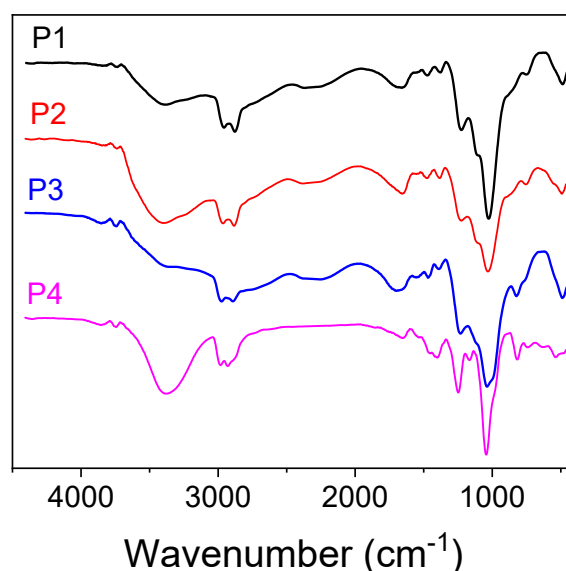


# Intrinsic bright green emission from hyperbranched polyphosphate esters: preparation, film fabrication and Fe<sup>3+</sup> sensing

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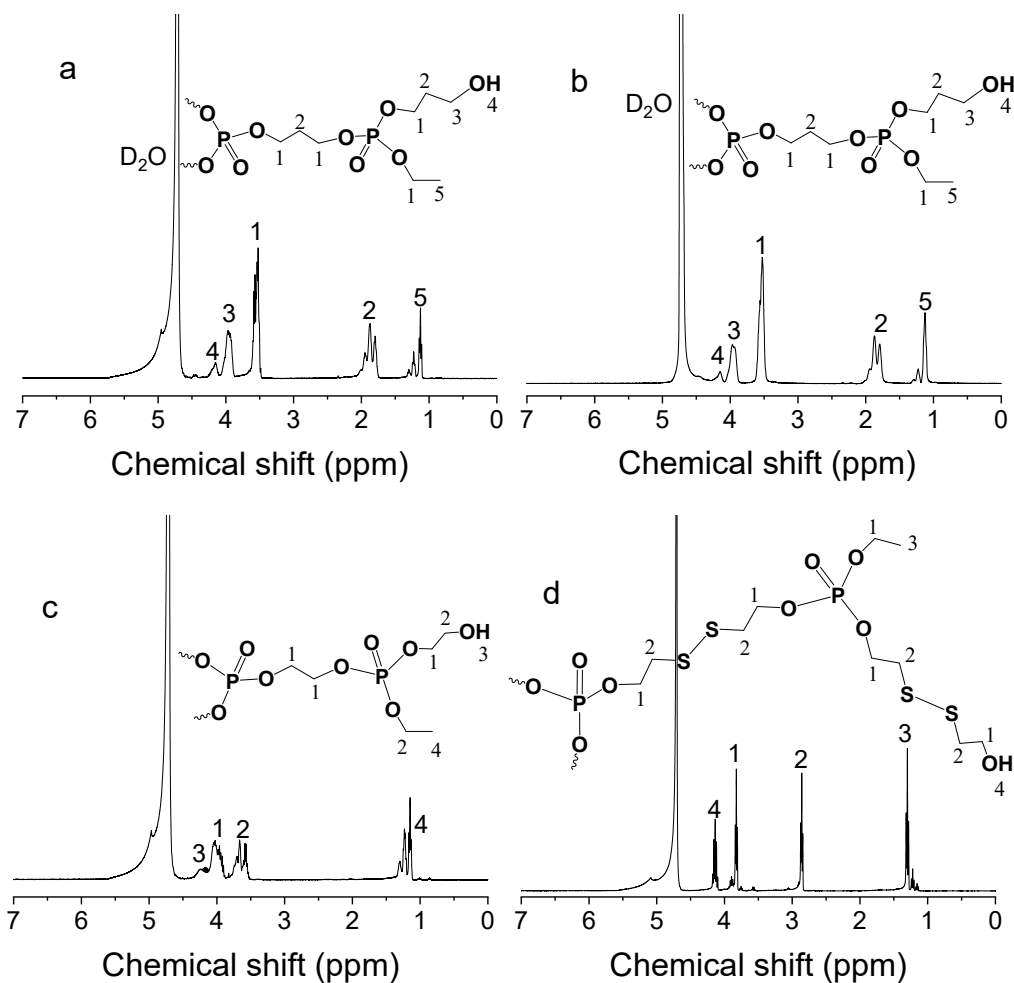
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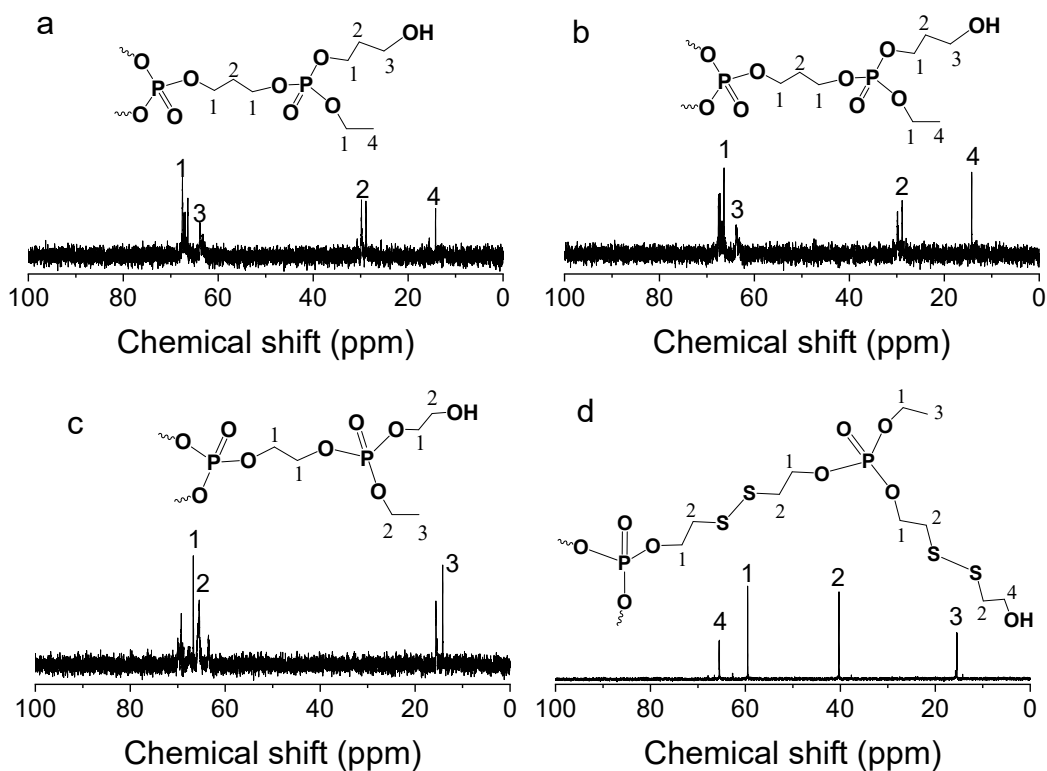
**Figure S1.** FTIR spectra of P1, P2, P3 and P4.

