

Water soluble non-conjugated fluorescent polymers: Aggregation induced emission, solid-state fluorescence, and sensor array applications

Anna Jose ^a, Adithya Tharayil ^a, Mintu Porel ^{a,b*}

^aDepartment of Chemistry; ^bEnvironmental Sciences and Sustainable Engineering Centre; Indian Institute of Technology Palakkad, Kerala, India

*Corresponding author E-mail address: mintu@iitpkd.ac.in

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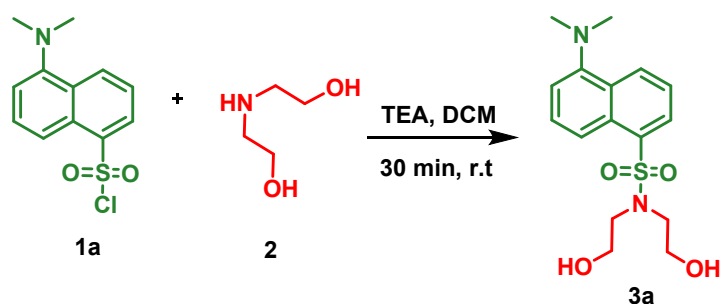
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Materials and methods

All the chemicals were purchased from Sigma Aldrich, Alfa Aesar, Spectrochem, Merck and TCI and used without further purification. The PerkinElmer FL 6500 instrument was used for fluorescence studies. The fluorescence and absorbance spectra were plotted in OriginPro 8.5.1. The absorbance was measured in BioTek EPOCH2 microplate reader. PerkinElmer STA (Simultaneous Thermal Analyser) 8000 was used for TG DTA measurements. The Carl Zeiss Gemini SEM 300 scanning electron microscope equipped with 2000000X magnification and 0.8 nm resolution at 15 kV, and 1.3 nm at 1 kV recorded the SEM images. The Fluorocube - Life Time System from JOBIN-VYON M/S was used for the time-correlated single photon counting (TCSPC) analysis to obtain the lifetime of the sample.

Synthesis of D1

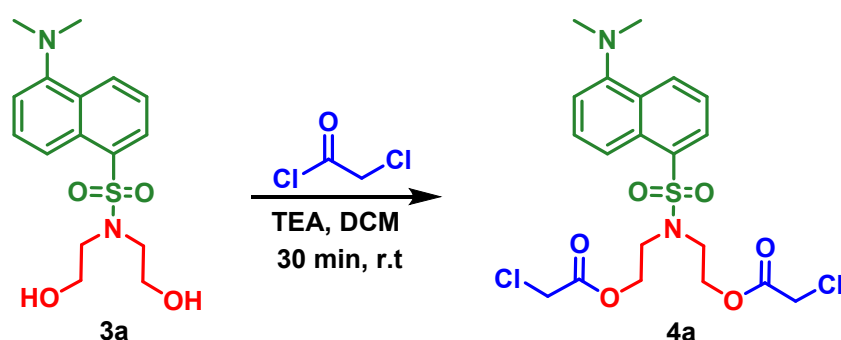
Step 1: Synthesis of 3a



Scheme 1: Synthesis of 3a

Procedure: Dansyl chloride, **1a**, (1 mmol) was dissolved in 10 mL of DCM and was kept in an ice bath for 5 minutes. To this, triethylamine (1.5 mmol) was added followed by dropwise addition of diethanolamine, **2**, (1 mmol). The reaction mixture was allowed to stir for 30 min. After the completion of the reaction, it was extracted with 1: 1 DCM: water mixture. The product was obtained in the DCM layer and was evaporated to obtain the pure product, **3a**, with 98% yield.

Step 2: Synthesis of 4a



Scheme 2: Synthesis of 4a

Procedure: The product, **3a**, (1 mmol) was dissolved in 10 mL of DCM and was kept in an ice bath for 5 minutes. To this, triethylamine (3 mmol) and chloroacetyl chloride, (4 mmol) was added dropwise over half an hour. The reaction mixture was allowed to stir for 30 min. After the completion of the reaction, it was extracted with 1: 1 DCM: water mixture. The product was obtained in the DCM layer and was evaporated to obtain the pure product, **4a**, with 98% yield.

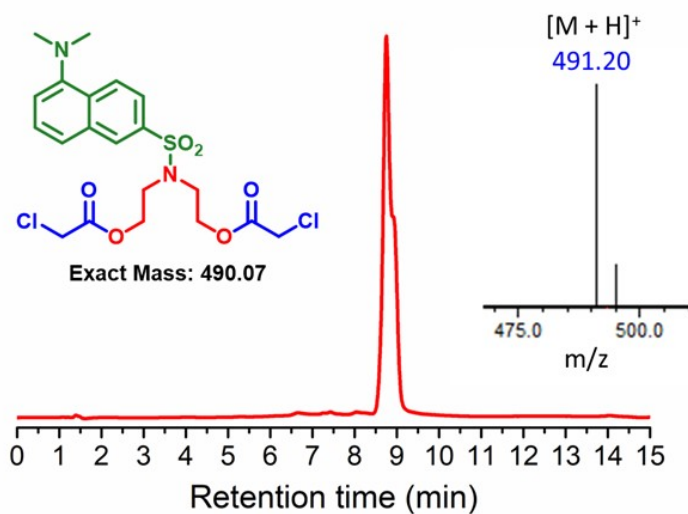
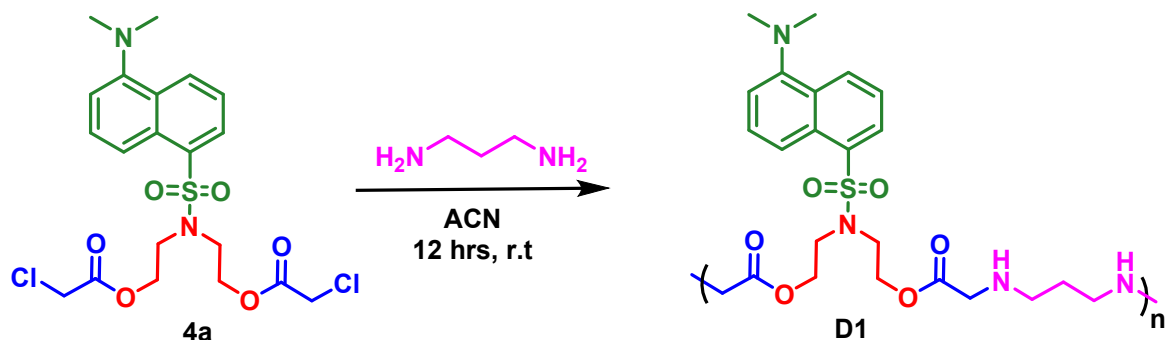


Figure S1: The HPLC trace and MS data showing $[M + H]^+$ ion for **4a**.

Step 3: Synthesis of **D1**

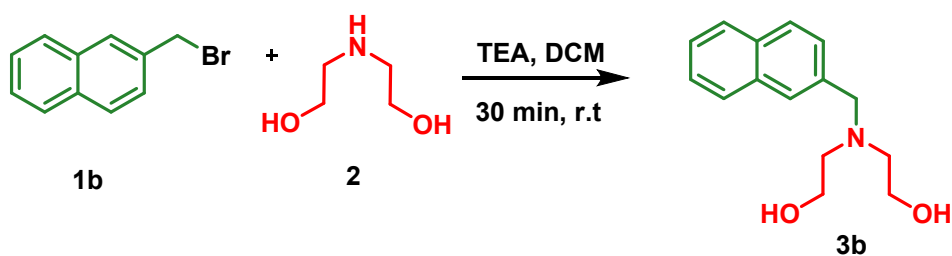


Scheme 3: Synthesis of **D1**

Procedure: The product, **4a**, (1 mmol) was taken in acetonitrile. To this 1, 3 propane diamine (1.5 mmol) was added and reaction mixture was allowed to stir for 12 hours at room temperature. The progress of the reaction is confirmed by the formation of solid powder in the round bottom flask. After 12 hours, the powder was filtered and was washed with ethyl acetate and acetone multiple times to remove any impurities. Further it was dried in the oven.

Synthesis of **N1**

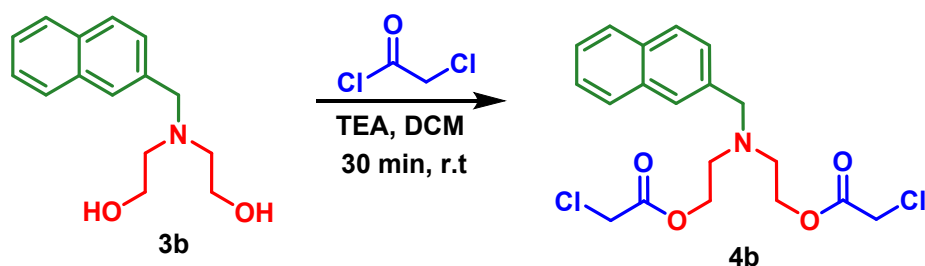
Step 1: Synthesis of **3b**



Scheme 4: Synthesis of **3b**

Procedure: Naphthyl bromide, **1b**, (1 mmol) was dissolved in 10 mL of DCM and was kept in an ice bath for 5 minutes. To this, triethylamine (1.5 mmol) was added followed by dropwise addition of diethanolamine, **2**, (1 mmol). The reaction mixture was allowed to stir for 30 min. After the completion of the reaction, it was extracted with 1: 1 DCM: water mixture. The product was obtained in the DCM layer and was evaporated to obtain the pure product, **3b**, with 98% yield.

