Solvophobic Control of Core-Substituted Naphthalene Diimide Nanostructures
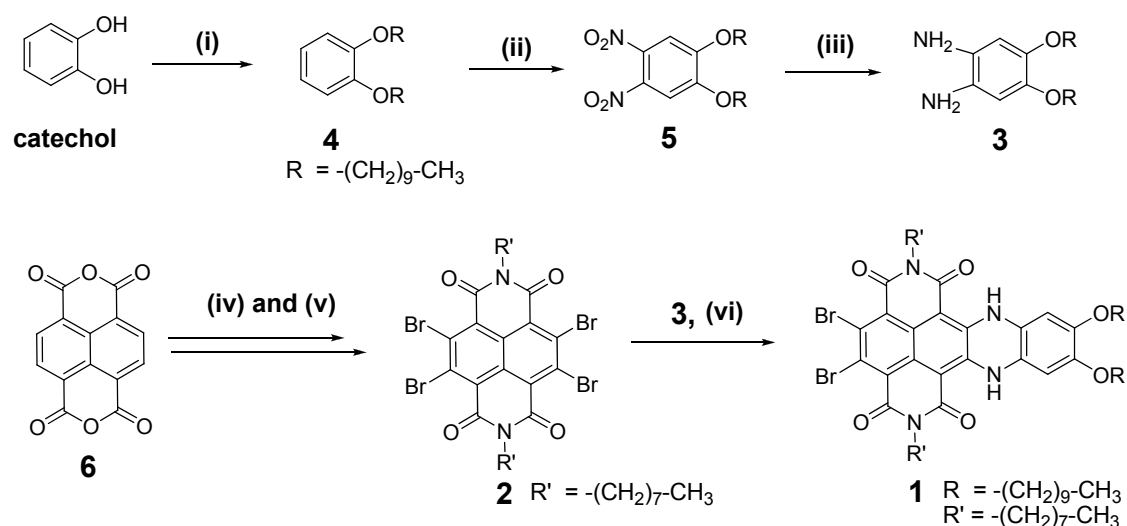
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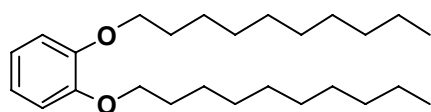## 1. Material and measurements

Catechol, naphthalene tetracarboxy dianhydride, DMF, chloroform, methanol and dichloromethane were purchased from Aldrich and used without purification, unless otherwise specified. UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 40p spectrometer. ^{1}H NMR, ^{13}C-NMR spectra were recorded on a Bruker spectrometer using chloroform-d as solvent and tetramethylsilane as an internal standard. The solvents for spectroscopic studies were of spectroscopic grade and used as received. The mixed aggregate system was prepared by dissolving NDI **1** in CHCl$_3$ and methanol injected over on it (10%-80%). The sample solution was kept at room temperature for one day before AFM measurements.

2. Synthesis and Characterisation for 1

Scheme 1. Synthesis of one-side-di-core-substituted naphthalene diimide 1. Reagents and conditions: (i) Br-(CH$_2$)$_{11}$-CH$_3$, DMF, K$_2$CO$_3$, 90°C, 3d; (ii) HNO$_3$, H$_2$SO$_4$, DCM, 16h; (iii) Pd/C, hydrazine hydrate, rt. 16h; (iv) 30% SO$_3^-$, H$_2$SO$_4$, NaBr, overnight, 130°C; (v) octylamine, AcOH, 90°C, overnight; (vi) DMF, 135°C, 15 min.
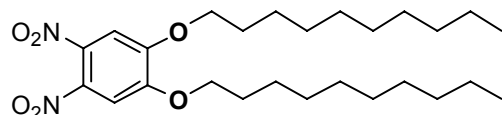
1,2-bis(dodecyloxy)benzene (4).

