

PCCP

“Bottom-up” Self-assembly and “Cold Crystallization” of Butterfly Shaped Tetrabenzofluorene Molecules**

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Experimental Details

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Section A. NMR studies of 1 and 2

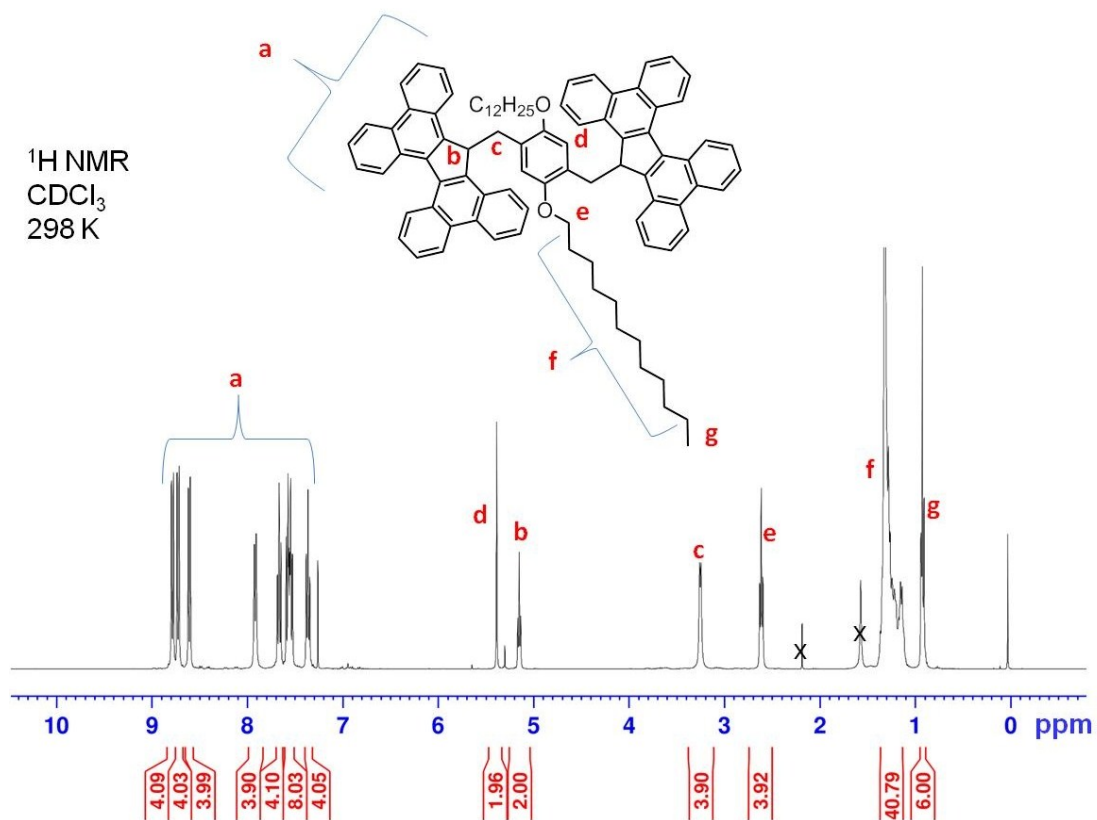


Fig. S1. ¹H NMR spectrum of **1** in CDCl₃ at 298 K. x : water and acetone

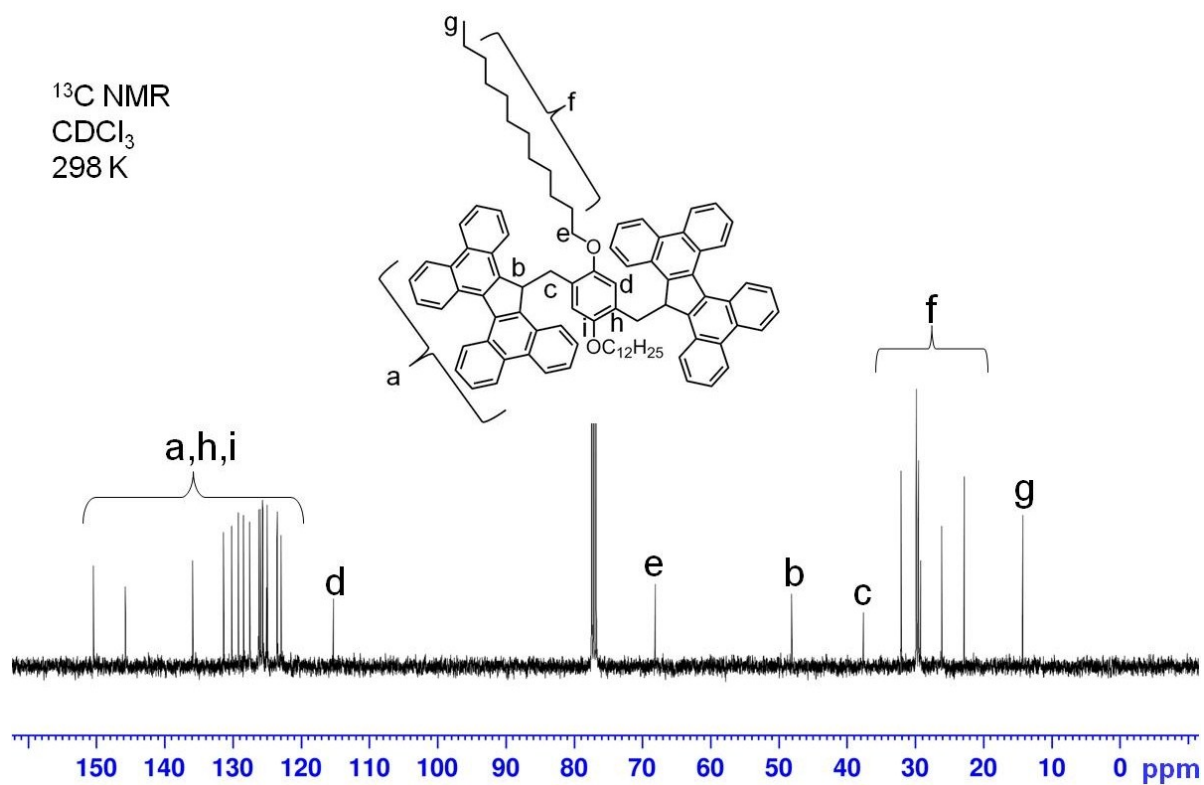


Fig. S2. ¹³C NMR spectrum of **1** in CDCl₃ at 298 K.

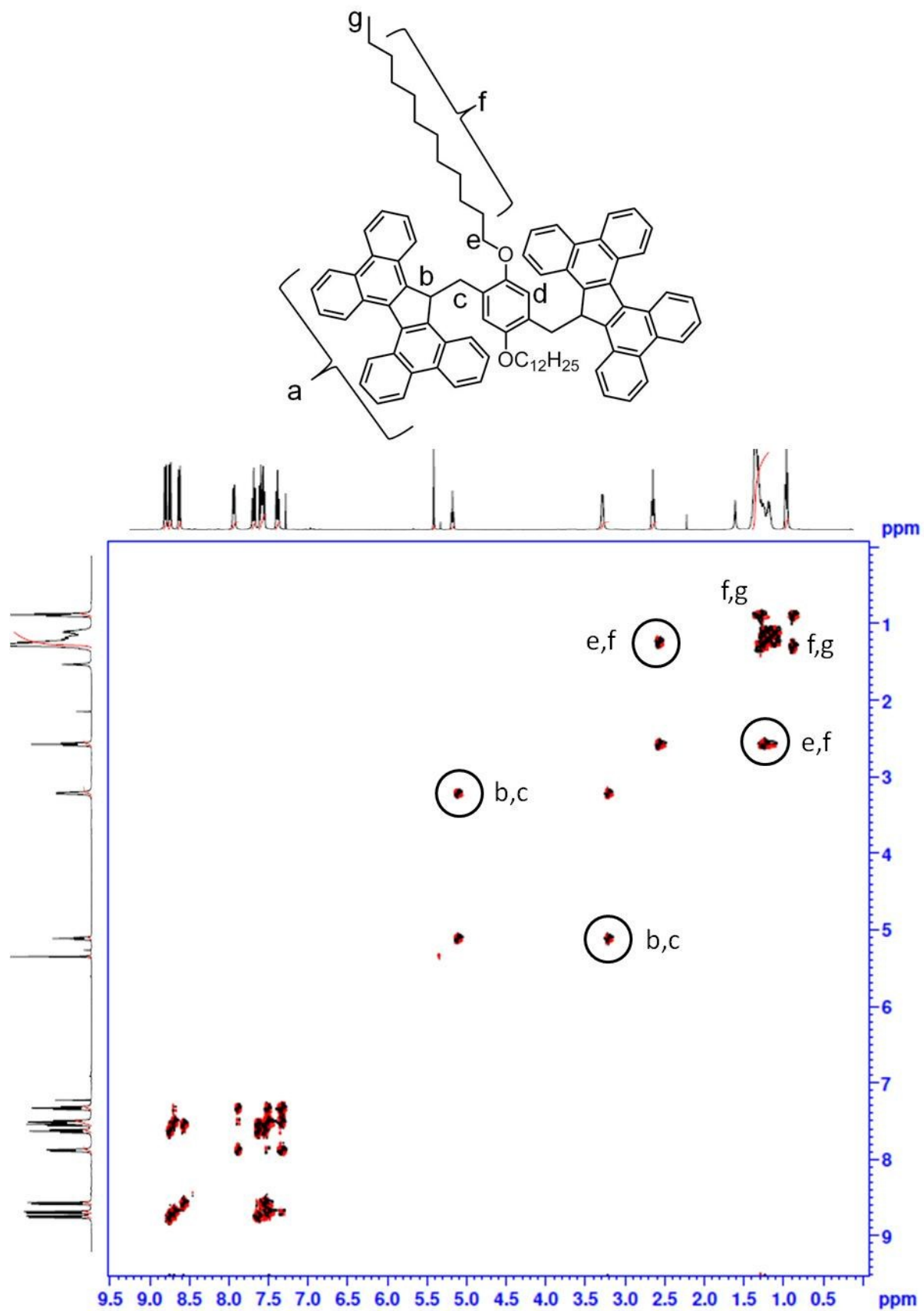


Fig. S3. ^1H - ^1H DQF COSY NMR spectrum of **1** in CDCl_3 at 298 K.

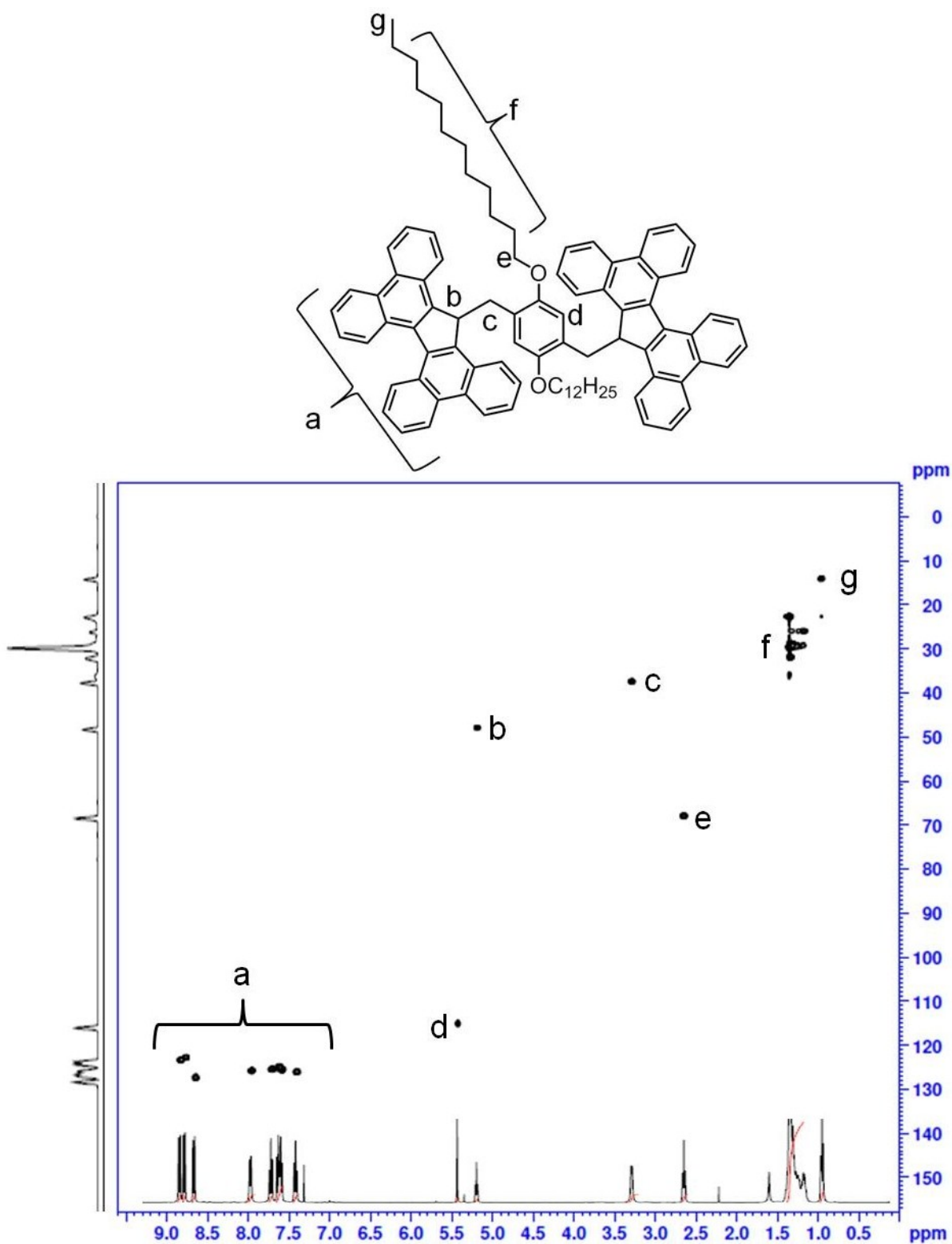


Fig. S4. ^1H - ^{13}C HSQC NMR spectrum of **1** in CDCl_3 at 298 K.