Step 2: Synthesis of **4b**



Scheme 5: Synthesis of **4b**

Procedure: The product, **3b**, (1 mmol) was dissolved in 10 mL of DCM and was kept in an ice bath for 5 minutes. To this, triethylamine (3 mmol) was added and chloroacetylchloride, (4 mmol) was added dropwise over half an hour. The reaction mixture was allowed to stir for 30 min. After the completion of the reaction, it was extracted with 1: 1 DCM: water mixture. The product was obtained in the DCM layer and was evaporated to obtain the pure product, **4b**, with 98% yield.

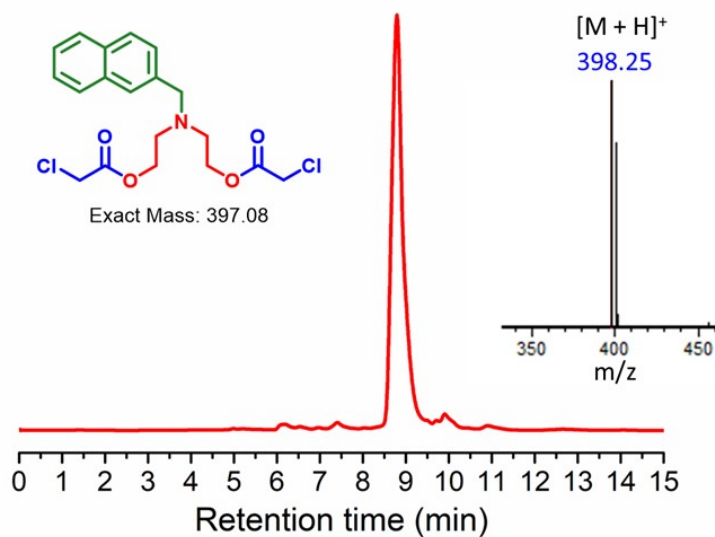
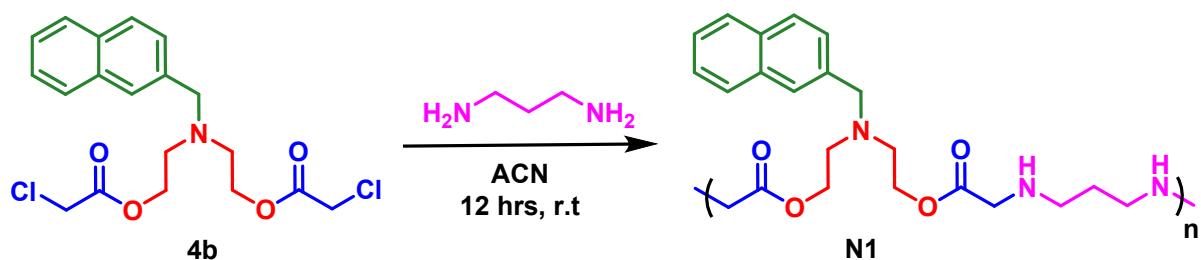


Figure S2: The HPLC trace and MS data showing [M + H]⁺ ion for **4b**.

Step 3: Synthesis of N1



Scheme 6: Synthesis of N1

Procedure: The product, **4b**, (1 mmol) was taken in acetonitrile. To this 1, 3 propane diamine (1.5 mmol) was added and reaction mixture was allowed to stir for 12 hours at room temperature. The progress of the reaction is confirmed by the formation of solid powder in the round bottom flask. After 12 hours, the powder was filtered and was washed with ethyl acetate and acetone multiple times to remove any impurities. Further it was dried in the oven.

GPC (gel permeation chromatography)

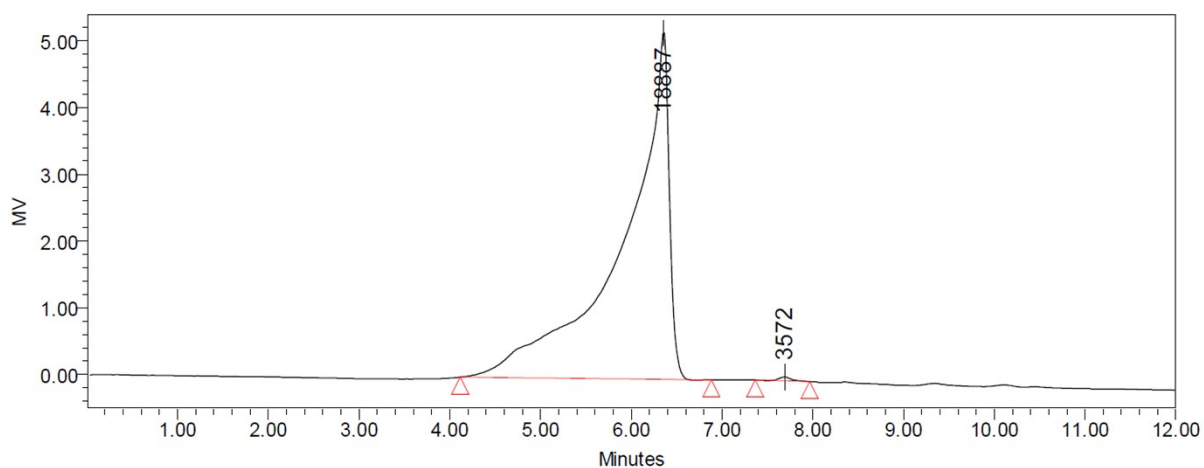


Figure S3: The molecular weight distribution obtained for **D1**.
For **D1** the molecular weight obtained was 18887 Da with a polydispersity index of 1.41.

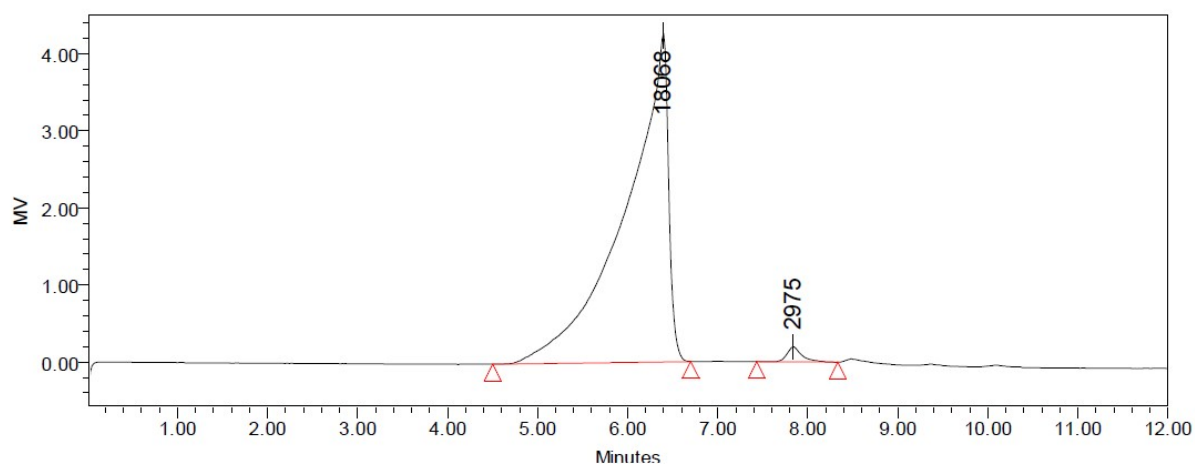


Figure S4: The molecular weight distribution obtained for **N1**.
For **N1** the molecular weight obtained was 18068 Da with a polydispersity index of 1.22.

