

Well-organized Supramolecular Self-Assembly of a Novel Acene Diimide Derivatives

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Methods, Materials

All reagents were purchased either from Sigma Aldrich Chemical Co. or Merck and used as such without any further purification. All the solvents were received from commercial sources and purified by standard methods. Melting points were determined in capillaries and are uncorrected. 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. ^1H 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. Mass spectrometric data were obtained by electron spray ionization (ESI-MS) technique on an Agilent Technologies 1100 Series (Agilent Chemstation Software) mass spectrometer. High-resolution mass spectra (HRMS) were obtained by using ESI-QTOF mass spectrometry. FTIR spectra were obtained on a Perkin Elmer FT-IR 400 spectrometer.

UV-VIS absorption spectroscopy

A 0.2 mL aliquot of the stock solution of **1** ($c = 10^{-3}$ M) or **2** ($c = 10^{-3}$ M) was transferred to various ratios of CHCl_3 /hexane, CHCl_3 /MeOH in different volumetric flasks, and made up to 2 mL volume. The solutions were allowed to equilibrate for 2 h prior to the spectroscopic measurements. Fig. S1 shows the absorption spectra of NDI **1** in various solvents. Fig. S2 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 650 to 775 nm that is characteristic for the S_0 – S_1 transition of the isolated NDIs chromophore. In contrast, methanol is a bad solvent for the solvation of the π system of NDI. Aggregation is observed at higher volume

ratios of CHCl_3 / as evidenced by distinct spectral changes (Fig. S1). The most prominent features are a reduction in the peak intensity along with a significant redshift 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 mono-annulated c-NDIs.^{1,2}

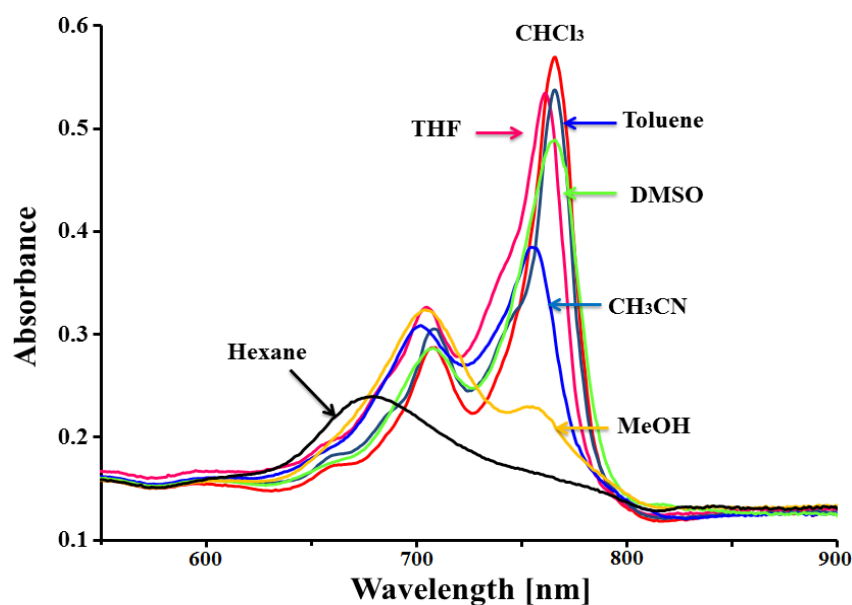


Fig. S1. UV-Vis absorption spectra of **2** (10^{-4} M) in various solvents.

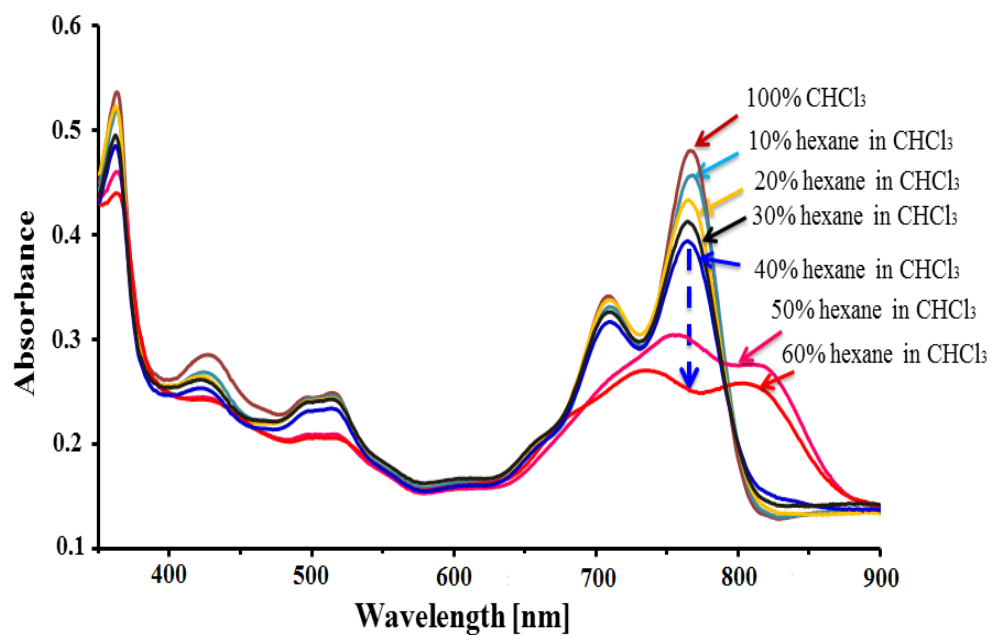


Fig. S2. UV/Vis spectra of acene diimides (**2** = 1.2×10^{-4} M) in various ratios of CHCl_3 /hexane at room temperature; blue arrow indicate the trend of absorption intensity changes upon increasing the methanol percentage.

