

Novel C_3 -Symmetric *n*-Type Tris(aryleneimidazole) and Its Analogs: Synthesis, Physical Properties and Self-Assembly

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Electronic Supplementary Information

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Experimental Section

General Methods: Reagents were purchased from Aldrich or synthesized as described. Thin-layer chromatography (TLC) was carried out using aluminum sheets, precoated with silica gel 60F (Merck 5554). The plates were inspected by UV-light. Proton and carbon nuclear magnetic resonance spectra ($^1\text{H-NMR}$ and $^{13}\text{C-NMR}$) spectra were recorded on a Bruker Avance500 II, using the deuterated solvent as lock and tetramethylsilane as internal standard. All chemical shifts are quoted using the δ scale, and all coupling constants (J) are expressed in Hertz (Hz). Matrix-assisted laser desorption ionization (MALDI) mass spectra were measured on 4800 MALDI TOF/TOF analyzer from Applied Biosystems. SEM images were recorded on a Zeiss Gemini Ultra-55 Analytic Scanning Electron Microscope. UV-vis absorption and fluorescence spectra were recorded on Cary 500 UV-vis-NIR spectrophotometer and Nanolog spectrofluorometer, respectively. All the thin-film samples were prepared by spincoating the corresponding CH_2Cl_2 solution ($\sim 5 \text{ mg / mL}$) onto a quartz substrate. The electrochemical experiments were carried out in N_2 -purged CH_2Cl_2 solutions at concentrations ranging from 1.0×10^{-4} to 1.0×10^{-3} M and with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF_6) as supporting electrolyte. Cyclic voltammetric (CV) experiments were performed with a Princeton 265A instrument interfaced to a PC using a glassy carbon working electrode, a Pt electrode as the counter electrode, and a silver wire as a pseudo-reference electrode. The surface of the working electrode was polished routinely with a $0.05 \mu\text{m}$ alumina-water slurry on a felt surface immediately before use. In all cases ferrocene ($E_{1/2} = +0.395 \text{ V vs SCE}$) was present as internal standard for the potential values. TGA and DSC curves were obtained using QA5000IR and Q200 from

TA Instruments, respectively. Compound **1**^{s1} and **2a-b**^{s2} were synthesized according to literature procedures. Optical and polarized optical images were taken using a Leica DM4500P microscope. Powder XRD data was collected on a Bruker-AXS D8 Discover with GADDS powder X-ray diffractometer with Cu K_α radiation.

Computational Methodology

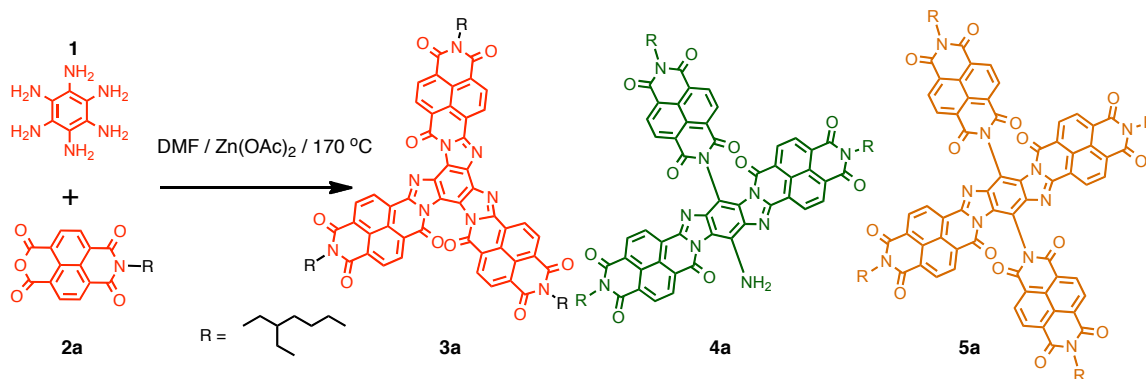
All calculations were performed using Q-Chem 3.2.^{s3} The free softwares Avogadro and Q-Chem User Interface (QUI) were used as the molecular builder and the script editor, respectively. To simplify the calculation, methyl was used as the side chains that attached to the **TAI** core, which should have a minimal effect on the optimized molecular structure and the frontier orbitals. The energy level of the HOMO and the LUMO of the **TAI** molecule was carried out at the DFT level^{s4,s5} using B3LYP/6-311G* basis set. DFT/B3LYP/6-311G* has been found to be an accurate formalism for calculating the structural and electronic properties of many molecular systems.^{s6} No symmetry constraints were imposed during the optimization process. The electrostatic potential was plotted with an ISO value of 0.01.

Materials Synthesis

Method A – Condensation Reaction in DMF. A mixture of **1** (102 mg, 0.607 mmol), **2a** (0.690 g, 1.82 mmol) and Zn(OAc)₂ (180 mg, 0.981 mmol) was dissolved in degassed DMF (30 mL) under N₂ and stirred at 170 °C for 18 hs. The reaction mixture was concentrated under reduced pressure and subsequently partitioned between CH₂Cl₂ and water (50 mL each). After extracting the aqueous layer twice with CH₂Cl₂ (2 × 30 mL), the organic layers were combined, dried over MgSO₄, filtered and evaporated to dryness. The residue was subjected to column chromatography (Silica, CH₂Cl₂ 100% to 3%

MeOH in CH₂Cl₂) to get a mixture (450 mg) of the tetramer **5a**, the acyclic trimer **4a**, and the asymmetric cyclic trimer **3a**. A portion of the mixture (60 mg) was subjected to preparative TLC (1.5% (v/v) MeOH in CH₂Cl₂) to get **5a**, **4a** and **3a** as an orange-red, green and red solid in a yield of 24%, 22% and 16%, respectively.

Scheme S1. Condensation reaction using DMF as the solvent



3a: ¹H NMR (C₆D₅Cl, 500 MHz, 373 K): δ = 8.60 (d, *J* = 8.0 Hz, 2 H), 8.55 (d, *J* = 8.0 Hz, 2 H), 8.52 (d, *J* = 8.0 Hz, 2 H), 8.45 (d, *J* = 8.0 Hz, 2 H), 8.42 (d, *J* = 8.0 Hz, 4 H), 8.37 (m, 6 H), 8.33 (d, *J* = 8.0 Hz, 2 H), 8.31 (m, 4 H), 4.05 (m, 6 H), 1.95 (m, 3 H), 1.32–1.11 (m, 33 H), 0.85 (m, 9 H). MS (MALDI-TOF): [M + H]⁺ calcd. 1198.4827, found 1198.6910 (100%).

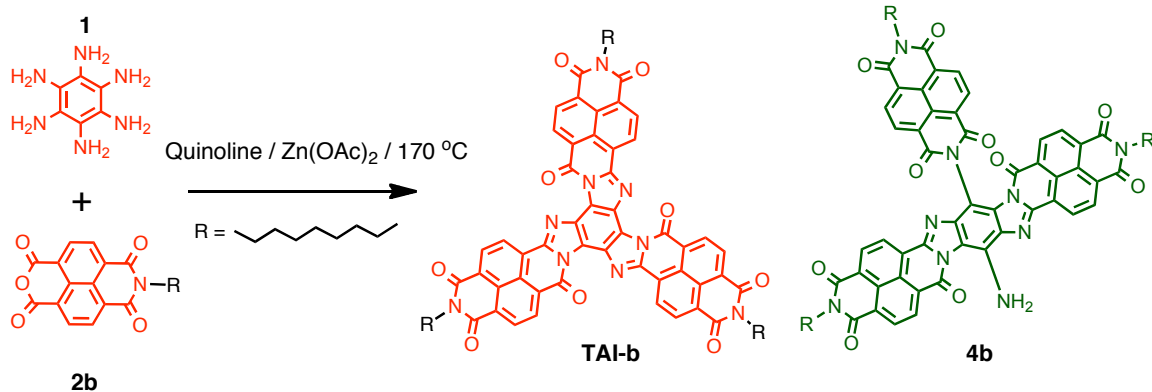
4a: ¹H NMR (CDCl₃, 500 MHz, 298 K): δ = 8.95 (d, *J* = 8.0 Hz, 4 H), 8.81 (d, *J* = 6.0 Hz, 1 H), 8.66 (d, *J* = 6.0 Hz, 1 H), 8.51 (d, *J* = 6.0 Hz, 1 H), 8.48 (d, *J* = 6.0 Hz, 1 H), 8.31 (d, *J* = 6.0 Hz, 1 H), 8.26 (d, *J* = 6.0 Hz, 1 H), 8.10 (d, *J* = 6.0 Hz, 1 H), 7.94 (d, *J* = 6.0 Hz, 1 H), 6.39 (br s, 2 H), 4.35 (br s, 2 H), 4.08 (br s, 2 H), 3.65 (br s, 2 H), 1.89 (br s, 2 H), 1.70–1.23 (m, 34 H), 0.96 (br s, 3 H), 0.87 (t, *J* = 7.0 Hz, 6 H). ¹³C NMR (CDCl₃, 125 MHz, 298 K): δ = 163.9, 163.1, 162.5, 162.2, 162.1, 161.7, 158.7, 158.2, 149.2, 145.7, 143.9, 132.6, 131.7, 131.4, 131.1, 131.0, 130.8, 130.6, 130.1, 129.9, 127.9, 127.6, 127.3, 127.1, 126.9, 126.8, 126.6, 125.9, 125.3, 125.2, 125.0, 124.8, 124.8, 122.7, 121.5,

117.7, 102.1, 41.1, 40.9, 40.4, 31.9, 31.8, 31.8, 29.7, 29.4, 29.3, 29.3, 29.2, 29.2, 28.3, 28.1, 27.9, 27.2, 27.1, 27.0, 22.7, 22.6, 22.6, 14.2, 14.1, 14.1; MS (MALDI-TOF): $[M]^+$ calcd. 1215.4854, found 1215.6841 (100%).