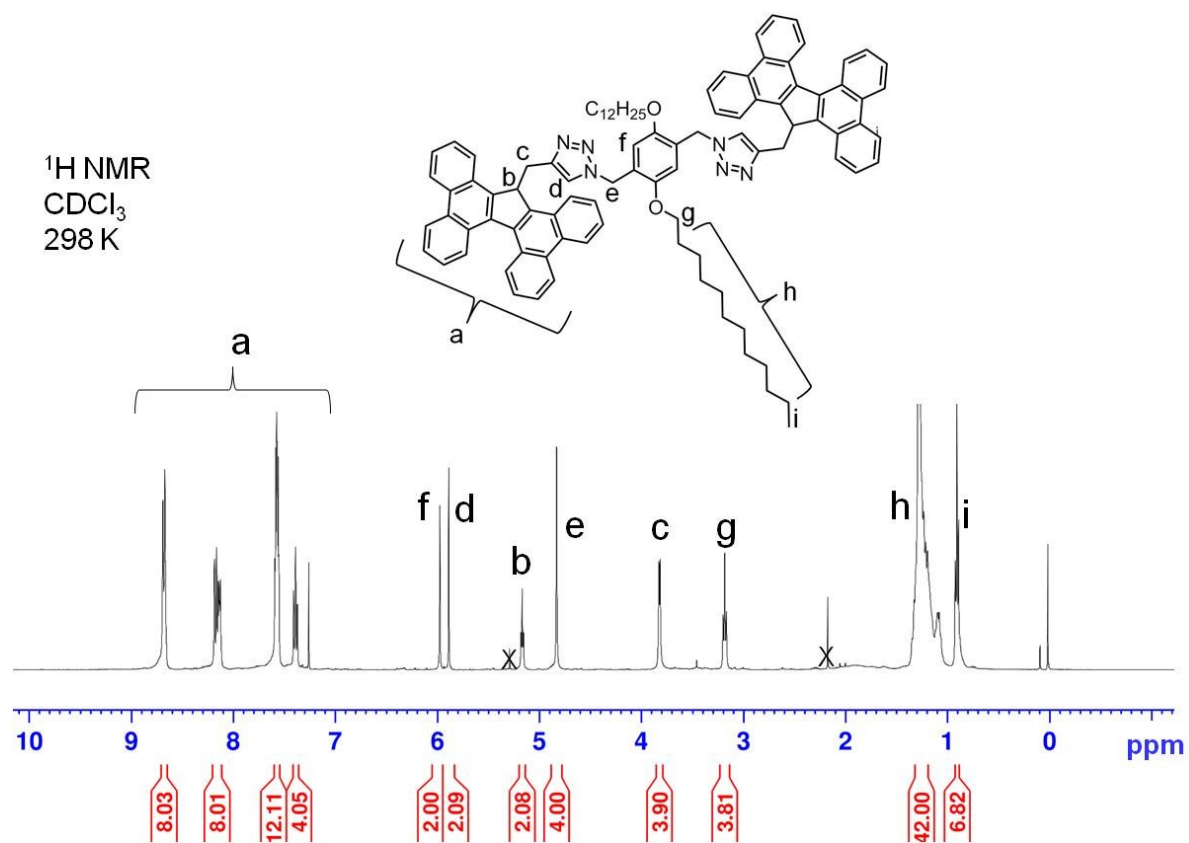


Fig. S5. ¹H NMR spectrum of **2** in CDCl₃ at 298 K. x : dichloromethane and acetone.

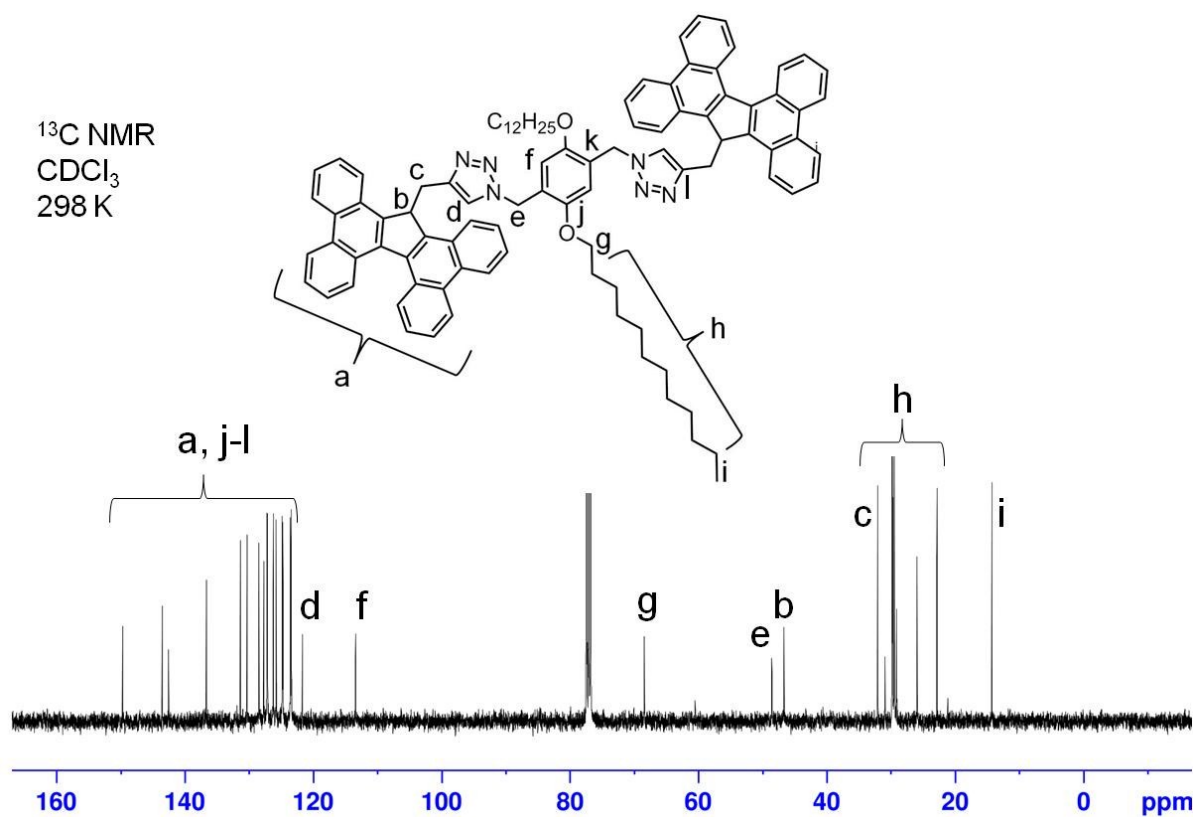


Fig. S6. ¹³C NMR spectrum of **2** in CDCl₃ at 298 K.

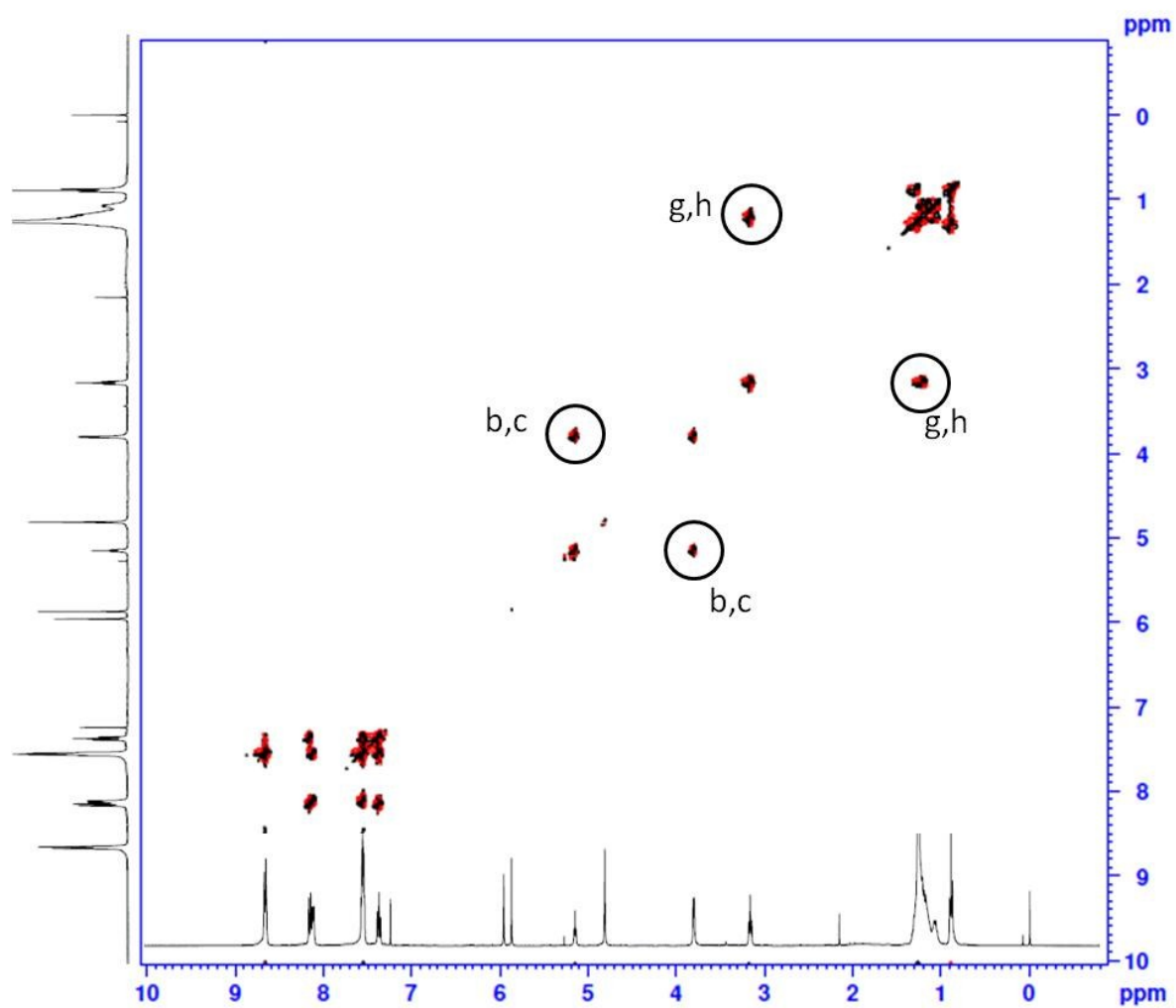
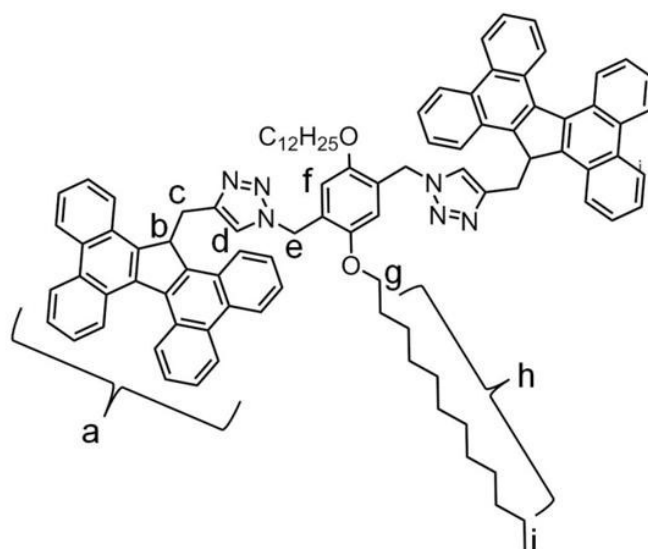


Fig. S7. ¹H-¹H DQF COSY NMR spectrum of **2** in CDCl₃ at 298 K.

