Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information (SI)

Aggregation Induced Emission and Volatile Acid Vapour Sensing in Acridine Appended Poly (Aryl Ether) Based Low Molecular Weight Organogelator

Srikanta Kumar Patra,[a] Malay Krishna Mahato[a] and Edamana Prasad[a]*

a. *Department of Chemistry, Indian Institute of Technology Madras (IITM), Chennai 600036, India*

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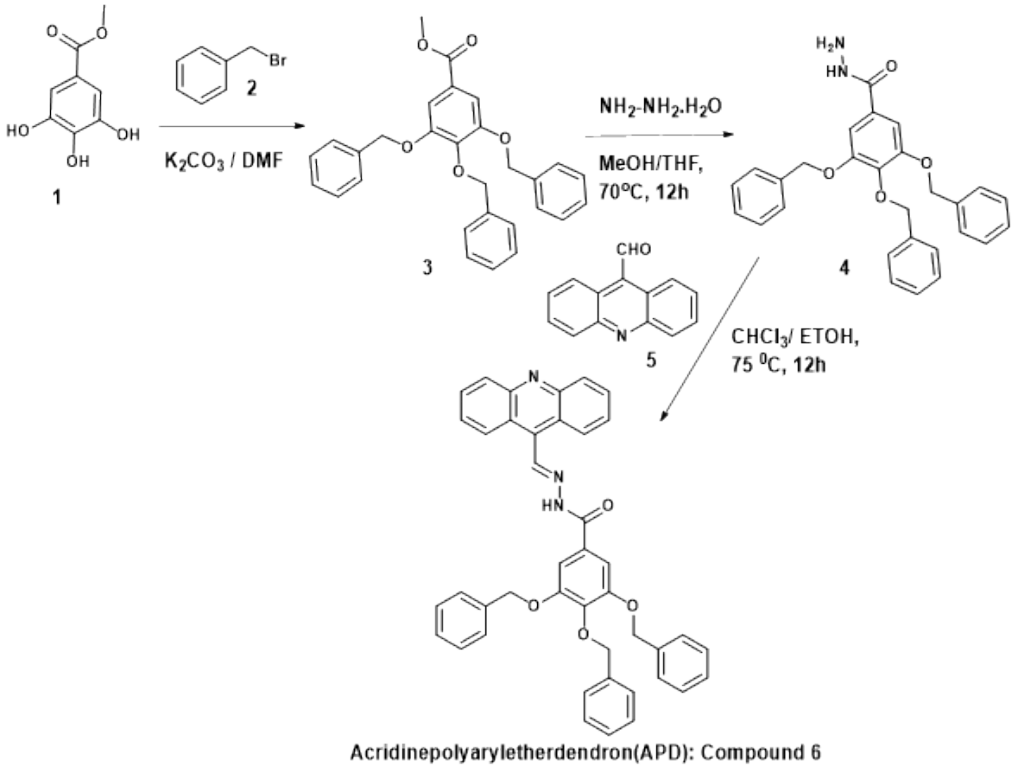
1. Synthetic scheme and characterization of APD with intermediate steps



Scheme S1: The overall synthetic scheme of the gelator APD (compound 6)

The detailed synthetic procedure for each steps is explained as follows,

Synthesis of Compound 3 (Benzylation reaction): Step-1

Methyl- 3,4,5- trihydroxybenzoate (compound 1, 2 g, 0.01 mole, 1 equivalent) and potassium carbonate (9.67g, 0.07 mole, 7 equivalent) is dissolved with 30 mL of DMF in a 250 mL round bottom flask. Benzyl chloride (6.46 mL, 0.054 mole, 5 equivalent) is added to the above reaction mixture under stirring. The reaction is run in a reflux condition at 90 ^{0}C for 24hrs. After completion of the reaction, the solvent is then removed under vacuum using rotary evaporator, leaving an oily substance, which turns into a solid upon standing. The solid is recrystallized from methanol to obtained 85% yield of the product 3. **^{1}H NMR (400MHz, $CDCl_3$) δ(ppm)**: 3.86 (s, COOC**H_3**, 3H), 5.09 (s, ArC**H_2**O, 2H), 5.11 (s, ArC**H_2**O, 4H), 7.22- 7.42(m, Ar**H,** Ph**H,** 17H); **^{13}C NMR (100**

MHz, $CDCl_3$) δ: 52.37, 71.37, 75.27, 109.22, 125.36, 127.69,128.08, 128.17, 128.33, 128.68, 136.79, 137.84,141.43, 152.70, 166.80. **HRMS (ESI+):** m/z Calculated M for $C_{29}H_{26}O_5$: 454.1778, $[M+H]^+ = C_{29}H_{27}O_5^+$: 455.1853 found: $[M]^+ = 454.1724$, $[M + H]^+ = 455.1852$, $[M + NH_4]^+ = 472.2113$, $[M + Na]^+ = 477.1664$, $[M + K]^+ = 493.1403$.

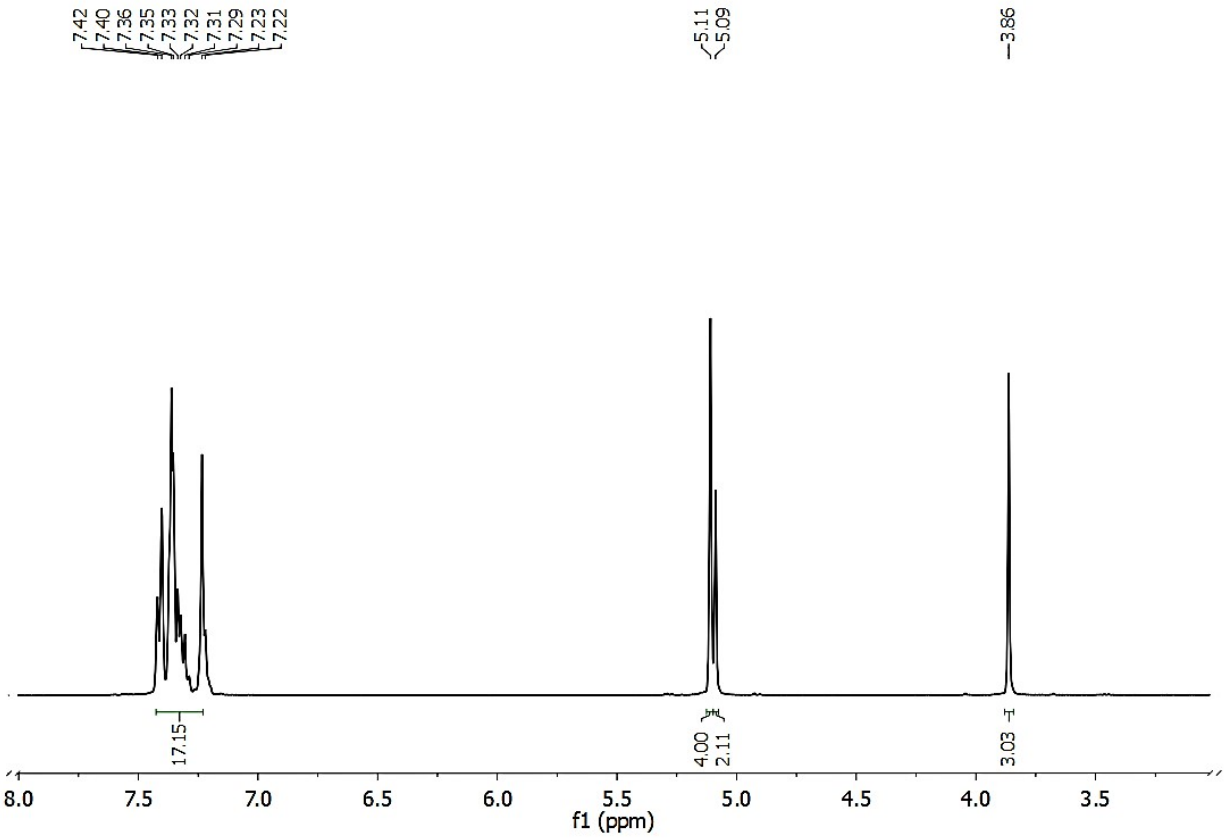


Figure S1: ^1H NMR spectra (400 MHz) of Compound 3.

