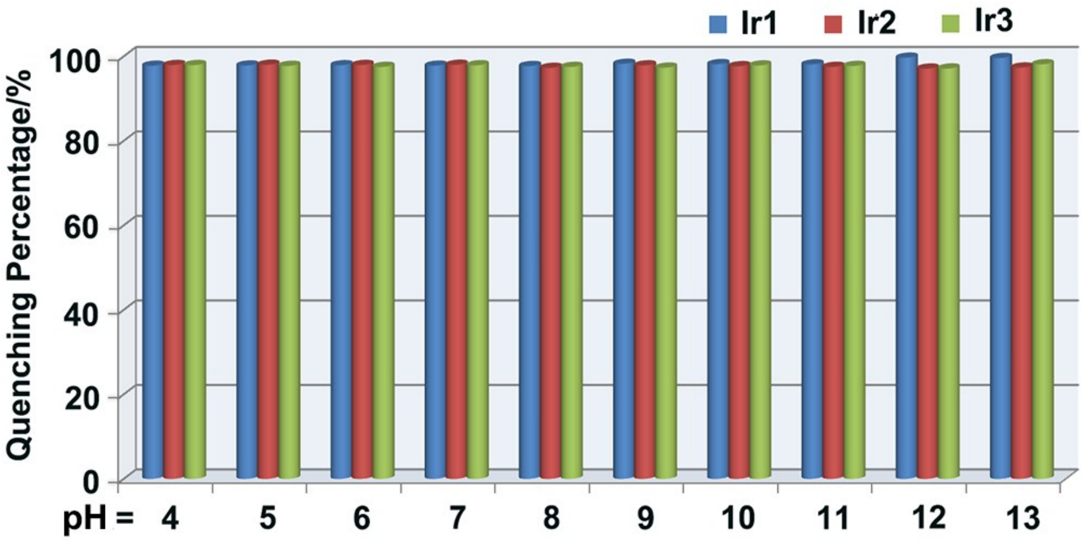


Fig. S8 The effect of pH on percentage of emission quenching of all complexes in CH_3CN/H_2O (v/v = 1 : 9) containing 2 ppm TNP. Buffer solutions: pH (4.0, 5.0), $CH_3COOH-CH_3COONa$; pH (6.0−8.0), $NaH_2PO_4-Na_2HPO_4$; pH (9.0−11.0), $NaHCO_3-Na_2CO_3$; pH 12.0, NaH_2PO_4-NaOH; and pH 13.0, KCl−NaOH.

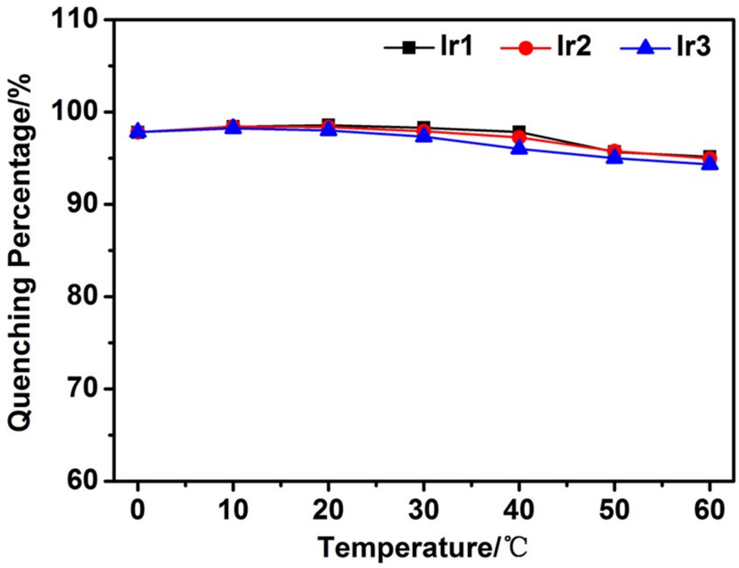


Fig. S9 The effect of temperature on percentage of emission quenching of all complexes in CH_3CN/H_2O (v/v = 1 : 9) containing 2 ppm TNP.

Table S1 Statistical comparison of the AIE dyes used to detect TNP.

