Supporting Information

Ultra-trace Detection of Nitroaromatics: Picric Acid Responsive Aggregation - Disaggregation of Self-assembled *p*-Terphenyl-benzimidazolium based Molecular Baskets

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1. Experimental Details

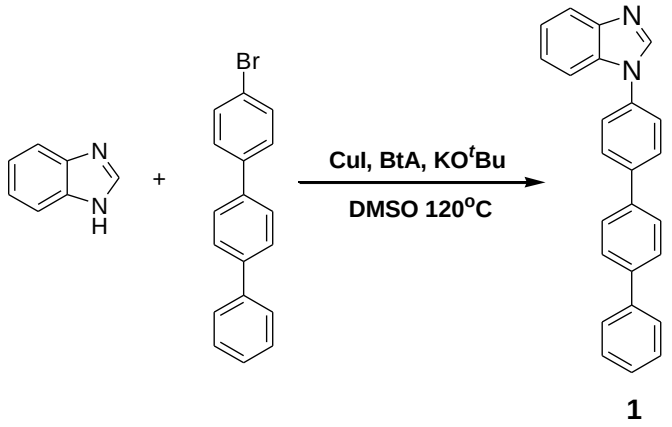
1.1 General Remarks: All chemicals were obtained from common suppliers (Aldrich, Across, SDFCL, Spectrochem etc.) and were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on Bruker-500 and JEOL-300 NMR instruments using the resonance of solvents having TMS as internal standard. Chemical shifts are given in ppm; coupling constants in Hz. UV-Vis studies of compounds were performed on Shimadzu-2450 and fluorescence studies were carried out on BH-CHRONOS spectrophotometers.

TRIPOD-TP coated paper strips. Whatman filter paper strips (1 cm x 1 cm) were dipped into aqueous DMSO solution of **TRIPOD-TP** (1 mM) and were dried under vacuum at room temperature. These paper strips were used for naked eye (under 365 nm light) visualisation of 10^{-17} to 10^{-9} M PA solution. The 10^{-17}, 10^{-15}, 10^{-13} and 10^{-9} M solutions of PA were prepared in water and 10 μl aliquot of each of these solutions was added on separate paper strip. For control experiment, drop of water alone was added on the **TRIPOD-TP** coated paper strip. The fluorescence spectrum of these paper strips was also recorded using front surface steady-state fluorescence on Chronos BH spectrophotometer.

TRIPOD-TP thin films on glass plate. 20 μl of **TRIPOD-TP** solution (10 μM, H_2O-2% DMSO) was placed on glass plate and was allowed to evaporate at 25^{o}C in the incubator.

SEM and TEM sample preparation. Solutions of **TRIPOD-TP** (5 μM, H_2O-2% DMSO) and its mixtures with varying concentrations of PA were prepared. These solutions were filtered through 0.2 micron filter membrane to remove interfering impurities. 10 μl of each of these solutions was added on .the pre-cleaned surface of the separate glass slides and was allowed to dry in the incubator at 25^{o}C. SEM images were taken on SEM-Zeiss-SUPRA^{TM} 55 after coating with silver particles. For preparation of samples for recording TEM images, the filtered solutions were added on copper grid which was allowed to dry in the incubator at 25^{o}C.

1.2 Synthesis of compound 1



Scheme 1: Synthesis of **1**

p-Bromoterphenyl (4.3 g, 14 mmol), CuI (267 mg, 1.4 mmol) and benzotriazole (333 mg, 2.8 mmol) were dissolved in DMSO (10 ml). To this stirred mixture benzimidazole (4.2 g, 35 mmol) and K-O^{t}Bu (4.3 g, 38.5 mmol) were added under N_2 and resulting solution was heated at 120ºC for 24h. The reaction mixture was cooled to room temperature and aqueous solution of EDTA (2.8 mmol) was added. The compound was extracted with ethyl acetate (3 × 30 ml). The solvent was distilled off, and residue on column chromatography with hexane-chloroform (9:1) mixture as eluent gave pure compound **1**, white solid (2.9 g). Yield 60 %; M**.** pt. 192^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) : δ 7.35 - 7.41 (m, 3H, ArH), 7.49 (t, 2H, *J* = 7.35 Hz, ArH), 7.61 - 7.69 (m, 5H, ArH), 7.74 (s, 4H, ArH), 7.85 (d, 2H, *J* = 8.4 Hz, ArH), 7.90 - 7.93 (m, 1H, ArH), 8.18 (s, 1H, Bim C2-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 110.6, 120.7, 123.0, 123.8, 124.4, 127.1, 127.4, 127.5, 127.6, 127.6, 127.8, 128.6, 128.6, 128.9, 132.0, 133.8, 135.5, 138.6, 140.5, 140.6, 140.8, 142.3, 144.2. HRMS-ESI : calcd for $C_{25}H_{18}N_2$, m/z = 347.1504 [M]; found, 347.1518 [M].

