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. ^{1}H and ^{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 $CDCl_3$ as solvent in all cases. X-ray crystallography was recorded on CAD4 DIFFACTIS 586 diffractormeter. 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 ($TBAPF_6$, 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^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 $Ag/AgNO_3$ (0.01 M) reference electrode. All electrochemical measurements were carried out under an atmospheric pressure of

argon.

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 □ in a flask with a reflux condenser. The solution was then heated at 160 □ 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%). ^{1}H NMR (400 Hz, $CDCl_3$): δ 8.05 (1 H, s,-C_6H_2)

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 ℃ 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 CH_2Cl_2. The combined organic fractions were washed with 10% NaOH and water until neutrality, dried over $MgSO_4$ and recrystallised from CH_2Cl_2/Et_2O. The product was obtained as white solid (1.26 g, 45.9%). ^{1}H NMR (400 Hz, $CDCl_3$) δ 8.70 – 8.62(m, 2H, S-Py-*H*-6), 8.30 (s, 1H,Ph), 7.78 (qd, 4H, $^{3}J_{H\text{-}H}$=5.7 Hz, $^{4}J_{H\text{-}H}$ =1.4 Hz, S-Py-*H*-4,5), 7.35 (m, 2H, S-Py-*H*-3); ^{13}C 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 ℃ 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%). ^{1}H NMR (400 Hz, $CDCl_3$): δ 8.05 (s, 1H, Ph), 7.74 (dd, 2 H, $^{3}J_{H\text{-}H}$ = 4.9 Hz, $^{4}J_{H\text{-}H}$ = 1.1 Hz, Th-*H*-5), 7.57 (dd, 2 H, $^{3}J_{H\text{-}H}$ = 3.9

Hz, *J* =1.1, Th-*H*-3), 7.12 (dd, 2 H, $^{3}J_{H\text{-}H}$ = 4.9 Hz, $^{3}J_{H\text{-}H}$ = 3.9 Hz, Th-*H*-4); ^{13}C 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-trimethylsiylthiophene (1.88 g, 7.99 mmol) in THF (10 ml) was slowly added to a mixture of iodine activated magnesium (0.23g, 9.58mmol) 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 □ 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 Mg_2SO_4 and the solvent was removed under reduced pressure. After purification by column chromatography with CH_2Cl_2/ petroleum as eluent, the product was obtained as white solid (0.74 g, 63.4%). ^{1}H NMR (400Hz, $CDCl_3$): δ 8.03 (s, 1 H, Ph), 7.62 (d, $^{3}J_{H\text{-}H}$=3.6 Hz, 2H, Th-*H*-3), 7.22 (d, $^{3}J_{H\text{-}H}$=3.6 Hz, 2H, Th-*H*-4), 0.32 (s, 18H, C*H*$_3$); ^{13}C NMR (100Hz, $CDCl_3$): 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, 9.7 1 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 □ 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 Mg_2SO_4 and the solvent was removed under reduced pressure. After purification by column chromatography with CH_2Cl_2/ petroleum as eluent, the product was obtained as white solid (0.43 g, 31.1%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.36 (d, 2H, $^{3}J_{H\text{-}H}$ =3.8 Hz), 6.79 (d, 2H, $^{3}J_{H\text{-}H}$ = 3.9 Hz), 2.82 (t, 4H, $^{3}J_{H\text{-}H}$ =7.6 Hz), 1.77 – 1.44 (m, 4H), 1.42 – 1.05 (m, 8H), 0.98 – 0.63 (m, 6H); ^{13}C NMR (100Hz, $CDCl_3$): δ 186.57, 158.63, 141.04, 140.92,

136.48, 129.69, 126.15, 31.69, 31.49, 31.00, 28.91, 22.75, 14.28.

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 (50ml) was stirred for 2d at room temperature. The solvent was removed under reduced pressure. After purification by column chromatography with CH_2Cl_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, $^3J_{H\text{-}H}$ = 3.7 Hz, $^3J_{H\text{-}H}$ = 1.1 Hz, Th-C-*H*-5), 7.72 (dd, 2H, $^3J_{H\text{-}H}$ = 5.1 Hz, $^3J_{H\text{-}H}$ = 1.1 Hz, Th-C*H*-5), 7.34 (dd, 2H, $^3J_{H\text{-}H}$ = 5.1 Hz, $^3J_{H\text{-}H}$ = 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 $C_{26}H_{15}N_4S_4$, 511.0180; found, 511.0183； M. p. >300℃.

Synthesis of 1,4,6,9-tetra(5-trimethylsilyl-thien-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 tirred for 2d at room temperature. The solvent was removed under reduced pressure. After purification by column chromatography with CH_2Cl_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, $^3J_{H\text{-}H}$ = 3.5 Hz, Th-*H*-3), 7.44 (d, 2H, $^3J_{H\text{-}H}$ =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 $C_{38}H_{47}N_4S_4Si_4$; 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** (1.5g, 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_2Cl_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, $^3J_{H\text{-}H}$=3.7 Hz, Th-*H*-3), 6.98 (dt, 2 H, $^3J_{H\text{-}H}$=3.6, $^4J_{H\text{-}H}$=0.8 Hz, Th-C*H*-4), 2.94 (t, 4H, $^3J_{H\text{-}H}$ =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 (100Hz,

$CDCl_3$): δ 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 $C_{50}H_{63}N_4S_4$, 848.3936; found, 847.3930； M. p. 193-195□.

Crystallography. Crystal data for $C_{13}H_7N_2S_2$, M=255.33, monoclinic, a=12.6998(16) Å, b=7.4627(10) Å, c=12.8404(16) Å, α=90°, β=114.132(2)°, γ=90°, V=1110.6(2) Å^3, T=296(2)K, Space group $P2(1)/n$, Z=4, λ(Mo-Kα)=0.71073 Å, 2053 reflections measured, 1082 independent reflections (R_{int}=0.0640). The final R_1 values were 0.0773 (I>2σ(I)). The final $wR(F^2)$ values were 0.2114 (I>2σ(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 $C_{50}H_{62}N_4S_4$, M=847.28, monoclinic, a=6.3583(3) Å, b=41.420(2) Å, c=8.9592(5) Å, α=90°, β=104.922(2)°, γ=90°, V=2280.0(2) Å^3, T=173(2) K, Space group $P2(1)/n$, Z=2, λ(Mo-Kα)=0.71073 Å, 4035 reflections measured, 3533 independent reflections (R_{int}=0.0456). The final R_1 values were 0.0794 (I>2σ(I)). The final $wR(F^2)$values were 0.1683 (I>2σ(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).

Compd	isosbestic λ_1 (nm)	Isosbestic λ_2 (nm)	λ_{onset} [a] （nm）	E_g^{opt} [a] （eV）
5a	393	446	579	2.14
5b	401	452	614	2.02
5c	413	470	649	1.91

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