Electronic Supplementary Information

Tunable Multi-color Luminescence from a Self-assembled Cyanostilbene and Cucurbit[7]uril in Aqueous Media

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SUPPORTING INFORMATION

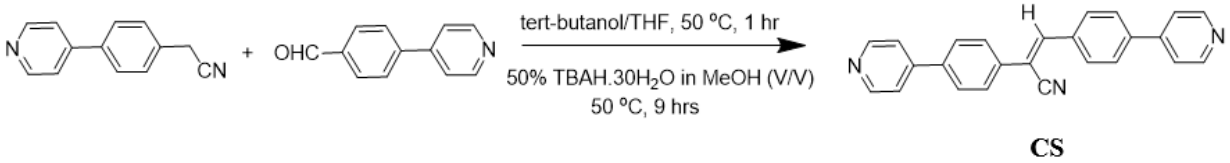
Contents:

1 General Experimental Methods

All starting materials were purchased from commercially available sources and used without further purification. 4-(pyridin-4-yl)benzaldehyde, (4-(cyanomethyl)phenyl)boronic acid and 4-

bromopyridine hydrochloride were purchased from Combi-Blocks. Cucurbit[7]uril, 1-adamantylamine, Tetrabutylammonium hydroxide 30-hydrate, 1-bromoethane, 1-bromododecane and tert-butanol were purchased from Sigma-Aldrich. UV-Vis spectroscopic measurements were carried out in Agilent Technologies Cary 8454 spectrophotometer. Emission spectroscopic measurements were carried out in Horiba Fluoromax 4 spectrofluorometer. ITC experiments were performed in a Malvern MICROCAL PEAQ-ITC instrument. Fluorescence images were taken under 365 nm UV lamp. SEM images was recorded by using the CARL ZEISS (Model- SUPRA 55VP) instrument. DLS measurement was carried out using Malvern Zetasizer NanoZS. A Horiba Jobin Yvon Fluorocube instrument fitted with a 340 nm diode laser excitation source (with a temporal resolution of 70 ps) was used for the time-resolved fluorescence experiments applying the time correlated single photon counting (TCSPC) method. ^{1}H and ^{13}C NMR were performed on Jeol 400 MHz and Bruker 500 MHz spectrometers.

2 Synthetic Procedures

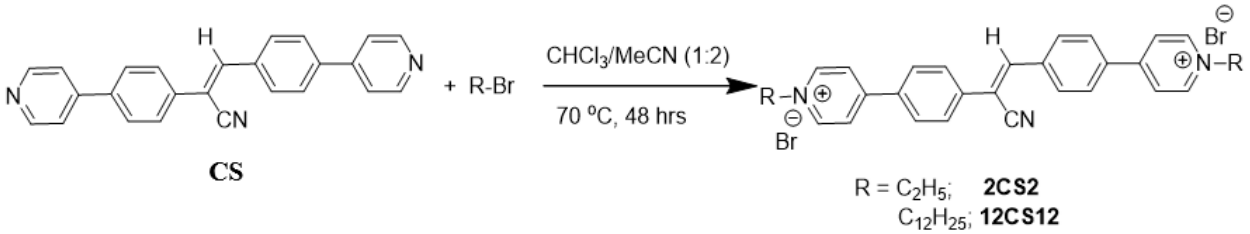


CS

Scheme S1. Synthetic scheme of **CS**

Procedure for synthesis of CS: 2-(4-(pyridin-4-yl)phenyl)acetonitrile was first synthesized from (4-(cyanomethyl)phenyl)boronic acid and 4-bromopyridine hydrochloride according to the literature procedure[1]. Then, (Z)-2,3-bis(4-(pyridin-4-yl)phenyl)acrylonitrile (**CS**) was prepared by slight modification as reported in the literature[1]. 4-(pyridin-4-yl)benzaldehyde (340 mg, 1.86 mmol) and 2-(4-(pyridin-4-yl)phenyl)acetonitrile (360 mg, 1.86 mmol) were taken in a 10 mL round bottom flask and dissolved in 6 mL *tert*-butanol and 0.30 mL tetrahydrofuran mixture. The reaction mixture was stirred for 1 hour at 50 °C. 0.8 mL 50% TBAH.30H_2O in methanol (V/V) was then added dropwise over a period of 15 min at 50 ^{0}C until the reaction mixture color became maroon in color. Stirring was continued for 9 more hours at 50 °C and then allowed to cool at room temperature. The yellowish white precipitate formed was then filtered and washed with *tert*-butanol for 3-4 times and finally dried under vacuum. Yield ~ 50%. ^{1}H NMR (400 MHz, $CDCl_3$):

δ (ppm) = 8.71 (d, J = 1 Hz, 4H), 8.05 (d, J = 8 Hz, 2H), 7.84 (d, J = 8 Hz, 2H), 7.76 (t, J = 8 Hz, 4H), 7.66 (s, 1H), 7.56 (t, J = 4 Hz, 4H).



Scheme S2. Synthetic scheme of N**CSN** (N = 2, 12)

General procedure for the synthesis of NCSN (N = 2, 12): CS (55 mg, 1.5 mmol) and corresponding alkyl halide (15 mmol) were taken in 10 mL reaction tube and dissolved in 2 mL acetonitrile and 1 mL chloroform solvents mixture. The reaction mixture was stirred at 70 ^{0}C under sealed condition for 48 hours and then allowed to cool at room temperature. The yellow precipitate formed was filtered and washed with cold chloroform for 3-4 times and finally dried under vacuum. 80% - 90% yields were obtained.

^{1}H NMR for **2CS2** (400 MHz, DMSO-D_6): δ(ppm) = 9.20 (t, J = 8 Hz, 4H), 8.63 (d, J = 8 Hz, 4H), 8.46 (s, 1H), 8.31 (t, J = 8 Hz, 4H), 8.24 (d, J = 8 Hz, 2H), 8.09 (d, J = 8 Hz, 2H), 4.66 (q, J= 8 Hz, 4H), 1.59 (t, J = 8 Hz, 6H); ^{13}C NMR for **2CS2** (500 MHz, DMSO-D_6): δ(ppm) = 153.30, 153.27, 144.75, 144.70, 143.25, 136.69, 130.33, 129, 128.73, 127.06, 124.67, 124.58, 117.30, 111.23, 55.57, 16.29; MS (ESI): m/z calculated for $C_{29}H_{27}N_3^{2+}$: 208.6097; found: 208.6097.

^{1}H NMR for **12CS12** (400 MHz, DMSO-D_6): δ(ppm) = 9.17 (t, J = 8 Hz, 4H), 8.62 (d, J = 8 Hz, 4H), 8.44 (s, 1H), 8.31 (t, J = 8 Hz, 4H), 8.23 (d, J = 8 Hz, 2H), 8.08 (d, J = 8 Hz, 2H), 4.60 (q, J= 8 Hz, 4H), 1.95 (br s, 4H), 1.31-1.23 (br s, 36H), 0.85 (t, J = 8 Hz, 6H); ^{13}C NMR for **12CS12** (500 MHz, DMSO-D_6): δ(ppm) = 153.34, 153.31, 144.92, 144.87, 143.26, 136.72, 130.34, 129.02, 128.75, 127.06, 124.67, 124.57, 117.30, 111.27, 60.06, 60.01, 31.24, 30.65, 28.84, 28.76, 28.61, 28.38, 25.42, 22.06, 13.92; MS (ESI): m/z calculated for $C_{49}H_{67}N_3^{2+}$: 348.7662; found: 348.7662.

3 Preparation of Stock Solutions

Preparation of stock solution of cucurbit[7]uril: A stock solution of **CB[7]** (2 mM) was prepared by dissolving required amount of **CB[7]** in Milli-Q water.

Preparation of stock solution of 2CS2 and 12CS12: Stock solutions of **2CS2** and **12CS12** were prepared by dissolving the solid powder of them in spectroscopic grade dimethyl sulfoxide (DMSO).

4 Titration Procedures

Titration of 2CS2 with CB[7]: At first, a stock solution of **2CS2** (1mM) in HPLC grade DMSO was diluted 100 times by Milli-Q water to obtain a 10 µM solution of **2CS2** in 99 % water-DMSO which was equilibrated for 10 min. Addition of **CB[7]** was done using fresh equilibrated aqueous solution of **2CS2** (10 µM) every time to avoid the chance of any possible photoreaction of the cyanostilbene backbone during the titration procedure. After the addition of **CB[7]**, each sample was equilibrated for 10 min before the spectra were recorded.

