

Diphenylpyrimidinone-salicylideneamines – New ESIPT based AIEgens with applications in latent fingerprinting

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EXPERIMENTAL SECTION

Materials and Methods

Chemicals and solvents were of reagent grade and used without further purification unless otherwise stated. All reactions were performed under N₂ atmosphere. Ethanol and Toluene solvents were of HPLC grade. Chromatographic purification was done with silica gel 60-120 mesh. TLC was performed on aluminium sheets coated with silica gel 60 F254 (Merck, Darmstadt). Deionized water was obtained from ULTRA UV/UF Rions Lab Water System Ultra 370 series.

Instrumentations

- NMR spectra were recorded on Bruker and JEOL (operating at 500 and 300 for ¹H; (125, 100) and 75 MHz for ¹³C, respectively). The peak values were obtained as ppm (δ), and referenced to the TMS as reference in ¹H NMR and deuterated solvent in ¹³C NMR spectra. Abbreviations used for splitting patterns are s = singlet, bs = broad singlet, t = triplet, q = quartet, m = multiplet.
- The absorption spectra were recorded on Shimadzu-2450 spectrophotometer from Shimadzu equipped with Peltier system as temperature controller. Quartz cells of appropriate length were used for sample measurement. The spectral bandwidth and the scan rate were fixed at 2 nm and 140 nm min⁻¹, respectively. The fluorescence titrations were performed on Varian Carey Eclipse fluorescence spectrophotometer using slit width (excitation = 10 nm, emission = 2.5 nm) with excitation at 500 nm, unless otherwise stated.
- Fourier transform infrared (FT-IR) spectra were recorded on Perkin Elmer 92035.
- High resolution mass spectra were recorded on a BRUKER DALTONIK micrOTOF-Q11 spectrometer.
- WXRDS were recorded using a Rigakudiffractometer with CuKα (λ = 1.54 Å) emission and spectra were recorded in the (2θ) range of 5-50°C. The radiation used was with a Ni filter and a data collection was carried out using flat holder in Bragg Brentano geometry.
- Dynamic Light Scattering (DLS) and Zeta Potential Measurements. DLS measurements were performed at 25.0 ± 0.1°C using a light-scattering apparatus (Zetasizer Nano ZS Malvern Instrument Ltd., U.K.). The solutions were filtered with a Millipore membrane filter (Acrodisc syringe filter, 0.45 μm Supor membrane) before measurements. The samples were thermally equilibrated for 10 min before each measurement, and an average of 10 measurement runs were considered to be data. The temperature was controlled to an accuracy of ±0.1 °C using an inbuilt Peltier device. Data was analyzed using the standard algorithms.

- Confocal microscopy imaging was performed on NIKON AIR machine using laser with excitation at 488 nm. Imaging was done with 60X objective lens with oil-emersion.
- Theoretical calculations were carried out using density functional theory (DFT) at B3LYP/6-31G* basis set using Gaussian package.
- SEM measurements were performed on a ZEISS SUPRATM55 operating at an acceleration voltage of 10 KV with tungsten filament as electron source.
- The TEM images were obtained with a JEOL JEM-2100 electron microscope operating at an acceleration voltage of 200 kV.

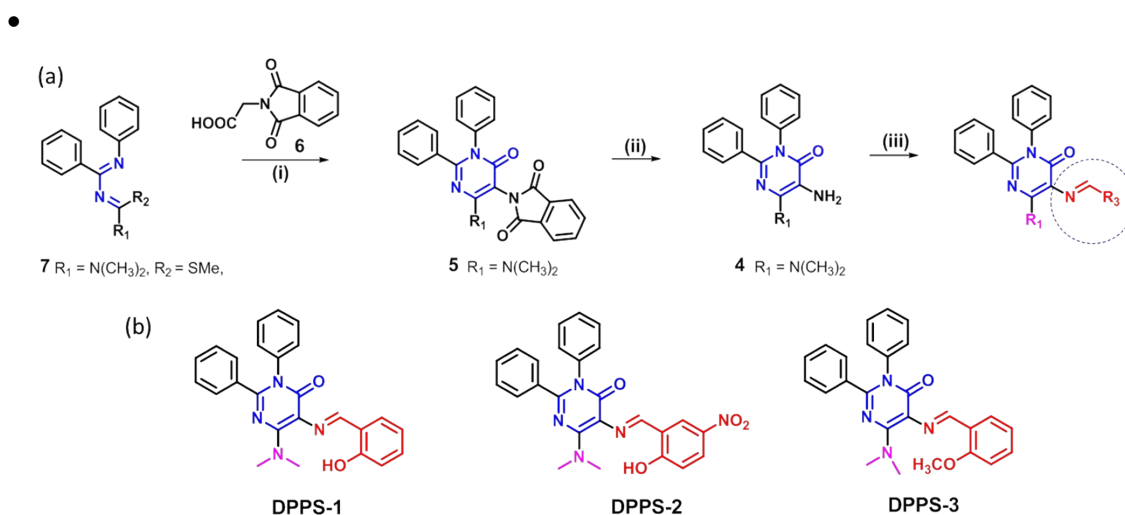


Figure 1: Structures of pyrimidone-schiff base derivatives.

Derivative **7** has been synthesized by following the literature procedure involving multi step synthesis.

Synthesis of **5**

To a solution of 1,3-diazabutadiene **7** (5 g, 1eq.), phtholylglycine **6** (2 eq.) and triethylamine (4 eq.) in dry dichloromethane (100 mL) at 0°C was added drop wise a solution of *p*-TsCl (2.5 eq.) in dry dichloromethane. The progress of the reaction was monitored with the help of tlc. After completion of reaction, a usual workup was performed using chloroform and brine solution. The organic layers were collected, dried over sodium sulphate and evaporated to get crude product. The crude product was recrystallized using 10% chloroform in diethyl ether to get pure 5-isoindole-1, 3-dione pyrimidinones **5**; Yield 94 %; m.pt 135-136°C; IR (KBr) ν 1658 cm^{-1} ; ¹H NMR (300 MHz) δ 3.17 (m, 6H, -CH₃), 7.29 (m, 10H, H aromatic); 7.78 (m, 2H, H-aromatic), 7.95 (m, 2H, H-aromatic), ¹³C NMR (75.5 MHz, CDCl₃): δ

45.99, 123.74, 125.97, 127.80, 128.17, 128.61, 128.63, 129.05, 129.25, 129.71, 132.44, 134.15, 134.99, 137.20, 156.50, 158.60, 160.72, 168.96; m/z 437 (M+1)⁺ HRMS calcd for C₂₆H₂₁N₄O₃ (M+1)⁺: 437.1614, found 437.171

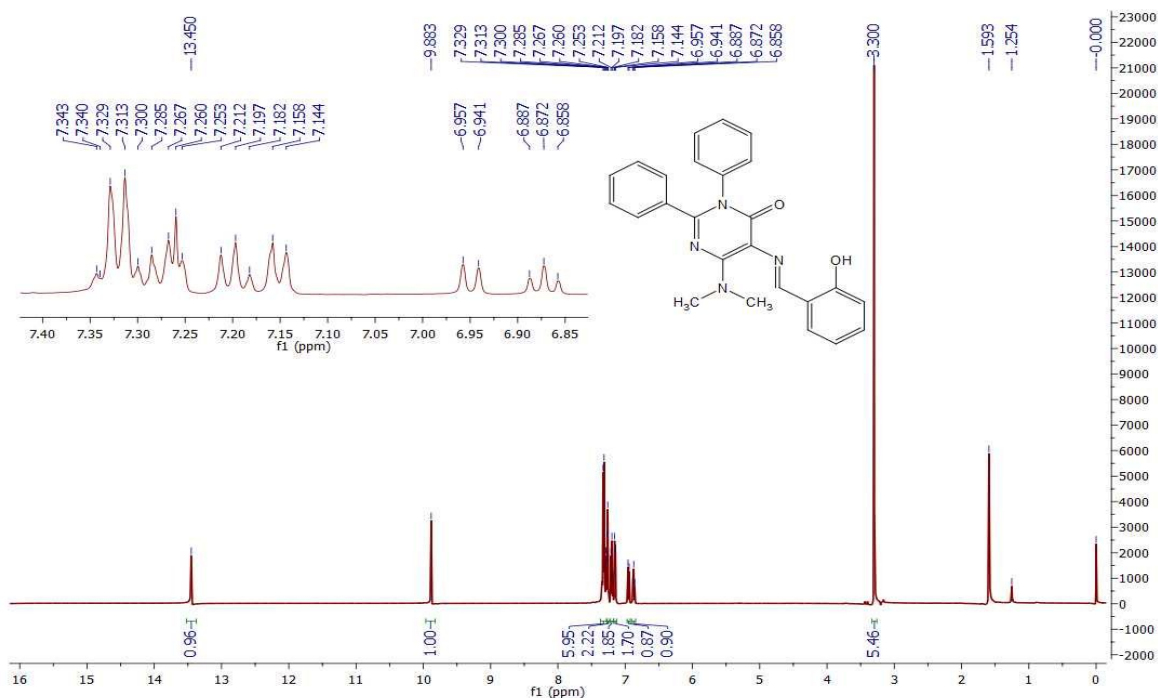


Figure S1a. ¹H NMR spectrum of DPPS-1.