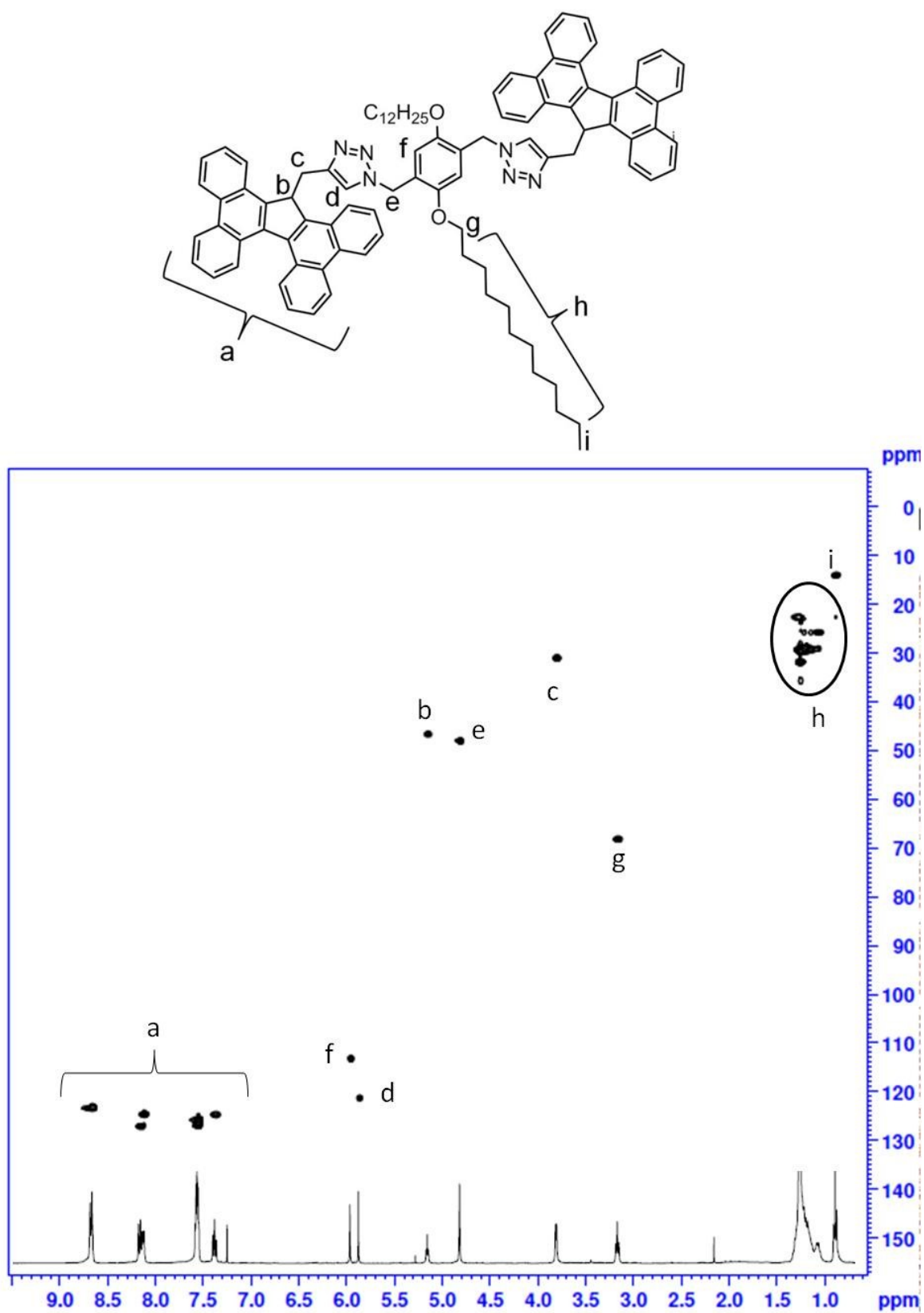


Fig. S8. ^1H - ^{13}C HSQC NMR spectrum of **1** in CDCl_3 at 298 K.

Section B. Single crystal X-ray structure of **1**

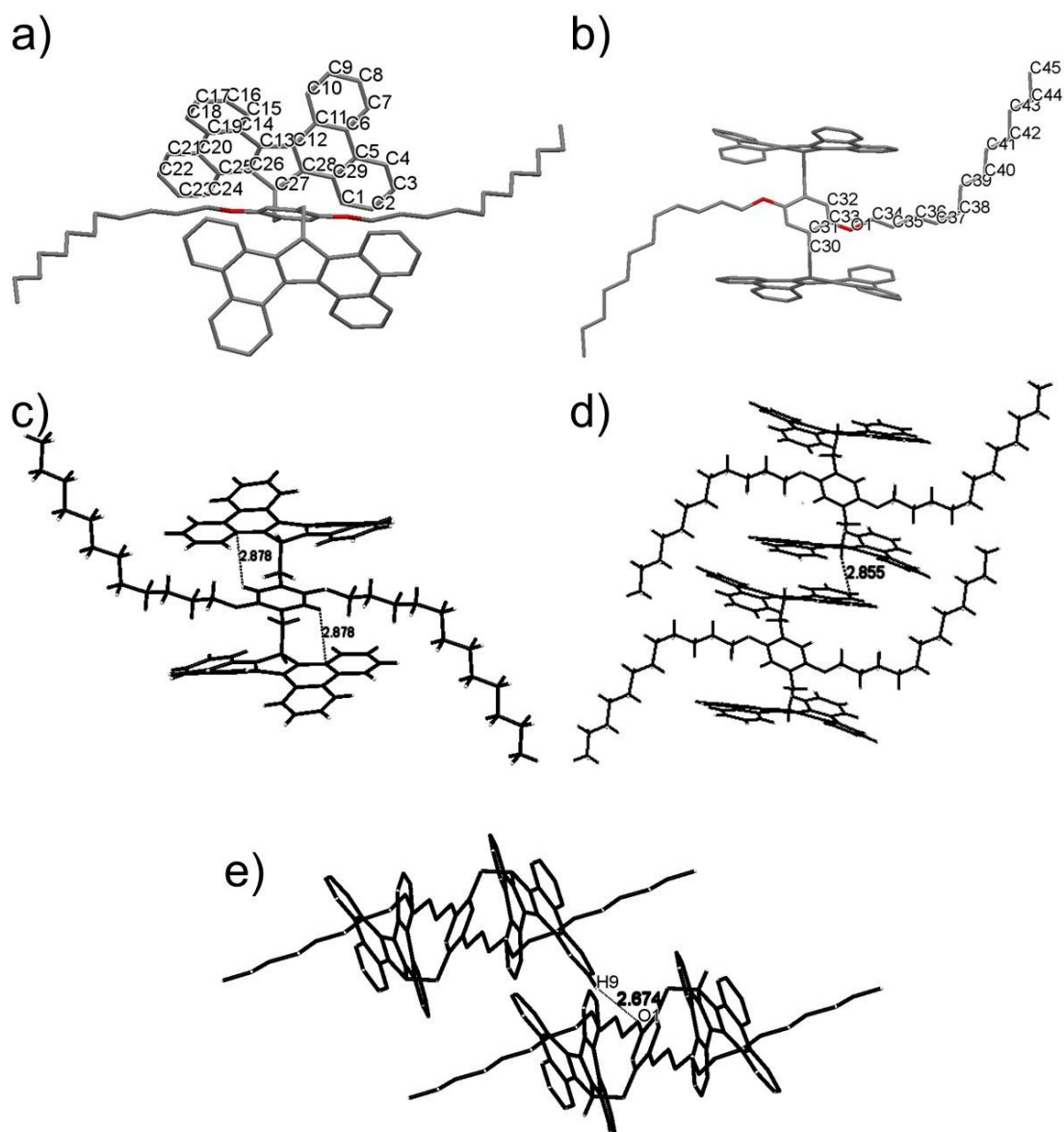


Fig. S9. Single crystal X-ray structure of **1** a) and b) shows the labelling of carbon atoms. c) shows the distance between C29 and H32, d) shows the intermolecular distance between C7 and H27 and e) shows the distance between O1 and H9.

Table S1. Hydrogen bond geometry for **1**.

S. No	D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)	Symmetry code: (i)
1	C27-H27...C7	0.981	2.855	3.654	139.19	1-x,3-y,1-z
2	C9-H9...O1	0.930	2.674	3.536	154.45	x, -1+y, z
3	C32-H32...C29	0.930	2.878	3.356	113.29	x, y, z

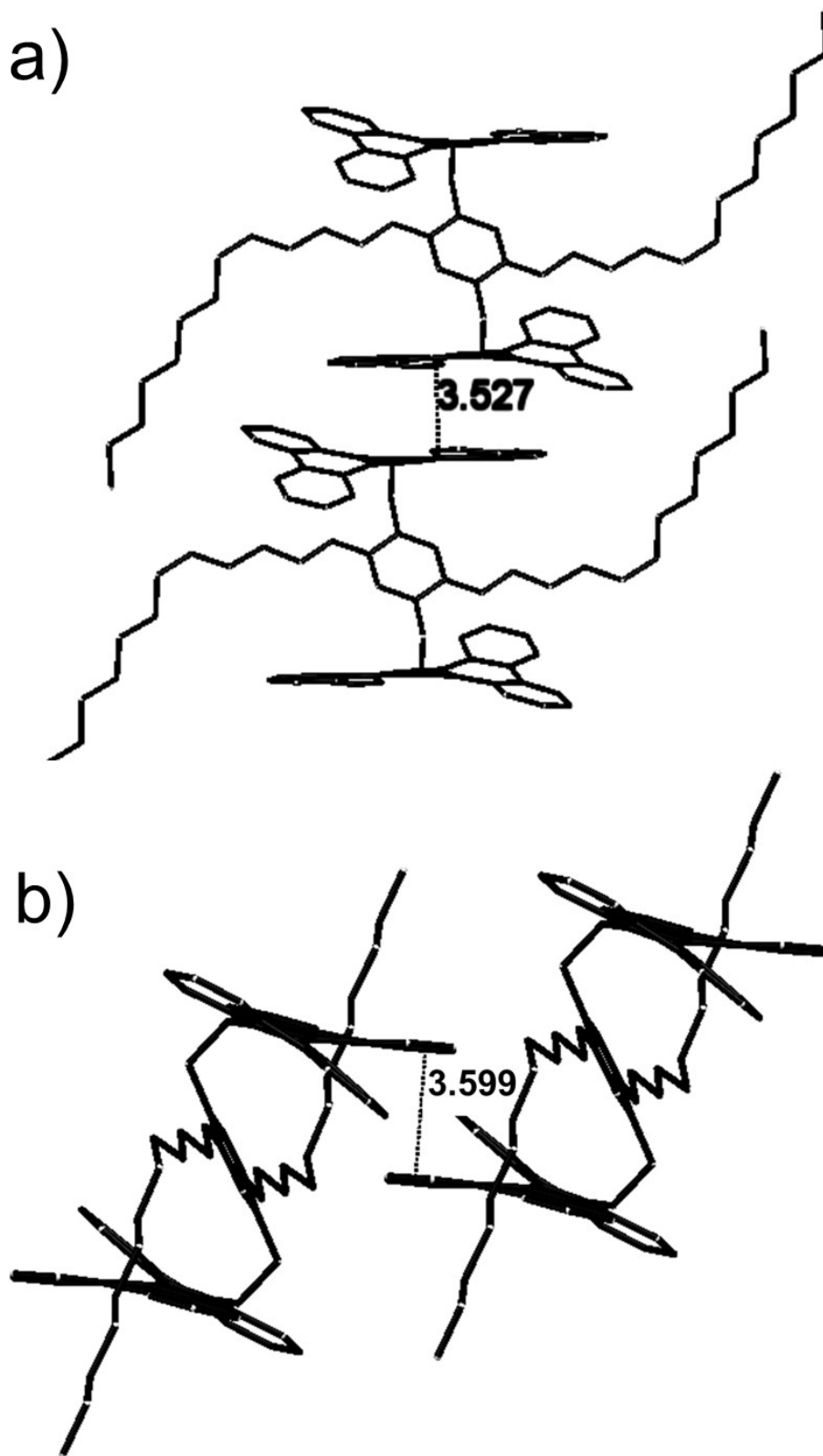


Fig. S10. Single crystal X-ray structure of **1** a) and b) shows the intermolecular π - π stacking.