Titration of 12CS12 with CB[7]: At first, a stock solution of **12CS12** (1mM) in HPLC grade DMSO was diluted 100 times by Milli-Q water to obtain 10 µM solution of **12CS12** in 99 % water-DMSO and equilibrated for 2 hrs. In this case also, addition of **CB[7]** was done using fresh equilibrated aqueous aggregated solution of **12CS12** (10 µM) every time to avoid the chance of any possible photoreaction of the cyanostilbene backbone during the titration procedure. Similarly, after the addition of **CB[7]**, each sample was equilibrated for 10 min before the spectra were recorded.

5 Spectroscopic Studies of 2CS2 and 12CS12

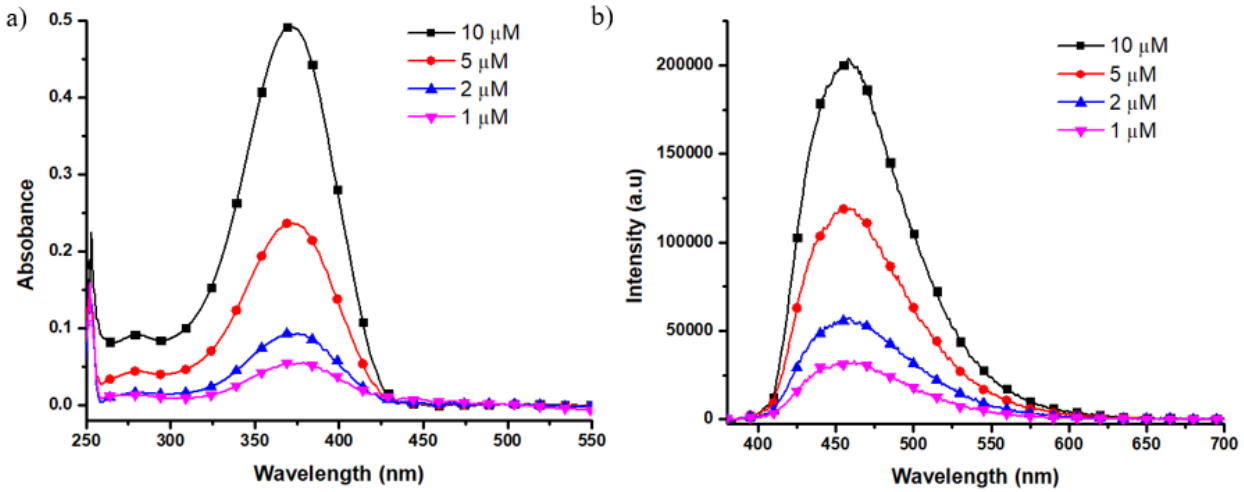


Figure S1. (a) Absorption and (b) emission spectra of **2CS2** at different concentrations in DMSO.

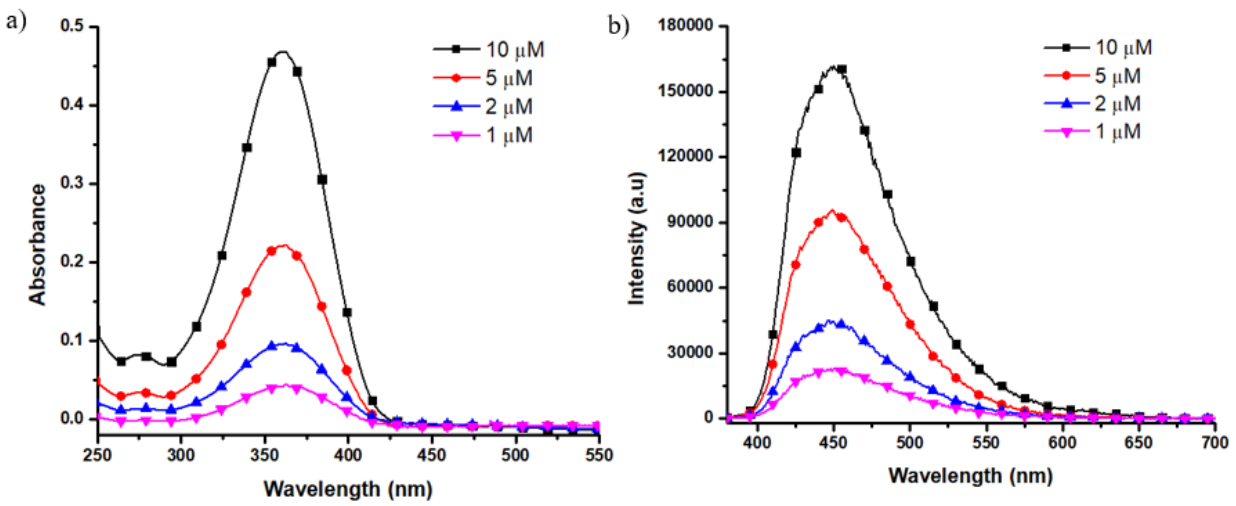


Figure S2. (a) Absorption and (b) emission spectra of **2CS2** at different concentrations in 99% water-DMSO.

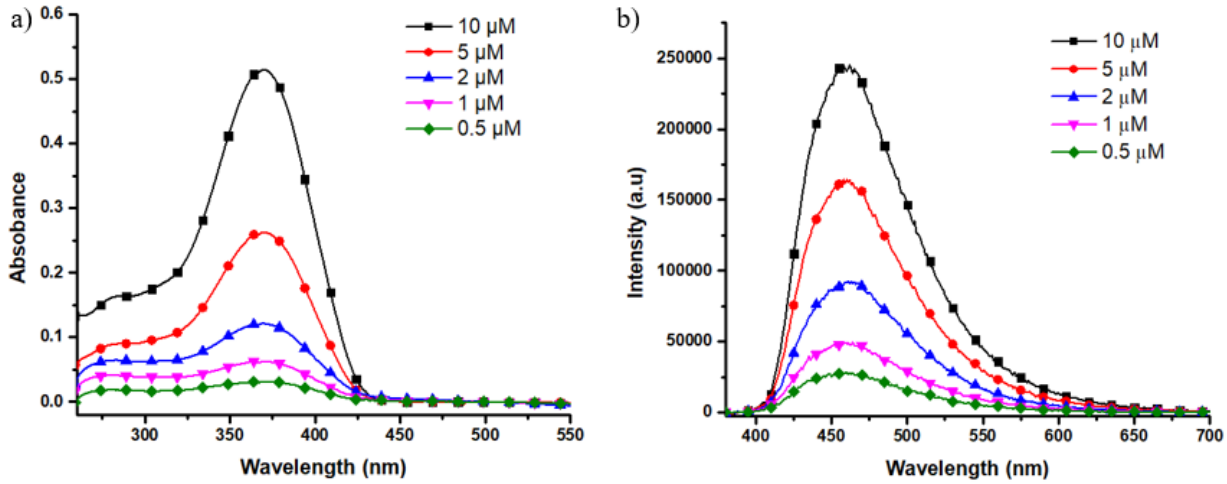


Figure S3. (a) Absorption and (b) emission spectra of **12CS12** at different concentrations in DMSO.

