Novel $C_3$-Symmetric $n$-Type Tris(aroyleneimidazole) 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 (1H-NMR and 13C-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 $\delta$ 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 spincasting the corresponding CH$_2$Cl$_2$ solution (~ 5 mg / mL) onto a quartz substrate. The electrochemical experiments were carried out in N$_2$-purged CH$_2$Cl$_2$ solutions at concentrations ranging from $1.0\times10^{-4}$ to $1.0\times10^{-3}$ 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 µm alumina-water slurry on a felt surface immediately before use. In all cases ferrocene ($E_{1/2}=+0.395$ 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 and 2a-b 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 Kα radiation.

**Computational Methodology**

All calculations were performed using Q-Chem 3.2. 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 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. 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 ºC 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, 29.7, 29.4, 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 (CDCl3, 500 MHz, 298 K): $\delta$ = 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). 13C NMR (CDCl3, 125 MHz, 298 K): $\delta$ = 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, 1268, 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 Zn(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$_2$Cl$_2$ and water (50 mL each). After extracting the aqueous layer twice with CH$_2$Cl$_2$ (2 × 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$_2$Cl$_2$ 100% to 3% MeOH in CH$_2$Cl$_2$) 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

\[ \text{1} \xrightarrow{\text{Quinoline/Zn(OAc)}_2/170 \degree C} \text{2b} \]

\[ \begin{align*}
4b: \text{H} \text{ NMR} (\text{CDCl}_3, 500 \text{ MHz, } 298 \text{ K}): & \delta = 8.95 (\text{m, 4 H}), 8.83 (\text{d, } J = 8.0 \text{ Hz, 1 H}), \\
& 8.66 (\text{d, } J = 8.0 \text{ Hz, 1 H}), 8.61 (\text{m, 2 H}), 8.55 (\text{d, } J = 8.0 \text{ Hz, 1 H}), 8.52 (\text{d, } J = 8.0 \text{ Hz, 1 H}), 8.48 (\text{d, } J = 8.0 \text{ Hz, 1 H}), 8.36 (\text{d, } J = 8.0 \text{ Hz, 1 H}), 6.71 (\text{br s, 2 H}), 4.34 (\text{t, } J = 8.0 \text{ Hz, 2 H}), 4.17 (\text{t, } J = 8.0 \text{ Hz, 2 H}), 3.99 (\text{t, } J = 8.0 \text{ Hz, 2 H}), 1.87 (\text{m, 2 H}), 1.74 (\text{m, 2 H}), 1.38–1.30 (\text{m, 32 H}), 0.98 (\text{t, } J = 7.5 \text{ Hz, 3 H}), 0.85 (\text{m, 6 H}). \\
\text{C NMR} (\text{CDCl}_3, 125 \text{ MHz, } 298 \text{ K}): & \delta = 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, 28.3, 28.1, 27.9, 27.2, 27.1, 27.0, 22.7, 22.6, 22.6, 14.2, 14.1, 14.1; \text{MS (MALDI-TOF): } [\text{M}]^+ \text{ calcd. 1215.4854, found 1215.6721 (100%).} \\
\text{TAI-b: } \text{H} \text{ NMR} (\text{C}_2\text{D}_2\text{Cl}_4, 500 \text{ MHz, } 413 \text{ K}): & \delta = 7.92 (\text{br s, 6 H}), 7.67 (\text{br s, 3 H}), 7.64 (\text{br s, 3 H}), 3.78 (\text{br s, 6 H}), 1.62 (\text{br s, 6 H}), 1.34–1.21 (\text{m, 30 H}), 0.86 (\text{br s, 9 H}). \\
\text{C NMR} (\text{C}_2\text{D}_2\text{Cl}_4, 125 \text{ MHz, } 413 \text{ K}): & \delta = 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, 28.3, 26.7, 25.4, 25.3, 24.9, 24.8, 24.7, 22.7, 22.6, 22.6, 14.2, 14.1, 14.1; \text{MS (MALDI-TOF): } [\text{M}]^+ \text{ calcd. 1215.4854, found 1215.6721 (100%).}
28.6, 23.9, 15.3. MS (MALDI-TOF): [M + H]$^+$ calcd. 1198.4827, found 1198.7484 (100%).

**Thermogravimetric 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 (x 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.
$^1$H NMR and $^{13}$C NMR Spectra

Figure S17. $^1$H NMR of 3a (298 K, C$_6$D$_5$Cl).
Figure S18. $^1$H NMR of 3a (373 K, C$_6$D$_5$Cl), The insert is a blow-up of the aromatic region.
Figure S19. $^1$H NMR of 4a (298 K, CDCl$_3$).

* Unknown impurity

Aromatic protons

12 H

$^6$ H $H_a + H_{a1} + H_{a2}$

$^4$2 H $H_{c-h} + H_{c1-h1} + H_{c2-h2}$

NH$_2$

S20
Figure S20. $^1$H NMR of 5a (298 K, CDCl$_3$). 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. $^1$H NMR of TAI-b (413 K, C$_2$D$_2$Cl$_4$).
Figure S23. $^{13}$C NMR of TAI-b (413 K, C$_2$D$_2$Cl$_4$).
Figure S24. $^1$H NMR of 4b (298 K, CDCl$_3$).
Figure S25. $^{13}$C NMR of 4b (298 K, CDCl$_3$).

References:


S3. Q-Chem is a product of Q-Chem. Inc.