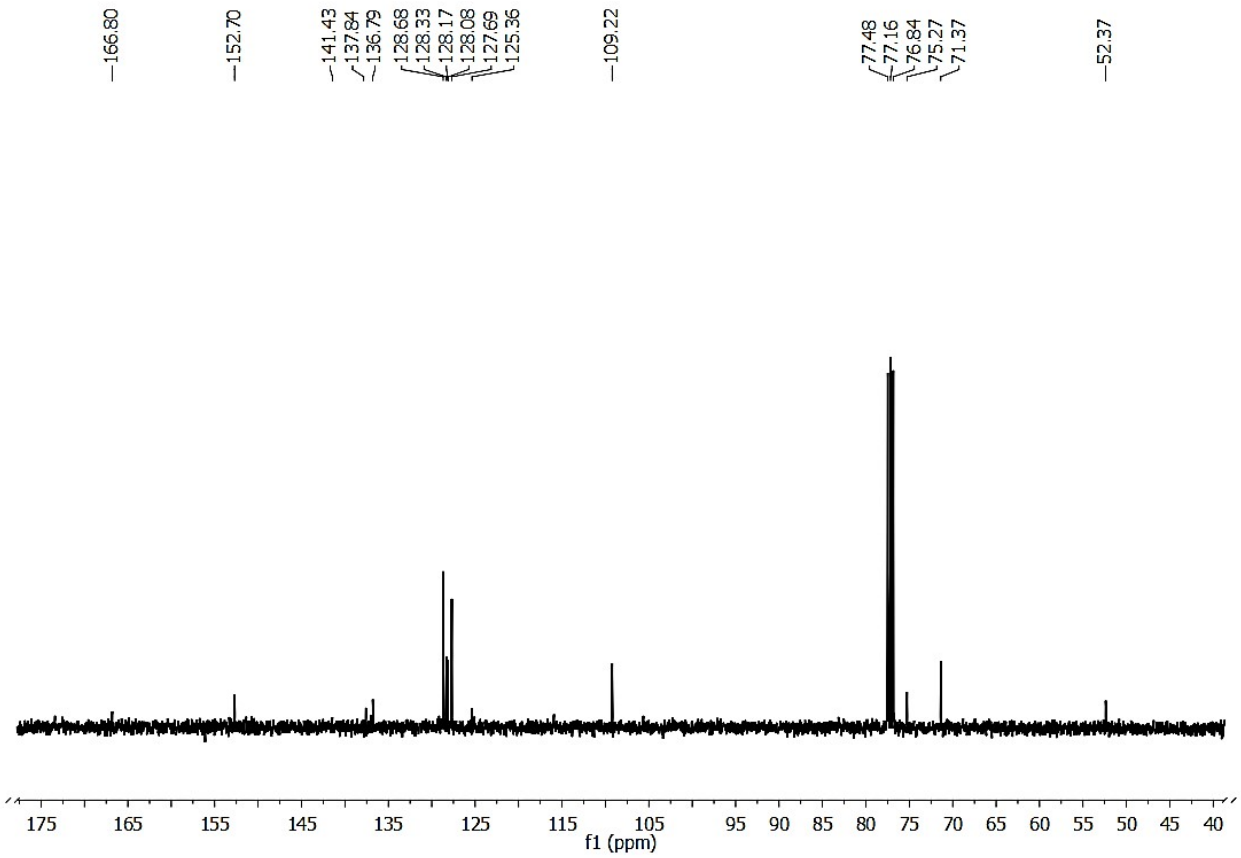


Figure S2: ^{13}C- NMR spectra (400 MHz) of Compound 3.

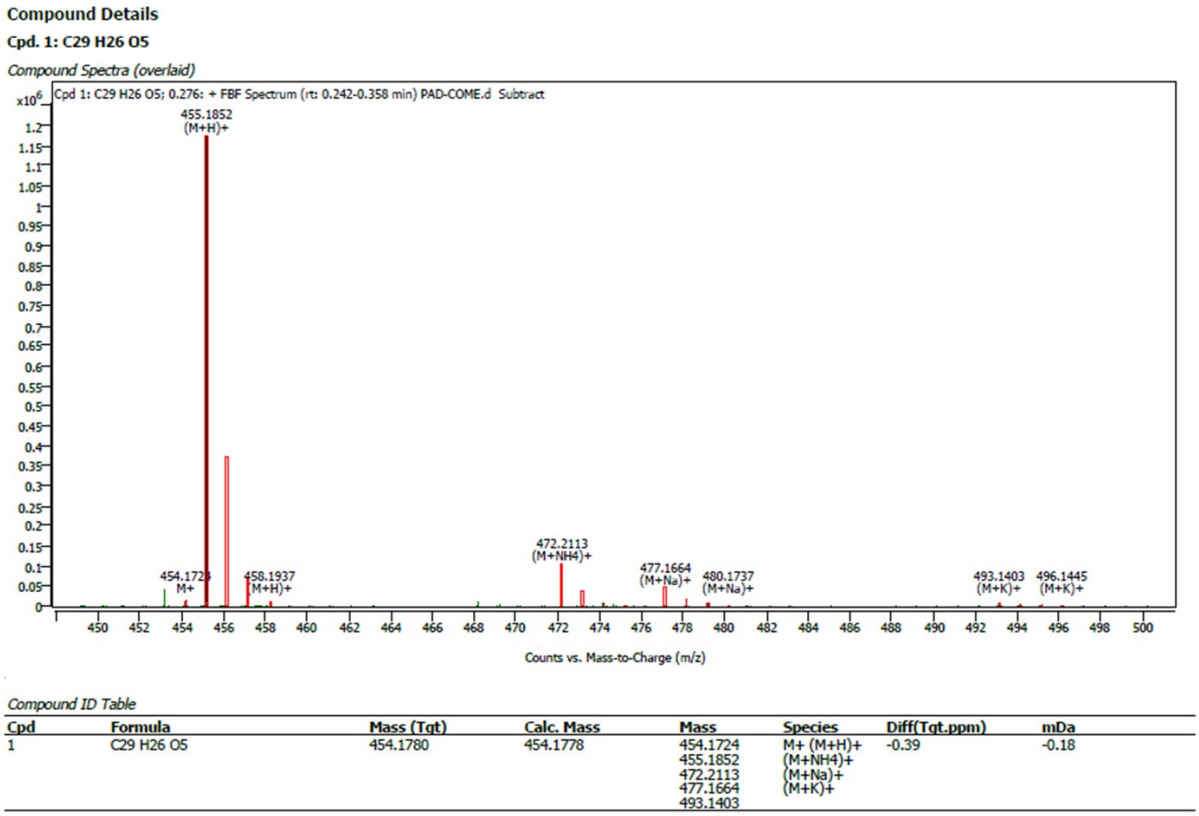


Figure S3: HR-MS spectrometry of compound 3

Synthesis of Compound 4 (Hydrazone reaction): Step-2

Compound 3 (3g, 0.006mole, 1 equivalent) and hydrazine monohydrate (16 mL, 0.33 mole, 50 equivalent) is dissolved in 40 mL methanol and 20 mL THF. The reaction is carried out under reflux condition at 70 ^{0}C with constant stirring for 12hrs. After completion of the reaction, the reaction mixture is allowed to cool to room temperature and the volatiles are removed under reduced pressure. The residue under goes fractional separation using DCM and water mixture. The collected organic layer is dried over anhydrous Na_2SO_4 and the solvent is evaporated to get crude product. It is purified by column chromatography using silica gel as the stationary phase and 5% methanol in DCM as the eluent to get pure white powder product 4 (weight = 3.626g). **^{1}H-**NMR (400 MHz, $CDCl_3$) δ: 3.96 (s, CONHN**H_2,** 2H), 5.01-5.02(d, PhC**H_2**O, 6H), 6.94 (s, Ar**H,** 2H), 7.17 – 7.23(dd, Ph**H**, 6H), 7.28 – 7.32(t, Ph**H**, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ**:** 71.52, 75.31,

106.88,127.61,128.07, 128.13, 128.23, 128.35, 128.73, 136.68, 137.49, 141.66, 153.04, 168.50.