This compound was synthesized using known literature method with slight modification.[S2]

Catechol (2.5 g, 0.02 mol) and K_2CO_3 (5.5 g, 0.1 mol) were placed in a two-necked RBF under a nitrogen atmosphere. DMF (100 ml) was added via a syringe. After stirring for 20 min. at room temperature, $C_{12}H_{25}Br$ (0.06 mmol) was added and the mixture was heated at 90°C for 3 days. The mixture was allowed to cool down to ambient temperature before pouring into de-ionised water (100 ml) into it. Diethyl ether (3x60 ml) was used to extract the product and the combined organic phases were dried over $MgSO_4$ and removed *in vacuo*. White needle-like crystals were obtained which were recrystallised from ethanol and dried *in vacuo* obtained **4** (60%). ^1H NMR (CDCl$_3$, 300 MHz) δ 6.88 (s, 4H, ArH), 3.99 (t, *J* 6.6 Hz, 4H, O-CH$_2$), 1.85-1.74 (m, 4H, CH$_2$), 1.46-1.20 (m, 24H, CH$_2$), 0.88 (t, *J* 6.8 Hz, 6H, CH$_3$). All spectra of 1,2-dialkoxybenzene agree with those in previous reports.[S2]

1,2-Bis(dodecyloxy)-4,5-dinitrobenzene (5).

This compound was synthesized using known literature method with slight modification.[S3]
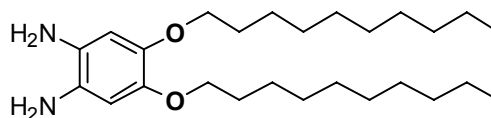
To a cooled (15 °C) mixture of 4.5 g (0.01 mol) of **4** and 70 mL of glacial acetic acid in 70 mL of dichloromethane was slowly added 10 mL of concentrated nitric acid (65%), while keeping the temperature below 40°C. After being stirred for 30 min, the solution was again cooled to 15 °C, 25 mL of fuming nitric acid (100%) was slowly added, and the mixture was stirred at room temperature for 3 days. The solution was poured into 250 g of ice water, and the organic layer was washed with water (3 × 150 mL), saturated NaHCO$_3$ solution (150 mL), and brine (150 mL). After the mixture was dried with MgSO$_4$, the solvent was evaporated. Recrystallization from acetone yields 4.0 g (75%) of **5**: mp 83-84 °C; ^1H NMR (CDCl$_3$, 300 MHz): δ 7.29 (s, 2H), 4.10 (t, *J* = 6.6 Hz, 4H,), 1.87 (m, 4H), 1.52-1.26 (m, 24H),0.88 (t, *J* = 6.4 Hz, 6H); ^{13}C NMR (CDCl$_3$): δ 151.8 (s), 136.5 (s), 107.9 (d), 70.2 (t), 31.9 (t), 29.7 (t), 29.6 (t), 29.4 (t), 29.2 (t), 28.7 (t), 25.8 (t), 22.7 (t), 14.1 (q); MS-FAB *m/z* 538.1 ((M + 2H)$^+$.
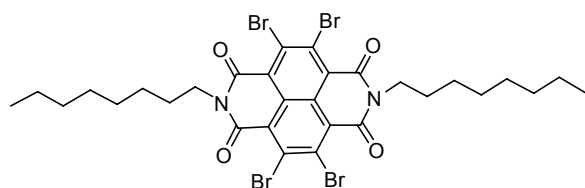
1,2-Bis(dodecyloxy)-4,5-diaminobenzene (3).

This compound was synthesized using known literature method with slight modification.[S3]

To a solution of 900 mg (1.7 mmol) of 5 in 25 mL of ethanol, 0.05 g of 10% Pd/C, and 3.6 mL (18 mmol) of hydrazine monohydrate were added. After overnight of refluxing, the hot solution was filtered over celite, while kept under N_2. After cooling, the white precipitate was filtered off and rinsed with cold, O_2-free methanol: yield 620 mg (80%); mp 73-74 °C; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 6.38 (s, 2H), 3.90 (t, J = 6.6 Hz, 4H), 1.80 (m, 4H), 1.52-1.26 (m, 24H), 0.88 (t, J = 6.4 Hz, 6H); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 143.4 (s), 128.4 (s), 106.8 (d), 70.7 (t), 31.9 (t), 29.7 (2 × t), 29.6 (t), 29.5 (t), 29.4 (t), 26.1 (t), 22.7 (t), 14.1 (q); MS-EI m/z 476.4 (M[+]).

