Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Mixed Donor-Acceptor Charge-Transfer Stacks via Hierarchical Self-Assembly of a Non-Covalent Amphiphilic Foldamer

Krishnendu Jalani, Mohit Kumar and Subi J. George*[a]

Supramolecular Chemistry Laboratory, New Chemistry Unit,
Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Bangalore,
India-560064. E-mail: george@jncasr.ac.in; Fax: +91 80 22082760; Tel: +91 80 22082964

Table of Contents

1. General Methods

Atomic Force Microscopy (AFM): AFM measurements were performed on a Veeco diInnova SPM operating in tapping mode regime. Micro - fabricated silicon cantilever tips doped with phosphorus and with a frequency between 235 and 278 kHz and a spring constant of 20-40 Nm^{-1} were used. The samples were prepared by drop casting 4 x 10^{-5} M solutions of the CT complex or individual molecules on glass substrates and dried in air followed by vacuum drying at room temperature.

Optical Measurements: Electronic absorption spectra were recorded on a Perkin Elmer Lambda 900 UV-Vis-NIR Spectrometer and emission spectra were recorded on Perkin Elmer Ls 55 Luminescence Spectrometer. UV-Vis and emission spectra were recorded in 10mm path length cuvette. Fluorescence spectra of solutions were recorded with 340 nm excitation wavelength.

NMR Measurements: NMR spectra were obtained with a Bruker AVANCE 400 (400 MHz) Fourier transform NMR spectrometer with chemical shifts reported in parts per million (ppm) with respect to residual solvent peak. Titration measurements were done in 35% D_2O in CD_3OD. The stock solutions were prepared in CD_3OD, which were then injected to appropriate volumes of D_2O and CD_3OD mixture.

High-Resolution Mass-Spectrometry (HR-MS): HRMS measurements were performed with Agilent Technologies Q-TOF-LCMS system, 6538 instrument. Measurements were done in ESI mode (positive mode).

Transmission Electron Microscopy (TEM): TEM measurements were performed on a JEOL, JEM 3010 operated at 300 kV. Samples were prepared by placing a drop of the solution on carbon coated copper grids followed by drying at room temperature. The images were recorded with an

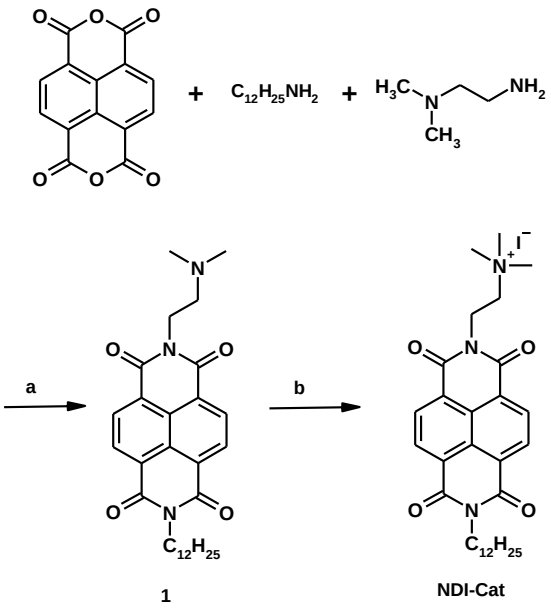
operating voltage 300 kV. In order to get a better contrast samples were stained with uranyl acetate (1 wt % in water) before the measurements**.**

Dynamic light scattering Experiments (DLS): The measurements were carried out using a NanoZS (Malvern UK) employing a 532 nm laser at a back scattering angle of 173^{o}. 10^{-3} M stock solutions of NDI-Cat and DIPY were prepared in methanol, which were injected into appropriate volumes of methanol-water solvent mixtures to obtain the required solution.

Sample preparation for optical measurements: Charge-transfer complexes were prepared by injecting pre-mixed **DIPY** and **NDI-Cat** in methanol to appropriate methanol-water solvent mixtures.

2. Synthesis and Procedures

NDI-Cat and **DIPY** molecules were synthesised according to Scheme S1 and Scheme S2 respectively.



Scheme S1: Synthetic Scheme for **NDI-Cat**. (a) Dry DMF, 100 ^{o}C, Argon, 24 h; b) CH_3I, 80 ^{o}C, 4 h.

Synthesis of (**1**)