	Solvent system	Quenching constants K_{sv} (M^{-1})	Limit of detection
This work	CH_3CN/H_2O (1 : 9 v/v)	3.79×10^6	10 ppb
Ref[1]	THF/H_2O (1 : 9 v/v)	2.10×10^4	NA
Ref[2]	THF/H_2O (1 : 9 v/v)	8.00×10^4	0.1 ppm
Ref[3]	Water or buffer	5.88×10^4	NA
Ref[4]	THF/H_2O (1 : 9 v/v)	1.00×10^5	NA
Ref[5]	THF/H_2O (1 : 9 v/v)	5.70×10^5	NA
Ref[6]	THF/H_2O (6 : 4 v/v)	3.20×10^6	NA
Ref[7]	THF/H_2O (1 : 9 v/v)	2.50×10^5	NA
Ref[8]	DMF/H_2O (1 : 9 v/v)	1.10×10^5	NA
Ref[9]	THF/H_2O (1 : 99 v/v)	2.90×10^5	NA
Ref[10]	CH_2Cl_2/hexane (1 : 9 v/v)	2.18×10^6	0.13 ppb
Ref[11]	THF/H_2O (1 : 9 v/v)	7.00×10^4	NA
Ref[12]	THF/H_2O (1 : 9 v/v)	5.65×10^4	NA
Ref[13]	THF/H_2O (1 : 9 v/v)	4.29×10^5	NA
Ref[14]	THF/H_2O (1 : 9 v/v)	NA	0.5 ppm
Ref[15]	THF/H_2O (1 : 9 v/v)	1.80×10^5	NA
Ref[16]	THF/H_2O (1 : 9 v/v)	3.39×10^4	NA
Ref[17]	THF/H_2O (1 : 9 v/v)	2.67×10^4	NA
Ref[18]	THF/H_2O (1 : 9 v/v)	3.47×10^5	NA
Ref[19]	THF/H_2O (1 : 9 v/v)	3.80×10^5	NA

[NA] Not available

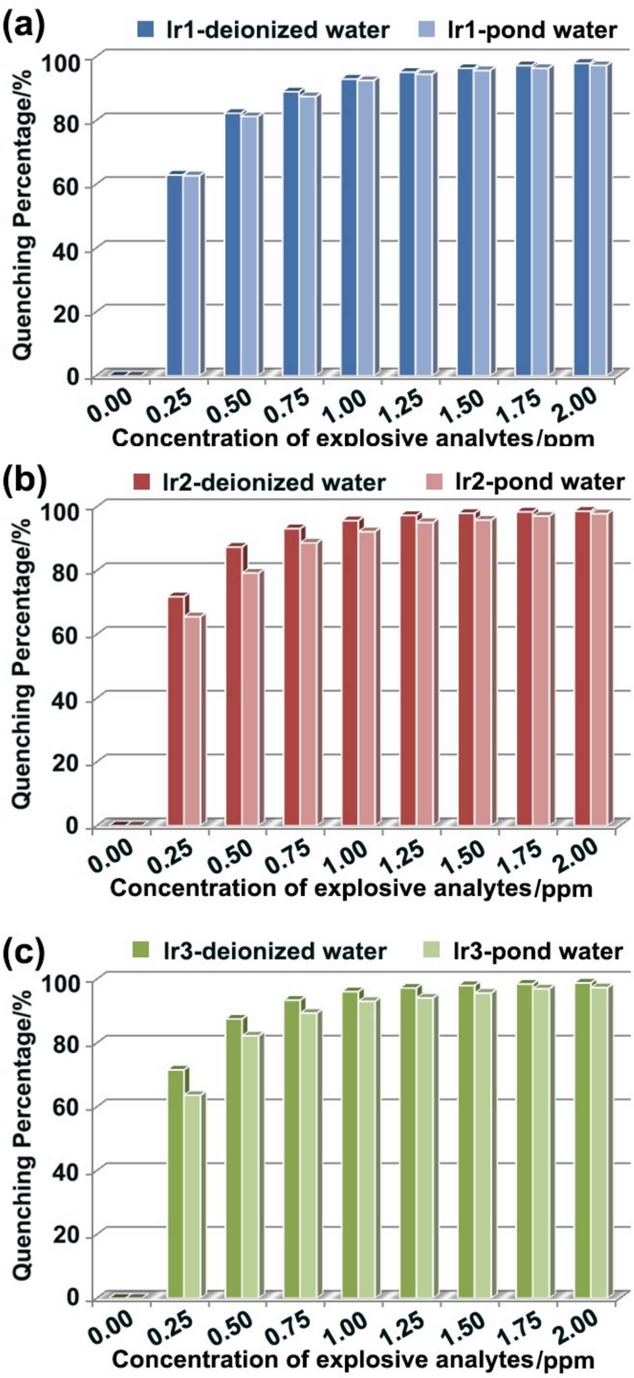


Fig. S10 The detection in pond water containing 2 ppm TNP.

