Supporting Information for

Efficient synthesis and physical properties of novel
H-shaped 2,3,7,8-tetraazaanthracene-based conjugated molecules

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General Procedure

All reagents were purchased from Aladdin and J&K Chemical. All solvents were supplied by Sinopharm Chemical Reagent. Tetrahydrofuran (THF) was refluxed with sodium. Triethylamine (TEA) was refluxed with calcium carbide. Dichloromethane for cyclic voltammetry (CV) and Ultraviolet-visible (UV-Vis) spectra studies was distilled from calcium hydride. All performances were carried out using standard Schlenk techniques. \textsuperscript{1}H and \textsuperscript{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Mercury Plus 400 (400 MHz for proton) spectrometer with tetramethylsilane as the internal reference using CDCl\textsubscript{3} as solvent in all cases. X-ray crystallography was recorded on CAD4 DIFFACTIS 586 diffractometer. Ultraviolet-visible (UV-Vis) spectra were recorded on a Beijing Purkinje TU-1901 spectrophotometer. Mass spectra were recorded on a Bruker microTOF-Q-II system. Cyclic voltammetry (CV) was performed on an Chenhua 650D electrochemical analyzer in distilled dichloromethane containing recrystallized tetra-n-butyl-ammoniumhexafluorophosphate (TBAPF\textsubscript{6}, 0.1M) as supporting electrolyte at 298 K. A conventional three-electrode cell was used with a platinum working electrode (surface area of 0.3 mm\textsuperscript{2}) and a platinum wire as the counter electrode. The Pt working electrode was routinely polished with a polishing alumina suspension and rinsed with acetone before use. The measured potentials were recorded with respect to a Ag/AgNO\textsubscript{3} (0.01 M) reference electrode. All electrochemical measurements were carried out under an atmospheric pressure of
Materials synthesis and characterization

Synthesis of 1,2,4,5-benzenetetracarbonyl tetrachloride (2)

A mixture of 1,2,4,5-Benzenetetracarboxylic anhydride (10.0 g) and phosphorus pentachloride (20.0 g) were melted together at 190°C in a flask with a reflux condenser. The solution was then heated at 160°C for 3h, allowed to cool, and distilled at reduced pressure to give a colorless fraction. The compound is white solid at room temperature (12.1 g, 80%). 1H NMR (400 Hz, CDCl3): δ 8.05 (1 H, s, -C6H2)

Synthesis of 1,2,4,5-tetra(S-(pyridine-2′-yl))benzenetetrathioate (3)

A solution of 2-mercaptopyridine (2.19 g, 19.7 mmol), TEA (5 ml) and THF (50 ml) was stirred at 0°C for 30 min. Then a solution of 1,2,4,5-benzenetetracarbonyl tetrachloride 2 (1.44 g, 4.38 mmol) in THF (50 mL) was quickly added. The reaction was quenched instantly with 1% HCl (100mL) and extracted with CH2Cl2. The combined organic fractions were washed with 10% NaOH and water until neutrality, dried over MgSO4 and recrystallised from CH2Cl2/Et2O. The product was obtained as white solid (1.26 g, 45.9%). 1H NMR (400 Hz, CDCl3) δ 8.70 – 8.62 (m, 2H, S-Py-H-6), 8.30 (s, 1H,Ph), 7.78 (qd, 4H, JH-H=5.7 Hz, 4JH-H =1.4 Hz, S-Py-H-4,5), 7.35 (m, 2H, S-Py-H-3); 13C NMR spectra can not be well-resolved due to its poor solubility in common organic solvents.

Synthesis of 1,2,4,5-tetra(thieno-2′-yl)benzene (4a)

A solution of 2-bromothiophene (2.29 g, 14.06 mmol) in THF (15 ml) was slowly added to a mixture of iodine activated magnesium (0.38 g, 15.63 mmol) in THF (5 ml) to form the Grignard reagent in 3 h. Afterwards, the cold reagent was slowly added to a flask containing 3 (2.00 g, 3.19 mmol) in absolute THF (100 mL) at 0°C and stirred overnight. The suspension became brown gradually. Solid precipitated after stirring. Then, the reaction was quenched with 10% HCl (100 mL). The solid was isolated by filtration. After washing by aqueous NaOH solution and water, the product was dried as white solid (1.41 g, 85.1%). 1H NMR (400 Hz, CDCl3): δ 8.05 (s, 1H, Ph), 7.74 (dd, 2 H, JH-H = 4.9 Hz, JH-H = 1.1 Hz, Th-H-5), 7.57 (dd, 2 H, JH-H = 3.9 Hz, 3JH-H = 5.7 Hz, 4JH-H = 1.4 Hz, S-Py-H-4,5), 7.35 (m, 2H, S-Py-H-3); 13C NMR spectra can not be well-resolved due to its poor solubility in common organic solvents.
Hz, J = 1.1, Th-H-3), 7.12 (dd, 2 H, 3 J_H-H = 4.9 Hz, 3 J_H-H = 3.9 Hz, Th-H-4); 13C NMR spectra can not be well-resolved due to its poor solubility in common organic solvents.