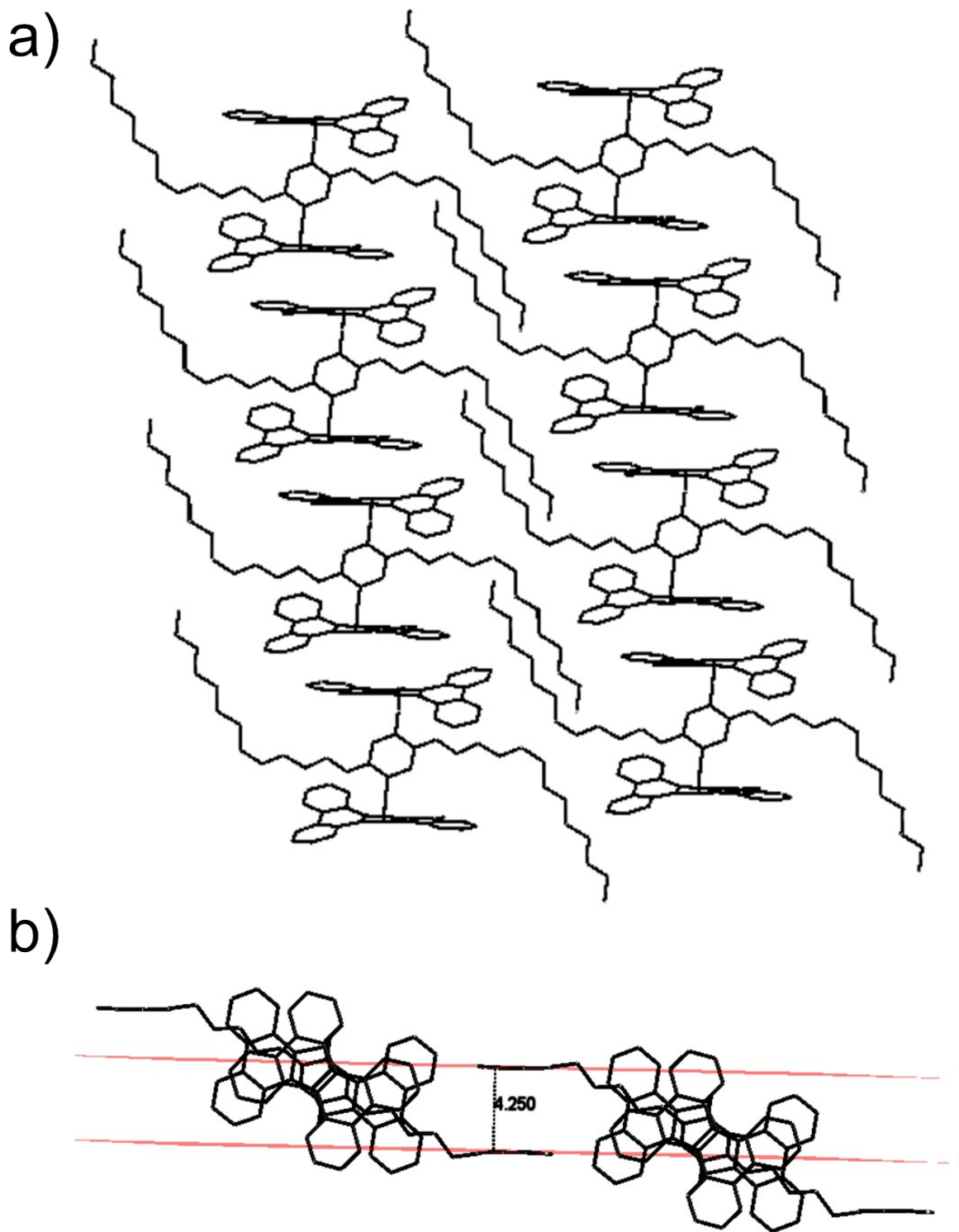


Fig. S11. Single crystal X-ray structure of **1** a) shows the molecular packing and b) shows the intermolecular distance between the planes of C40 to C45 alkyl chain.

Section C. Powder X-ray Diffraction spectra of 1 and 2

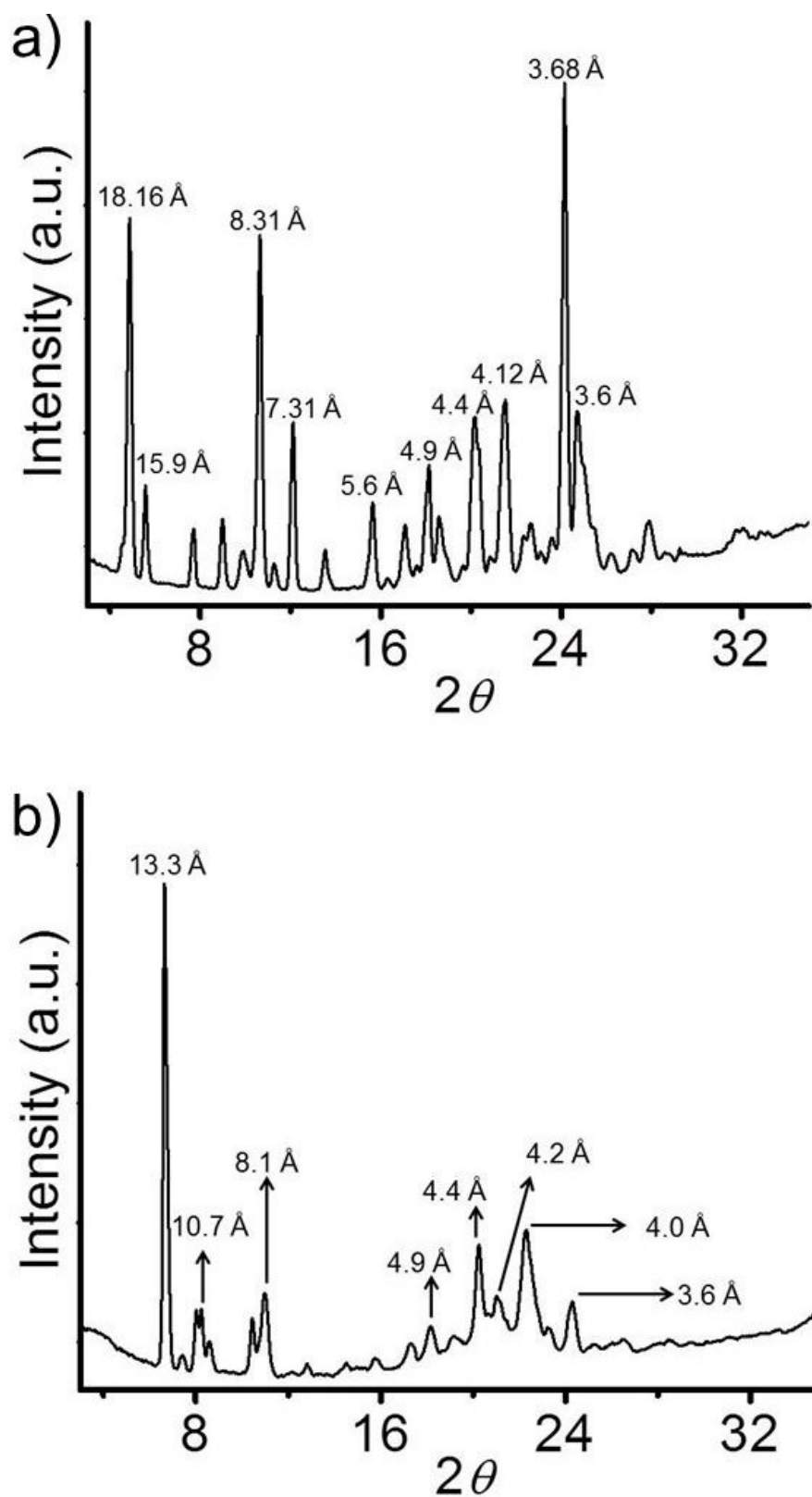


Fig. S12. Powder X-ray diffraction spectra of a) 1 and b) 2.

Section D. TGA spectra of 1 and 2

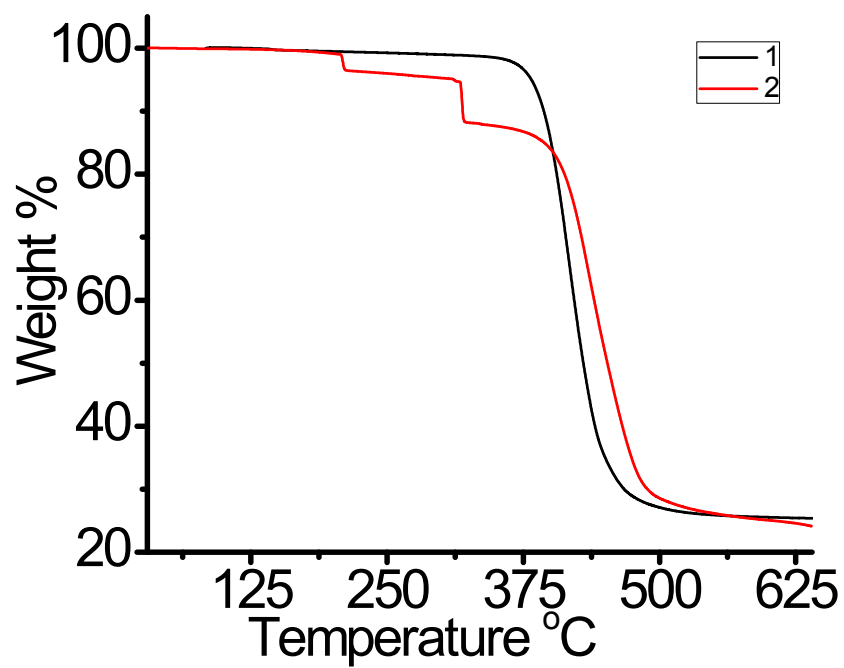


Fig. S14. TGA curves of 1 and 2 at heating rate of 10 °C/min under N₂ atmosphere.

Section E. DSC spectra and HOPM images of 1 and 2

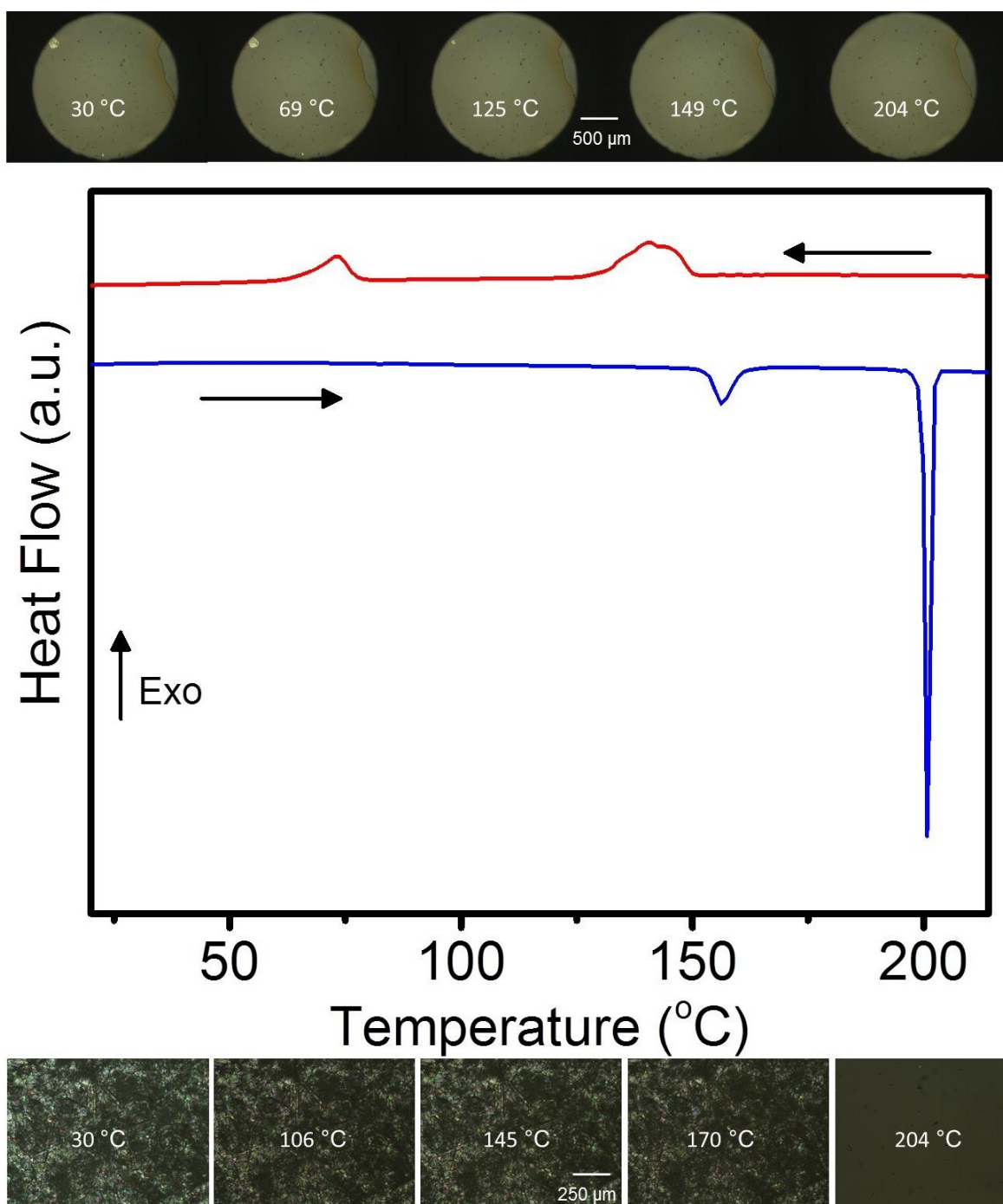


Fig. S15. DSC trace of **1** at heating and cooling cycle at 5 °C/min under N₂ atmosphere (first cycle). The inset shows the HOPM images at respective transition temperature in both heating and cooling cycle. HOPM images were recorded by placing the sample between glass covers on a temperature controlled hot stage