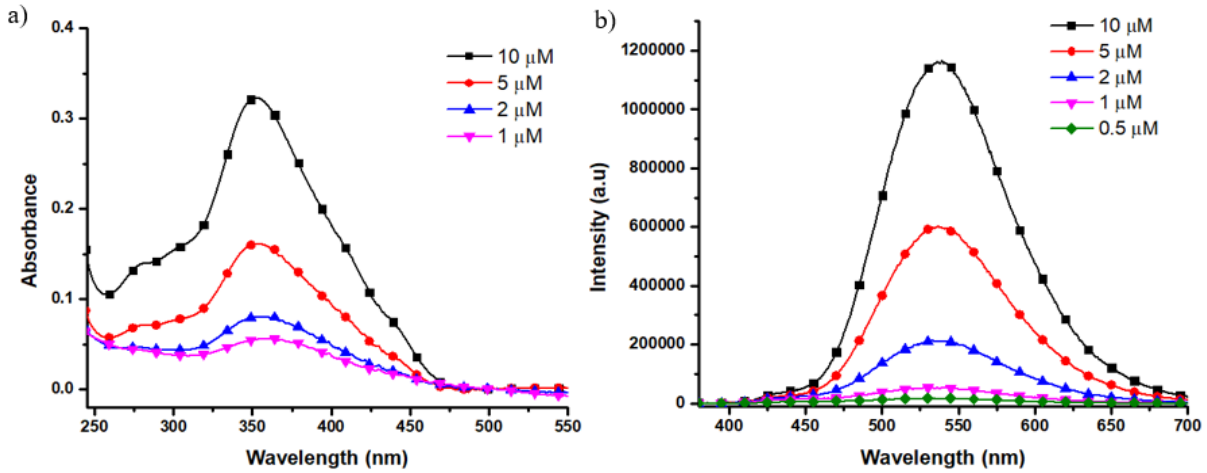


Figure S4. (a) Absorption and (b) emission spectra of **12CS12** at different concentrations in 99% water-DMSO.

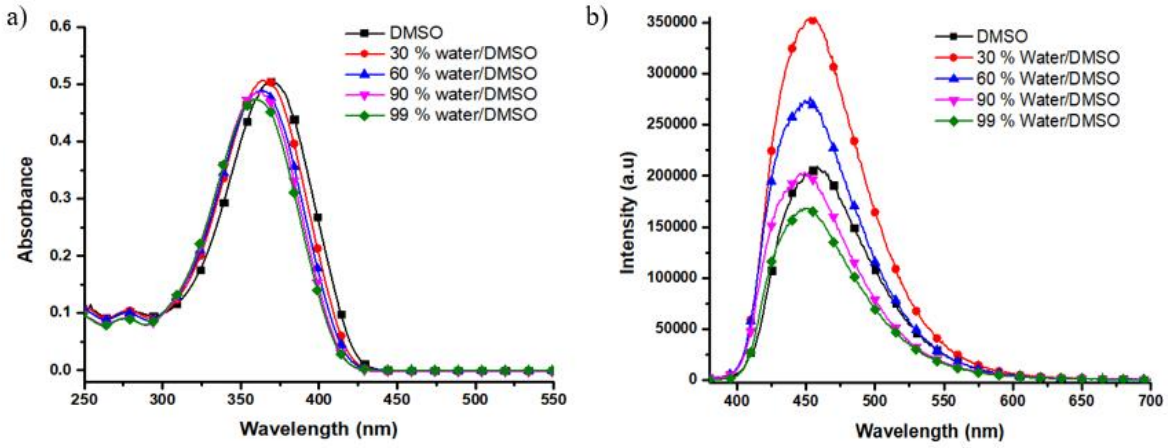


Figure S5. (a) Absorption and (b) emission spectra of **2CS2** (10 μM) at different water-DMSO fractions.

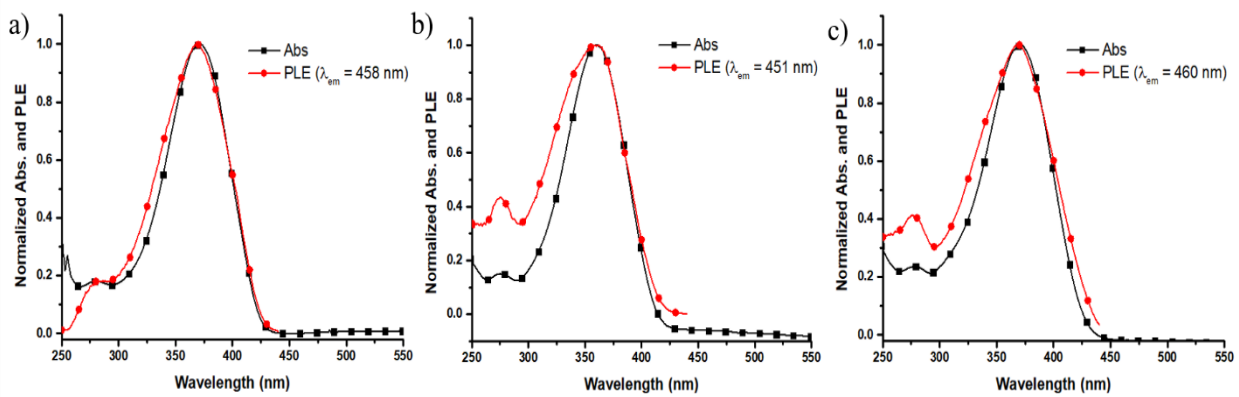


Figure S6. Normalized absorption and photoluminescence excitation spectra of **2CS2** (10 µM) in (a) DMSO, (b) 99% water-DMSO and (c) in presence of **CB[7]** (25 µM) in 99% water-DMSO.

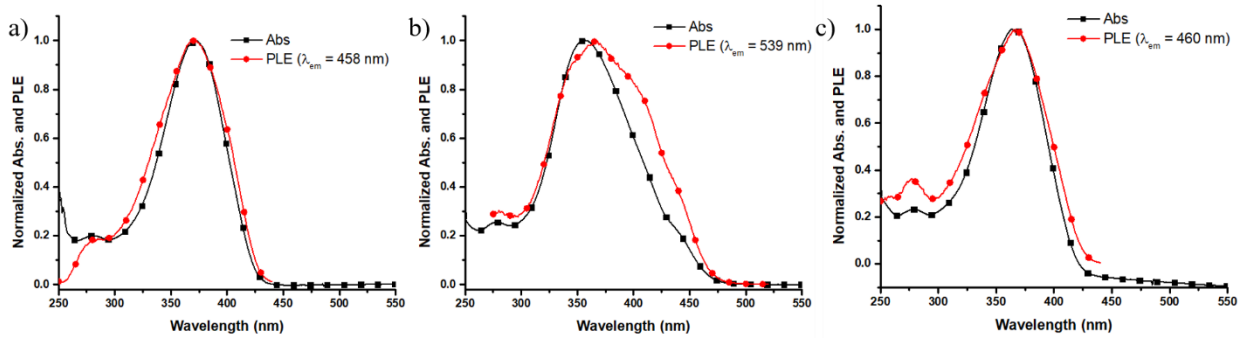


Figure S7. Normalized absorption and photoluminescence excitation spectra of **12CS12** (10 µM) in (a) DMSO, (b) 99% water-DMSO and (c) in presence of **CB[7]** (30 µM) in 99% water-DMSO.

6 Binding Studies with CB[7]

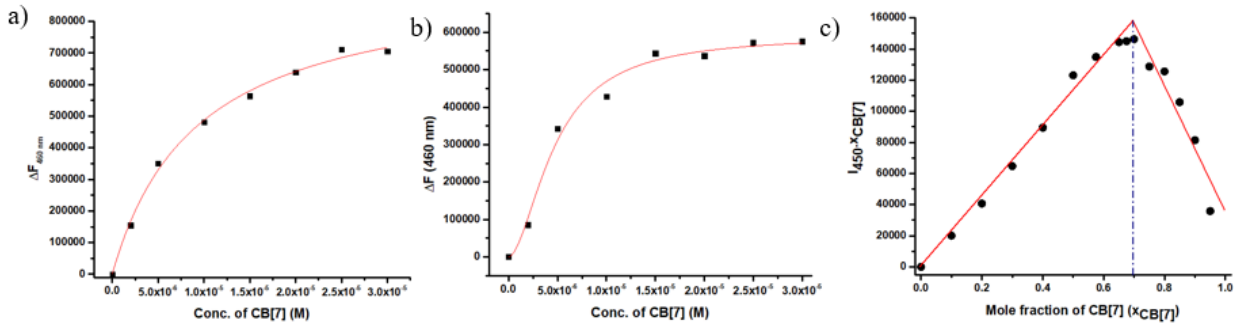


Figure S8. ΔF vs conc. of **CB[7]** for (a) **2CS2** (10 µM) and (b) **12CS12** (10 µM), (c) Job's plot for **2CS2** (10 µM) upon addition of **CB[7]** in aqueous medium (2:1 stoichiometry of **CB[7]** to **2CS2**).

