

Efficient detection of L-Aspartic acid and L-Glutamic acid by a self-assembled fluorescent microparticle with AIE and FRET activities

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Electronic Supplementary Information (9 pages)

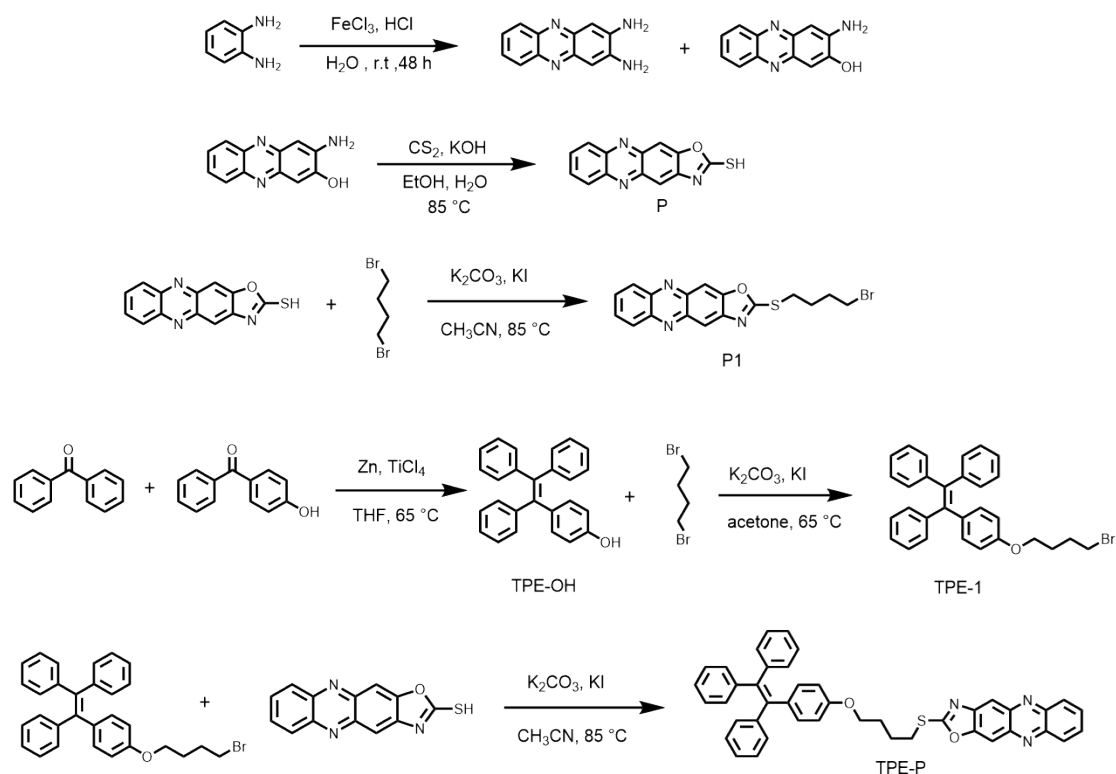
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1. Materials and methods

All reagents were analytical grade, commercially and without further purification. Melting points were measured on X-4 digital melting-point apparatus and were uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on an Agilent DD2 at 400 MHz and 150 MHz spectra. Electrospray ionization mass spectra (ESI-MS) were measured on an Agilent 1100 LC-MSD-Trap-VL system. UV-vis spectra were recorded on a Shimadzu UV-2550 spectrometer. Fluorescence spectra were recorded on a Shimadzu RF-5301PC fluorescence spectrometer. Study of scanning electron microscopy (SEM), determination of the SEM images was performed on a JSM-6701F FE-SEM microscope.

2. Synthesis of compounds

Oxazolo[4,5-b]phenazine-2-thiol **P1** and (2-(4-(4-bromobutoxy)phenyl)ethene-1,1,2-triyl)tribenzene **TPE-1** were prepared according to the literature procedures.^{S1-S4}



Scheme S1. Synthetic route to **TPE-P**.