HRMS (ESI+): m/z Calculated for $[M+H]^+ = C_{28}H_{27}N_2O_4^+$: 455.1965 Found: $[M+H]^+$ = 455.1976.

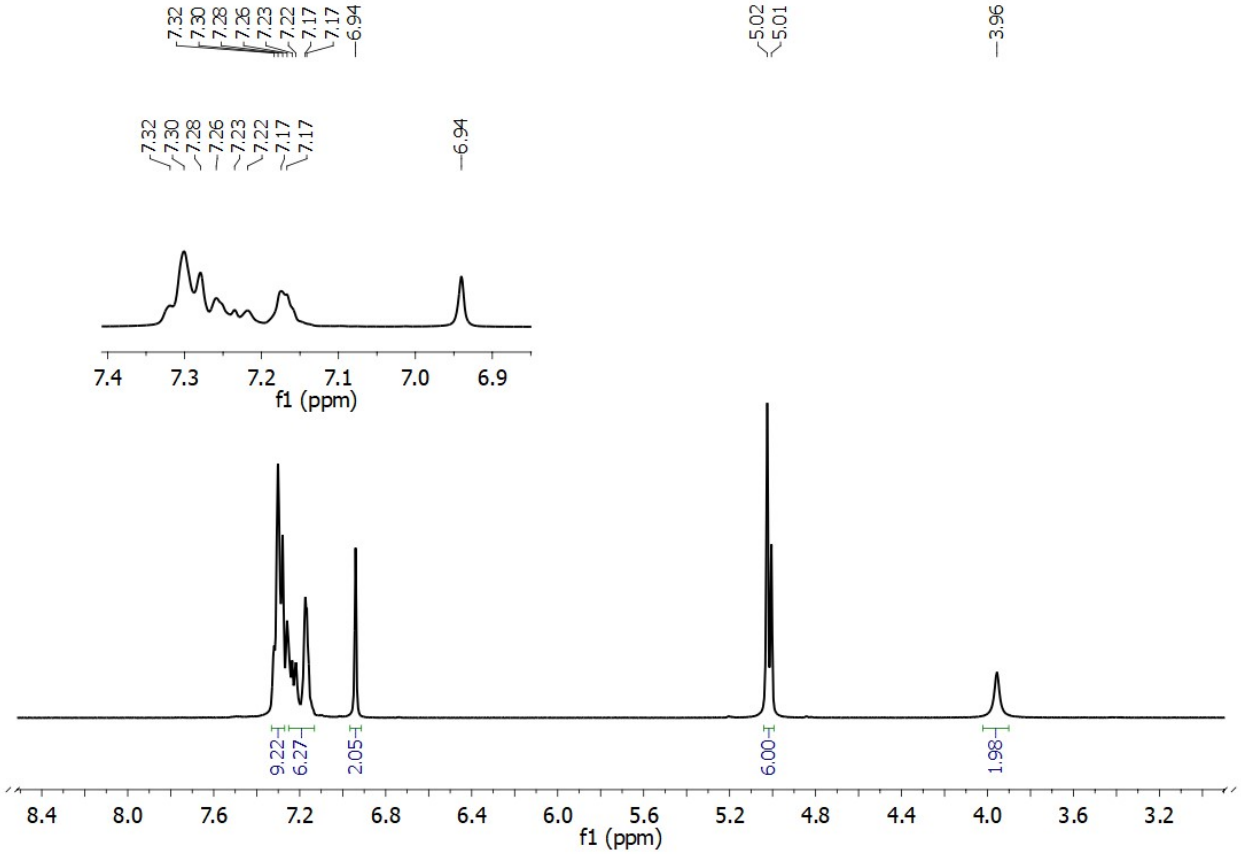


Figure S4: ^{1}H NMR spectra (400 MHz) of Compound 4.

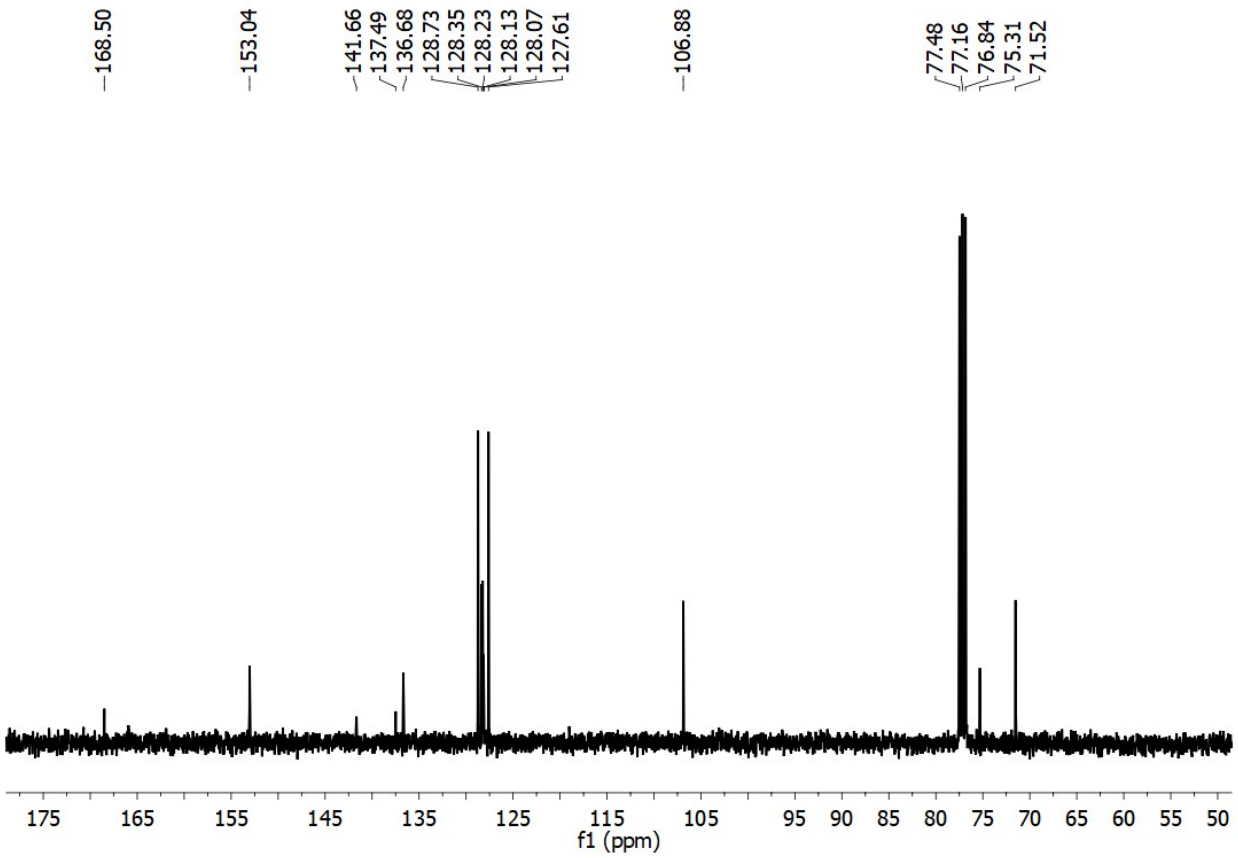


Figure S5: ^{13}C- NMR spectra (400 MHz) of Compound 4.