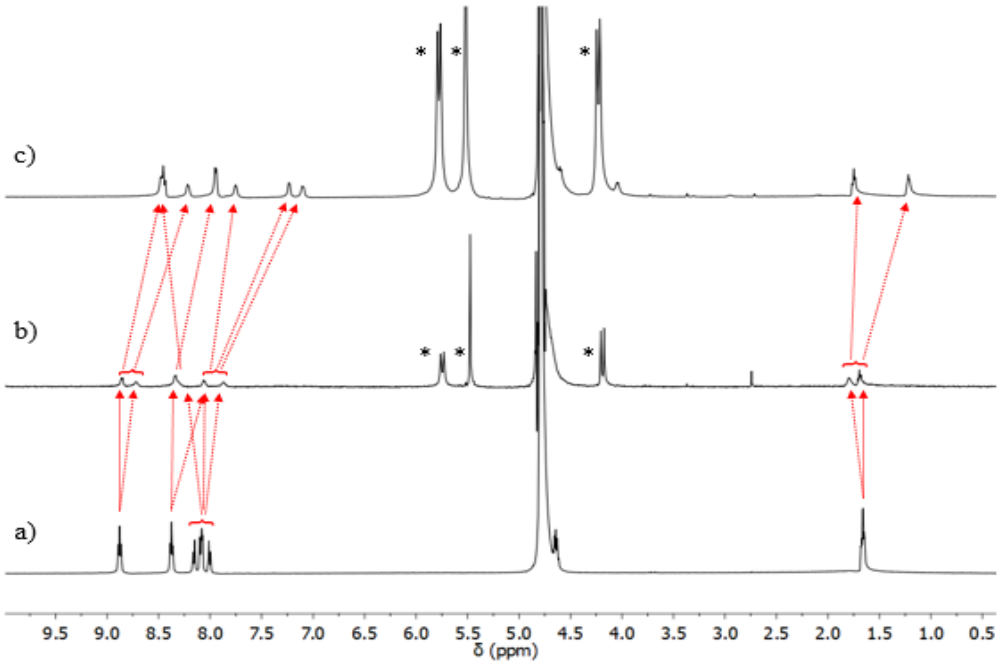


Figure S9. ^{1}H NMR spectra of **2CS2** (1 mM) (500 MHz, D_2O) in the absence (a) and in the presence of 1.0 equiv. (b) and 2.5 equiv. (c) of **CB[7]**. (* marked peaks are from **CB[7]**).

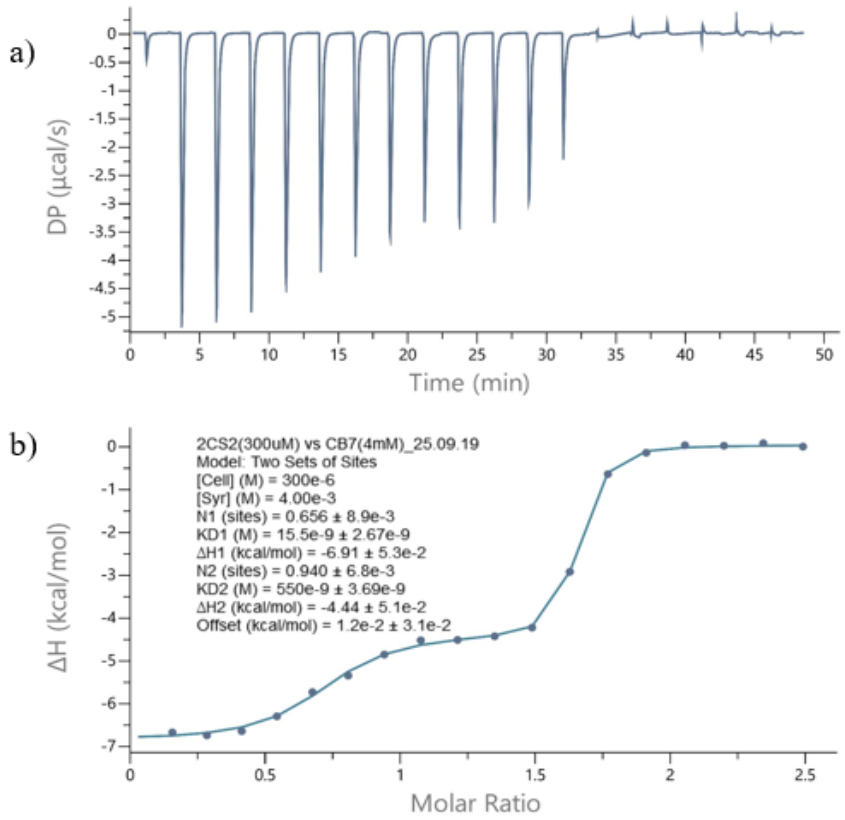


Figure S10. (a) Thermogram obtained during the titration of **2CS2** (300 µM) in the cell with **CB[7]** (4 mM) in the syringe in water (298.0 K). (b) Fitting of the data to a two sets of binding sites model.

7 Calculation of the Ratio of the Aggregate and Host-Guest Complex in the Aqueous Mixture of 12CS12 and CB[7] by Spectral Decomposition

In a mixture of **12CS12** and **CB[7]**, three species can co-exist: **12CS12** monomer, **12CS12** aggregate and **12CS12-CB[7]** host-guest complex. However, as the binding constants of the host-guest complex formation were in the order of 10^7 M^{-1} (as determined from ITC), we assume that in the examined concentration of **12CS12** (10 µM), there was no free monomer in the presence of **CB[7]** and everything is in host-guest complex. In order to determine the relative proportions of **12CS12** aggregate and **12CS12-CB[7]** complex in the mixtures of these two components in different ratios, the photoluminescence (PL) spectra of the mixture are expressed as a linear combination of the PL spectra of the aggregate and the PL spectra of the complex. Therefore we

fit the observed normalized PL spectra ($PL_{obs(\mathbf{12CS12})}$) upon addition of **CB[7]** by using the following equation:

$$PL_{obs(\mathbf{12CS12})} = aPL_{agg(\mathbf{12CS12})} + bPL_{com(\mathbf{12CS12@CB[7]})} \quad \ldots\ldots\ldots\ldots \text{ equation (1)}$$

$PL_{agg(\mathbf{12CS12})}$ and $PL_{com(\mathbf{12CS12@CB[7]})}$ are the normalized PL spectra of the aggregate and the host-guest complex of **12CS12-CB[7]**, respectively whereas a and b are their corresponding fractions in the mixture.

Now, substituting the $PL_{com(\mathbf{12CS12@CB[7]})}$ term in eq. 1 by $PL_{com(\mathbf{2CS2@CB[7]})}$, the following equation is obtained:

$$PL_{obs(\mathbf{12CS12})} = aPL_{agg(\mathbf{12CS12})} + bPL_{com(\mathbf{2CS2@CB[7]})} \quad \ldots\ldots\ldots\ldots \text{ equation (2)}$$

The approximate ratio of the aggregates to complex in each composition is calculated using equation 2 as shown in table S1 (spectral decomposition for a mixture with **12CS12** (10 µM) and **CB[7]** (10 µM) is shown in Fig. S11).

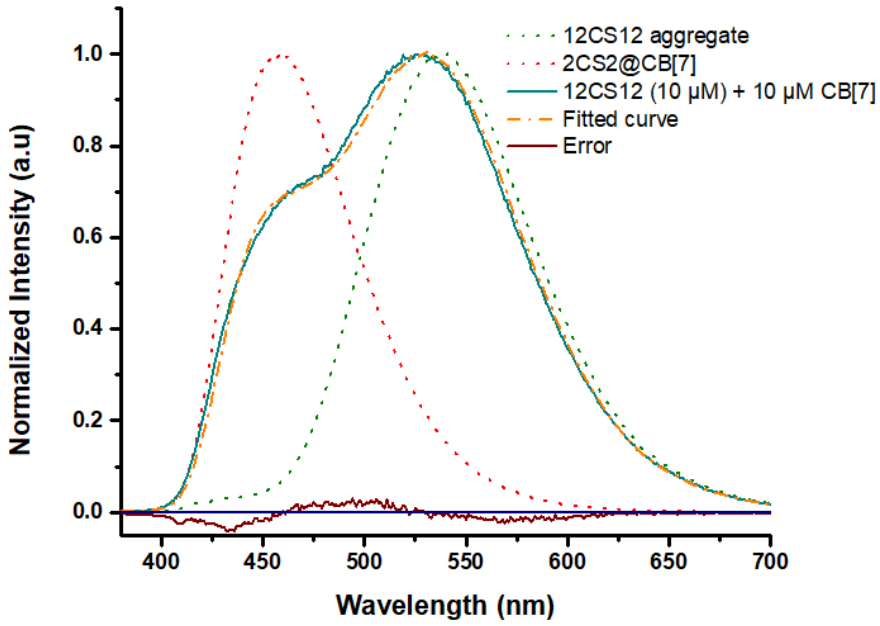


Figure S11. Fitting of PL spectra upon addition of 10 µM of **CB[7]** to the aggregated aqueous solution of **12CS12** (10 µM).