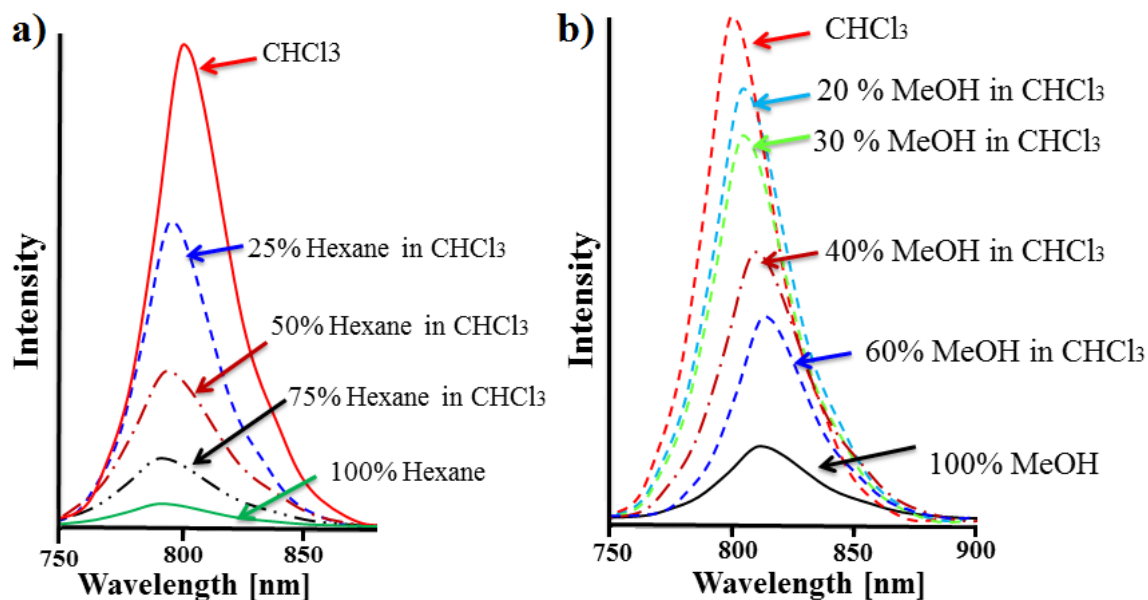


Fig. S3. Fluorescence spectra of (a) alkyl-annulated acene diimide (**2** = 1.0×10^{-4} M) in various ratios of CHCl_3 /hexane at room temperature, and (b) mTEG-annulated acene diimide (**1** = 1.5×10^{-4} M) increasing the methanol percentage in CHCl_3 .

Scanning Electron Microscopy (SEM): S Samples were sputter coated with gold for 10 s at 0.016 mA Ar plasma (SPI, West Chester, USA) for SEM imaging using a FEI Nova NanoSEM (Hillsboro, USA) operating at high vacuum and SEM and images were collected.

Sample preparation: Stock solutions (concentration 1×10^{-3} M) of alkyl-annulated acene diimide **1** dye were made in CHCl_3 . A 0.2 mL aliquot of the stock solution of **1** was transferred to four different volumetric flasks of (i) CHCl_3 /MeOH (4:6, v/v), (ii) CHCl_3 /MeOH (6:4, v/v), (iii) CHCl_3 /hexane (4:6, v/v), and (iv) CHCl_3 /hexane (4:6, v/v), and made up to 2 mL volume with respective solvents. The solutions were allowed to equilibrate

for 2 h prior to the Scanning Electron Microscopy (SEM) measurements. Similar procedure applied for the sample preparation of mTEG-annulated acene diimide **2**.

SEM images of alkyl-annulated acene diimide 1 in CHCl₃/MeOH (4:6, v/v):

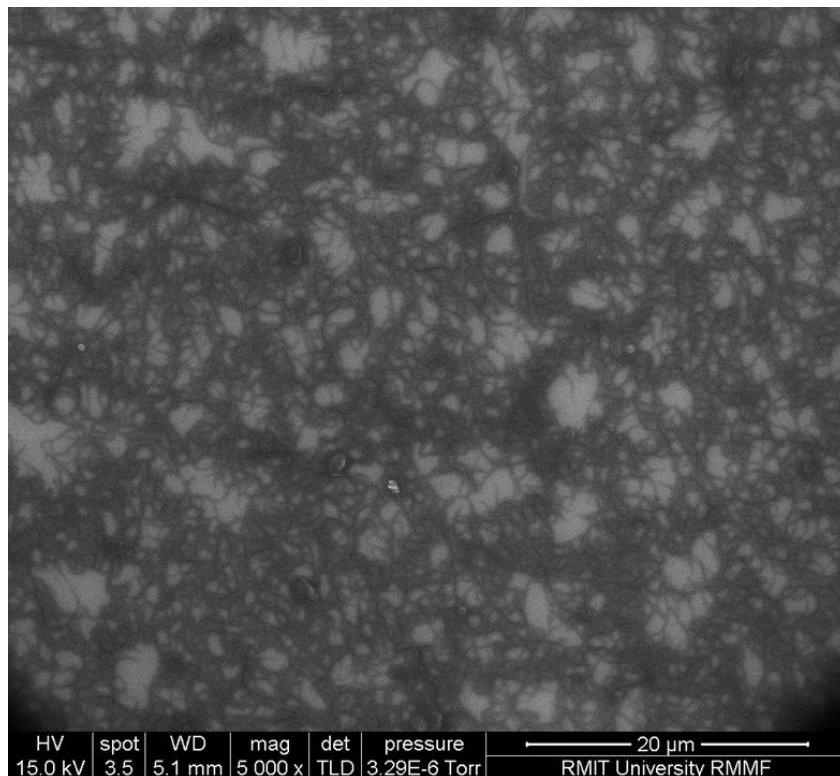


Fig. S4. SEM images of well-defined nanostructures formed by **1** from 1.2×10^{-4} M solution from 40% MeOH in CHCl₃.

SEM images of alkyl-annulated acene diimide 1 in CHCl₃/MeOH (6:4, v/v)

Fig. S4-S7. SEM images of well-defined nanostructures formed by **1** from 1.2×10^{-4} M solution from 60% MeOH in CHCl₃.