NMR characterisation

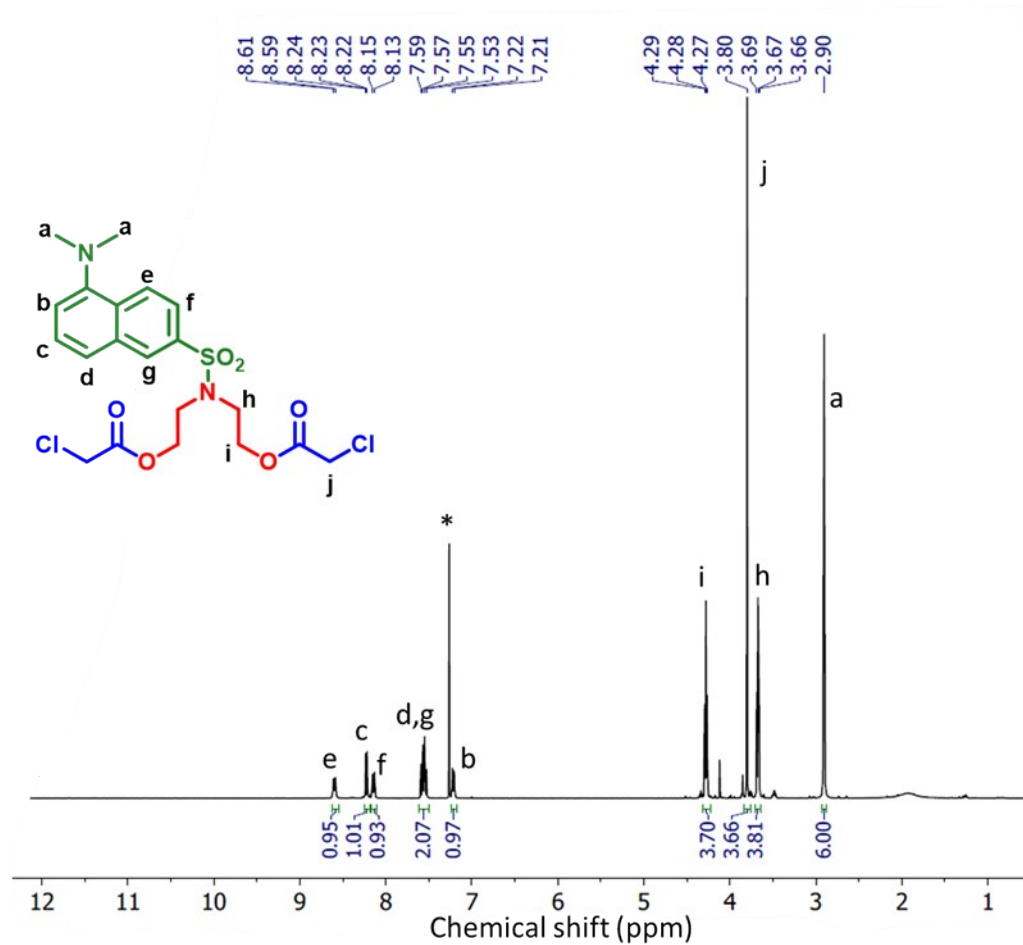


Figure S5: The ¹H-NMR (400 MHz) of **4a** in CDCl₃. δ (ppm) 2.90 (s, 6H), 3.66-3.69 (t, 4H), 3.80 (s, 4H), 4.27-4.29 (t, 4H), 7.21-7.22 (d, 1H), 7.53-7.59 (m, 2H), 8.13-8.15 (d, 1H), 8.22-8.24 (d, 1H), 8.59-8.61 (d, 1H). * represents the residual peaks of CDCl₃.

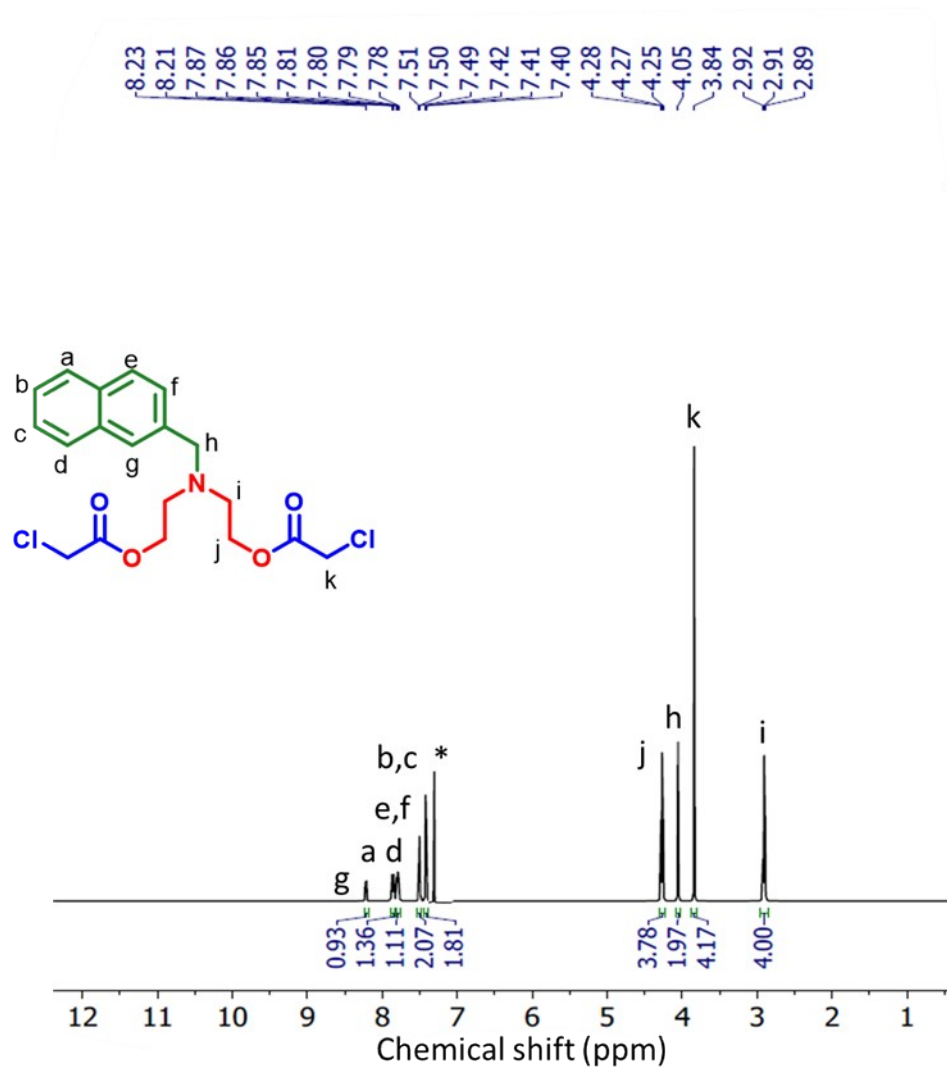


Figure S6: The ¹H-NMR (400 MHz) of **4b** in CDCl₃. δ (ppm) 2.89-2.92 (t, 4H), 3.84 (s, 4H), 4.05 (s, 2H), 4.25-4.28 (t, 4H), 7.40-7.42 (m, 2H), 7.49-7.51 (m, 2H), 7.78-7.81 (m, 1H), 7.85-7.87 (m, 1H), 8.21-8.23 (d, 1H). * represents the residual peaks of CDCl₃.

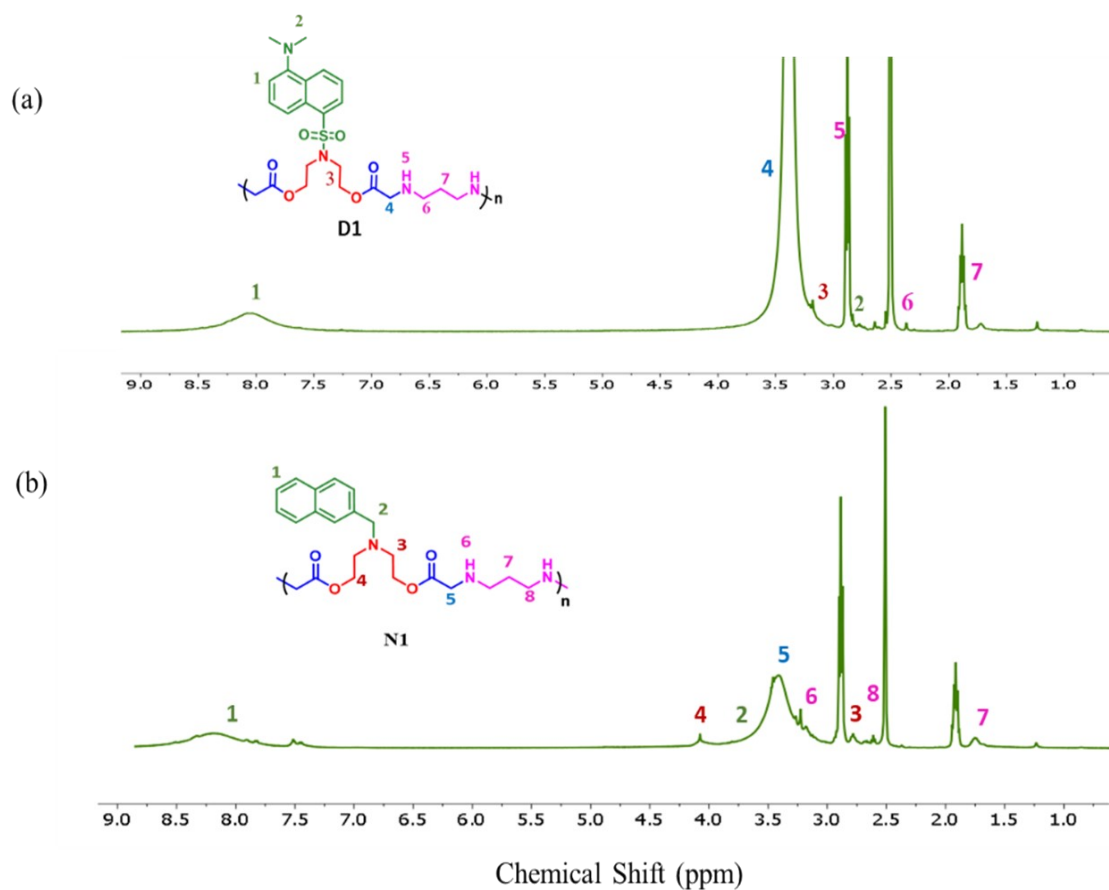


Figure S7: The ^1H -NMR (400 MHz) of (a) **D1** and (b) **N1** in DMSO-d_6 .