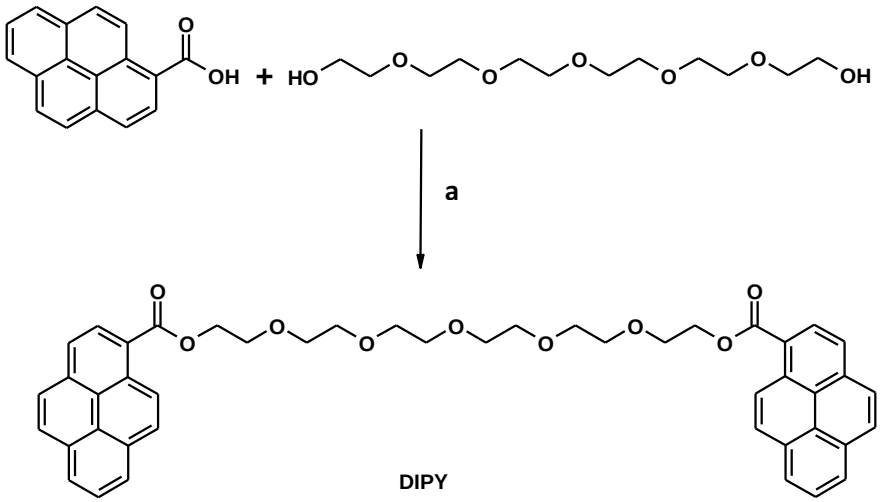
1,4,5,8-Naphthalenetetracarboxylic dianhydride (2 g, 7.45 mmol) was added to N,N-dimethylethylenediamine (0.66 g, 7.45 mmol) and dodecylamine (1.38 g, 7.45 mmol) in 50 ml of dry DMF and the reaction mixture was stirred at 100 °C for 24h under inert atmosphere. DMF was then evaporated under high vacuum. The resulting residue was purified by column chromatography (silica, 100-200 mesh, 100% chloroform to 5/95 v/v methanol/chloroform solvent mixture) followed by size exclusion chromatography (biobeads SX-3, $CHCl_3$,) to give 560 mg of **1** in 15% yield. The low yield of the reaction is due to the statistical formation of three possible products.

^{1}H NMR (400 MHz, $CDCl_3$ TMS): δ (ppm) 8.75 (s, 4H), 4.35 (t, J = 6.8 Hz, 2H), 4.18 (t, J = 7.6 Hz, 2H), 2.67 (t, J = 6.8 Hz, 2H), 2.34 (s, 6H), 1.62 (m, 2H), 1.45-1.25 (m, 18H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ (ppm) 163.1, 162.9, 131.2, 131.1, 126.9, 126.8, 126.7,57.1, 45.9,

41.2, 38.8, 32.1, 29.8, 29.77, 29.74, 29.67, 29.5, 28.2, 27.2, 22.8, 14.3. HRMS (ESI): m/z calcd: $C_{30}H_{39}N_3O_4$: 505.2940, found: 506.2994 $[M+H]^+$.

Synthesis of **NDI-Cat**

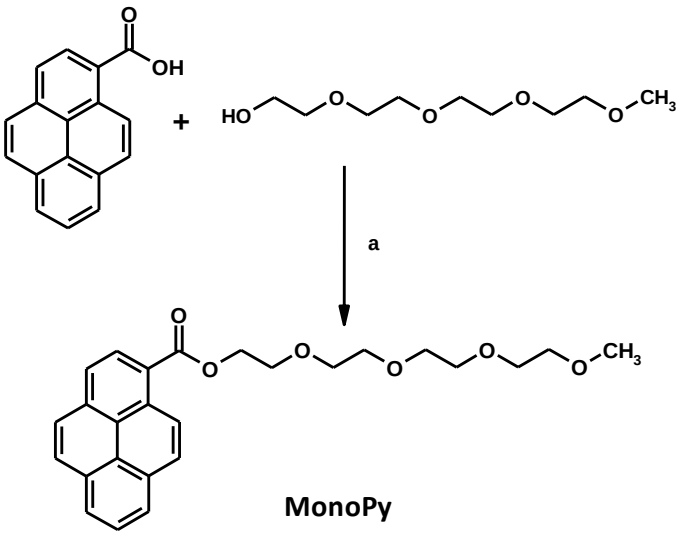
Methyl iodide (0.8 ml, 12.84 mmol) was added to 130 mg (0.26 mmol) of **1** in 20 ml of toluene, and stirred for 4 h at 80 ^oC under inert atmosphere. The shiny yellow precipitate formed during the reaction was filtered, washed with diethyl ether and dried under vacuum to give 160 mg of pure **NDI-Cat** in 95% yield. ^1H NMR (400 MHz, $CDCl_3$, TMS) : δ(ppm) 8.70 (s, 4H), 4.48 (t, J=7.2 Hz, 2H), 4.05 (t, J=7.6 Hz, 2H), 3.63 (t, J=6.8 Hz, 2H), 3.23 (s, 9H), 1.65 (m, 2H), 1.23 (m, 18H), 0.84 (t, J = 6.8 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) : δ (ppm) 162.7, 162.6, 130.5, 126.6, 126.3, 126.2, 61.7, 52.5, 33.9, 31.3, 29.0, 28.7, 27.3, 26.5, 22.1, 13.9; HRMS (ESI): m/z calcd: $C_{31}H_{42}N_3O_4$: 520.3169, found : 520.3279 $[M]^+$.



Scheme S2: Synthetic Scheme for **DIPY.** (a) Dry dichloromethane, EDC, DMAP, 24 h.