In the FTIR spectrum of P1, P2, P3 and P4 (**Figure S1**), the absorption peaks at 3381 cm<sup>-1</sup> is corresponded to the stretching vibration of OH. Peak at 1243 cm<sup>-1</sup> is ascribed to the vibration of P=O. Peaks at 1038 and 1160 cm<sup>-1</sup> are caused by the vibration of P-O and C-O, respectively.



**Figure S2.**  $^1\text{H}$  NMR spectra of P1 (a), P2 (b), P3 (c) and P4(d).

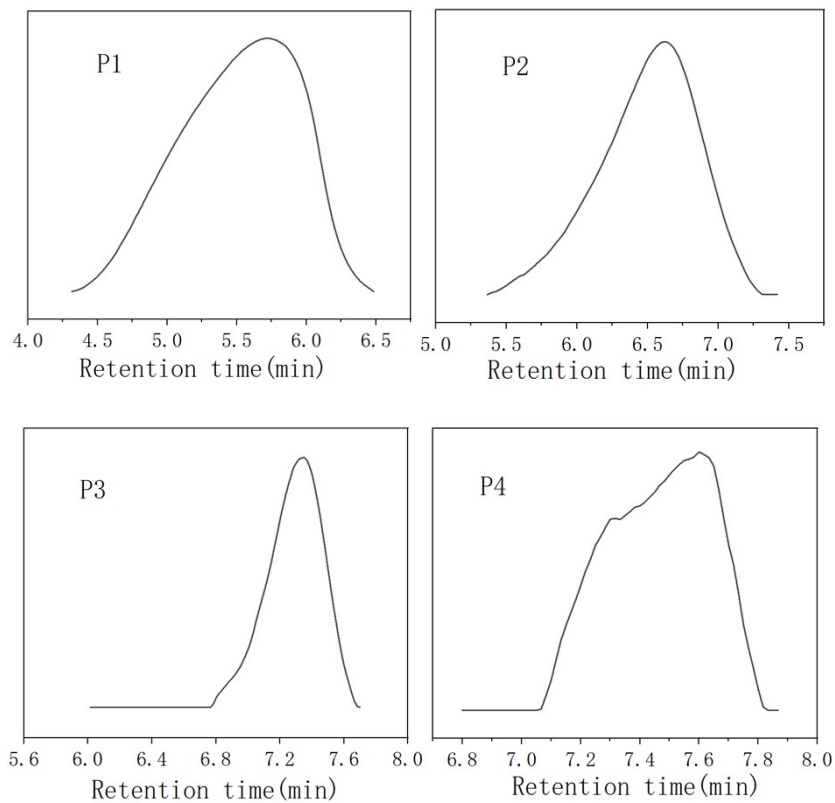
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of P1-P4 were also obtained to further confirm the structures. In the  $^1\text{H}$  NMR spectrum of P1 (**Figure S2a**), signals at 1.87, 3.54 and 3.95 ppm come from protons of methylene groups ( $-\text{CH}_2-$ ) of  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$  (H2),  $\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}$  (H1) and  $\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$  (H3), respectively. Peak at 1.12 comes from  $\text{P}-\text{O}-\text{CH}_2-\text{CH}_3$  (H5). The signal at 4.15 ppm is ascribed to the protons of  $-\text{OH}$  (H4). The  $^1\text{H}$  NMR spectrum of P2 (**Figure S2b**) is quite similar to that of P1, because they have the similar structures. In the  $^1\text{H}$  NMR spectrum of P3 (**Figure S2c**), the signals at 3.98 and 3.66 ppm come from protons of methylene groups ( $-\text{CH}_2-$ ) of  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$  (H1) and  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$  (H2), respectively. The signals at 1.14 and 4.24 ppm are ascribed to the protons of  $-\text{O}-\text{CH}_2-\text{CH}_3$  (H4) and  $-\text{OH}$  (H3), respectively. In the  $^1\text{H}$  NMR spectrum of P4 (**Figure S2d**), signals at 3.82 and 2.86 ppm come from protons of methylene groups ( $-\text{CH}_2-$ ) of  $\text{O}-\text{CH}_2-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-\text{CH}_2-\text{O}$  (H1) and  $\text{O}-\text{CH}_2-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-\text{CH}_2-\text{O}$  (H2), respectively. The signals at 4.12 and 1.30 ppm are ascribed to the protons of  $-\text{OH}$  (H4) and  $-\text{O}-\text{CH}_2-\text{CH}_3$  (H3), respectively.



**Figure S3.**  $^{13}\text{C}$  NMR spectra of P1 (a), P2 (b), P3 (c) and P4(d).

In the  $^{13}\text{C}$  spectrum of P1 and P2 (**Figure S3a** and **S3b**), the signals at 67.58, 63.82 and 29.64 ppm come from the secondary carbons ( $-\text{CH}_2-$ ) of C1 ( $\text{O}-\underline{\text{C}}\text{H}_2-\text{CH}_2-\underline{\text{C}}\text{H}_2-\text{O}$ ), C3 ( $\text{O}-\text{CH}_2-\text{CH}_2-\underline{\text{C}}\text{H}_2-\text{OH}$ ), C2 ( $\text{O}-\text{CH}_2-\underline{\text{C}}\text{H}_2-\text{CH}_2-\text{O}$ ), respectively. The signal at 14.30 ppm is ascribed to C4 ( $\text{O}-\text{CH}_2-\underline{\text{C}}\text{H}_3$ ). In the  $^{13}\text{C}$  spectrum of P3 (**Figure S3c**), the signals at 66.78 and 65.44 ppm come from the secondary carbons ( $-\text{CH}_2-$ ) of C1 ( $\text{O}-\underline{\text{C}}\text{H}_2-\underline{\text{C}}\text{H}_2-\text{O}$ ) and C2 ( $\text{O}-\text{CH}_2-\underline{\text{C}}\text{H}_2-\text{OH}$ ), respectively. The signal at 14.02 ppm is ascribed to C3 ( $\text{O}-\text{CH}_2-\underline{\text{C}}\text{H}_3$ ). In the  $^{13}\text{C}$  spectrum of P4 (**Figure S3d**), the signals at 65.37, 59.64 and 40.13 ppm are ascribed to the secondary carbons ( $-\text{CH}_2-$ ) of C4 ( $\text{O}-\text{CH}_2-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-\underline{\text{C}}\text{H}_2-\text{OH}$ ), C1 ( $\text{O}-\underline{\text{C}}\text{H}_2-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-\underline{\text{C}}\text{H}_2-\text{O}$ ) and C2 ( $\text{O}-\text{CH}_2-\underline{\text{C}}\text{H}_2-\text{S}-\text{S}-\underline{\text{C}}\text{H}_2-\text{CH}_2-\text{O}$ ), respectively. And the signal at 15.57 ppm is ascribed to C3 ( $\text{O}-\text{CH}_2-\underline{\text{C}}\text{H}_3$ ).