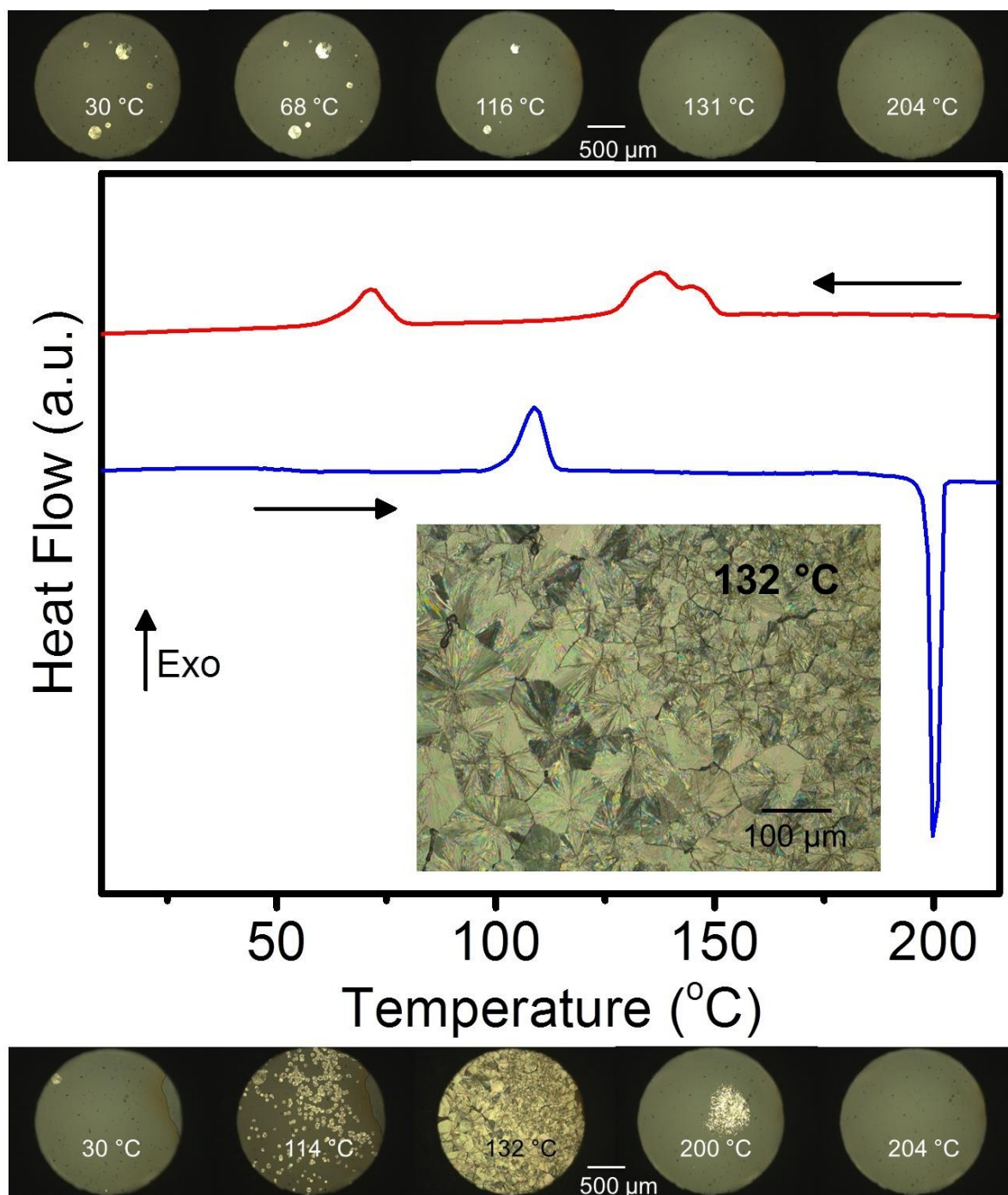


Fig. S16. DSC trace of **1** at heating and cooling cycle at 5 °C/min under N₂ atmosphere (second cycle). The inset shows the HOPM images at respective transition temperature in both heating and cooling cycle. HOPM images were recorded by placing the sample between glass covers on a temperature controlled hot stage.

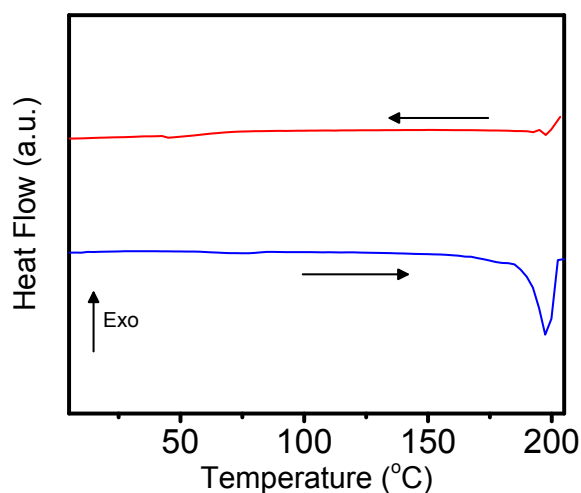


Fig. S17. DSC trace of **2** at heating and cooling cycle at 5 °C/min under N₂ atmosphere (first cycle).

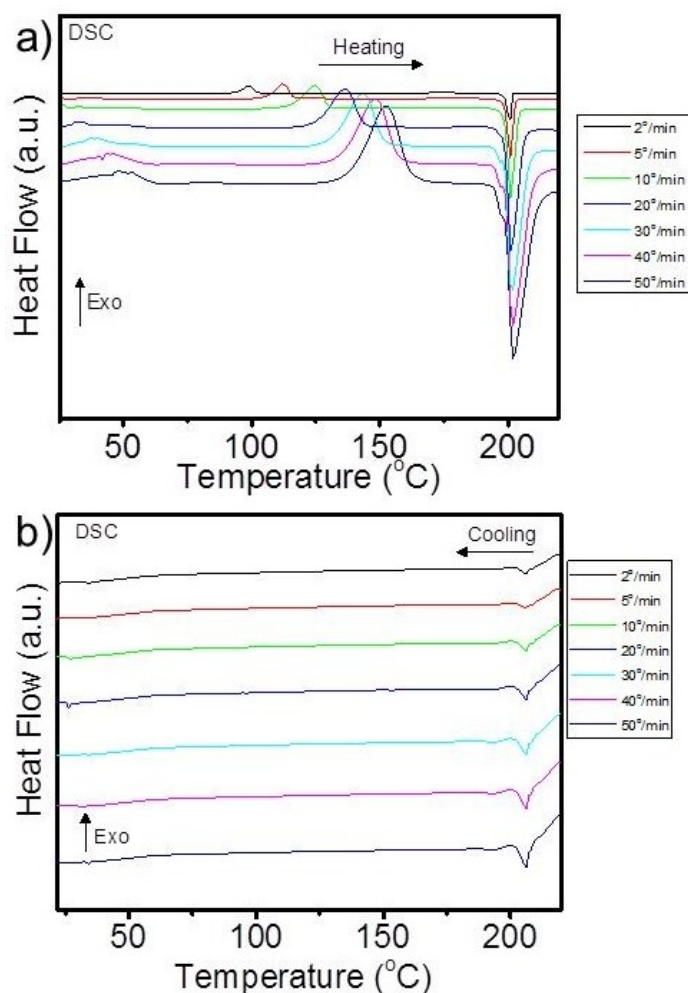


Fig. S18. The effect of heating rate on the cooling traces of **1** are studied by keeping the cooling rate constant (10 °C/min) and varying the previous step heating rates. a) Heating traces of **1** with varying heating rates while the cooling rate is kept constant at 10 °C/min. a) All cooling traces at a cooling rate of 10 °C/min, however, the different color curves indicate their earlier step's heating rate.

Table S2. DSC spectra details of **1** as a function of heating rate.

S. No	λ (K/min)	T_p (K)
1	2	371.8
2	5	385.2
3	10	397.8
4	20	409.3
5	30	416.3
6	40	421.2
7	50	425.4

Kissinger equation:¹

$$\ln(\lambda/T_p^2) = -E_a/RT_p + C \dots\dots\dots 1$$

Where R is gas constant, T_p is crystallization peak temperature, λ is DSC heating rate, E_a is the crystallization activation energy and C is a constant.¹ The slope of $\ln(\lambda/T_p^2)$ vs $1/T_p$ gives the value for E_a/R . The calculated E_a is 71 ± 0.8 kJ/mol ($R^2 = 0.999$).

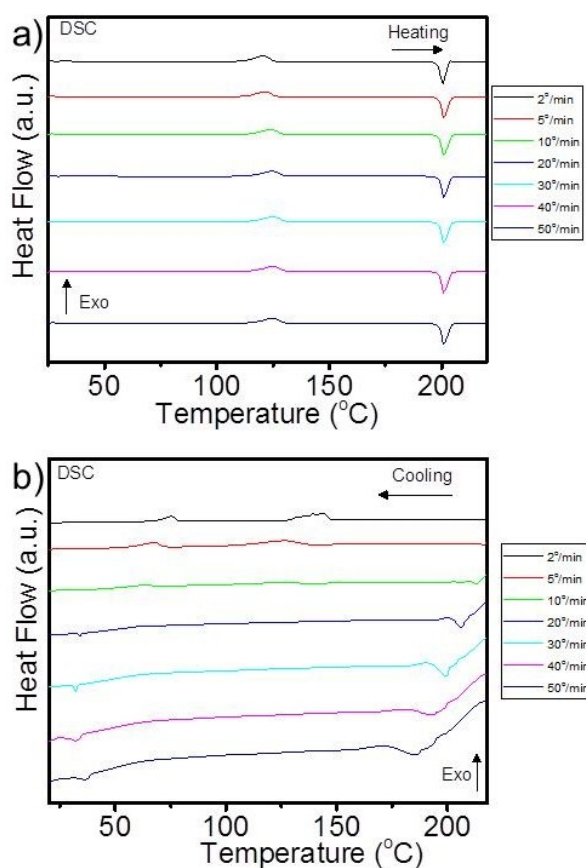


Fig. S19. The effect of cooling rate on the heating traces of **1** are studied by keeping the heating rate constant (10 °C/min), however, the different color curves indicate their earlier step's cooling rate. a) All heating traces at a heating rate of 10 °C/min, however, the different color curves indicate their earlier step's cooling rate. b) Cooling traces of **1** with varying cooling rates while the heating rate is kept constant at 10 °C/min.

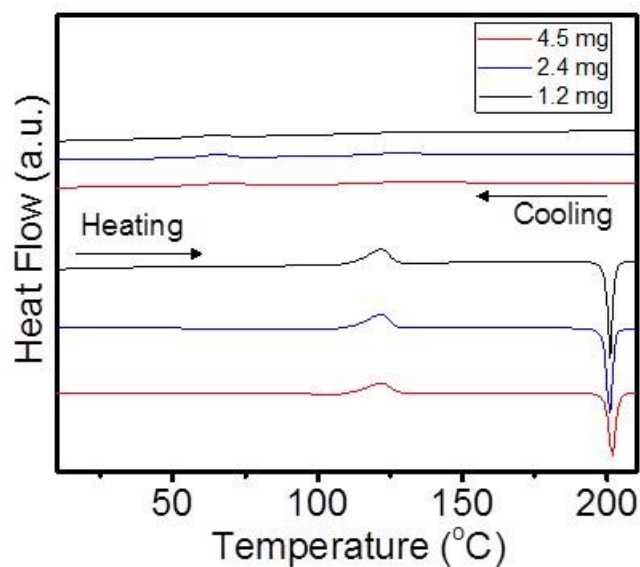


Fig. S20. DSC trace of **1** at heating and cooling cycle at 10 °C/min under N₂ atmosphere with different sample weight in the range of 1.2 mg to 4.5 mg (second cycle). The peak positions have negligible changes or trend with increase in the sample weight in the above analysed weight range.

Section F. NMR studies of **1** after DSC experiment

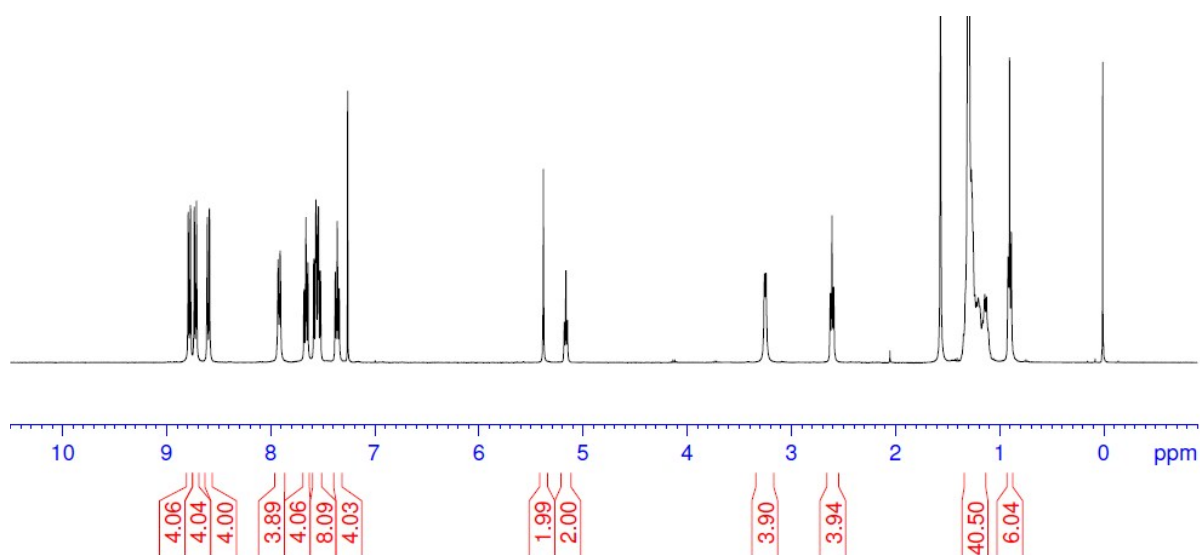


Fig. S21. ¹H NMR spectrum of **1** in CDCl₃ at 298 K. Sample preparation for ¹H NMR after DSC experiment, **1** was first subjected to heating up to 210 °C and subsequent cooling back to 25 °C with heating and cooling rate of 5 °C/min under N₂ atmosphere and then dissolved in CDCl₃.