Table S1. Ratio of the aggregates and the host-guest complex upon addition of **CB[7]** to the aggregated aqueous solution of **12CS12** (10 µM) as obtained by fitting the normalized PL spectra using equation 2

Experiment No.	Amount of CB[7] added	Aggregate (%)	Host-Guest Complex (%)
1.	2 µM	92.5	07.5
2.	5 µM	70.0	30.0
3.	10 µM	58.3	41.7
4.	15 µM	50.1	49.9
5.	20 µM	38.8	61.2
6.	25 µM	27.1	72.9
7.	30 µM	20.2	79.8

8 Reversible Luminescence Control

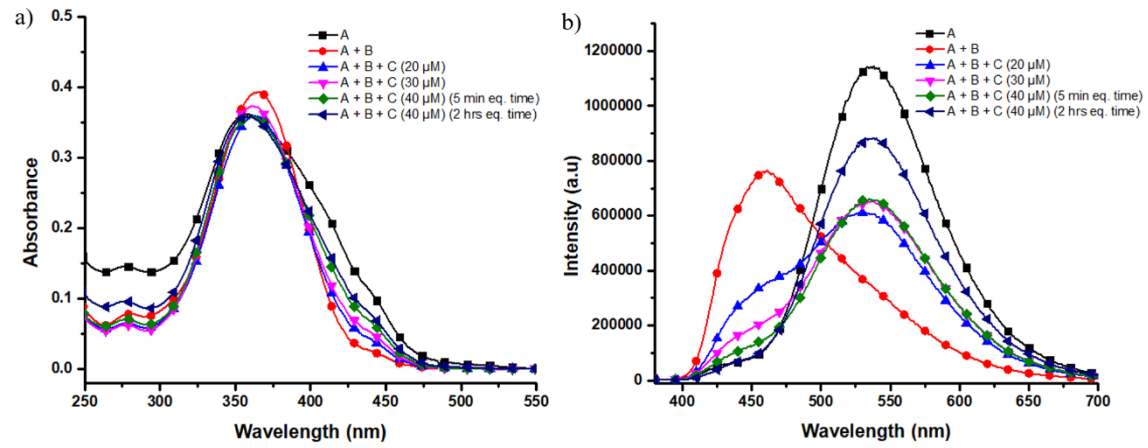


Figure S12. (a) Absorption and (b) emission spectral change of **12CS12** (10 µM)@**CB[7]** (25 µM) in water upon addition of 1-adamantylamine (**1-ADA**). **A** = **12CS12** (10 µM), **B** = **CB[7]** (25 µM) and **C** = **1-ADA**.

9 Computational Studies

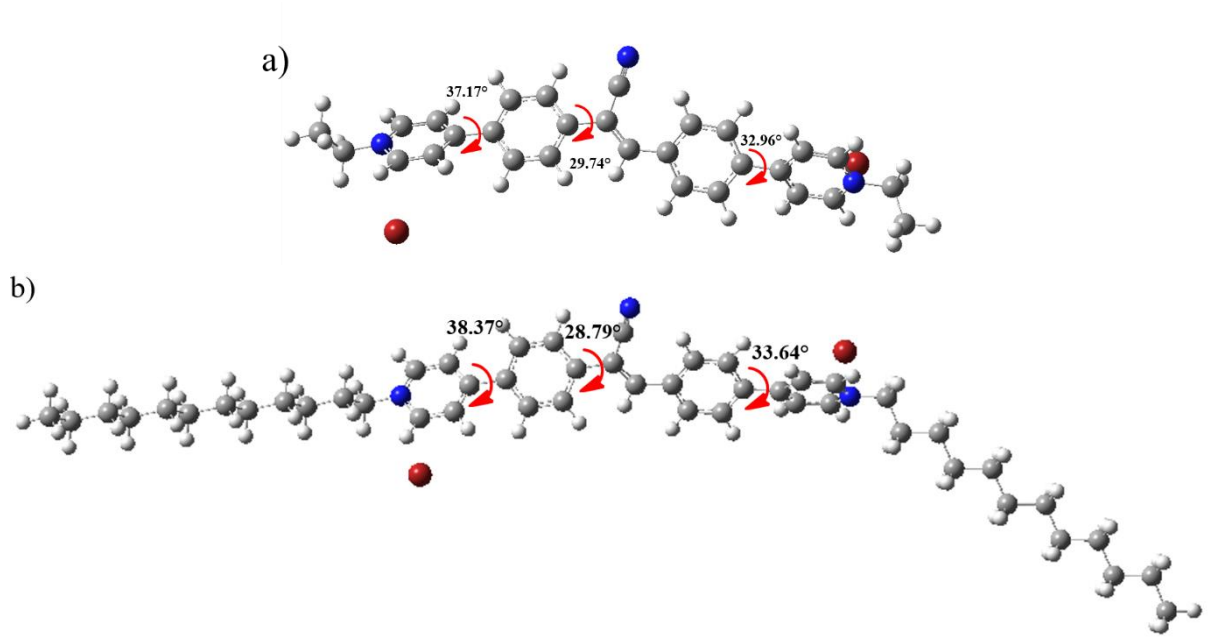


Figure S13. DFT optimized structures of (a) **2CS2** and (b) **12CS12**. Density functional theory (DFT) calculations were carried out to optimize the structure using the B3LYP/6-311++G** level of theory and without imposing any symmetry constraints. Frequency calculations were done at the same level of theory to confirm the nature of stationary points as the real minima (N_{img} = 0) level of theory.

10 Scanning Electron Microscope Images

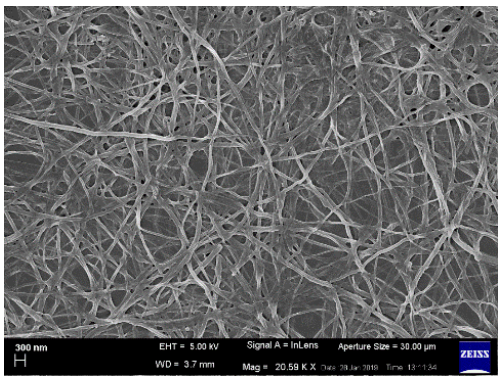


Figure S14. SEM image of aggregated **12CS12** (10 µM)

11 Dynamic Light Scattering (DLS) Measurement

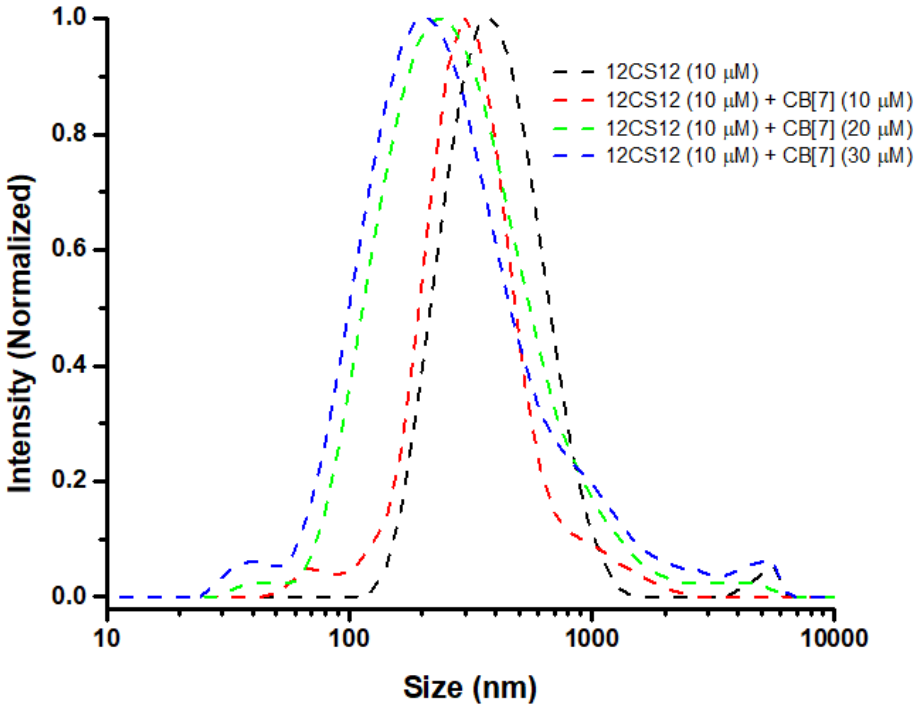


Figure S15. Change in hydrodynamic diameter upon addition of **CB[7]** to aggregated aqueous solution of **12CS12** (10 μM) as measured by DLS.