2. Absorption and emission spectra of TRIPOD-TP with increasing water ratio

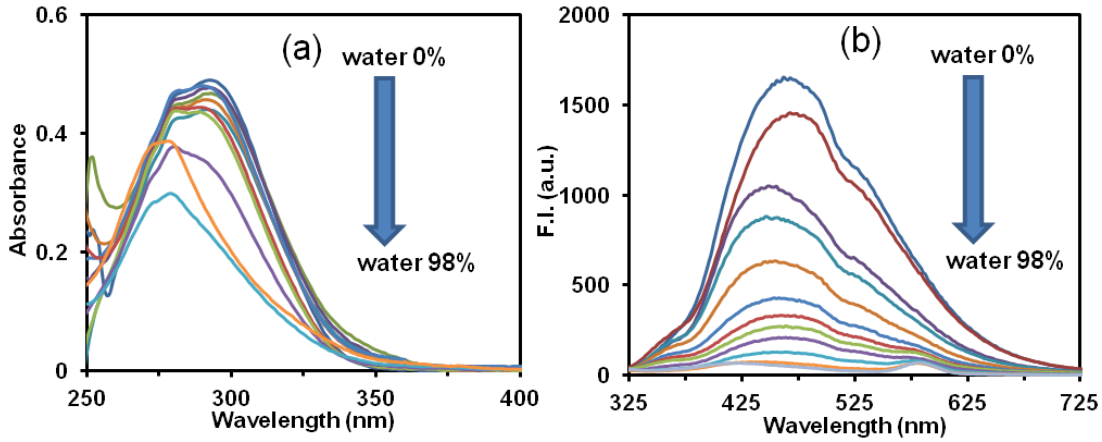
