Supplementary materials for:

Nickel(II) and Iron(III) Selective Off-On-Type Fluorescence Probes Based on Perylene Tetracarboxylic Diimide

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Figure S1. ^{1}H NMR spectrum of **PDI-1** in $CDCl_3$

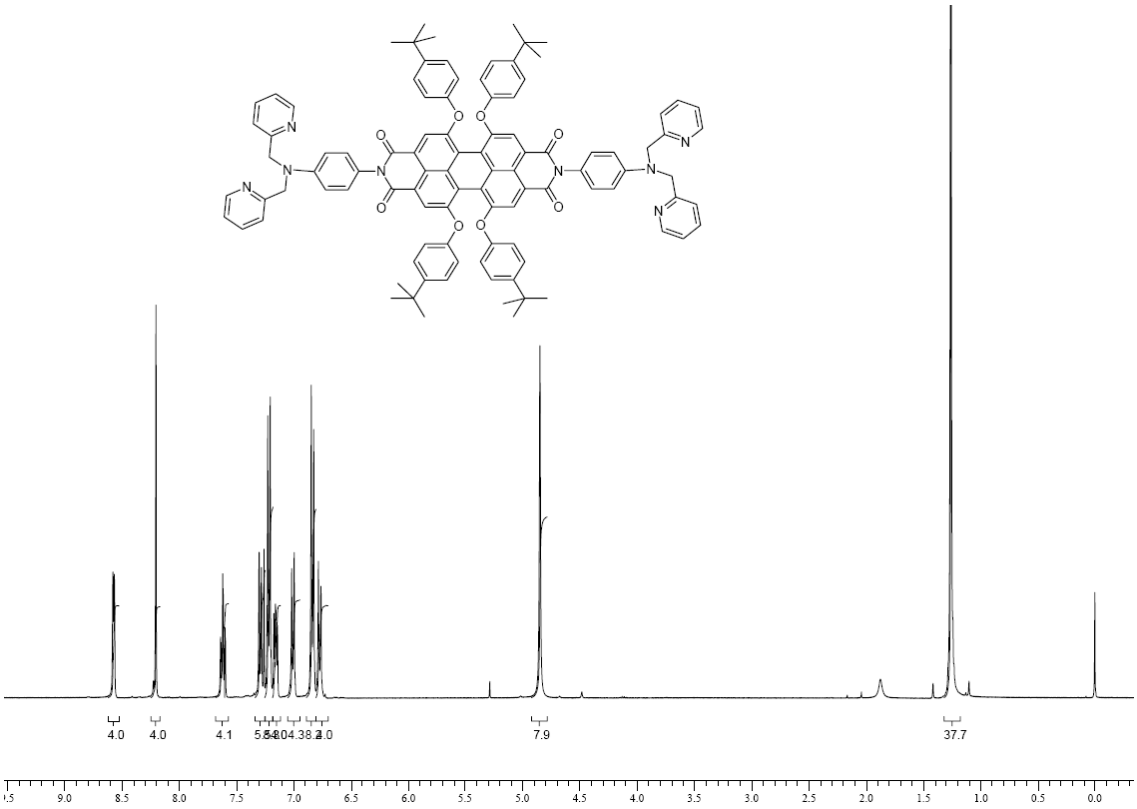


Figure S2. ^{13}C NMR spectrum of **PDI-1** in $CDCl_3$

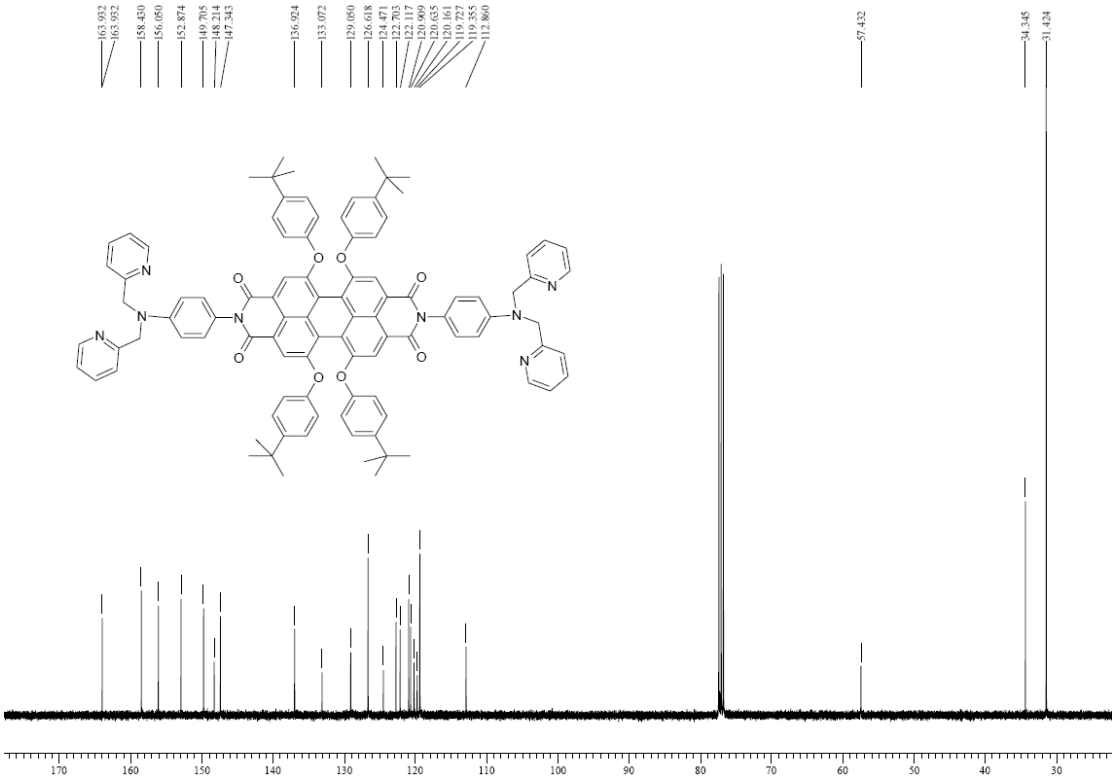


Figure S3. ^{1}H NMR spectrum of **PDI-2** in $CDCl_3$

