

Electronic supplementary information (ESI)

Benzimidazolium ionic liquid tagged phenazine salophen as
bifunctional 'off-on' PET based fluorescent sensor for aqueous
phase detection of trinitrotoluene and picric acid

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EXPERIMENTAL SECTION

Chemicals

Potassium bromide, o-phenylenediamine, salicylaldehyde, formaldehyde (Sigma, 37%), zinc chloride (Alfa, 99.99%), sodium hydride (60% dispersion in mineral oil), benzimidazole, 1-bromoethane and all nitro compounds used in the present work were purchased from Sigma-Aldrich. 2,4,6-TNT (250 mg) was prepared according to the reported procedure¹ from 2,4-DNT in small quantities. *Caution:* Since TNT and other nitroaromatics used in the present study are highly explosive, they should be handled in small quantities to avoid risks. All the chemicals and reagents were of analytical grade and used without any purification unless otherwise specified. Aqueous solutions were prepared using deionized water collected from Millipore water purification (18.2 MΩ cm at 25 °C) technique. Aqueous stock solutions of PS-IL (1.0 mM) and nitro compounds (1.0 mM) used in the present study were prepared by dissolving the necessary amount of corresponding compounds in water under sonication.

Characterization

Nuclear magnetic resonance (NMR) spectra were recorded on Avance Bruker 400 MHz spectrometer (TMS as internal reference). Mass spectral data were recorded using Waters high resolution Q-TOF mass spectrometer. Fourier transform infrared spectra (IR) were recorded using Shimadzu Affinity FT-IR spectrometer with attenuated total reflectance (ATR) setup within the range of 4000-400 cm⁻¹. UV-Visible absorption spectra were recorded using Jasco 4100 (UV-VIS-NIR-V-670) spectrophotometer. Fluorescence spectra were recorded with a Hitachi (F-7000FL) spectrophotometer. Electrospun (ES) nanofibers were collected from Espin nano, India, with the capacity of 60 kV using H₂O as solvent. The morphology of electrospun nanofibers was obtained using FEI Quanta 250 FEG field emission-scanning electron microscope (FE-SEM). Fluorescence lifetime measurements were recorded with a HORIBA

Jobin-Yvon spectrofluorometer. The mechanistic pathway of the sensor was studied theoretically using density functional theory (DFT) and the calculations were performed on Gaussian 09 program.

Synthesis of 5-(chloromethyl)-2-hydroxybenzaldehyde (1)

The synthesis of 5-(chloromethyl)-2-hydroxybenzaldehyde was carried out with a slight modification using the earlier reported procedure². In a round bottom flask containing 25 mL of conc. HCl, 6 mL of formaldehyde (37 wt% H₂O) and 40 mmol of salicylaldehyde (4.884 g) was added along with 0.3 g of ZnCl₂. The resulting mixture was allowed to stir at room temperature for 24 h under N₂ atmosphere, which forms a pink coloured precipitate. Thus, obtained precipitate was separated out and washed with several times of water to remove the unreacted reactants from the product. Finally, the resultant crude product was recrystallized using hot n-hexane, which forms the desired product (**1**) as white solid. Yield: 52%, M.P: 84 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ: 4.73 (s, 2H), 7.02 (d, 1H), 7.57 (d, 1H), 7.70 (s, 1H), 10.25 (s, 1H), 10.92 (s, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 46.22, 117.53, 122.25, 127.22, 133.98, 135.44, 160.25, 192.04. GC-MS *m/z* calculated for [M⁺] [C₈H₇ClO₂]⁺ 170.5910 and found 170.5955.

Synthesis of 1-ethyl-1H-benzimidazole (2)

To synthesize 1-ethyl-1H-benzimidazole, we have followed earlier reported procedure with a minor modification³. Benzimidazole (5.907 g, 50 mmol) in 75 mL of dry THF was added dropwise to a stirring THF (10 mL) solution of oil free NaH (2 g, 50 mmol) and refluxed at 60 °C for 2 h. Thereafter, THF (15 mL) solution of bromoethane (5.44 g, 50 mmol) was added dropwise and continued to stir at 60 °C for another 48 h. After completion, the reaction mixture was filtered off to remove the formed sodium bromide and the resulting solution was subjected to rotary evaporation. Thus, obtained yellowish brown liquid was redissolved in

chloroform and then washed with copious amount of deionized water. Thereafter, the organic layer was separated from water and dried over Na₂SO₄. Finally, chloroform was removed under reduced pressure to obtain **(2)** as a pale yellow liquid with 95% yield. ¹H NMR (400 MHz, DMSO-*d*₆) δ: 1.36 (t, *J*=7.7 Hz, 3H), 4.26 (q, *J*=7.2, 2H), 7.20 (d, *J*=1.6, 2H), 7.25 (d, 1H), 7.60 (d, *J*=7.6, 1H), 8.25 (d, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 15.64, 79.69, 110.71, 119.92, 121.89, 122.67, 134.04, 143.92, 144.04. GC-MS *m/z* calculated for [M⁺] [C₉H₁₀N₂]⁺ 146.19 and found 146.20.

Synthesis of 1-ethyl-3-(3-formyl-4-hydroxybenzyl)-1H-benzimidazol-3-ium chloride (**3**)

The mixture of compound 1 (2.922 g, 20 mmol) and compound 2 (3.4 g, 20 mmol) was dissolved in acetonitrile and then the reaction mixture was refluxed under 70 °C for 24 h. The resulting reaction mixture was allowed to cool at room temperature and then the obtained precipitate was filtered and washed with ethyl acetate (3 × 50 mL) followed by diethyl ether (2 × 50 mL). The product was obtained as white solid **(3)**. Yield: 6.01 g, 96%. M.P: 243 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ: 1.54 (t, *J*=7.20 Hz, 3H), 4.52 (q, *J*=7.20 Hz, 2H), 5.71(s, 2H), 7.16 (d, *J*=8.80 Hz, 2H), 7.64-7.73 (m, 3H), 7.99 (d, *J*=2.0 Hz, 1H), 8.09-8.10 (m, 1H), 8.11 (d, *J*=2.0 Hz, 1H), 10.05 (s, 1H), 10.27 (s, 1H), 11.20 (s, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 14.55, 42.67, 49.62, 114.30, 114.33, 118.60, 122.97, 125.17, 127.04, 127.13, 129.22, 131.32, 131.65, 136.96, 142.56, 161.69, 190.79.

Synthesis of 1-ethyl-3-(3-formyl-4-hydroxybenzyl)-1H-benzimidazol-3-ium bromide (**4**)

A mixture of potassium bromide (2.38 g, 20 mmol) in absolute ethanol was added dropwise to an ethanolic solution of compound 3 (3.16 g, 10 mmol) at room temperature for 12 h and filtered. The solvent was removed under reduced pressure and the obtained solid was washed with diethyl ether (3 × 50 mL), gives pale yellow solid **(4)** with 80% yield. M.P:

245 °C , ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ : 1.56 (t, $J=7.2$ Hz, 3H), 4.54 (q, $J=7.2$ Hz, 2H), 5.73 (s, 2H), 7.11 (d, $J=8.4$ Hz, 1H), 7.66-7.68 (m, 2H), 7.74 (q, $J=2.0$ Hz, 1H), 7.88 (d, $J=2.0$ Hz, 1H), 7.98 (q, $J=3.2$ Hz, 1H), 8.07 (q, $J=1.2$ Hz, 1H), 10.05 (s, 1H), 10.25 (s, 1H), 11.09 (s, 1H). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ : 14.54, 42.71, 49.60, 119.29, 119.31, 118.52, 122.87, 125.26, 127.05, 127.13, 129.43, 131.25, 131.61, 137.05, 142.46, 161.54, and 191.05.