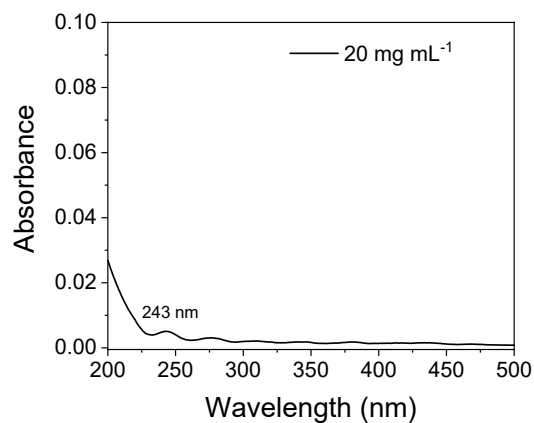
In the GPC curve of P1, P2, P3 and P4 (**Figure S4**), the average molecular weight ( $M_w$ ) are 789000, 95300, 14900, 10400  $\text{g mol}^{-1}$ , respectively, and number average weight ( $M_n$ ) are 399000, 57300, 13300 and 9190  $\text{g mol}^{-1}$ , separately, and thus, their polydispersity index (PDI) are 1.98, 1.66, 1.13 and 1.13, respectively. Therefore, the target polymers have been successfully synthesized. The GPC information of P1, P2, P3 and P4 has been listed in **Table S1**.



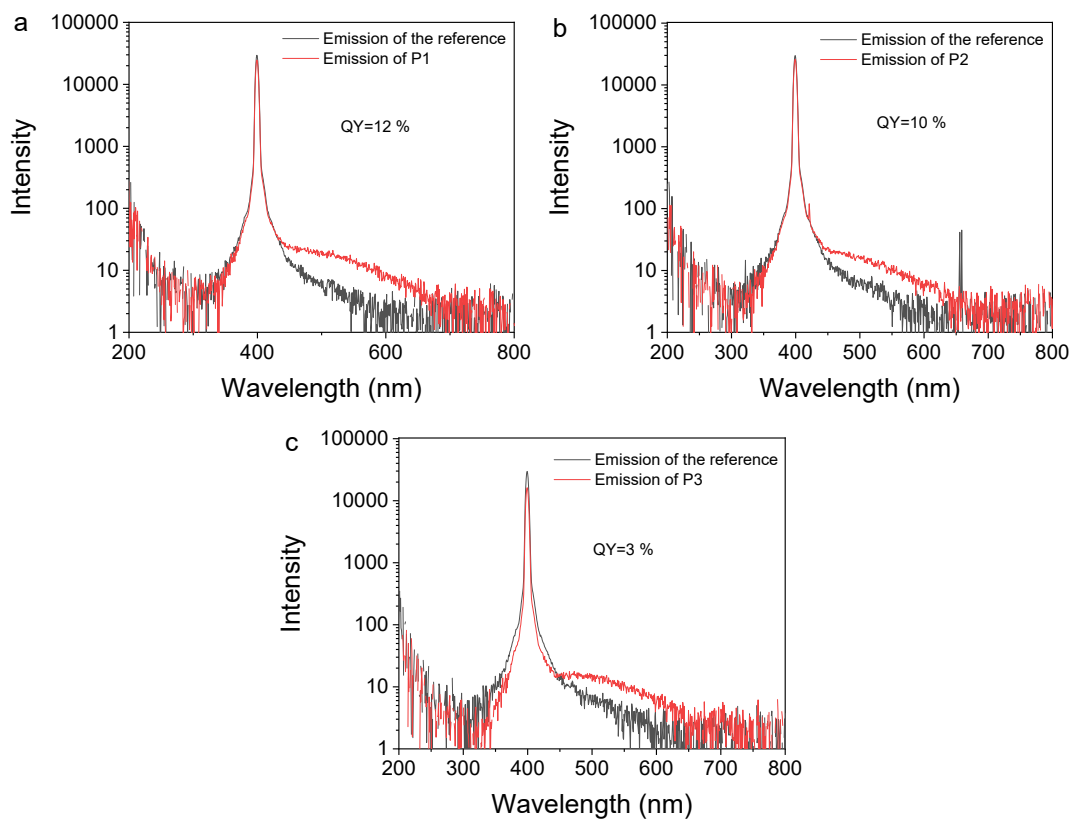
**Figure S4.** GPC curves of P1, P2, P3 and P4.