IR characterisation

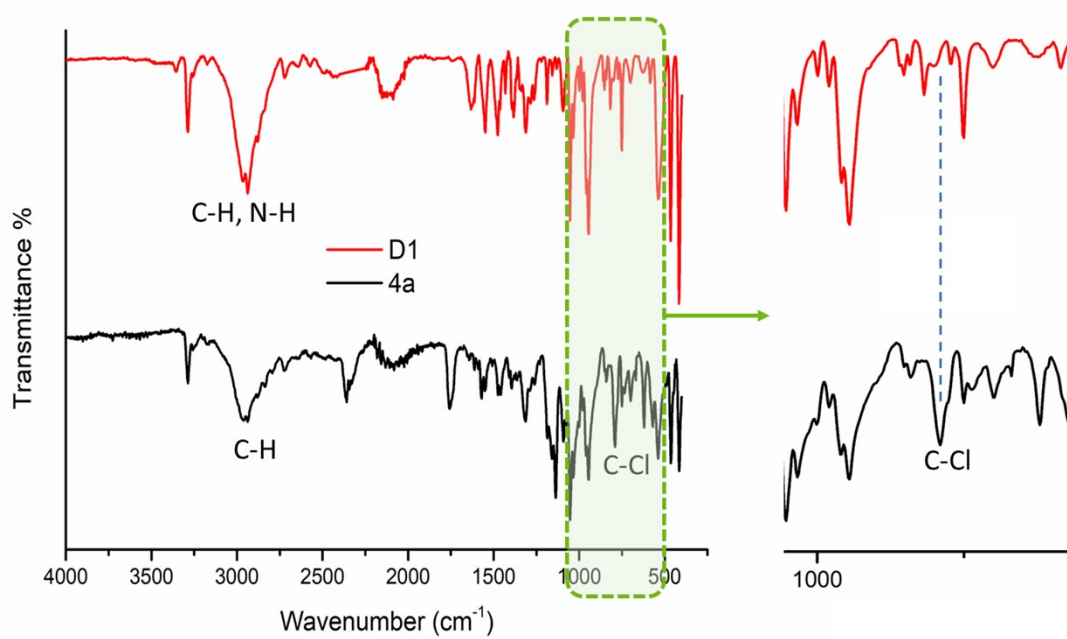


Figure S8: The IR spectra for **D1** (red) and 4a (black)

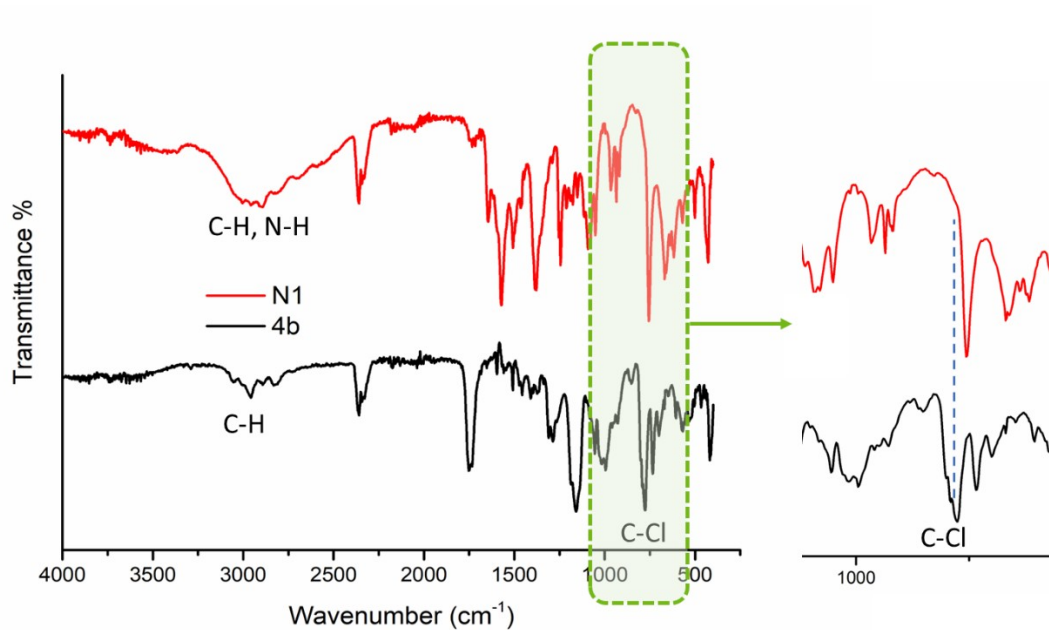


Figure S9: The IR spectra for **N1** (red) and 4b (black)

Scanning electron microscopy (SEM)

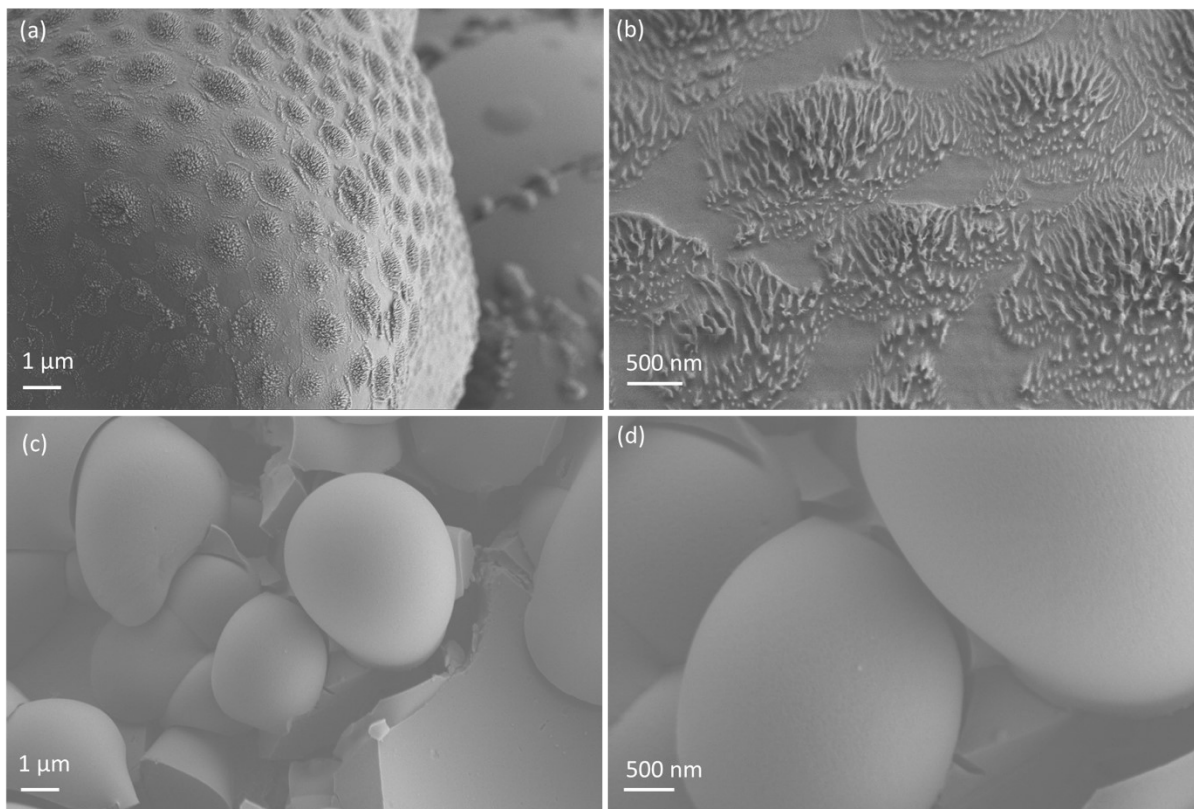


Figure S10: The SEM images obtained for **D1** (a, b) and **N1** (c, d).

TG DTA measurement

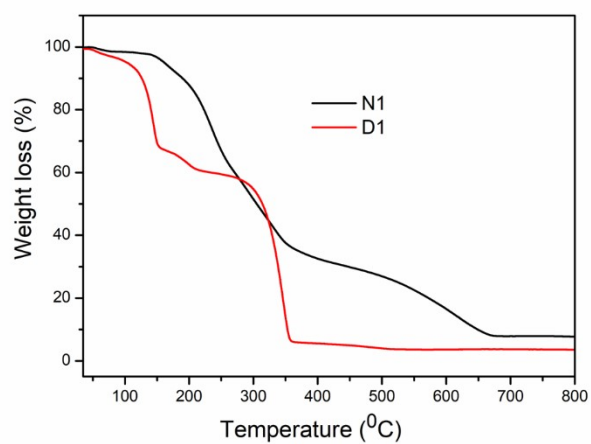


Figure S11: The TG DTA of polymer **D1** and **N1**.

Dynamic light scattering (DLS)

The dynamic light scattering experiment (DLS) of **D1** and **N1** were recorded in water-DMSO mixtures with DMSO fractions of 0%, 50%, and 90%.