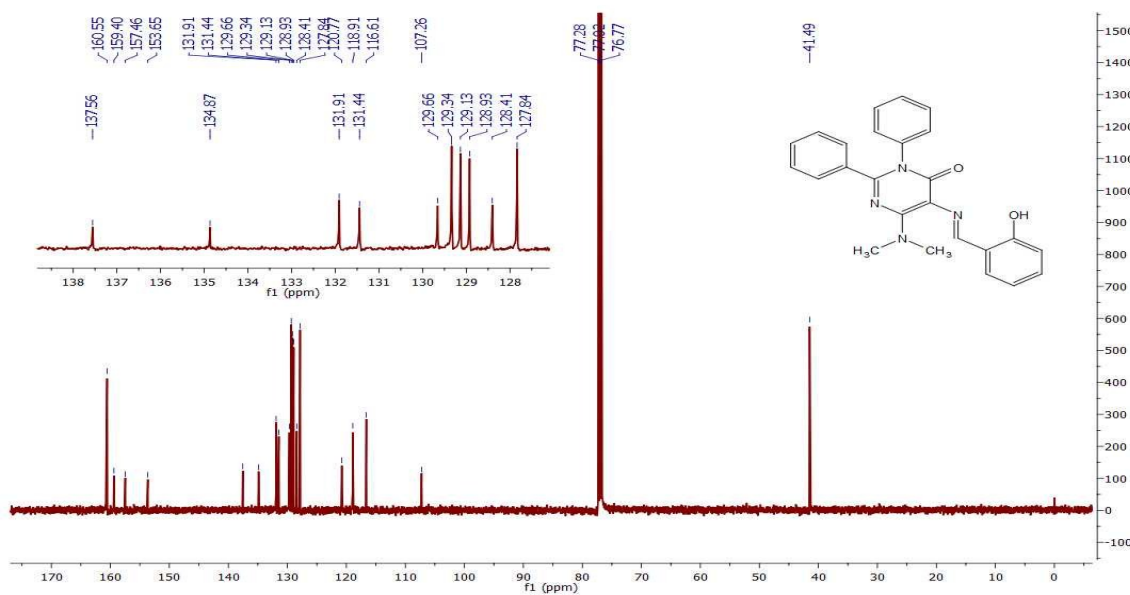


Figure S1b. ^{13}C NMR spectrum of **DPPS-1**.

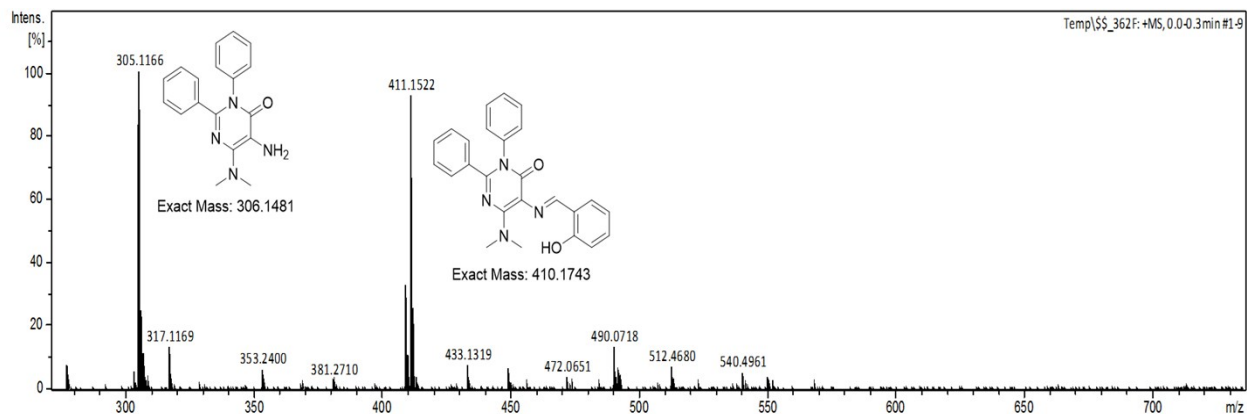


Figure S1c. Mass spectrum of **DPPS-1**.

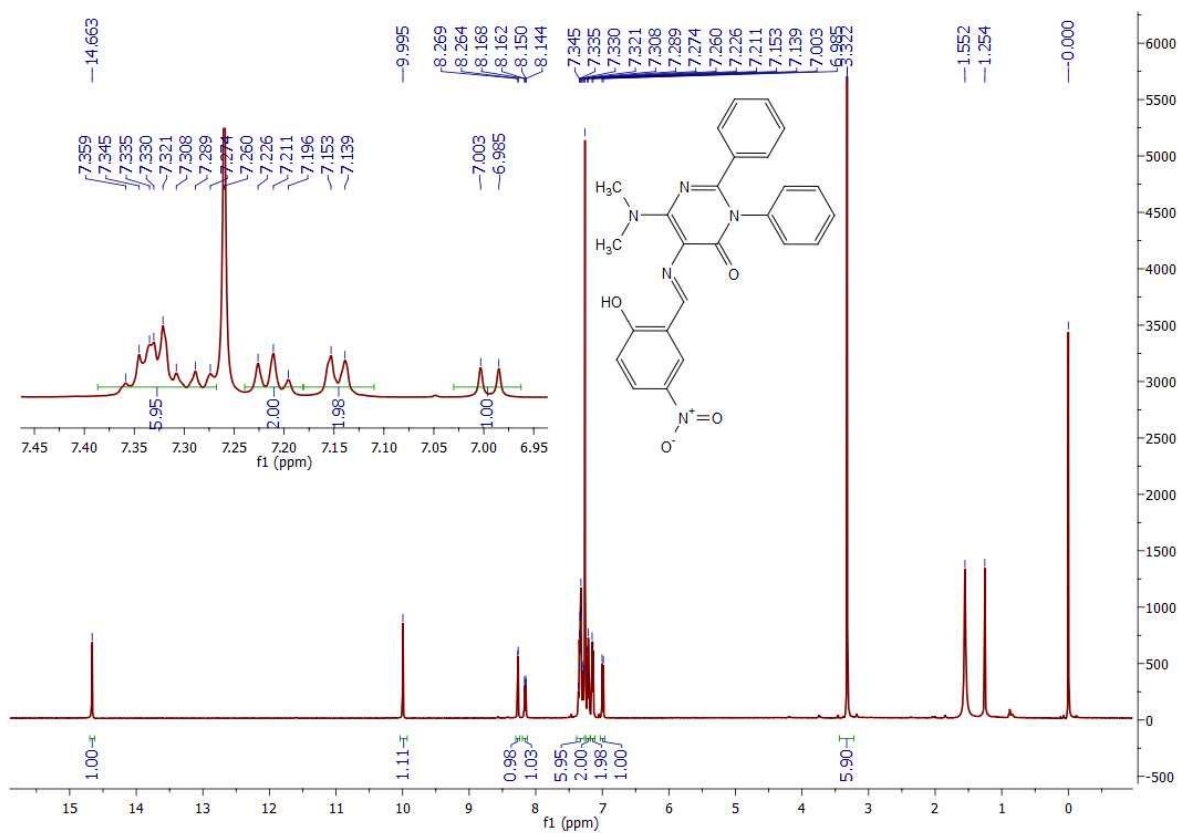


Figure S2a. ^1H NMR spectrum of **DPPS-2**.

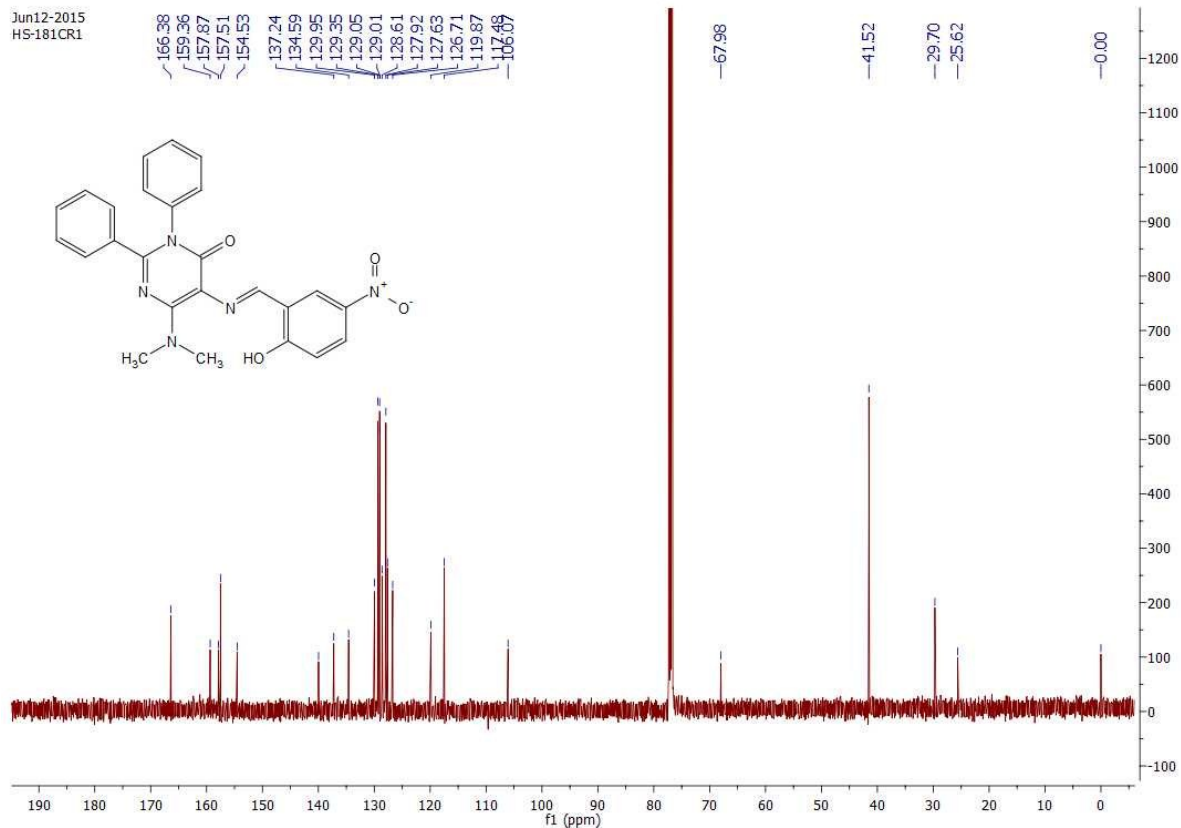


Figure S2b. ^{13}C NMR spectrum of DPPS-2.