Synthesis of Dipyrene (**DIPY**)

Hexaethylene glycol (91 mg, 0.32 mmol) and pyrene carboxylic acid (200 mg, 0.81 mmol) mixture were dissolved in dry dichloromethane and stirred at 0 ^oC. To the above solution, EDC (200 mg, 1.04 mmol), (N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride) and DMAP (50mg) were dissolved in 15 ml of dry DCM and added. Whole solution was stirred at room temperature for 1 day. The reaction mixture was then extracted with dichloromethane and water. The organic layer was concentrated under vacuum and purified by column chromatography (silica gel, 100-200 mesh) with 2 % methanol in chloroform to give 190 mg of the pure product (yield: 80%). ^1H NMR (400 MHz, $CDCl_3$, TMS) : δ (ppm) 9.2 (d, J=9.6 Hz, 2H), 8.6 (d, J=8.4 Hz, 2H), 8.2 (m, 6H) , 8.1 (m, 4H), 8.0 (t, J = 7.6 Hz, 4H), 3.5-3.8 (m, 22H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.1, 134.5, 131.3, 131.1, 130.5, 129.7, 129.5, 128.7, 127.3, 126.4, 126.4, 126.3, 125.0, 124.9, 124.30, 124.2, 123.6, 70.86, 70.80, 70.7, 69.5, 64.4; HRMS (ESI) m/z cald : $C_{46}H_{42}O_9Na$: 761.2726, found : 761.2718 $[M+Na]^+$.



Scheme S3: Synthetic scheme for **MonoPy.** (a) Dry Dichloromethane, EDC, DMAP, 12 hrs

Synthesis of TEG appended Monopyrene derivative **(MonoPy)**

150 mg of Pyrenecarboxylic acid (0.61 mmol) and 250 mg of tetraethylene glycol monomethyl ether (1.22 mmol) were mixed with 15 ml of dry dichloromethane and stirred continuously at ice cold temperature. To that the mixture of 150 mg (0.78 mmol) EDC (N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride) and 50 mg DMAP (Dimethyl amino pyridine in 15 ml dry dichloromethane was added. The whole solution was stirred at room temperature for 12 hrs under argon atmosphere. The reaction mixture was then extracted with dichloromethane and water. The organic layer was concentrated under vacuum and purified by column chromatography (silica gel, 100-200 mesh) with 5% methanol in chloroform to give 250 mg of pure product (yield: 94%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) : δ (ppm) 9.27 (d, J=9.6 Hz, 1H), 8.66 (d, J=8, 1H), 8.25 (m, 3H), 8.18 (d, J=3.6, 1H), 8.16 (d, J=3.6, 1H), 8.08 (m, 2H), 4.67 (t, J=4.8, 2H), 3.97 (t, J=4.8, 2H), 3.78 (m, 2H), 3.71 (m, 2H), 3.68 (m, 2H), 3.64 (m, 2H), 3.59 (m, 2H), 3.50 (m, 2H), 3.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.07, 134.46, 131.26, 131.10, 130.48, 129.72, 129.53, 128.65, 127.26, 126.39, 126.37, 126.26, 125.05, 124.91, 124.29, 124.21, 123.63, 72.00, 70.85, 70.80, 70.78, 70.71, 70.59, 69.45, 64.41, 59.00; HRMS (ESI) m/z cald : $C_{26}H_{28}O_6Na$: 459.1783 , found : 459.1780 $[M+Na]^+$.

3. Supporting Figures

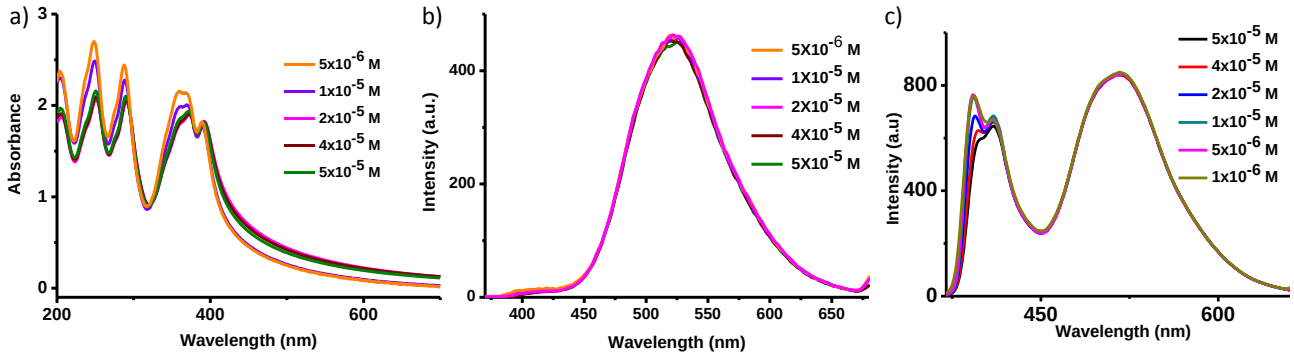


Fig. S1 Concentration dependent (normalized) a) absorption and b) emission spectra (λ_{exc} = 340 nm) of **DIPY** in methanol/water solvent mixture (30:70, v/v). Normalized spectra show that the excimer formation is independent of concentration confirming intramolecular folded conformation. c) Concentration dependent emission spectra (normalized at 520 nm) recorded in pure MeOH where both monomers and excimer emission is present. Absence of any significant change points to the fact that the excimer emission is indeed originated form intramolecular. Slight intensity variation at 390 nm could be due to self-absorption, which is evident as there are no changes seen for the vibronic band at 410 nm.