**Table S1.** GPC data of P1, P2, P3 and P4.

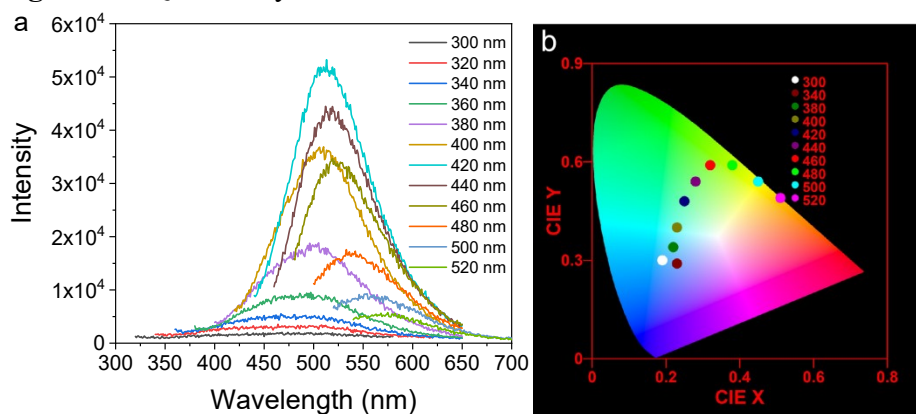
Samples	Raw materials	$M_n(10^3)$	$M_w(10^3)$	$M_w/M_n$	Water solubility
P1	TEP+EG	399.00	789.00	1.98	Excellent
P2	TEP+EG	57.30	95.30	1.66	Excellent
P3	TEP+1,3-PD	13.30	14.90	1.13	Excellent
P4	TEP+2-hydroxyethyl disulfide	9.19	10.40	1.13	Excellent



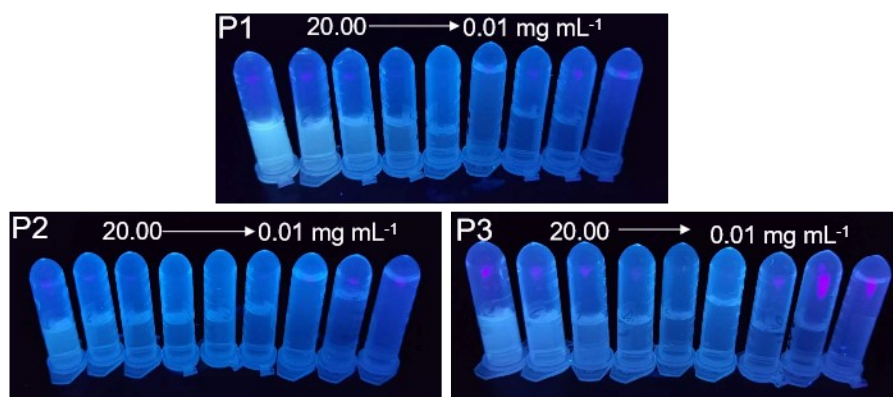
**Figure S5.** UV-vis absorbance of triethyl phosphate in water solution at 20 mg mL<sup>-1</sup>.



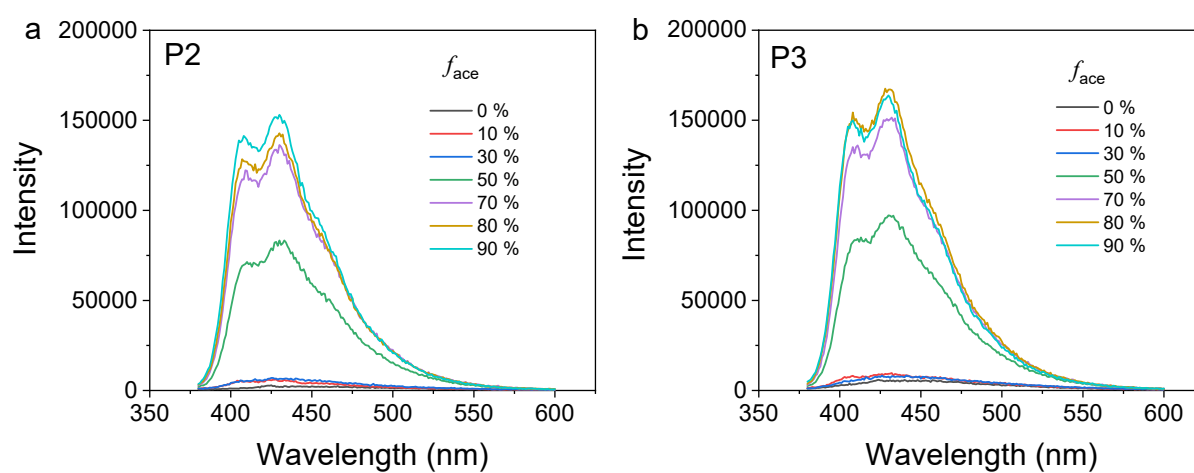
**Figure S6.** Quantum yields of P1, P2 and P3 under excitation of 400 nm.