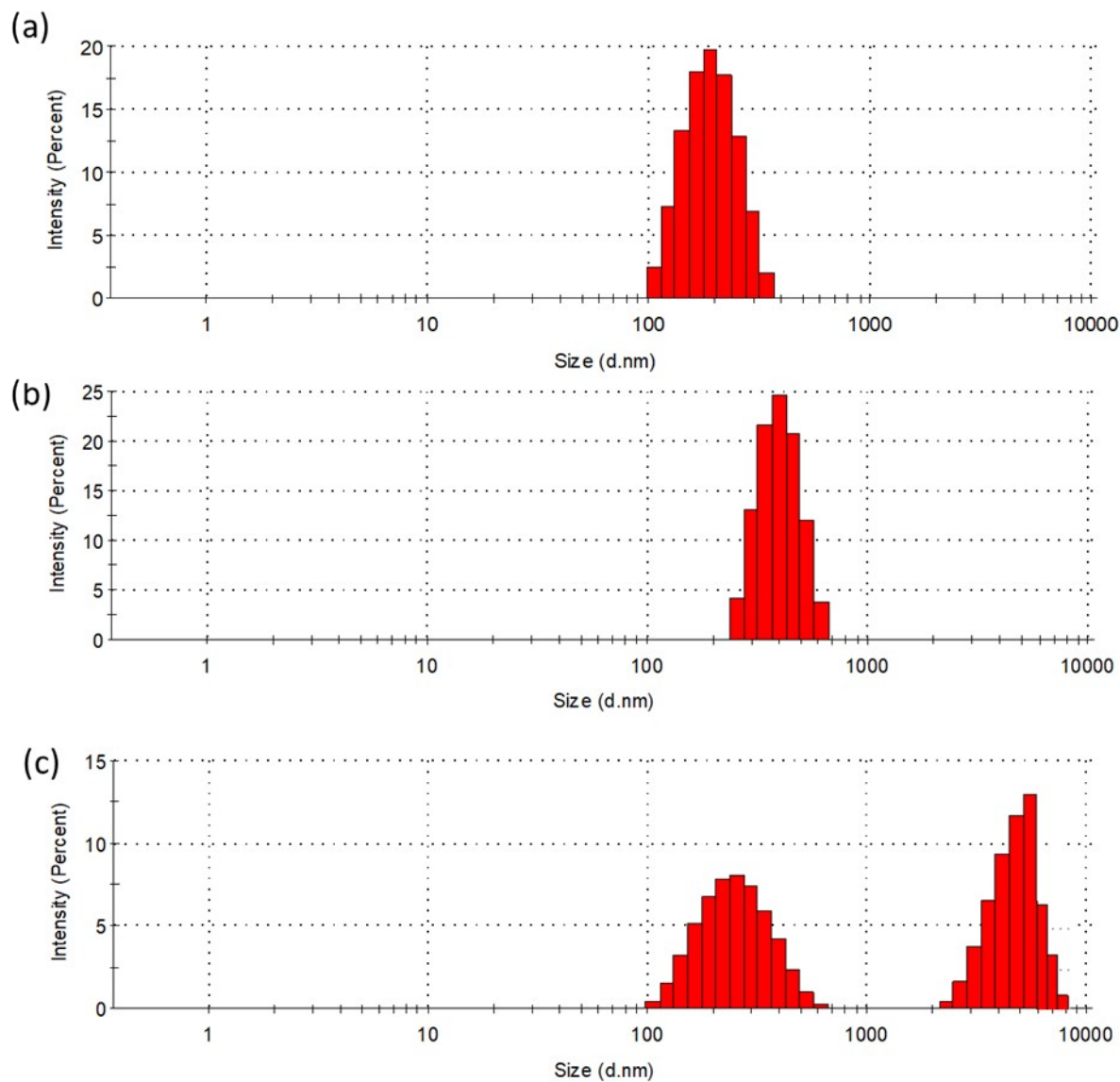


Figure S12: The DLS data obtained for (a) 0% (b) 50% and (c) 90% DMSO fractions of **D1** in water.

The water-DMSO fraction with 0% DMSO had a hydrodynamic diameter of 205.2 nm with a polydispersity index (PDI) of 0.308. For 50% DMSO fraction the value was 403 nm with PDI of 0.122. For 90%, a mixture of hydrodynamic diameters was observed with the highest value being 4472 nm (PDI is 0.759).

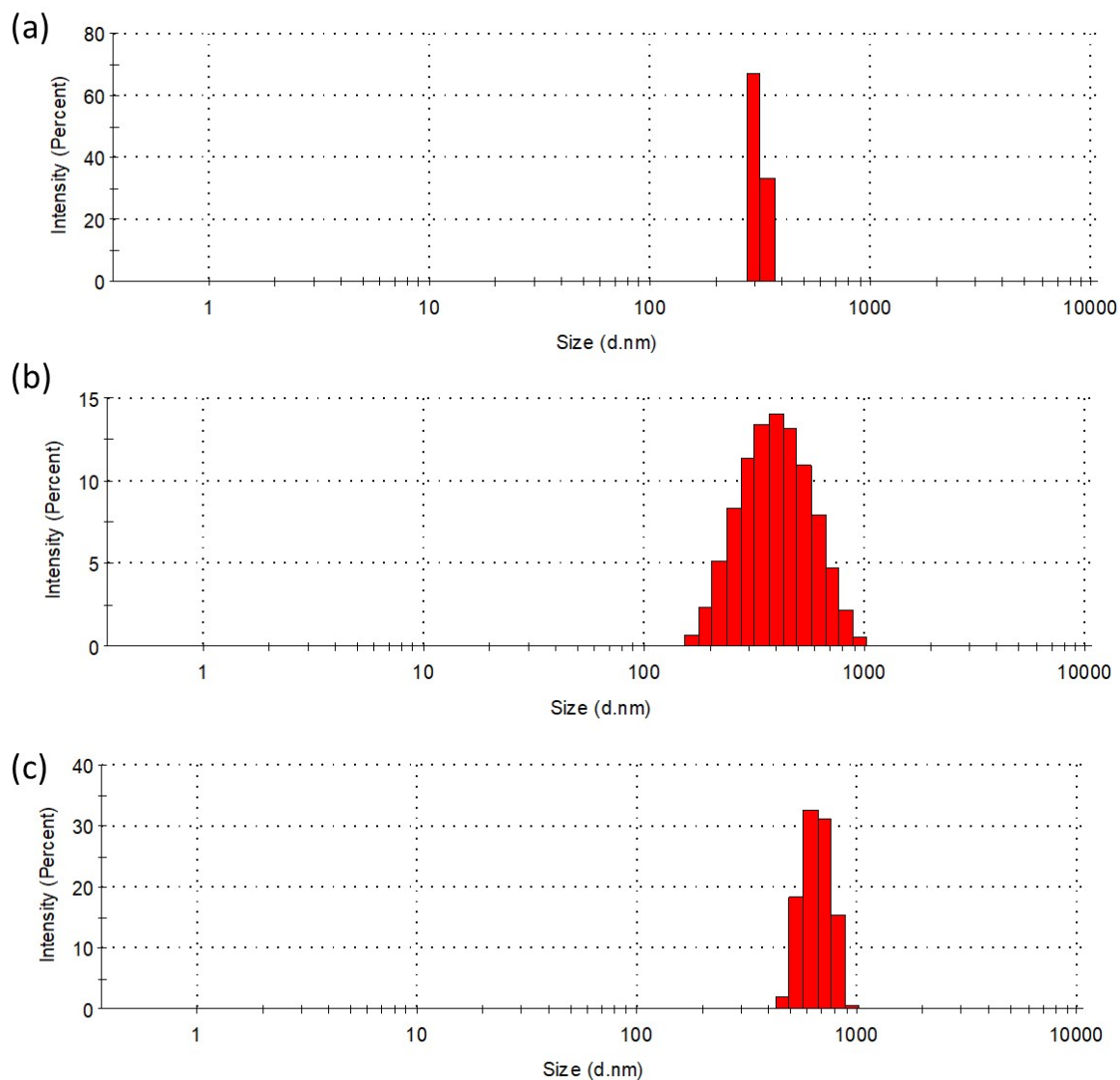


Figure S13: The DLS data obtained for (a) 0% (b) 50% and (c) 90% DMSO fractions of **N1** in water.

For **N1**, 0%, 50% and 90% DMSO fraction the obtained hydrodynamic diameter were 310.8 nm (PDI- 0.9), 418.6 (PDI- 0.275) and 661 nm (PDI-0.495) respectively.

The DLS of a solution of **D1** (3mg/mL) in water was compared with that obtained after the addition of 10 equivalents of Ag^+ ions.

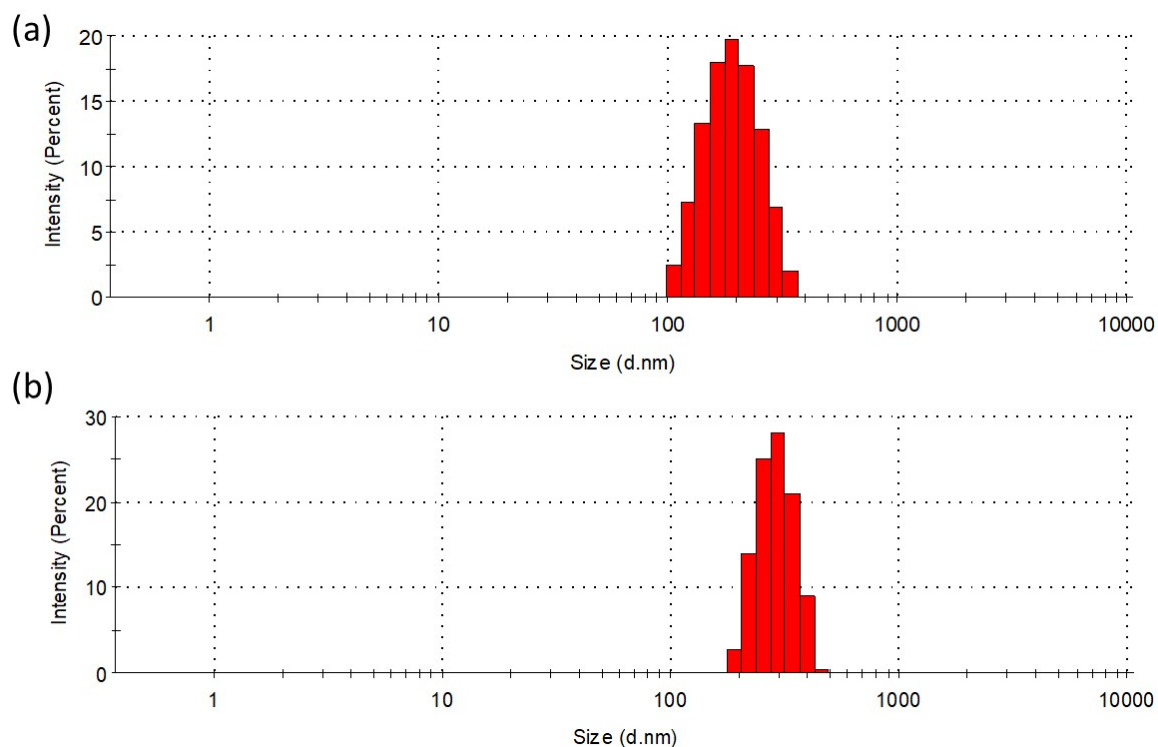


Figure S14: The DLS data obtained for (a) **D1** in water and (b) **D1** + Ag^+ . The hydrodynamic diameter of **D1** was obtained as 205.2 nm with a polydispersity index (PDI) of 0.308 and that of **D1** + Ag^+ was 383.6 nm with PDI of 0.738.