2,3,6,7-Tetrabromo-dioctyl-naphthalene diimide (2):[S4] Firstly 2,3,6,7-tetrabromo-naphthalene dianhydride was prepared from naphthalene dianhydride by literature method obtained yellow solid with 93% yield.[S4] Following a literature

method, compound **2** was synthesized in 30% yields as yellow crystalline solid. M.P. 259-260 °C. No fluorescence output. All spectroscopic data matches with literature.[S1]

Core-Substituted naphthalene diimide (1)

Mixture of 2,3,6,7-tetrabromo-dioctyl-naphthalene diimide **2** (100 mg, 1.2×10^{-4} mol) and 1,2-bis(dodecyloxy)-4,5-diamino benzene **3** (0.237 mg, 4.98×10^{-4} mol) in dry DMF (5 mL) heated at 135°C for 15 min. (colour change was observed yellowish to dark green), completion of the reaction was monitored by TLC. After completion DMF was removed on rotary evaporator, and purified by column chromatography on flash silica column eluate with 1:1 DCM/hexane. Dark green crystals were obtained **1** (89 mg, 74%). ^{1}H NMR (CDCl$_3$, 300 MHz) δ 12.75 (s, 2H), 6.3 (s, 2H), 3.93 (t, J = 7.8, 4H), 4.05 (t, J = 7.8, 4H), 1.88 (m, 4H), 1.65 (m, 4H), 1.5 (m, 6H), 1.31 (m, 40H), 0.87 (m, 12H). [13]C

NMR (CDCl$_3$, 125 MHz) δ 164.2, 160.0, 149.0, 128.0, 120.9, 120.4, 94.0, 32.1, 32.0, 29.9, 29.8, 29.7, 29.6, 20.5, 29.5, 29.3, 27.5, 26.2, 22.9, 22.8, 14.3, 14.2. FT-IR (KBr, Cm^{-1}) ν 2959, 2925, 2852, 1716, 1666, 1502, 1431, 1409, 1374, 1287, 1173, 1157, 1013, 910, 789, 768, 721, 582, 545. UV/vis (CH$_2$Cl$_2$): λ_{max} (ε/M^{-1}cm^{-1}) = 629 (36 000), 582 (15 550), 538 (5400), 431 (25 750), 408 (12 700), 388 nm (4250). Fluorescence (CH$_2$Cl$_2$): λ_{max} 699, 647 (λ_{ex} = 571 nm). HRMS (ESI): calcd. for C$_{56}$H$_{80}$Br$_2$N$_4$O$_6$: m/z 1062.4444; found 1062.4419.