Synthesis of 2,3-Diaminophenazine (5)

2,3-diaminophenazine was prepared according to the previous reported procedure⁴. 12 mL of 0.16 mol/L aqueous FeCl_3 solution was added to 60 mL of 0.04 mol/L aqueous o-phenylenediamine under continuous stirring at room temperature. A fast colour change from purple black to red-brown was observed with the addition of FeCl_3 . After 6 h, the obtained solid was filtered and washed with water (4×20 mL). The product (**5**) was yielded (95%) as brown solid. M.P: 300 °C. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ : 6.95 (s, 2H), 7.32 (s, 4H), 7.63 (s, 2H), 7.94 (s, 2H). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ : 99.35, 125.33, 128.31, 136.04, 140.49 and 147.36. GC-MS: m/z calculated for $[\text{M}^+]$ $[\text{C}_{12}\text{H}_{10}\text{N}_4]^+$ as 210.24; found : 210.21.

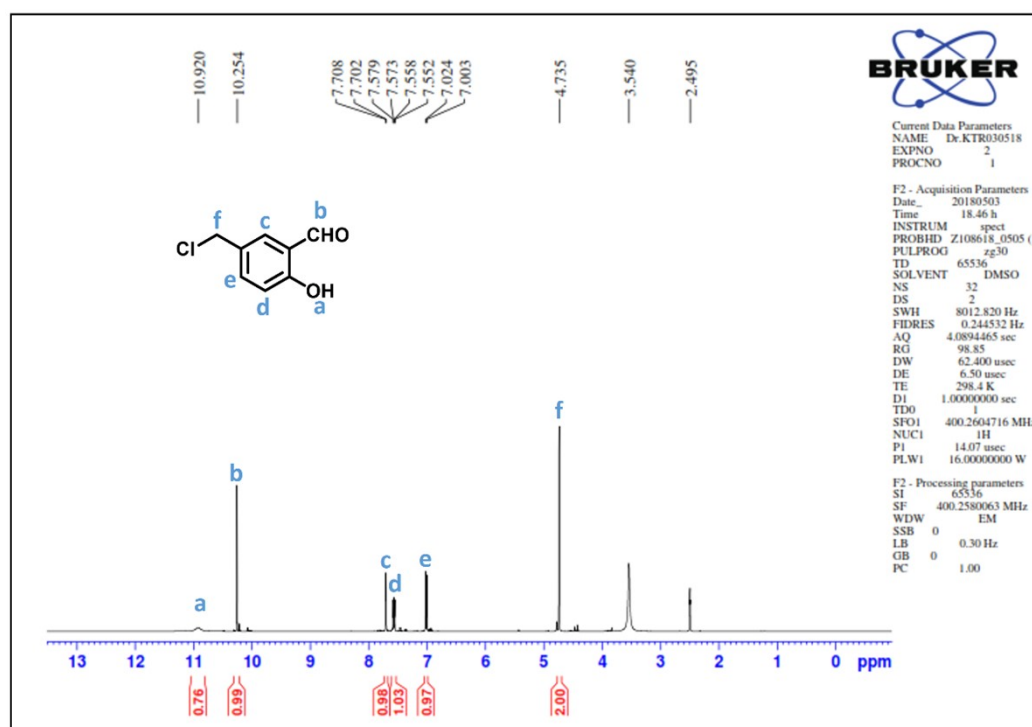


Fig. S1 ^1H NMR spectrum of 5-chloromethyl-2-hydroxybenzaldehyde (**1**)

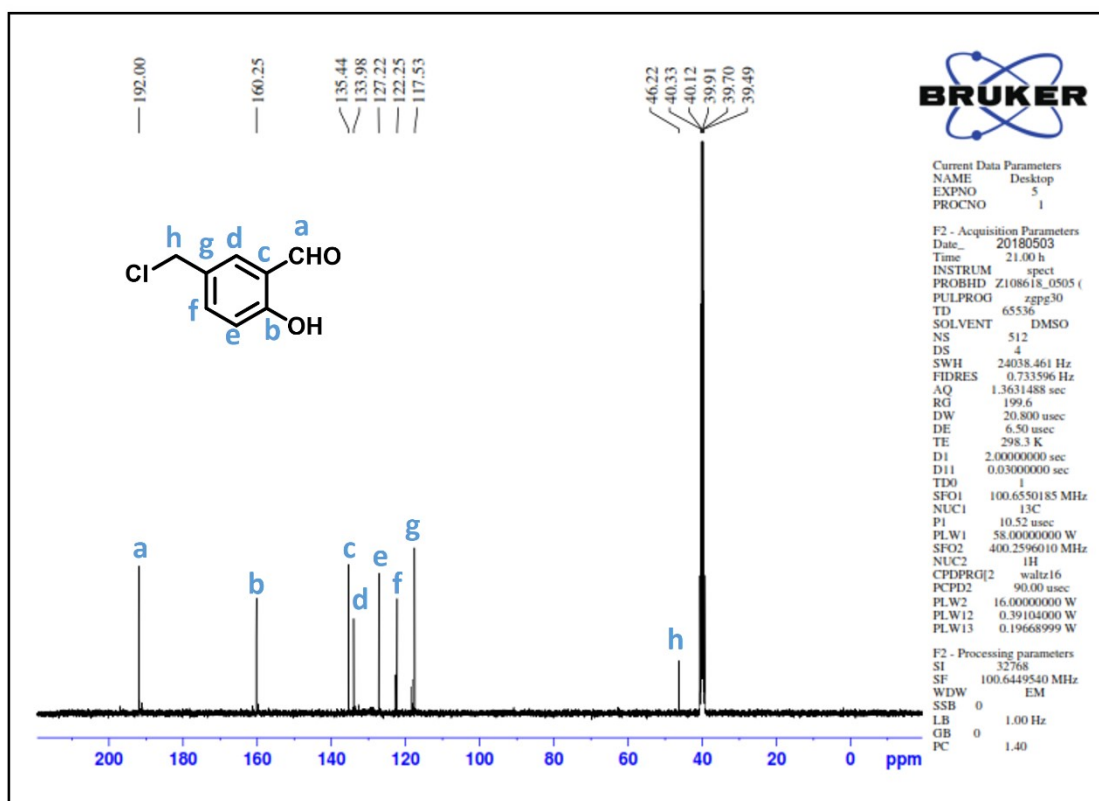


Fig. S2 ¹³C NMR spectrum of 5-chloromethyl-2-hydroxybenzaldehyde (1)