Further, the solution of **D1** + Ag^+ showed clear evidence of the Tyndall effect, demonstrating the formation of nanoscale aggregates.

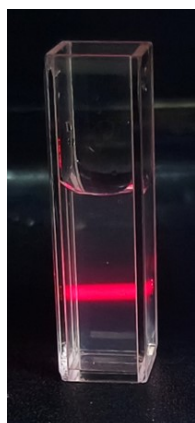


Figure S15: Photographic image of the solution of **D1** showing Tyndall effect with the addition of 10 equivalents of Ag^+ solution.

Quantum yield measurement

The quantum yield was calculated using the following equation:

$$Q_S = Q_R \frac{I_S A_R \eta_S^2}{I_R A_S \eta_R^2}$$

Where Q_S and Q_R represents the quantum yield of the sample and the reference respectively. I_S and I_R represents the integrated area under the emission spectra of sample and reference, A_R and A_S represents the absorption of reference and sample and η represents the refractive index of the medium. Quantum yield of the sensor was calculated via reference method, by taking quinine sulphide as the reference. The quantum yield for quinine sulphide is 0.54 (Fig S16). The integrated area under the curve obtained for the emission spectra of quinine sulphide is 2.103×10^7 .

For **D1**, the area under the curve obtained for 0, 30, 70 and 90% DMSO fractions were 4.97×10^6 and 2.63×10^5 respectively. Also, the absorbance value for these were 0.146, 0.135 and 0.097.

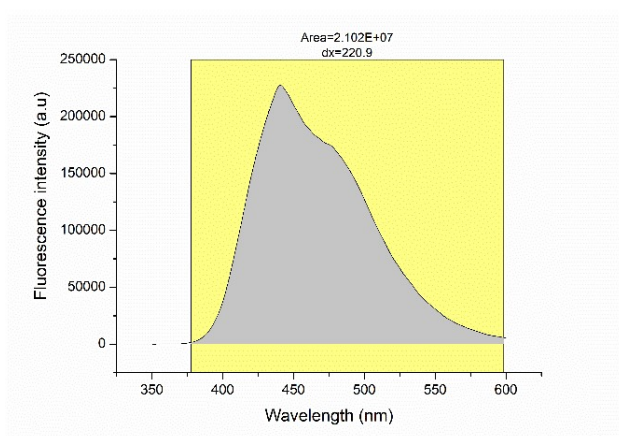


Figure S16: The area under the curve calculated for quinine sulphide

The quantum yield for quinine sulphide is 0.54

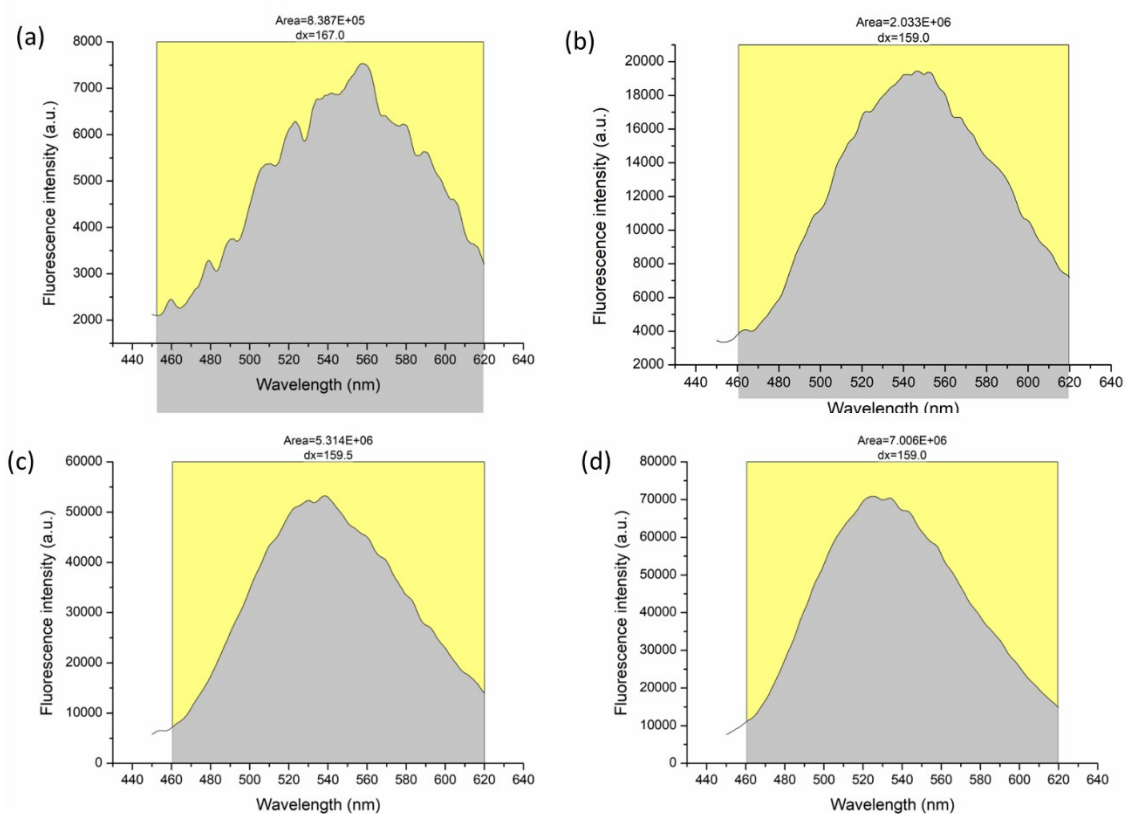


Figure S17: The area under the curve calculated for (a) 0%, (b) 30%, (c) 70% and (d) 90% DMSO fractions of **D1**

The quantum yield obtained for 0%, 30%, 70% and 90% DMSO fraction of **D1** are 0.023, 0.061, 0.183 and 0.243 respectively.

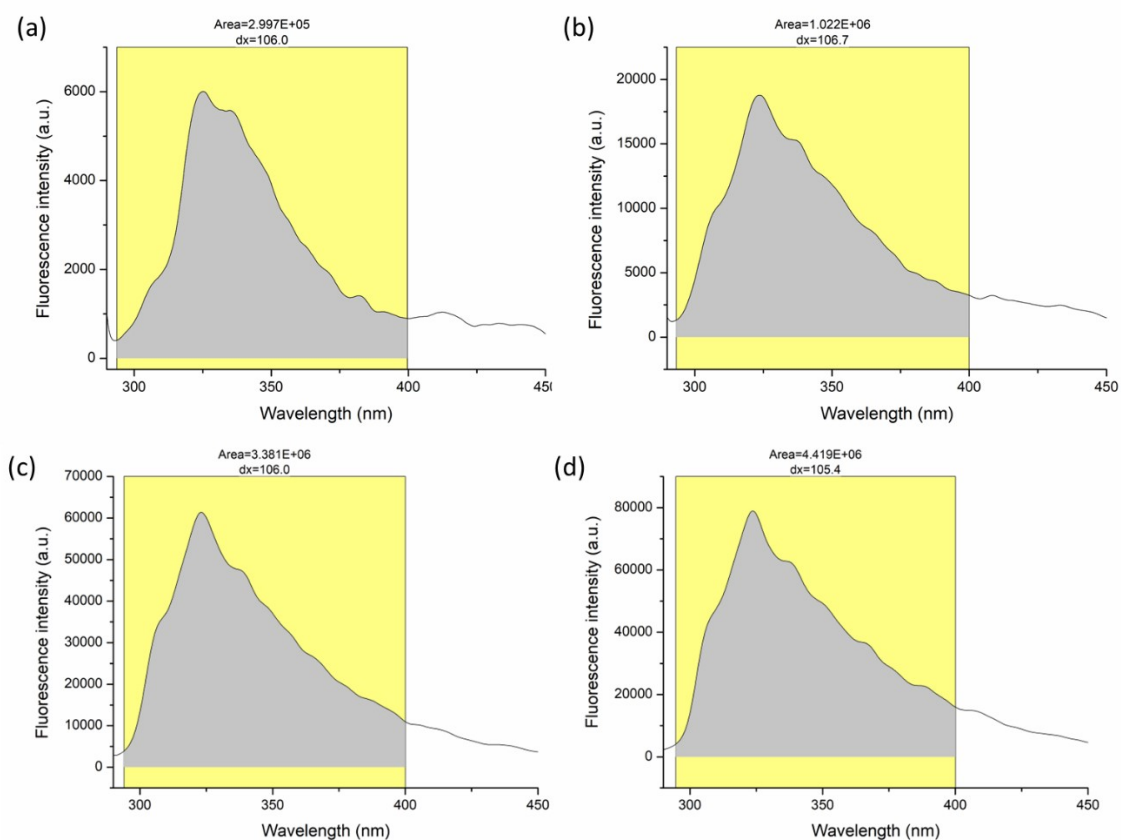


Figure S18: The area under the curve calculated for (a) 0%, (b) 30%, (c) 70% and (d) 90% DMSO fractions of N1

The quantum yield obtained for 0%, 30%, 70% and 90% DMSO fraction of N1 are 0.010, 0.032, 0.113 and 0.153 respectively.