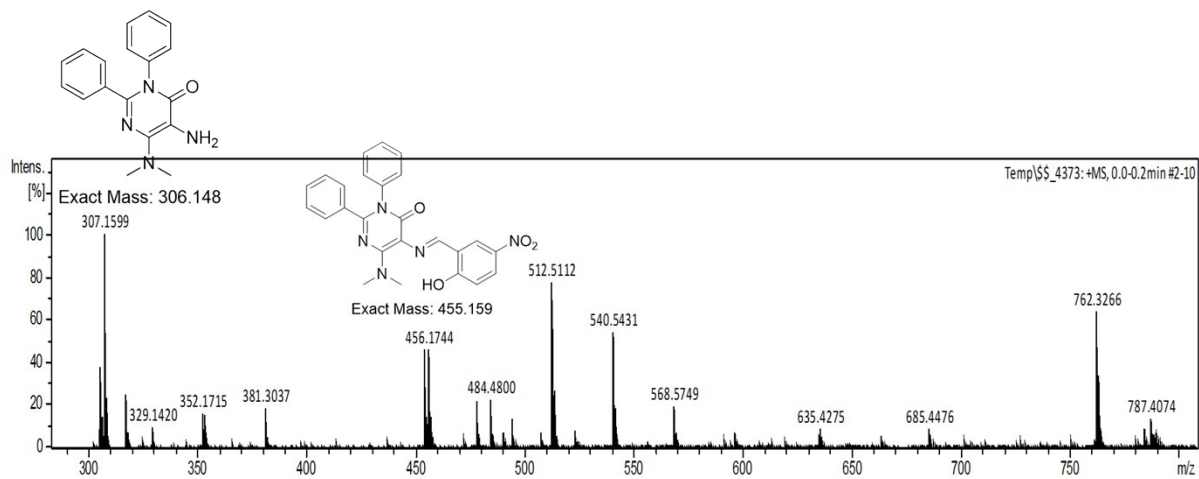


Figure S2c. Mass spectrum of DPPS-2.

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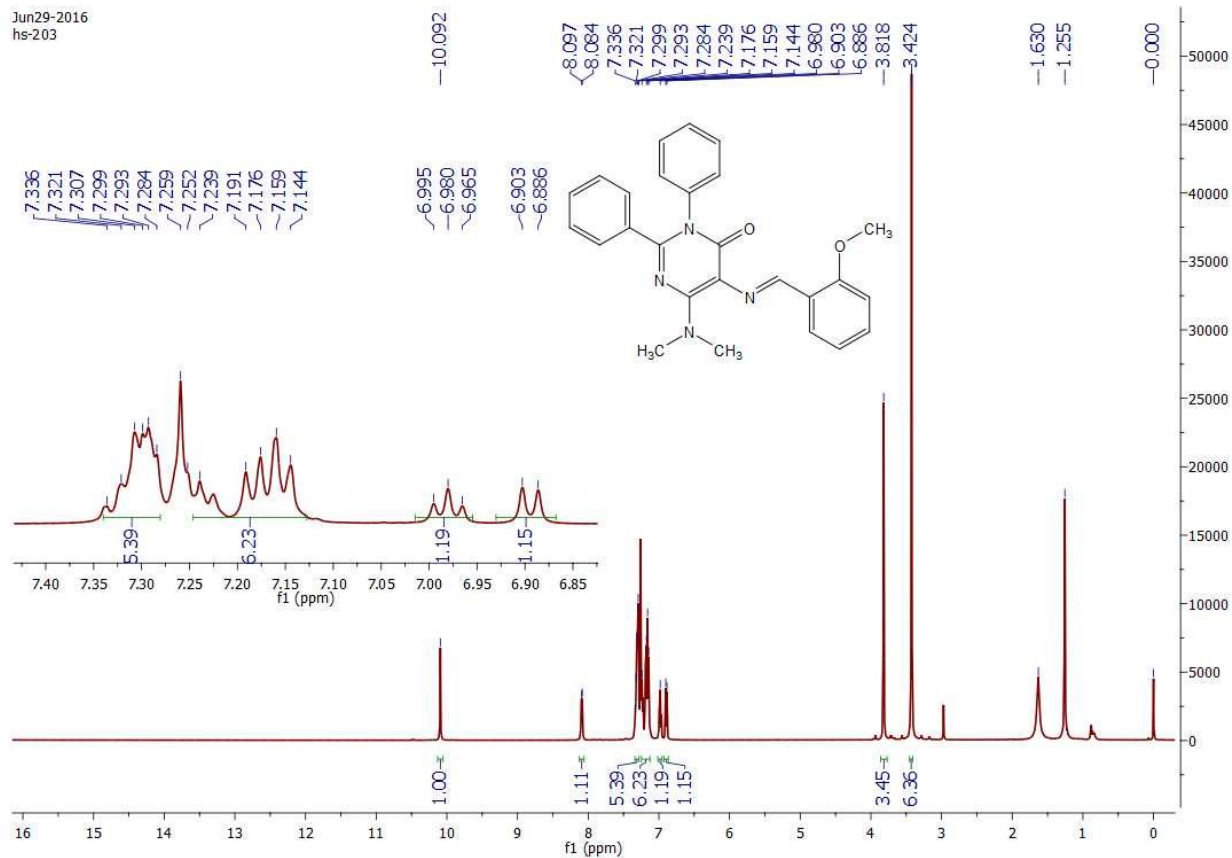


Figure S3a. ¹H NMR spectrum of DPPS-3.

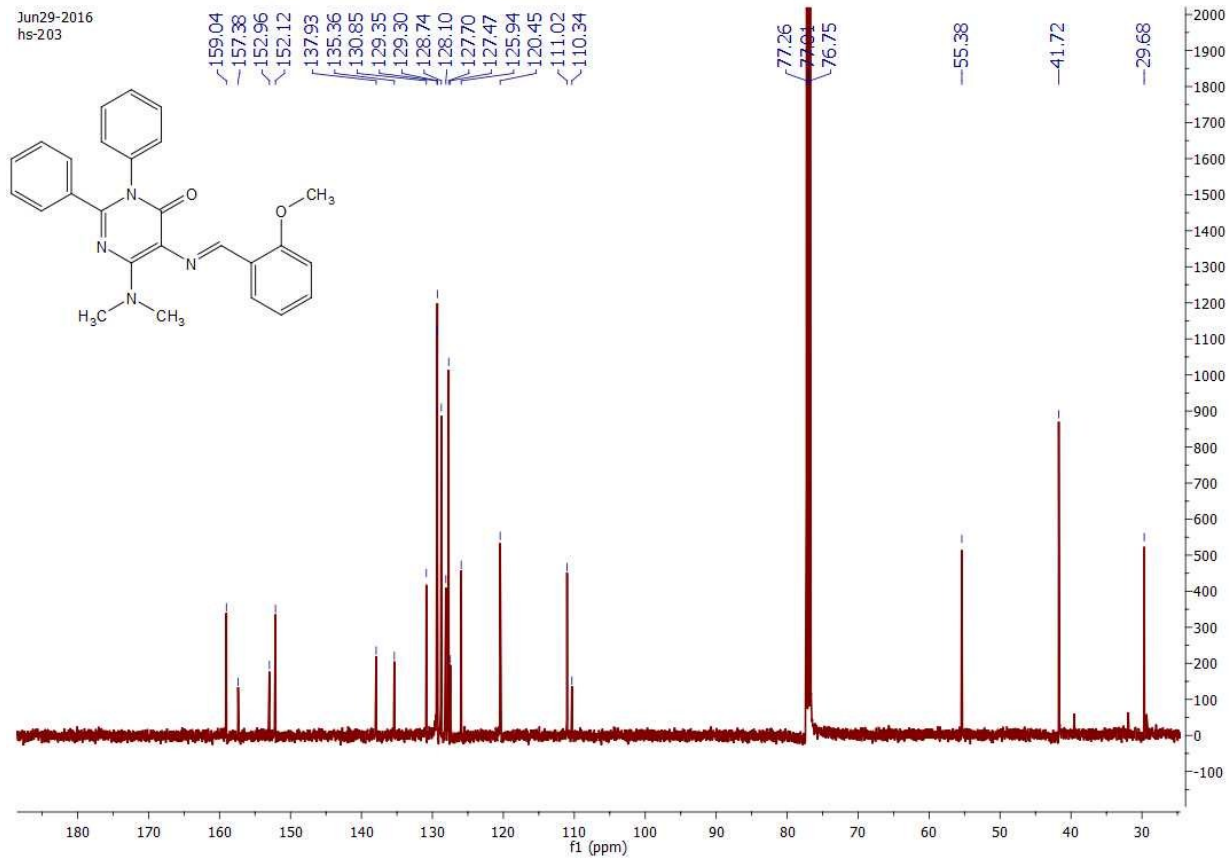


Figure S3b. ^{13}C NMR spectrum of DPPS-3.