5a: ^1H NMR (CDCl_3 , 500 MHz, 298 K): δ = 8.92 (m, 8 H), 8.63 (d, J = 8.0 Hz, 2 H), 8.61 (d, J = 8.0 Hz, 2 H), 8.60 (d, J = 8.0 Hz, 2 H), 8.51 (d, J = 8.0 Hz, 2 H), 4.26 (m, 4 H), 4.12 (m, 4 H), 2.03 (m, 2 H), 1.90 (m, 2 H), 1.47 (m, 8 H), 1.37 (m, 16 H), 1.30 (m, 8 H), 1.02 (t, J = 7.5 Hz, 6 H), 0.96 (t, J = 7.5 Hz, 6 H), 0.91 (t, J = 7.5 Hz, 6 H), 0.86 (t, J = 7.5 Hz, 6 H). ^{13}C NMR (CDCl_3 , 125 MHz, 298 K): δ = 163.4, 163.1, 163.1, 162.9, 158.6, 150.7, 143.4, 132.1, 131.6, 131.4, 131.2, 130.8, 130.2, 127.9, 127.8, 127.3, 127.2, 127.1, 127.0, 126.8, 125.7, 125.1, 124.9, 115.0, 44.7, 44.6, 38.1, 38.0, 30.8, 30.7, 28.7, 28.6, 24.1, 24.0, 23.1, 23.0, 14.2, 14.1, 10.7, 10.5; MS (MALDI-TOF): $[M + H]^+$ calcd. 1577.6176, found 1578.1060 (25%).

Method B – Condensation Reaction in Quinoline. A mixture of **1** (0.100 g, 0.590 mmol) and $\text{Zn}(\text{OAc})_2$ (0.163 mg, 0.888 mmol) was dissolved in degassed quinoline (20 mL). A solution of **2b** (0.632 g, 1.67 mmol) in quinoline (10 mL) was added slowly into the above mixture over 30 min under N_2 and stirred at 170 °C for 18 hs. The reaction mixture was concentrated under reduced pressure and subsequently partitioned between CH_2Cl_2 and water (50 mL each). After extracting the aqueous layer twice with CH_2Cl_2 (2 \times 30 mL), the organic layers were combined, dried over MgSO_4 , filtered and evaporated to dryness. The residue was subjected to column chromatography (Silica, CH_2Cl_2 100% to 3% MeOH in CH_2Cl_2) to get a mixture (520 mg) of **4b** and **TAI-b**. A portion of the mixture (60 mg) was subjected to recycling GPC (CHCl_3) to give **4b** and **TAI-b** as a green and red solid in a yield of 35% and 25%, respectively.

Scheme S2. Condensation reaction using quinoline as the solvent



4b: ¹H NMR (CDCl₃, 500 MHz, 298 K): δ = 8.95 (m, 4 H), 8.83 (d, J = 8.0 Hz, 1 H), 8.66 (d, J = 8.0 Hz, 1 H), 8.61 (m, 2 H), 8.55 (d, J = 8.0 Hz, 1 H), 8.52 (d, J = 8.0 Hz, 1 H), 8.48 (d, J = 8.0 Hz, 1 H), 8.36 (d, J = 8.0 Hz, 1 H), 6.71 (br s, 2 H), 4.34 (t, J = 8.0 Hz, 2 H), 4.17 (t, J = 8.0 Hz, 2 H), 3.99 (t, J = 8.0 Hz, 2 H), 1.87 (m, 2 H), 1.74 (m, 2 H), 1.38–1.30 (m, 32 H), 0.98 (t, J = 7.5 Hz, 3 H), 0.85 (m, 6 H). ¹³C NMR (CDCl₃, 125 MHz, 298 K): δ = 163.8, 163.1, 162.5, 162.1, 162.0, 161.7, 158.6, 158.2, 149.2, 145.7, 143.9, 132.5, 131.6, 131.1, 130.9, 130.8, 130.6, 130.1, 129.9, 127.9, 127.5, 127.3, 127.1, 126.8, 126.7, 126.5, 125.8, 125.1, 125.0, 124.8, 124.7, 122.7, 121.1, 116.0, 108.6, 102.2, 41.1, 40.9, 40.4, 31.9, 31.8, 31.8, 29.7, 29.4, 29.3, 29.3, 29.2, 29.2, 28.3, 28.1, 27.9, 27.2, 27.1, 27.0, 22.7, 22.6, 22.6, 14.2, 14.1, 14.1; MS (MALDI-TOF): [M]⁺ calcd. 1215.4854, found 1215.6721 (100%).

TAI-b: ¹H NMR (C₂D₂Cl₄, 500 MHz, 413 K): δ = 7.92 (br s, 6 H), 7.67 (br s, 3 H), 7.64 (br s, 3 H), 3.78 (br s, 6 H), 1.62 (br s, 6 H), 1.34–1.21 (m, 30 H), 0.86 (br s, 9 H). ¹³C NMR (C₂D₂Cl₄, 125 MHz, 413 K): δ = 162.9, 162.8, 156.4, 147.0, 139.9, 132.1, 131.6, 131.1, 128.1, 127.7, 127.4, 127.0, 125.5, 124.9, 123.5, 121.8, 33.1, 31.1, 30.6, 30.5, 29.4,

28.6, 23.9, 15.3. MS (MALDI-TOF): $[M + H]^+$ calcd. 1198.4827, found 1198.7484
(100%).

Thermogravitic Analysis

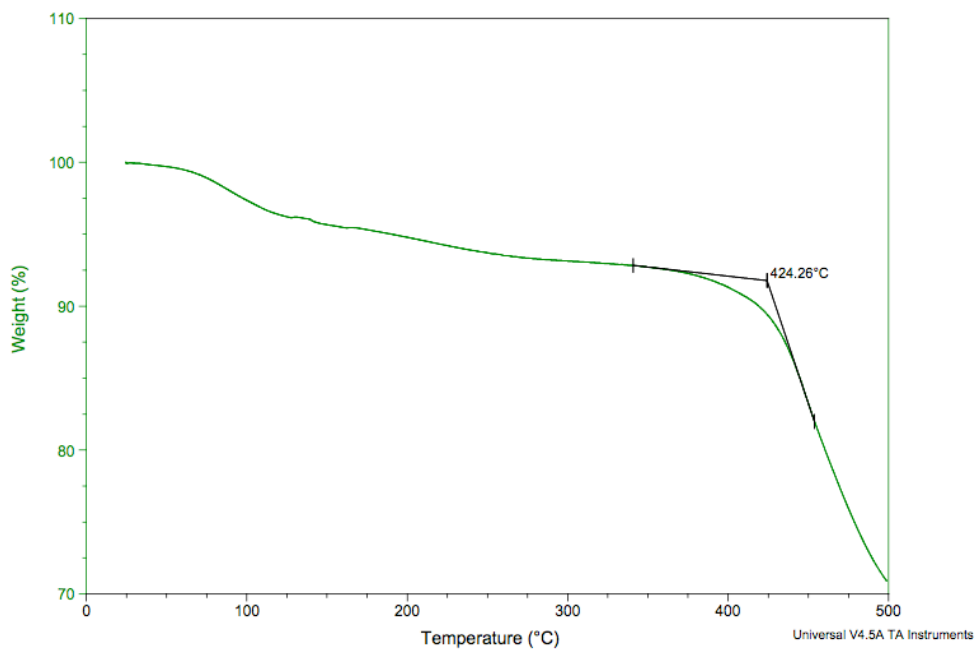


Figure S1. TGA of **3a**.

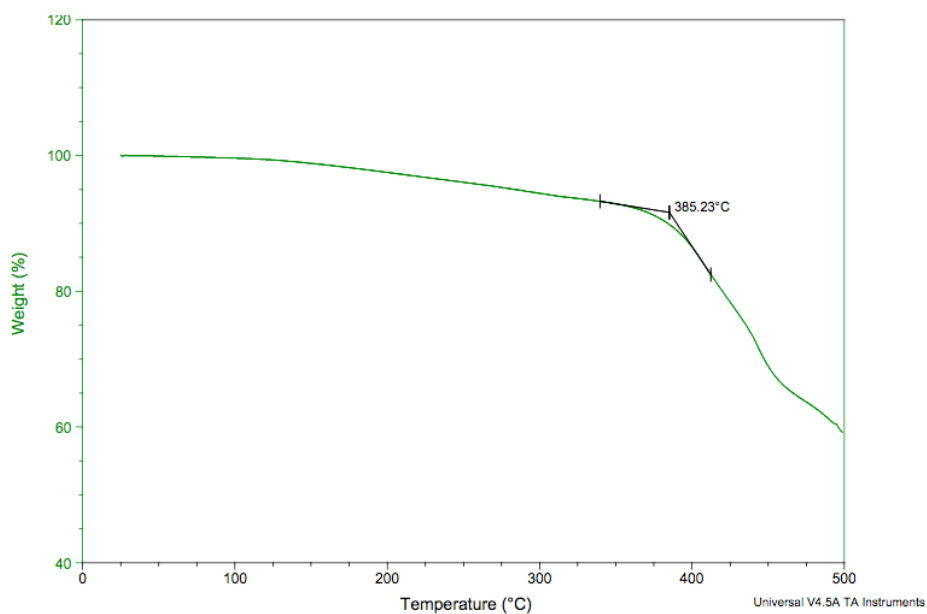


Figure S2. TGA of **4a**.

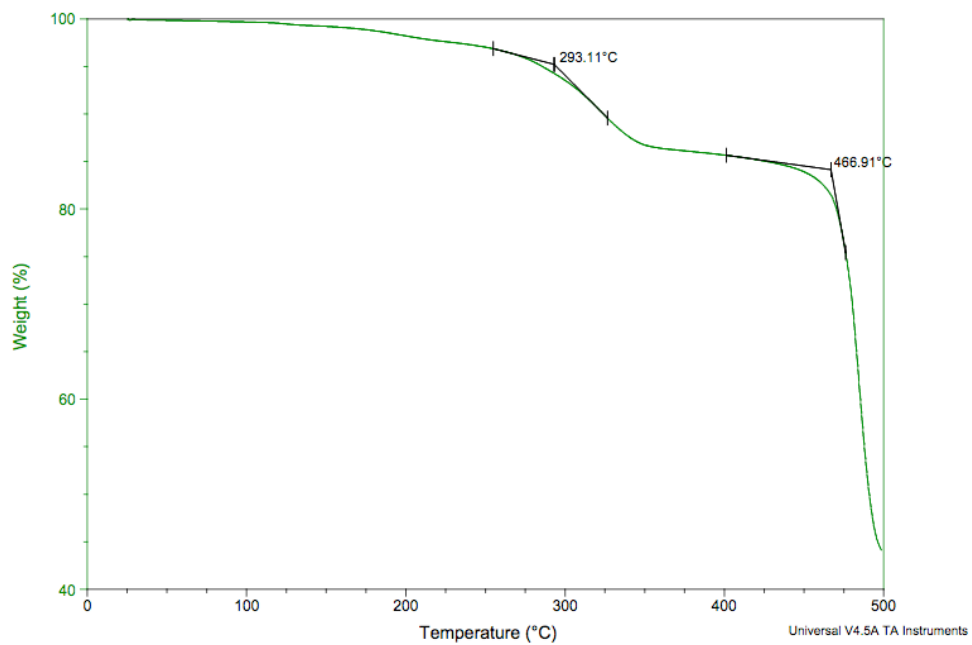


Figure S3. TGA of **5a**.