Lifetime measurements

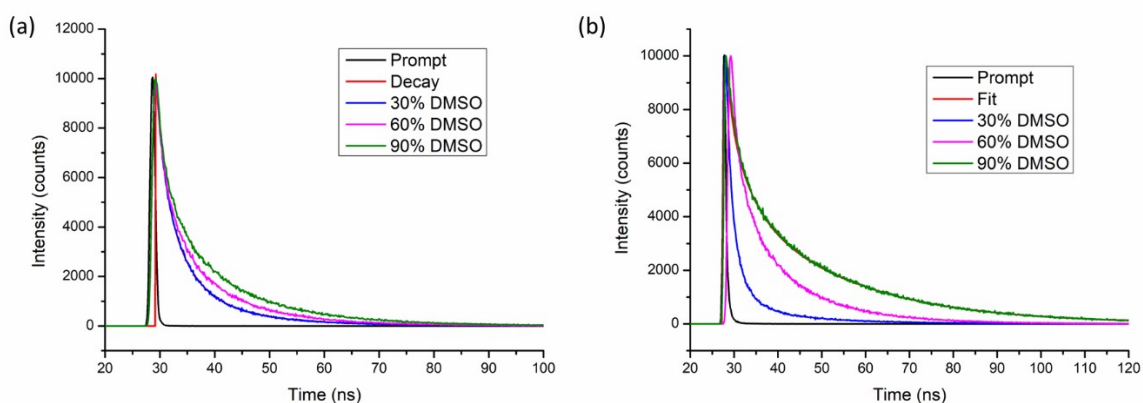


Figure S19: Fluorescence decay curve obtained for (a) D1 and (b) N1

The average lifetime (τ) obtained for 30%, 60% and 90% DMSO fraction of D1 are 3.5 ns, 4.73 ns and 5.63 ns and that obtained for N1 are 5.21 ns, 7.04 ns and 8.86 ns.

Absorption spectra of D1 with metal ions

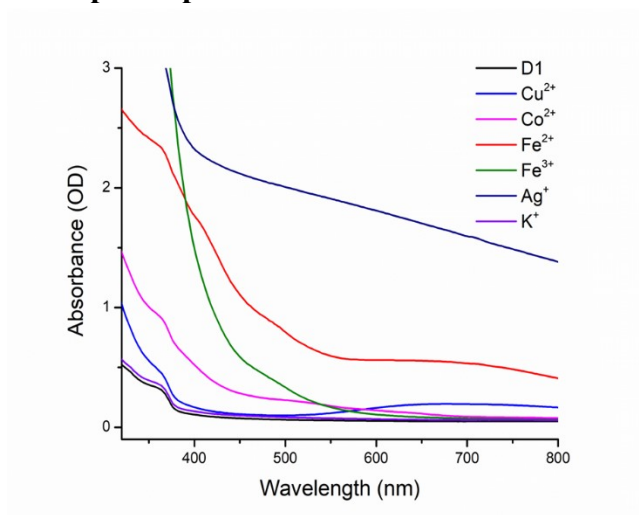


Figure S20: The absorption spectra for the addition of different metal ions to **D1**

Fluorescence titration of N1 with metal ions

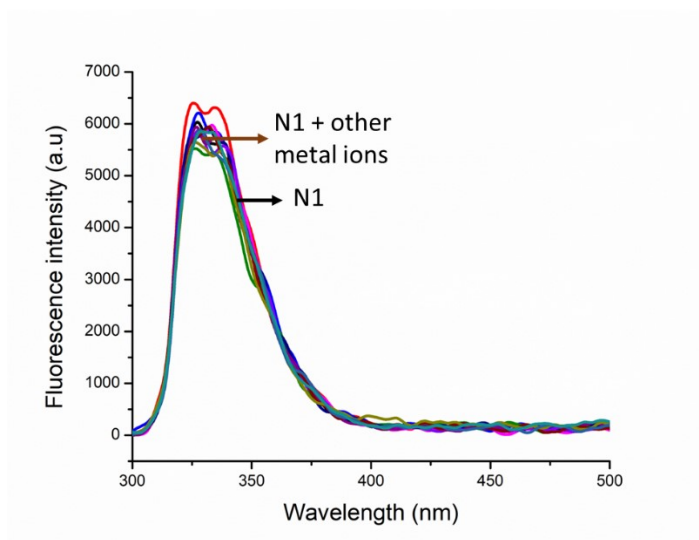


Figure S21: The fluorescence spectra for the addition of different metal ions to **N1**

LDA plot for D1 in nanomolar range

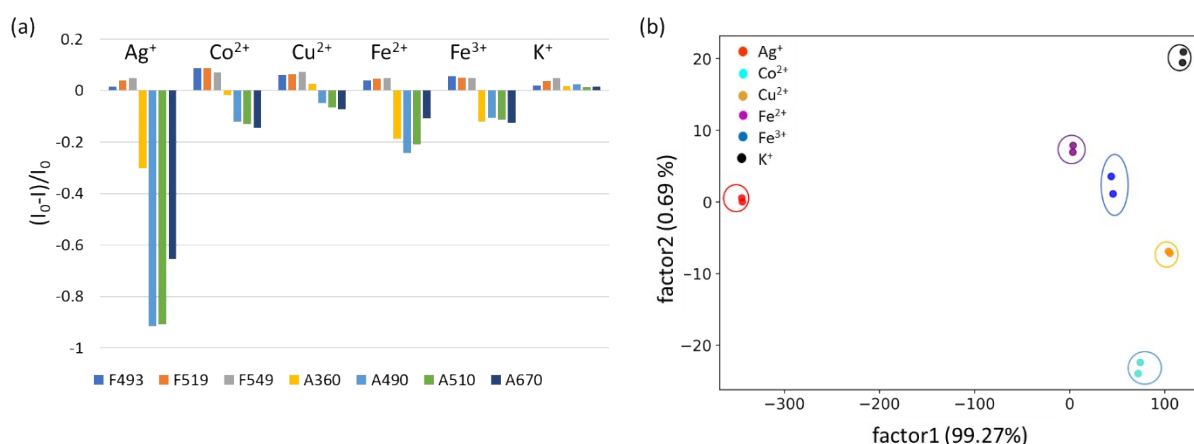


Figure S22: (a) The absorption and fluorescence response patterns of six metals with **D1** and (b) LDA plot obtained from the absorbance and fluorescence responses of **D1** with Ag^+ , Cu^{2+} , Co^{2+} , Fe^{2+} , Fe^{3+} and K^+ .

Limit of detection (LOD)

The limit of detection (LOD) was obtained by titrating the aqueous solution of **D1** (1mg/mL) with different metal ions namely, Co^{2+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Ag^+ and K^+ . The emission spectra obtained for each of these cases and its respective linear plot are shown in figure S23-S28. The LOD obtained for each of these metal ions are tabulated below:

Metal ion	LOD (nM)
Co^{2+}	4.05
Cu^{2+}	5.01
Fe^{2+}	1.40
Fe^{3+}	4.67
Ag^+	4.48
K^+	1.02

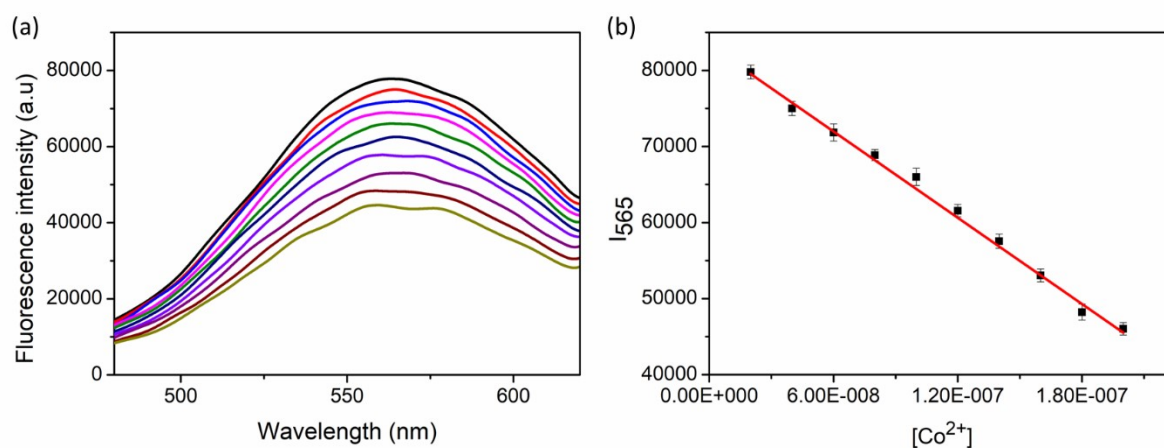


Figure S23: (a) The emission spectra obtained for the addition of Co^{2+} to **D1** and (b) linear plot for the fluorescence intensity at 565 nm against the concentration of Co^{2+} added.