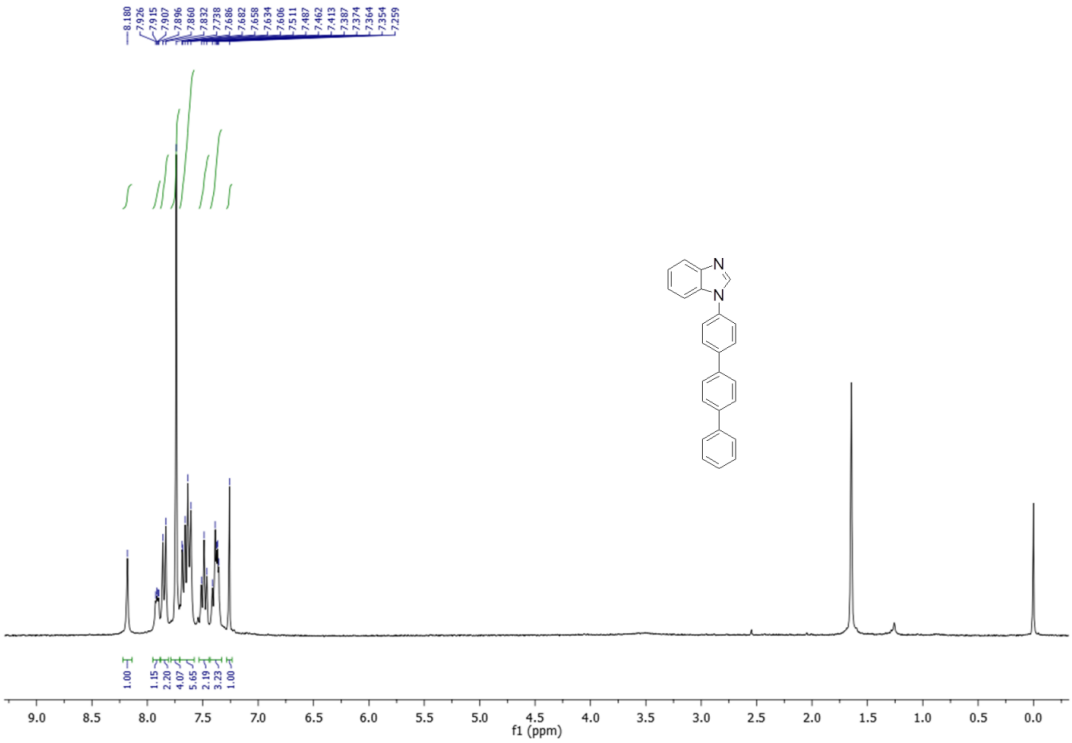
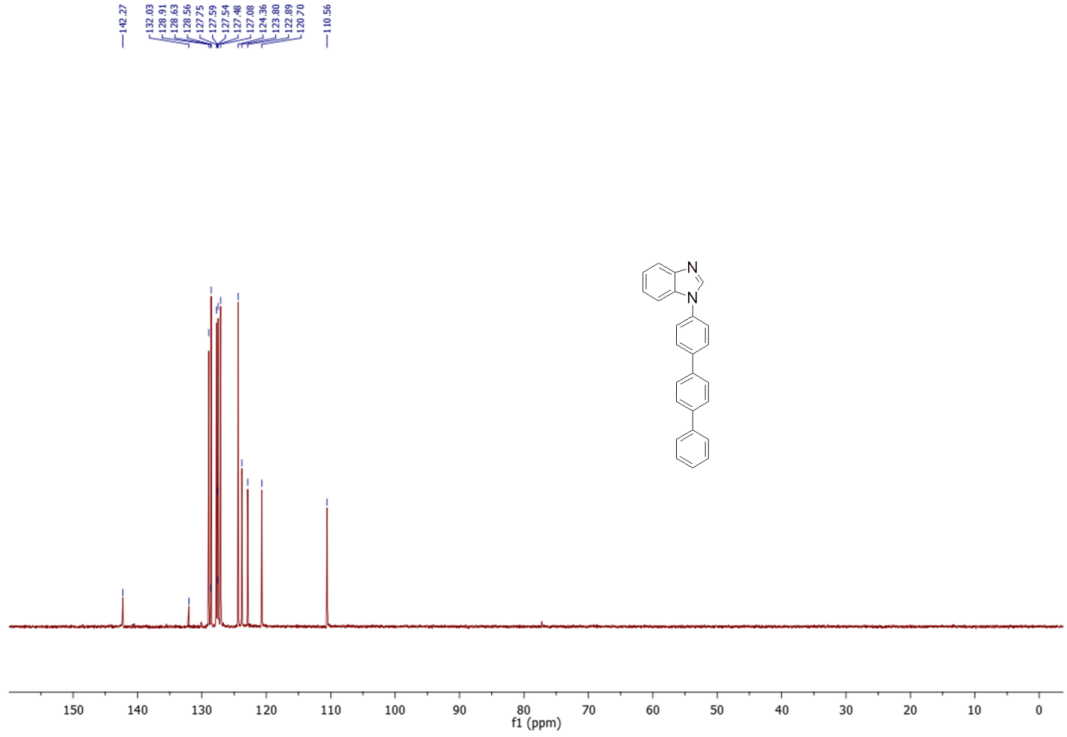