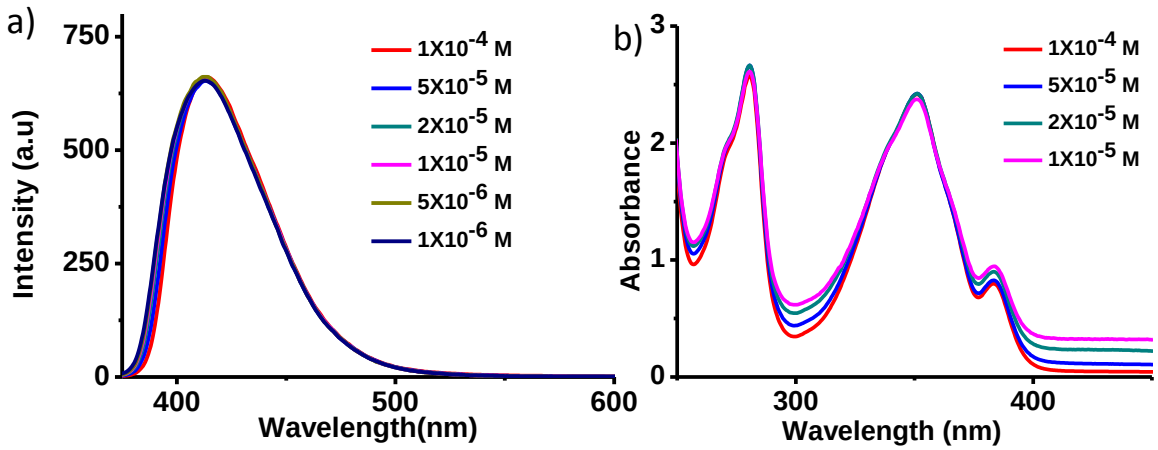


Fig. S2 Concentration dependent (normalized) a) emission (λ_{exc} = 340 nm) and b) absorption spectra of **MonoPy** in methanol/water solvent mixture (30:70, v/v). Normalized spectra show that lack of excimer formation is independent of concentration confirming the role of intramolecular folded conformation in **DiPY** being responsible for excimer formation.

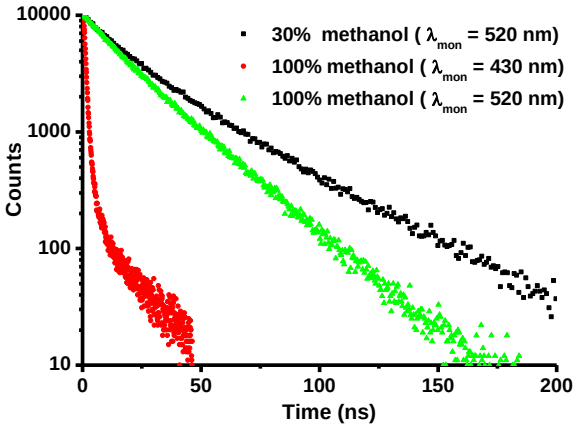


Fig. S3 Fluorescence lifetime decay profiles of **DIPY** in 30 % methanol in water and in 100 % methanol (λ_{exc} = 405 nm) while collecting at monomer (430 nm) and excimer emission (λ_{exc} = 520 nm). Whereas in MeOH, when collected at 430 nm, the major contribution is from a very fast decay (1.02 ns) characteristic of monomeric form. 30 % MeOH in water shows a very high lifetime of 40.17 ns indicating formation of preassociated excimer. See the below table for the life-time values.

Solvent	τ_1 (ns)	τ_2 (ns)
MeOH (430 nm)	1.02 (80%)	8.97 (20%)
MeOH (520 nm)	11.81 (16%)	25.03 (84%)
30% MeOH (430 nm)	16 (30%)	40.17 (70%)

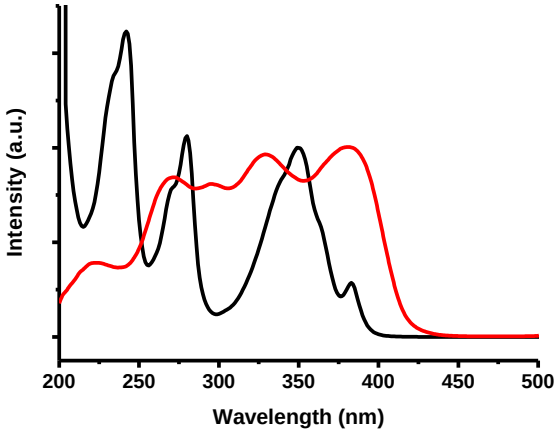


Fig. S4 Normalized absorption spectrum (black) of **DIPY** in 100 % methanol compared with that of excitation spectrum (red) in 30 % methanol in water, collected at excimer emission (520 nm). The red-shifted excitation spectrum compared to monomeric absorption spectrum is clearly an indication of the static excimer formation with inter chromophoric interactions in the ground state.

