

Supporting Information

**All-thiophene Dendrimers Based on Cyclooctatetrathiophene :
Synthesis and Aggregation-induced Emission (AIE) Features**

Pengfei Wang ^{1,†}, Chunmei Zhao ^{1,†}, Shuai Qiu ¹, Wan Xu ^{1,*}, Chunli Li ¹, Zhiying Ma ¹, Wei Cao ¹, Li Xu ² and Hua Wang ^{1,*}

¹ Institute of Nanoscience and Engineering, Henan University, Kaifeng 475004, China

² College of Chemistry and Molecular Sciences, Henan University, Kaifeng 475004, China

E-mail: 40070005@henu.edu.cn; hwang@henu.edu.cn

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1. Experimental Section

General Procedures and Materials: Ether and tetrahydrofuran (THF) for use were freshly distilled from sodium/benzophenone prior to use. Concentration of *n*-BuLi (hexane) was determined by titration with *N*-pivaloyl-*o*-toluidine¹. Column chromatography was carried out on silica gel (300-400 or 200-300 mesh). Analytical thin-layer chromatography was performed on glass plates of Silica Gel GF-254 with detection by UV. Standard techniques for synthesis under inert atmosphere, using gasbag and Schlenk glassware equipped with an 8-mm PTFE vacuum stop-cock were employed. All starting materials and reagents were commercially available. NMR spectra were obtained using chloroform-*d* (CDCl₃) as solvent. The chemical shift references were as follows: (¹H) CDCl₃, 7.26 ppm (CHCl₃); (¹³C) CDCl₃, 77.00 ppm (CDCl₃). IR spectra were obtained using an FT-IR instrument, equipped with an ATR sampling accessory. HRMS spectra were carried out at TOF MS (EI⁺) or FTMS (ESI). Melting point determination was taken on a Melt-Temp apparatus and was uncorrected. UV-vis spectra were obtained with a double-beam spectrophotometer at room temperature. PL spectra were recorded on HORIBA JY FluoroLog-3 or FLS980 at room temperature. Field-emission scanning electron microscopy (FESEM) images were acquired with a JSM-7610F electron microscope operating at 5 kV. Solvents for UV-vis and emission spectroscopic measurements were spectrographically pure as received. The ground and excited states were optimized using density functional theory and time-dependent density functional theory. The solution phase in tetrahydrofuran (THF) was modeled by the polarizable continuum model (PCM)² as implemented in Gaussian 09 package³. The aggregation state was modeled using a quantum mechanics and molecular mechanics (QM/MM) approach. The QM/MM calculations were carried out using the ChemShell 3.5 package⁴ integrating Turbomole 7.0^{5,6} (QM part) with DL-POLY⁷ (MM part) programs. The quantum calculations were carried out using B3LYP method with 6-31G* (for solution state) or def2-SV(P) (for solid state) basis sets. For the MM treatment, the general Amber force field (GAFF)⁸ was used. The model of

aggregation phase was set up on the basis of the X-ray crystal structure, which consists of one central molecule for the QM part and 71 surrounding molecules (5472 atoms) for the MM part. The reorganization energies were obtained by the MOMAP program⁹⁻¹¹. The molecular geometries were optimized at the B3LYP/6-31G(d) level of theory. Subsequently, we performed TD-DFT calculations to simulate the UV-vis spectra of these compounds at BMK/6-31G(d) level of theory. The primary π -electron delocalization channels were obtained by the Multiwfn¹² and VMD program¹³, as determined by the localized orbital locator (LOL)^{14,15}.

*Synthesis of COTh-4Br*¹⁶

COTh-(TMS)₄ (2.74 g, 4.44 mmol) was dissolved in 40 mL HOAc/CHCl₃ (v/v = 1:1), NBS (3.56 g, 20.00 mmol, 4.5 equiv) was added under good stirring at room temperature. The reaction process was monitored by TLC analysis. Four hours later, the reaction mixture was quenched with saturated NaHCO₃ aqueous. After being extracted with CHCl₃, the combined organic phase was washed with saturated NaHCO₃ aqueous and water orderly. Drying over anhydrous MgSO₄ was sequenced by solvent evaporation to give crude product. Pure **COTh-4Br** (2.60 g) was obtained by recrystallization from CHCl₃/CH₃OH in 90% yield. M.p. > 300 °C.