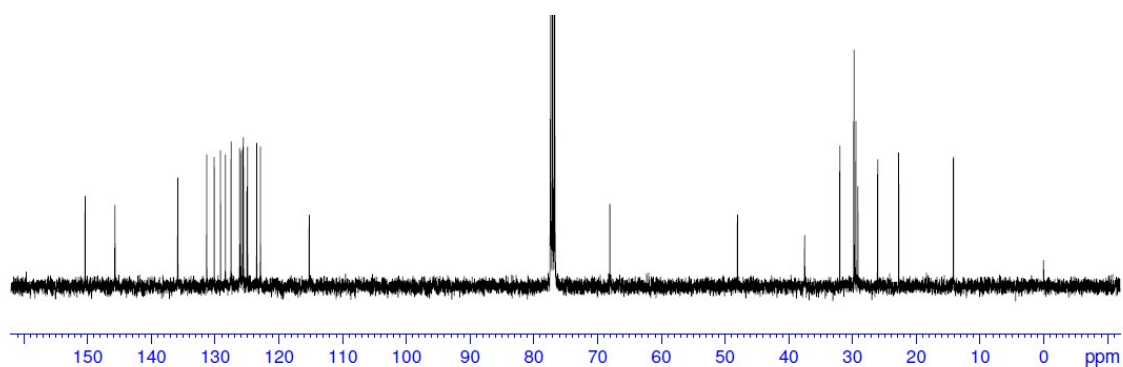


Fig. S22. ^{13}C NMR spectrum of **1** in CDCl_3 at 298 K. Sample preparation for ^{13}C NMR after DSC experiment, **1** was first subjected to heating up to 210 $^\circ\text{C}$ and subsequent cooling back to 25 $^\circ\text{C}$ with heating and cooling rate of 5 $^\circ\text{C}/\text{min}$ under N_2 atmosphere and then dissolved in CDCl_3 .

Section G. Optical studies of **1** and **2**

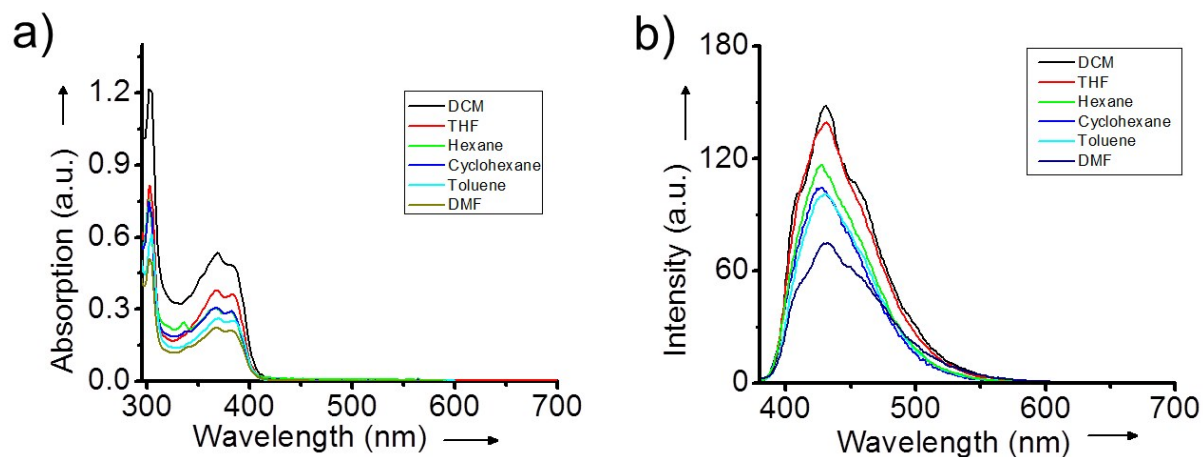


Fig. S23. a) Absorption and b) Fluorescence spectra of **1** in dichloromethane (DCM), tetrahydrofuran (THF), hexane, cyclohexane, toluene and dimethylformamide (DMF) at 25 $^\circ\text{C}$. $\lambda_{\text{ex}}=360$ nm ($l = 1$ cm, $c = 1 \times 10^{-5}\text{M}$).

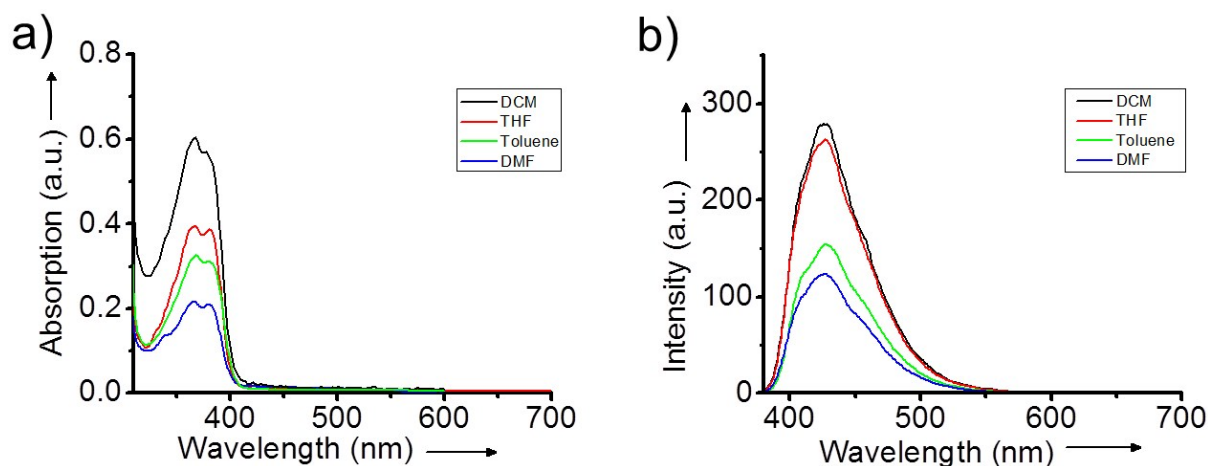


Fig. S24. a) Absorption and b) Fluorescence spectra of **2** in dichloromethane (DCM), tetrahydrofuran (THF), toluene and dimethylformamide (DMF) at 25 °C. $\lambda_{\text{ex}}=360$ nm ($l = 1$ cm, $c = 1 \times 10^{-5}$ M).

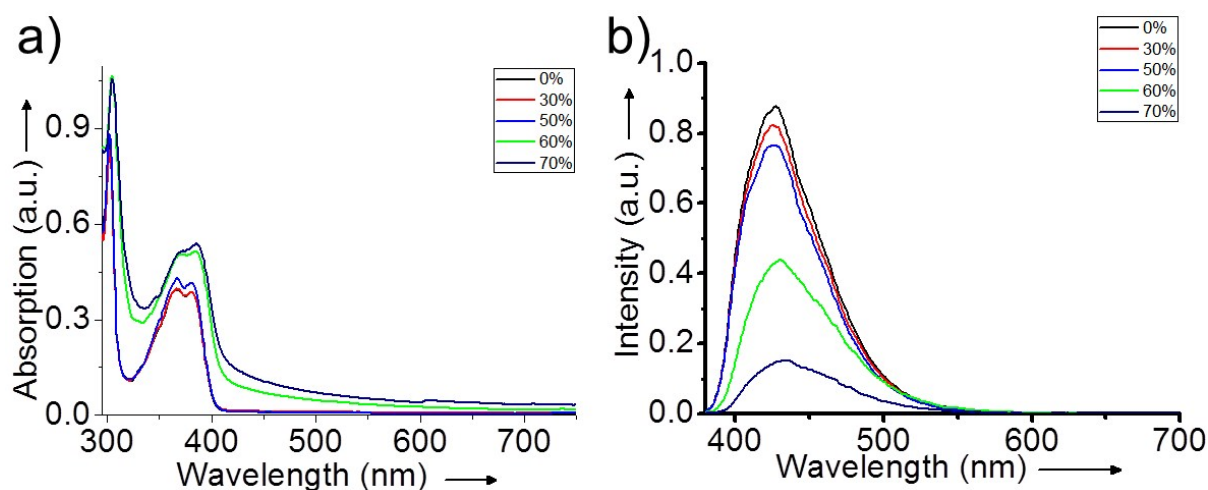


Fig. S25. a) Absorption and b) Fluorescence spectra of **2** in various tetrahydrofuran (THF) water mixture ratio (From 0 % water to 70 % water in THF) at 25 °C. $\lambda_{\text{ex}}=360$ nm ($l = 1$ cm, $c = 1 \times 10^{-5}$ M).

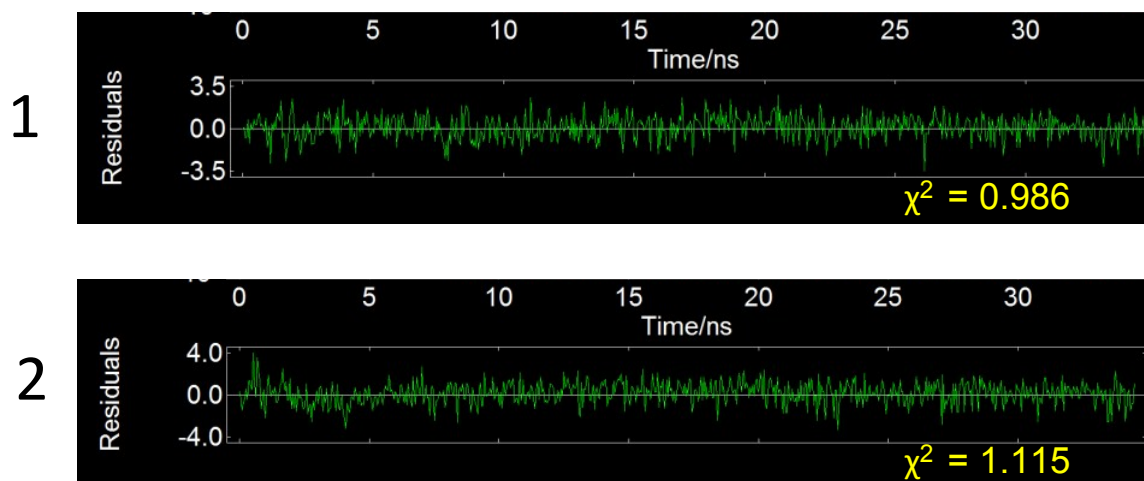
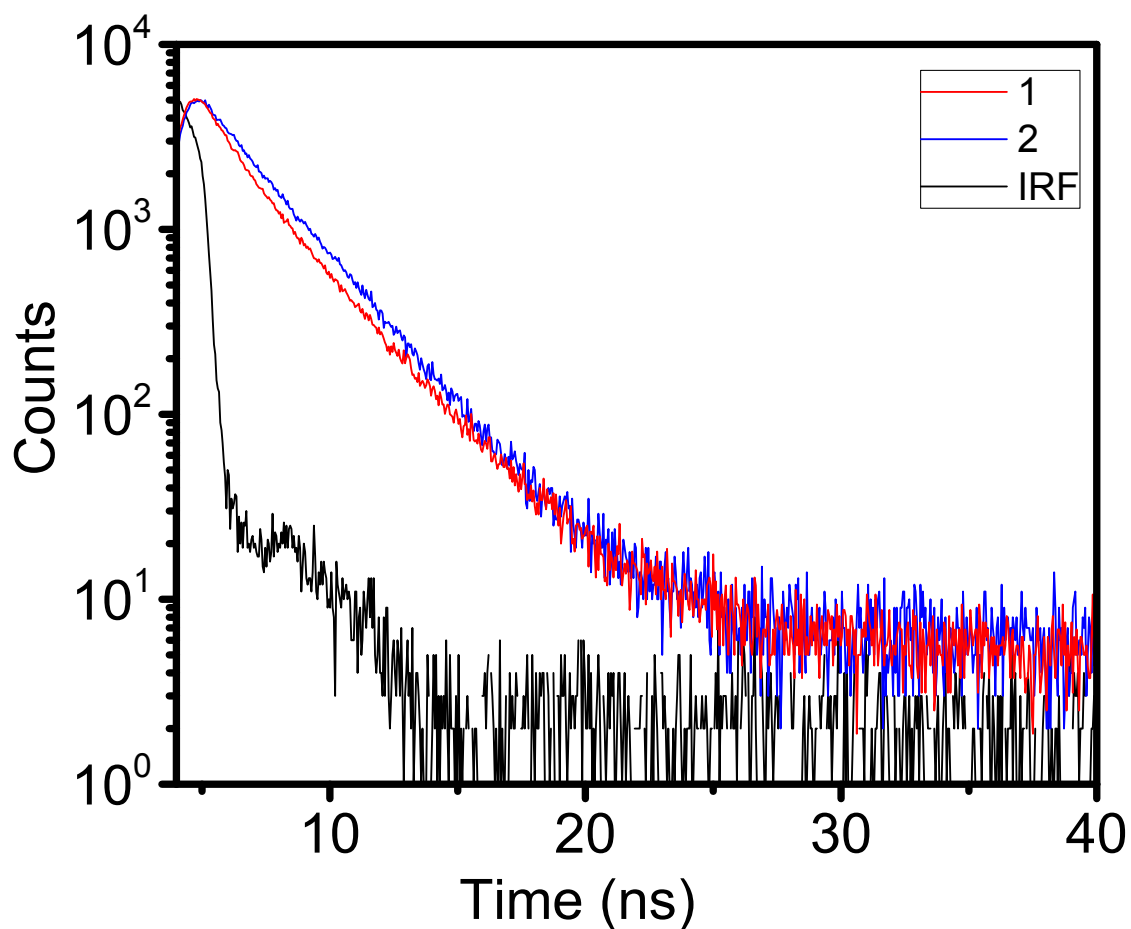


Fig. S26. Fluorescence decay curves of **1** and **2** in THF solution, emission monitored at 430 nm, $\lambda_{\text{ex}} = 375$ nm at 25 °C. ($l = 1$ cm, $c = 1 \times 10^{-5}$ M). Bottom panel shows the residual traces of fluorescence decay curves fitting along with their corresponding χ^2 values.