Figure S1: The effect of increasing ratio of water on (a) absorbance and (b) emission spectra of **TRIPOD-TP** (5 µM)

3. Spectral data of Compound 1





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Analysis Info

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Sample Name	sh-35	Instrument	micrOTOF-Q II 10356
Comment			

Acquisition Parameter

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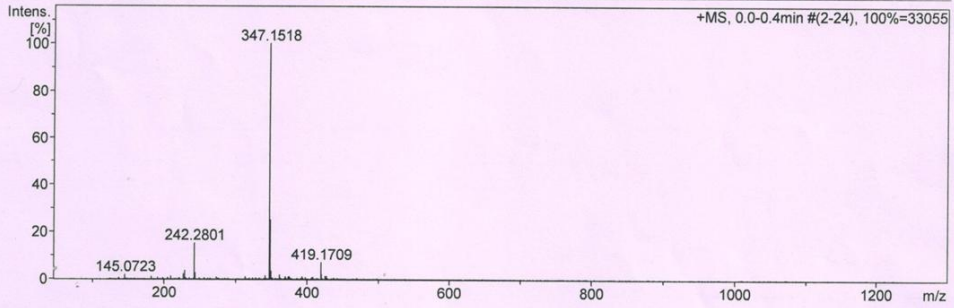
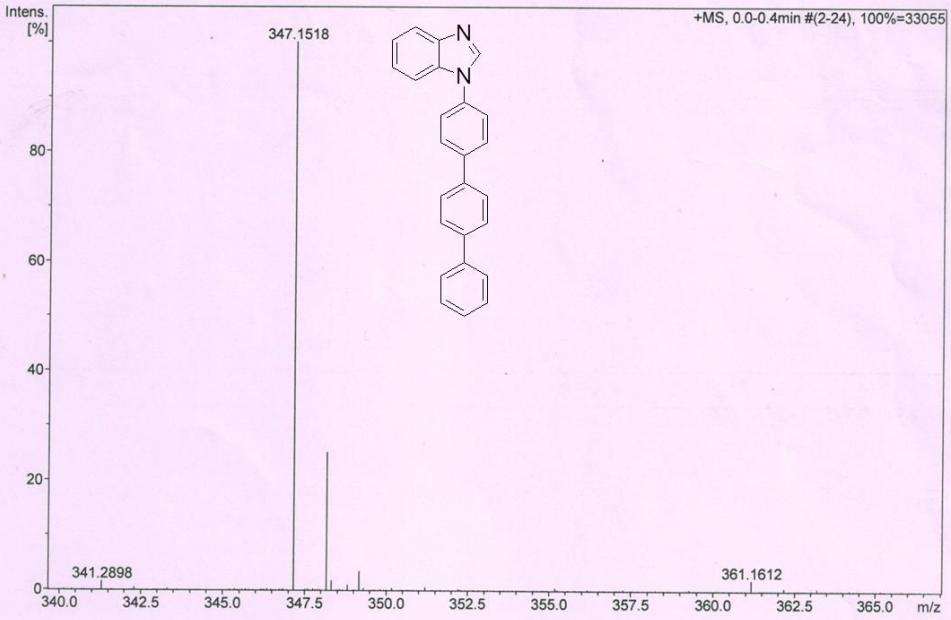
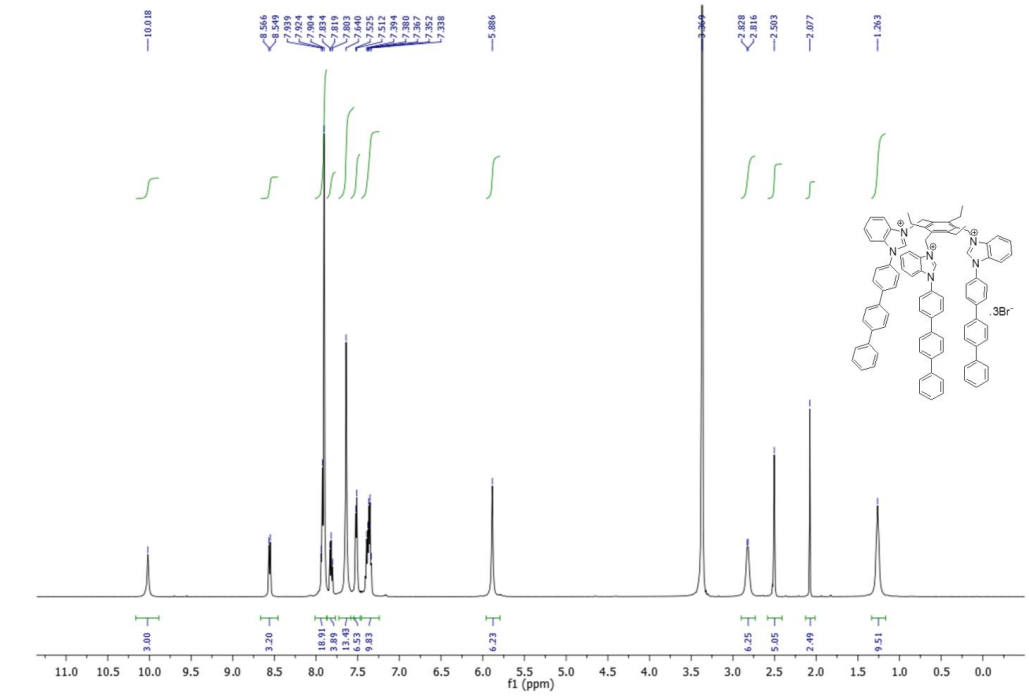
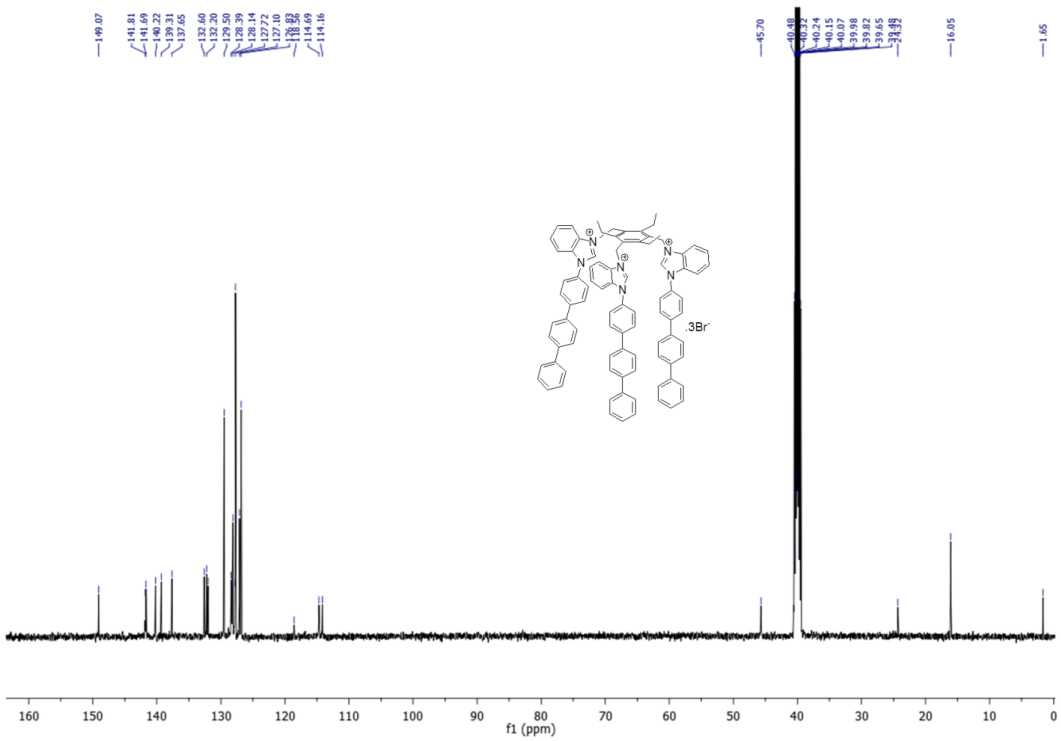
Scan End	3000 m/z	Set Collision Cell RF	250.0 Vpp	Set Divert Valve	Waste