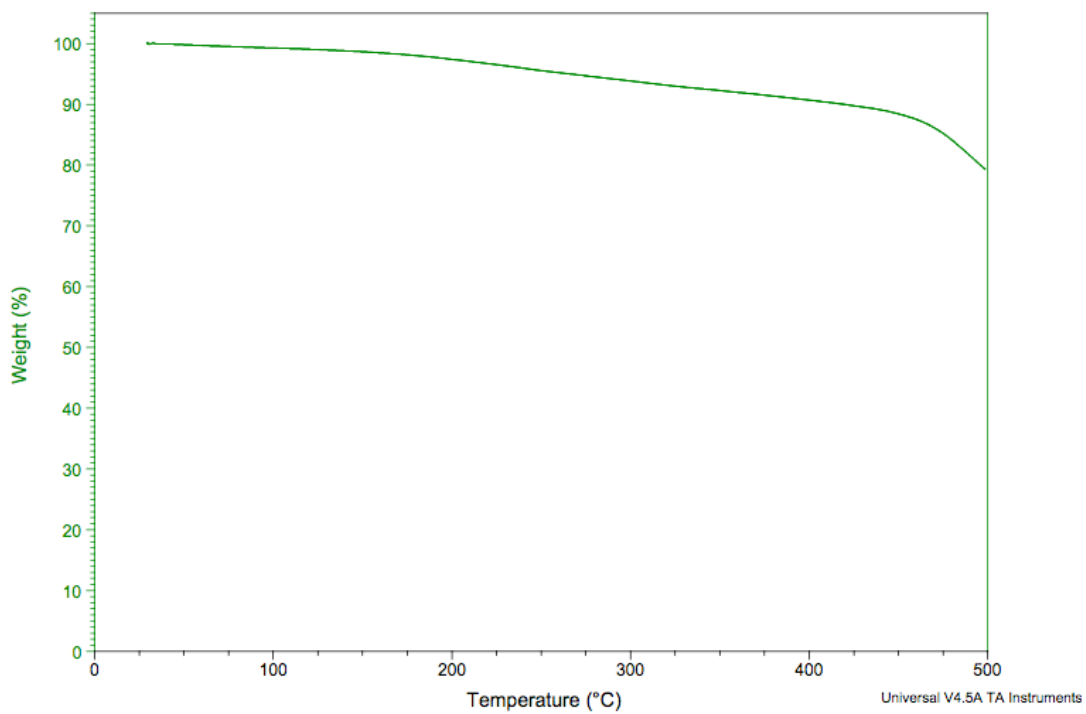


Figure S4. TGA of **TAI-b**.

DSC trace of TAI-b

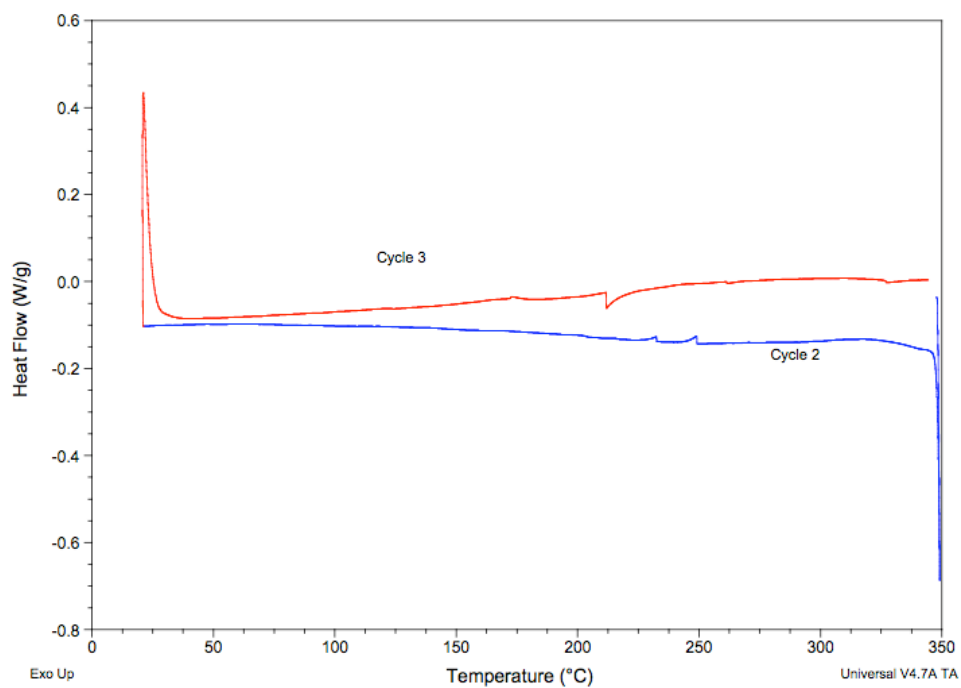


Figure S5. DSC of **TAI-b**. Note that the bumps are system artifacts from the instrument rather than real phase transitions.

Optical Images

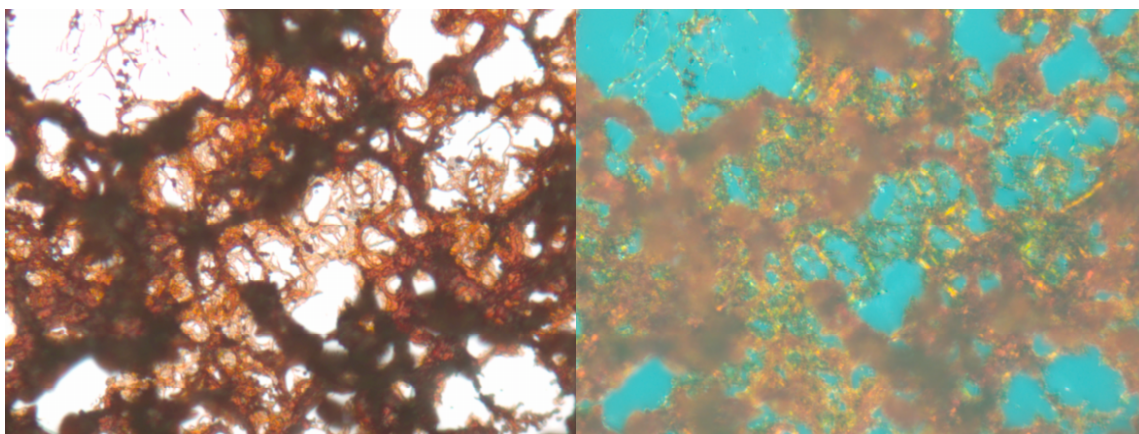


Figure S6. Normal optical image (left) and polarized optical image (right) of **TAI-b** nanofibers ($\times 500$).

Electrochemical Measurements

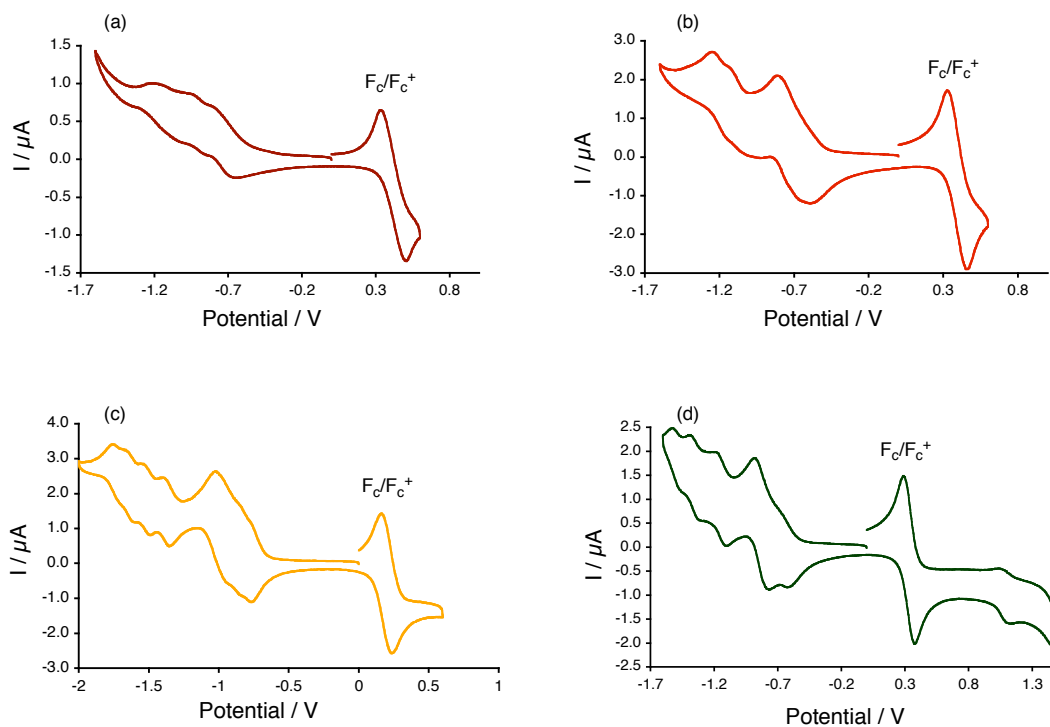


Figure S7. CV of (a) **TAI-b**, (b) **3a**, (c) **5a** and (d) **4b**. Ferrocene/ferrocenium redox couple was used as the internal standard in all cases.