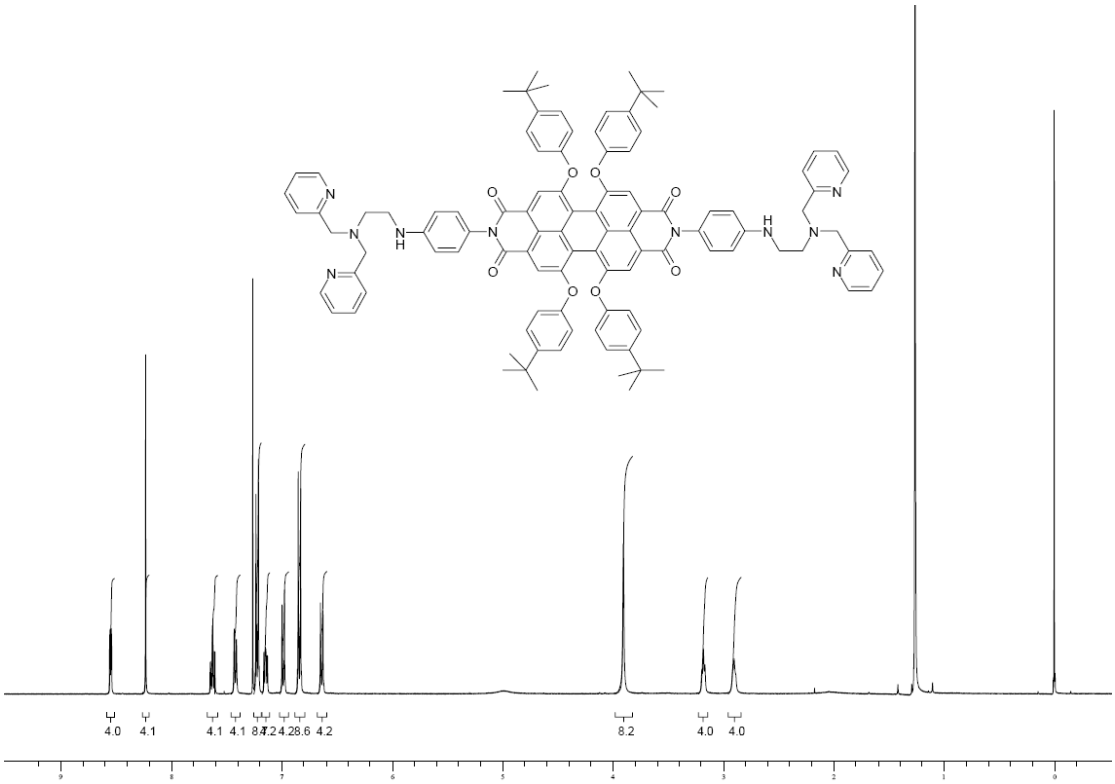
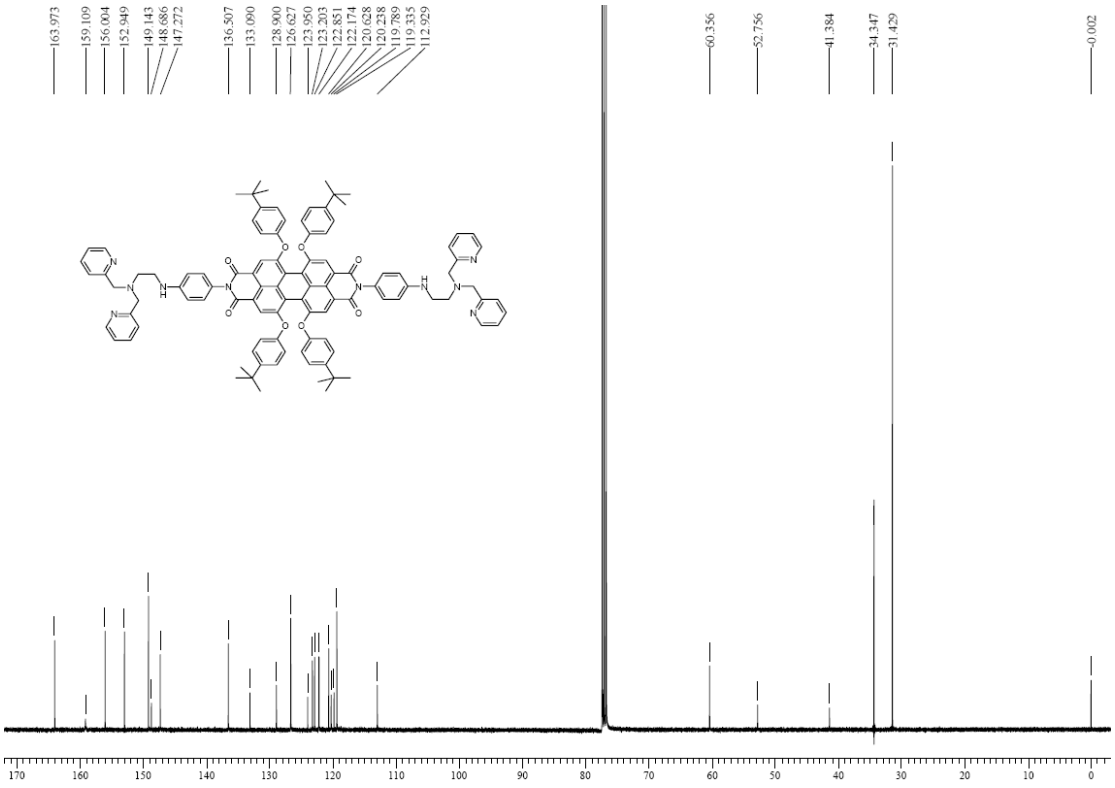


Figure S4. ^{13}C NMR spectrum of **PDI-2** in $CDCl_3$



Free energy calculation for the photoinduced electron transfer from DPA to PDI.