4. Spectral data of TRIPOD-TP





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Analysis Info

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Sample Name	sh-35	Instrument	micrOTOF-Q II 10356
Comment			

Acquisition Parameter

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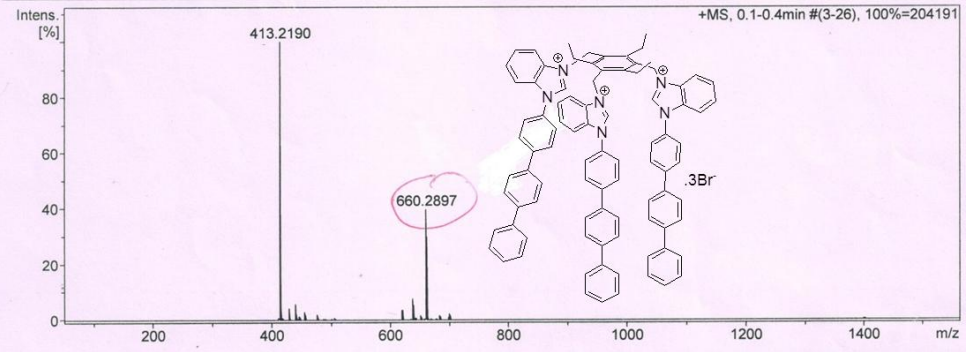
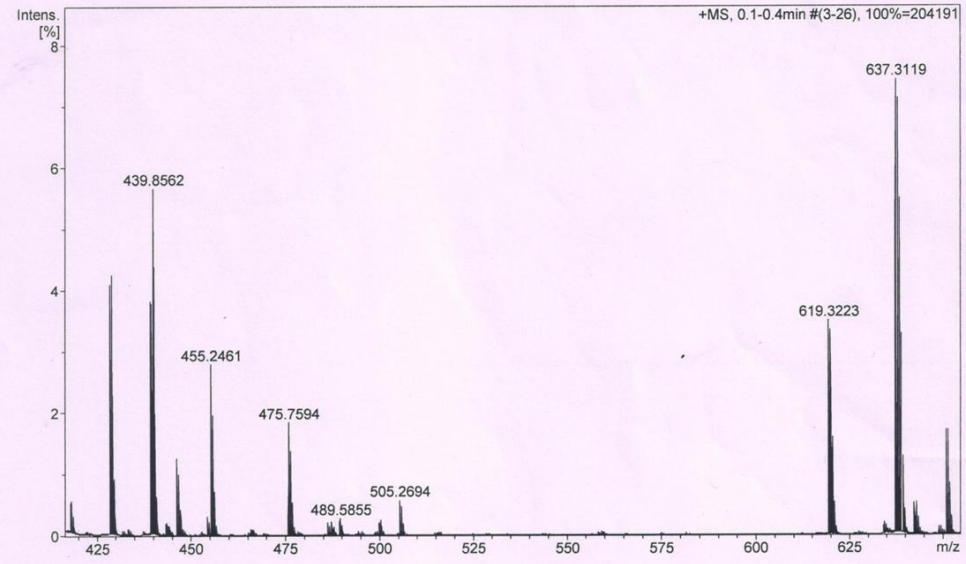
Scan End	3000 m/z	Set Collision Cell RF	650.0 Vpp	Set Divert Valve	Waste





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5. SAED and XRD analysis of TRIPOD-TP (rods)