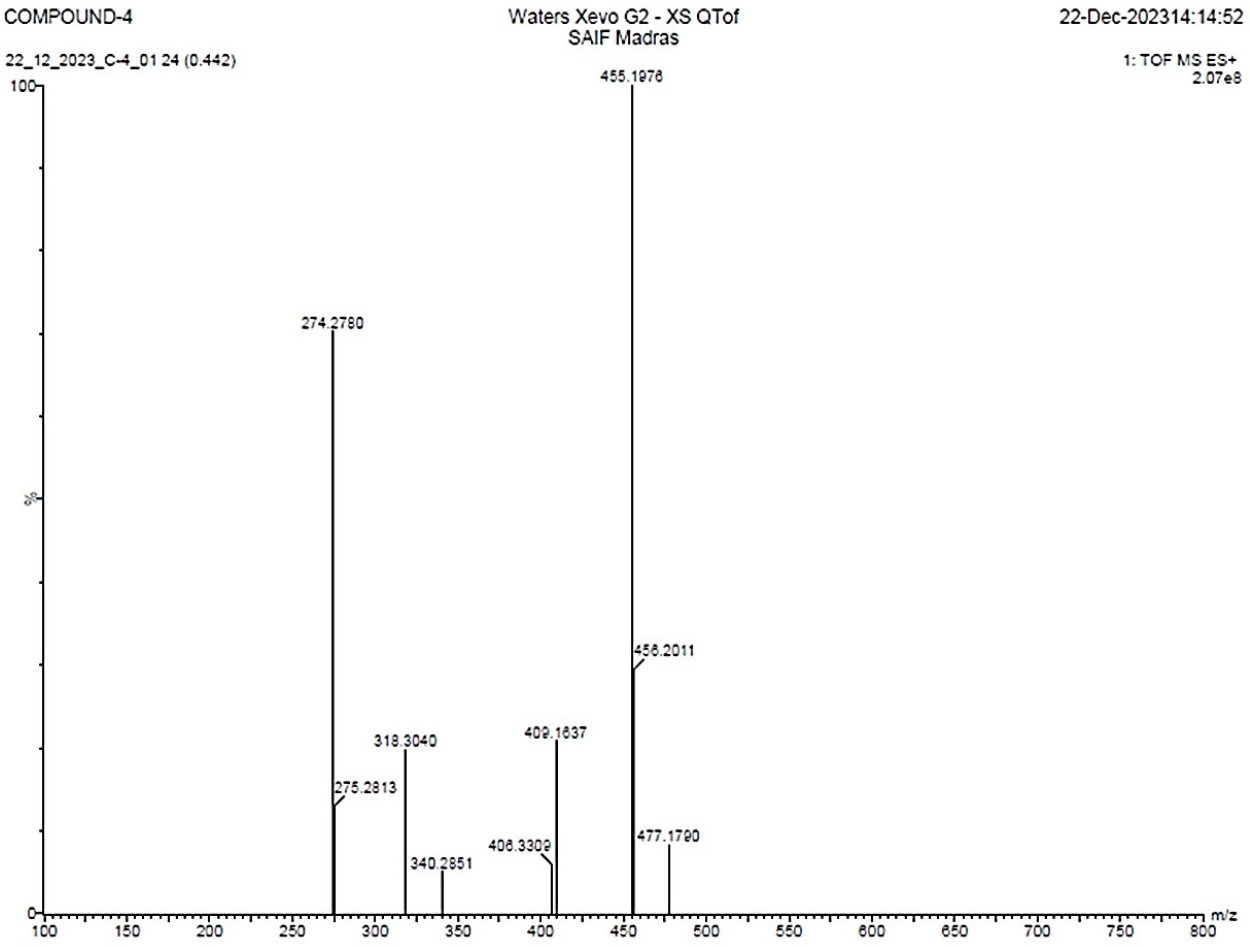


Figure S6: HR-MS spectrometry of compound 4

Synthesis of Compound 6, APD (Condensation reaction): Step -3

Acridine aldehyde (Compound 5, 0.100g, 0.00048mole) is dissolved in 30 mL of ethanol under hot condition. Then the compound 4 (0.219g, 0.00048 mole) is dissolved in 10 mL of chloroform in a vial and transferred drop by drop to the hot solution of compound 5. A catalytic amount of acetic acid is added to catalyze the reaction. The solution become green color. After completion of the reaction, yellow precipitate is formed. It is separated through vaccum filtration and washed with ethanol to get required pure APD gelator (product 6). The formation of product 6 i.e. APD gelator is confirmed by ^{1}H- NMR and HR-MS spectrometry (Figure S7 & S8).

^{1}H-NMR (400 MHz, DMSO-d_6) δ: 5.07 (s, PhC**H**$_2$O, 2H), 5.27 (s, PhC**H**$_2$O, 4H), 7.29-7.30 (d, Ph-H, 2H) 7.36- 7.39(m, Ph-H, 5H), 7.42-7.45 (t, Ph-H, 4H), 7.51-7.53 (m, Ph-H, 6H), 7.73-7.76 (t, ArH,2H), 7.90-7.93(t, ArH,2H), 8.22-8.24 (d, ArH, 2H), 8.76-8.78(d, ArH,2H), 9.67(s, -C**H**=N-, 1H), 12.26 (s, -CON**H**N-, 1H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ: 70.61, 74.34, 107.15, 123.43, 125.34, 127.21, 127.77, 127.97, 128.05, 128.14, 128.27, 128.53, 129.88, 130.35, 134.74, 136.76, 137.39, 144.60, 148.39, 152.26, 162.84. **HRMS (ESI+):** m/z Calculated for $[M+H]^+$ = $C_{42}H_{34}N_3O_4^+$: 644.2544: Found: $[M+H]^+$ = 644.2543.