3. UV-vis absorption spectroscopy

Stock solutions (concentration 1×10^{-3} M) of NDI **1** dye were made in CHCl$_3$. A 0.2 mL aliquot of the stock solution was transferred to two different volumetric flasks of CHCl$_3$ and MeOH, or hexane, and made up to 2 mL volume. The solutions were allowed to equilibrate for 2 h prior to the spectroscopic measurements. For variable-temperature UV-visible spectroscopic experiments, a 25 min interval was given before each measurement after the desired temperature was reached. Furthermore, Figure S1 shows the absorption spectra of NDI **1** in various ratios of hexane and chloroform. The latter is a good solvent for solvation of the π system of NDI dyes, hence the dyes do not form aggregates at a high CHCl$_3$ 90% content at the concentration (1×10^{-4} M) applied in these experiments. Thus, for a CHCl$_3$/MeOH or hexane (v/v 9:1) ratio the major absorption band shows the well-resolved vibronic structure ranging from 410 to 660nm that is characteristic for the S0–S1 transition of the isolated NDIs chromophore. In contrast, methanol is a bad solvent for the solvation of the π system of NDI. As a consequence, the dye is not soluble in pure MeOH and aggregation is observed at higher volume ratios of CHCl$_3$/hexane (v/v 1:1 and 0:1) as evidenced by distinct spectral changes (Figure S1). The most prominent features are a reduction in the peak intensity along with a significant blueshift of the absorption maximum and a loss of the fine structure. These features suggest the formation of face-to-face π stacks of rotationally displaced NDI chromophores, similar effect observed in the case of perylenediimides[5] and other systems.[S6]
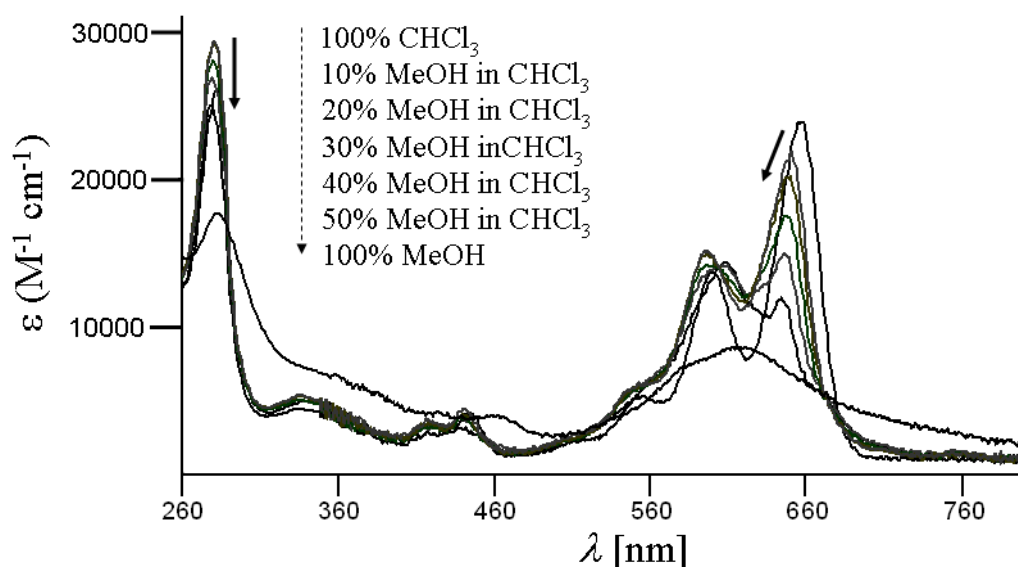
Figure S1. UV/vis spectroscopy of NDI **1** in CHCl$_3$ ([**1**] = 1x10^{-4} M) and with increasing concentration of methanol at 20°C.
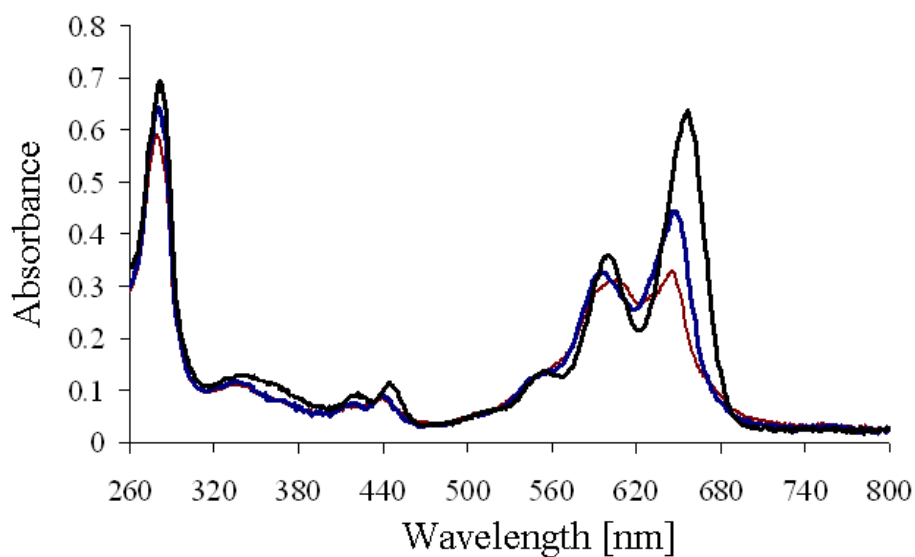

Figure S2. UV/vis spectroscopy of NDI **1** in CHCl$_3$ (black), 1:1 CHCl$_3$/hexane and only hexane (dark red).

4. Atomic force microscopy (AFM) of NDIs 1

The samples were characterised using an Atomic Force Microscope (AFM) from Agilent Technologies (5500 AFM). Micromach Ultrasharp probes with silica wafer coating for enhanced reflectivity (NSC15/AIBS), with a typical resonance frequency of 325 kHz and