Compound TPE-P: A mixture of oxazolo[4,5-b]phenazine-2-thiol **P1** (1.00 mmol, 0.253 g), (2-(4-(4-bromobutoxy) phenyl) ethene-1,1,2-triyl) tribenzene **TPE-1** (0.50 mmol, 0.241 g), K₂CO₃ (3 mmol, 0.414 g) and KI (3 mmol, 0.498 g) was added to a 100 mL round-bottom flask, and the reaction mixture was stirred at 85 °C for 24 h under nitrogen atmosphere. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (v:v = 10:1) as the eluent to isolate the compound **TPE-P** as yellow solid (0.082 g, yield 25%). M.p. > 300 °C. The proton NMR spectrum of compound **TPE-P** is shown in Figure S1. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.34 (s, 1H), 8.27–8.23 (m, 2H), 8.15 (s, 1H), 7.86–7.83 (m, 2H), 7.09 (m, 7H), 7.05–7.00 (m, 7H), 6.93 (d, *J* = 8.8 Hz, 3H), 6.64 (d, *J* = 8.7 Hz, 2H), 3.99 (t, *J* = 5.9 Hz, 2H), 3.50 (d, *J* = 7.2 Hz, 2H), 2.11 (d, *J* = 7.6 Hz, 2H), 2.00 (m, 2H). The ¹³C NMR spectrum of compound **TPE-P** is shown in Figure S2. ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 157.33, 153.79, 143.94, 140.46, 140.11, 136.24, 132.55, 131.36, 131.33, 130.28, 129.30, 129.13, 127.70, 127.57, 127.04, 115.12, 115.02, 113.55, 105.93, 105.86, 77.22, 77.01, 76.80, 66.86, 32.36, 28.24, 26.07. The ESI-MS of compound **TPE-P** is shown in Figure S3 *m/z*: Calcd for C₄₃H₃₃N₃O₂S [1 + H]⁺: 656.2371, found 656.2356, error = -1.80 × 10⁻⁶.

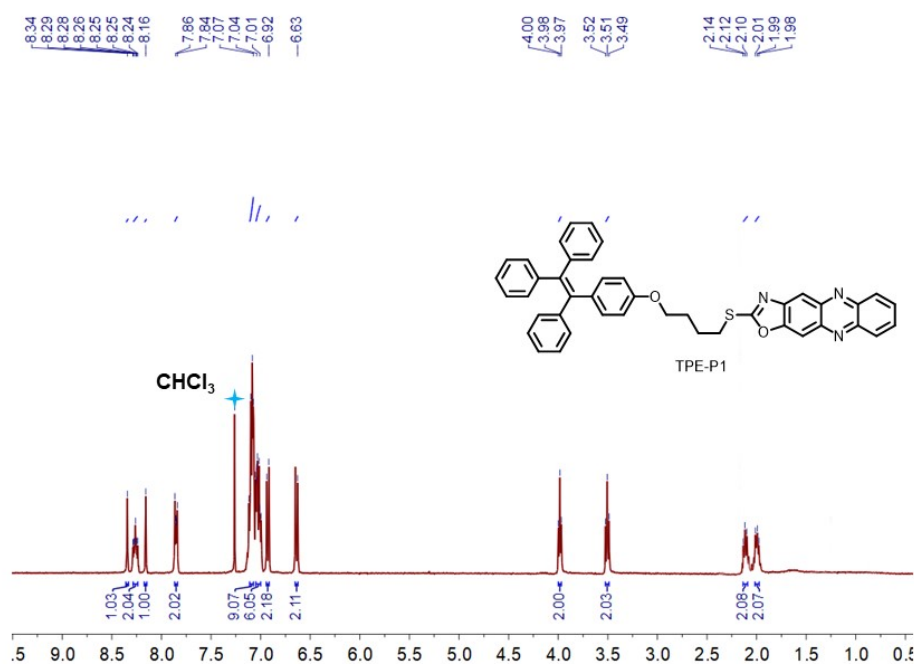


Fig. S1. ¹H NMR spectrum of **TPE-P** in CDCl₃.