12 Quantum Yield Calculation

Quantum yield of **2CS2** and **2CS2-CB[7]** complex were measured by employing reference method using the following equation[2]

$$Q_f = Q_{ref} \times \frac{a_{ref}}{a_{sam}} \times \frac{A_{smp}}{A_{ref}} \times \left(\frac{n_{sam}}{n_{ref}} \right)^2$$

Where Q_f and Q_{ref} are quantum yields (QY), A_{sam} and A_{ref} are the areas under the fluorescence spectrum, a_{sam} and a_{ref} are the absorbance at excitation wavelength (λ_{ex} = 366 nm) of the sample and the reference, respectively. η_{sam} and η_{ref} are the refractive indices of the solvents where the sample and the reference were dissolved, respectively. Quinine sulfate in 0.1 M H_2SO_4 was used as the reference dye.

13 Time-correlated Single Photon Counting (TCSPC) Measurement

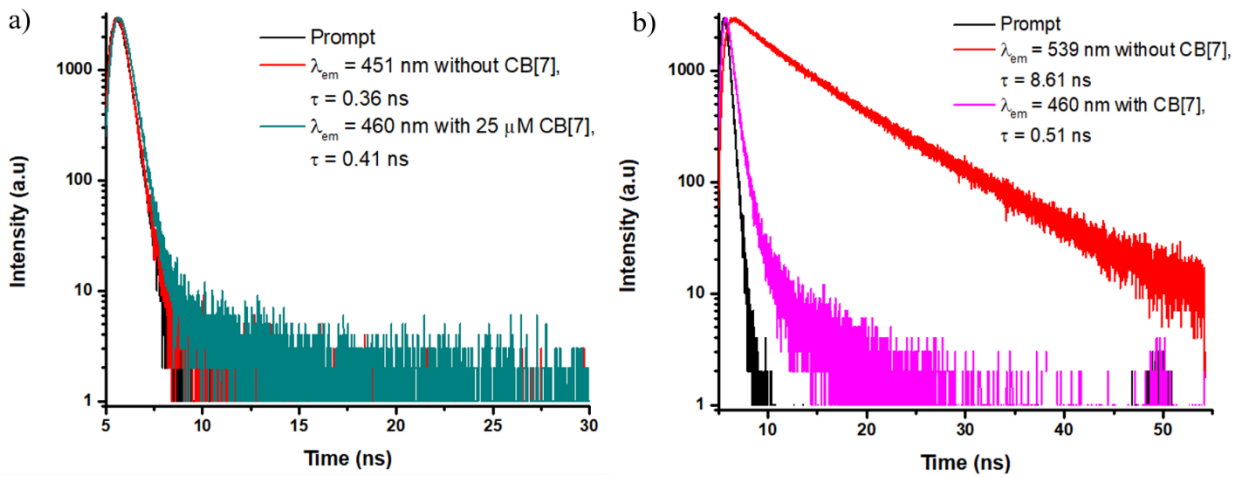


Figure S16. Time resolved decay curves (λ_{ex} = 340 nm) of a) **2CS2** (10 µM) and b) **12CS12** (µM) with and without **CB[7]** in water.

14 NMR Spectral Characterization

NMR Characterization of 2-(4-(pyridin-4-yl)phenyl)acetonitrile:

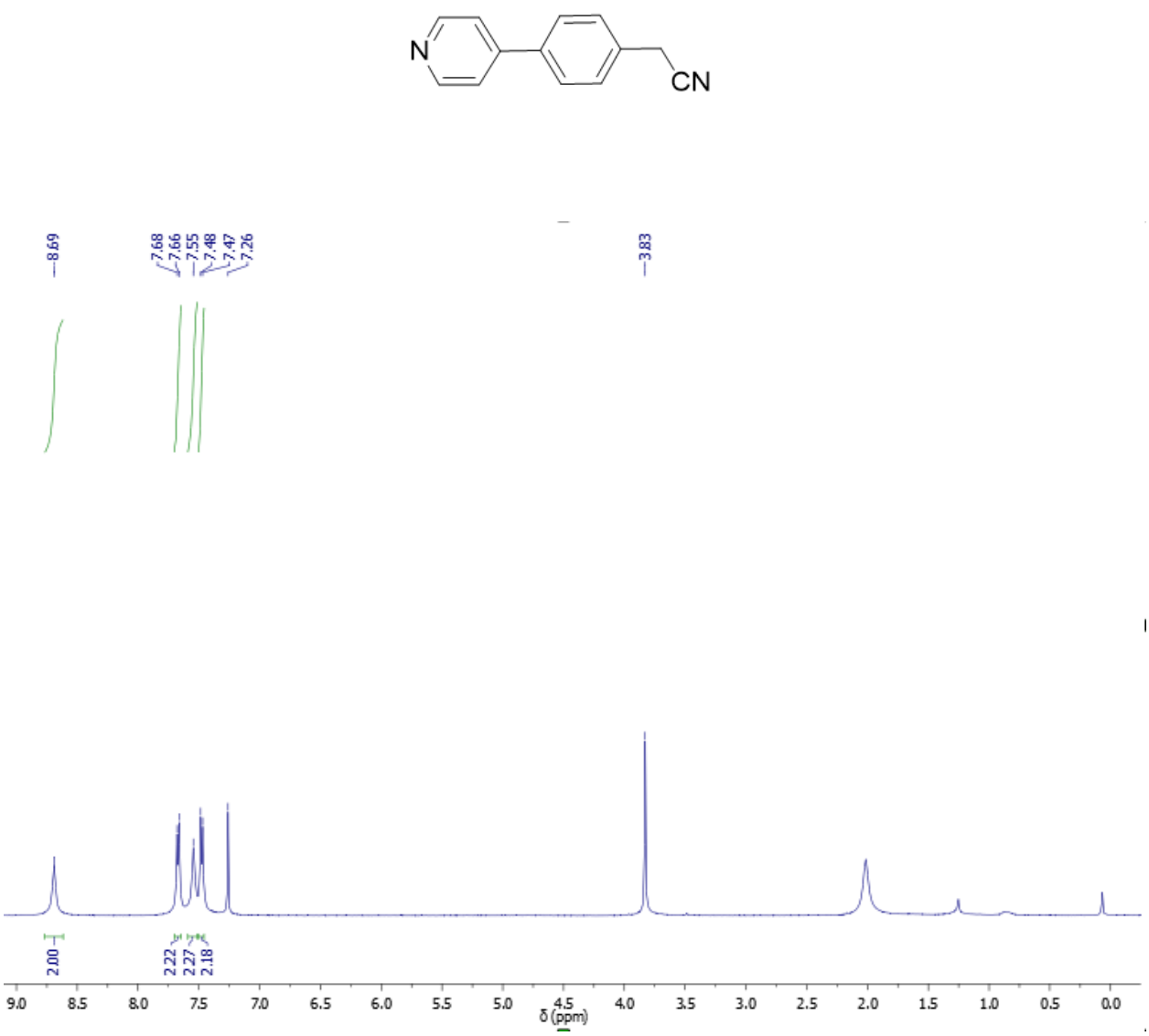
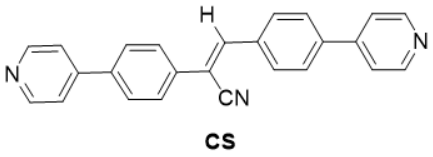