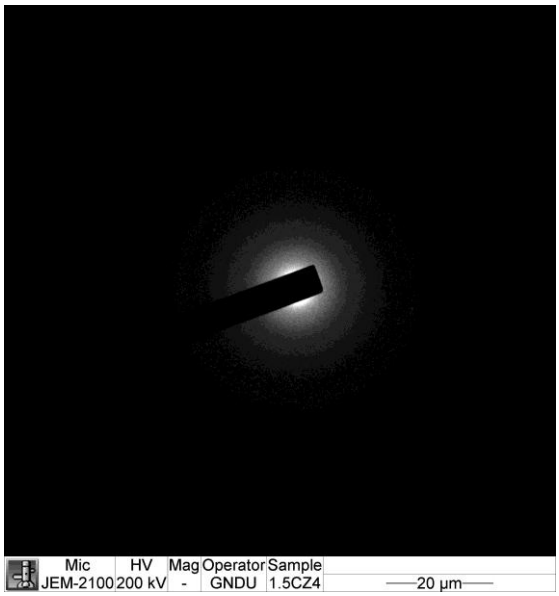

Figure S2: SAED pattern of TRIPOD-TP rods section

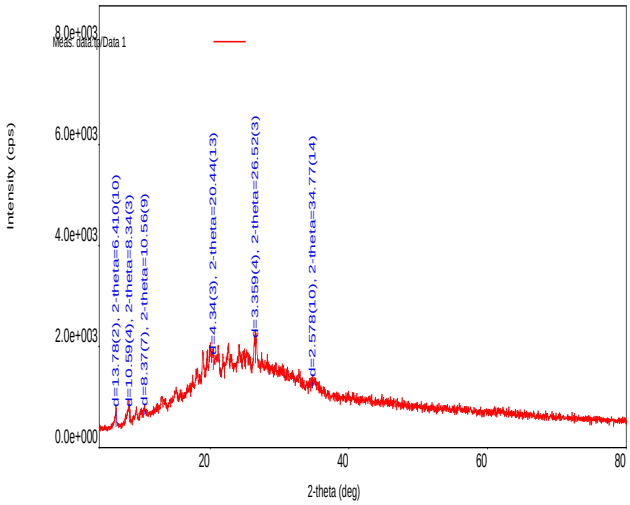

Figure S3: X-ray diffraction analysis of TRIPOD-TP powder

6. Energy Minimized structure of TRIPOD-TP

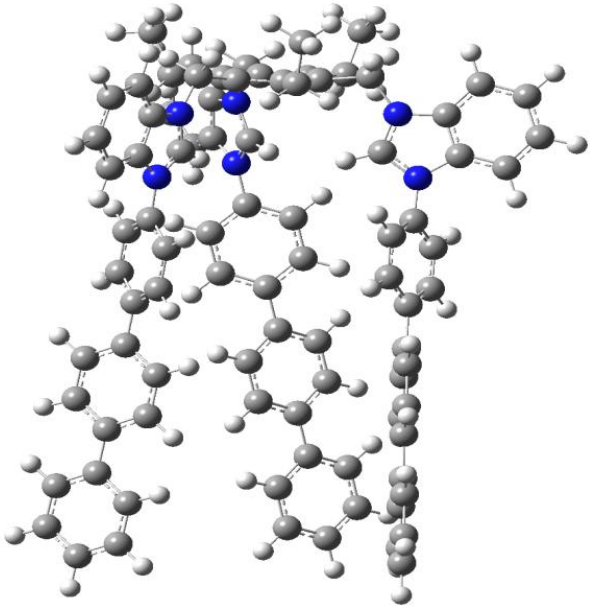

Figure S4: Energy minimized structure of TRIPOD-TP. Carbon (black spheres); nitrogen (blue spheres); hydrogen (white spheres). The structure has been optimized by DFT/B3LYP calculations and 6-31G basis set on TmoleX platform