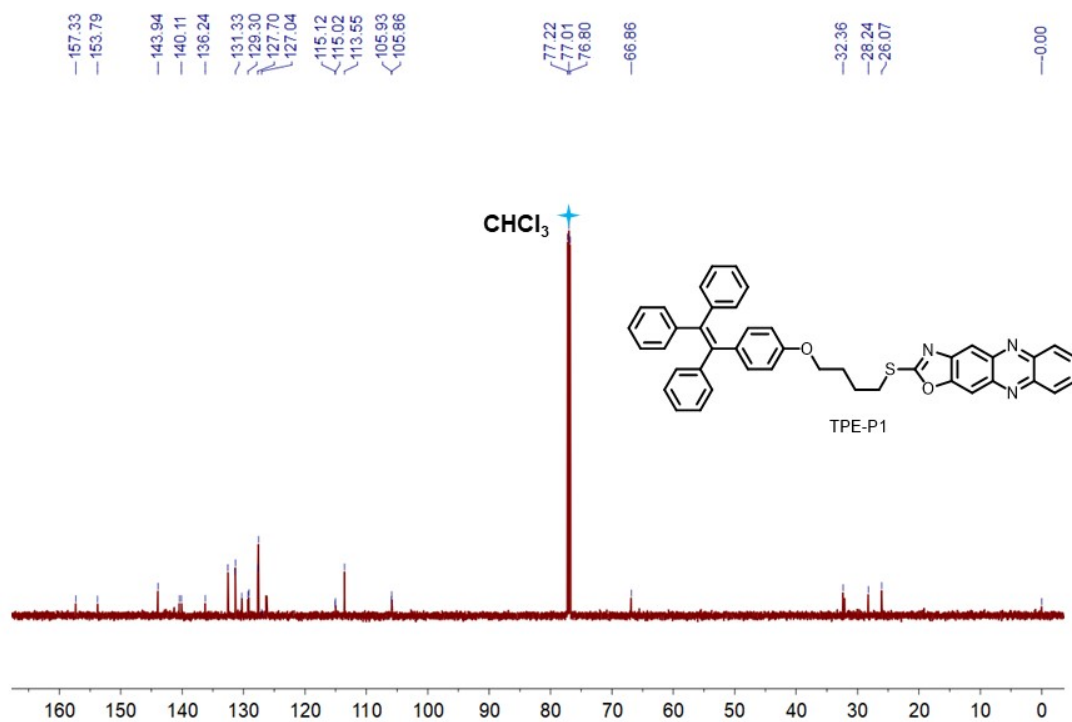


Fig. S2. ^{13}C NMR spectrum of TPE-P in CDCl_3 .