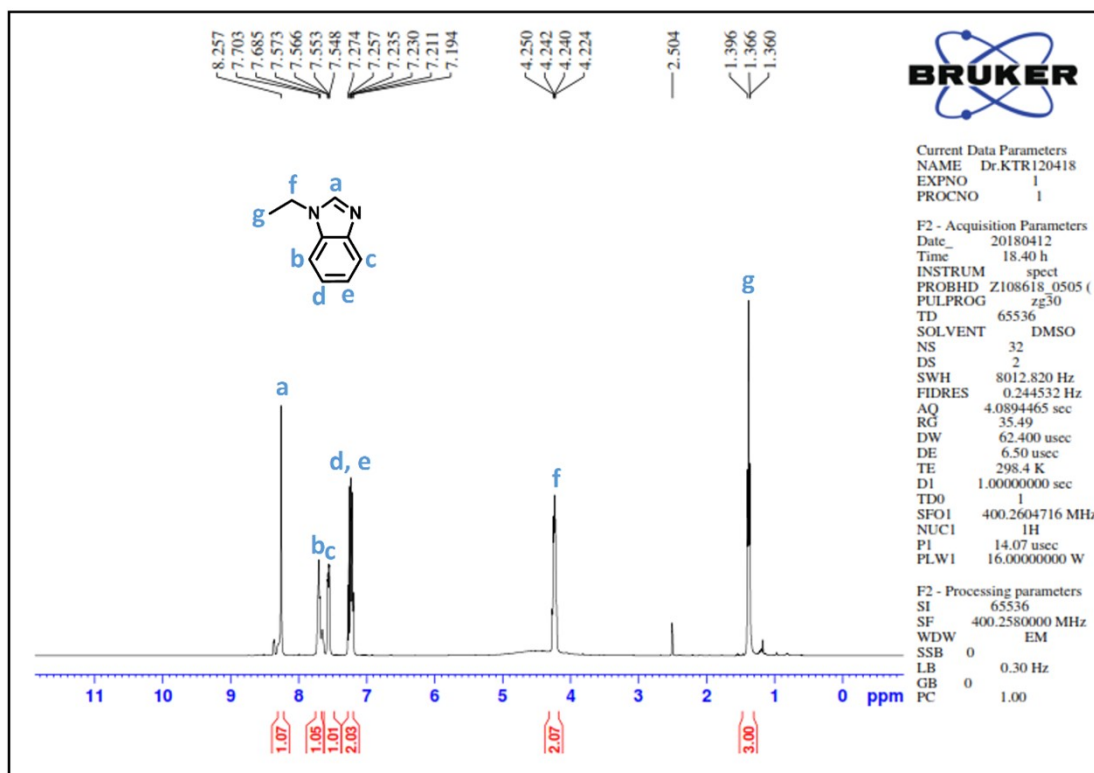


Fig. S3 ¹H NMR spectrum of 1-ethylbenzimidazole (2)

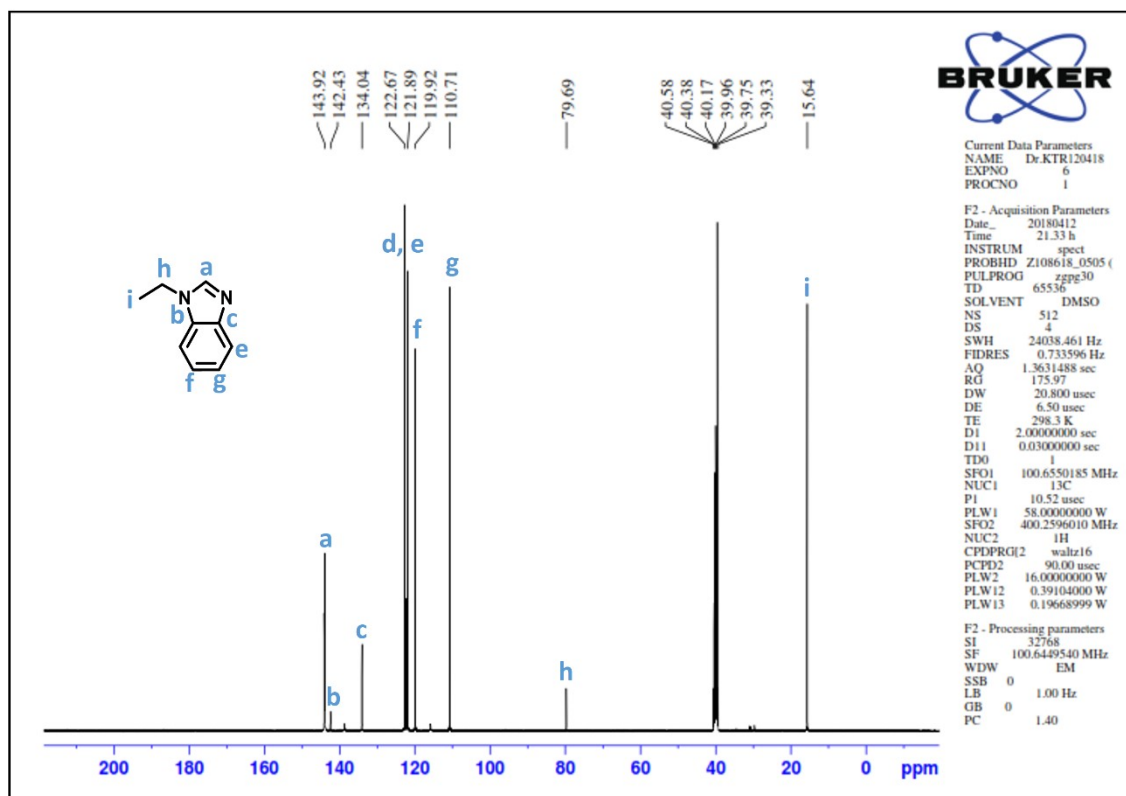


Fig. S4 ^{13}C NMR spectrum of 1-ethylbenzimidazole (2)

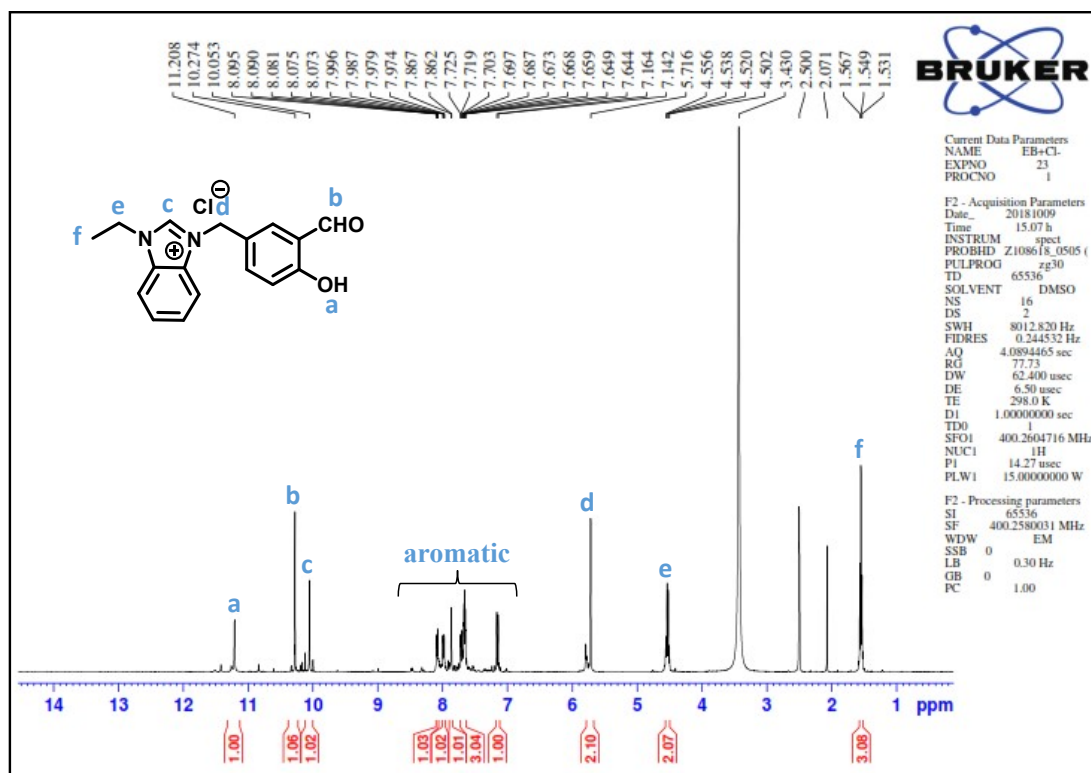


Fig. S5 ^1H NMR spectrum of 1-(3-formyl-4-hydroxybenzyl)-3-ethylbenzimidazolium chloride (3)