*Synthesis of COTh*¹⁶

To a solution of **COTh-(TMS)₄** (105.8 mg, 0.17 mmol) in CHCl₃ (5 mL), TFA (0.3 mL, 10 equiv) was added at room temperature with stirring. The reaction process was monitored by TLC analysis. After stirring at room temperature for 4 h, the reaction mixture was quenched with saturated NaHCO₃ and extracted with CHCl₃, then washed with saturated NaHCO₃ and water. The organic layer was dried over anhydrous MgSO₄. After removing the solvent in vacuo, the residue was purified by column chromatography with petrol ether (60–90 °C) as eluent to yield **COTh** (53.0 mg, 94 %) as a white solid.

Synthesis of COTh-3Br from COTh-4Br

n-BuLi (0.46 M in hexane, 0.46 mL, 0.21 mmol, 1.2 equiv) was added dropwise to a solution of **COTh-4Br** (113.0 mg, 0.18 mmol) in dry THF (250 mL) at -78 °C. The reaction process was monitored by TLC analysis. After stirring at -78 °C for 4 h, methanol was used to quench the reaction, and the reaction mixture was extracted with CHCl_3 . The resulting organic layer was washed with water and then dried over MgSO_4 . The solvent was removed in vacuo to give crude product. A white powder **COTh-3Br** (58.3 mg, 69%) was obtained by column chromatography with petrol ether (60 – 90 °C) as eluent. M.p.: 265 – 268 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.41 (d, $J = 5.2$ Hz, 1H), 6.93 (s, 1H), 6.91 (d, $J = 5.2$ Hz, 1H), 6.90 (s, 1H), 6.89 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 137.19, 136.29, 135.70, 135.69, 133.73, 132.67, 132.38, 132.12, 131.90, 131.44, 129.57, 128.13, 114.69, 114.62, 114.39; HRMS (MALDI/DHB) m/z calcd for $[\text{C}_{16}\text{H}_5\text{Br}_3\text{S}_4]$ 561.6824, found 561.6818. IR (KBr): 3106, 3083, 2922, 2852, 831, 733 (C–H) cm^{-1} .

Synthesis of COTh-3Br from COTh

n-BuLi (2.40 M in hexane, 0.48 mL, 1.16 mmol, 3.5 equiv) was added dropwise to a solution of **COTh** (108.9 mg, 0.33 mmol) in dry THF (100 mL) at -78 °C. After keeping at -78 °C for 4 h, then solution of $\text{C}_2\text{Br}_2\text{Cl}_4$ (0.54 g, 1.66 mmol, 3.5 equiv) in THF was added dropwise. The reaction was warmed slowly to ambient temperature overnight. The reaction mixture was quenched with water at room temperature, extracted with CHCl_3 . The organic layer was washed with water and then dried over MgSO_4 . The light yellow solid **2** (67.0 mg, 36%) was obtained by column chromatography with petrol ether (60 – 90 °C) as eluent. M.p. >300 °C.

Synthesis of COTh-3TMS from COTh

To a solution of **COTh** (401.8 mg, 1.22 mmol) in dry THF (100 mL), *n*-BuLi (2.28 M in hexane, 2.04 mL, 4.65 mmol, 3.5 equiv) was added dropwise at -78 °C. After keeping at -78 °C for 4 h, the reaction mixture was quenched with trimethylchlorosilane (0.62 mL, 4.89 mmol, 4.0 equiv), then warmed slowly to ambient temperature and stirred overnight. The resulted mixture was quenched with water and extracted with CHCl_3 . The

organic layer was washed with water and then dried over MgSO₄. The light yellow solid **COTh-3TMS** (360.0 mg, 54%) was obtained by column chromatography with petrol ether (60–90 °C) as eluent. M.p.: 115–116 °C.