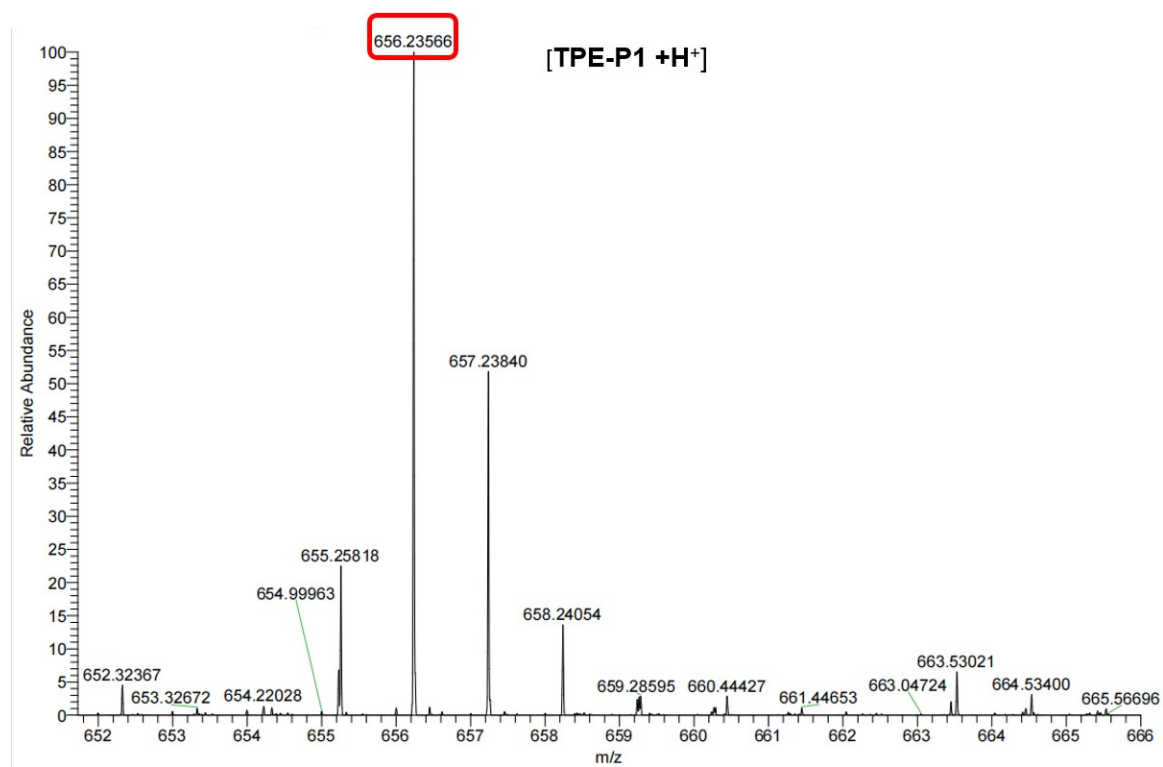


Fig. S3. The ESI-MS of TPE-P: $[\text{M} + \text{H}]^+ = 656.23566$.

3. Normalized spectral overlap

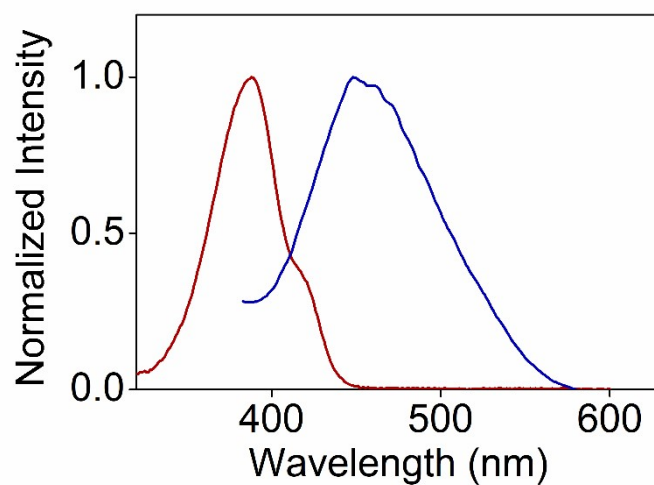


Fig. S4. Normalized spectral overlap between absorption spectrum of **P1** (red line) and emissive spectrum of **TPE-1** (blue line) in THF/ H₂O (v:v = 1:1).

4. TEM experiments

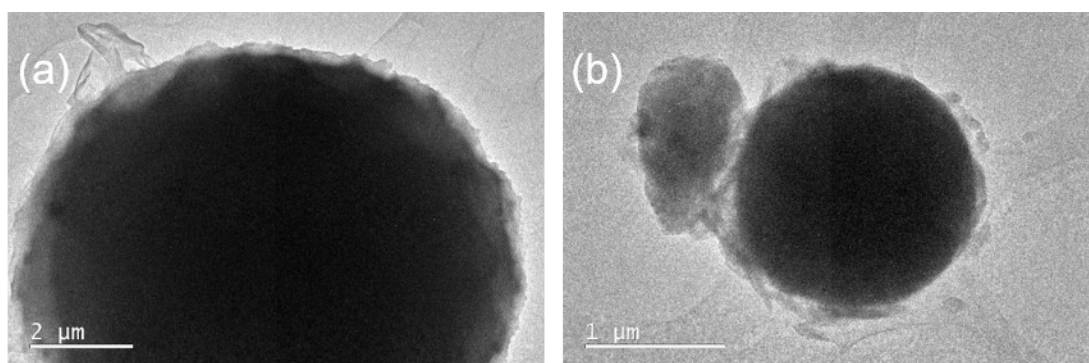


Fig. S5 (a) TEM image of **TPE-P** (2×10^{-5} M) in THF/H₂O (1/1; v/v). (b) TEM image of **TPE-P** (2×10^{-5} M) in THF/H₂O (1/1; v/v) after 36 hours.