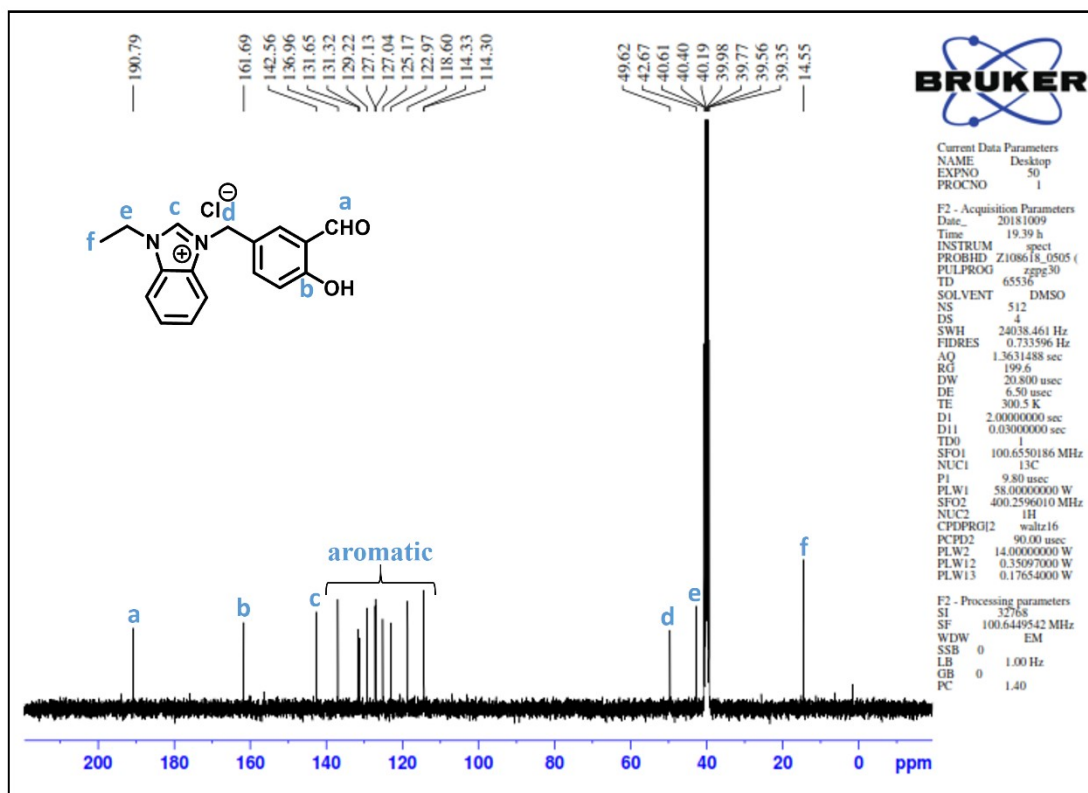


Fig. S6 ¹³C NMR spectrum of 1-(3-formyl-4-hydroxybenzyl)-3-ethylbenzimidazolium chloride (3)

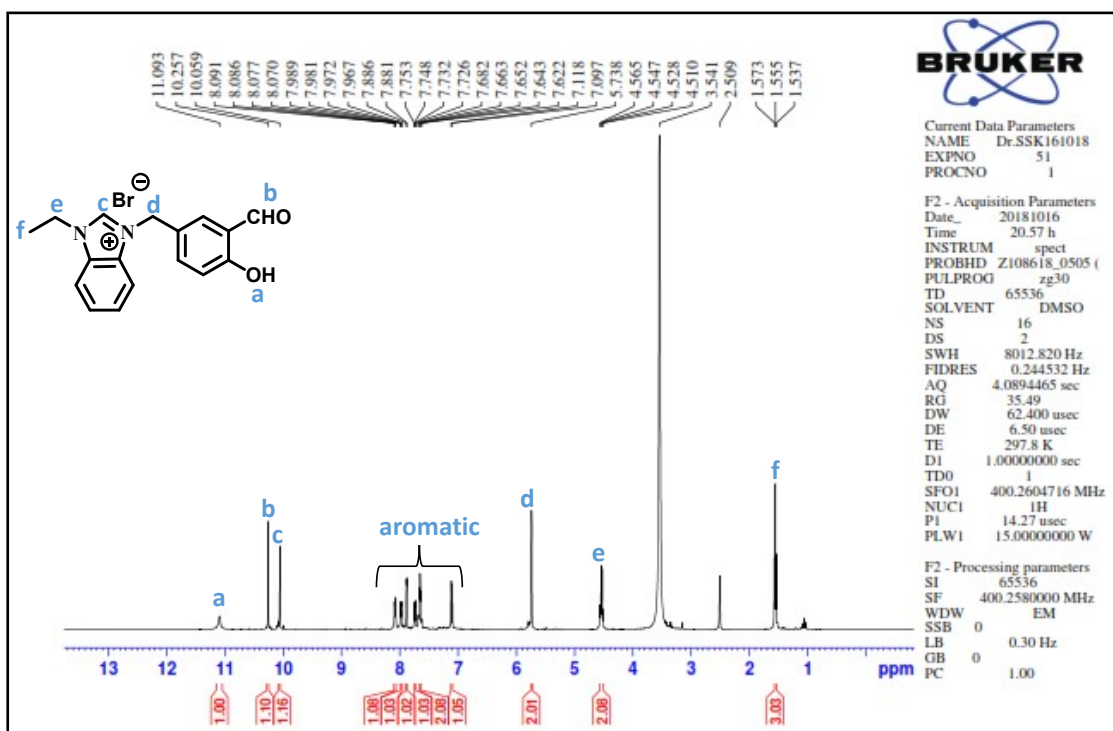


Fig. S7 ¹H NMR spectrum of 1-(3-formyl-4-hydroxybenzyl)-3-ethylbenzimidazolium bromide (4)