**Synthesis of 1,2,4,5-tetra(5-trimethylsilyl-thieno-2'-yl)benzene (4b)**

A solution of 2-bromo-5-trimethylsilylthiophene (1.88 g, 7.99 mmol) in THF (10 ml) was slowly added to a mixture of iodine activated magnesium (0.23 g, 9.58 mmol) in THF (5 ml) to form the Grignard reagent in 5 h. Afterwards, the cold reagent was slowly added to a flask containing 3 (1.0 g, 1.60 mmol) in absolute THF (50 mL) at 0 °C and stirred overnight. Then, the reaction was quenched with 10% HCl (100 mL) and extracted with ether. The combined organic fractions were washed with 1M NaOH and water until neutrality, dried over MgSO4 and the solvent was removed under reduced pressure. After purification by column chromatography with CH2Cl2/petroleum as eluent, the product was obtained as white solid (0.74 g, 63.4%). 1H NMR (400Hz, CDCl3): δ 8.03 (s, 1 H, Ph), 7.62 (d, 3 J_H-H = 3.6 Hz, 2H, Th-H-3), 7.22 (d, 3 J_H-H = 3.6 Hz, 2H, Th-H-4), 0.32 (s, 18H, C6H18); 13C NMR (100Hz, CDCl3): δ 186.47, 153.63, 141.70, 141.49, 136.34, 129.66, 124.72, -0.221.

**Synthesis of 1,2,4,5-tetra(5'-hexyl-thieno-2'-yl)benzene (4c)**

A solution of 2-bromo-5-hexylthiophene (2.0 g, 8.09 mmol) in THF (10 ml) was slowly added to a mixture of iodine activated magnesium (0.24 g, 9.71 mmol) in THF (5 ml) to form the Grignard reagent in 4 h. Afterwards, the cold reagent was slowly added to a flask containing 3 (1.01 g, 1.62 mmol) in absolute THF (50 mL) at 0 °C and stirred overnight. Then, the reaction was quenched with 10% HCl (100 mL) and extracted with ether. The combined organic fractions were washed with 1M NaOH and water until neutrality, dried over MgSO4 and the solvent was removed under reduced pressure. After purification by column chromatography with CH2Cl2/petroleum as eluent, the product was obtained as white solid (0.43 g, 31.1%). 1H NMR (400 MHz, CDCl3): δ 7.98 (s, 1H), 7.36 (d, 3 J_H-H = 3.8 Hz, 2H, Th-H-3), 6.79 (d, 3 J_H-H = 3.9 Hz, 2H, Th-H-4), 2.82 (t, 4H, 3 J_H-H = 7.6 Hz), 1.77 – 1.44 (m, 4H), 1.42 – 1.05 (m, 8H), 0.98 – 0.63 (m, 6H); 13C NMR (100Hz, CDCl3): δ 186.57, 158.63, 141.04, 140.92,
Synthesis of 1,4,6,9-tetra(thien-2-yl)-2,3,7,8-tetraazaanthracene (5a)
A suspension of hydrazine hydrate (1.54 g, 30.8 mmol) and 4a (2.0 g, 3.9 mmol) in ethanol (50 ml) was stirred for 2d at room temperature. The solvent was removed under reduced pressure. After purification by column chromatography with CH$_2$Cl$_2$/petroleum, the product was obtained as orange solid (1.28 g, 65.0%). $^1$H NMR (400 MHz, CDCl$_3$): δ 9.87 (s, 1H, Ph), 7.87 (dd, 2H, $^3$J$_{H-H}$ = 3.7 Hz, $^3$J$_{H-H}$ = 1.1 Hz, Th-C-H-5), 7.72 (dd, 2H, $^3$J$_{H-H}$ = 5.1 Hz, $^3$J$_{H-H}$ = 1.1 Hz, Th-CH-5), 7.34 (dd, 2H, $^3$J$_{H-H}$ = 5.1 Hz, $^3$J$_{H-H}$ = 3.7 Hz, Th-H-4); $^{13}$C NMR spectra can not be well-resolved due to its poor solubility in common organic solvents. HRMS-ESI m/z: [M+H] calcd. for C$_{26}$H$_{15}$N$_4$S$_4$, 511.0180; found, 511.0183; M. p. >300℃.