5. Fluorescent spectrum of **P1**

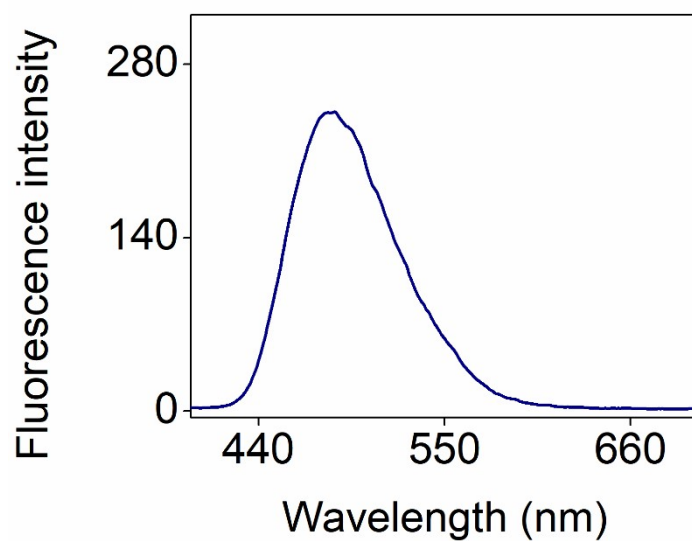


Fig. S6 Fluorescent spectrum of **P1** in THF/H₂O (1/1; v/v).

6. Time dependent ¹H NMR spectrum of **TPE-P**

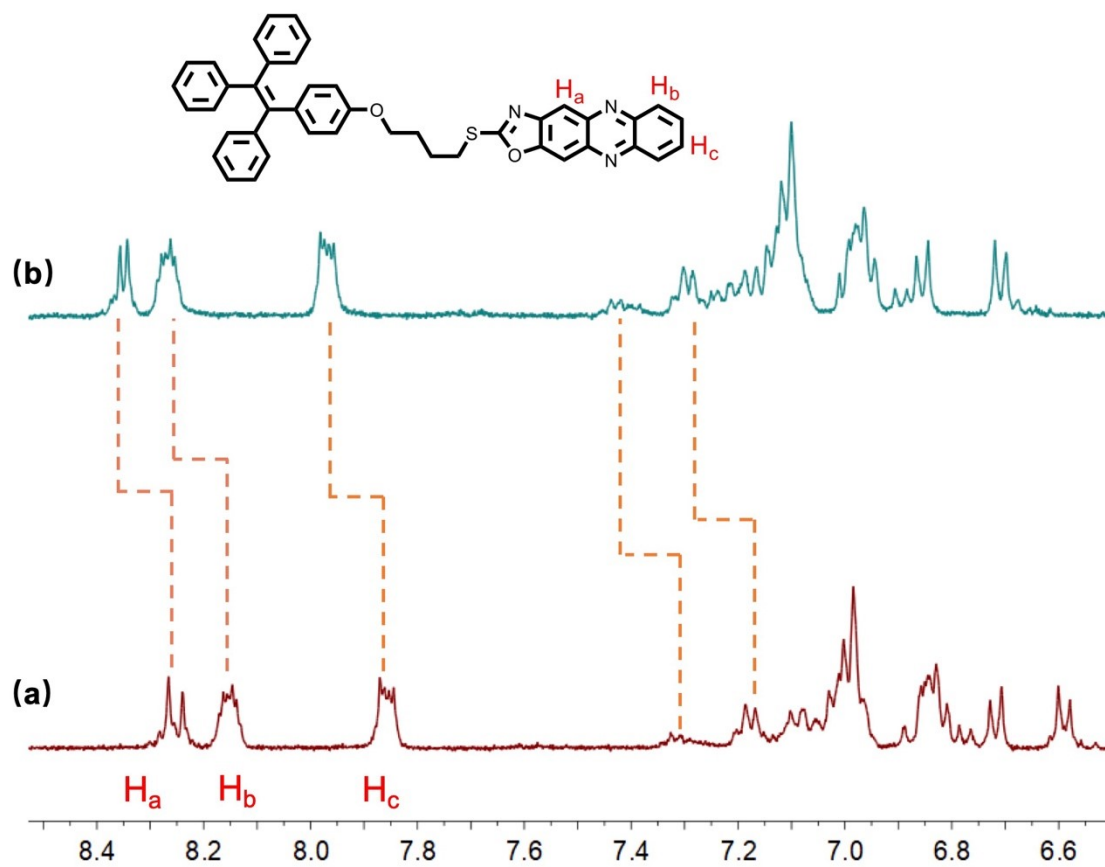


Fig. S7 Time dependent ¹H NMR spectrum of **TPE-P** in DMSO-*d*₆ at 293 K. (a) 0 hour, (b) 36 hours.