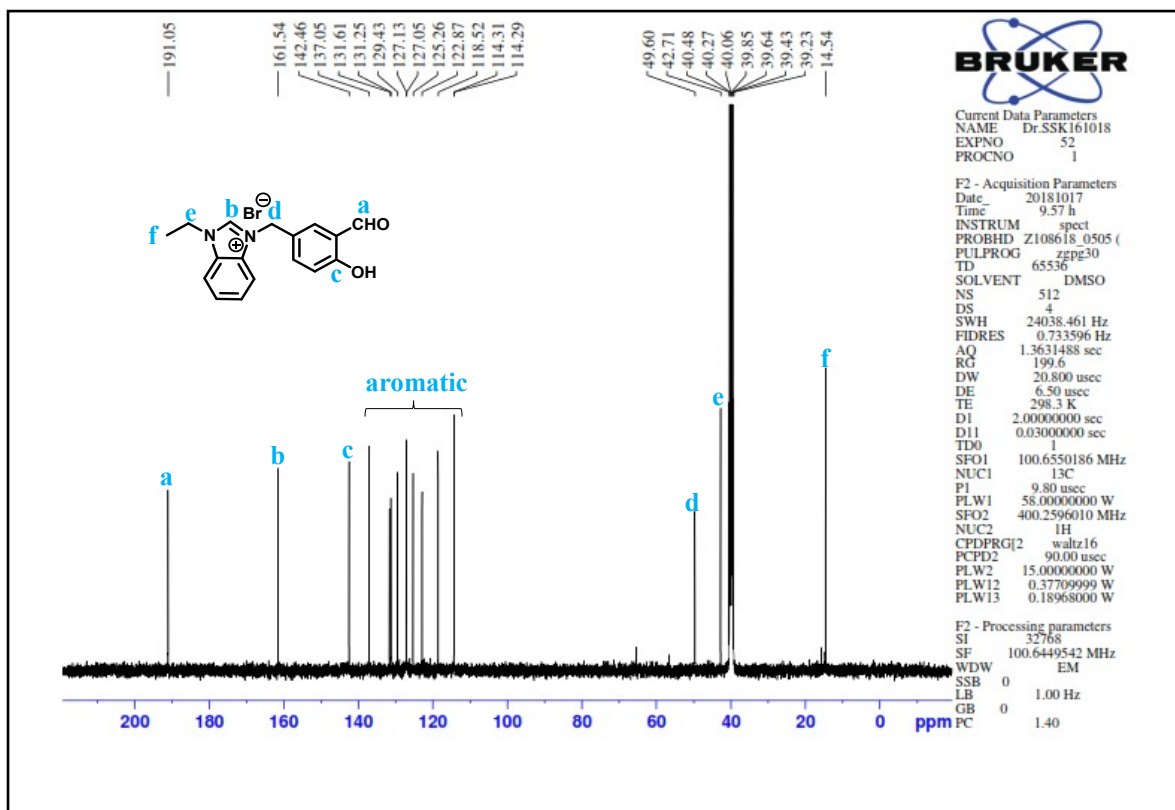


Fig. S8 ^{13}C NMR spectrum of 1-(3-formyl-4-hydroxybenzyl)-3-ethylbenzimidazolium bromide (4)

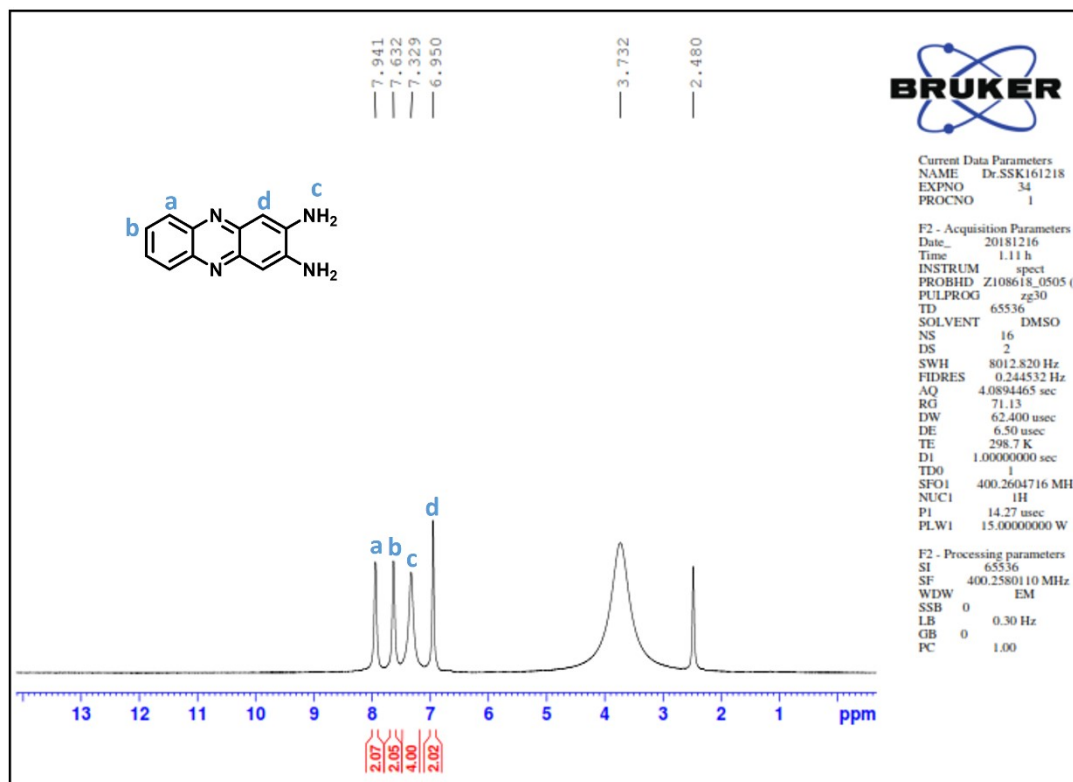


Fig. S9 ^1H NMR spectrum of 2,3-diaminophenazine (5)

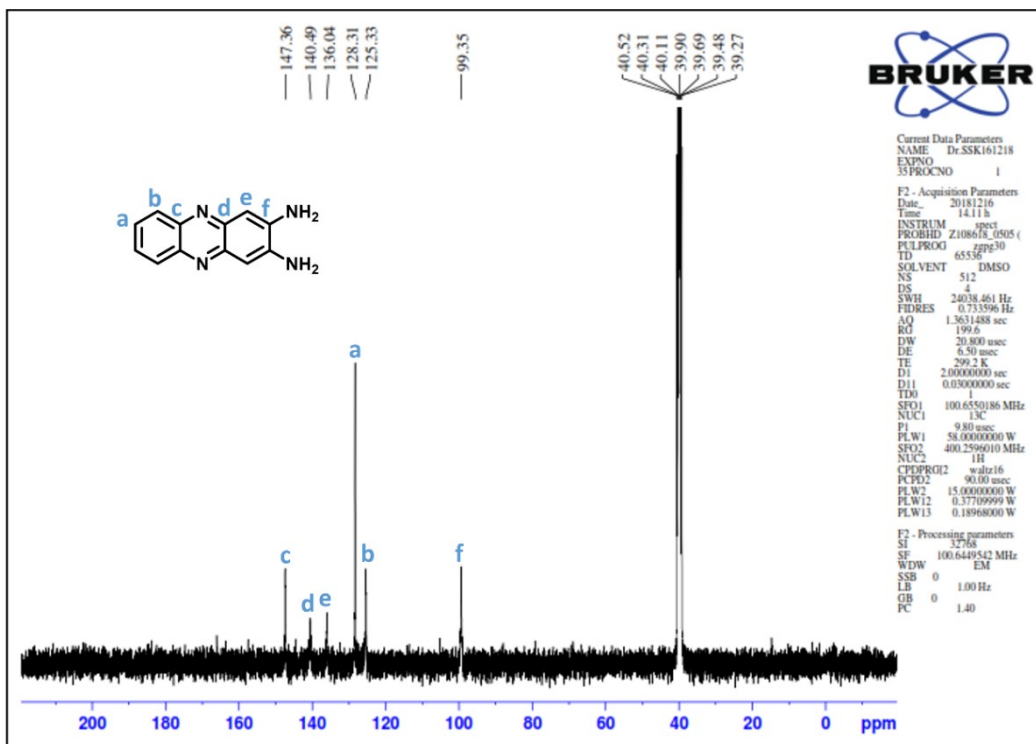


Fig. S10 ^{13}C NMR spectrum of 2,3-diaminophenazine (5)