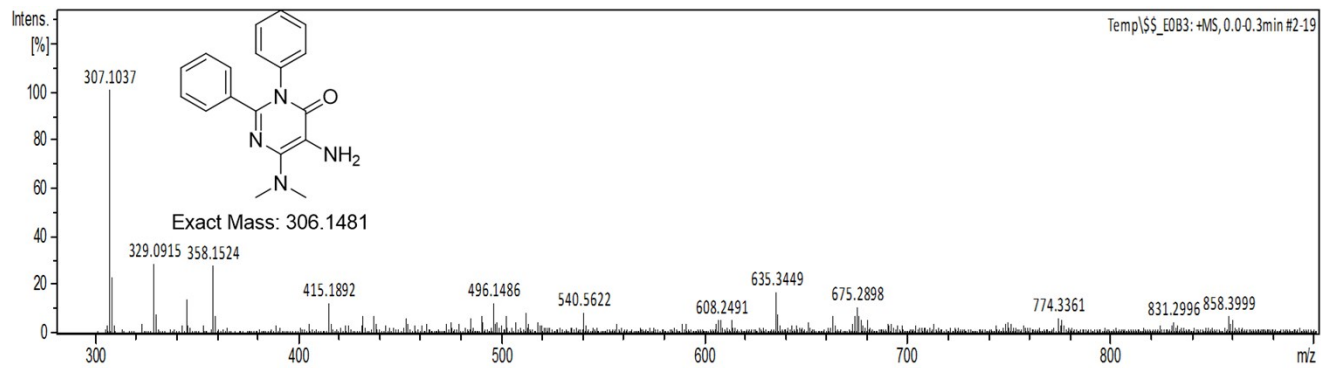


Figure S3c. Mass spectrum of DPPS-3.

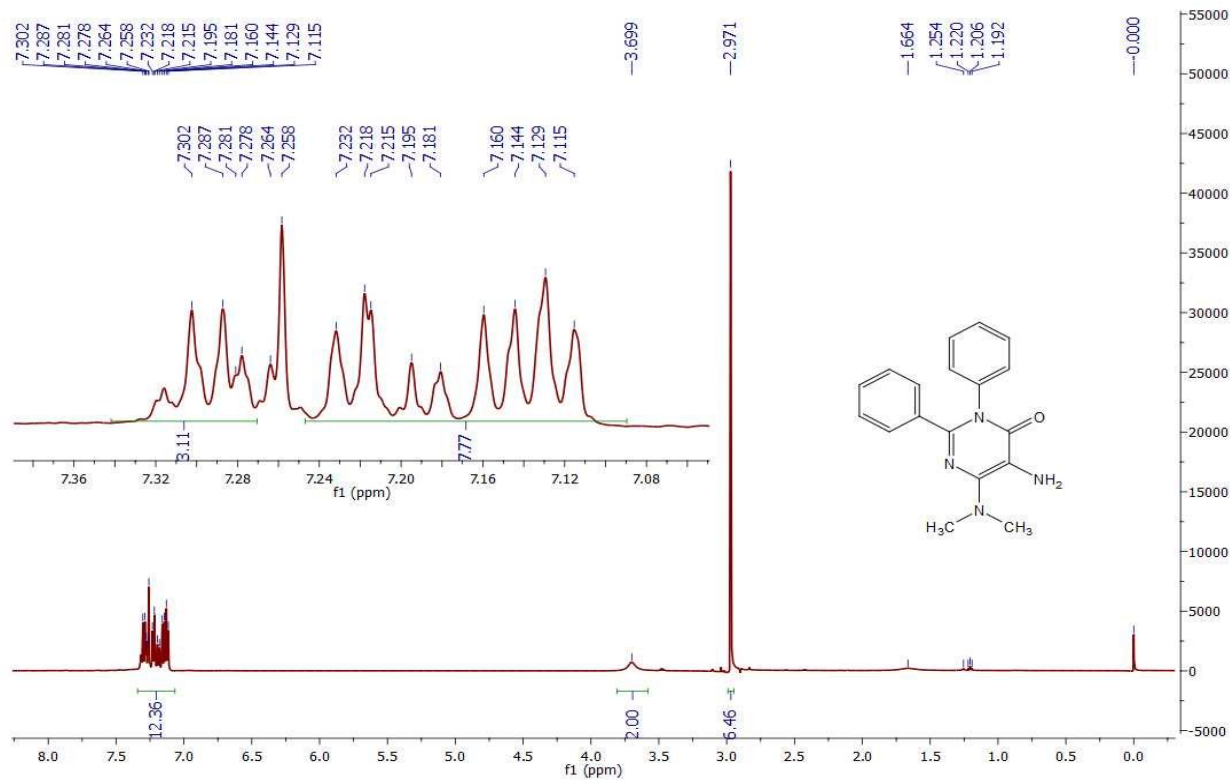


Figure S4a. ¹H NMR spectrum of 4.

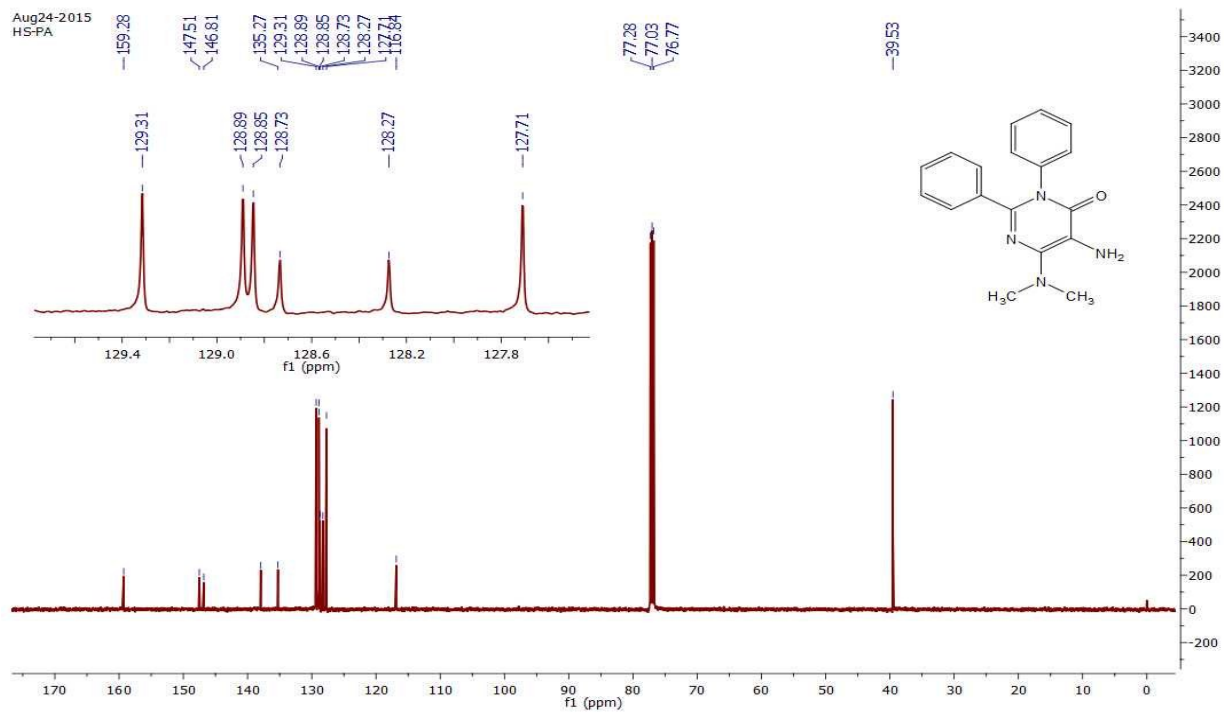


Figure S4b. ¹³C NMR spectrum of 4.

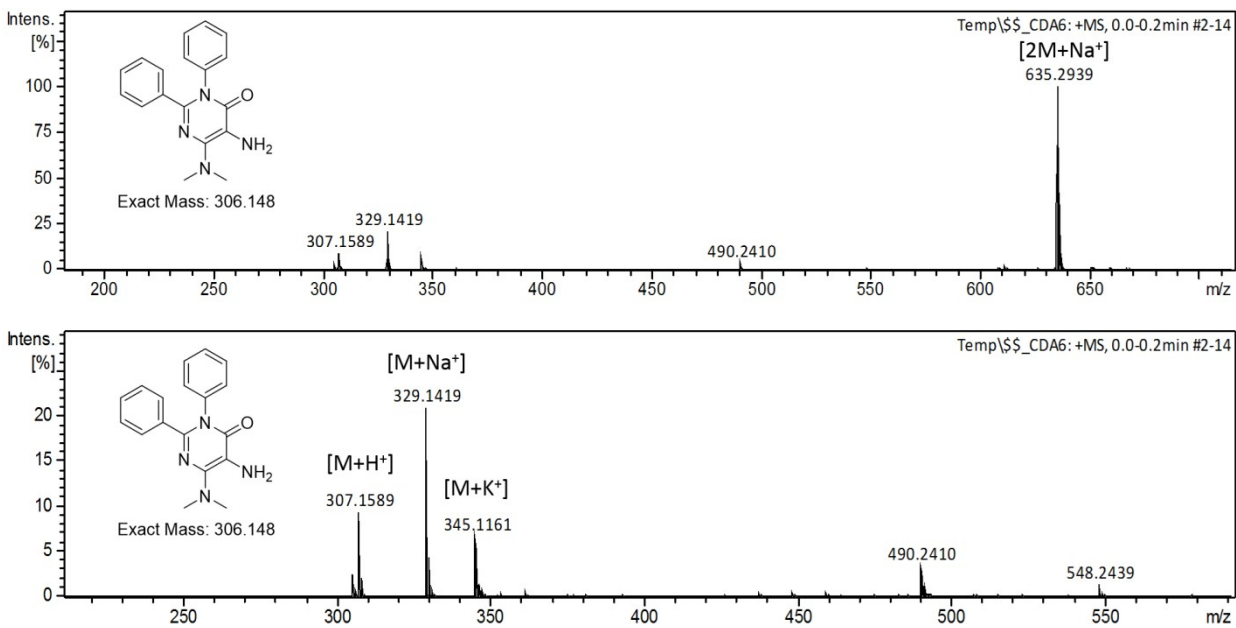


Figure S4c. Mass spectrum of 4.