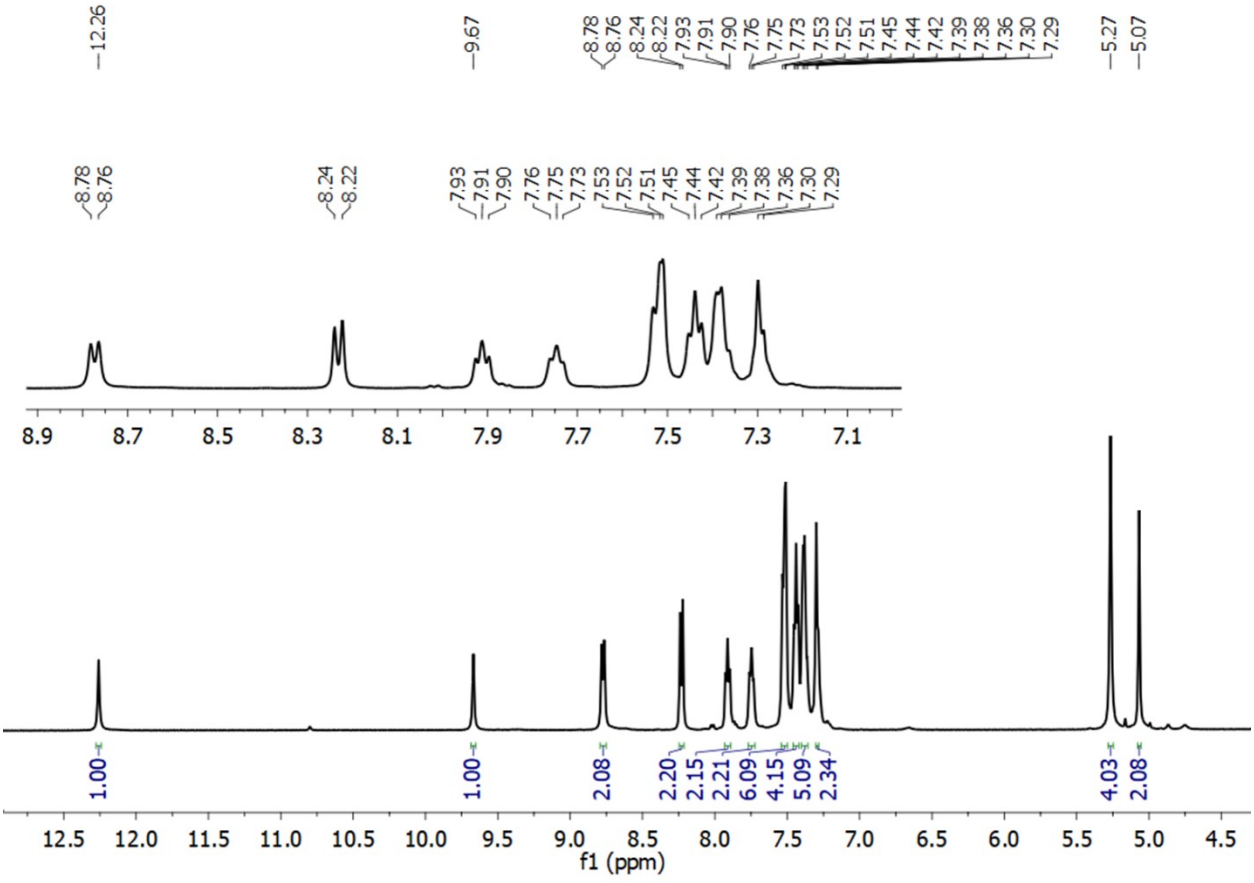


Figure S7: ^{1}H NMR spectra (400 MHz) of APD gelator (Compound 6)

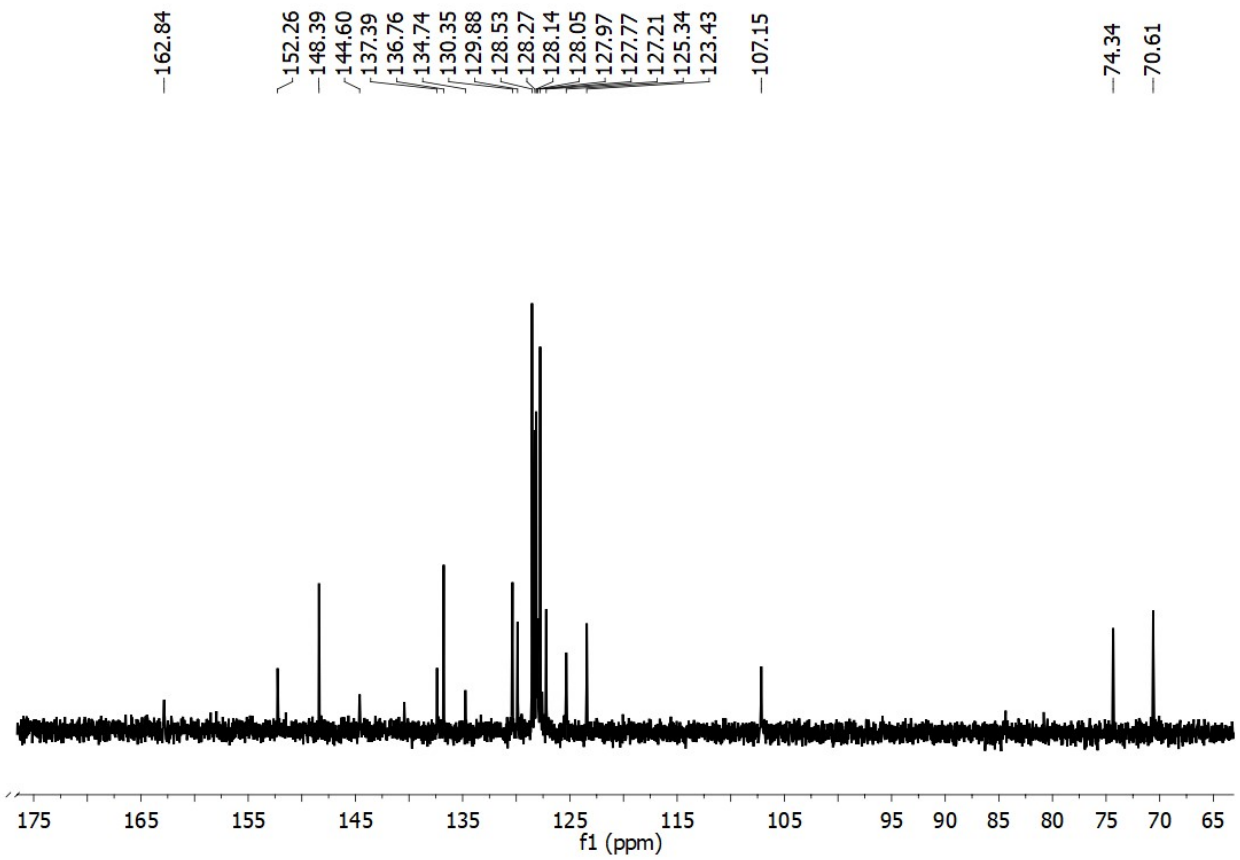


Figure S8: ^{13}C NMR spectra (400 MHz) of APD gelator (Compound 6)

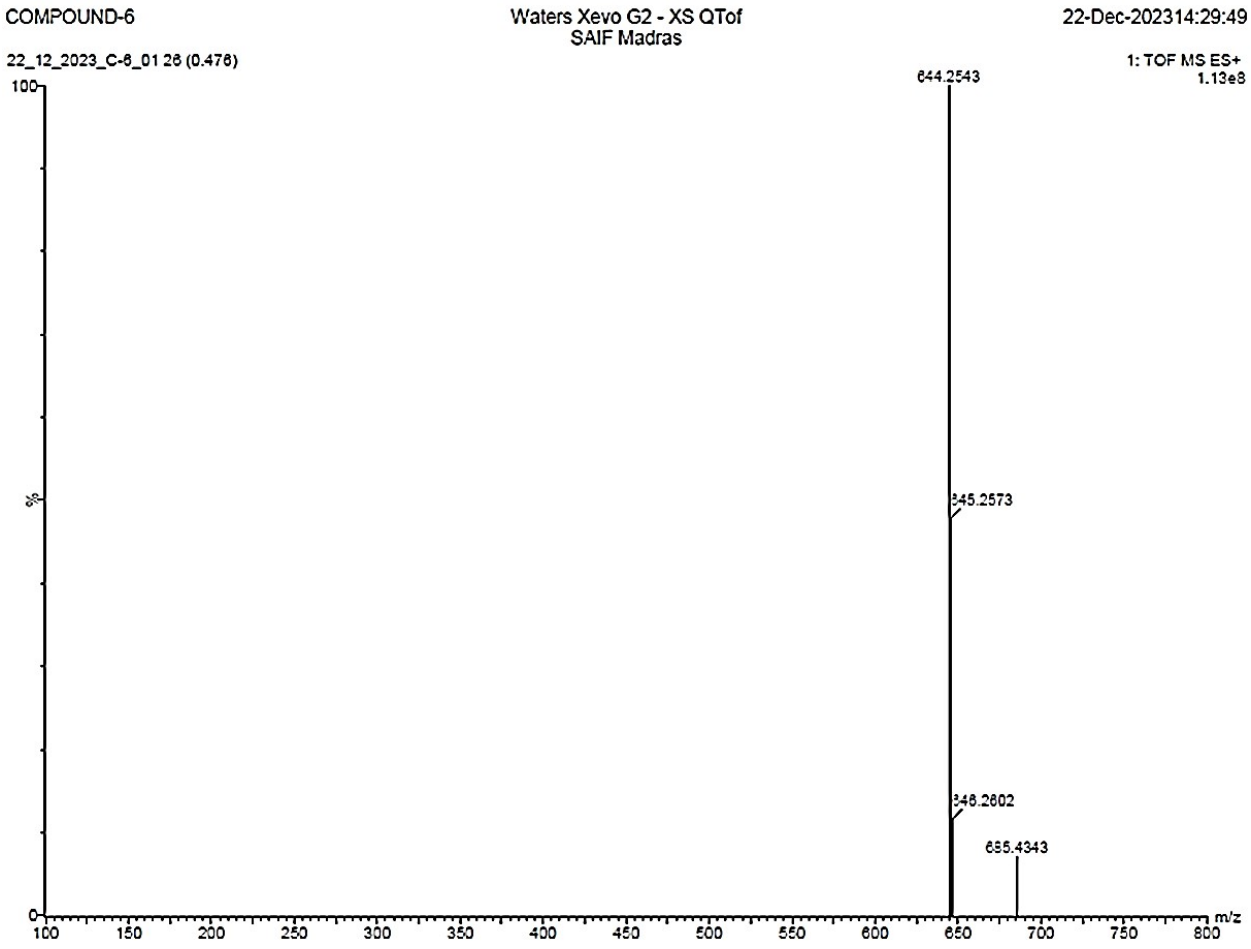


Figure S9: HR-MS spectrometry of APD gelator (compound 6)