Powder XRD

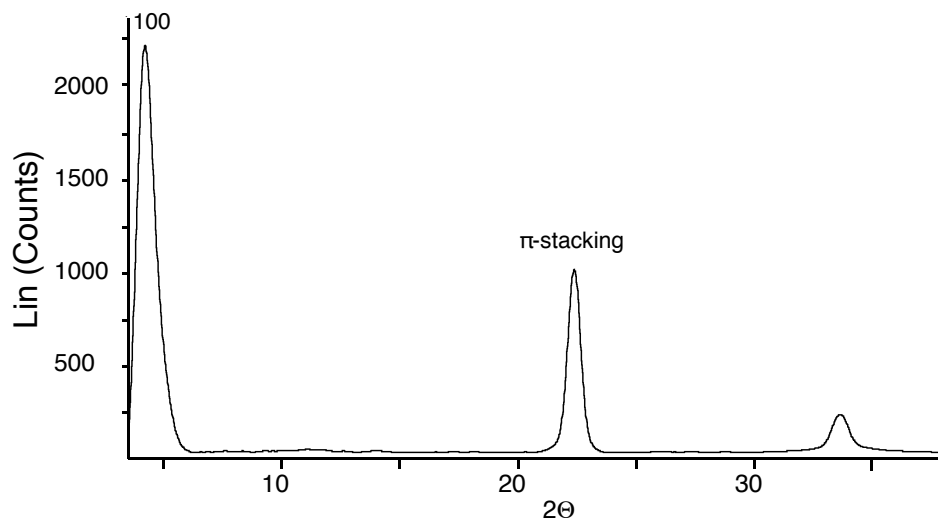


Figure S8. Powder XRD of the **TAI-b** nanofibers.

Thin-Film UV-vis Spectra

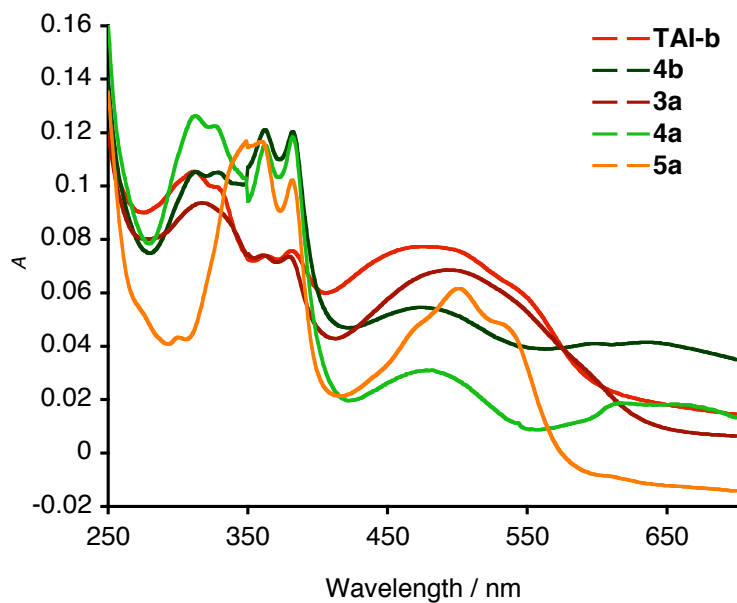


Figure S9. Thin film UV-vis spectra of **TAI-b** (red), **4b** (green), **3a** (deep red), **4a** (light green) and **5a** (orange).

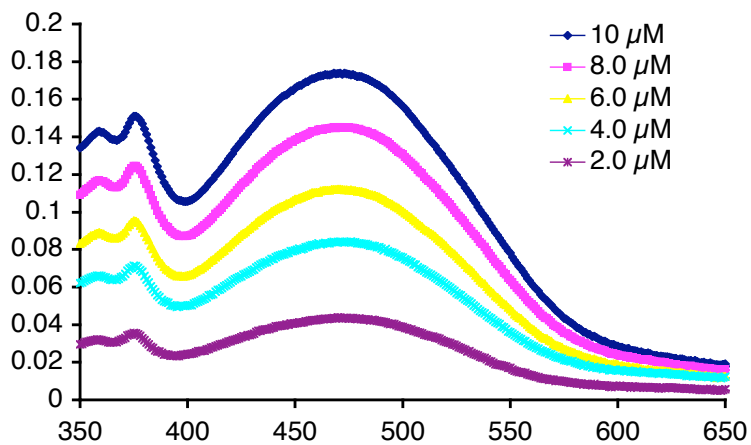


Figure S10. UV-vis spectra of **TAI-b** at 10 μM , 8.0 μM , 6.0 μM , 4.0 μM and 2.0 μM .

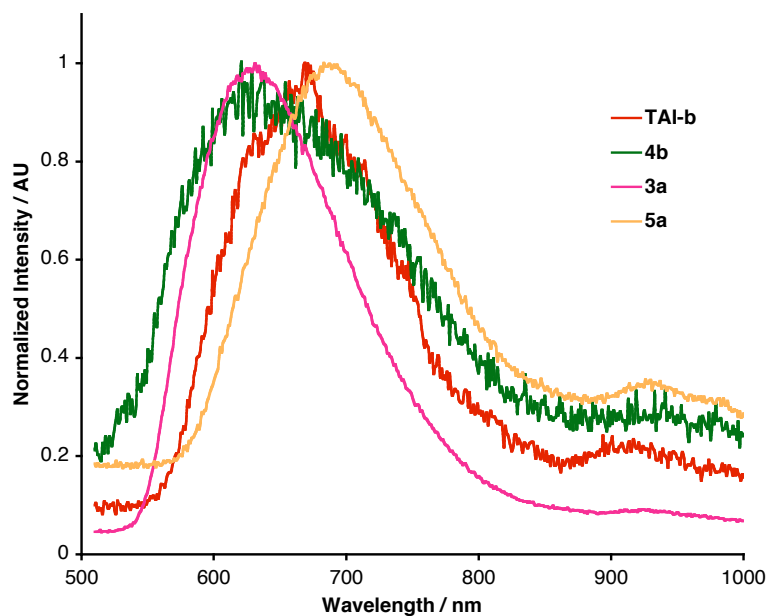


Figure S11. Fluorescence spectra of **TAI-b**, **4b**, **3a**, **4a** and **5a**.

MALDI-TOF Spectra

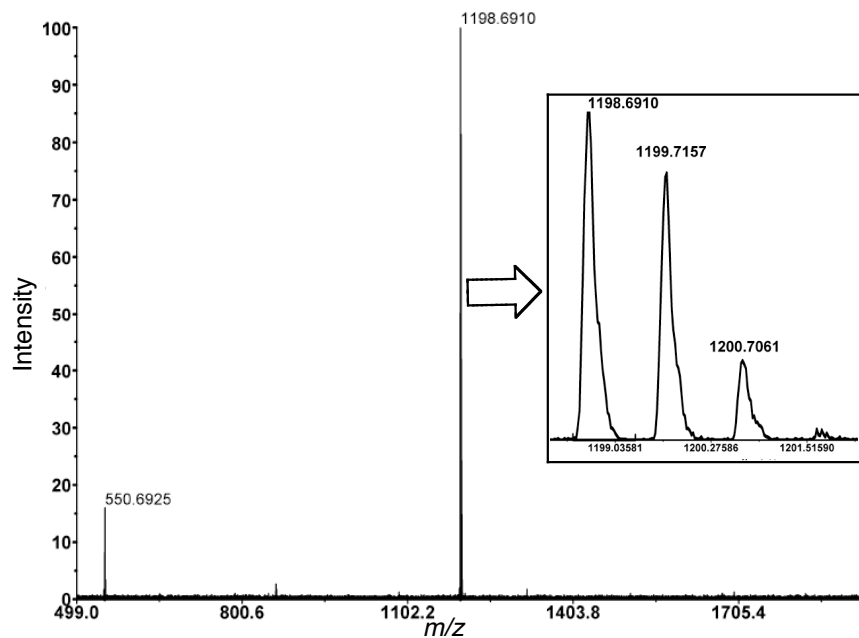


Figure S12. MALDI-TOF spectrum of asymmetric cyclic trimer **3a**. The insert indicates the isotopic distribution of the molecular ion peak.

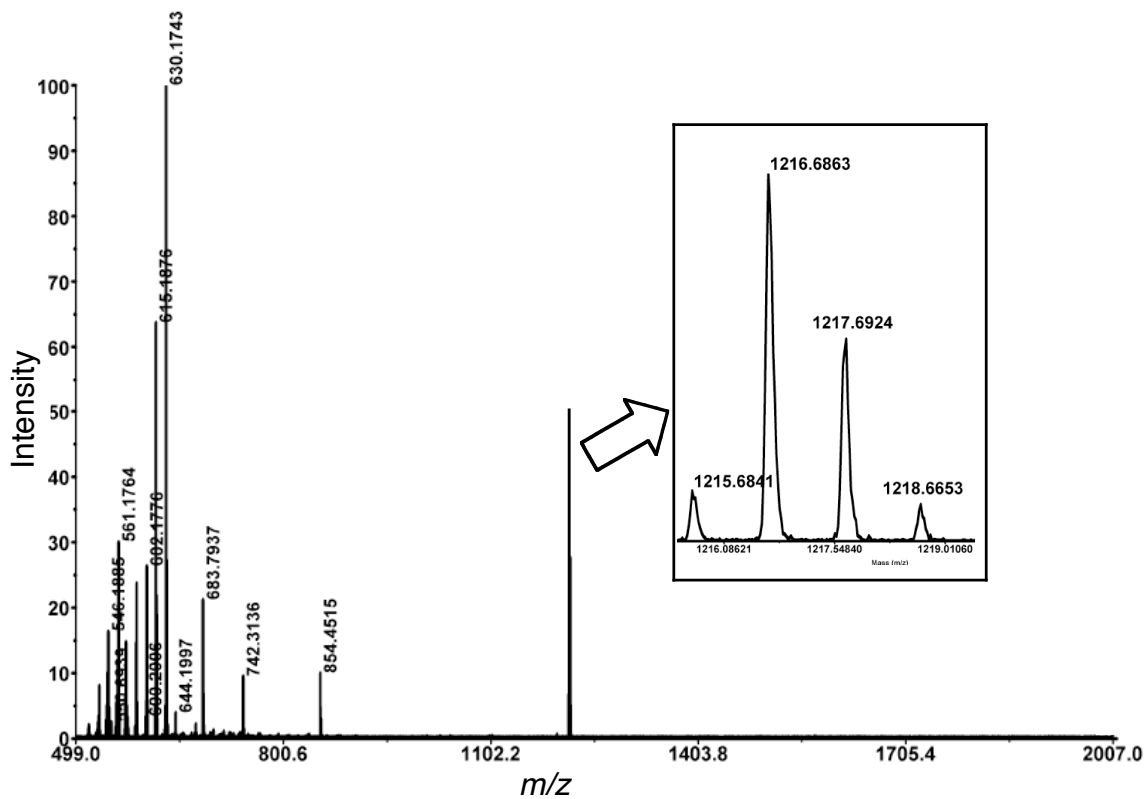


Figure S13. MALDI-TOF spectrum of acyclic trimer **4a**. The insert indicates the isotopic distribution of the molecular ion peak.