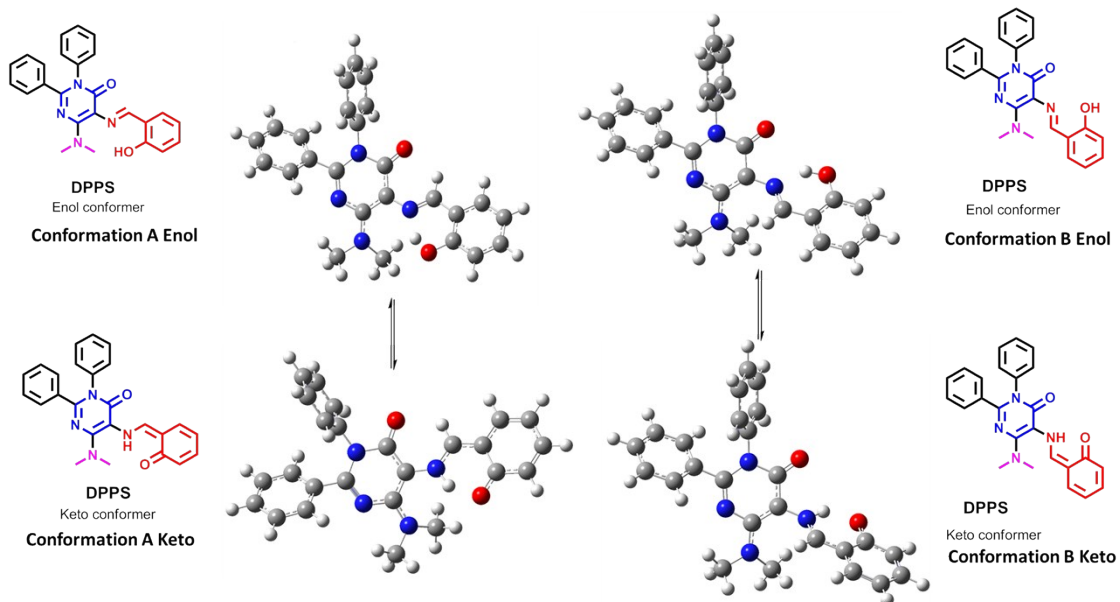


Figure S5 The energy minimized structures (DFT 6-31G*) of diphenylpyrimidone-schiff base derivative DPPS.

1. Solvent Dependent Absorption and Emission spectrum of DPPS

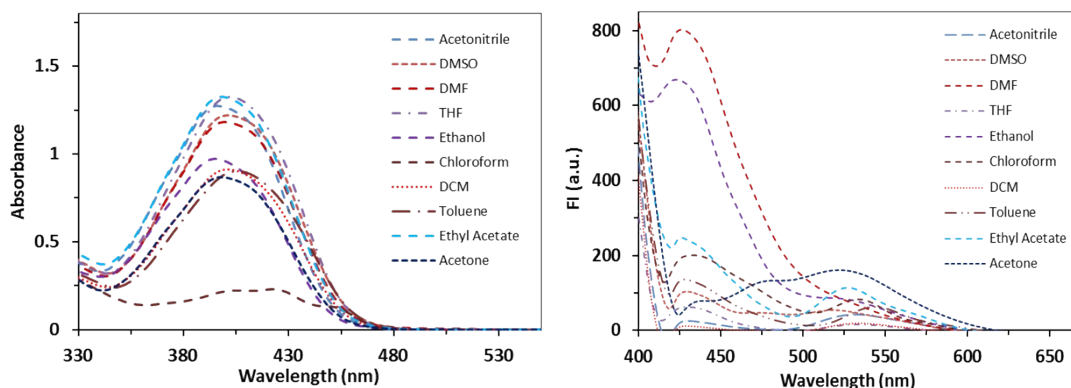


Figure S6. (a) Solvent dependent absorption spectrum of **DPPS-1** (50 μM) and (b) fluorescence spectrum of **DPPS** (1 μM) recorded in different polarity solvents; λ_{ex} 390 nm; slit width (Ex/Em = 10/10 nm).

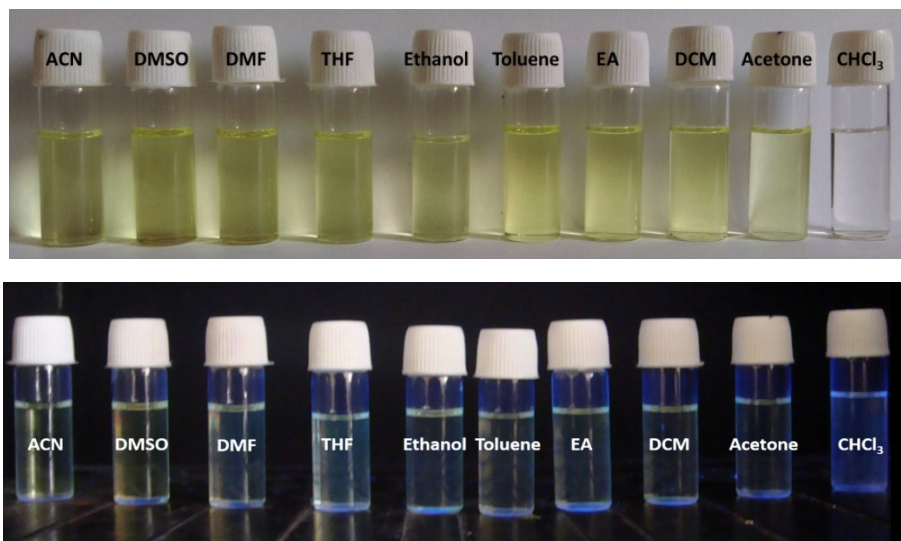


Figure S7. Color images of **DPPS-1** (50 μM) (above) and fluorescent images of **DPPS-1** (1 μM, under 365 nm UV lamp) (below) in various polarity solvents.

Table S1. Photophysical Characteristics of **DPPS-1** in different solvents.

	Absorption λ_{\max} (nm)	Emission λ_{\max} (nm)	Stokes Shift (cm^{-1})
Acetonitrile	400	526	5988.593
DMSO	405	430	1435.544
DMF	400	430	1744.186
THF	400	430	1744.186
Ethanol	395	430	2060.642
Toluene	400	545	6651.376
EA	398	430	1869.814
Acetone	398	526	6114.221

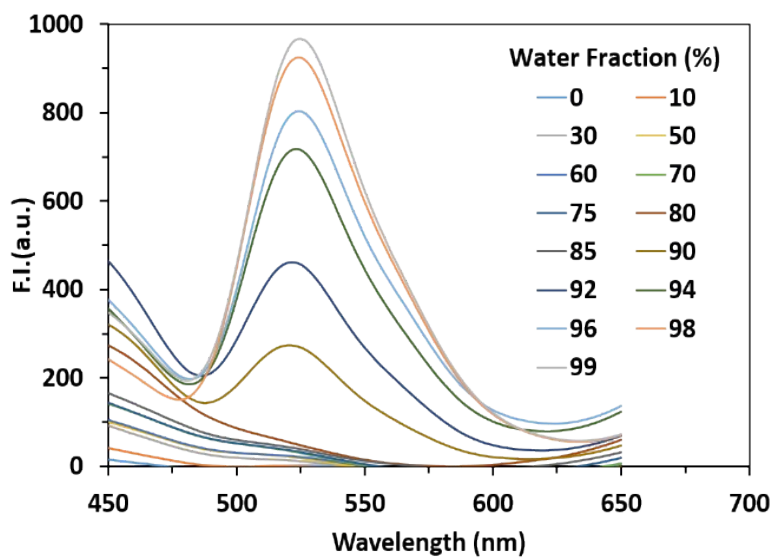


Figure S8: Emission changes of **DPPS-1** after incremental addition of 10 vol% of H_2O in CH_3CN at a concentration of $1 \mu\text{M}$ ($\lambda_{\text{ex}} = 345 \text{ nm}$, slit width Ex/Em = 10/20 nm).