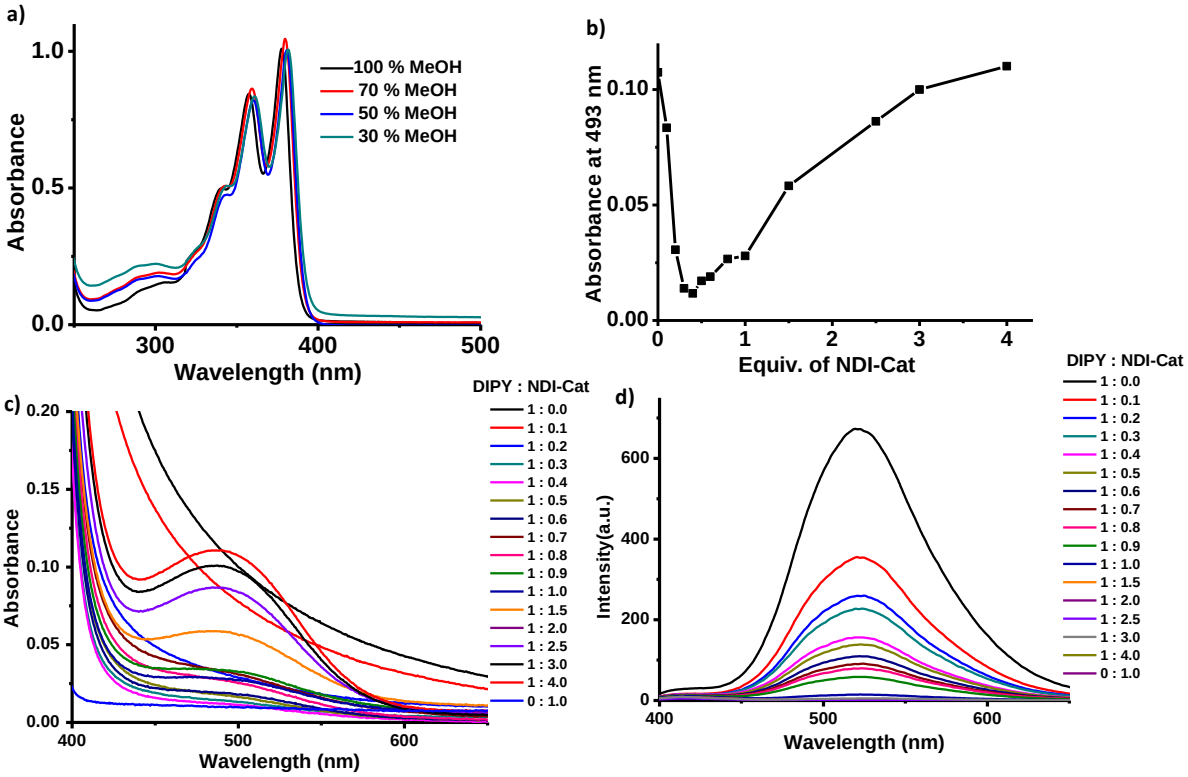


Fig. S5 a) Absorption spectra of **NDI-Cat** (4 x 10^{-5} M, 30 % methanol in water) showing molecularly dissolved features with no significant effect of change in solvent composition. b) shows the titration points obtained by plotting the absorption changes monitored at 489 nm. c) absorption and d) emission spectra showing titration of **DIPY (**4 X 10^{-5} M) with increasing equivalents of **NDI-Cat** to form CT complex in 30 % Methanol in water. High absorption values at initial stages of titration (upto 0.4 equiv. of **NDI-Cat** in Fig. S4 a) originates from the scattering of aggregated **DIPY**, which diminishes with subsequent addition of **NDI-Cat** due to improved solubilization of amphiphilic CT foldamer.

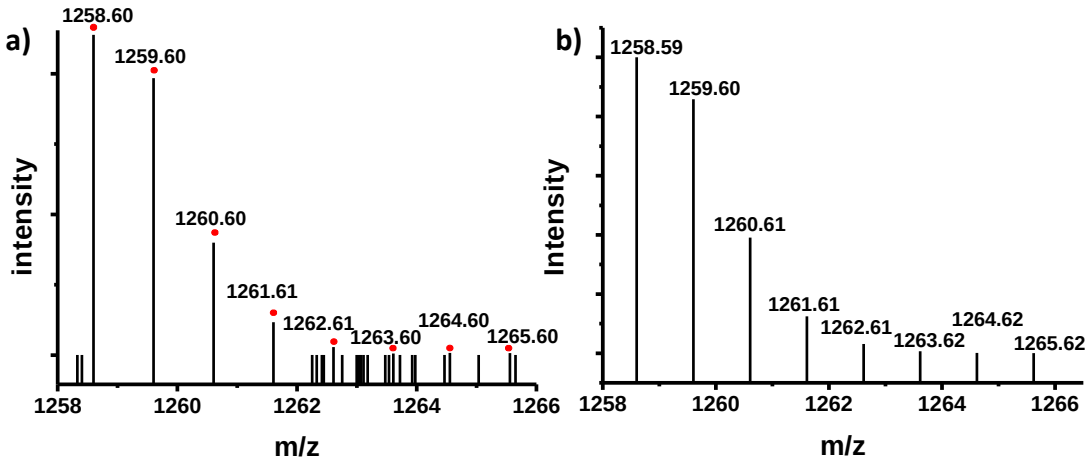


Fig. S6 ESI – HRMS spectra of a) obtained and b) simulated isotopic abundance for 1:1 CT complex ion, which is in good agreement with each other confirming CT complex formation. Extra lines in a) is due to background noise interfering with weak isotopic peaks.