The Rehm-Weller equation:

$\Delta G_{PET} = E^0_{ox} - E^0_{red} - E_S - e^2/\varepsilon r$

where the E^0_{ox} is the oxidation potential of the electron donor (amino group), the E^0_{red} is the reduction potential of the electron acceptor (PDI unit), E_s is the energy of the lowest excited singlet state of the PDI, and the part $-e^2/\varepsilon r$ corresponds to the energy of stabilization of the solvent to the ion pair.

The values of the E^0_{ox}, E^0_{red}, E_s and $e^2/\varepsilon r$ were 0.97 eV[1], $-$0.72 eV[2], 2.07 eV and -0.12 eV[3], respectively.

Reference:

1. B. Rybtchinski, L. E. Sinks, M. R. Wasielewski, *J. Phy. Chem. A*, **2004**, *108*, 7497-7505.

2. J. Feng, Y. Zhang, C. Zhao, R. Li, W. Xu, X. Li, J. Jiang, *Chem. Eur. J.* **2008**, *14*, 7000-7010.

3. R. Zhang, Z. Wang, Y. Wu, H. Fu, J. Yao, *Org. Lett.*, **2008**, *10*, 3065-3068.

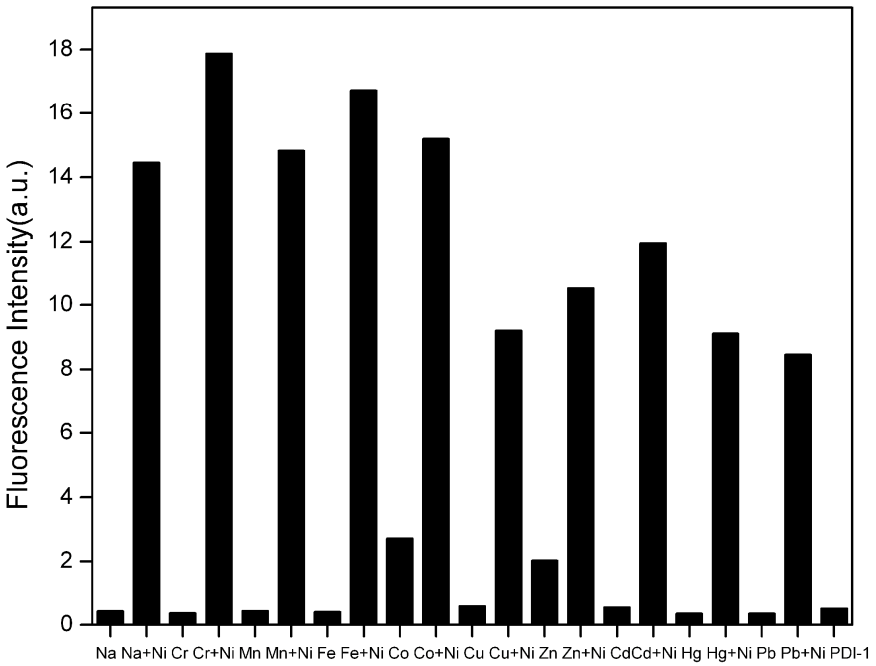


Figure S5. Fluorescence responses of PDI-1 (8 μM) to various metal cations (12 equiv) and equimolar mixtures of these cations with a second transition metal cation, respectively, in DMF solution (λ_{ex} = 440 nm).