2. Table S1: Gelation test of APD in different solvents

Solvent Used	Critical Gel concentration	remarks
DMSO+ WATER(1:1 v/v)	7mg/mL	Partial and unstable gel
DMSO+ CHLOROFORM (1:1v/v)	5mg/mL	sol
DMF+ WATER(1:1 v/v)	5mg/mL	Stable gel
DMF + CHLOROFORM (1:1v/v)	5mg/mL	Sol
THF	5mg/mL	Sol(Δ)
ACN	5mg/mL	Sol(Δ)

3. Optimized structure of APD by DFT

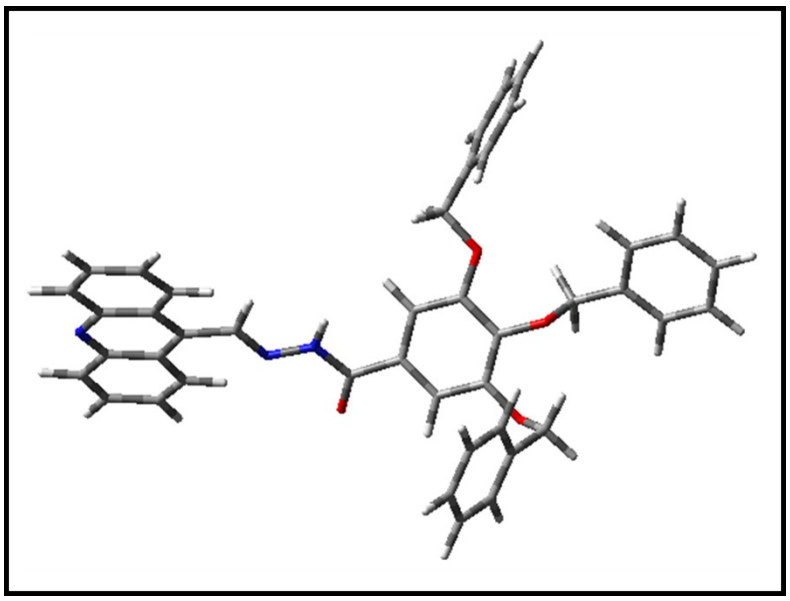


Figure S10: Optimized structure of APD by DFT.

4. Dynamic Light Scattering (DLS) experiment

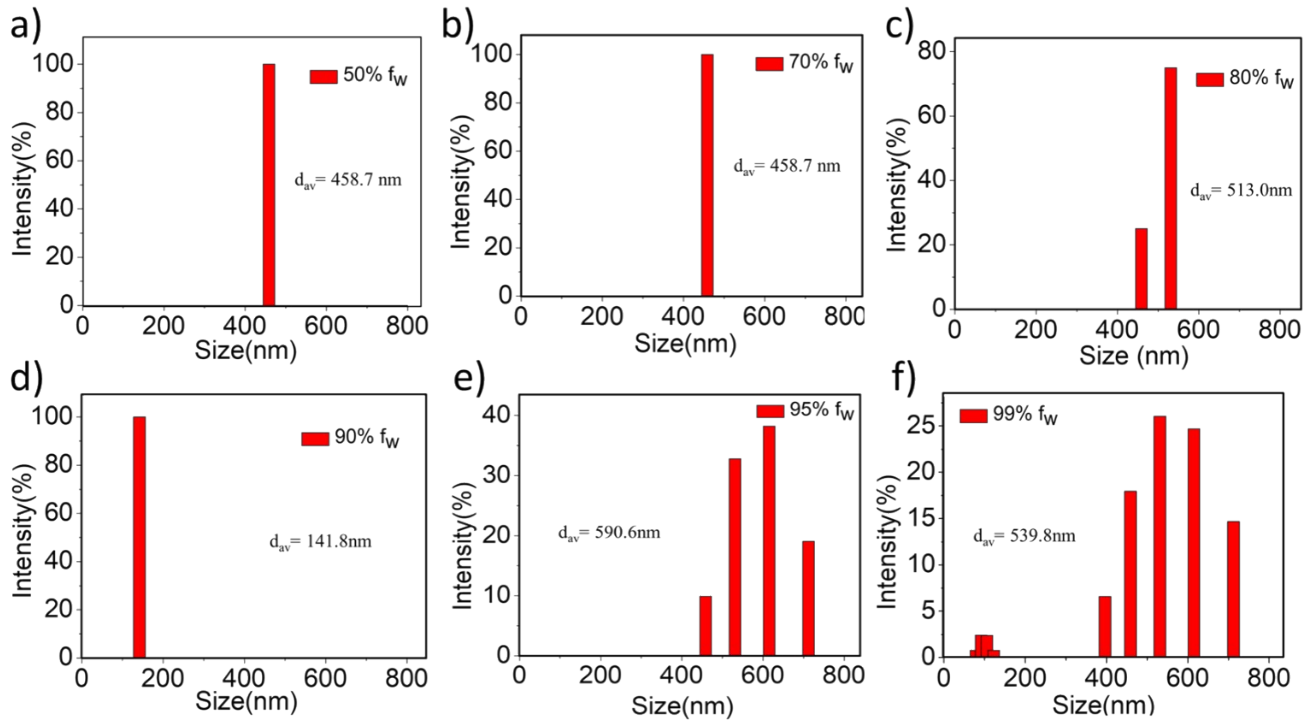


Figure S11. DLS traces of APD in DMF/ Water mixture at different water fraction (fw).

5. Visual detection of TFA vapour on APD solid film.

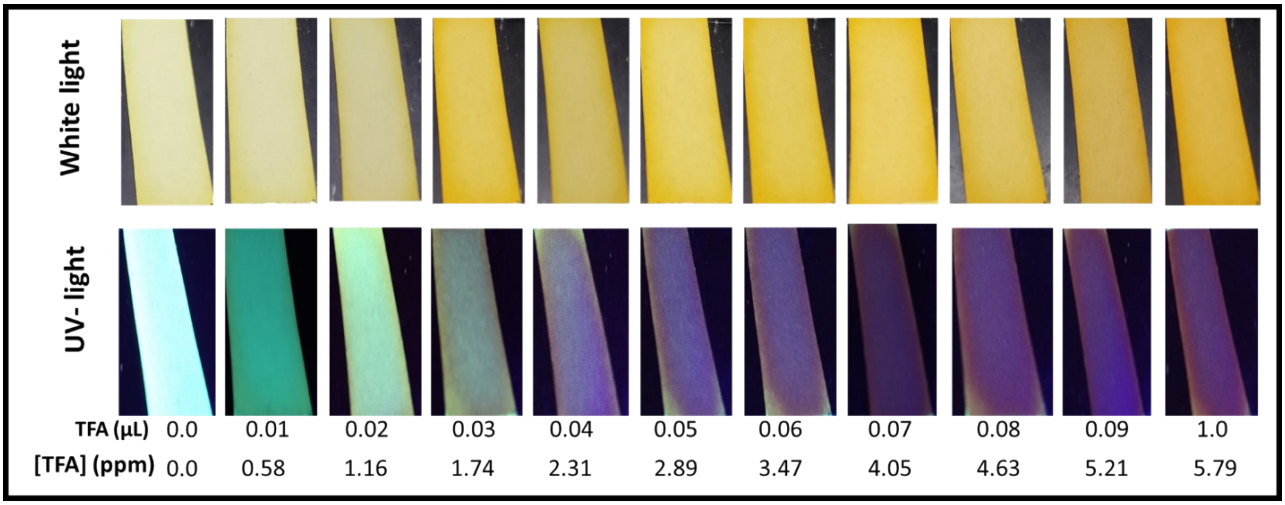


Figure S12. Naked eye detection of TFA vapours at different concentration on APD solid film exposed for 10s.