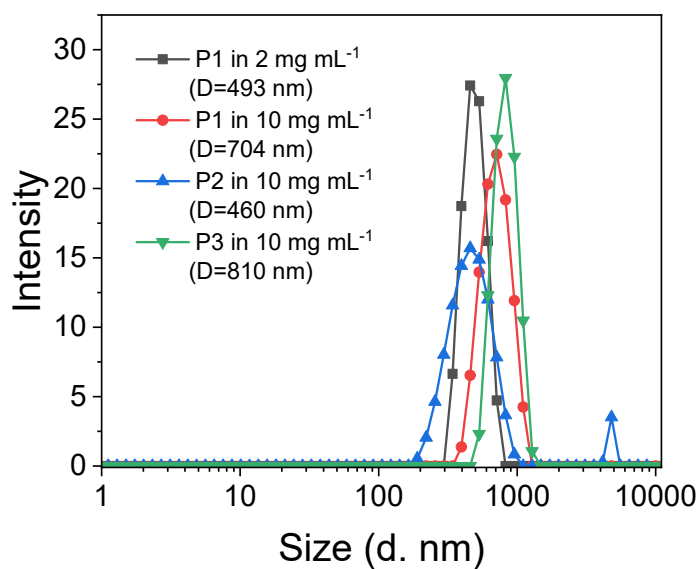
**Figure S7.** Emission spectra (a) and CIE plots (b) of P4 obtained under different excitations.



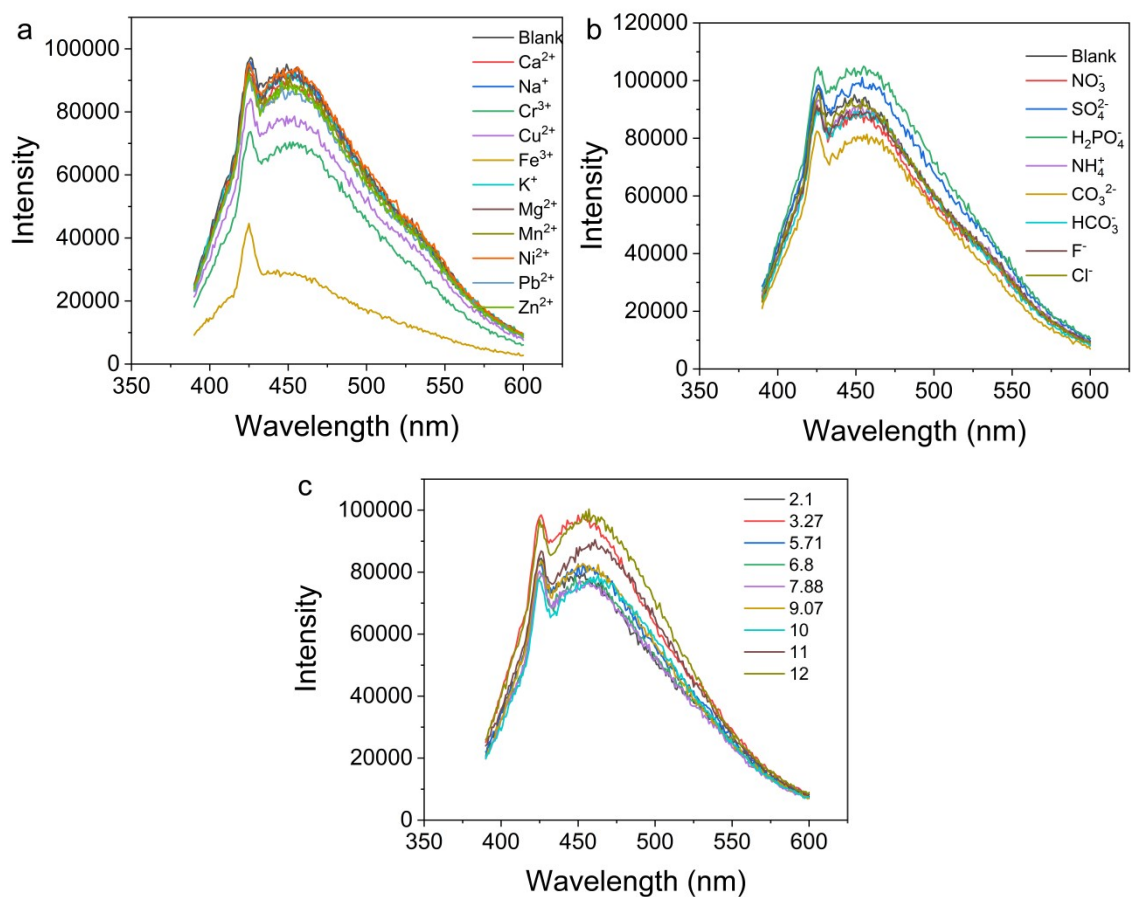
**Figure S8.** Digital pictures of P1, P2 and P3 aqueous solution with different concentrations under 365 nm UV light.