7. ^1H NMR spectra of **TPE-P** in the presence of L-Glu and L-Asp

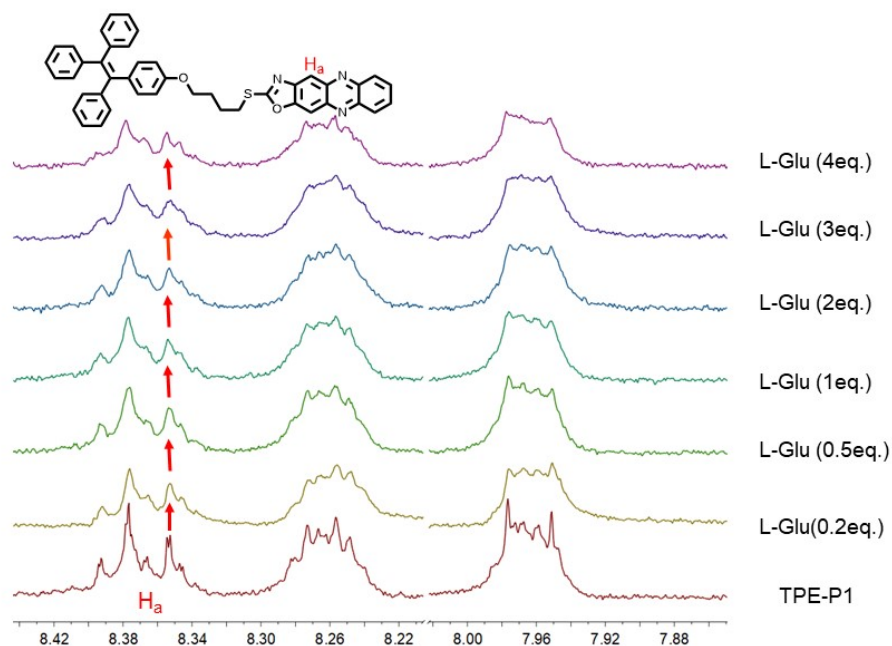


Fig. S8. Partial ^1H NMR spectra of **TPE-P** (400 MHz) in the presence of various molar equivalents of L-Glu in $\text{DMSO-}d_6$ at 293 K.

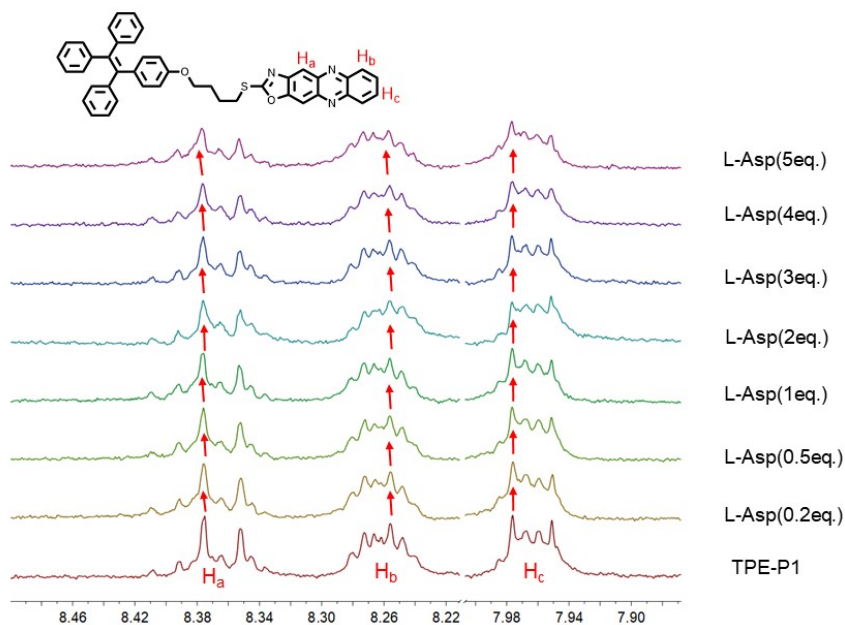


Fig. S9. Partial ^1H NMR spectra of **TPE-P** (400 MHz) in the presence of various equivalents of L-Asp in $\text{DMSO-}d_6$ at 293 K.