a force constant of 40 N/m, were used for imaging. Sample of NDIs were prepared by spin-coating the freshly prepared solution (1×10^{-4} M in CHCl3/MeOH v/v 6:4) onto silica coating at 2000 rpm. The vesicle diameter and height was performed by measuring the mean horizontal distance and height of particles (see Figure 2 in manuscript and Figure S2-S4). AFM images showing evolution of self-assembling supramolecular structures of **1** through increasing amounts of methanol in chloroform 10-40% (a-d) respectively as shown in figure S3.
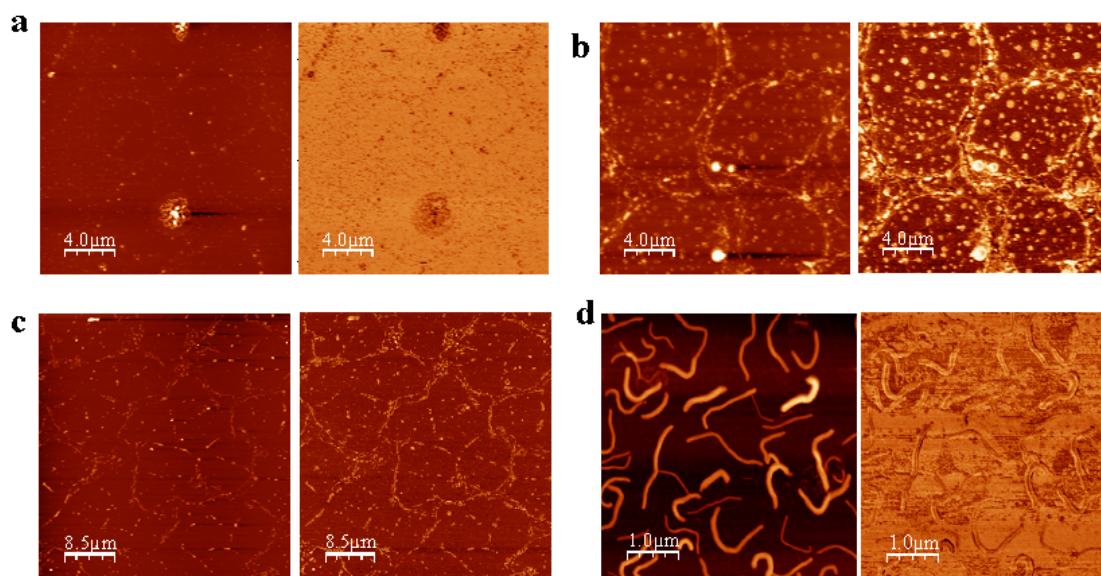

Figure S3: AFM images showing evolution of self-assembling supramolecular structures of **1** through increasing amounts of methanol in chloroform (a) 10% (b) 20% (c) 30% (d) 40% respectively, (Topography images on left and phase images on right).

4.1. *3-D topology and phases of 1*

The hypothesis for the formation of worm-like aggregates from molecules of **1** is further supported by 3D phase images of the worms. Phase images in AFM are simulated graphic contrasts created as a result of difference in responses during the interaction of the probe tip with different material properties (especially elasticity). For example the interaction of the tip with the aliphatic regions invokes a response different to that with the aromatic region. Figure S4 shows 3D topography and phase images of the aggregates.
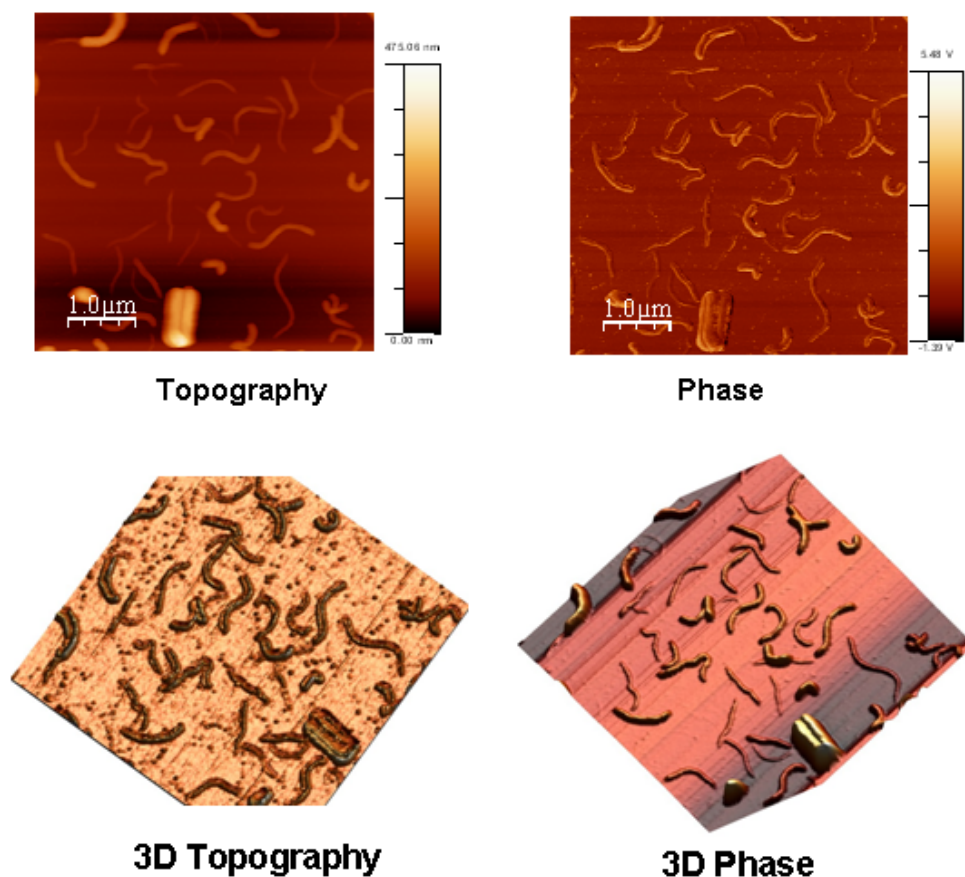
Figure S4: Topography, phase as well as 3D topography and 3D phase AFM images of self-assembled structures of **1** at 40% v/v methanol/chloroform