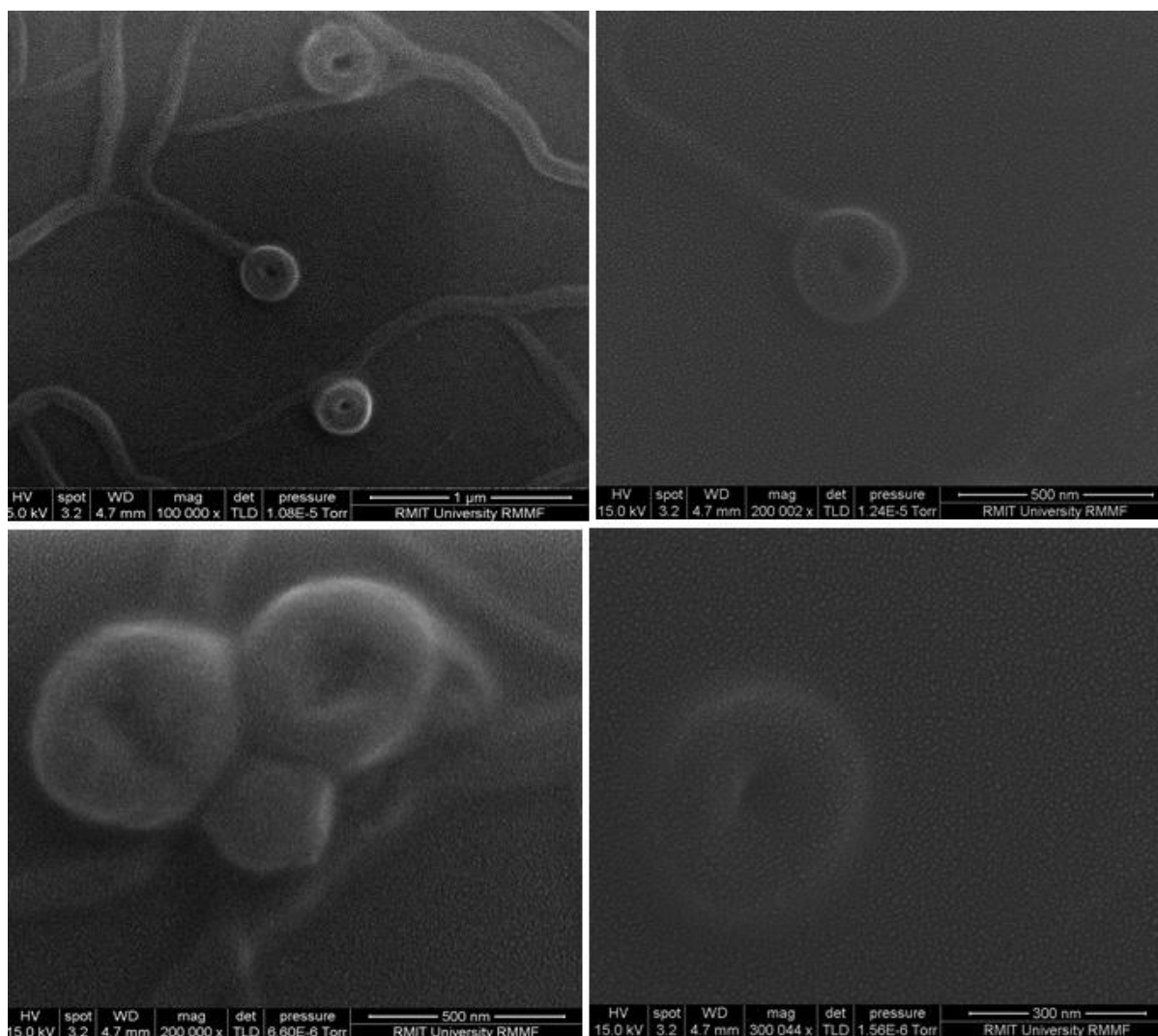


Fig. S5. SEM images of donut-like nanostructures formed by **1** from 1.2×10^{-4} M solution from 60% MeOH in CHCl_3 with proposed steps.

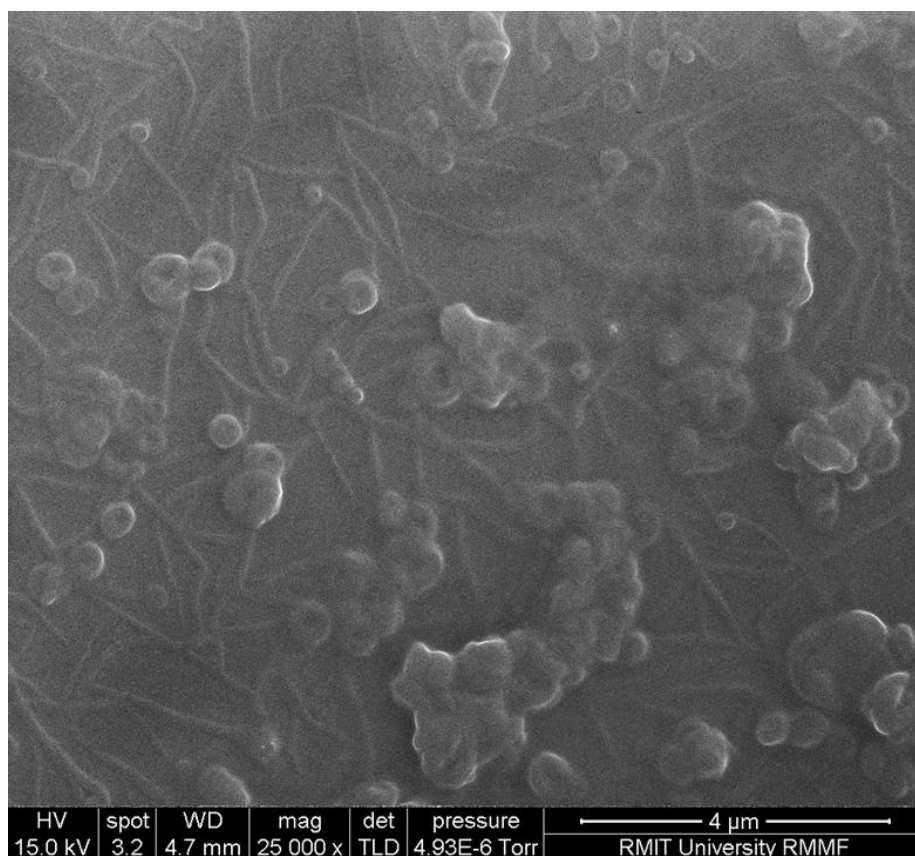


Fig. S6.

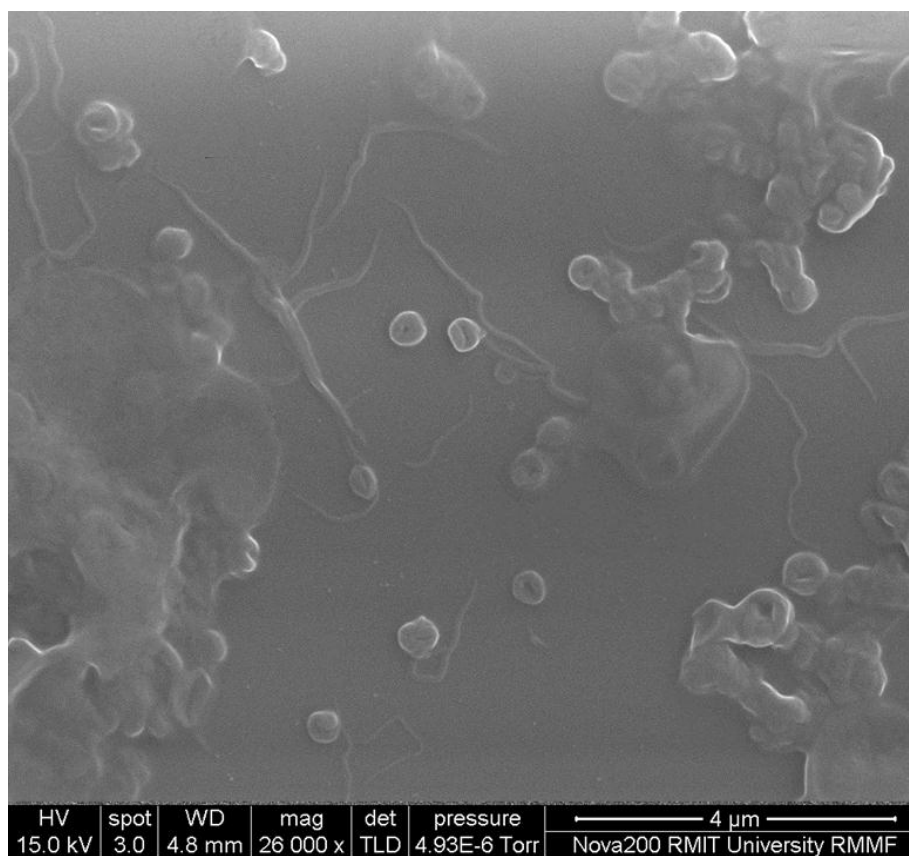


Fig. S7.

