Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Molecular Recognition Driven Self-Assembly and Chiral Induction in Naphthalene Diimide Amphiphiles

Mohit Kumar, Narendra Jonnalagadda 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

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 sample was stained with uranyl acetate (1 wt % in water) before the measurements. For TEM, water was used instead of aq. HEPES solution to avoid masking of nanostructures due to HEPES deposition upon drying.

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 10 mm path length cuvettes. Fluorescence spectra of solutions were recorded with 350 nm excitation wavelength. Circular Dichroism measurements were performed on a Jasco J-815 spectrometer where the sensitivity, time constant and scan rate were chosen appropriately. Corresponding temperature dependent measurements were performed with a CDF – 426S/15 Peltier-type temperature controller with a temperature range of 263-383 K and adjustable temperature slope.

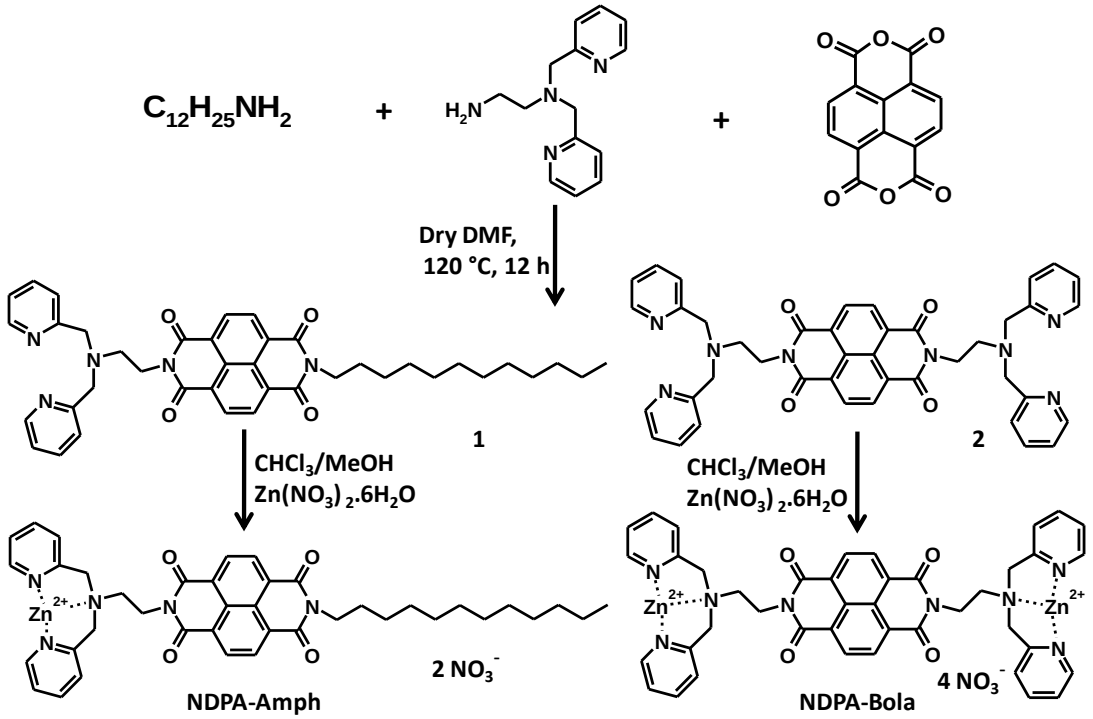
NMR Measurements: NMR spectra were obtained with a Bruker AVANCE 400 (400 MHz) Fourier transform NMR spectrometer with chemical shifts reported in parts per million (ppm) with respect to TMS.

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}. The samples were measured in a 10 mm glass cuvette.

Sample Preparation: All samples for spectroscopic measurements were prepared by injecting the stock solution of **NDPA-Amph** or **NDPA-Bola** into required volume of solvent (aq. HEPES buffer and THF, wherever applicable). To that required amount of phosphates were injected and the solution was mixed by manual shaking before measurements.