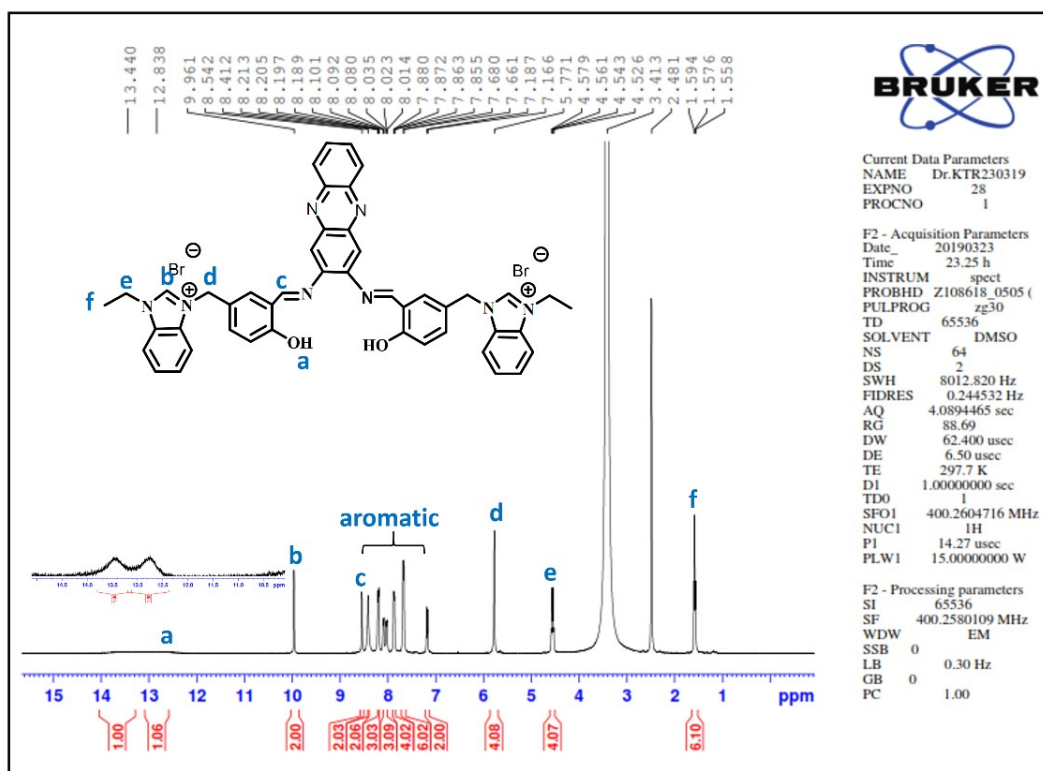


Fig. S11 ^1H NMR spectrum of 3,3'-((((1E,1'E)-(phenazine-2,3-diylbis(azanylylidene))bis(methanylylidene))bis(4-hydroxy-3,1-phenylene))bis(methylene))bis(1-ethyl-1H-benzoimidazol-3-ium) bromide (PS-IL) (6).

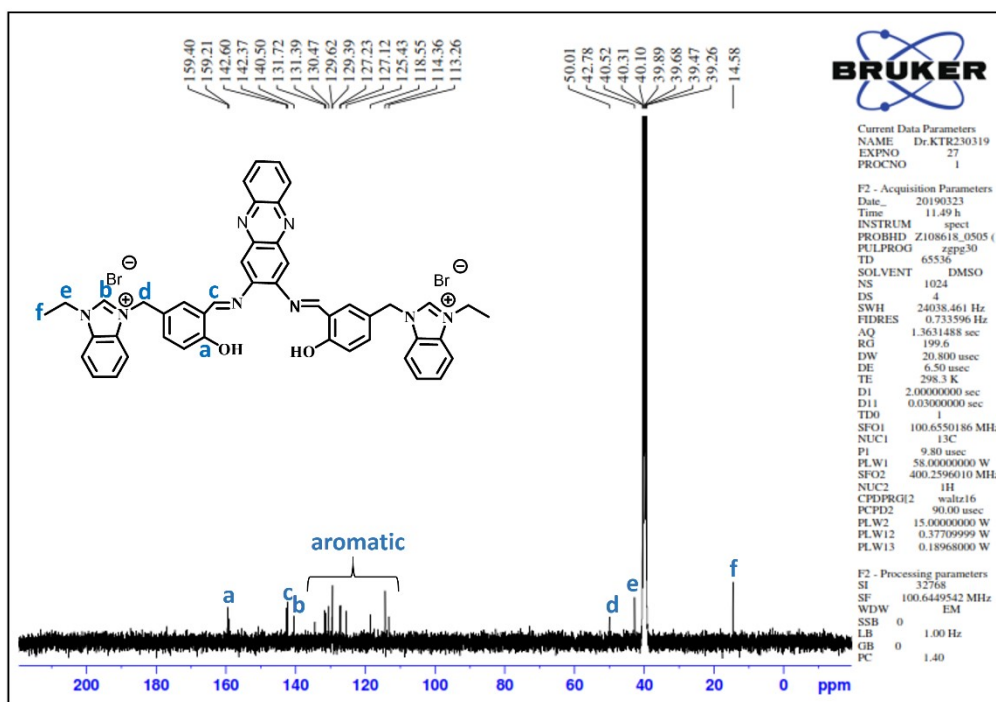


Fig. S12 ¹³C NMR spectrum of 3,3'-((((1E,1'E)-(phenazine-2,3-diylbis(azanylylidene))-bis(methanylylidene))bis(4-hydroxy-3,1-phenylene))bis(methylene))bis(1-ethyl-1H-benzimidazol-3-ium) bromide (PS-IL) (6).

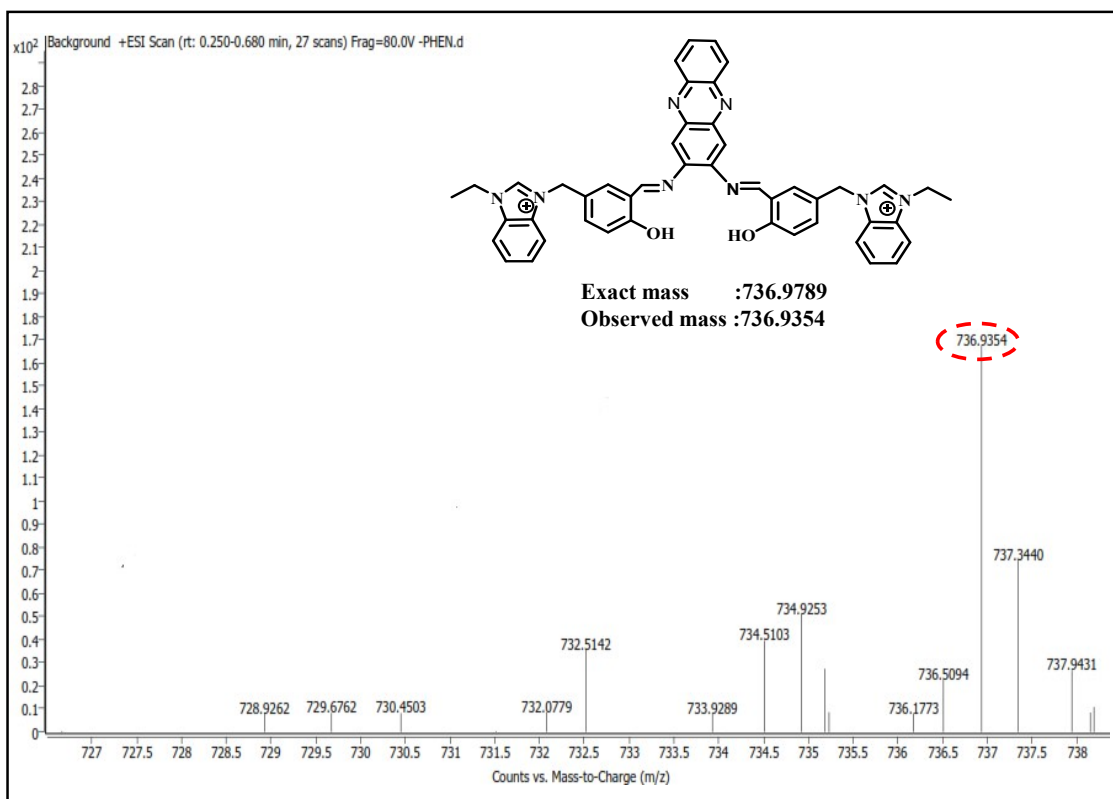


Fig. S13 ESI-QTOF-MS mass spectrum of [C₄₆H₄₀N₈O₂]²⁺ PS-IL.