8. Calculated structures of TPE-P + L-Glu and TPE-P + L-Asp

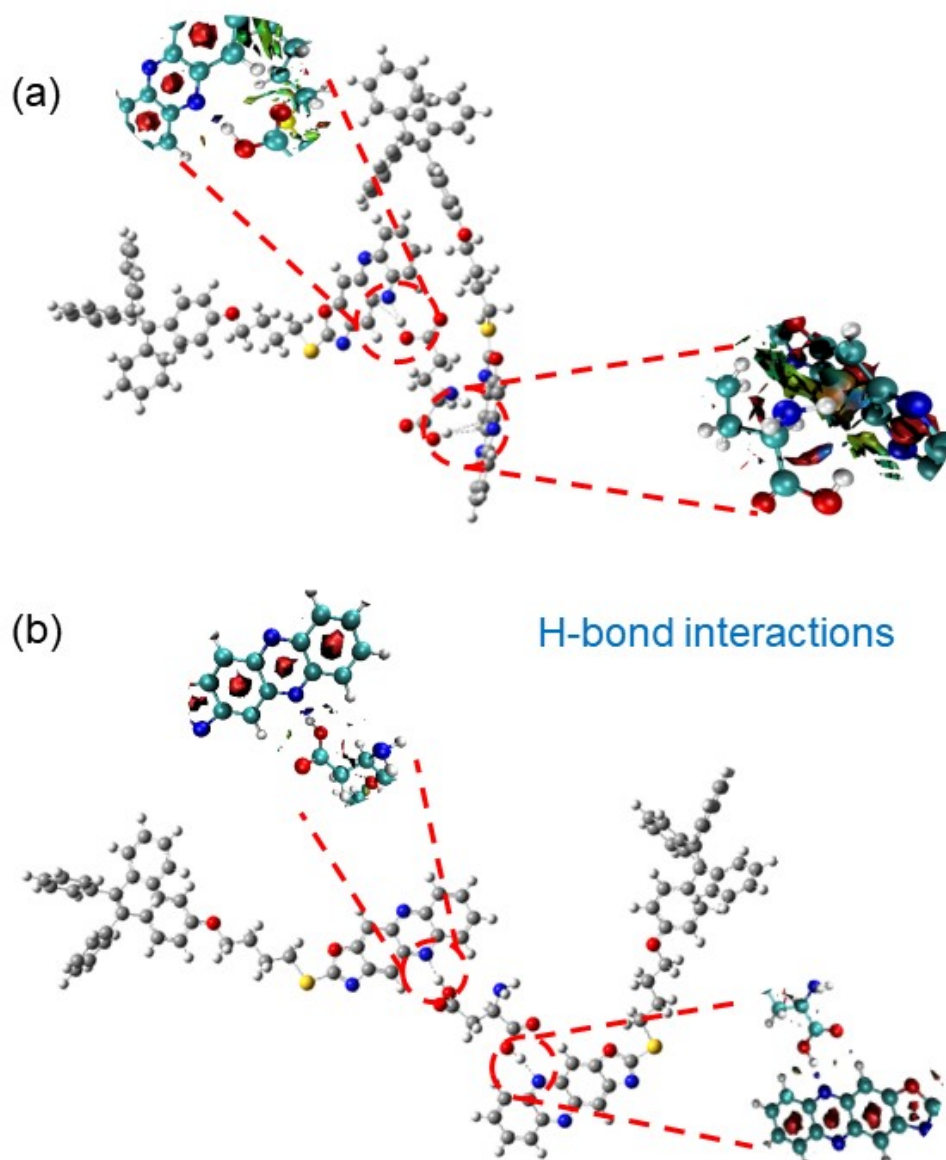


Fig. S10 The calculated structures of (a) TPE-P + L-Glu, (b) TPE-P + L-Asp, L-Glu and L-Asp interact with phenazine group by hydrogen bonding.