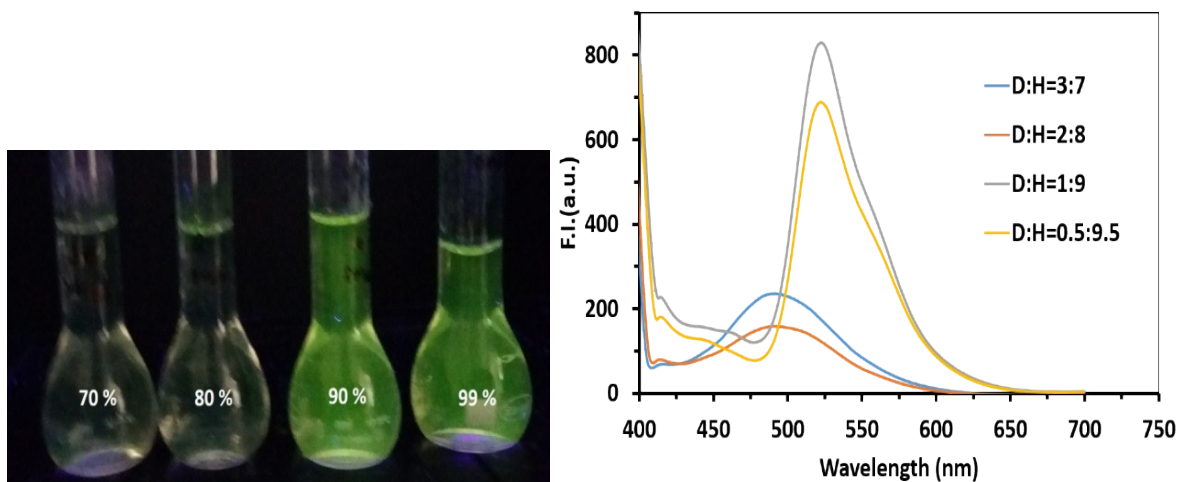


Figure S9: (Left) fluorescent images of **DPPS** ($10\ \mu\text{M}$) on addition of 70-99% H_2O in DMSO under 365 nm UV light; (Right) Emission changes of **DPPS** after incremental addition of 10 vol% of H_2O in DMSO at a concentration of $10\ \mu\text{M}$ ($\lambda_{\text{ex}} = 390\ \text{nm}$, slit width Ex/Em = 10/10 nm).

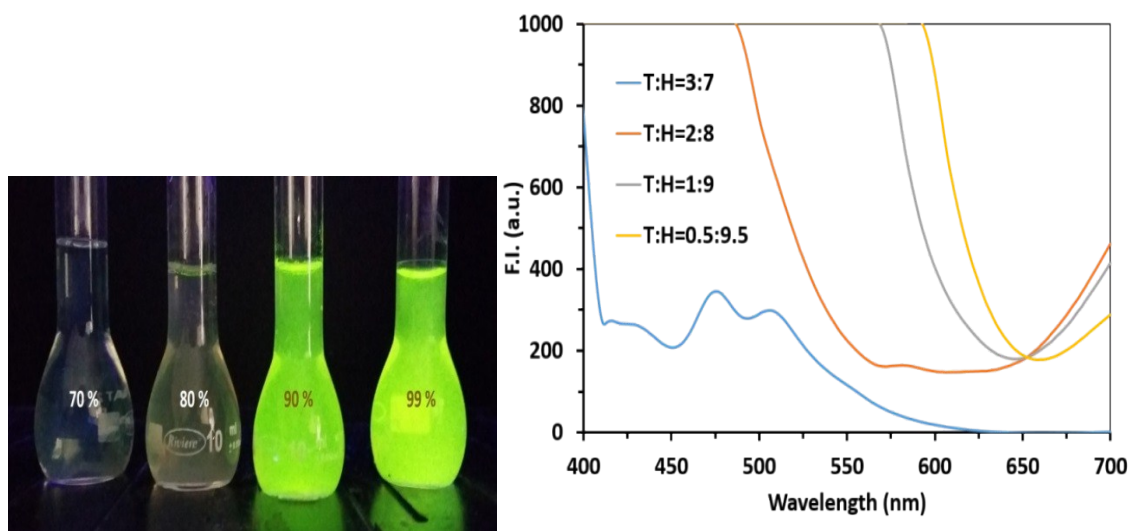


Figure S10: (Left) fluorescent images of **DPPS** ($10\ \mu\text{M}$) on addition of 70-99% H_2O in THF under 365 nm UV light; (Right) Emission changes of **DPPS** after incremental addition of 10 vol% of H_2O in THF at a concentration of $10\ \mu\text{M}$ ($\lambda_{\text{ex}} = 390\ \text{nm}$, slit width Ex/Em = 10/10 nm).

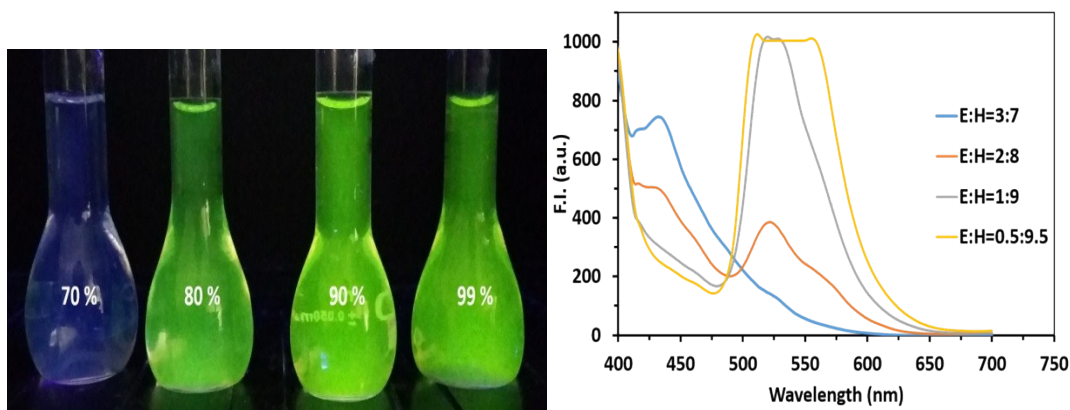


Figure S11: (Left) fluorescent images of **DPPS-1** (10 μ M) on addition of 70-99% H₂O in ethanol under 365 nm UV light; (Right) Emission changes of **DPPS-1** after incremental addition of 10 vol% of H₂O in ethanol at a concentration of 10 μ M ($\lambda_{\text{ex}} = 390$ nm, slit width Ex/Em =10/10 nm).

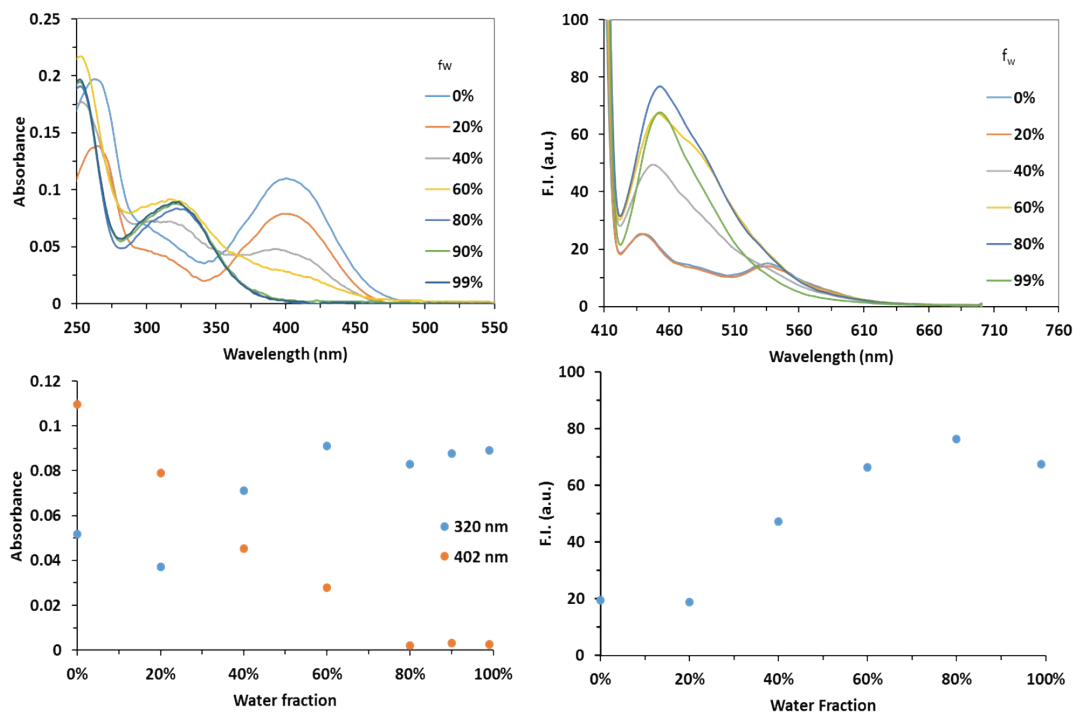


Figure S12: (Upper panel, Left) Absorbance changes of **DPPS-3** after incremental addition of H₂O in Acetonitrile at a concentration of 10 μ M; (Upper panel, Right) Emission changes of **DPPS-3** after incremental addition of H₂O in Acetonitrile at a concentration of 1 μ M; (Lower panel, Left) Behavior of **DPPS-3** in absorbance at 320 and 402 nm on incremental addition of H₂O in Acetonitrile at a concentration of 10 μ M; (Lower panel, right) Behavior of **DPPS-3** in emission at 470 nm on incremental addition of H₂O in Acetonitrile at a concentration of 1 μ M.

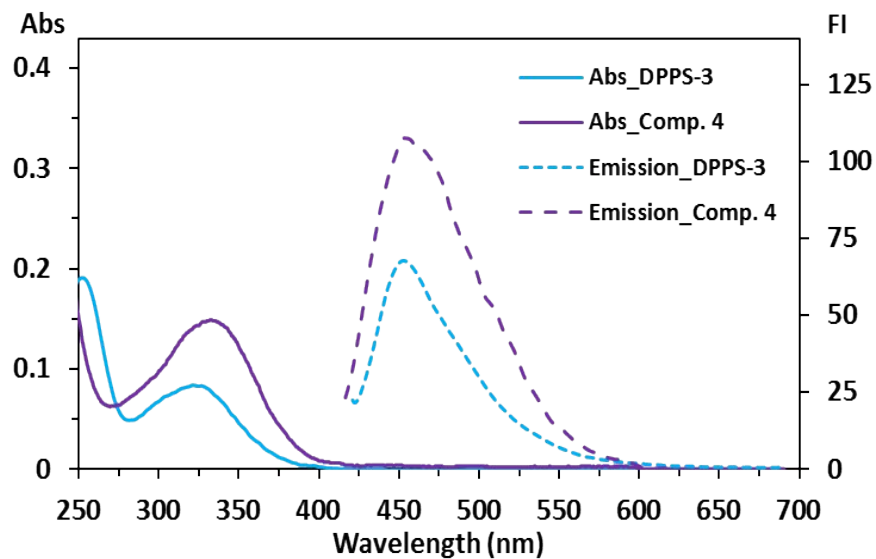


Fig. S13 Comparison of UV-Vis (10 μ M) and Emission behavior (1 μ M) of **DPPS-3** and compound **4** in 99% $\text{H}_2\text{O}:\text{CH}_3\text{CN}$ mixture.