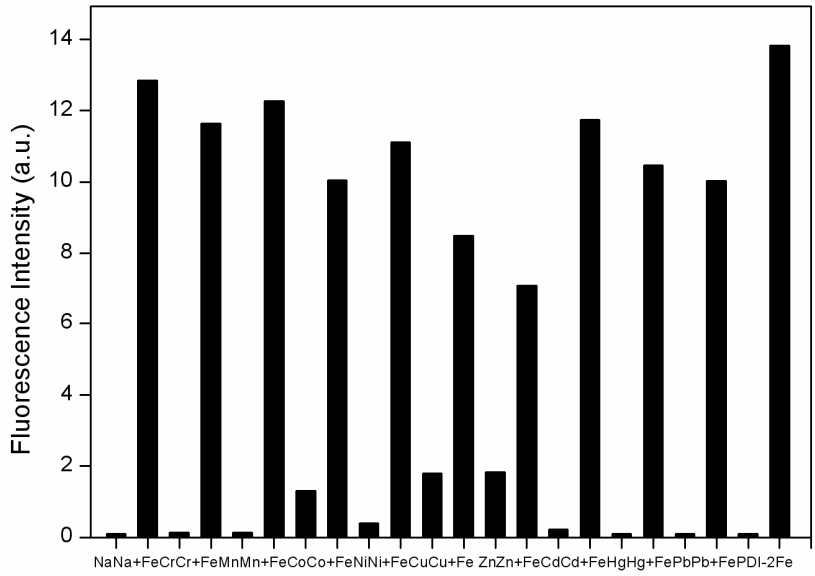


Figure S6. Fluorescence responses of PDI-2 (5 μM) to Fe^{3+}(4 equiv) and other metal cations (8 equiv) in DMF solution and PDI-2 in the presence of Fe^{3+}(4 equiv) plus other metal cations (8 equiv) in DMF solution, respectively. Bars represent the integrated fluorescence emission. The excitation was 440 nm

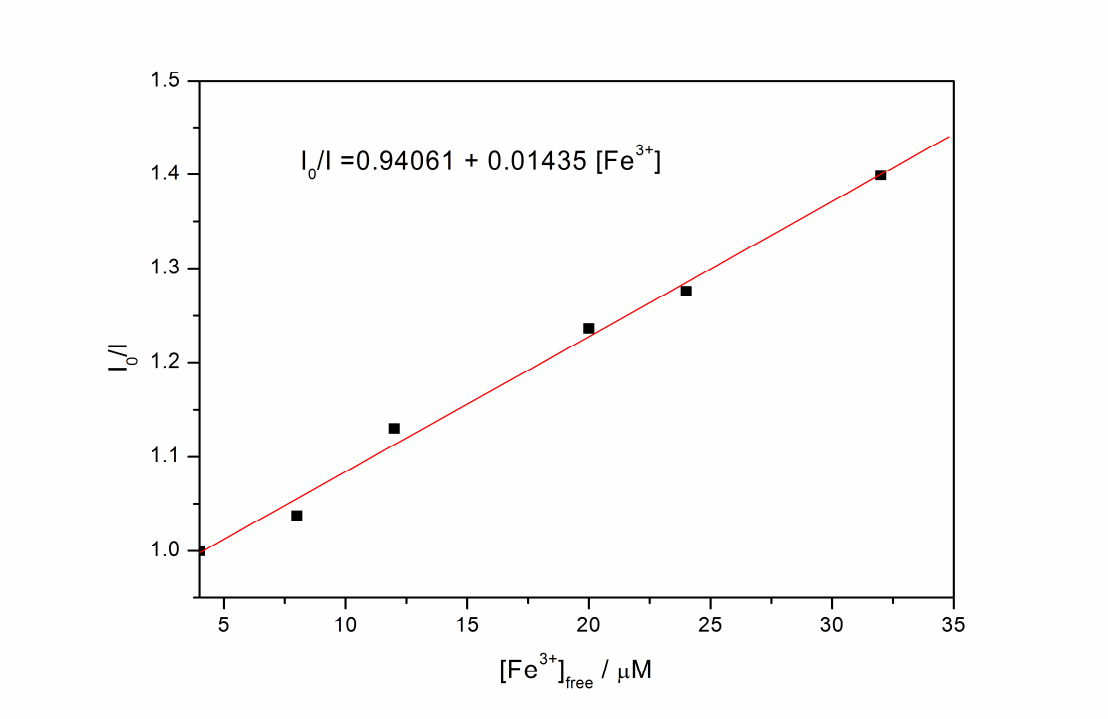


Figure S7. Stern-volmer plot of the fluorescence quenching of **PDI-2** in the presence of excess of Fe^{3+}