6. Photoluminescence study of APD film in presence of HCl vapour

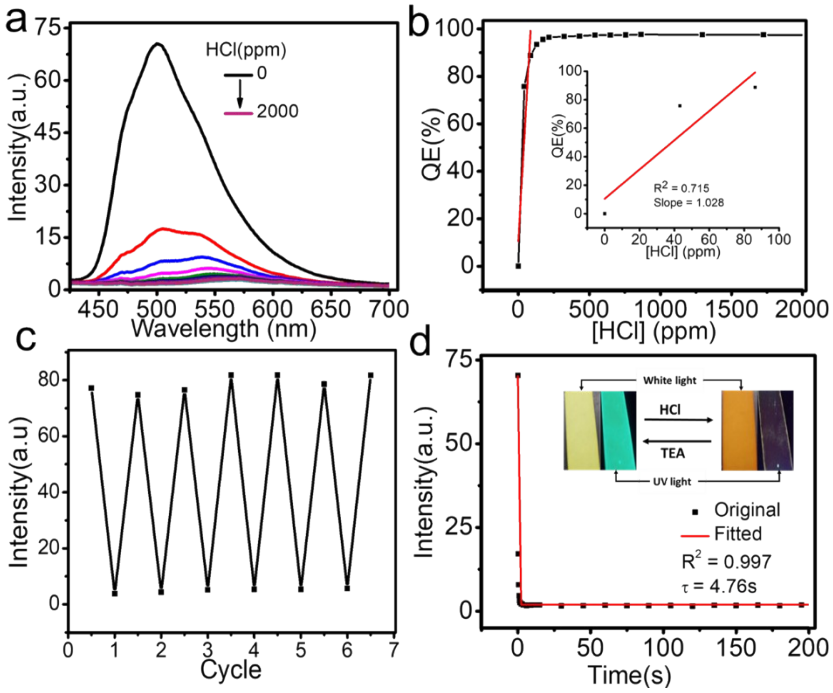


Figure S13: a) Changes in the emission intensity of the APD film after exposure to HCl vapour at different concentrations for 10sec. b) The concentration dependent fluorescence quenching efficiency ($1-I/I_0$) for APD film. Inset: The linear fitting at low concentration of HCl below 90ppm.c) Reversibility PL study of APD probe through fluorescent "on or off" by alternate exposer of saturated HCl (for10sec) and saturated TEA (for 70 min). (d) Time course of intensity quenching of the thin film upon exposure to saturated HCl vapors. . Inset: fluorescence color change of the thin film upon alternated expose to saturated HCl acid vapour and TEA.

7. Photoluminescence study of APD film in presence of HNO_3 vapour

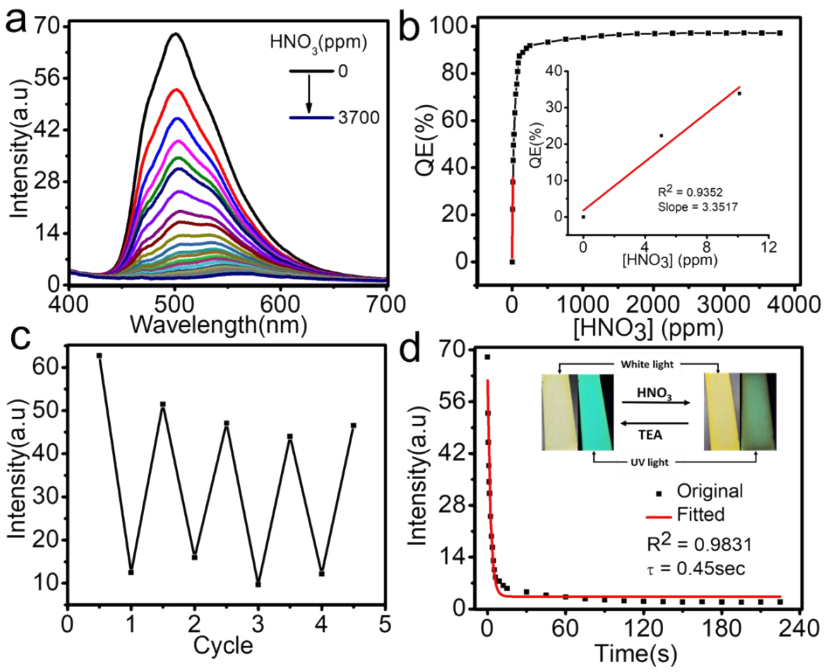


Figure S14: a) Changes in the emission intensity of the APD film after exposure to HNO_3 vapor at different concentrations for 10sec. b) The concentration dependent fluorescence quenching efficiency ($1-I/I_0$) for APD film. Inset: The linear fitting at low concentration of TFA below 10ppm. c) Reversibility PL study of APD probe through fluorescent "on or off" by alternate exposer of saturated HNO_3 (for10sec) and saturated TEA (for 10 min). (d) Time course of intensity quenching of the thin film upon exposure to saturated HNO_3 vapors. Inset: fluorescence color change of the thin film upon alternated expose to saturated HNO_3 acid vapour and TEA.

8. HOMO and LUMO calculation of APD and APDH using DFT

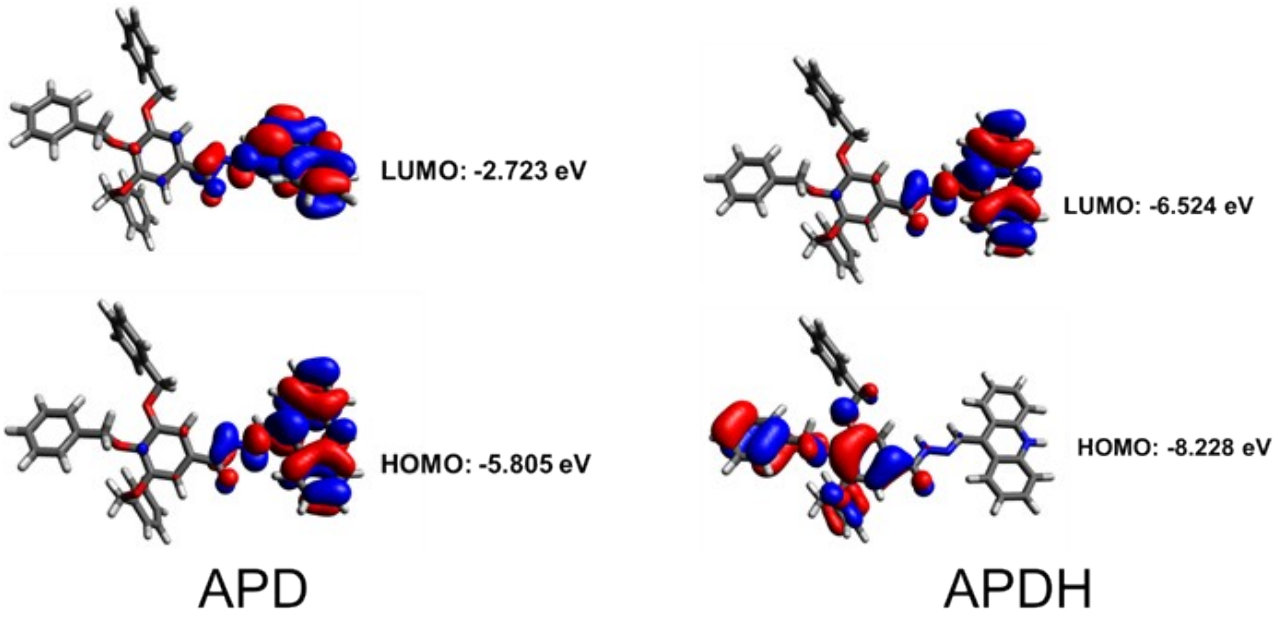


Figure S15: HOMO and LUMO calculation of APD and APDH using DFT.