It can be observed in the phase images that each worm appears to have a hollow central region. This means that the edges of the worms are of a different elastic nature than the central region. This fits well with the proposed structure in which there is a central aromatic region surrounded by the aliphatic chains. Individual worms were imaged in order to elucidate further the nature of the aggregates and hence that of the self-assembly process (Figure S5).
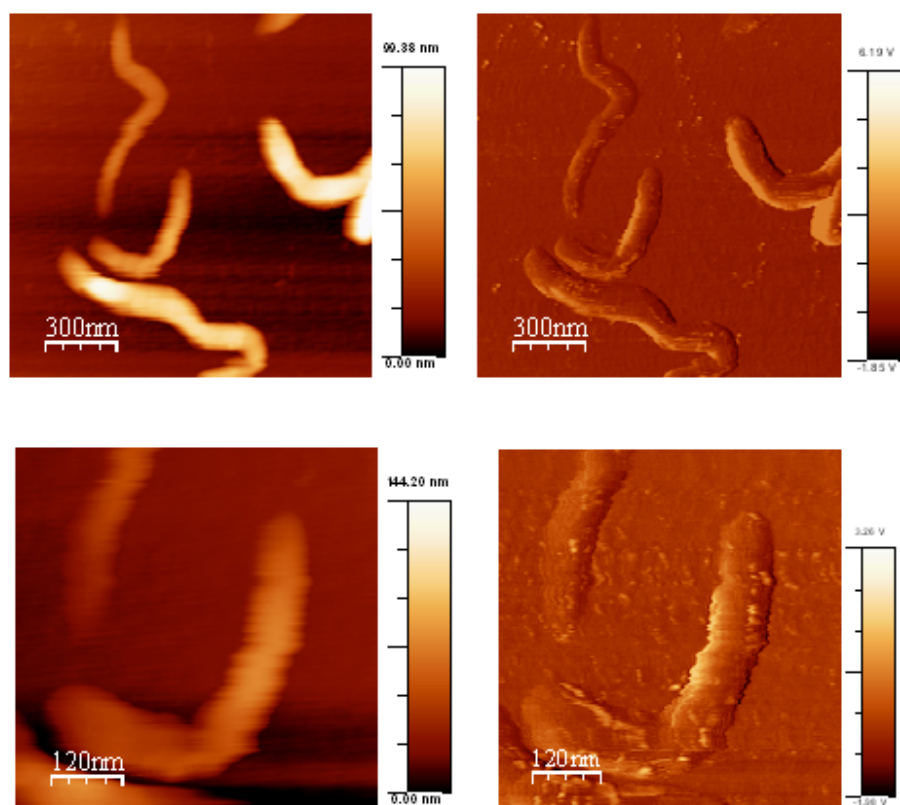
Figure S5: AFM images of individual self-assembled aggregates of **1** at 40% v/v methanol/chloroform (topography on left, phase on right)