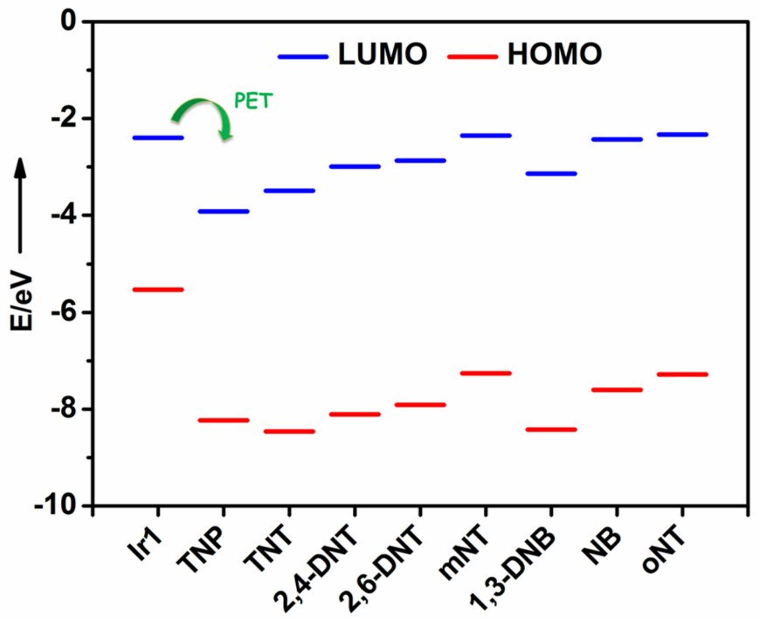
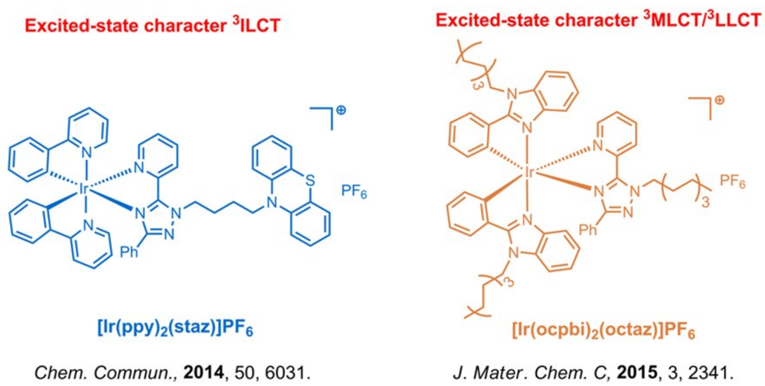


Fig. S11 Calculated HOMO and LUMO energies of **Ir1** and the analytes.



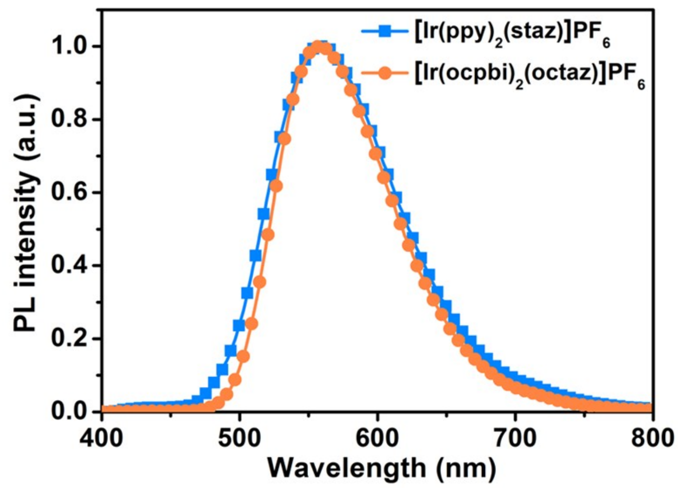


Fig. S12 Chemical structures and PL spectra of the reported complexes **[Ir(ppy)$_2$(staz)]PF$_6$** and **[Ir(ocpbi)$_2$(octaz)]PF$_6$**.

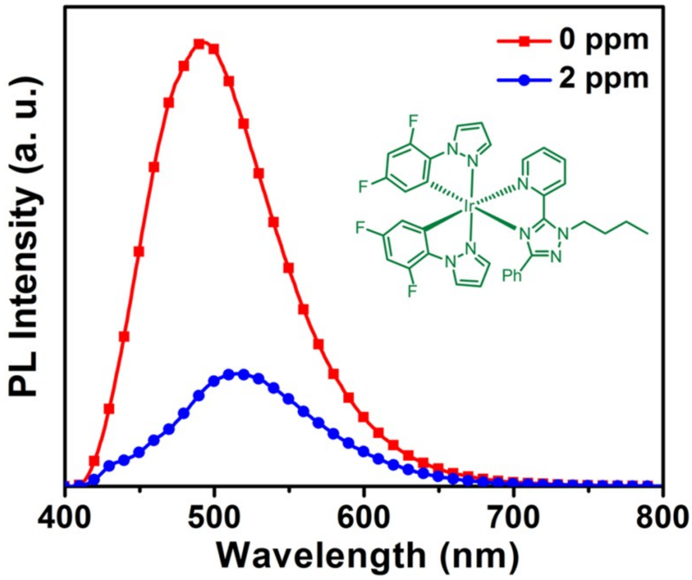


Fig. S13 PL spectra of **Ir4** with addition of 0 and 2 ppm TNP in CH_3CN/H_2O mixtures (v/v = 1 : 9).

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