9. Photoluminescence study of APD film in presence of AcOH vapour

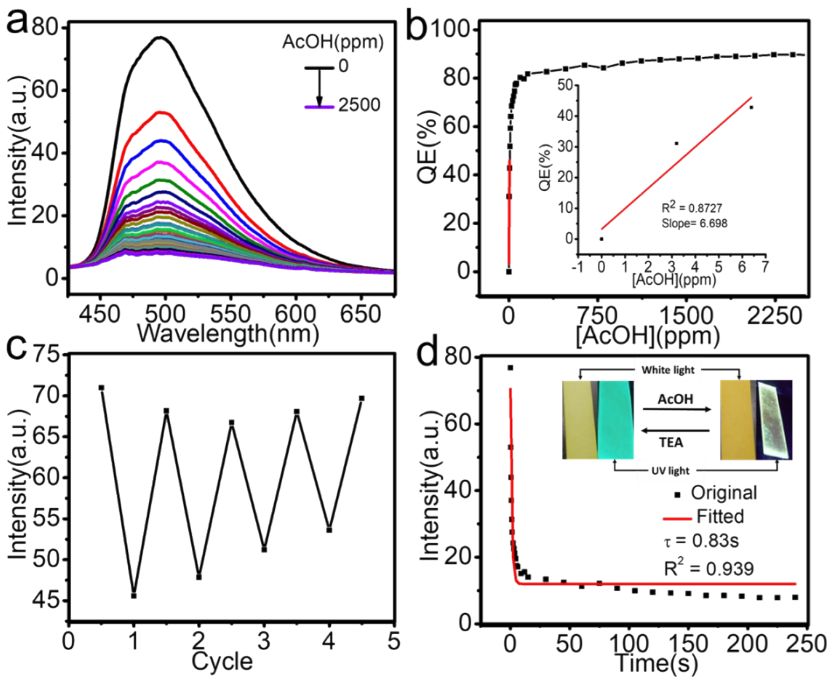


Figure S16: a) Changes in the emission intensity of the APD film after exposure to AcOH vapor at different concentrations for 10sec. b) The concentration dependent fluorescence quenching efficiency ($1-I/I_0$) for APD film. Inset: The linear fitting at low concentration of TFA below 7ppm. c) Reversibility PL study of APD probe through fluorescent "on or off" by alternate exposer of saturated AcOH (for60sec) and saturated TEA (for 10 min). (d) Time course of intensity quenching of the thin film upon exposure to saturated AcOH vapors. Inset: fluorescence color change of the thin film upon alternated expose to saturated acetic acid vapour and TEA

10. Behaviour of APD solid film in acid and alkali solution:

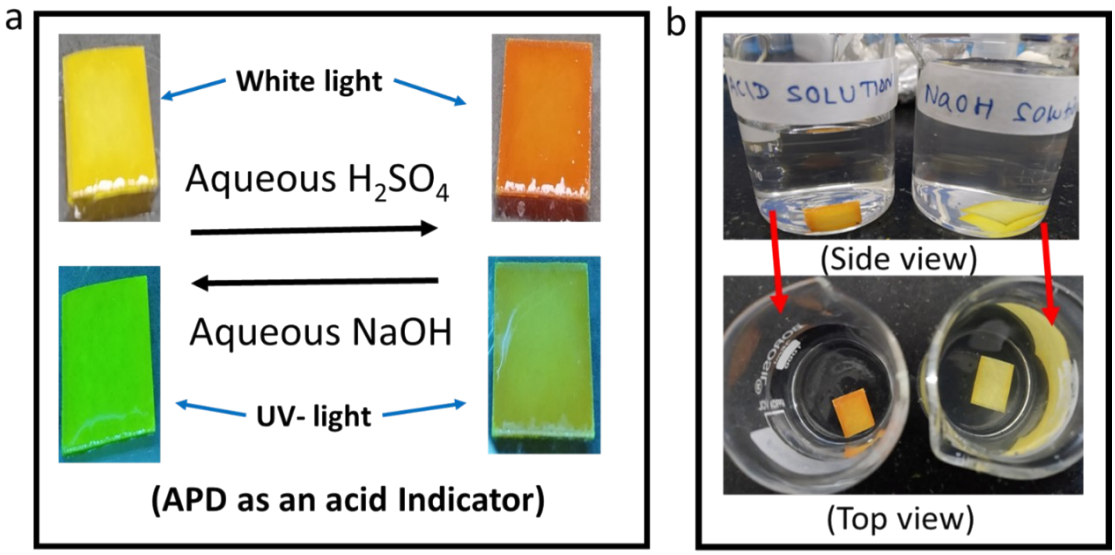


Figure S17: APD as an acid indicator a) Changes on the APD film on treating with aqueous solution of acid and alkali. b) Experimental setup demonstrating the colour change in different solution.

11. Response of APD gel in presence of different acids

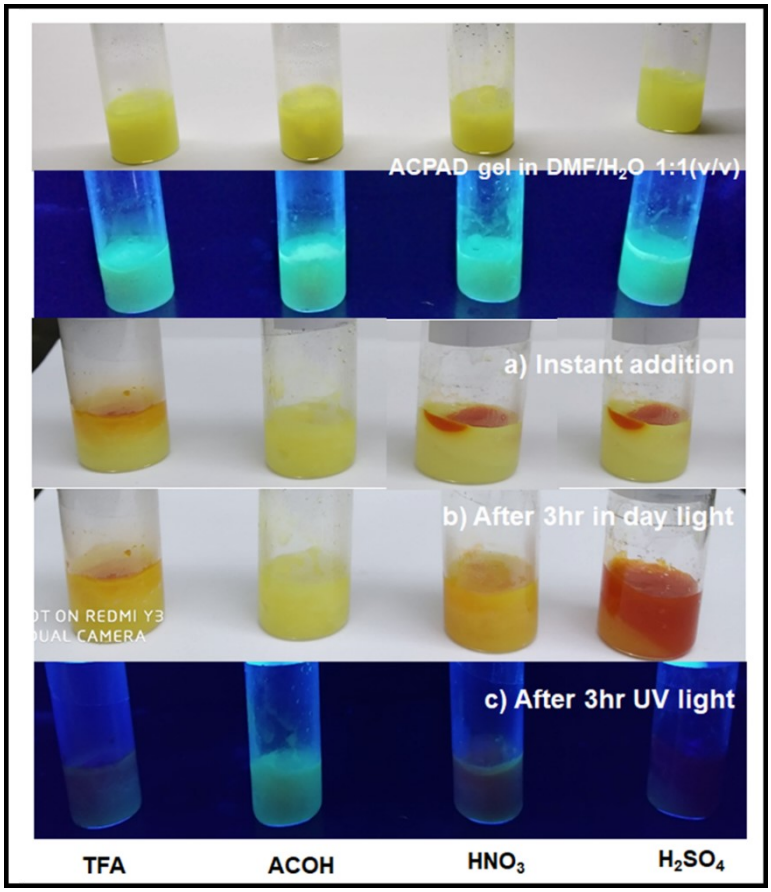


Figure S18: Addition of 1eq of different acid on APD gel in DMF/H_2O 1:1(v/v)