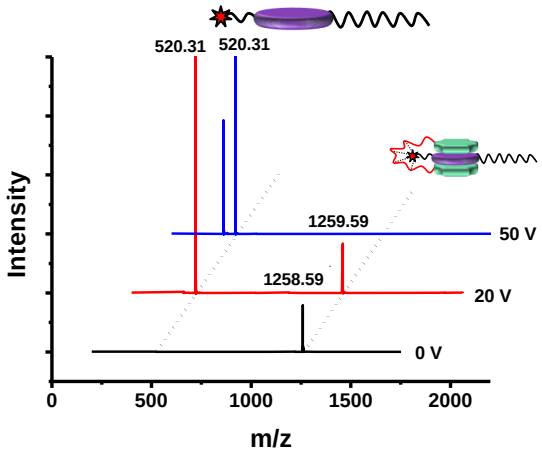


Fig. S7 ESI tandem MS/MS pattern of 1:1 CT complex between **DIPY** and **NDI-Cat** (1258.59 m/z) upon varying accelerating voltage. At low voltage (0 V), there was no observed fragmentation, whereas on increasing voltage (50 V), we see the appearance of peak at 520.31 (m/z) corresponding to **NDI-Cat** with gradual disappearance of CT signal. Appearance of another peak at 461.33 (m/z) at 50 V is due to fragmentation of **NDI-Cat** with loss of $N(CH_3)_3$. **DIPY** (761.26 m/z) is hardly detected in MS/MS experiments, probably due to lack of inherent charge in the molecule and its inability to gain charge inside collision cell under solvent-free conditions.

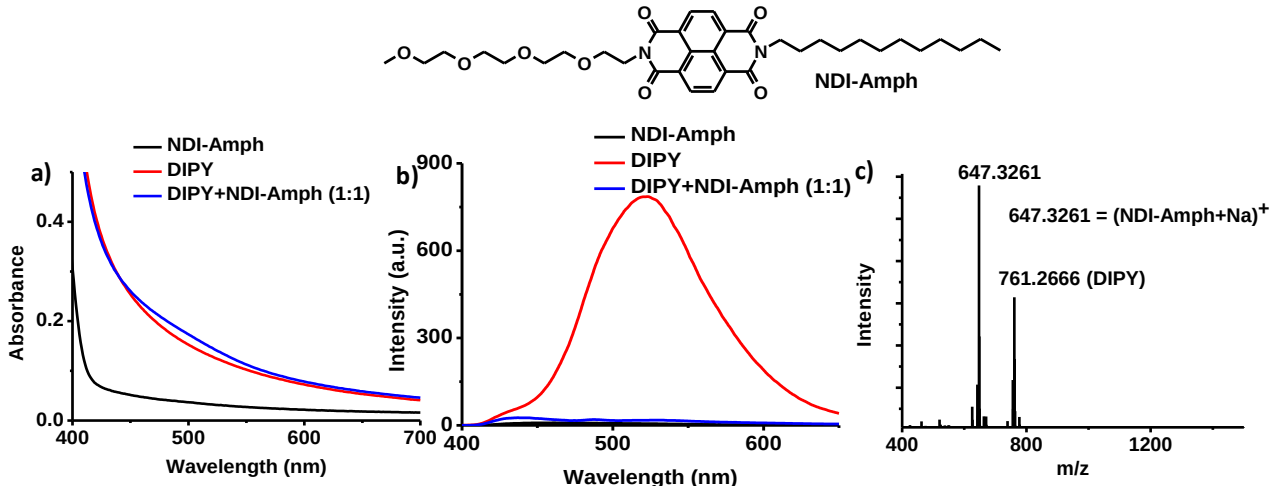


Fig. S8 Molecular structure of **NDI-Amph** and steady state a) absorption and b) emission spectra of individual **DIPY** and **NDI-Amph** as well as its 1:1 CT complex (4×10^{-5} M, 2 % THF, 28 % methanol in water). Fig c) shows the mass spectrum of **DIPY** and **NDI-Amph** (1:1) CT complex**.** Although absorption and fluorescence measurements show the formation of CT complex through the CT band in a) and emission quenching in b), but absence of any mass (m/z) corresponding to CT complex in c) indicates that they are much weaker compared to that of **NDI-Cat**- **DIPY** pair. This also proves the interaction of HEG chain and quaternary nitrogen in stabilizing the D-A pair.