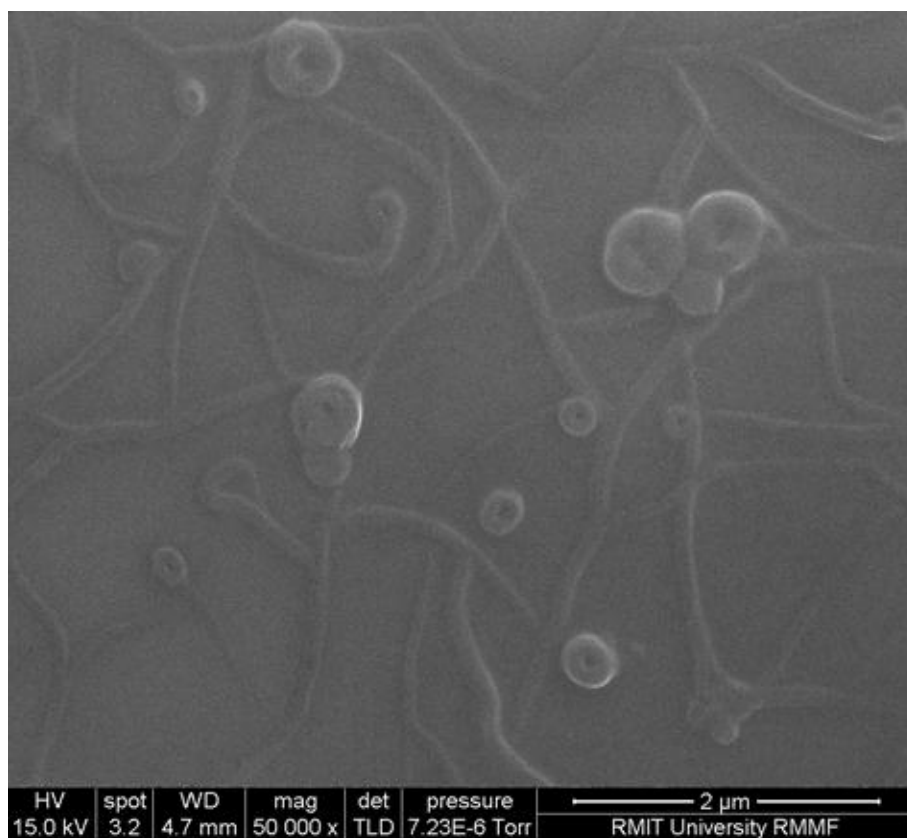


Fig. S8.

SEM images of mTEG-annulated acene diimide 2 in CHCl₃/MeOH (4:6, v/v)

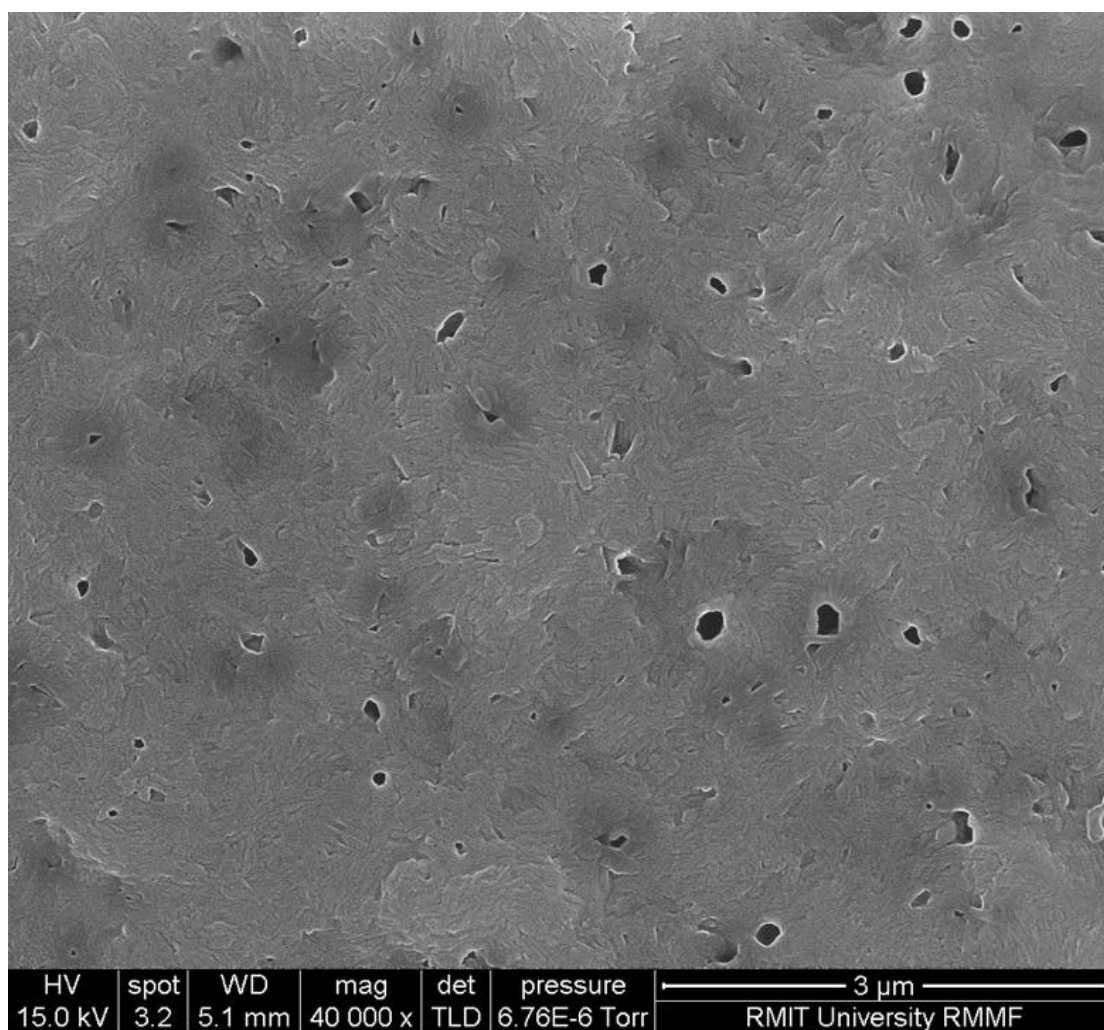


Fig. S9. SEM images of work-like nanostructure formed by **2** from 1.2×10^{-4} M solution from 40% MeOH in CHCl₃

SEM images of mTEG-annulated acene diimide 2 in CHCl₃/hexane (6:4, v/v)

Fig. S9-S12. SEM images of leaf-like nanostructure formed by **2** from 1.2×10^{-4} M solution from 60% hexane in chloroform.