Materials: N,N-Bis(2-pyridylmethyl)ethane-1,2-diamine was synthesized based on reported procedure.[9] All other chemicals were purchased from the commercial sources and were used as such. Spectroscopic grade solvents were used for all optical measurements.

2. Synthesis and Procedures



Scheme S1. Synthetic scheme for **NDPA-Amph** and **NDPA-Bola** amphiphiles.

Synthesis of 1

1,4,5,8-Naphthalenetetracarboxylic dianhydride (1 g, 3.73 mmol) was added to N,N-Bis(2-pyridylmethyl)ethane-1,2-diamine (1.08 g, 4.47 mmol) and dodecylamine (0.82 g, 4.47 mmol) in 20 ml DMF and the reaction mixture was stirred at 120 $^{\circ}$C overnight. DMF was evaporated under vacuum and residue was extracted with chloroform and water. Organic layer was dried over anhydrous Na_2SO_4, and solvent was evaporated. Compound was purified by column chromatography to give 110 mg of desired product **1** (Yield = 5 %). Low yield was mainly due to a) statistical three possible products, b) presence of basic pyridine group in the compound which tend to stick to silica gel during column chromatography. ^{1}H NMR (400MHz, $CDCl_3$, TMS) : δ 8.77 (d, 2H, J = 7.6 Hz), 8.67 (d, 2H, J = 7.6 Hz), 8.36 (m, 2H), 7.30 (m, 4H), 7.00 (m, 2H), 4.40 (t, 2H, J = 6.2 Hz), 4.20 (m, 2H), 3.90(s, 4H), 2.95 (t, 2H, J = 6.2 Hz), 1.25 (m, 20H), 0.87 (t, 3H, J =7 Hz); ^{13}C NMR δ_C (100 MHz, $CDCl_3$): 163.00, 162.76, 159.55, 149.05, 136.24, 131.07, 130.99, 126.84, 126.79, 126.76, 123.00, 121.98, 60.42, 51.42, 41.20, 38.63, 32.05, 29.78, 29.76, 29.73, 29.67, 29.48, 29.25, 27.25, 22.82, 14.25; MS (ESI): m/z calcd for $C_{40}H_{45}N_5O_4$: 659.84 [M^+], found: 659.0.

Synthesis of NDPA-Amph

50 mg (0.07 mmol) of **1** was taken in $CHCl_3$ (3 ml) and was added drop wise to a solution of $Zn(NO_3)_2.6H_2O$ (42 mg, 0.1 mmol) in methanol (1 ml). The reaction mixture was then stirred for 30 minutes at room temperature and then the solvent was evaporated. The residue obtained was dissolved in $CHCl_3$ and filtered to remove the unreacted $Zn(NO_3)_2.6H_2O$. Filtrate was distilled under low pressure to get 50 mg of the desired product **NDPA-Amph** as white solid (Yield = 78.5 %). ^{1}H NMR (400MHz, $CDCl_3$, TMS) : δ 8.82 (d, 2H, J = 4.9 Hz), 8.70 (d, 2H, J = 7.6 Hz), 8.62 (d, 2H, J = 7.6 Hz), 8.04 (dt, 2H, J = 7.7, 1.6 Hz), 7.58 (m, 4H), 4.70 (m, 2H, J = 15 Hz), 4.50 (m, 2H), 4.40 (m, 2H), 4.16 (t, 2H, J = 7.6 Hz), 2.82 (t, 2H, J = 7.6 Hz), 1.24-1.72 (m, 20H), 0.86 (t, 3H, J = 6.8 Hz); ^{13}C NMR δ_C (100 MHz, $CDCl_3$): 162.70, 162.66, 153.9, 149.07, 140.95, 131.31, 130.99, 127.23, 126.74, 126.72, 125.95, 125.59, 124.43, 56.42, 47.68, 41.22, 33.52, 32.04, 29.75, 29.74, 29.71, 29.64, 29.46, 29.43, 28.18, 27.21, 22.81, 14.24; HRMS (ESI): m/z: calcd for M-$Zn(NO_3)_2$ i.e. $C_{40}H_{45}N_5O_4$: 659.8134, found : 660.3562.