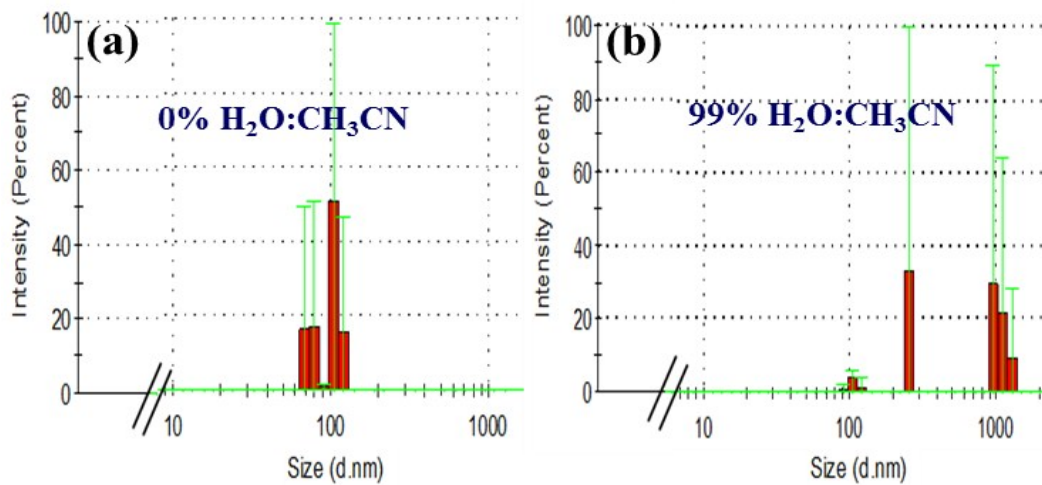


Figure S14 DLS bar graph of **DPPS-2** in (a) 0%; (b) 99% $\text{H}_2\text{O}:\text{CH}_3\text{CN}$ mixture.

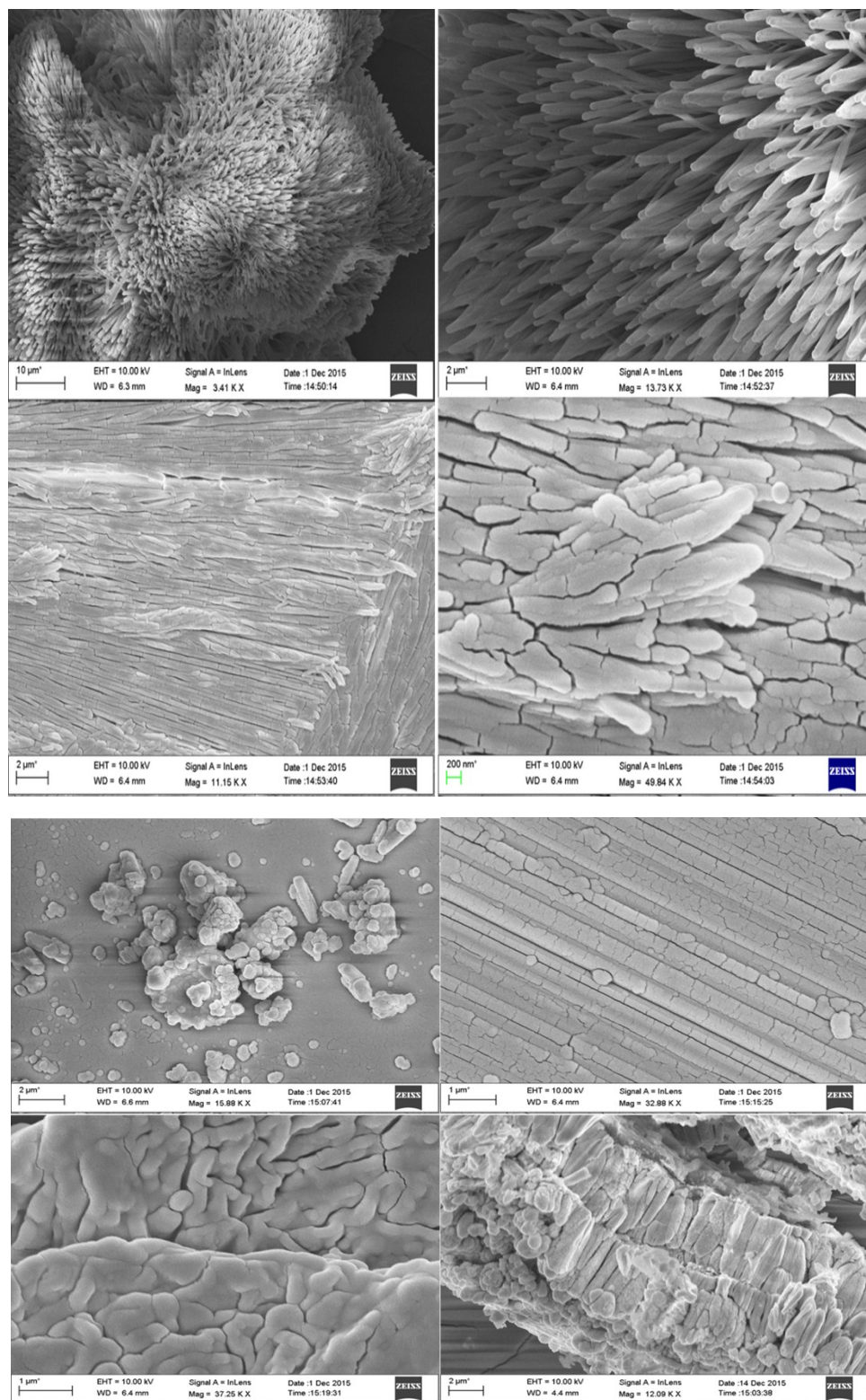


Figure S15. SEM micrographs of DPPS-1 at 1 μM concentration showing the self-assembled 3D nano rods morphology and at 10 μM concentration showing nano spherical morphology.

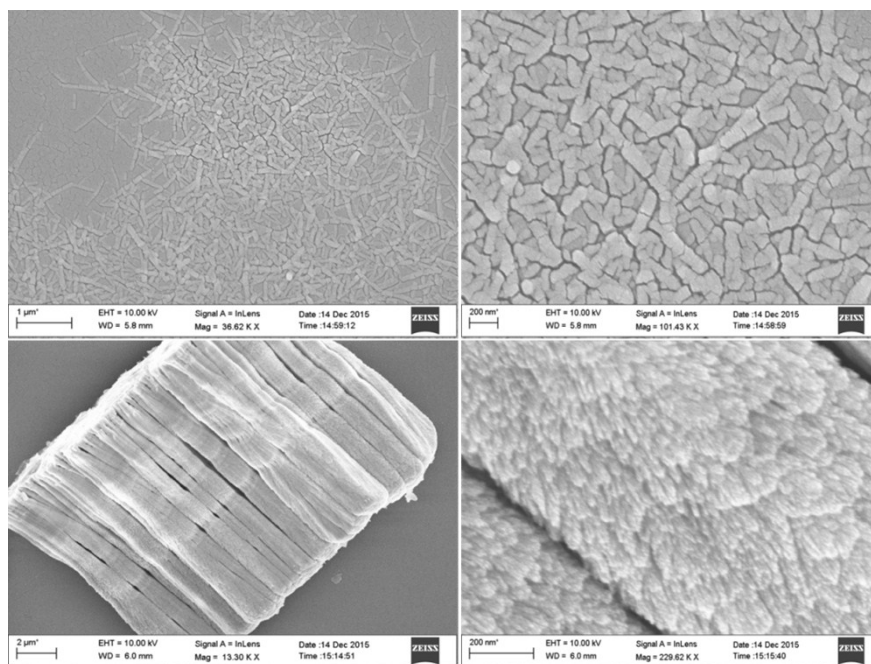


Figure S16. SEM micrographs of DPPS-1 at 10 μM concentration showing nano rods morphology.