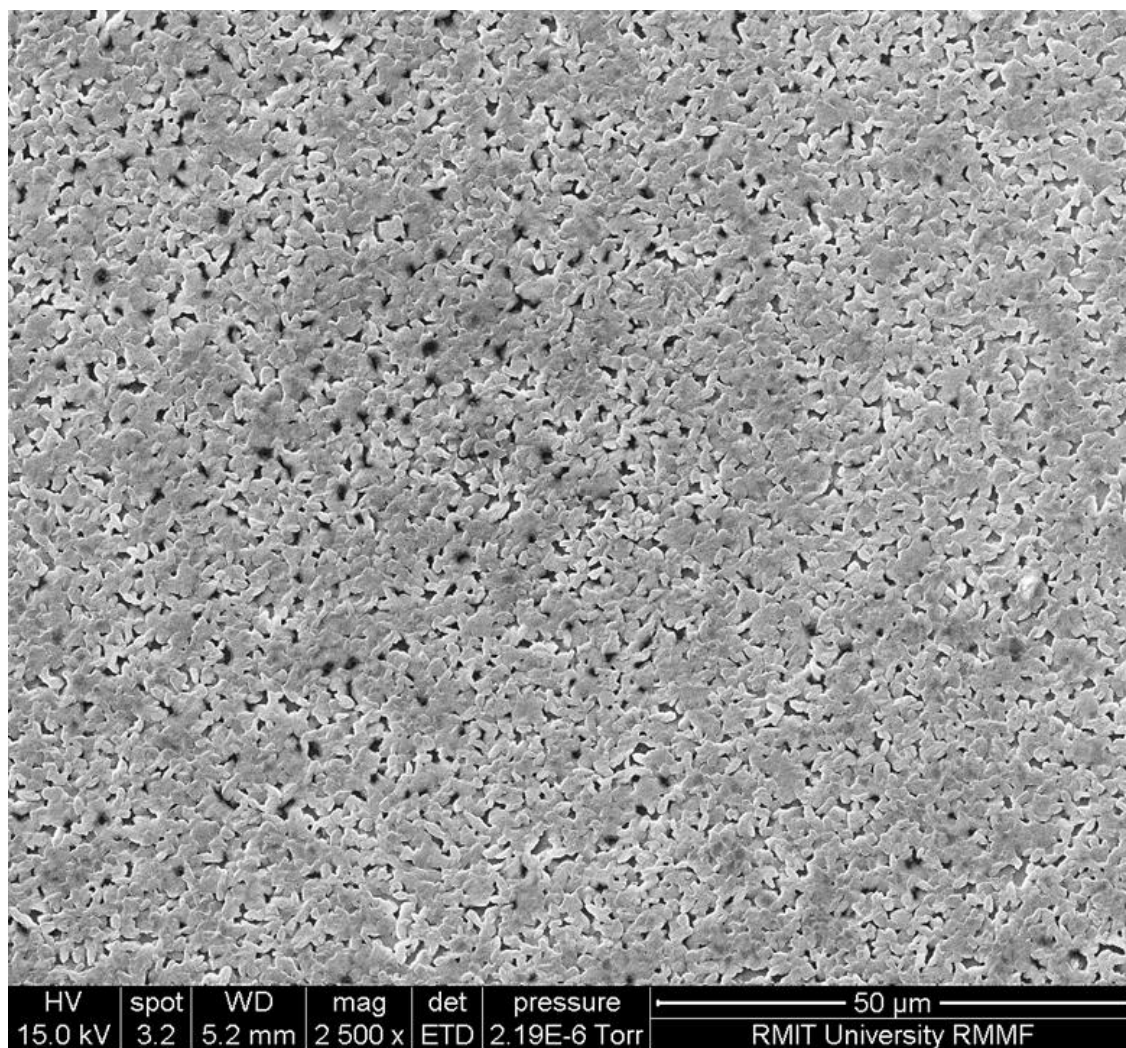


Fig. S10.

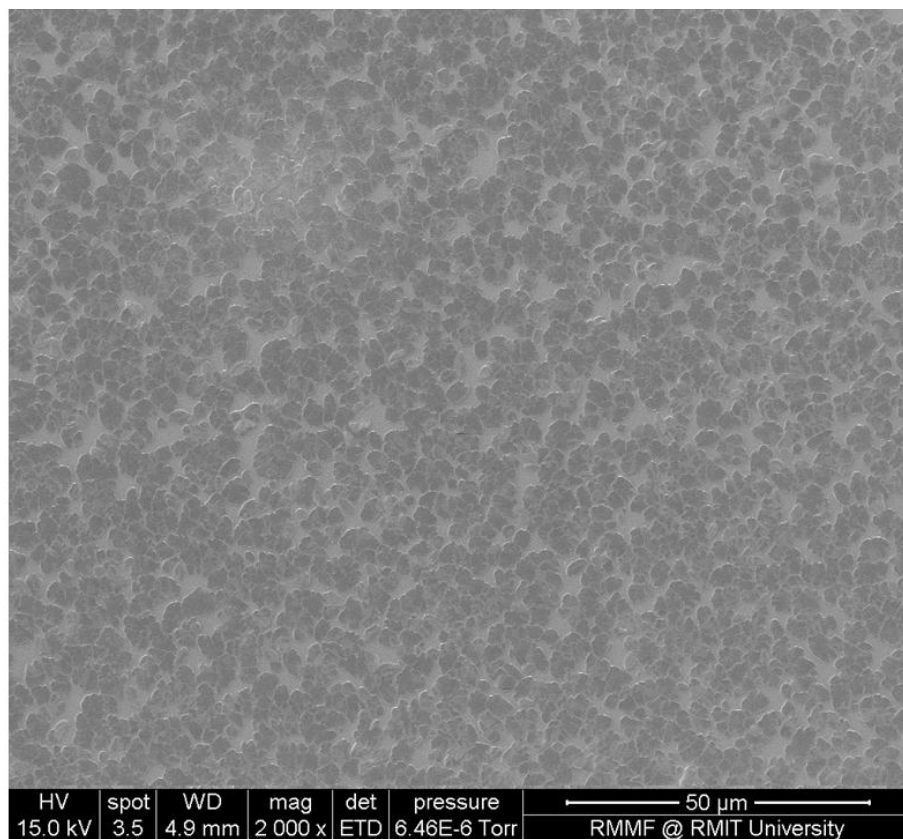


Fig. S11.