Synthesis of NDPA-Bola

This compound was synthesized following the reported procedure and all characterization were done accordingly.[9]

3. Supporting Figures

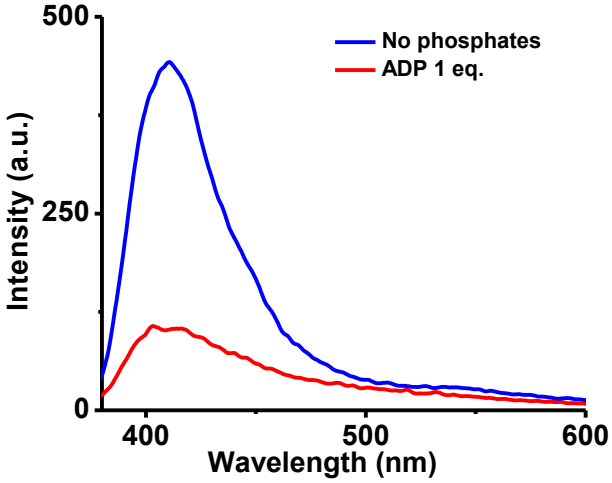


Fig. S1 Change in the emission intensity upon binding of ADP to **NDPA-Bola** (λ_{exc} = 350 nm, c= $5x10^{-5}$ M, 10 mM aq. HEPES buffer). The decrease in fluorescence is indication of guest induced NDI self-assembly.

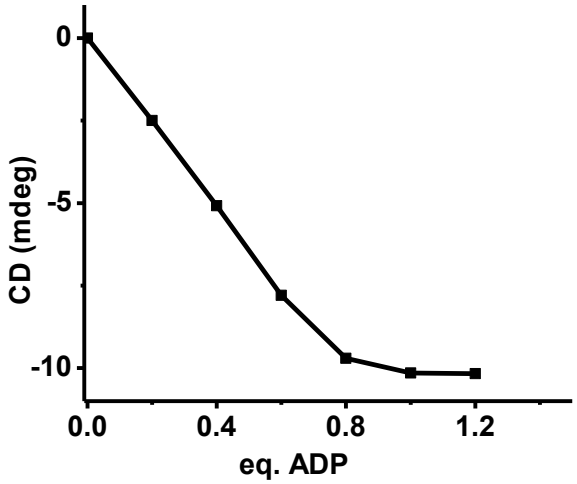


Fig. S2 CD titration data of **NDPA-Bola** with varying equivalents of ADP, (c = $5x10^{-5}$ M, 10 mM aq. HEPES buffer).