Synthesis of COTh-B3TMS

To the solution of **COTh-3TMS** (483.4 mg, 0.89 mmol) in dry ether (35 mL), *n*-BuLi (2.33 M, 0.46 mL, 1.2 equiv) was added dropwise at 0 °C. After stirring for 2 h, the solution of bis(pinacolato)diboron (292.8 mg, 1.3 equiv) in dry Et₂O (5 mL) was added to the reaction mixture at –78 °C. Then warmed slowly and stirred overnight. Quenching with water was sequenced by extraction with ether (3×10 mL), then washed with water (3×50 mL). After being dried over dried over MgSO₄, the solvent was removed to give crude product. **COTh-B3TMS** (510.0 mg) with white solid was obtained by column chromatography with petrol ether (60–90 °C) as eluent in 86% yield. M.p. > 300 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.48 (s, 1H), 7.08 (s, 1H), 7.07(s, 1H), 7.05 (s, 1H), 1.34 (s, 6H), 1.32 (s, 6H), 0.32 (s, 9H), 0.31 (s, 9H), 0.30 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): 142.85, 142.44, 142.42, 139.75, 139.61, 137.76, 137.70, 137.46, 137.41, 137.31, 137.05, 136.96, 136.92, 136.74, 136.66, 84.22, 24.85, 24.56, –0.18, –0.20, –0.21. HRMS (TOF MS ES⁺) *m/z* calcd for [C₃₁H₄₃BO₂S₈Si₃] 670.1547, found [M+1]⁺ 671.1629. IR(KBr): 3053, 2977, 2956, 2897 (C–H) cm^{–1}.

Synthesis of 2COTh

n-BuLi (2.53 M in hexane, 0.14 mL, 0.36 mmol, 1.2 equiv) was added dropwise to a solution of **COTh-3TMS** (162.6 mg, 0.30 mmol) in dry THF (25 mL) at –78 °C. After keeping at –78 °C for 2 h, dry CuCl₂ (80.2 mg, 0.60 mmol, 2.0 equiv) was added quickly. The reaction mixture was kept at –78 °C for 2 h, then warmed up slowly to ambient temperature. The reaction mixture was quenched with water, and extracted with CHCl₃. The organic layer was washed with water and then dried over MgSO₄. The solvent was removed by rotary evaporation to give crude product. A light yellow solid **2COTh** (72.0 mg, 44.4%) was obtained by column chromatography on silica gel with petrol ether

(60–90 °C) as eluent. M.p. > 300 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.08 (s, 2H), 7.07 (s, 2H), 7.06 (s, 2H), 7.02 (s, 2H), 0.36–0.30 (m, 54H). ¹³C NMR (75 MHz, CDCl₃): 142.99, 142.92, 142.86, 138.31, 138.27, 137.88, 137.70, 137.42, 137.22, 137.11, 137.07, 137.04, 136.97, 136.9, 136.90, 136.82, 126.97, 0.97, 0.05. HRMS (DART Postive) *m/z* calcd for [C₅₀H₆₂S₈Si₆] 1086.1233, found 1087.1288. IR(KBr): 2957, 2925, 2898, 2853 (C–H) cm⁻¹.

Synthesis of 4COTH via Negishi coupling

n-BuLi (2.28 M in hexane, 0.33 mL, 0.75 mmol, 1.02 equiv) was slowly added to a solution of **COTH-3TMS** (0.40 g, 0.73 mmol, 1.0 equiv) in dry THF (20 mL) in a Schlenk vessel at –78 °C. 2 h later, the resulted pale yellow mixture was treated with ZnCl₂ (0.151 g, 1.10 mmol, 1.5 equiv), and stirred for 30 min. Then warmed to room temperature and kept for 2 h. **COTH-3Br** (103.8 mg, 0.18 mmol, 0.25 equiv) and Pd(PPh₃)₄ (51.0 mg, 0.04 mmol, 0.06 equiv) were added to the reaction mixture under argon. The reaction mixture was refluxed for 3 days at 110 °C. After being quenched with water, the reaction mixture was extracted with CHCl₃ and dried over MgSO₄. The solvent was removed in vacuo to provide crude product. It was purified by silica chromatography with petrol ether (60–90 °C) as eluent to give **4COTH** (180.0 mg, 50%) as a yellow solid. M.p. > 300 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.42 (d, *J* = 4.0 Hz, 1H), 7.08–6.97 (m, broad peaks, 16H), 0.35–0.32 (m, 81H); ¹³C NMR (100 MHz, CDCl₃): δ 143.23, 143.20, 143.19, 143.14, 143.12, 143.11, 143.04, 138.68, 138.65, 138.63, 138.59, 138.55, 138.49, 137.83, 137.75, 137.71, 137.67, 137.66, 137.52, 137.45, 137.43, 137.37, 137.25, 137.17, 137.16, 137.12, 137.05, 136.98, 136.93, 136.71, 136.67, 136.63, 136.59, 132.45, 132.31, 132.28, 132.22, 132.11, 132.09, 132.05, 131.81, 131.60, 131.55, 131.33, 131.28, 131.08, 130.87, 130.42, 130.37, 127.96, 127.75, 127.24, 127.20, 127.11, 127.06, 127.01, 126.81, 126.77, 126.68, 126.62, 126.59, 0.17; HRMS (MALDI/DHB) *m/z* calcd for [C₉₁H₉₈S₁₆Si₉] 1954.1123, found 1954.1121. IR(KBr): 3058, 2955, 2897, 2853(C–H) cm⁻¹.