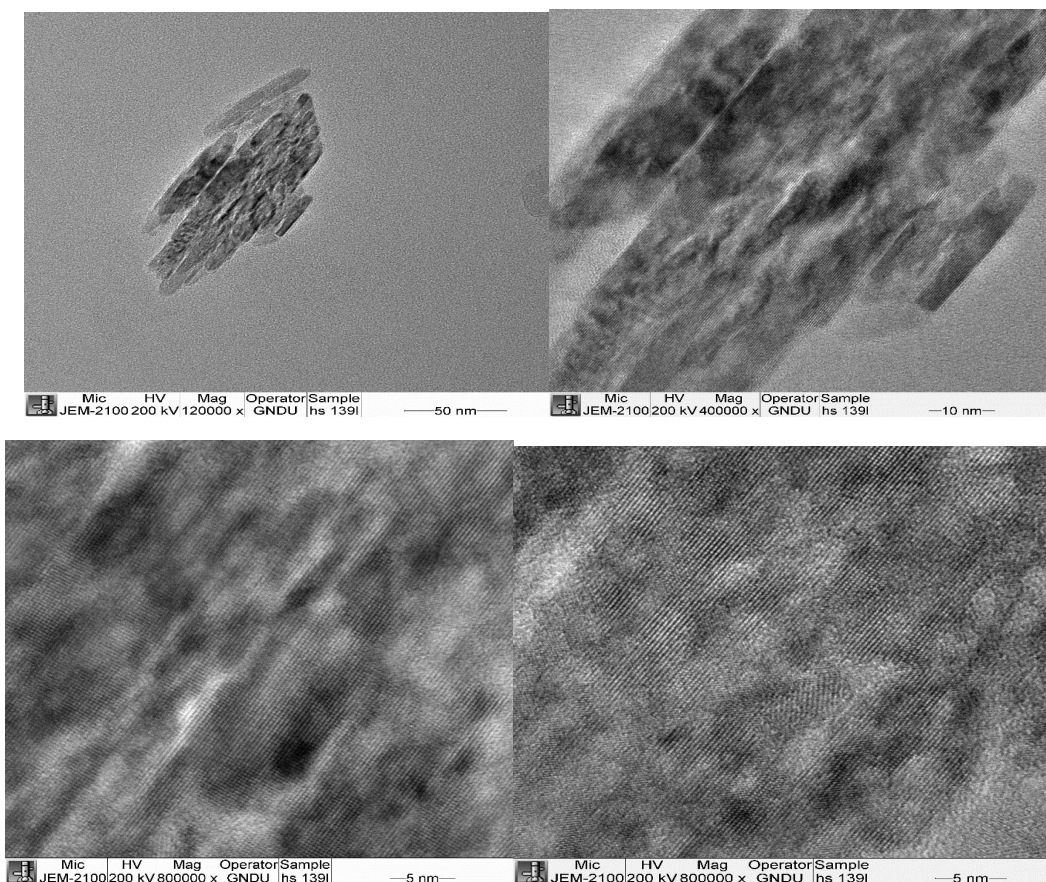


Figure S17. TEM micrograph of DPPS-1 (1 μM) recorded on copper grid.

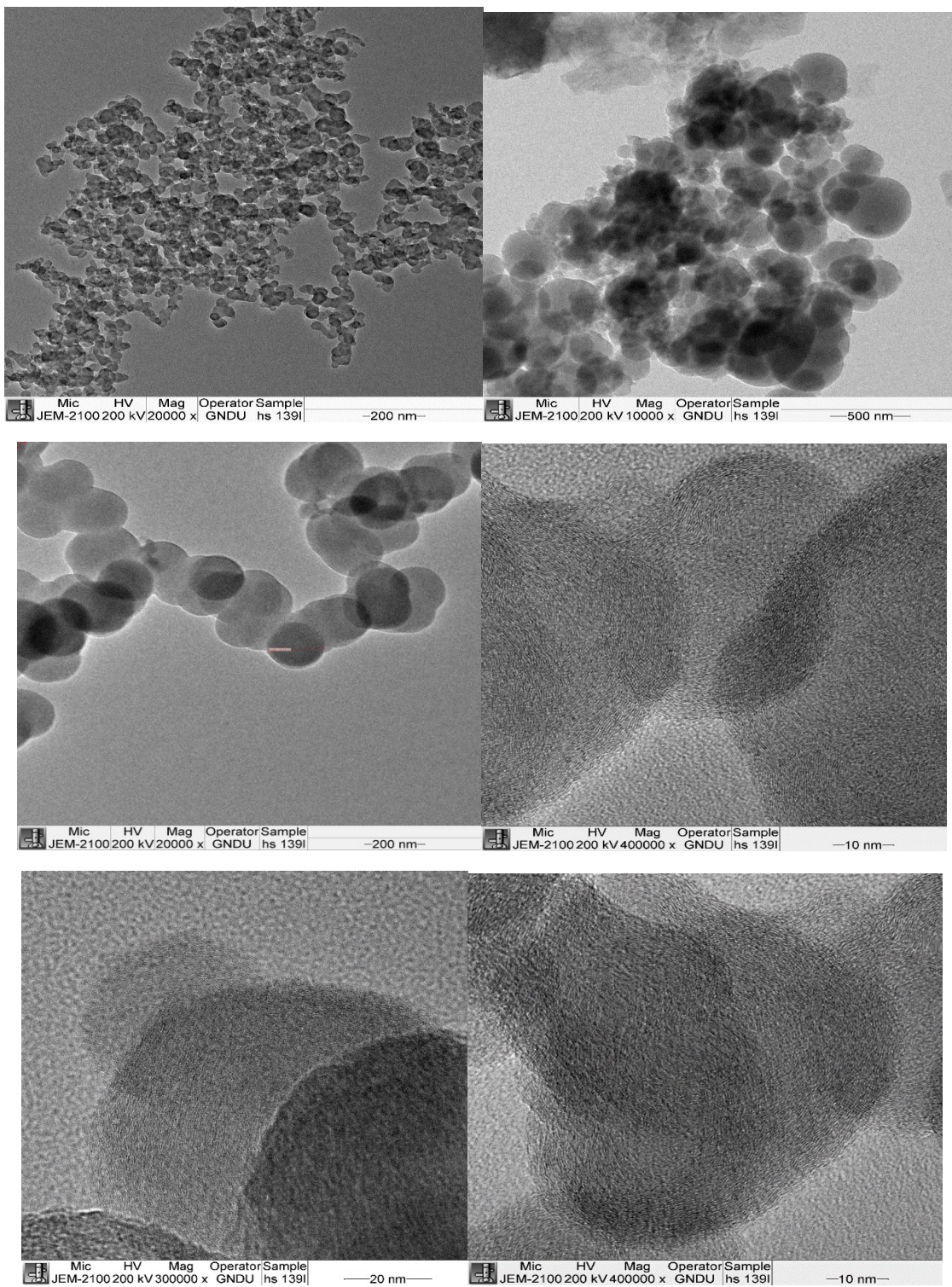


Figure S18. TEM micrograph of DPPS-1 (1 μM) recorded on copper grid showing spherical morphology and layer-by-layer self-assembly.

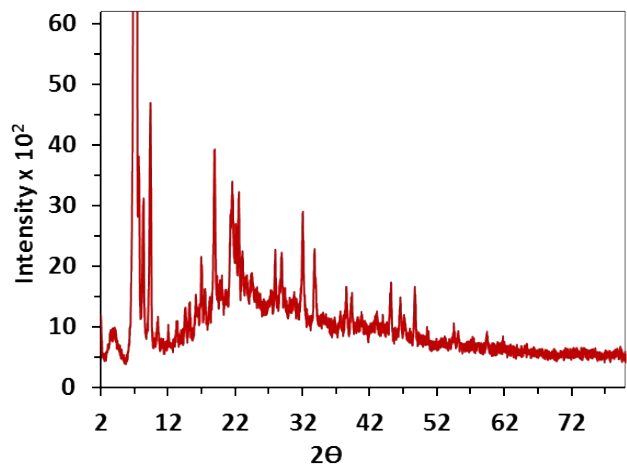


Figure S19. Wide angle X-ray diffraction (WXR) powder spectrum of **DPPS**



Figure S20 Fluorescence images of 24 h aged fingerprints of all fingers on aluminium substrates. All substrate samples were developed using **DPPS-2** in 40% H₂O:CH₃CN mixture and then visualized under 365 nm UV lamp.

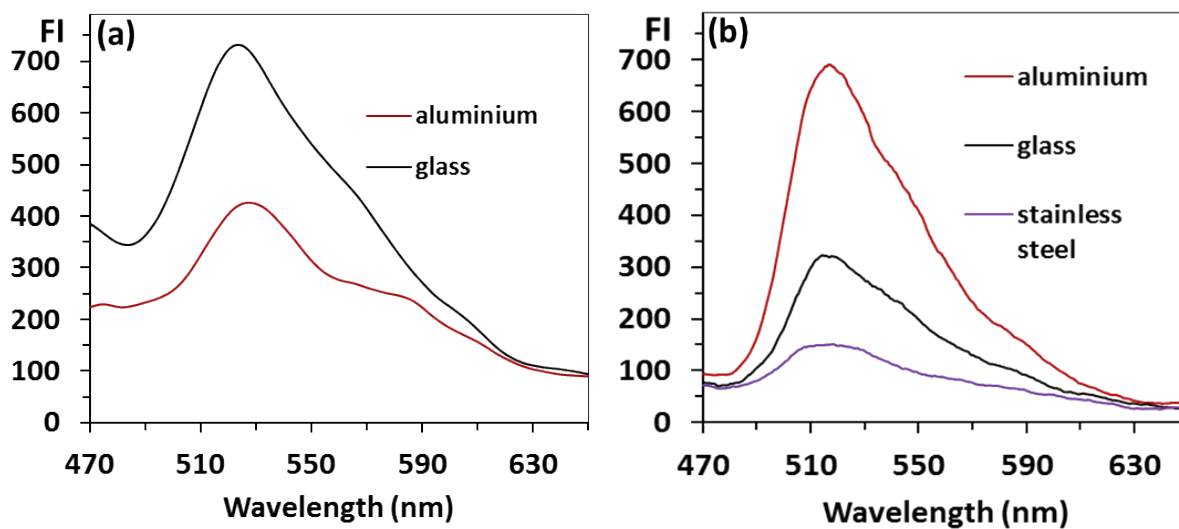


Figure S21 Recording of solid state fluorescence emission of finger prints stamped on different substrates.