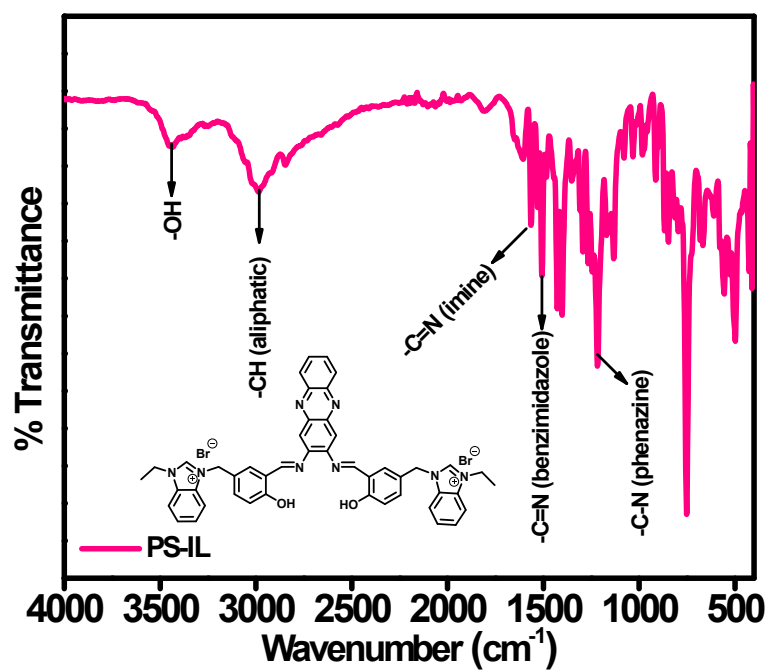


Fig. S14 FTIR spectrum of PS-IL.

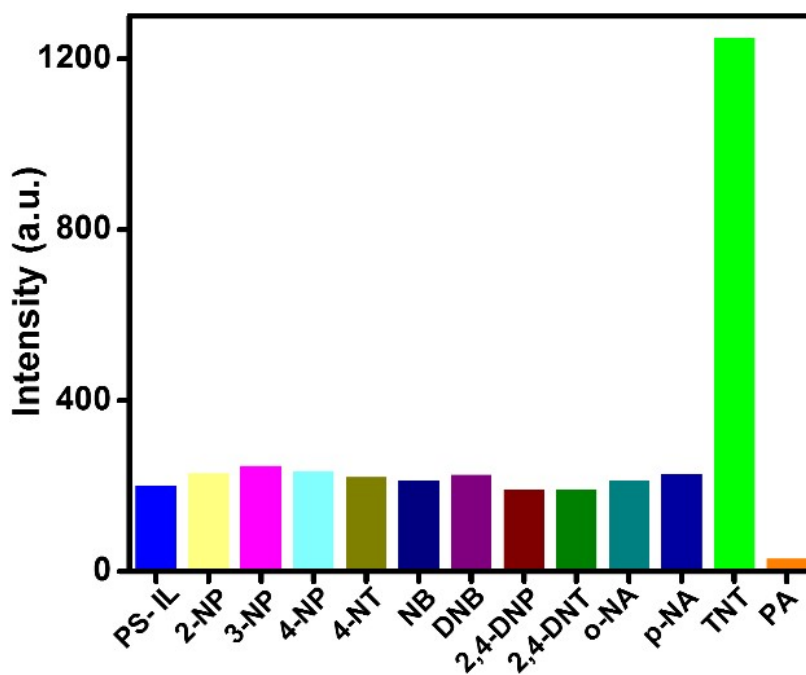


Fig. S15 Selectivity graph of PS-IL towards various nitroaromatics at 1 μ M concentration.

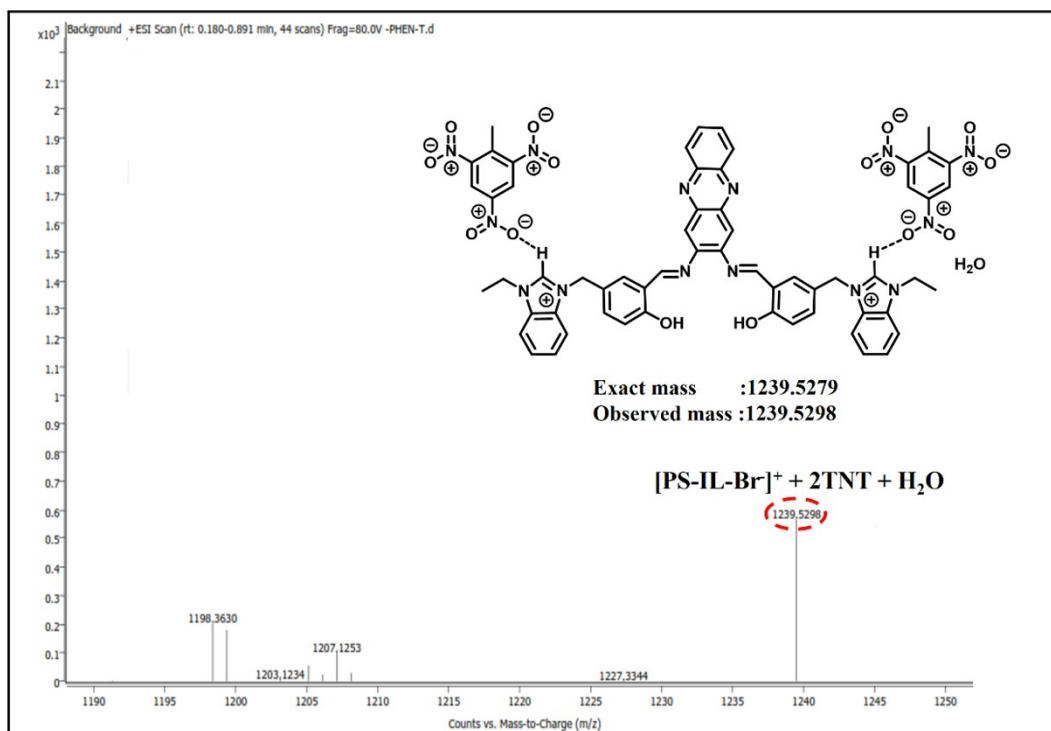


Fig. S16 ESI-QTOF-MS spectrum of PS-IL+TNT.