Table S3. Optical properties of **1** in various solvents.

S. No	Solvent	Absorption Maxima λ_{abs} (nm)	Emission Maximum λ_{em} (nm)	Stokes Shift $\Delta\nu_{\text{st}}$ cm ⁻¹	molar extinction coefficient (ϵ) x 10 ⁴ M ⁻¹ cm ⁻¹	Quantum Yield (Φ_f)
1	DCM	368, 382	431	3971	5.33	0.32
2	THF	368, 382	431	3971	3.78	0.33
3	Hexane	366, 380	427	3903	3.05	0.35
4	Cyclohexane	366, 382	427	3903	3.06	0.33
5	Toluene	370, 384	430	3772	2.63	0.31
6	DMF	368, 382	432	4025	2.22	0.33

[a] $\Delta\nu_{\text{st}} = \lambda_{\text{abs}} - \lambda_{\text{em}}$, and is the difference in absorption and emission frequencies, or the Stokes shift. $\lambda_{\text{ex}} = 360$ nm. Quinine sulphate in 0.5M H₂SO₄ used as quantum yield reference. Fluorescence quantum yields ($\pm 5\%$ error) were determined using quinine sulfate as the standard ($\Phi_f = 0.546$ in 0.1 N H₂SO₄).²

Table S4. Optical properties of **2** in various solvents.

S.No	Solvent	Absorption Maxima λ_{abs} (nm) _x	Emission Maximum λ_{em} (nm)	Stokes Shift $\Delta\nu_{\text{st}}$ cm ⁻¹	molar extinction coefficient (ϵ) X 10 ⁴ M ⁻¹ cm ⁻¹	Quantum Yield (Φ_f)
1	DCM	368, 378	426	3699	6.04	0.39
2	THF	367, 381	427	3828	3.94	0.38
3	Toluene	368, 380	427	3754	3.26	0.38
4	DMF	366, 380	425	3793	2.16	0.39

[a] $\Delta\nu_{\text{st}} = \lambda_{\text{abs}} - \lambda_{\text{em}}$, and is the difference in absorption and emission frequencies, or the Stokes shift. $\lambda_{\text{ex}} = 360$ nm. Quinine sulphate in 0.5M H₂SO₄ used as quantum yield reference. Fluorescence quantum yields ($\pm 5\%$ error) were determined using quinine sulfate as the standard ($\Phi_f = 0.546$ in 0.1 N H₂SO₄).²

Table S5. Optical properties of **1** and **2** in THF solution.

Compound	Quantum Yield (Φ_f)	Lifetime τ (ns)	Average Lifetime τ_{av} (ns)	k_r (s ⁻¹)	k_d (s ⁻¹)	k_r/k_d
1	0.33	1.26 (35 %) 2.85 (65 %)	2.54	1.3 x 10 ⁸	2.6 x 10 ⁸	0.50
2	0.38	2.55 (100 %)	-	1.5 x 10 ⁸	2.4 x 10 ⁸	0.63

The average life time (τ_{av}) of the biexponential decay was calculated based on the equation $\tau_{\text{av}} = (a_1\tau_1^2 + a_2\tau_2^2) / (a_1\tau_1 + a_2\tau_2)$, where 'a' is the amplitude and 'τ' is the corresponding life time of the decay components.³

Section H. DLS spectra of 1 and 2

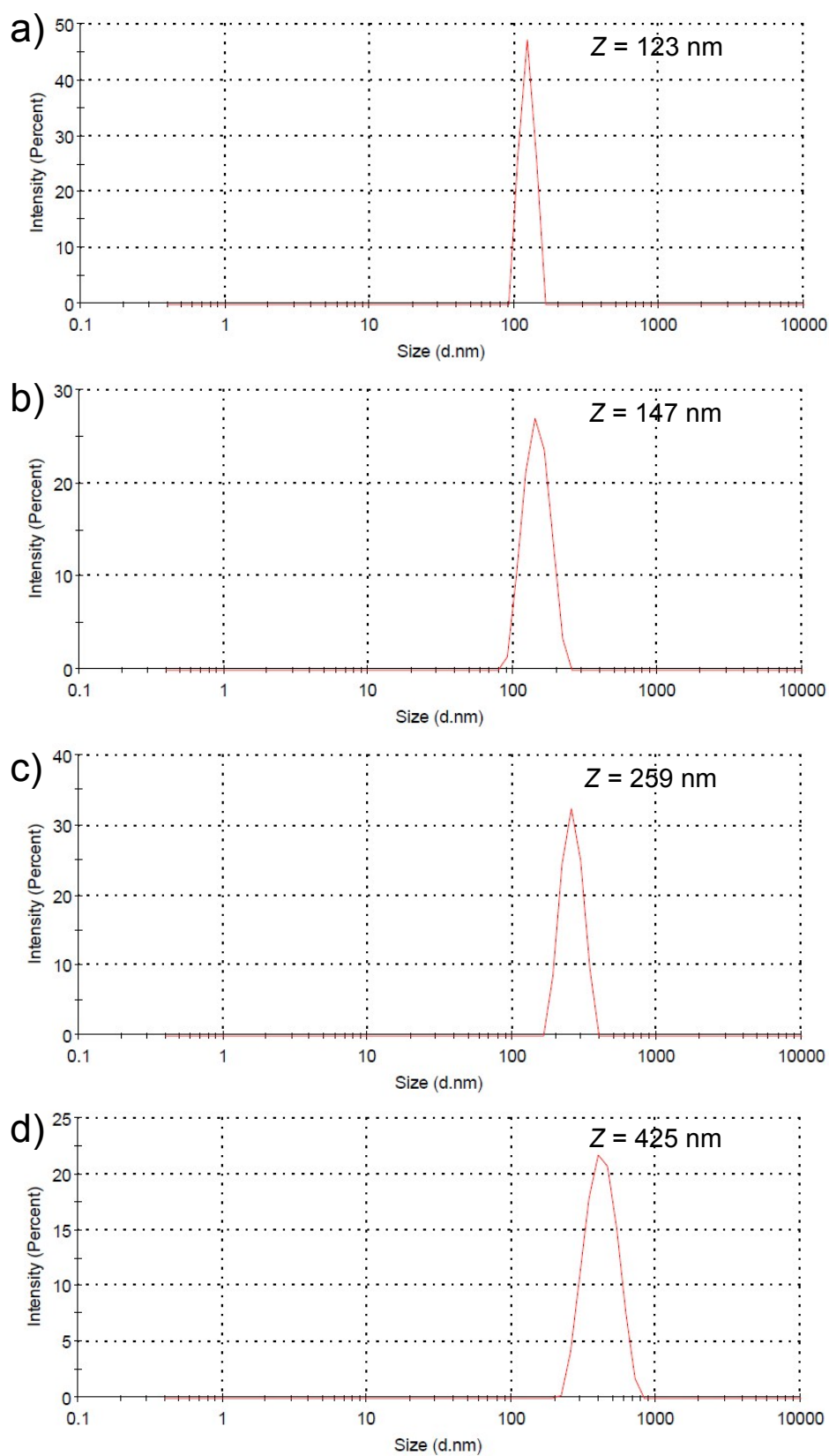


Fig. S27. Dynamic light scattering (DLS) spectra of **1** in a) THF, b) 10, c) 30 and d) 50% water:THF mixture at 25 °C ($l=1$ cm, $c = 1 \times 10^{-5}$ M).

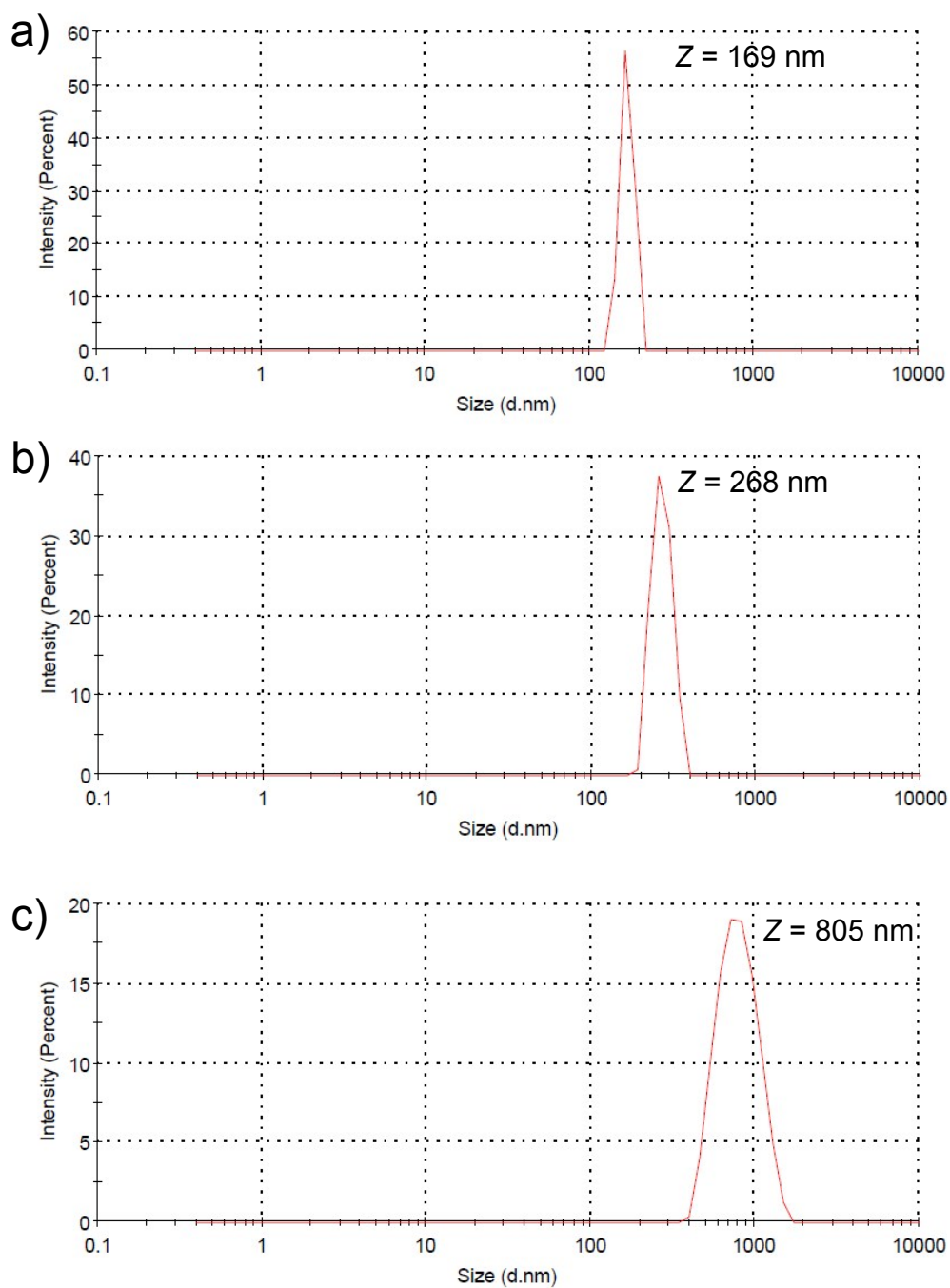


Fig. S28. Dynamic light scattering (DLS) spectra of **2** in **1** in a) THF, b) 10 and c) 30% water:THF mixture at 25 °C ($l = 1$ cm, $c = 1 \times 10^{-5}$ M).

Section I. Microscopic images of 1 and 2

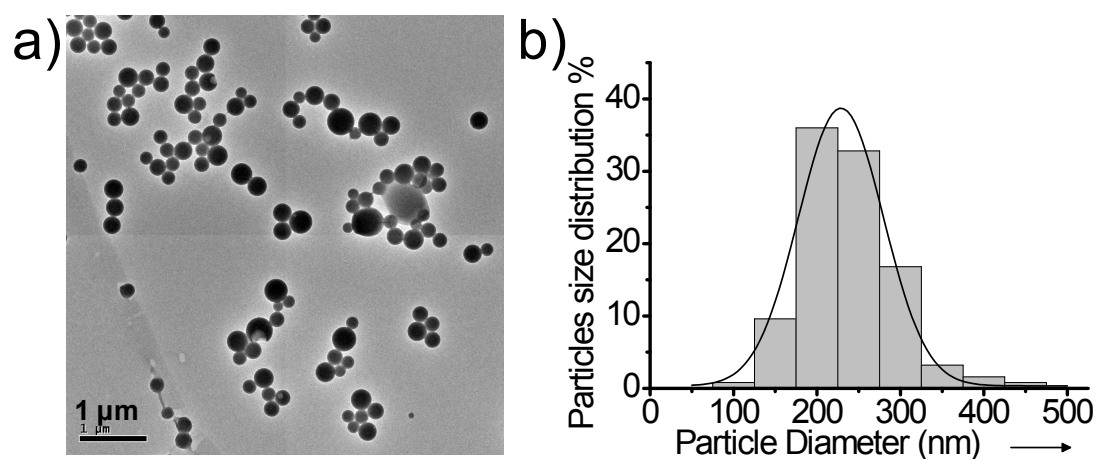


Fig. S29. a) HRTEM images of **1** drop casted from 1×10^{-4} M water:THF (30:70) solution mixture, b) Particle size distribution bar diagram of **1** obtained by analysing the particle size from HRTEM image of **1**.