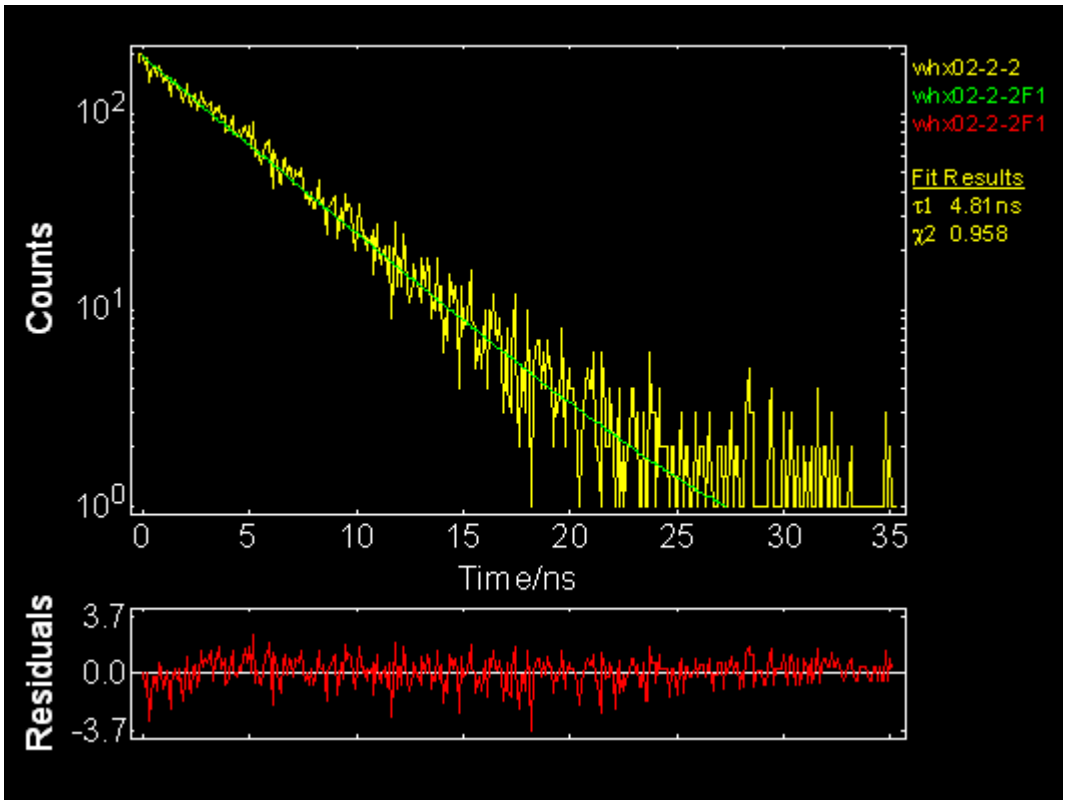


Figure S8. Fluorescence lifetime measurement of PDI-2 in the presence of Fe^{3+}. [PDI-2] = 6μM**,** [Fe^{3+}] = 24μM (4equ.), the excitation was at 440 nm, τ = 4.81 ns.