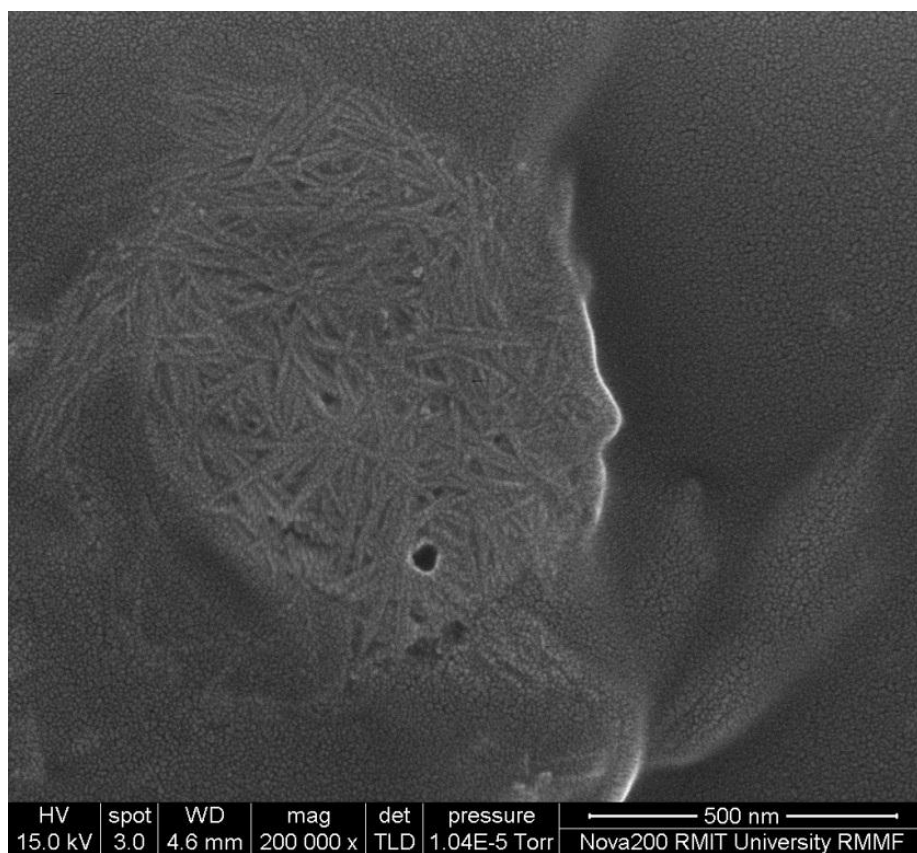


Fig. S12.

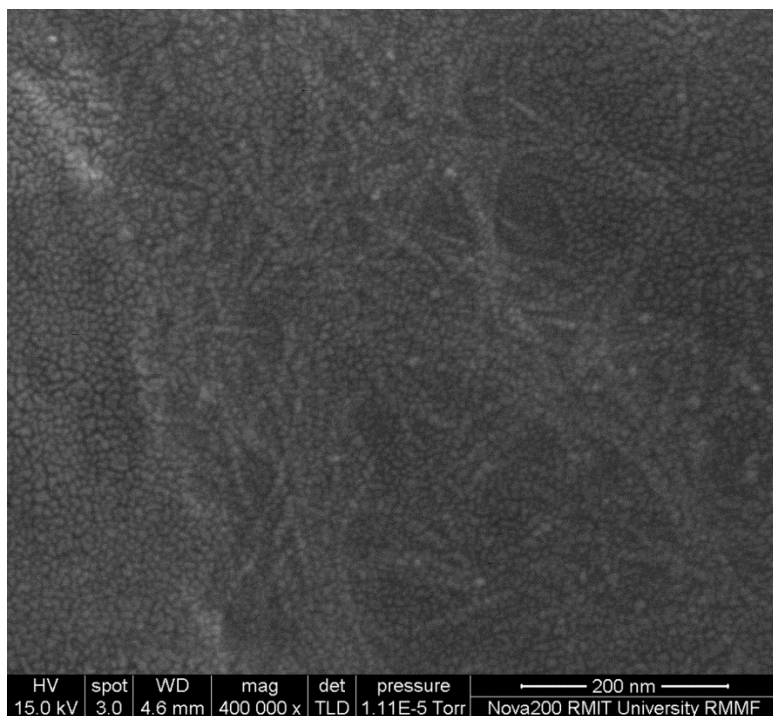
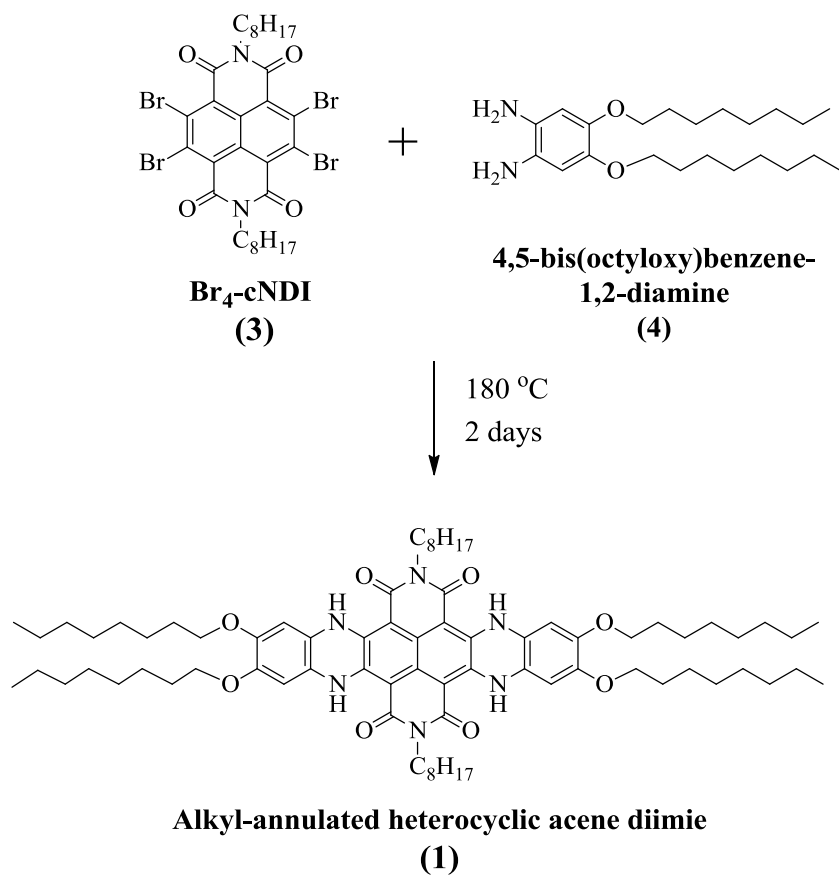


Fig. S13.