Synthesis of 1,4,6,9-tetra(5-trimethylsilylethien-2-yl)-2,3,7,8-tetraazaanthracene (5b)
A suspension of hydrazine hydrate (0.75 g, 15.0 mmol) and 4b (1.0 g, 1.23 mmol) in ethanol (50 ml) was stirred for 2d at room temperature. The solvent was removed under reduced pressure. After purification by column chromatography with CH$_2$Cl$_2$/petroleum, the product was obtained as orange solid (0.62 g, 62.6%). $^1$H NMR (400 MHz, CDCl$_3$): δ 9.90 (s, 1H), 7.98 (d, 2H, $^3$J$_{H-H}$ = 3.5 Hz, Th-H-3), 7.44 (d, 2H, $^3$J$_{H-H}$ = 3.5 Hz, Th-H-4), 0.44 (s, 18H, CH$_3$); $^{13}$C NMR (100 Hz, CDCl$_3$): δ 152.76, 146.76, 143.07, 134.99, 131.89, 126.67, 125.87, 0.126; HRMS-ESI m/z: [M+H] calcd. for C$_{38}$H$_{47}$N$_4$S$_4$Si$_4$, 799.1761; found, 799.1763; M. p. >300℃.

Synthesis of 1,4,6,9-tetra(5-hexyl-thien-2-yl)-2,3,7,8-tetraazaanthracene (5c)
A suspension of hydrazine hydrate (0.1 g, 15.0 mmol) and 4c (1.5 g, 1.23 mmol) in ethanol (50 ml) was stirred for 2d at room temperature. The solvent was removed under reduced pressure. After purification by column chromatography with CH$_2$Cl$_2$/petroleum, the product was obtained as orange-red solid (0.61 g, 62.0%). $^1$H NMR (400 MHz, CDCl$_3$): δ 9.81 (s, 1H, Ph), 7.69 (d, 2H, $^3$J$_{H-H}$ = 3.7 Hz, Th-H-3), 6.98 (dt, 2H, $^3$J$_{H-H}$ = 3.6 Hz, $^4$J$_{H-H}$ = 0.8 Hz, Th-CH-4), 2.94 (t, 4H, $^3$J$_{H-H}$ = 7.6 Hz, CH$_2$), 1.54–1.43 (m, 4H, CH$_2$), 1.40–1.32 (m, 8H, CH$_2$), 1.31–1.21 (m, 6H, CH$_3$); $^{13}$C NMR (100 Hz,
CDCl$_3$): \( \delta \) 152.24, 151.93, 136.09, 130.66, 126.31, 125.64, 31.82, 30.66, 29.92, 29.12, 22.83, 14.33; HRMS-ESI m/z: [M+H] calcd. For C$_{50}$H$_{63}$N$_4$S$_4$, 848.3936; found, 847.3930; M. p. 193-195.

Crystallography. Crystal data for C$_{13}$H$_7$N$_2$S$_2$, \( M=255.33 \), monoclinic, \( a=12.6998(16) \) Å, \( b=7.4627(10) \) Å, \( c=12.8404(16) \) Å, \( \alpha=90^\circ \), \( \beta=114.132(2)^\circ \), \( \gamma=90^\circ \), \( V=1110.6(2) \) Å$^3$, \( T=296(2)K \), Space group \( P2(1)/n \), \( Z=4 \), \( \lambda(\text{Mo-K}\alpha)=0.71073 \) Å, 2053 reflections measured, 1082 independent reflections (\( R_{\text{int}}=0.0640 \)). The final \( R_1 \) values were 0.0773 (I>2\( \sigma(I) \)). The final \( wR(F^2) \) values were 0.2114 (I>2\( \sigma(I) \)). The final \( R_1 \) values 0.1361 (all data). The final \( wR(F^2) \) values 0.2456 (all data). The goodness of fit on \( F^2 \) was 0.945. CCDC number: 860020.

Crystal data for C$_{50}$H$_{62}$N$_4$S$_4$, \( M=847.28 \), monoclinic, \( a=6.3583(3) \) Å, \( b=41.420(2) \) Å, \( c=8.9592(5) \) Å, \( \alpha=90^\circ \), \( \beta=104.922(2)^\circ \), \( \gamma=90^\circ \), \( V=2280.0(2) \) Å$^3$, \( T=173(2) \) K, Space group \( P2(1)/n \), \( Z=2 \), \( \lambda(\text{Mo-K}\alpha)=0.71073 \) Å, 4035 reflections measured, 3533 independent reflections (\( R_{\text{int}}=0.0456 \)). The final \( R_1 \) values were 0.0794 (I>2\( \sigma(I) \)). The final \( wR(F^2) \) values were 0.1683 (I>2\( \sigma(I) \)). The final \( R_1 \) values 0.0890 (all data). The final \( wR(F^2) \) values 0.1734 (all data). The goodness of fit on \( F^2 \) was 1.154. CCDC number: 860021.

Table 1S Optic properties of 5a-c upon titration with trifluoroacetic acid (TFA).

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$^a$ Calculated on the basis of the saturated values of the absorption maxima upon addition of a large excess amount of TFA.