9. ^1H NMR spectra of **TPE-P** in the presence of other amino acids

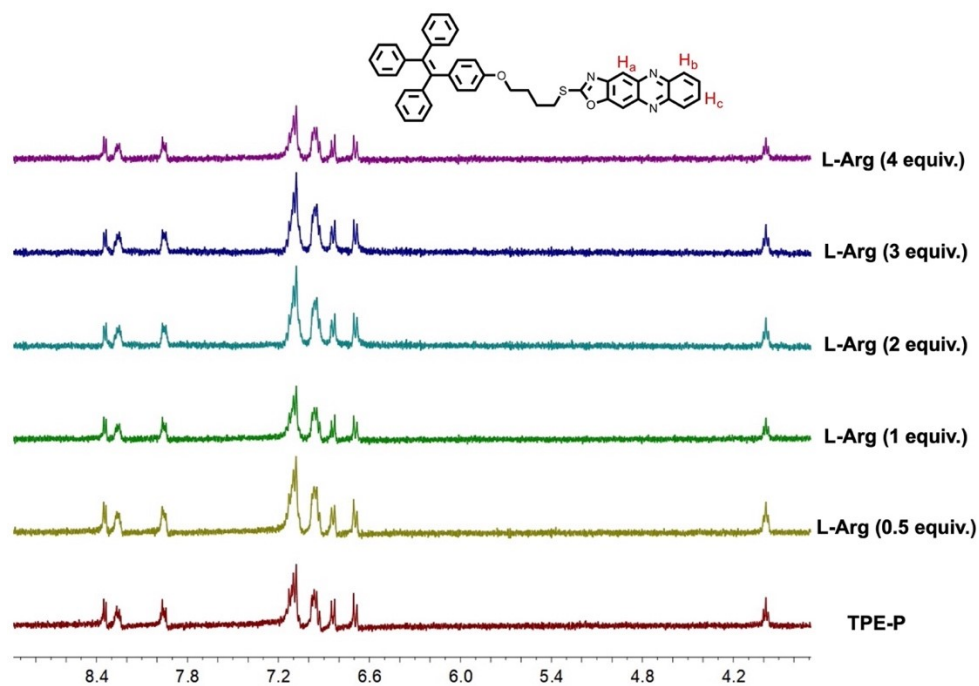


Fig.S11 Partial ^1H NMR spectra of **TPE-P** (400 MHz) in the presence of various molar equivalents of L-Arg in $\text{DMSO-}d_6$ at 293 K.

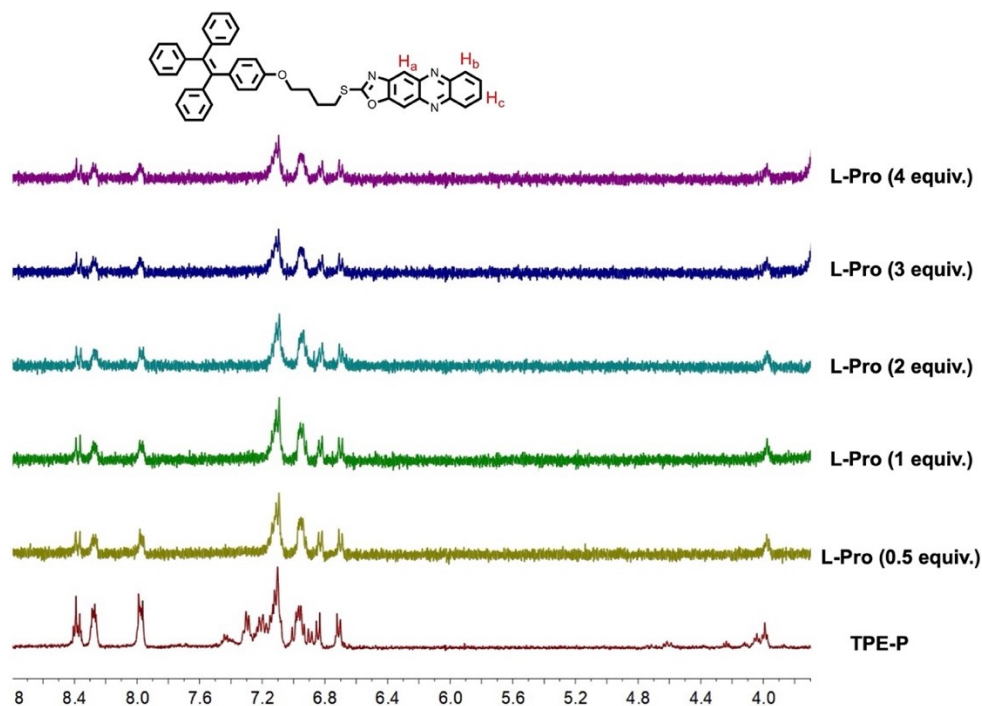


Fig. 12 Partial ^1H NMR spectra of **TPE-P** (400 MHz) in the presence of various molar equivalents of L-Pro in $\text{DMSO-}d_6$ at 293 K.

10. References

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