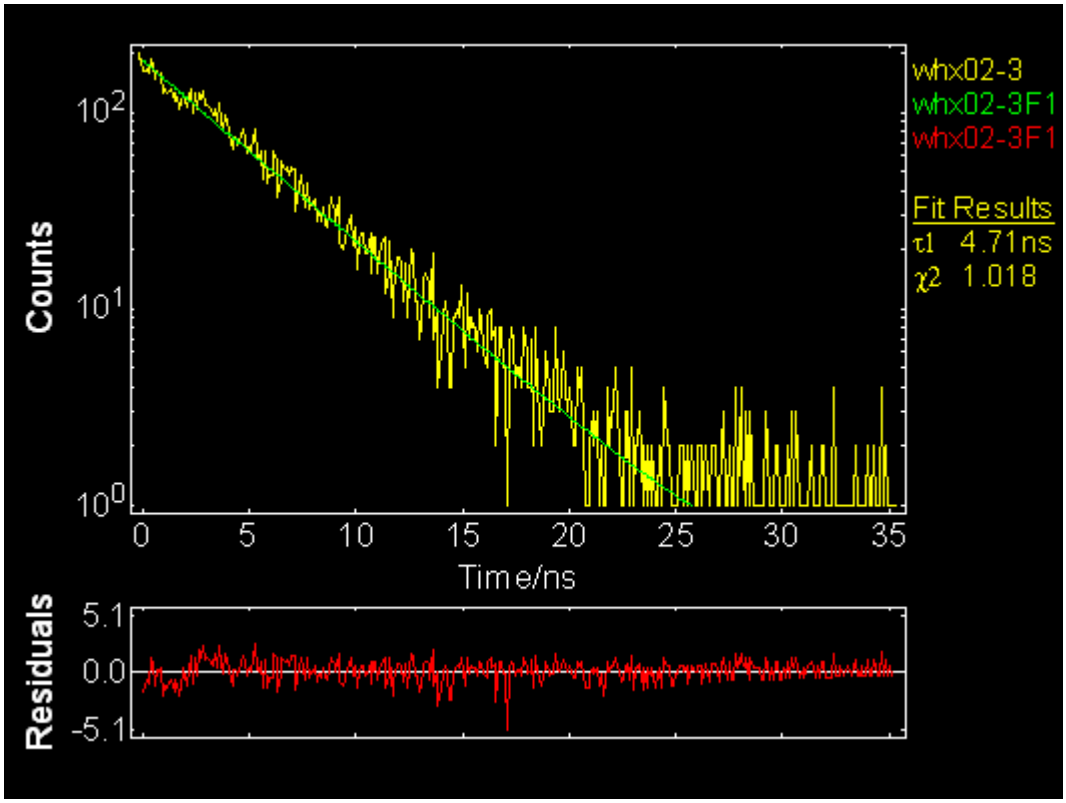


Figure S9. Fluorescence lifetime measurement of PDI-2 in the presence of Fe^{3+}. [PDI-2] = 6μM**,** [Fe^{3+}] = 42μM (7equ.), the excitation was at 440 nm, τ = 4.71 ns.