Figure S17. ^{1}H NMR Spectra of **2-(4-(pyridin-4-yl)phenyl)acetonitrile** (500 MHz, $CDCl_3$)

NMR Characterization of CS:



CS

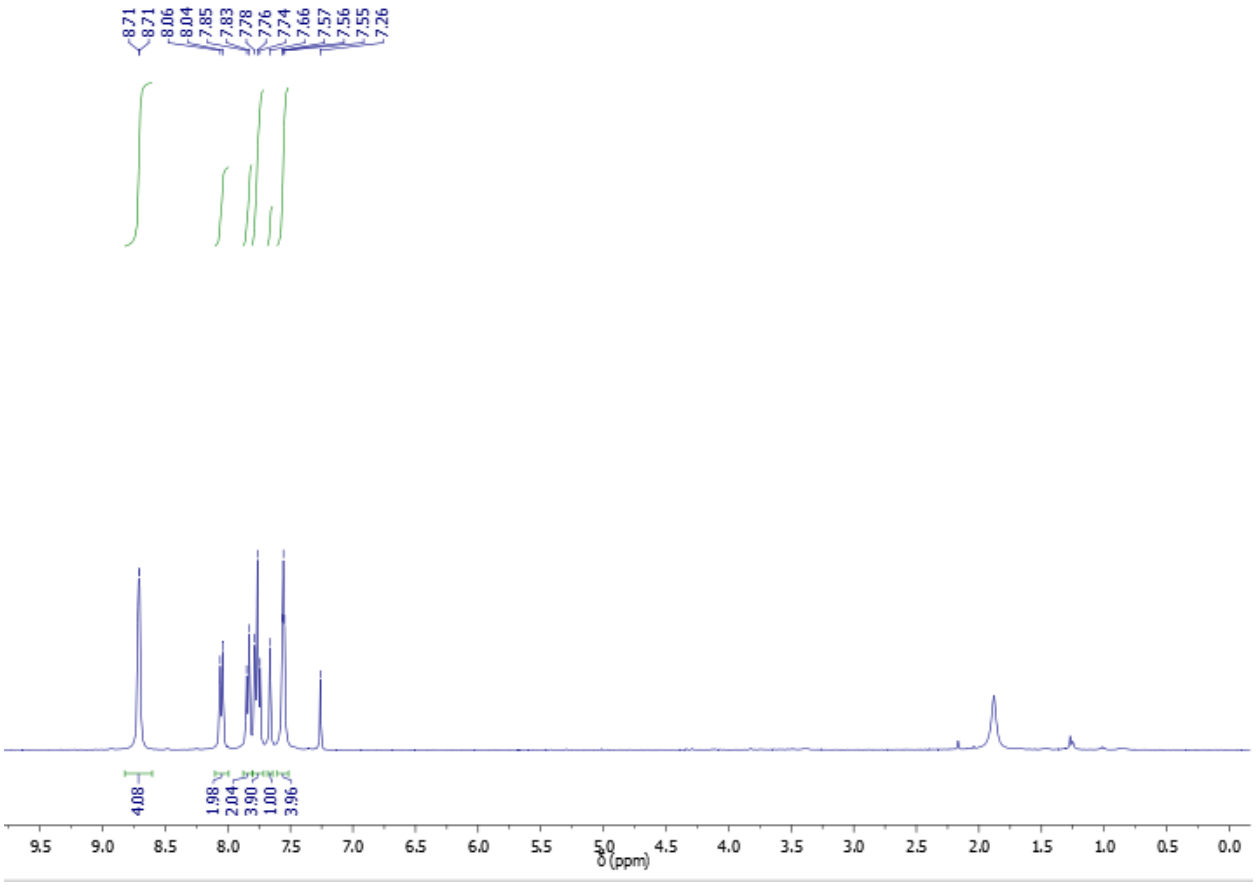
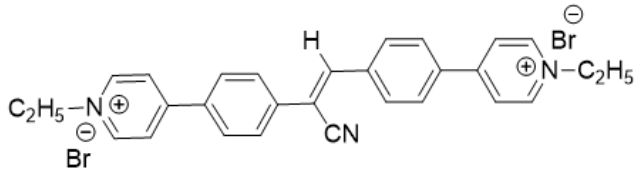


Figure S18. ^{1}H NMR Spectra of **CS** (400 MHz, $CDCl_3$)

NMR Characterization of 2CS2:



2CS2

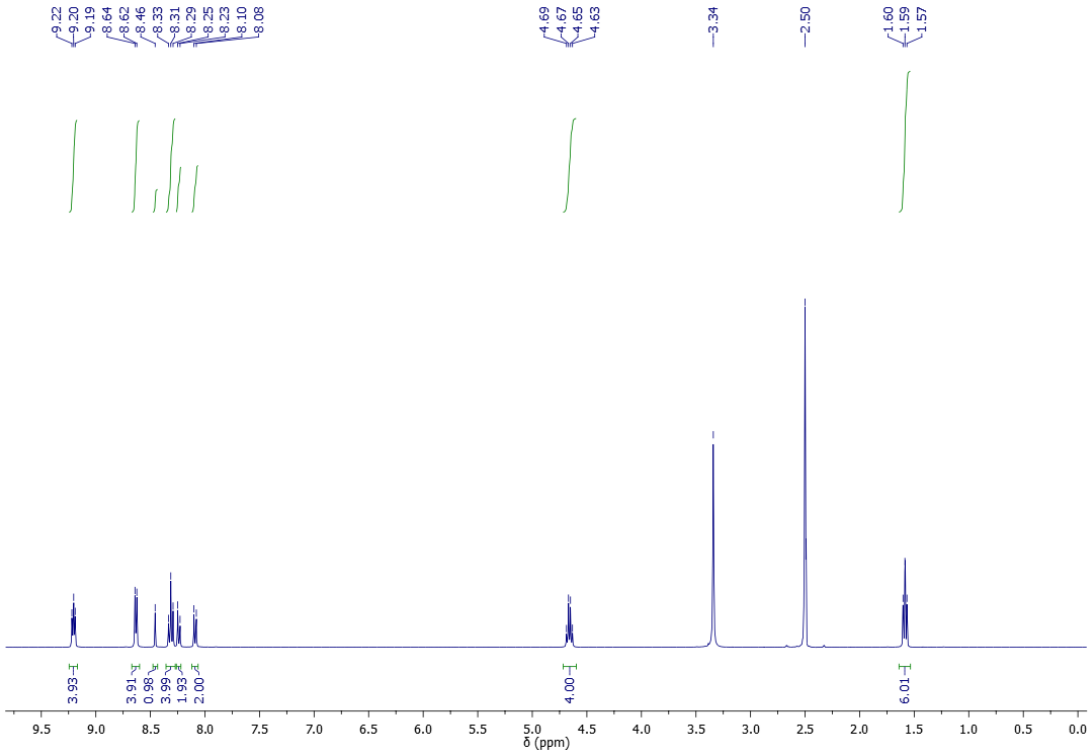


Figure S19. ^{1}H NMR Spectra of **2CS2** (400 MHz, DMSO-D_6)