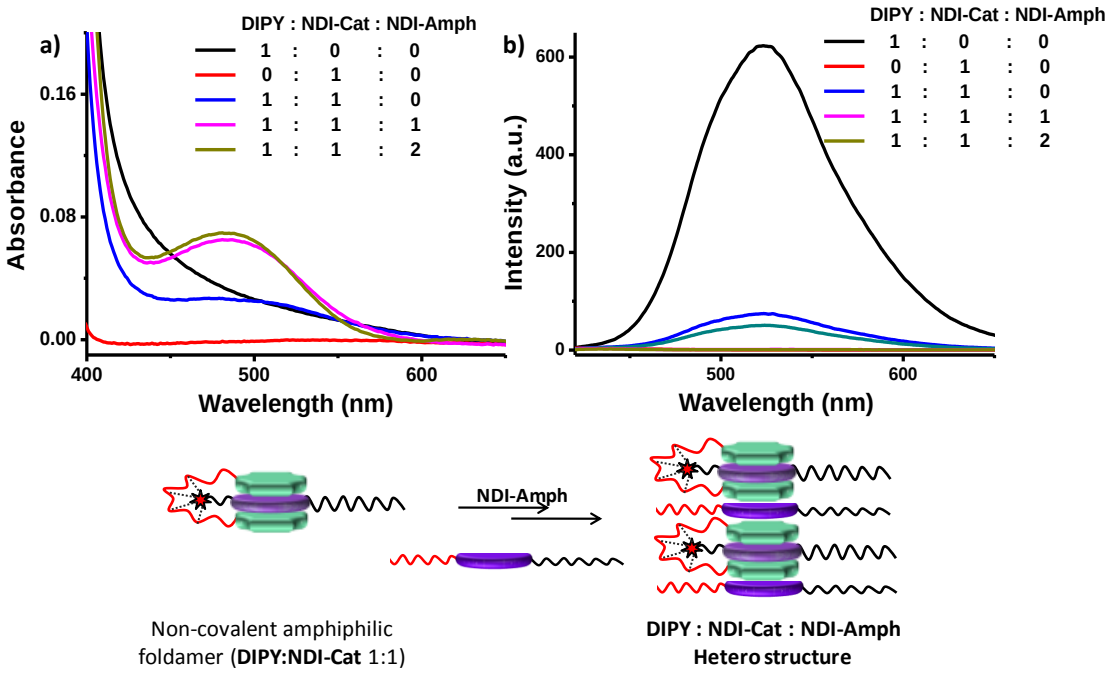


Fig. S9 Steady state a) absorption and b) emission spectra showing two step process leading to formation of heterostructure. Addition of **NDI-Amph** to pre-formed 1:1 CT complex of **NDI-Cat** and **DIPY** shows further enhancement of CT absorption band with quenching of fluorescence intensity indicating formation of hetero CT stack. Schematic illustration of the two step process is also shown.