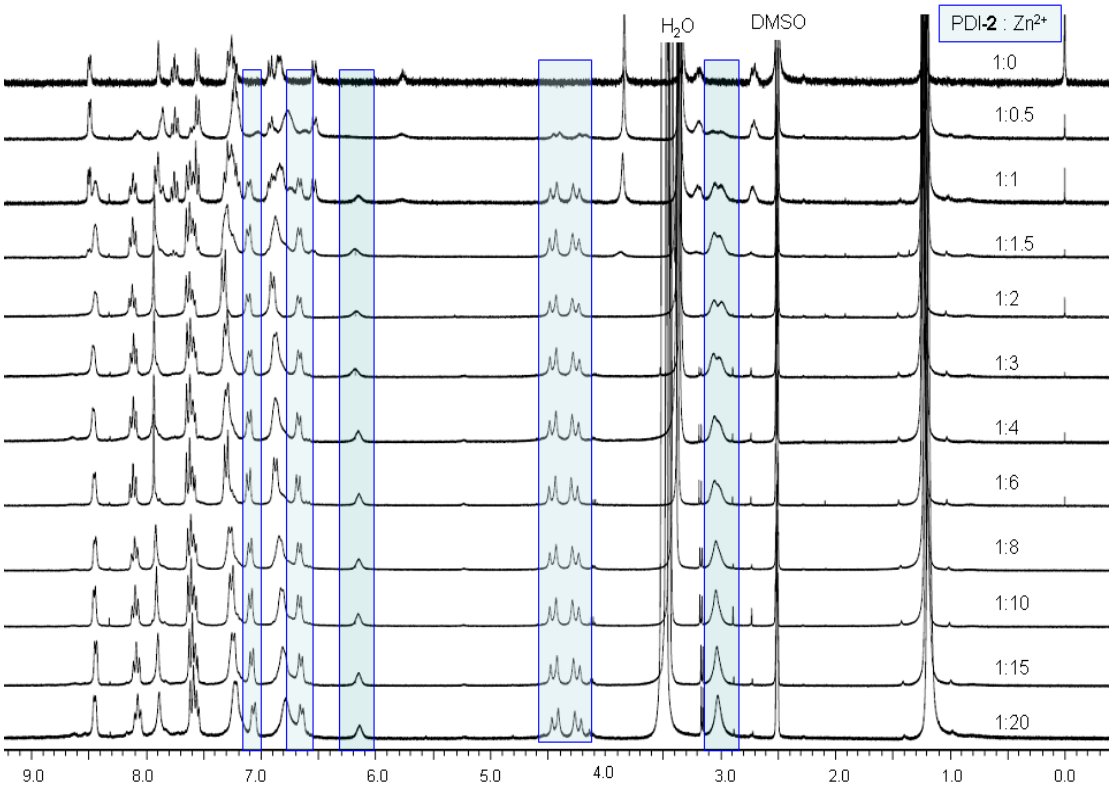


Figure S10. ^{1}H NMR (300MHZ) spectra of **PDI-2** obtained during the titration with zinc (Ⅱ) ions measured in DMSO-d_6. The ratio of [PDI-2] to [Zn^{2+}] varied from 1/0 to 1/20. The squares indicate the new peaks formed in the presence of Zn^{2+}.

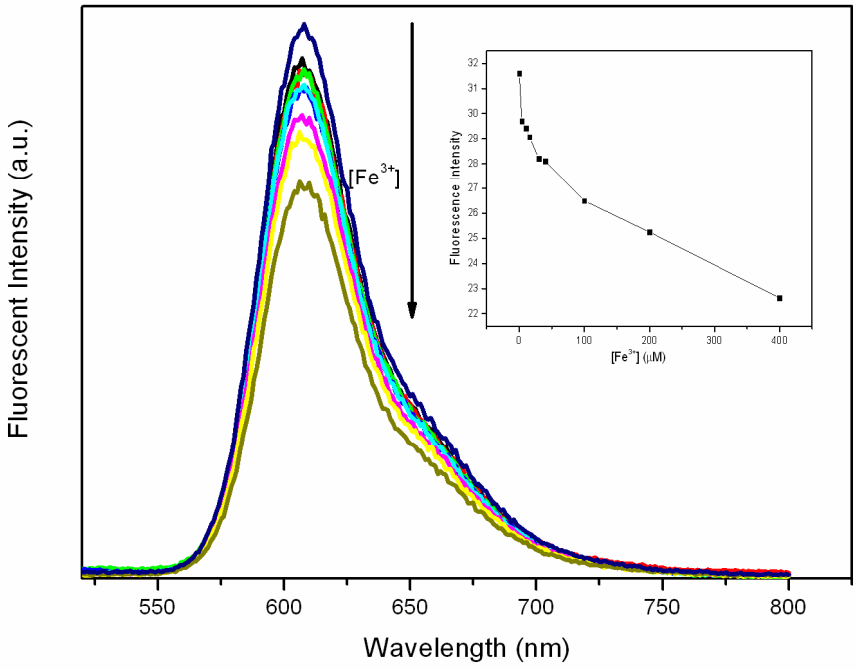


Figure S11. Fluorescence spectra of **PDI-2** analog N,N'-di-*n*-butyl-1,6,7,12 -tetra(4-***tert***-butylphenoxy)perylene-3,4:9,10-tetracarboxylic-diimide (4 μM) with the increasing concentration of $FeCl_3$ in DMF at room temperature. The excitation wavelength was 440 nm. Inset showed the plot of integrated fluorescent intensity of the compound with the concentration of Fe^{3+} in DMF.