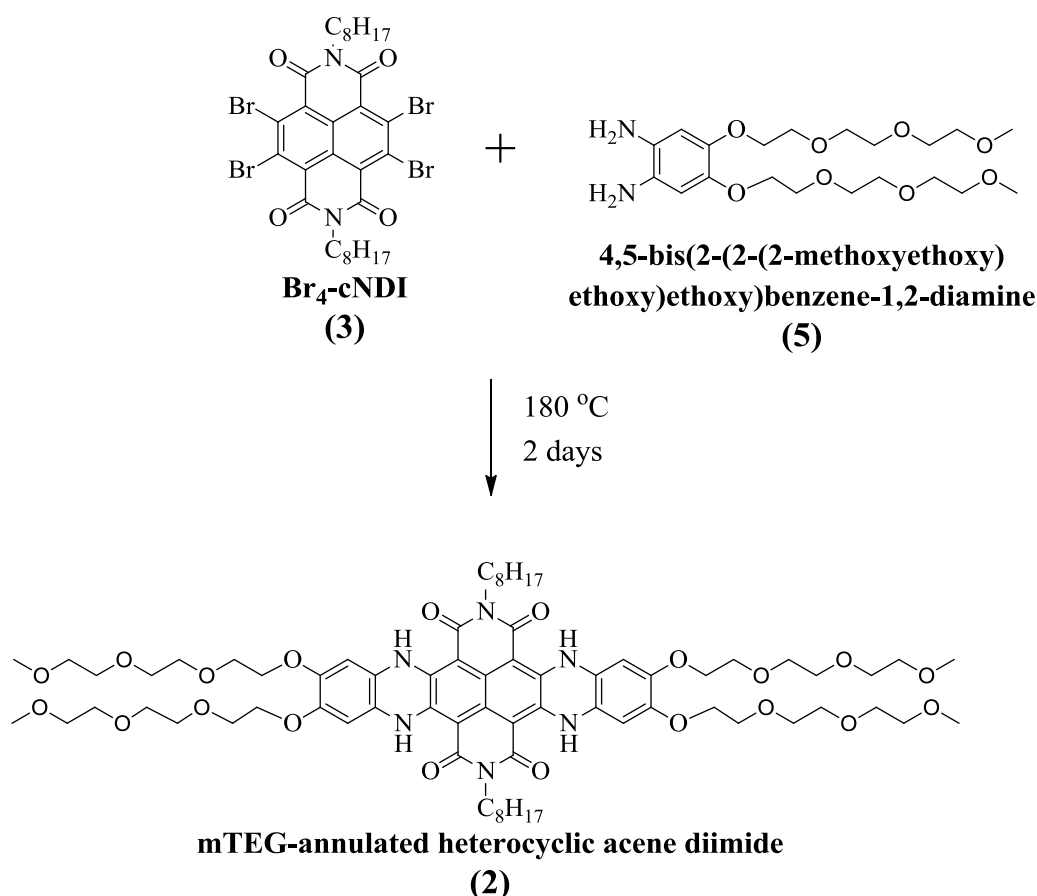
Synthesis of 1 and 2:

Preparation of alkyl-annulated acene diimide (1).



A mixture of Br₄-cNDI **3**³ (250 mg, 31 mmol) and 4,5-bis(octyloxy)benzene-1,2-diamine² **4** (1.8 g, 49 mmol) was mixed well before heated at 180 °C under nitrogen for 2 days. Thereafter, water (25 mL) was added, and the resultant mixture was extracted with chloroform (3 times x 100 mL). The resultant combined organic layer was dried over anhydrous sodium sulphate and removed under reduced pressure. The crude product was purified by column chromatography over silica gel and column eluted with hexane/ethyl acetate (5:1, v/v), obtained a deep green solid of **1** in 29% yield (110 mg). M.p. > 300 °C; ¹H NMR (CDCl₃, 300 MHz) δ 12.84 (s, 4H), 6.31 (s, 4H), 4.07 (t, *J* = 6.8 Hz, 8H), 3.93 (t, *J* = 7.2 Hz, 4H), 1.89 (br, 4H), 1.67 (br, 8H), 1.32-1.19 (m, 60H), 0.90-0.84 (m, 18H); ¹³C NMR (CDCl₃, 75 MHz) δ 165.71, 142.21, 133.79, 133.82, 106.71, 109.32, 102.01, 98.9, 43.35, 36.7, 31.92, 31.84, 31.7, 30.25, 29.68, 29.36, 22.81, 26.49, 22.68, 14.20, 14.11; FT-IR (KBr, Cm⁻¹) ν: 2961, 2934, 2849, 1719, 1661, 1514, 1456, 1413, 1374, 1287, 1179, 1153, 1010, 912, 791, 767, 729, 569, 565. HRMS (ESI): calcd. for C₇₄H₁₁₀N₆O₈ (M⁺): *m/z* 1210.8385; found 1210.8385. Elem. Anal.: for C₇₄H₁₁₀N₆O₈: C, 73.35; H, 9.15; N, 6.94. Found: C, 73.31; H, 9.13; N, 6.97.

Preparation of mTEG-annulated acene diimide (**2**):



Following above protocol mTEG-annulated acene diimide was prepared from condensation of Br₄-cNDI **3**³ (31 mmol) and 4,5-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene-1,2-diamine² **5** (50 mmol) heated at 180 °C for 2 days. The crude product was purified by column chromatography over silica gel and column eluted with chloroform/methanol (10:0.1, v/v),

obtained a deep green solid of **2** in 31% yield. M.p. > 300 °C, ^1H NMR (CDCl_3 , 300 MHz) δ 12.88 (s, 4H), 6.38 (s, 4H), 4.18 (m, 8H), 4.05 (t, $J = 7.8$, 8H), 3.92 (t, $J = 6.8$, 4H), 3.91-3.33 (m, 32H), 3.25 (s, 12H), 1.88 (m, 4H), 1.31 (m, 20H), 0.89 (m, 6H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 162.5, 142.3, 133.86, 133.56, 109.78, 106.49, 102.08, 71.61, 70.41, 70.11, 70.01, 69.61, 59.31, 40.91, 31.91, 30.08, 29.39, 26.71, 29.34, 22.72, 14.1; FT-IR (KBr, Cm^{-1}) ν : 2963, 2929, 2852, 1722, 1668, 1581, 1439, 1411, 1378, 1279, 1168, 1152, 1011, 911, 784, 762, 719, 581, 543; HRMS (ESI): calcd. for $\text{C}_{70}\text{H}_{102}\text{N}_6\text{O}_{20}$ (M^+): m/z 1346.7149; found 1346.7148; Elem. Anal.: for $\text{C}_{70}\text{H}_{102}\text{N}_6\text{O}_{20}$: C, 62.39; H, 7.39; N, 6.24. Found: C, 62.39; H, 7.65; N, 6.26.