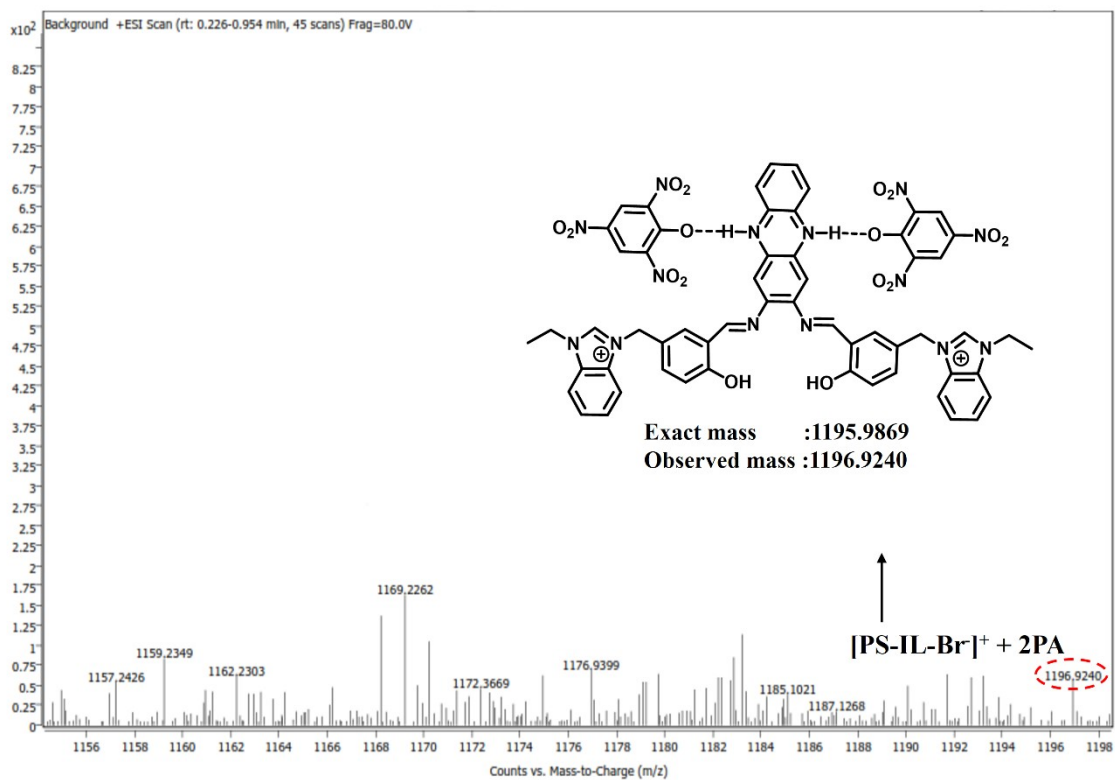


Fig. S17 ESI-QTOF-MS spectrum of PS-IL+PA.

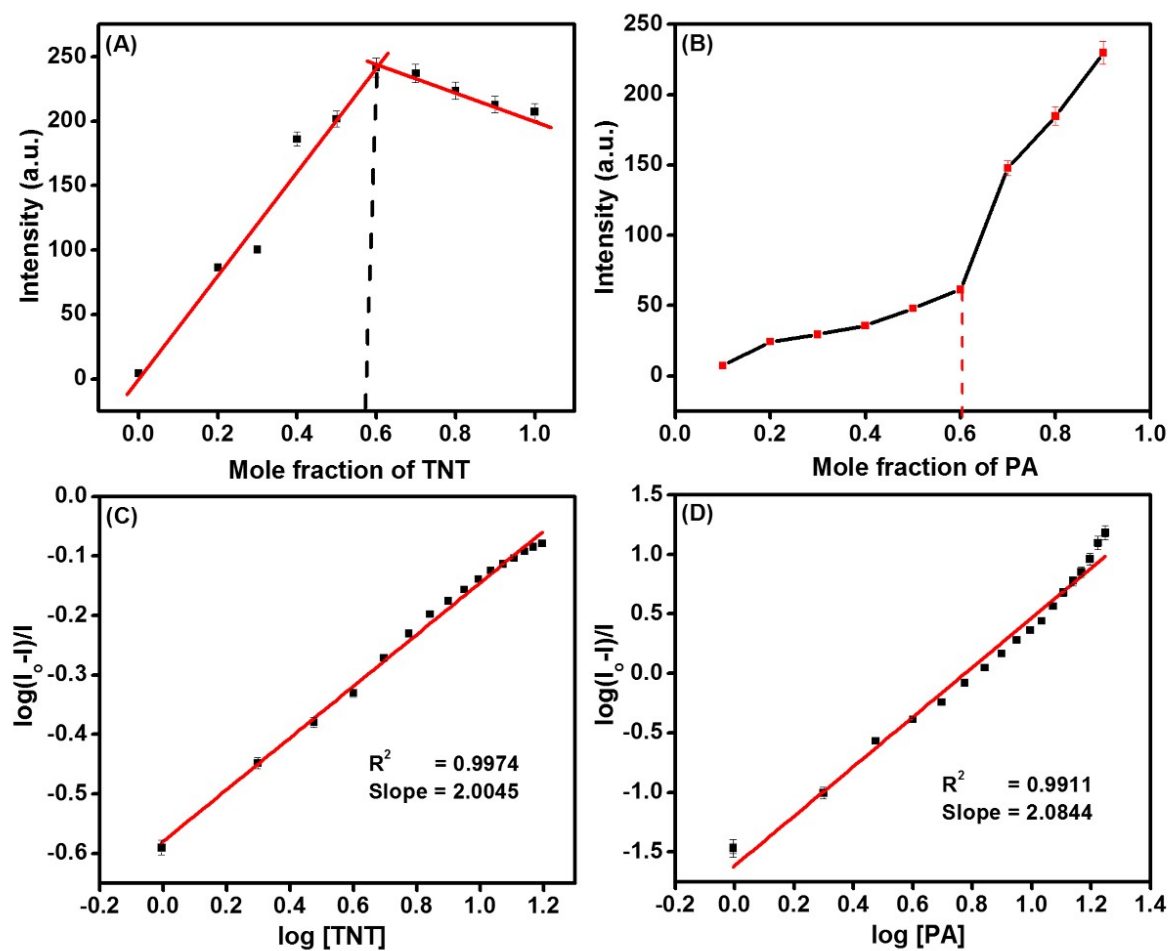


Fig. S18 Job's plot for PS-IL with (A) TNT and (B) PA. Hill's plot for PS-IL towards (C) TNT and (D) PA.

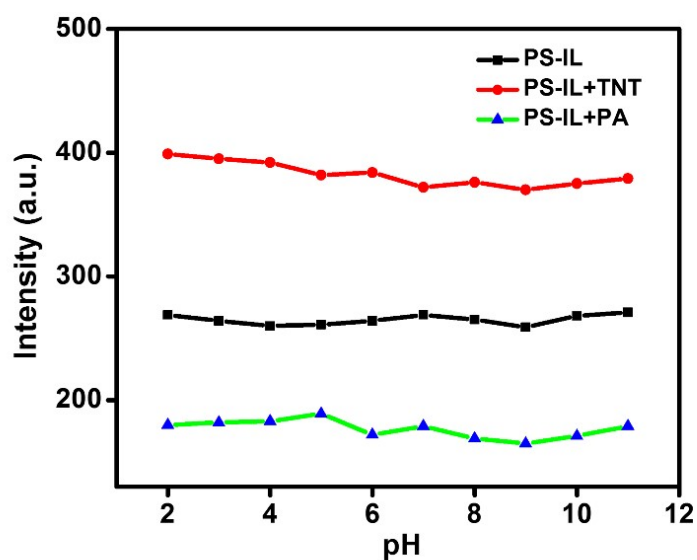


Fig. S19 pH measurements of PS-IL in the presence and absence of (A) TNT and (B) PA at 562 nm.

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