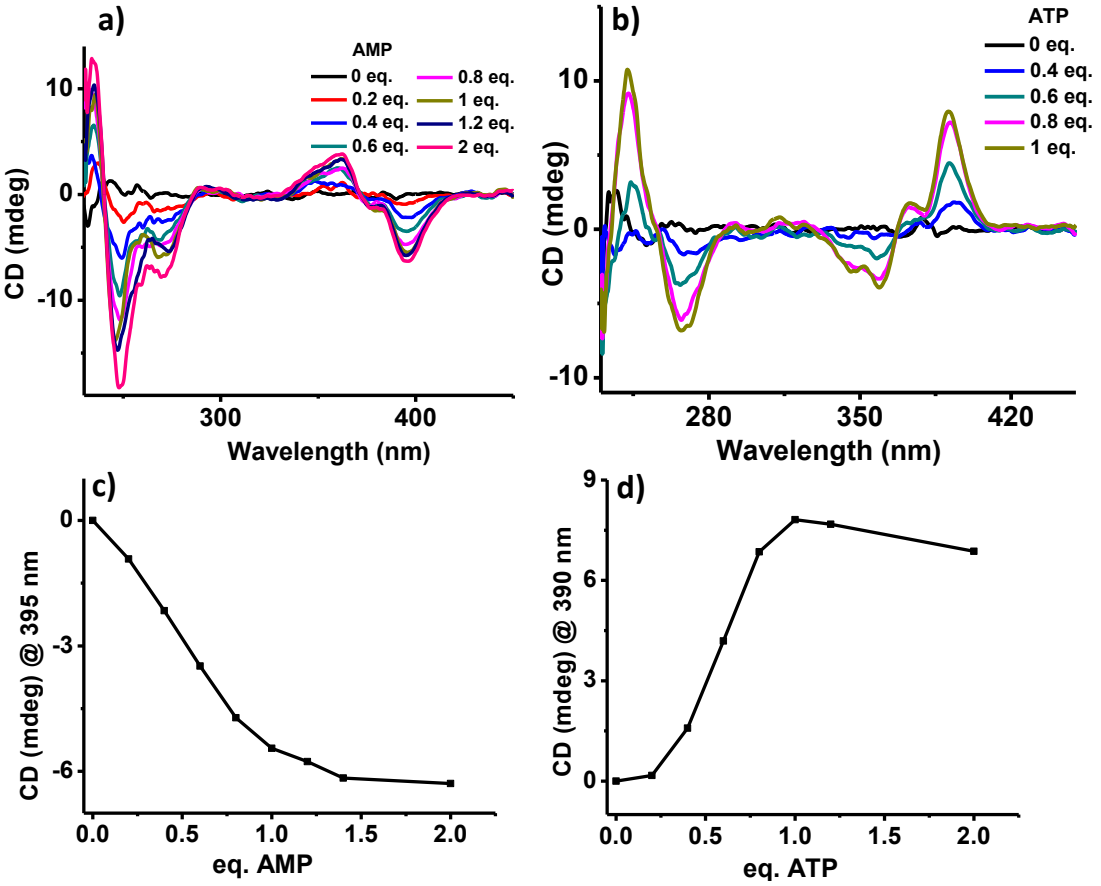


Fig. S3 Evolution of CD signals upon binding of a) AMP and b) ATP to **NDPA-Bola.** c) and d) show corresponding CD titration data with varying equivalents of AMP and ATP respectively, (c = $5x10^{-5}$ M, 10 mM aq. HEPES buffer).

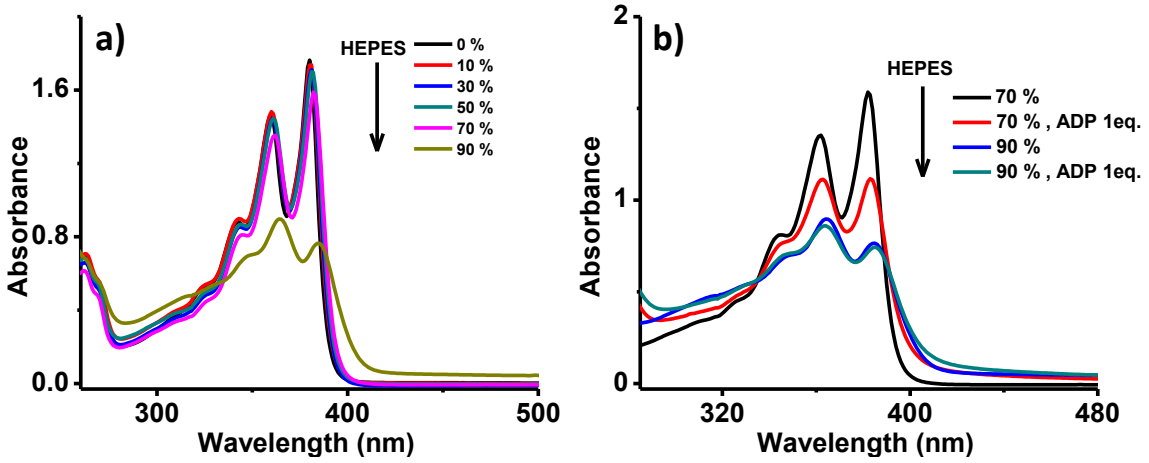


Fig. S4 Absorption changes of **NDPA-Amph** upon a) increasing the percentage of aq. HEPES buffer in THF and b) binding of molar equivalent of ADP at varying solvent compositions (c = $7x10^{-5}$ M).