5. Transmission electron microscopy (TEM) of NDI 1

TEM measurements were performed on an electron microscopy Igor 1200EX, operating at an accelerating voltage of 80 kV. 0.5 Microliter freshly prepared sample solution (1×10^{-4} M in hexane) was dropped onto a TEM grid (400-mesh copper grid coated with carbon) and the solvent was allowed to evaporate before introduction into the vacuum system. Negative stained was performed by addition of a drop of uranyl acetate onto the carbon grid, after few min. remaining solvent was removed by tapping with filter paper and images were collected. A representative image is shown in Figure S7.
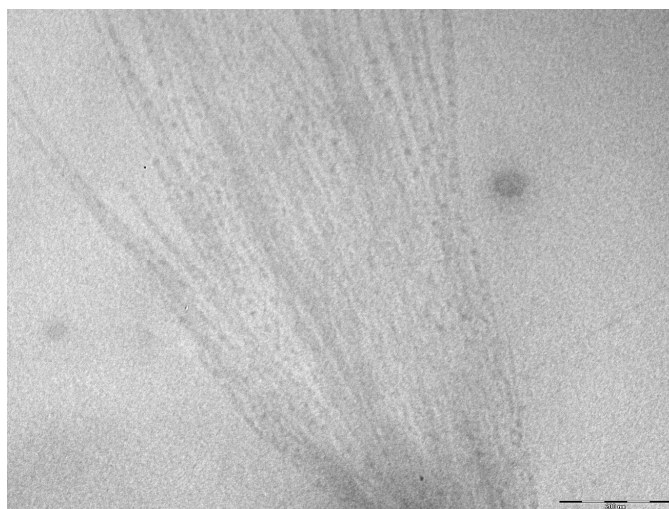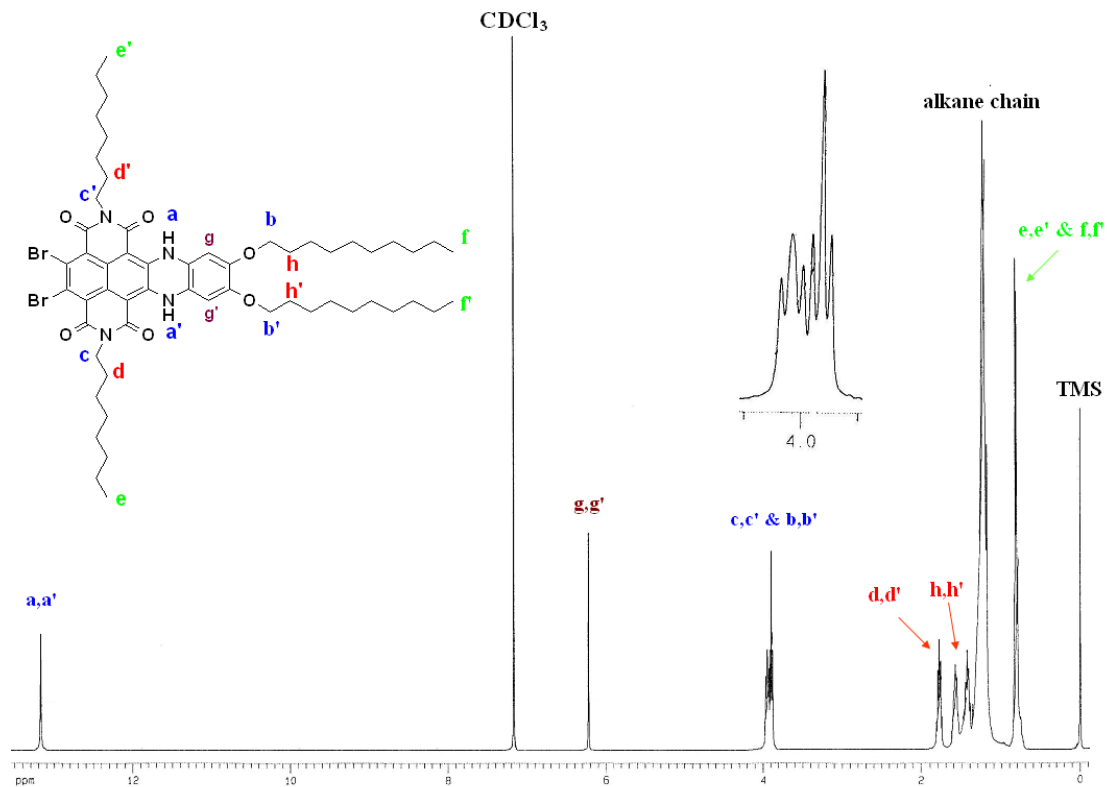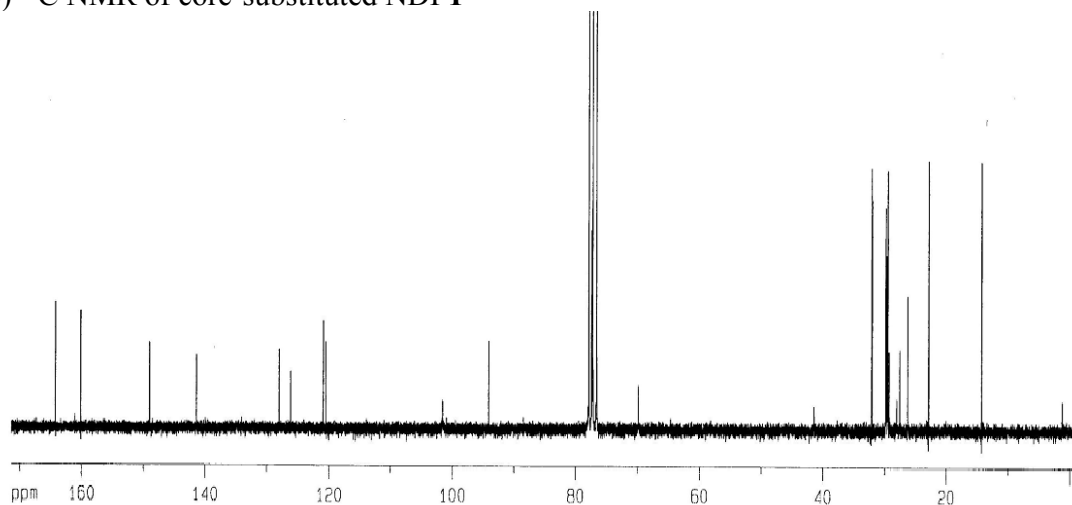
Figure S7. Transmission electron microscopy (TEM) micrograph of **1** (1×10^{-4} M) on holey, carbon-coated copper grids (scale bar are 100 nm), sample prepared in hexane.