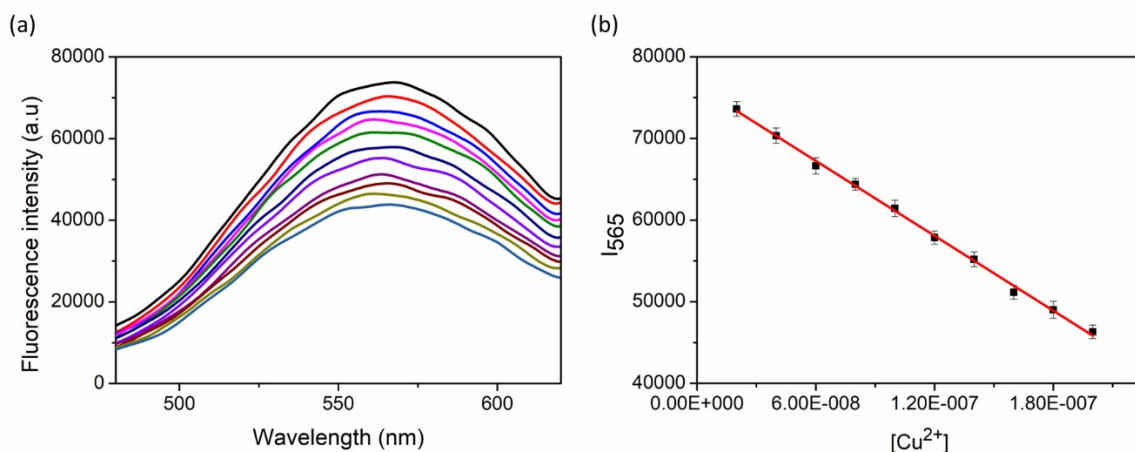


Figure S24: (a) The emission spectra obtained for the addition of Cu^{2+} to **D1** and (b) linear plot for the fluorescence intensity at 565 nm against the concentration of Cu^{2+} added.

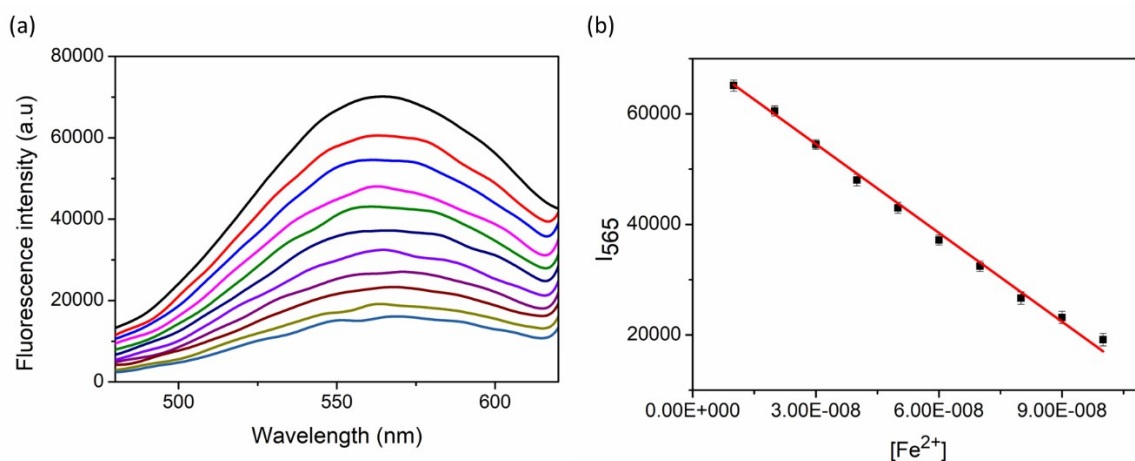


Figure S25: (a) The emission spectra obtained for the addition of Fe^{2+} to **D1** and (b) linear plot for the fluorescence intensity at 565 nm against the concentration of Fe^{2+} added.

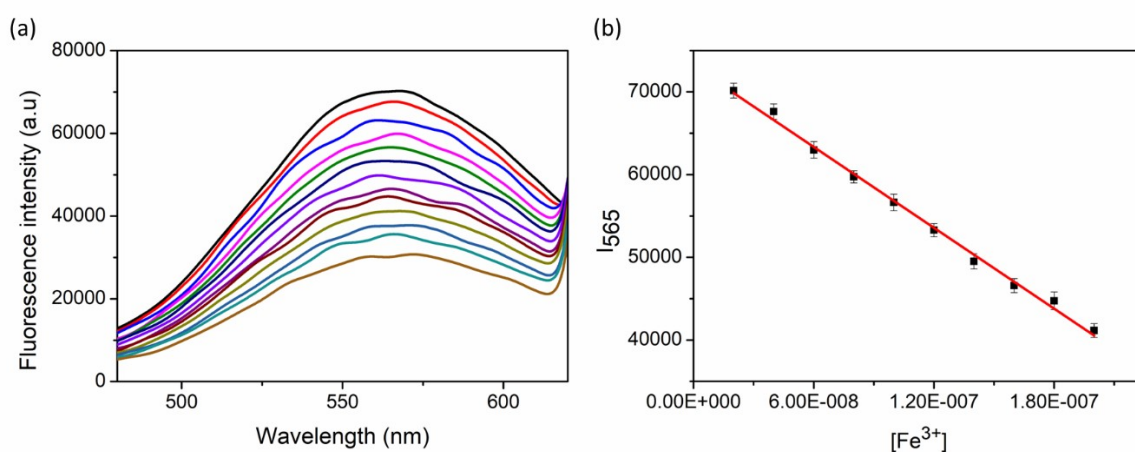


Figure S26: (a) The emission spectra obtained for the addition of Fe^{3+} to **D1** and (b) linear plot for the fluorescence intensity at 565 nm against the concentration of Fe^{3+} added.

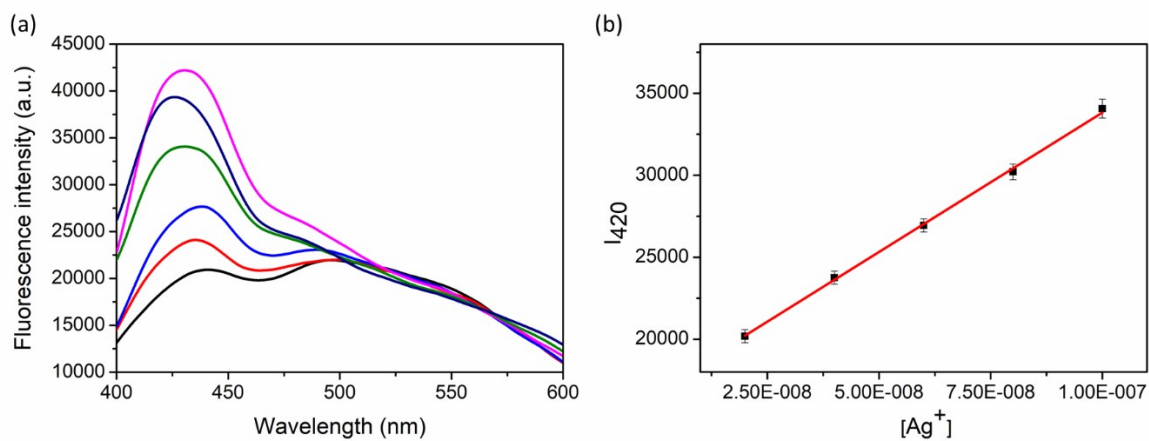


Figure S27: (a) The emission spectra obtained for the addition of Ag^+ to **D1** and (b) linear plot for the fluorescence intensity at 420 nm against the concentration of Ag^+ added.

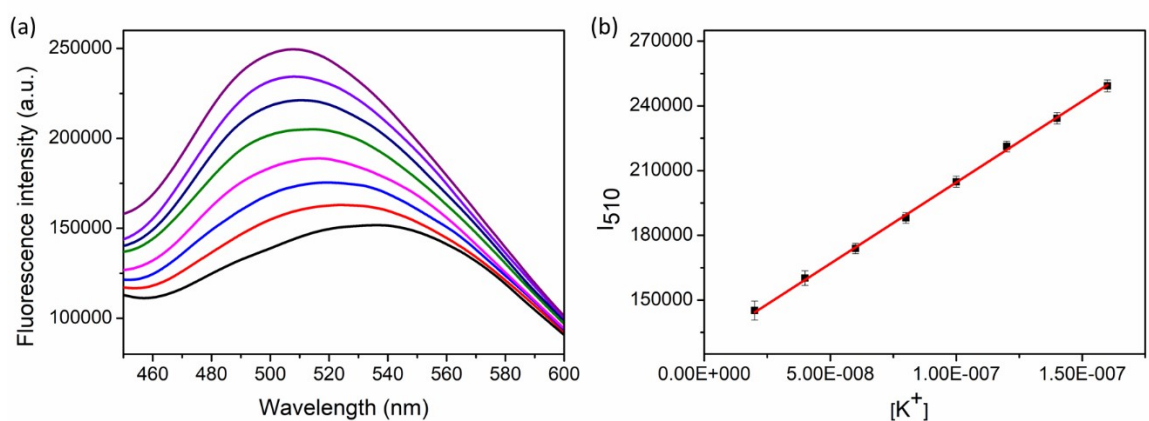


Figure S28: (a) The emission spectra obtained for the addition of K^+ to **D1** and (b) linear plot for the fluorescence intensity at 510 nm against the concentration of K^+ added.