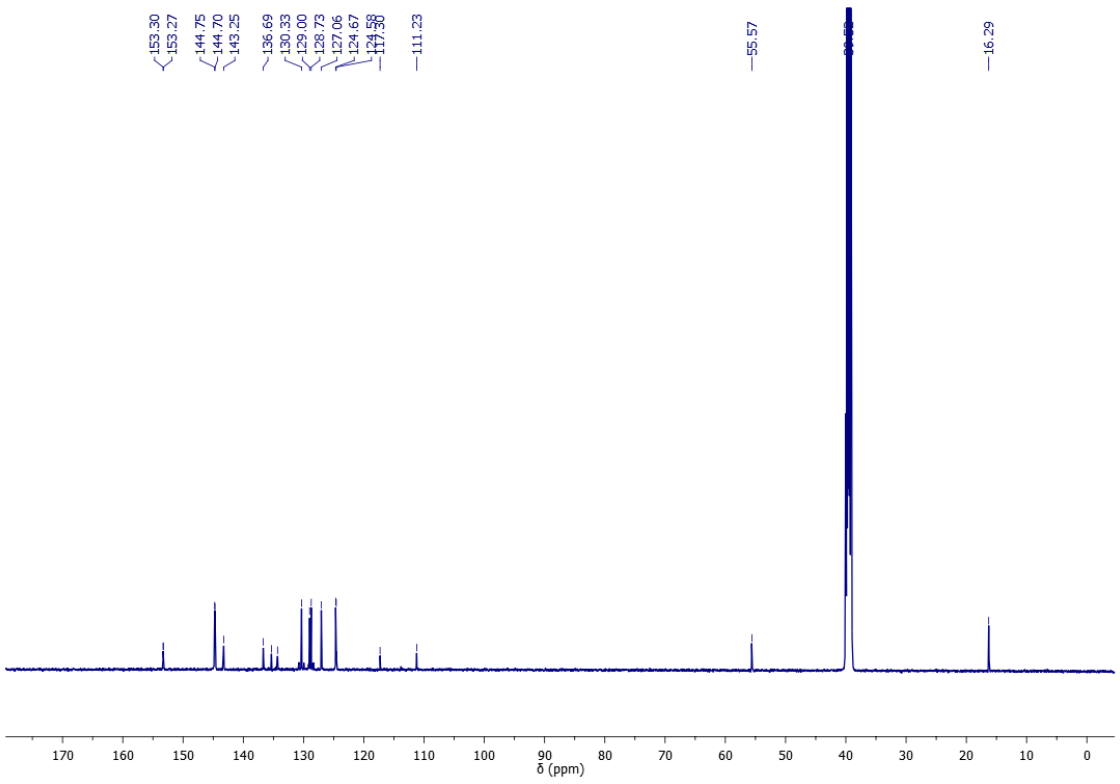
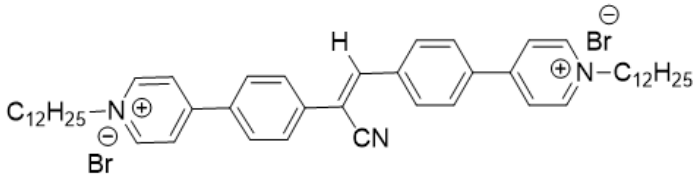


Figure S20. ^{13}C NMR Spectra of **2CS2** (500 MHz, DMSO-D_6)

NMR Characterization of 12CS12:



12CS12

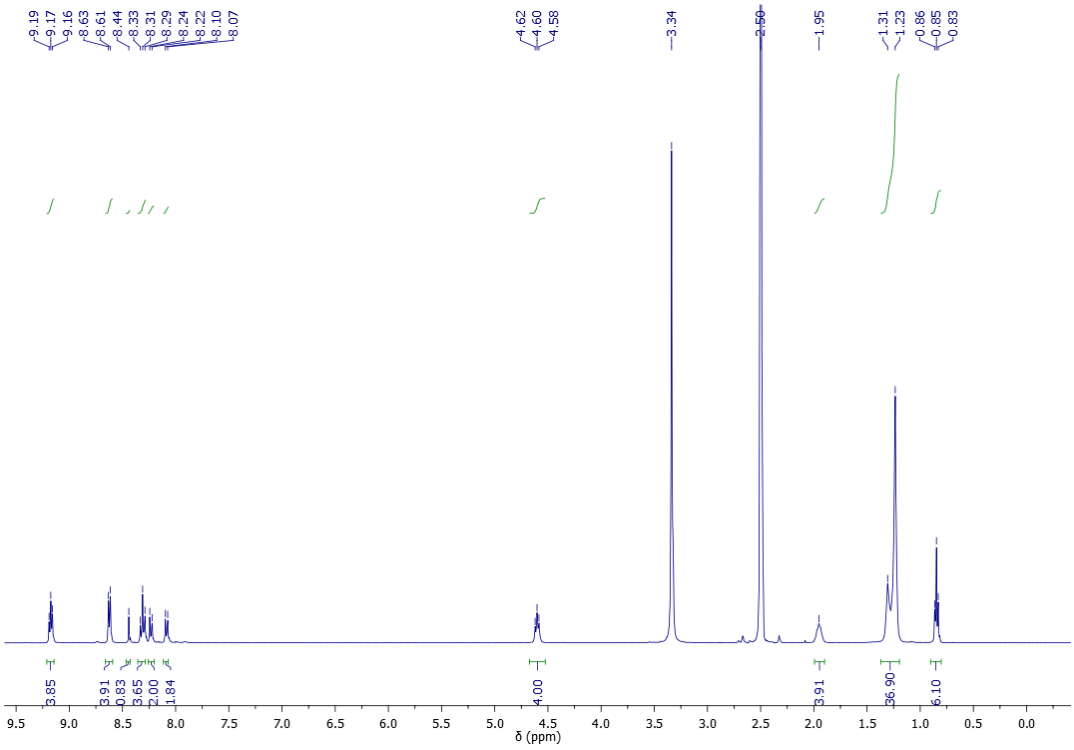


Figure S21. ^{1}H NMR Spectra of **12CS12** (400 MHz, DMSO-D_6)

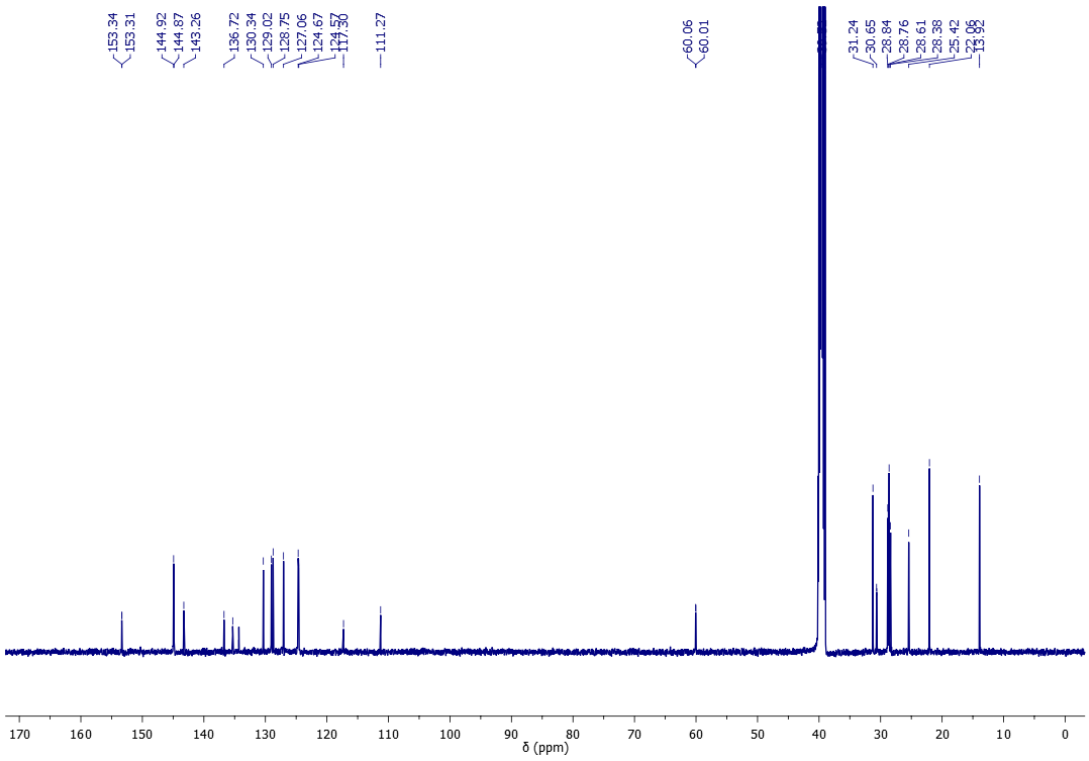


Figure S22. ^{13}C NMR Spectra of **12CS12** (500 MHz, DMSO-D_6)

References:

1 Y. You, H. Yang, J. W. Chung, J. H. Kim, Y. Jung, S. Y. , Park, *Angew. Chem. Int. Ed.*, 2010, **49**, 3757.

2 E. Austin, M. Gouterman, *Bioinorg. Chem.*, 1978, **9**, 281.