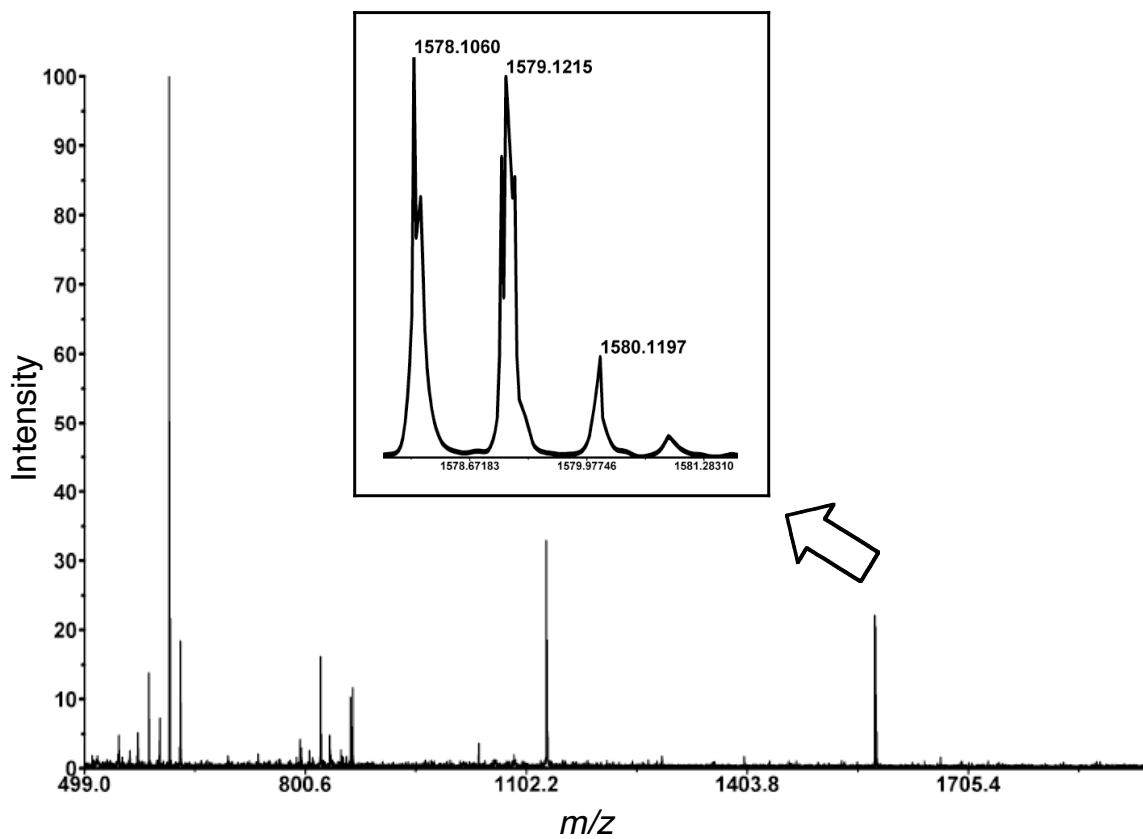


Figure S14. MALDI-TOF spectrum of tetramer **5a**. The insert indicates the isotopic distribution of the molecular ion peak.

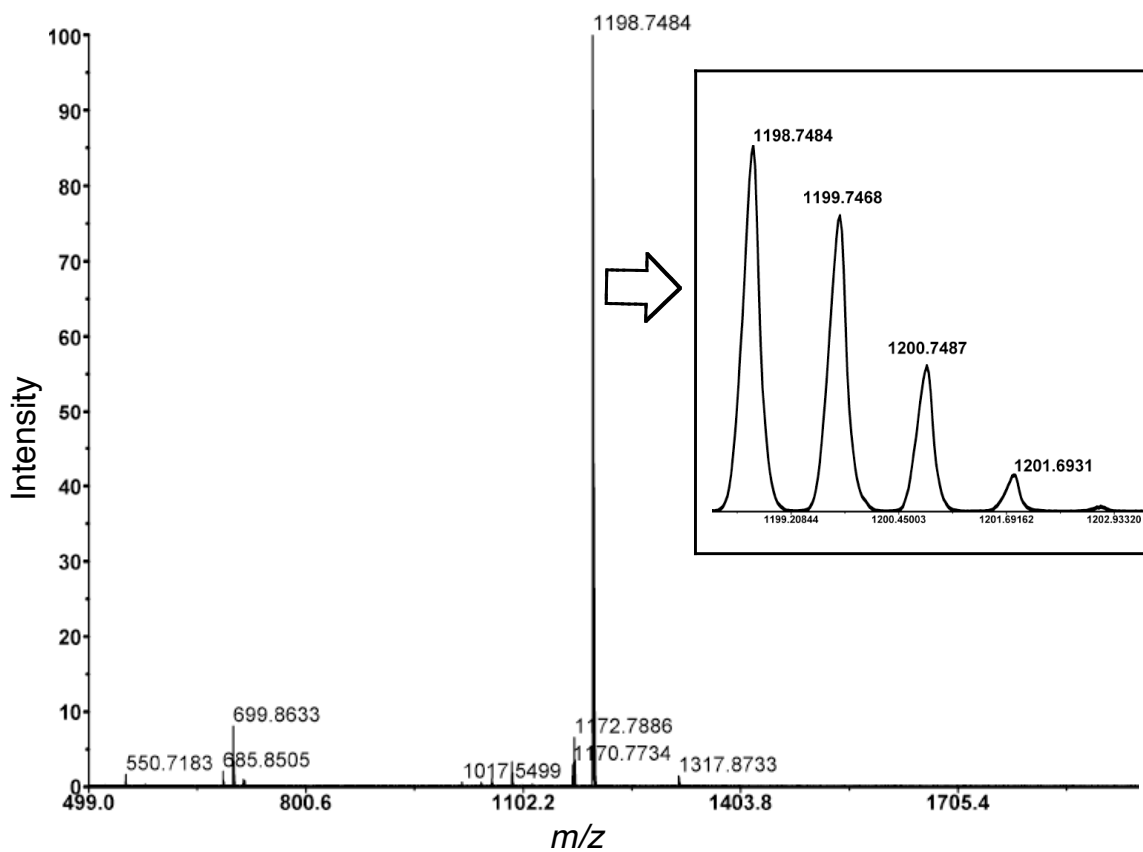


Figure S15. MALDI-TOF spectrum of **TAI-b**. The insert indicates the isotopic distribution of the molecular ion peak.

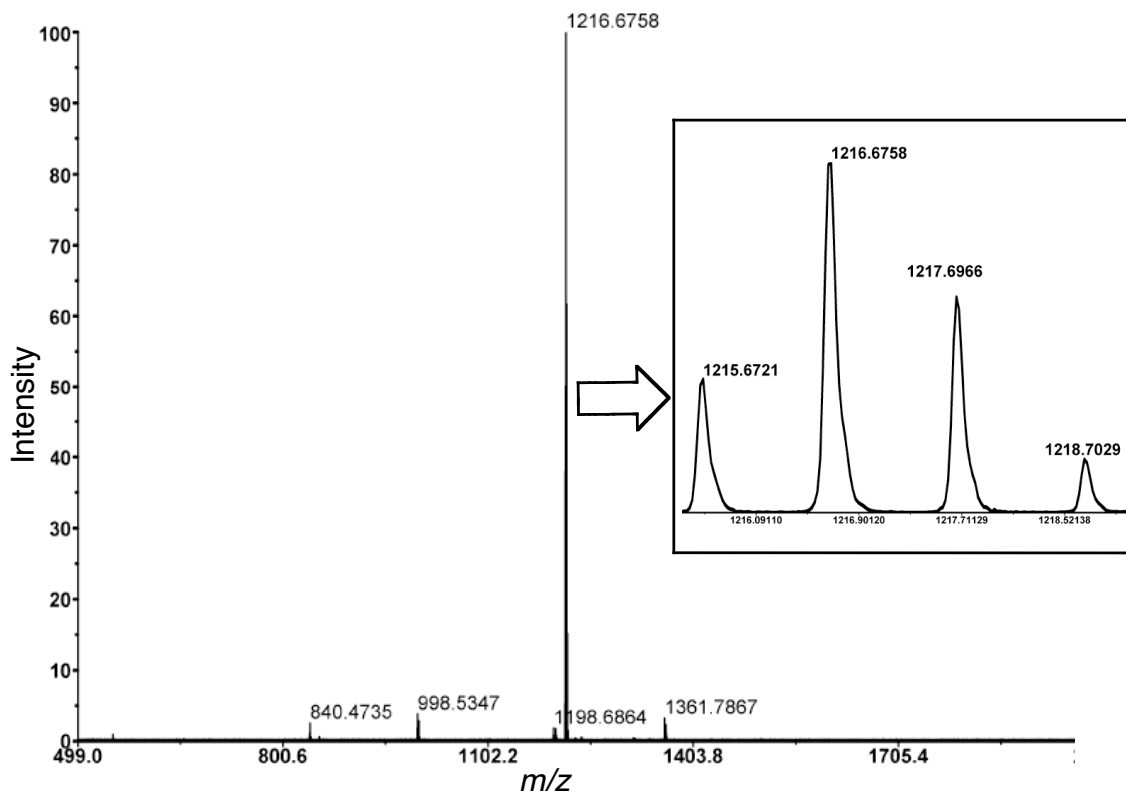


Figure S16. MALDI-TOF spectrum of acyclic trimer **4b**. The insert indicates the isotopic distribution of the molecular ion peak.