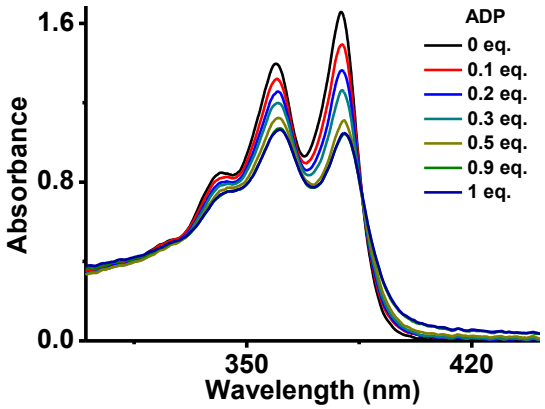


Fig. S5 Changes in absorption spectra of **NDPA-Amph** upon titration with ADP (70 % aq. HEPES buffer, 7x10^{-5} M).

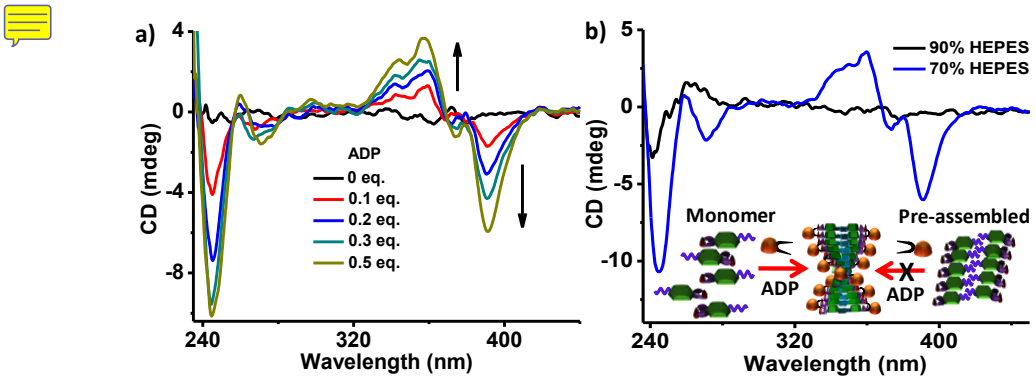


Fig. S6 CD spectra of **NDPA-Amph** (c = 7x10^{-5} M) a) upon ADP titration, 70% aq. HEPES buffer in THF and b) varying solvent composition (0.5 eq. ADP). Inset of b shows the schematic of chiral induction process.