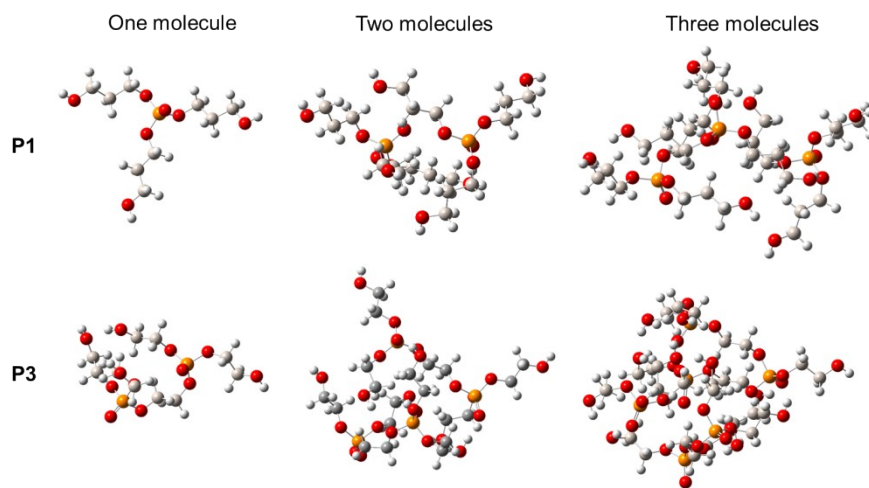
**Figure S9.** Effect of acetone on the emission spectra of P2 (a) and P3 (b).



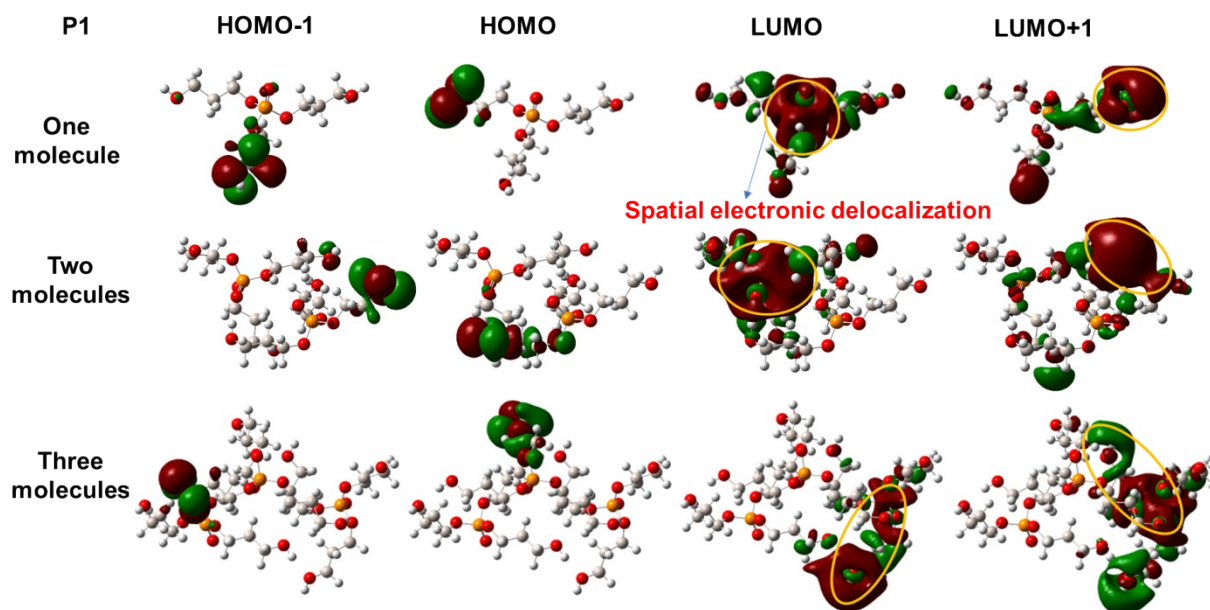
**Figure S10.** DLS results of the aggregate of P1, P2 and P3.