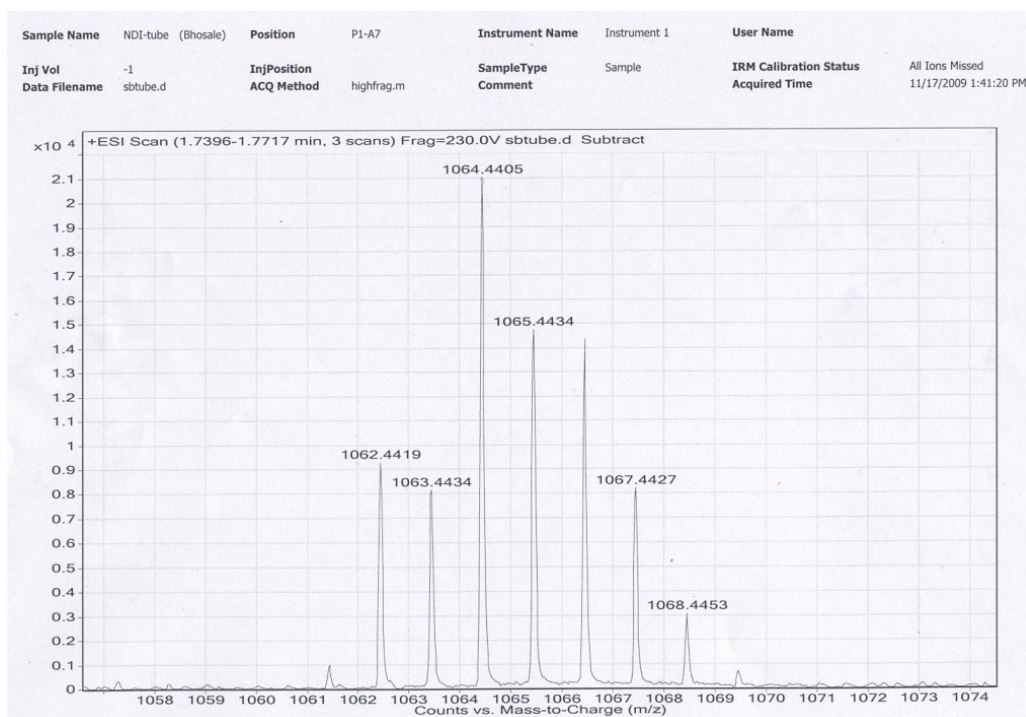## 6. Characterisation of core-substituted NDI

(a) ^{1}H NMR of core-substituted NDI **1**

(b) ^{13}C NMR of core-substituted NDI **1**

HRMS (ESI) of core-substituted NDI **1**

7. References

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