^1H NMR and ^{13}C NMR Spectra

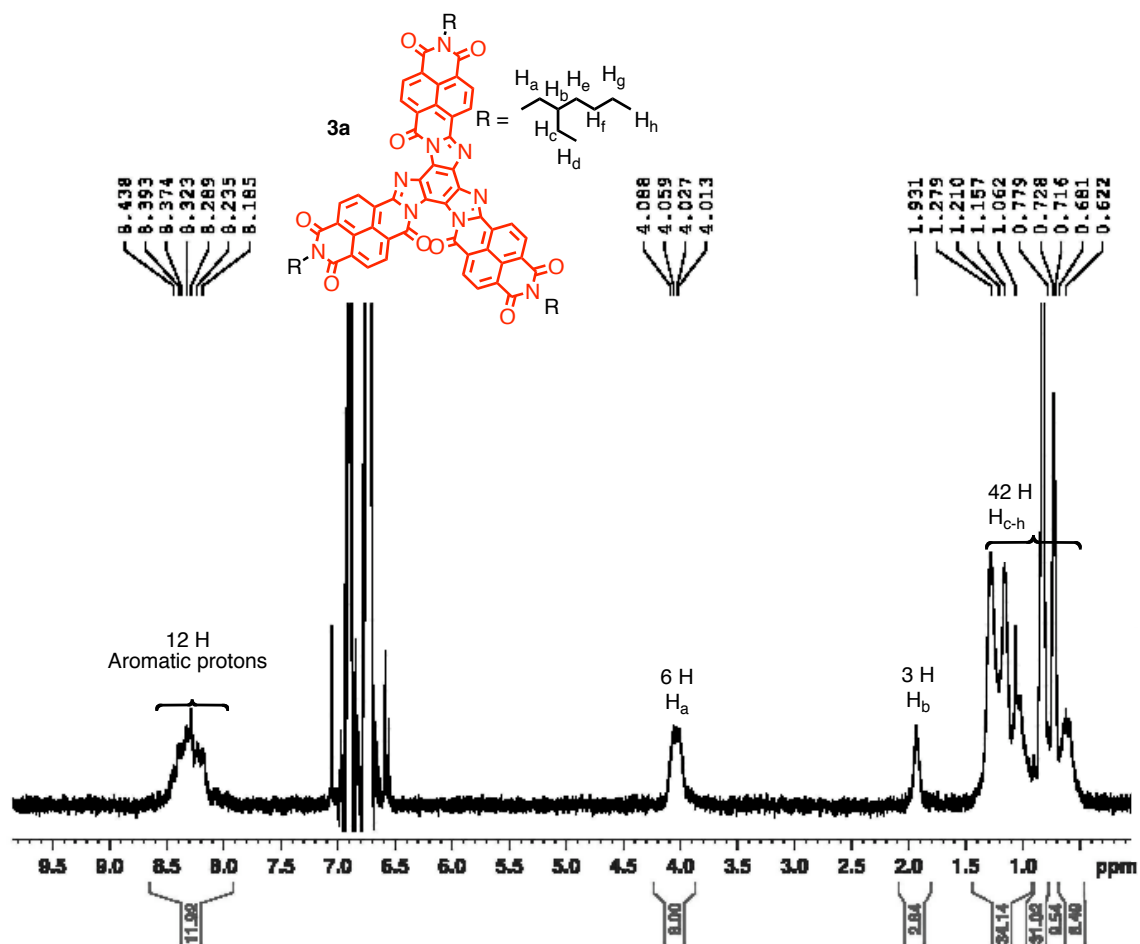


Figure S17. ^1H NMR of **3a** (298 K, $\text{C}_6\text{D}_5\text{Cl}$).

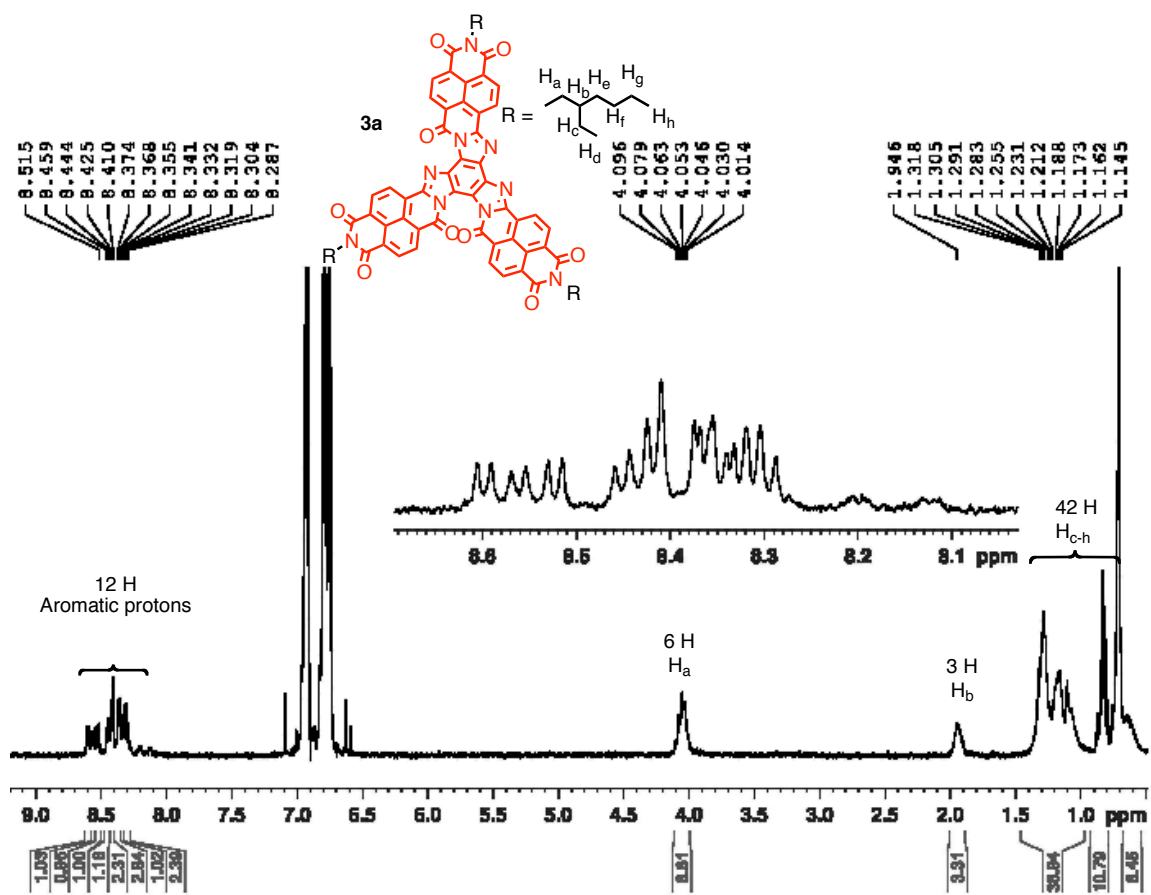


Figure S18. ^1H NMR of **3a** (373 K, $\text{C}_6\text{D}_5\text{Cl}$), The insert is a blow-up of the aromatic region.

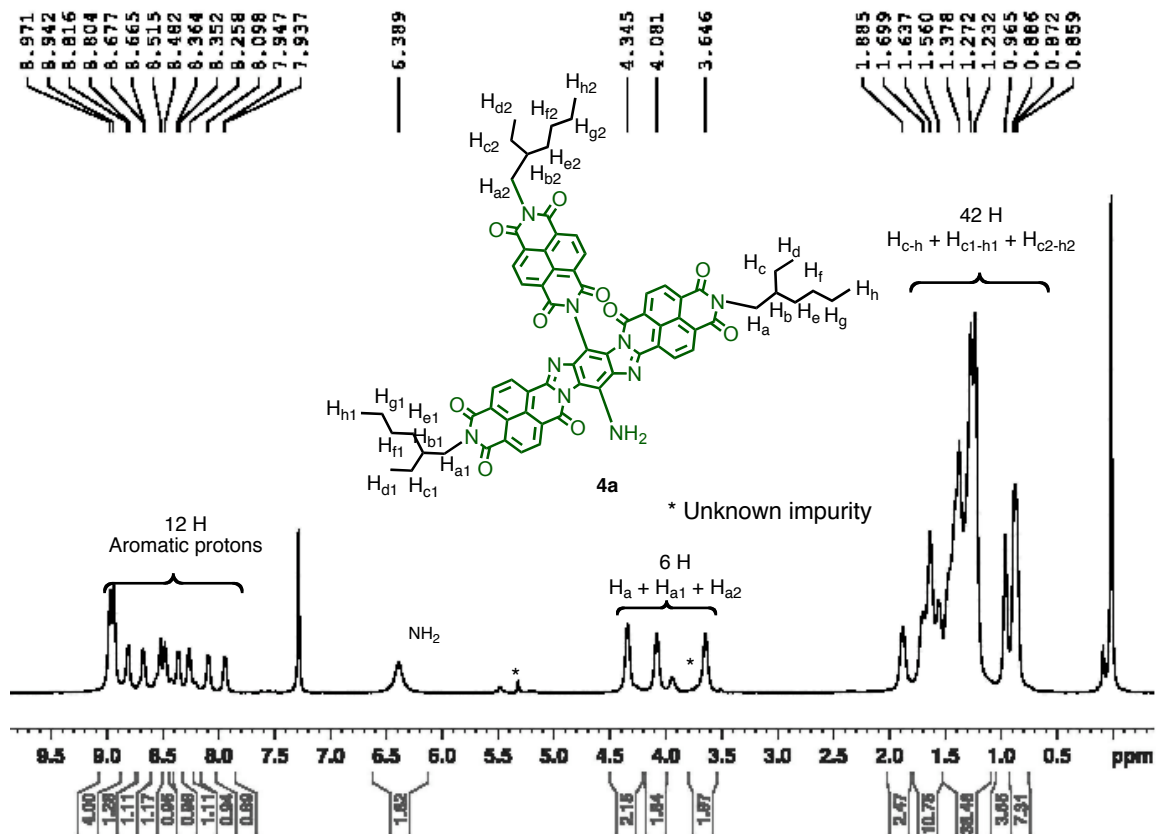


Figure S19. ¹H NMR of **4a** (298 K, $CDCl_3$).