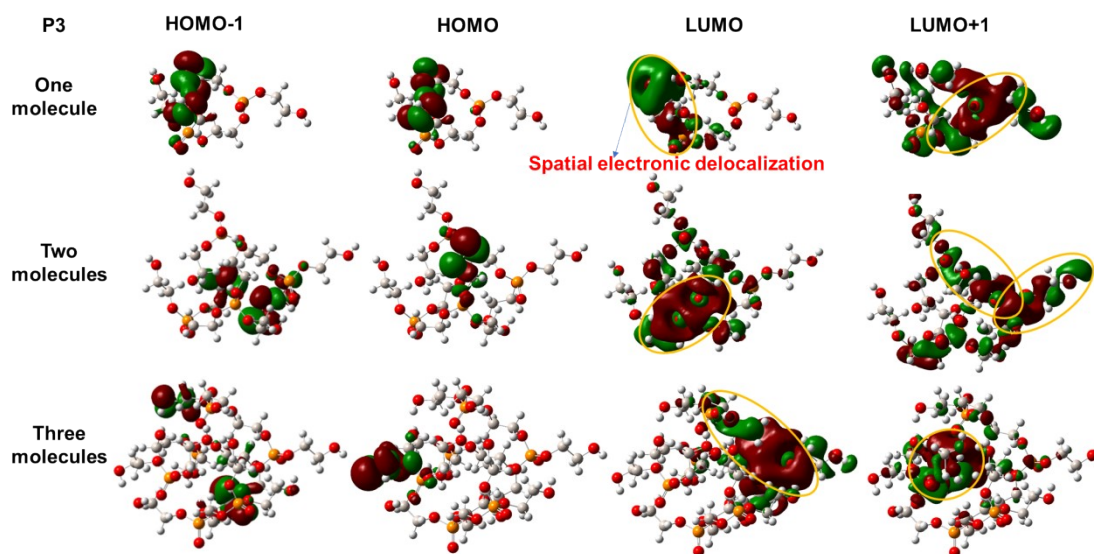
**Figure S11.** Emission spectra of P1 aqueous solutions with metal ions, non-metal ions and different pH values.



**Figure S12.** Optimized structure of P1 and P2 with one, two and three molecules.

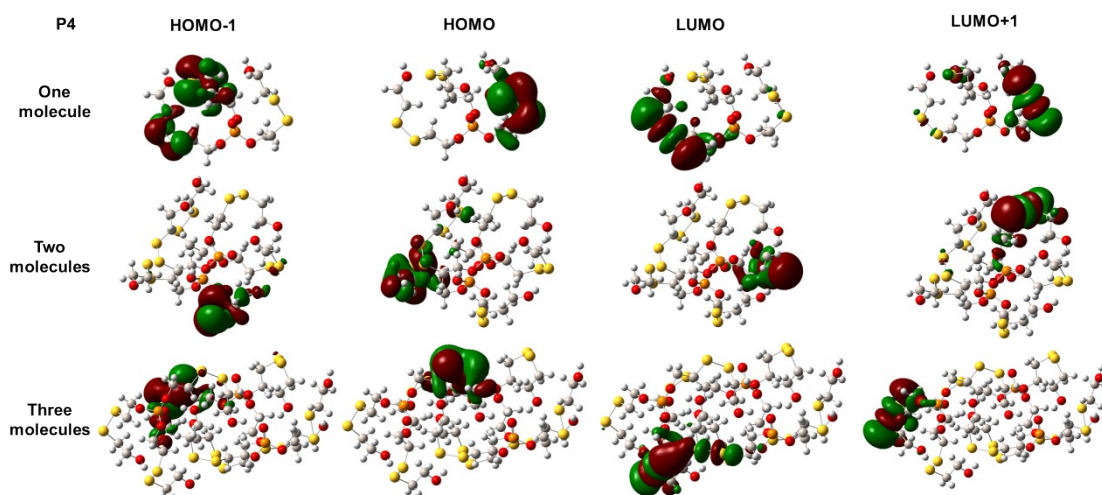


**Figure S13.** Frontier molecular orbitals of P1 with different molecules at  $S_0$  geometries using DFT method at B3LYP-D3/6-31G(d,p) level.



**Figure S14.** Frontier molecular orbitals of P3 with different molecules at  $S_0$  geometries using DFT method at B3LYP-D3/6-31G(d,p) level.





**Figure S15.** Frontier molecular orbitals of P4 with different molecules at  $S_0$  geometries using DFT method at B3LYP-D3/6-31G(d,p) level.