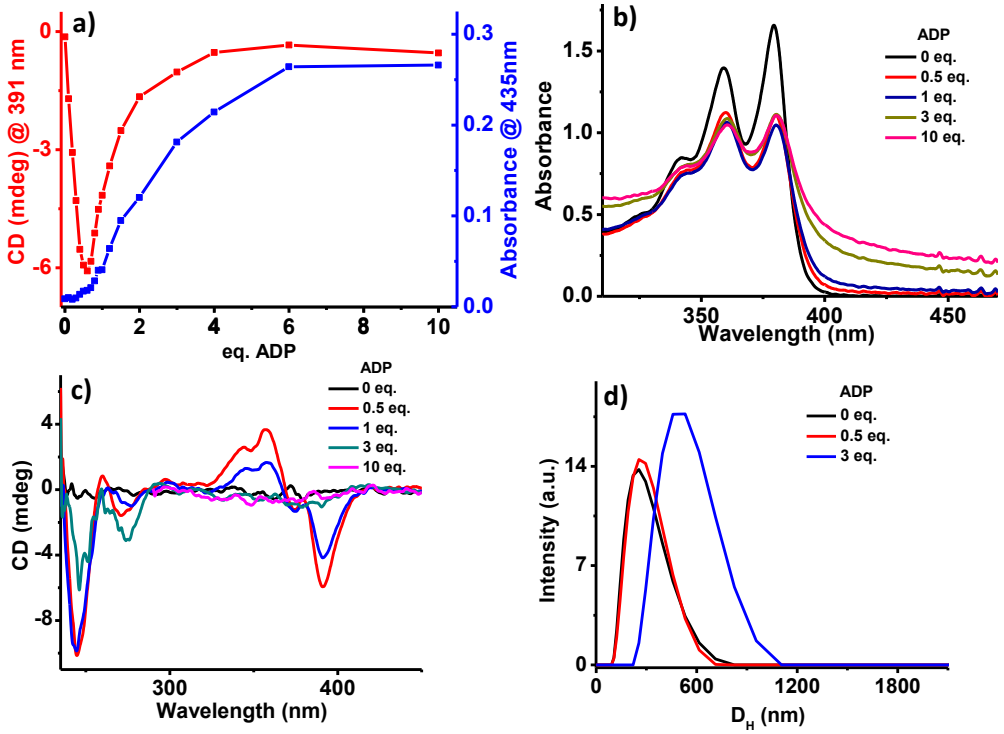


Fig. S7 a) Plots of CD intensity at 391 nm and absorbance at 435 nm of **NDPA-Amph** (7x10^{-5} M, 70 % HEPES in THF) upon titration with ADP. Changes in b) absorbance, c) CD spectra and

d) hydrodynamic size distribution measured using DLS with varying equivalents of ADP are also shown. The saturation of CD signal at 0.5 equivalents of ADP suggests the clip type binding of ADP to NDI molecules, similar to that of **NDPA-Bola**. Increase in scattering intensity and particle size with the simultaneous disappearnce of CD signal at higher equivalents of ADP indicates the formation of higher order aggregates, probably due to the cross-linking.

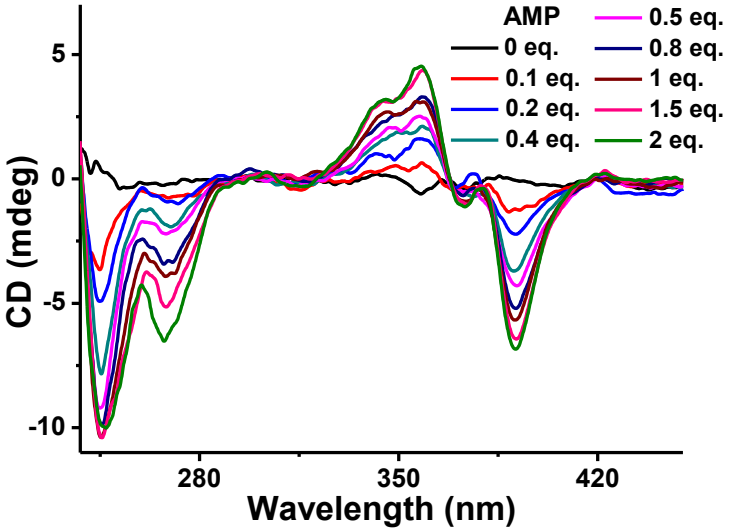


Fig. S8 Evolution of CD signal of **NDPA-Amph** with varying equivalents of AMP, (c = $7x10^{-5}$ M, 70% aq. HEPES buffer in THF).

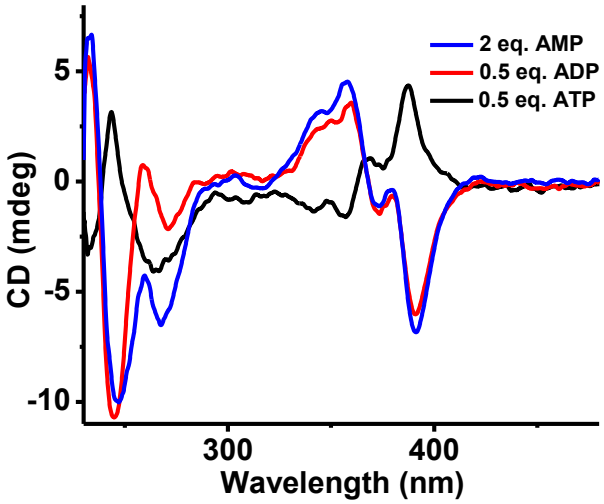


Fig. S9 Saturated, mirror image CD spectra of **NDPA-Amph** upon binding with various adenosine phosphates. (c = $7x10^{-5}$ M, 70% aq. HEPES buffer in THF).