7. SAED and XRD analysis of TRIPOD-TP + PA (spherical aggregates)

Figure S5: SAED pattern of spherical aggregates of TRIPOD-TP + PA

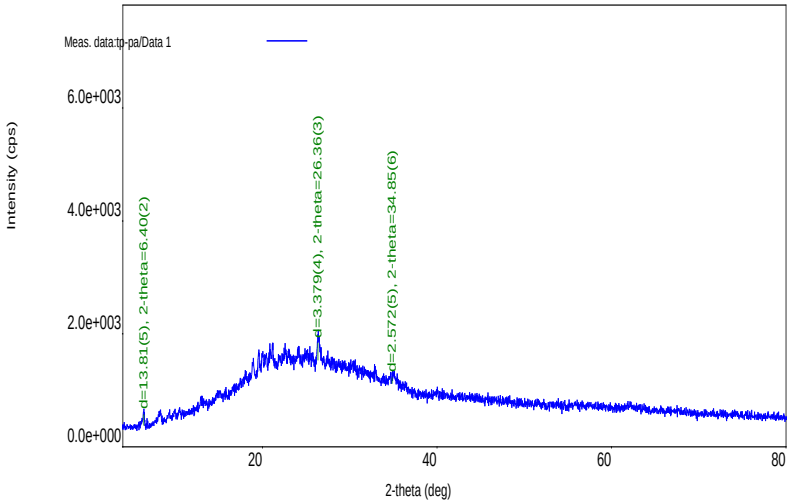

Figure S6: X-ray diffraction analysis of TRIPOD-TP + PA

8. ^{1}H NMR spectra of TRIPOD-TP and Picric acid

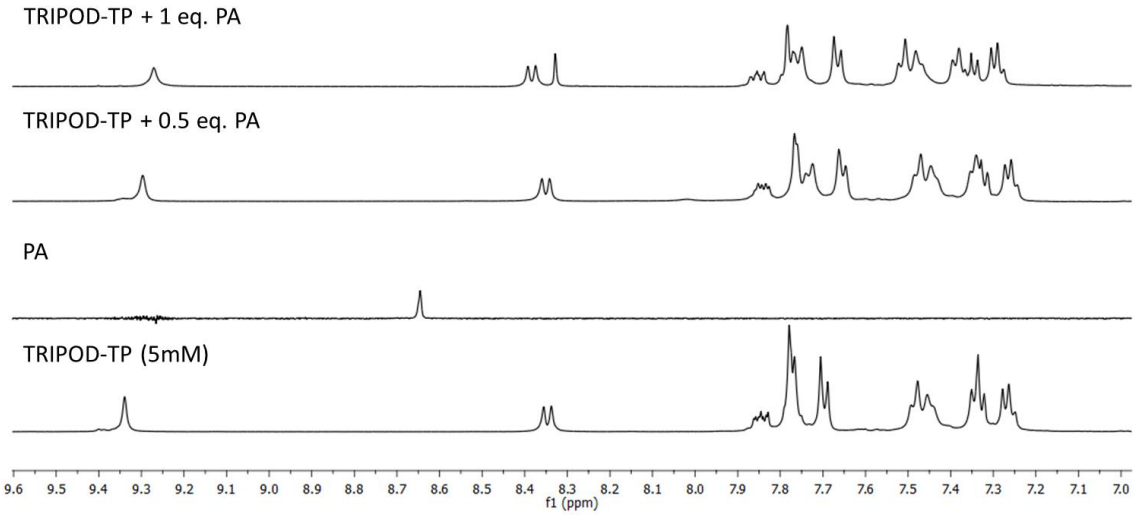

Figure S7: Effect of addition of PA on ^{1}H NMR spectrum of **TRIPOD-TP** (5 mM, DMSO + H_2O; 7:3)

9. Comparison of HOMO and LUMO of TRIPOD-TP and NACs

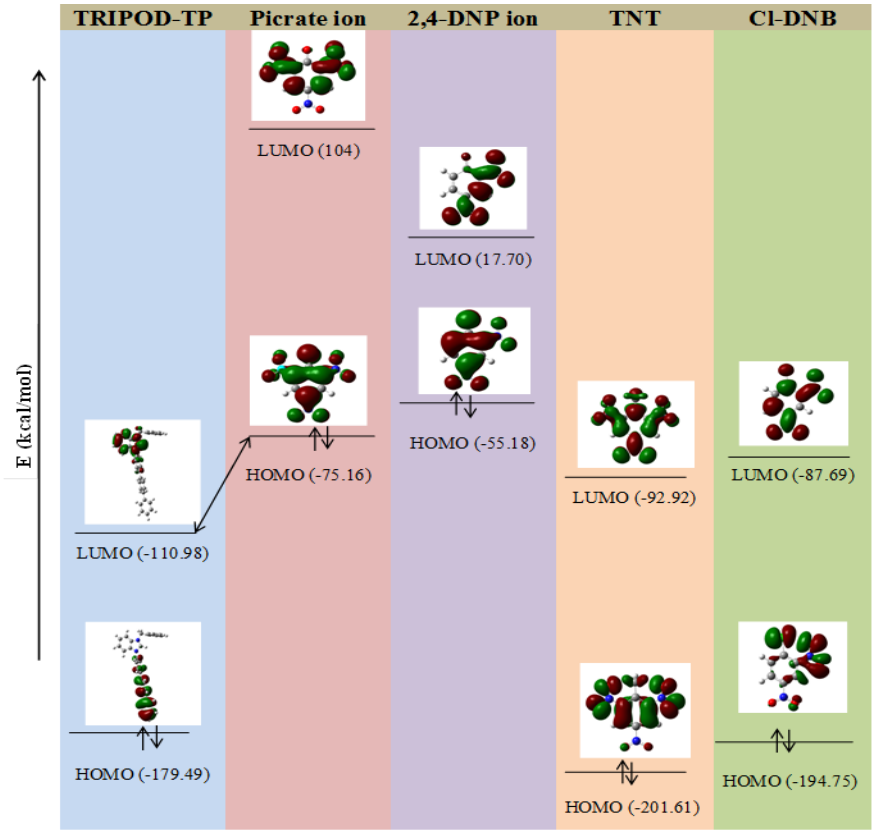

Figure S8: Pictorial representation of the electron transfer phenomenon which occurs from the HOMO of picrate anion to the LUMO of **TRIPOD-TP**. All theoretical calculations are performed using density functional theory at B3LYP/ 6-31 G basis set