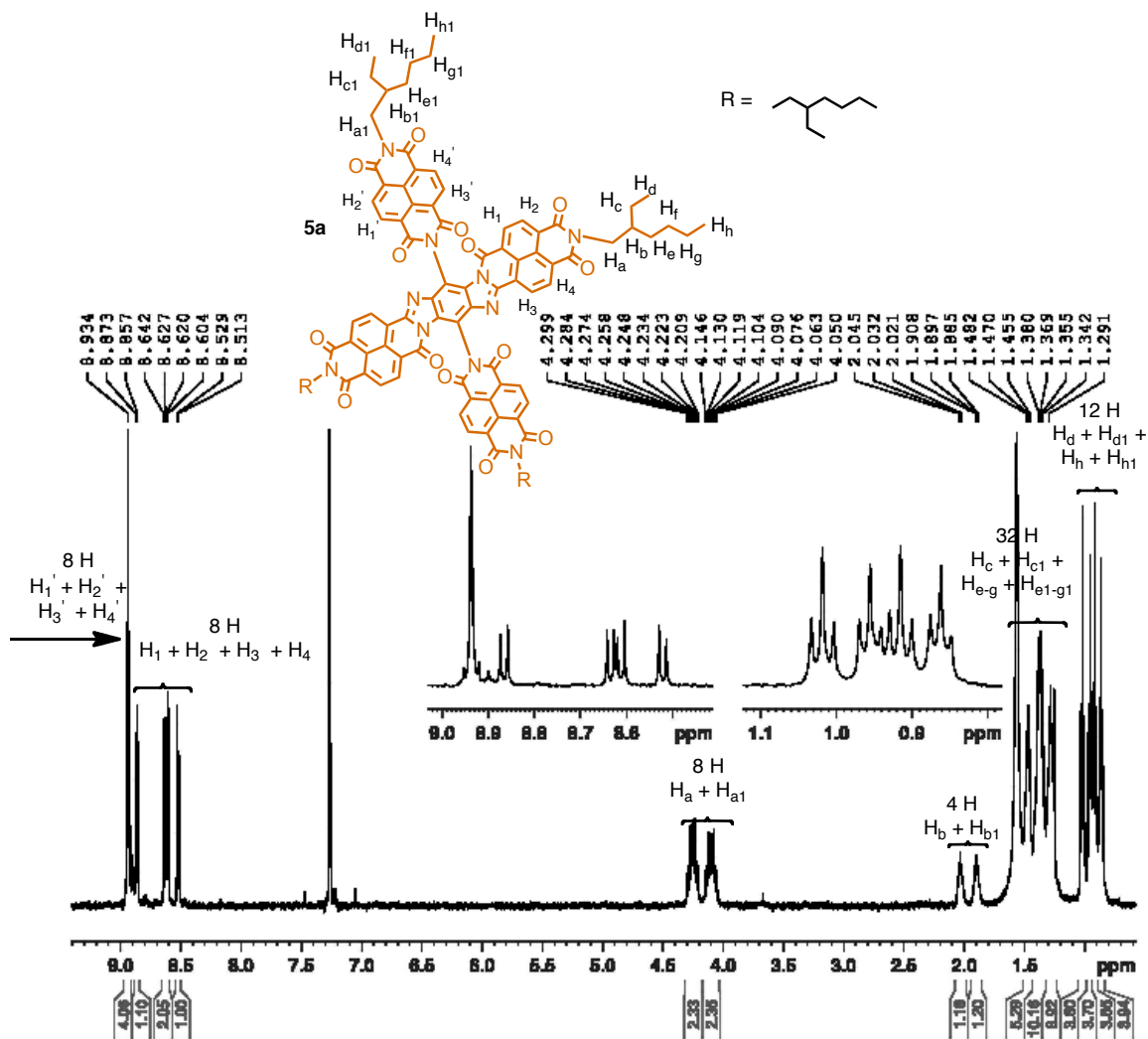


Figure S20. ¹H NMR of **5a** (298 K, CDCl₃). The insert is a blow-up of the aromatic region and the methyl protons.

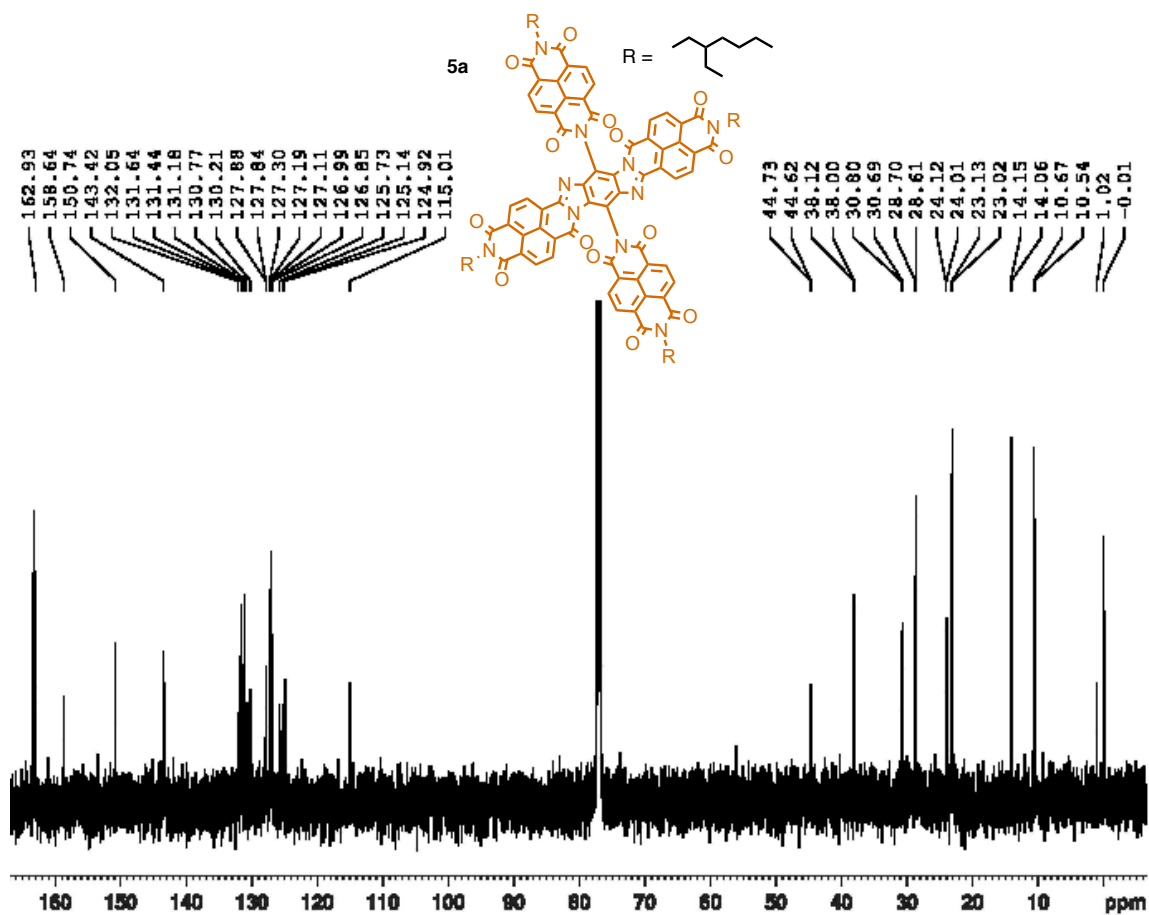


Figure S21. ^{13}C NMR of **5a** (298 K, CDCl_3).

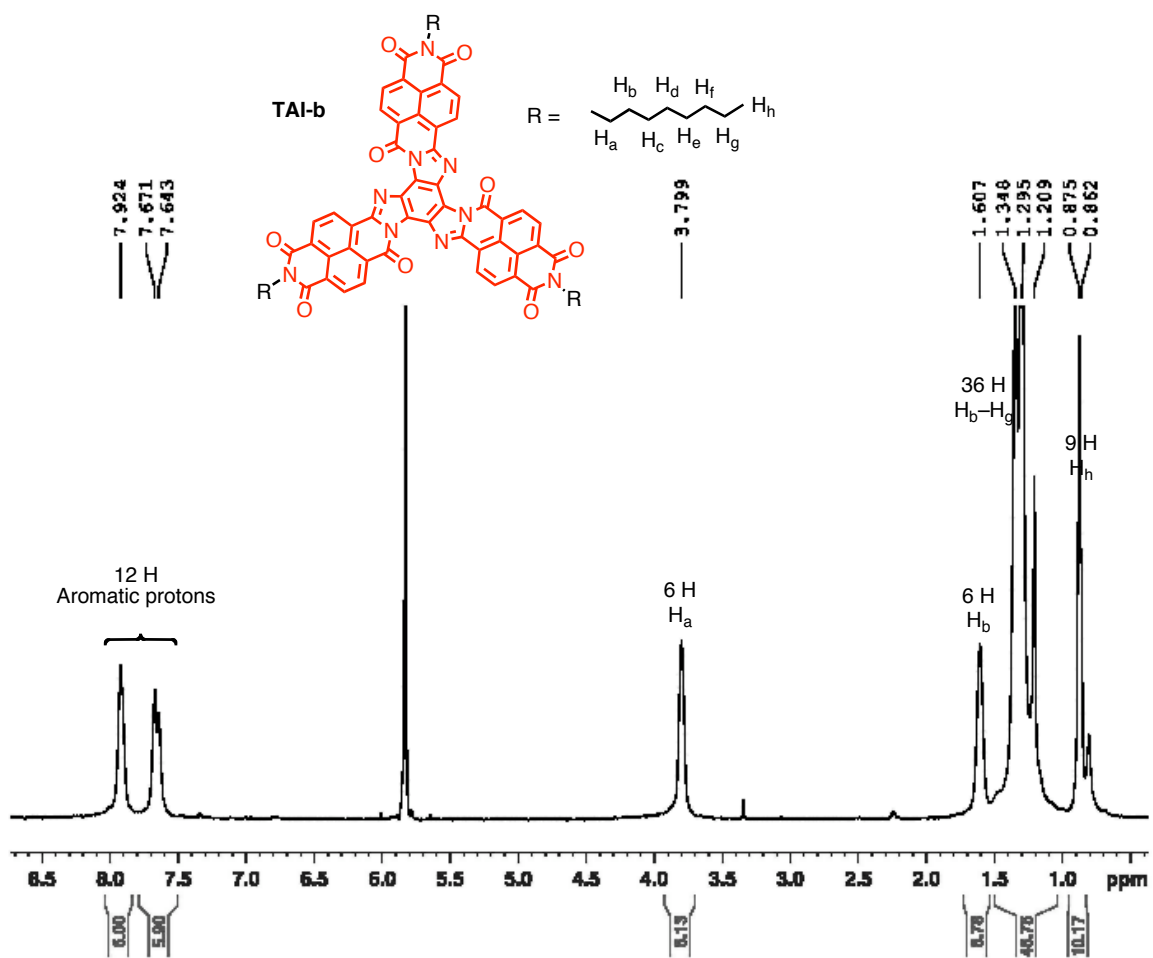


Figure S22. ¹H NMR of TAI-b (413 K, C₂D₂Cl₄).