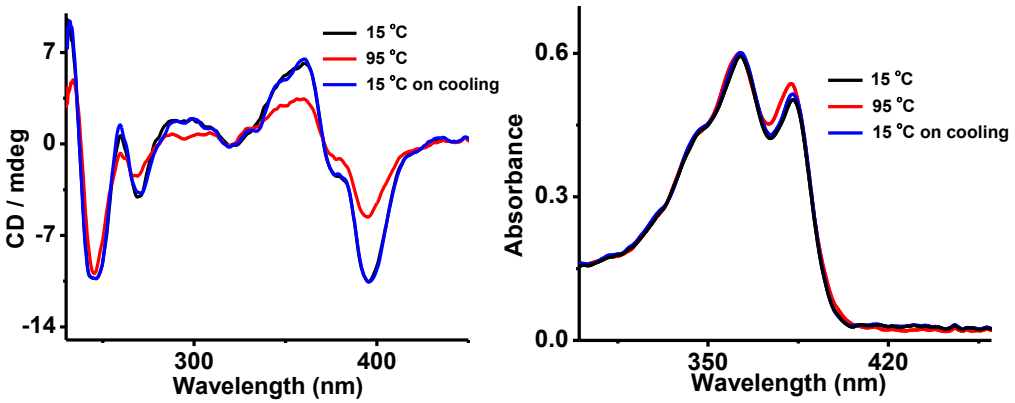


Fig. S10 Temperature dependent a) CD and b) absorption spectra of **NDPA-Bola** upon addition of 1 eq. ADP, (c = $5x10^{-5}$ M, 10mM aq. HEPES buffer).

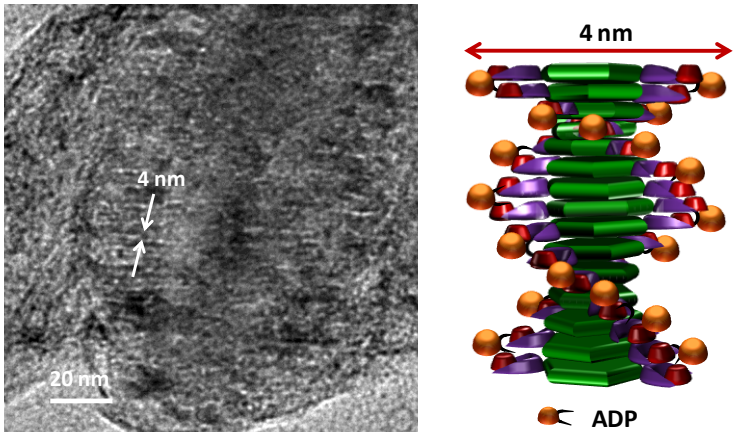


Fig. S11 TEM images obtained by drop casting 5 x 10^{-5} M aqueous solution of **NDPA-Amph** on copper grid with 1 eq. ADP. The sample was post stained with uranylacetate (1 wt % in water).

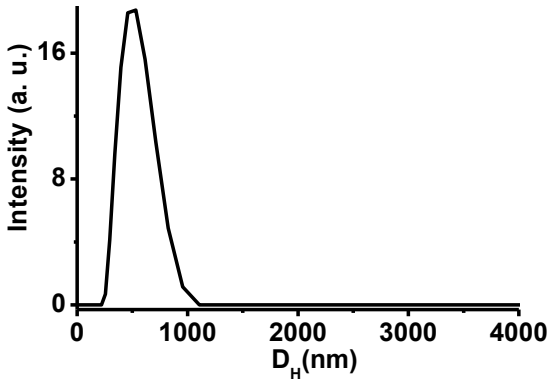


Fig. S12 Dynamic light scattering measurement showing hydrodynamic size distribution of **NDPA-Bola** assembly with 1 eq. ADP (c = $5x10^{-5}$ M, 10 mM aq. HEPES buffer).

Note : With ref. to **Fig. 3** Absence of chiral induction in pre-assembled NDPA-Amph assemblies is probably due to different energy minima of either achiral stack or solvent composition compared to helical co-assembled counter-parts with ADP which allow CD reversal even in aggregated state.