^1H -NMR spectrum of **1** and **2**

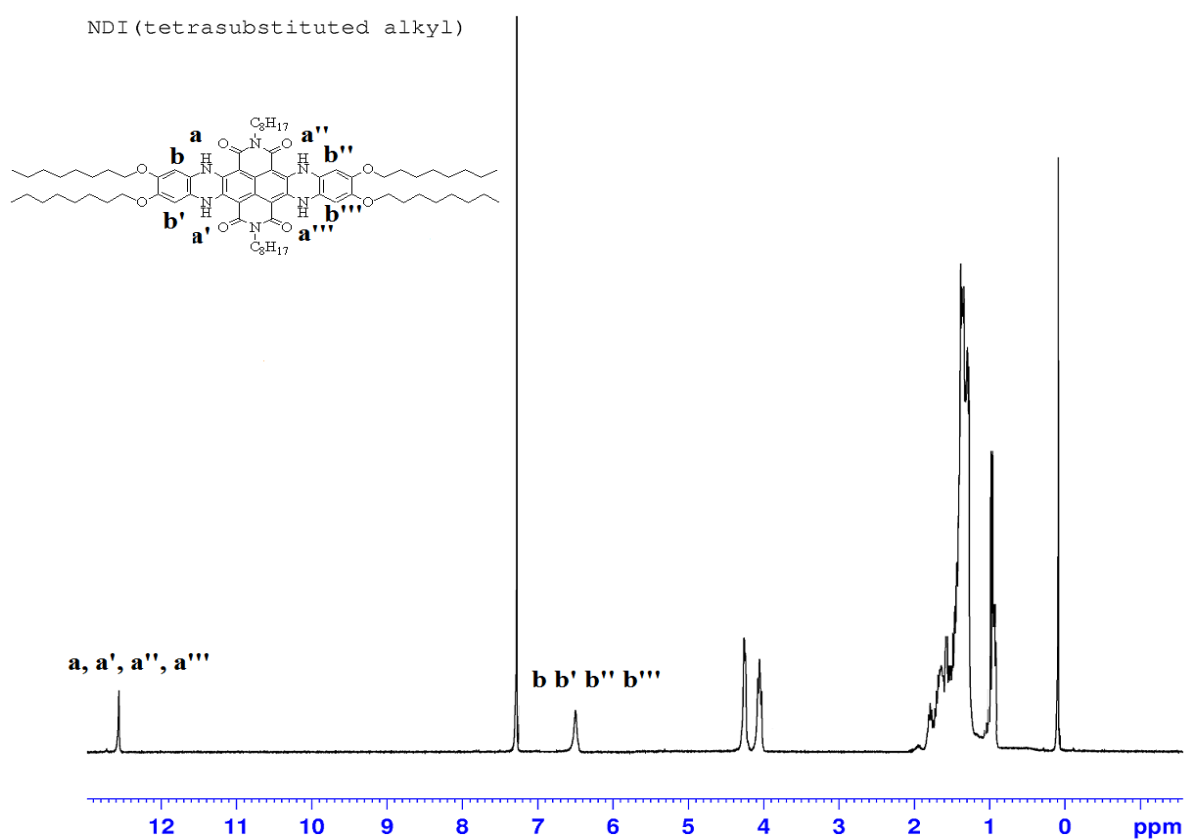


Fig. S14. ^1H NMR of acene diimide **1**

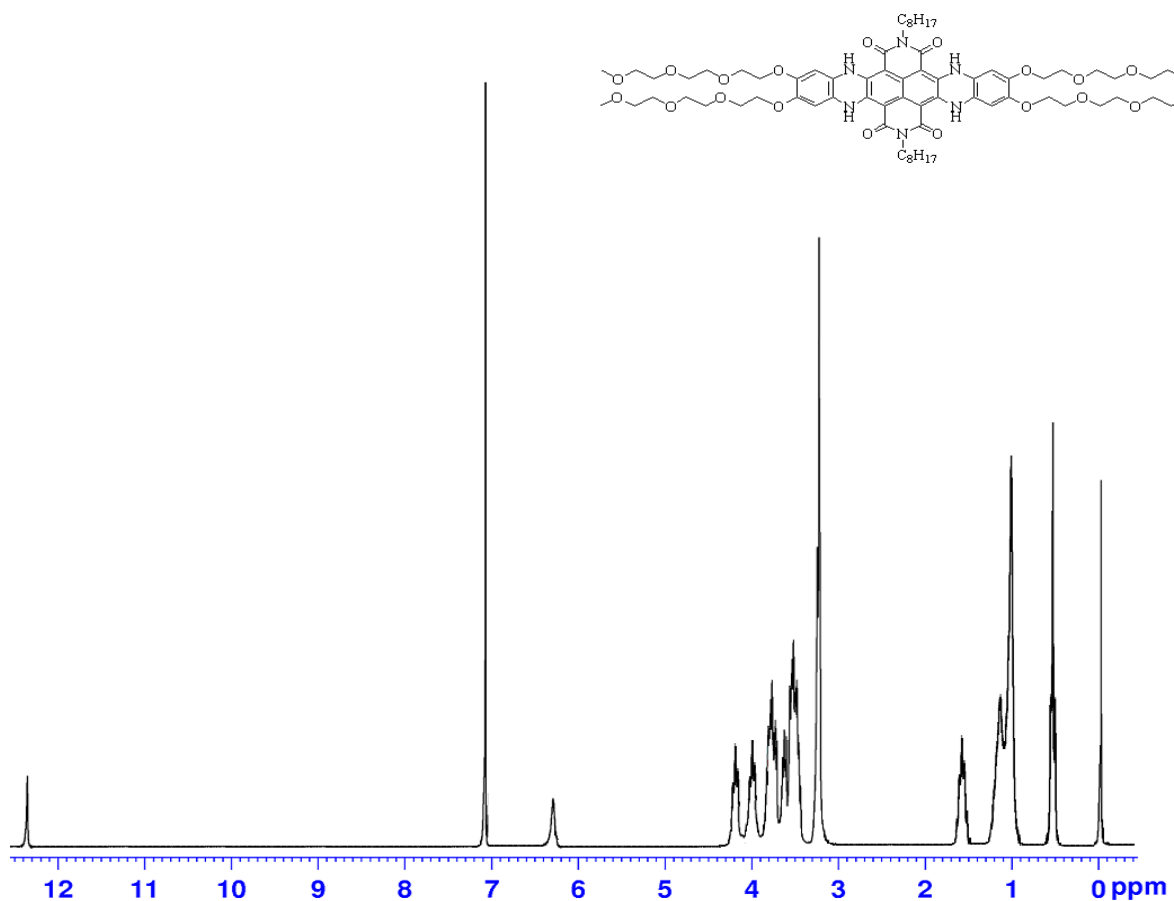


Fig. S15. ¹H NMR of acene diimide **2**

References:

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3. X. Gao, W. Qiu, X. Yang, Y. Liu, Y. Wang, H. Zhang, T. Qi, Y. Liu, K. Lu, C. Du, Z. Shuai, G. Yu, D. Zhu, *Org. Lett.*, 2007, **9**, 3917.