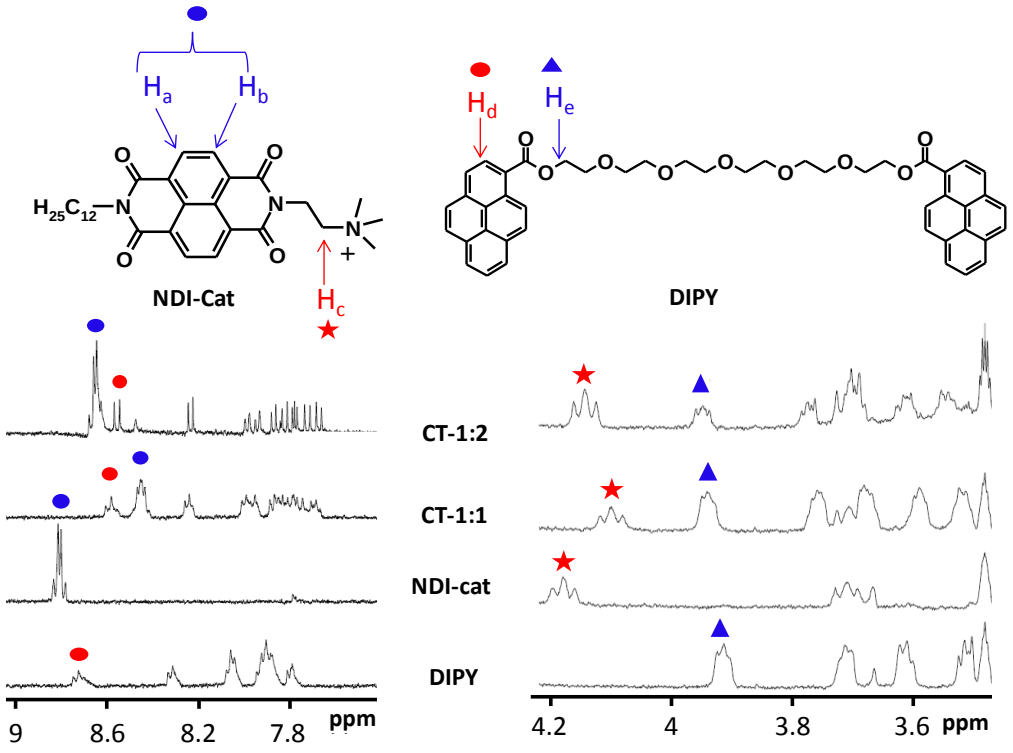


Fig. S10 Variation in the ^{1}H NMR spectra of **DIPY** and **NDI-Cat** upon CT complex formation (35 % D_2O in CD_3OD at 1.2 X 10^{-4} M). Protons of interest are colour coded to guide the eye. Interestingly, 1:2 complex show sharpening of **DIPY** and NDI peaks along with slight downfield shift. Sharpening of peak could be due to the improved ordering of CT complex in the extended organization leading to 1-D fibers. Downfield shift of protons in the 1:2 complex could be due to the time average signal of two types of NDI involved in two step processes. High concentration and lower D_2O composition (compared to optical studies) was required to get significant NMR signal in the aggregated state.

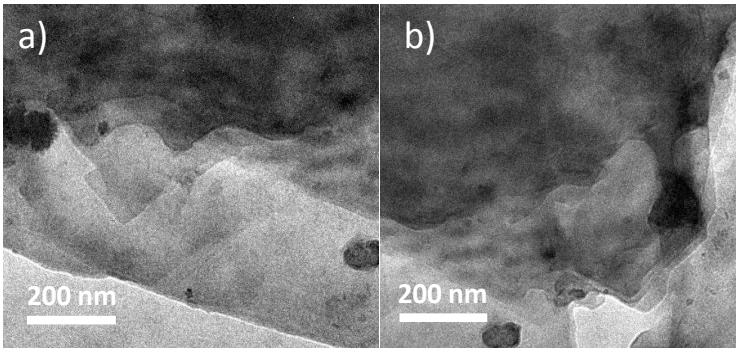


Fig. S11 Additional TEM images of **DIPY** sheets (4X10^{-5} M, 30% methanol in water).

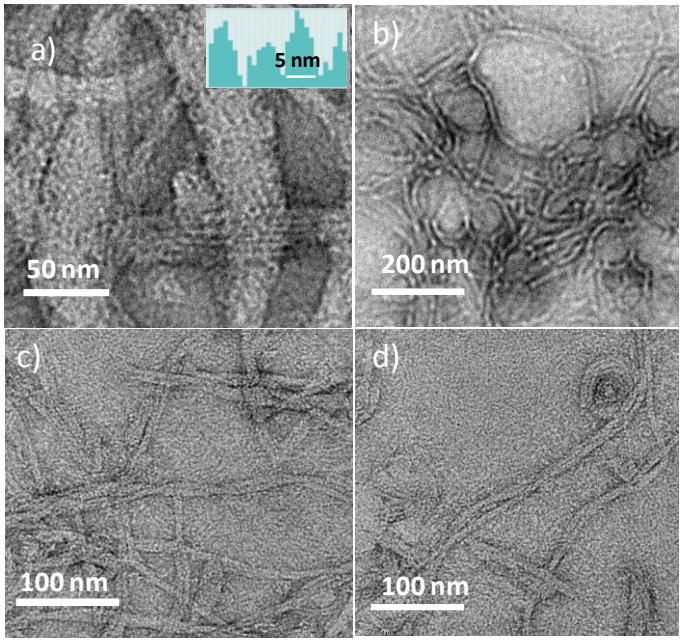


Fig S12 TEM images of a), b) 1:1 CT complex showing nanofibers of width 5 nm as seen from the electron density profile in inset of a) whereas c), d) are nanofibers formed by 1:2 charge transfer complex of **DIPY** and **NDI-Cat** in 4 X 10^{-5} M (30% methanol in water). Although the self-assembled amphiphilic CT foldamer in 1:1 ratio also showed 1-D nanofibers, they showed slight variation of width to around 5 nm as compared to 6 nm obtained with 1:2 CT complex, which could be due to the differences in the volume fraction of hydrophobic and hydrophilic components in two cases.

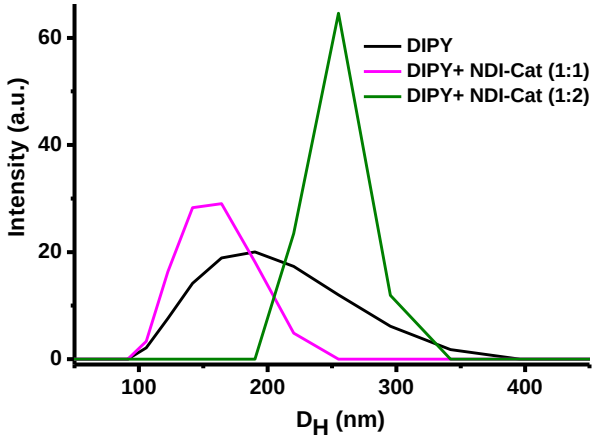


Fig. S13 Dynamic light scattering (DLS) measurements showing the hydrodynamic size distribution of **DIPY** and its CT co-assembly with **NDI-Cat** (c = 4 x 10^{-5} M, 30 % Methanol in water). Alone **NDI-Cat** being molecularly dissolved do not scatter.