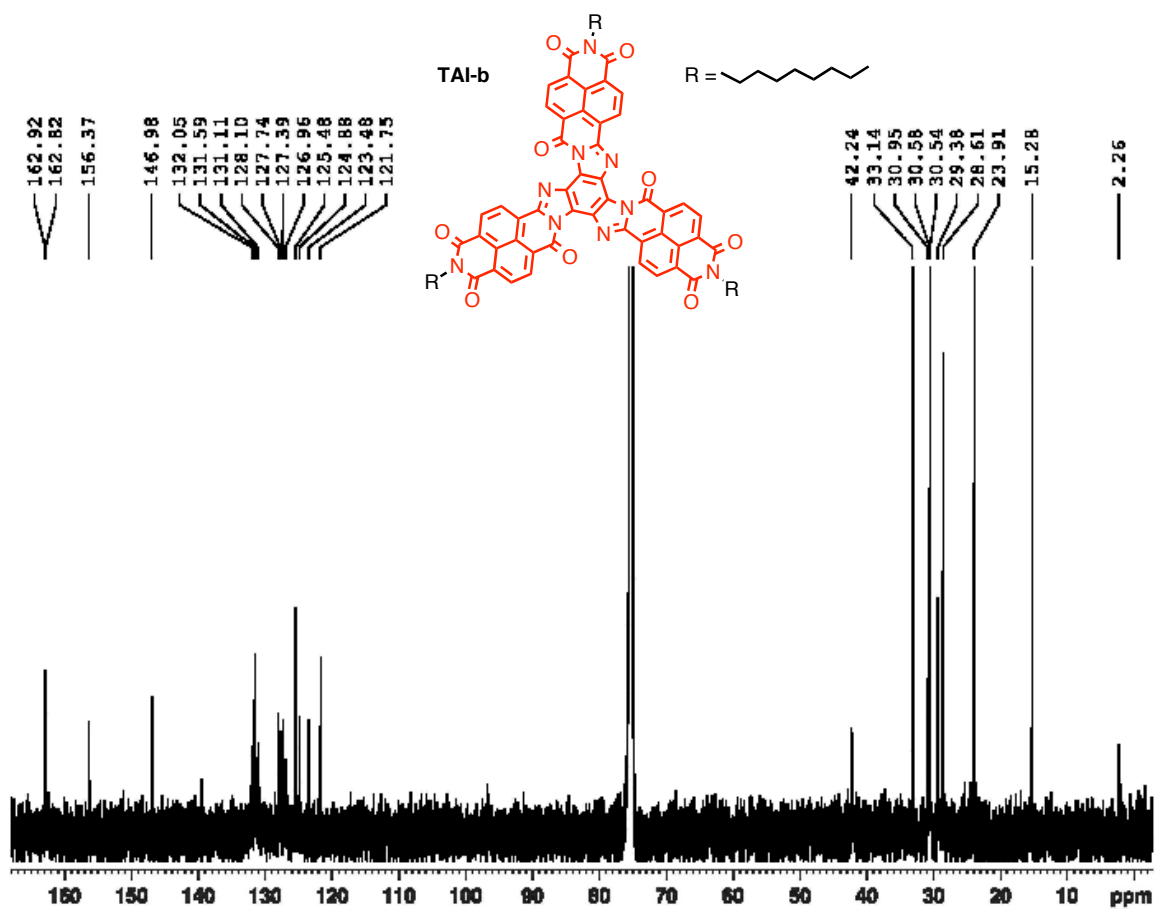


Figure S23. ¹³C NMR of TAI-b (413 K, C₂D₂Cl₄).

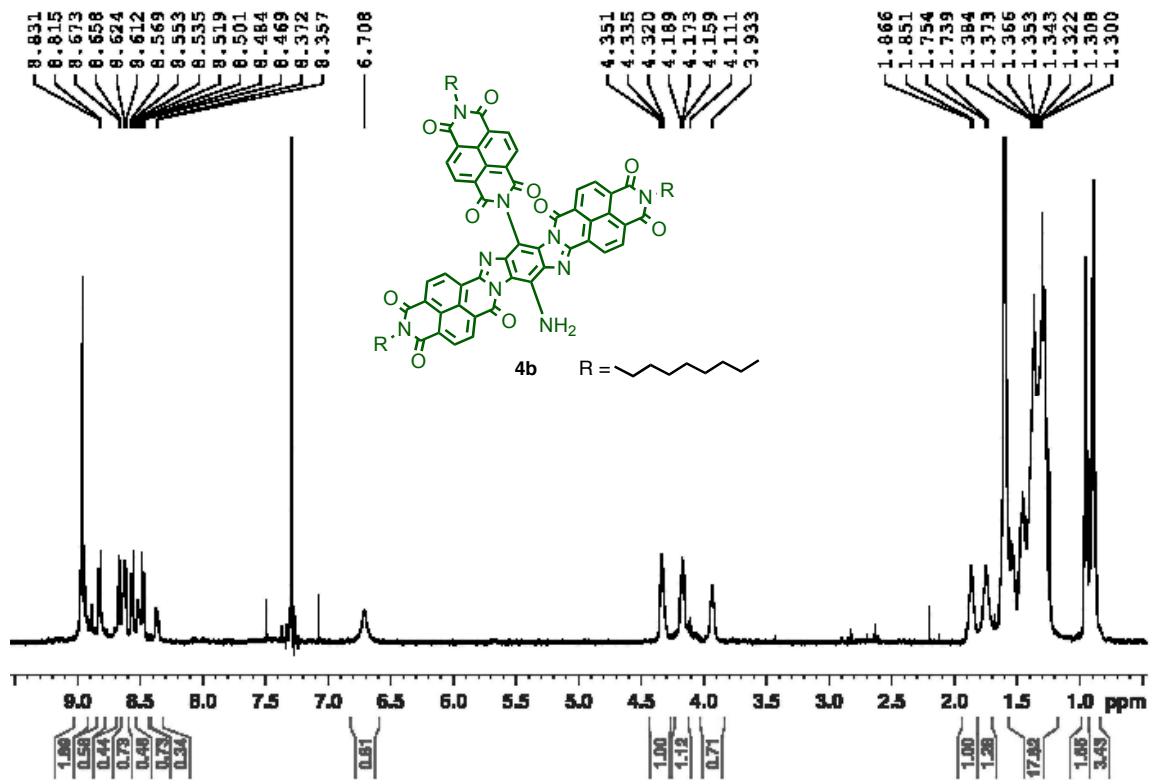


Figure S24. $^1\text{H NMR}$ of **4b** (298 K, CDCl_3).

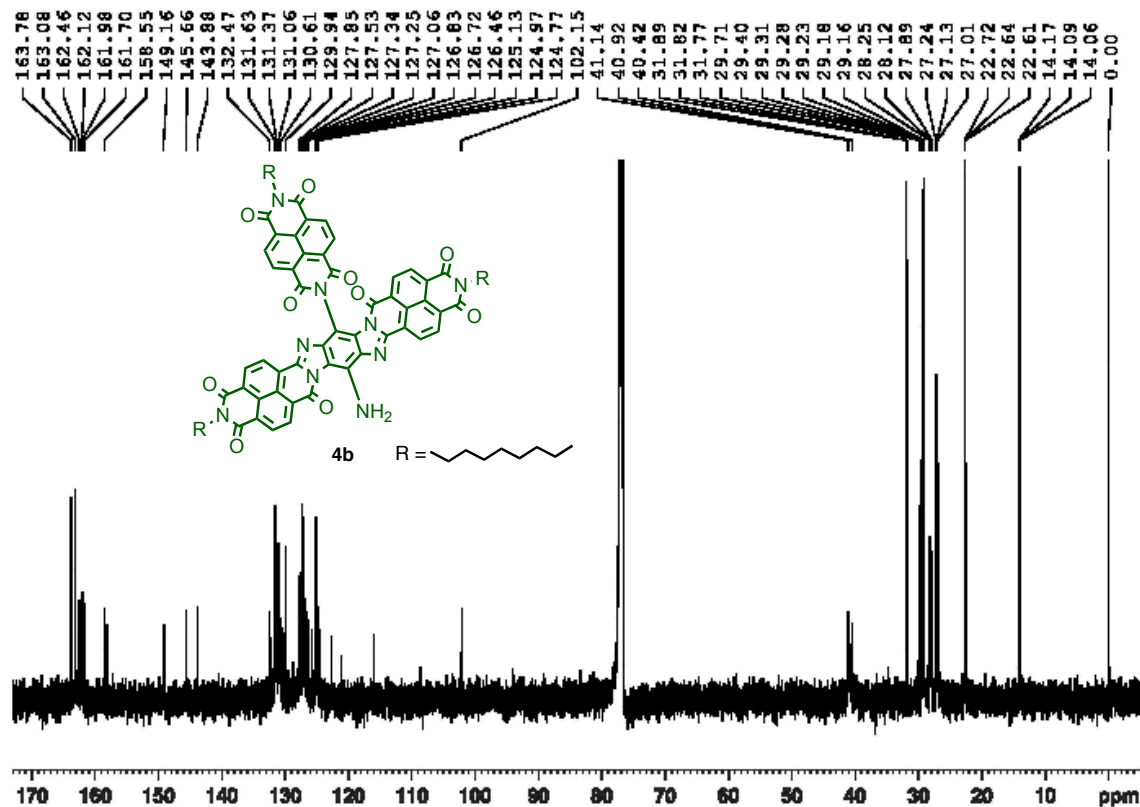


Figure S25. ^{13}C NMR of **4b** (298 K, CDCl_3).

References:

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