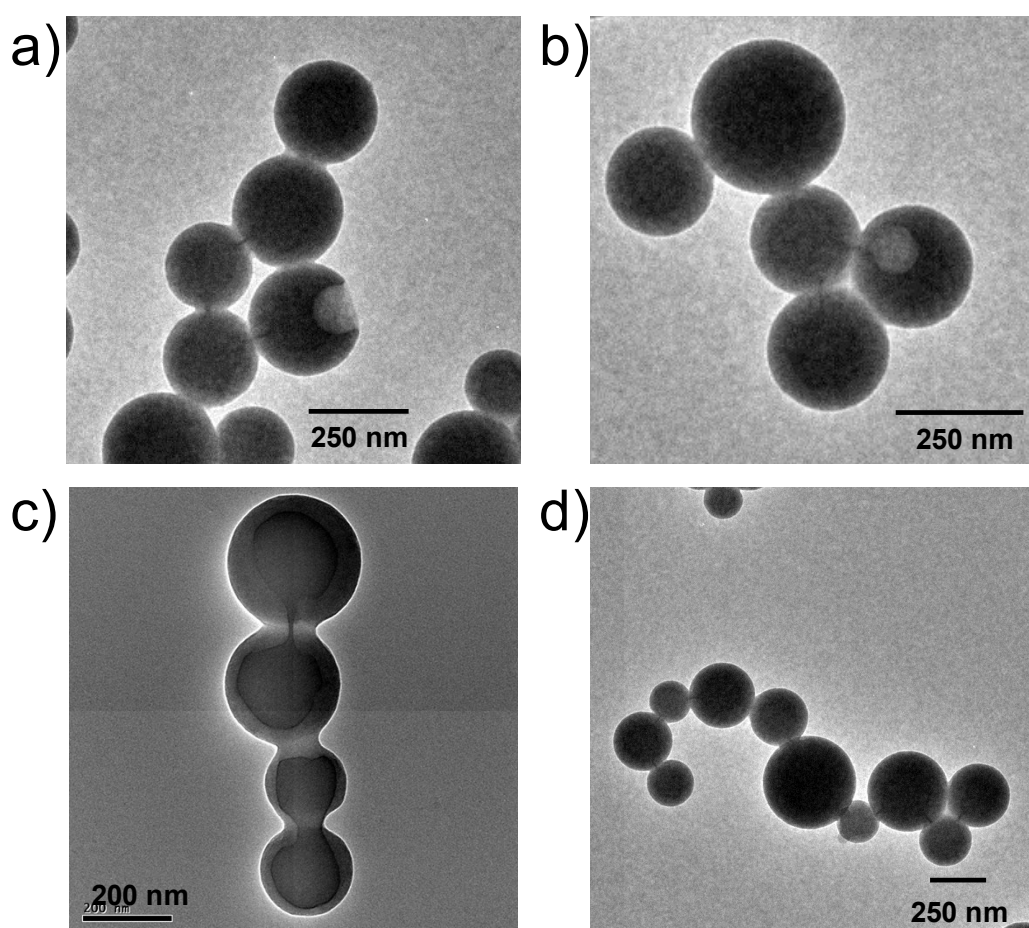


Fig. S30. a)-d) HRTEM images of **1** drop casted from 1×10^{-4} M water:THF (30:70) solution mixture at various location and magnification. The sample is drop casted on carbon-coated TEM grids and solvents are removed by keeping the samples under vacuum at room temperature for 24 hours.

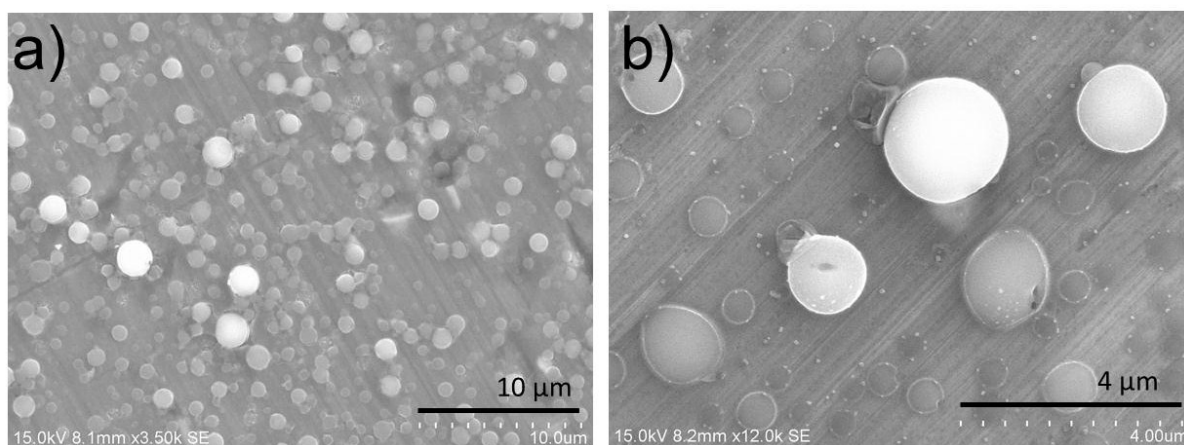


Fig. S31. FESEM images of a) **1** drop casted from 1×10^{-4} M water:THF (30:70) solution mixture, b) **2** drop casted from 1×10^{-4} M water:THF (30:70) solution mixture.

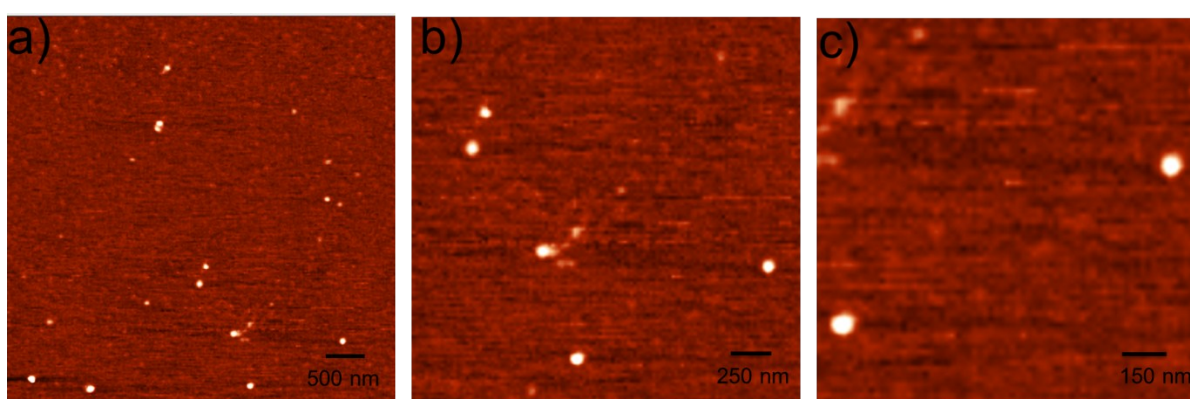


Fig. S32. a)-c) AFM images of **1** drop casted from 1×10^{-4} M water:THF (30:70) solution mixture at various magnification. The sample is drop casted on freshly cleaved mica surface and solvents are removed by keeping the samples under vacuum at room temperature for 24 hours.

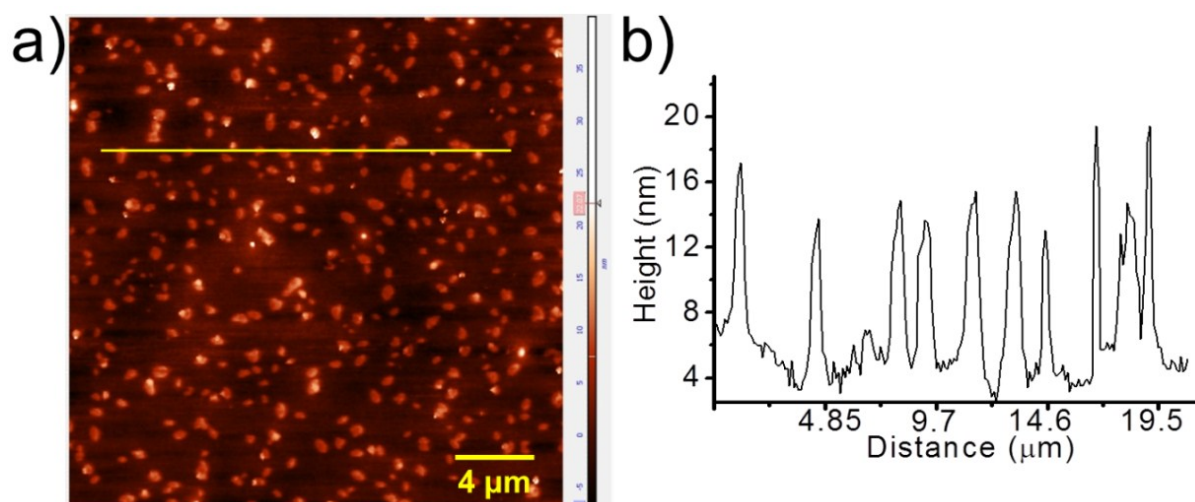


Fig. S33. a) AFM height images of **1** drop casted from 1×10^{-4} M toluene solution. b) the height profile of line shown in (a). The sample is drop casted on freshly cleaved mica surface and solvent was removed by keeping the samples under vacuum at room temperature for 24 hours.

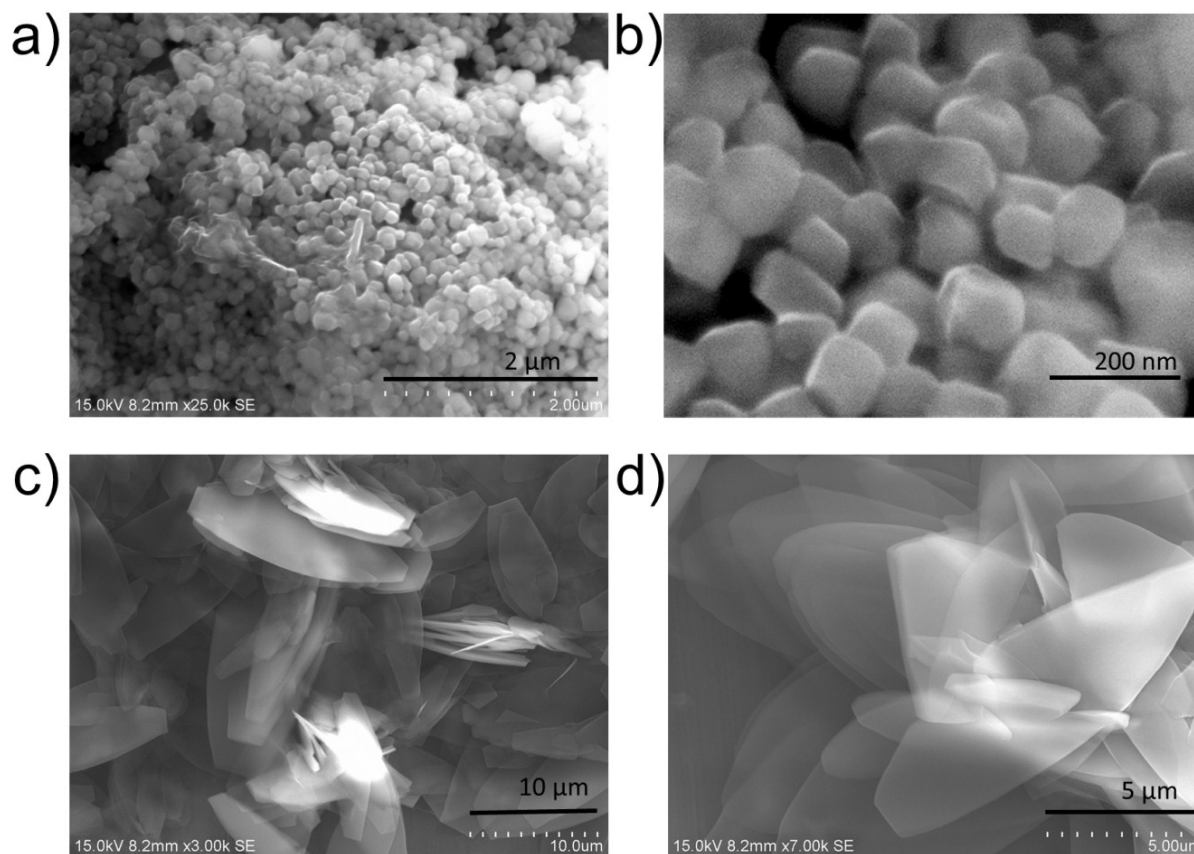


Fig. S34. a) and b) FESEM images of **1** drop casted from 1×10^{-4} M toluene solution at different magnification. c) and d) FESEM images of **2** drop casted from 1×10^{-4} M toluene solution at various location and magnification. The samples are drop casted on aluminum foil and solvent was removed by keeping the samples under vacuum at room temperature for 24 hours.

Section J. References

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