Synthesis of 4COTh via Suzuki coupling

COTh-3Br (42.4 mg, 0.08 mmol 1.0 equiv), **COTh-B3TMS** (226.5 mg, 0.34 mmol, 4.5 equiv), K_2CO_3 (77.6 mg, 0.56 mmol, 7.5 equiv) and $Pd(PPh_3)_4$ (21.7 mg, 18.76 μ mol, 0.25 equiv) were mixed with 15 mL THF and 2 mL water under argon. The mixture was stirred at 80 °C for 15 h. After being quenched with water, the reaction mixture was extracted with $CHCl_3$, and dried over anhydrous $MgSO_4$. After the solvent was removed in vacuo, the residue was purified by column chromatography on silica gel with petroleum ether (60–90 °C) as eluent to yield **4COTh** (54.0 mg, 37%) as a yellow solid. M.p. > 300 °C.

Synthesis of 5COTh¹⁶

n-BuLi (2.50 M in hexane, 0.17 mL, 0.43 mmol, 1.02 equiv) was slowly added to a solution of **COTh-B3TMS** (240.0 mg, 0.44 mmol, 1.0 equiv) in dry THF (20 mL) at –78 °C. After stirring for 2 h, the pale yellow reaction mixture was treated with $ZnCl_2$ (90.0 mg, 0.66 mmol, 1.5 equiv), kept stirring at for 30 min, then warmed to room temperature and kept for 2 h. **COTh-4Br** (56.7 mg, 0.09 mmol, 0.2 equiv) and $Pd(PPh_3)_4$ (30.5 mg, 0.03 mmol, 0.06 equiv) were added to the reaction mixture under argon. Finally, The reaction mixture was refluxed for 2 days at 110 °C. After quenching with water, the reaction mixture was extracted with $CHCl_3$ and dried over $MgSO_4$. The product was purified by silica chromatography with petrol ether (60–90 °C) as eluent. **5COTh** (47.0 mg, 21.0%) was obtained as a yellow solid. M.p. > 300 °C.

Synthesis of 8COTh

n-BuLi (0.36 M in hexane, 0.22 mL, 0.08 mmol, 2.0 equiv) was added dropwise to a solution of **4COTh** (78.3 mg, 0.04 mmol) in dry THF (20 mL) at –78 °C. 2 h later, dry $CuCl_2$ (0.0161 g, 0.12 mmol, 3.0 equiv) was added quickly. The reaction mixture was stirred at –78 °C for 2 h, –55 °C for 2 h, and then warmed slowly to ambient temperature. The reaction mixture was quenched with water, extracted with $CHCl_3$. The organic layer was washed with water and then dried over $MgSO_4$. The yellow solid

8COTh (21.0 mg, 27%) was obtained by column chromatography on silica gel with petrol ether (60–90 °C) as eluent. M.p. > 300 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.22 (s, broad, 2H) 7.13–6.99 (m, broad, 30H), 0.39–0.26 (m, 162H); ^{13}C NMR (100 MHz, CDCl_3): δ 143.11, 143.06, 143.00, 142.98, 142.94, 142.90, 138.79, 138.43, 138.35, 138.31, 137.70, 137.62, 137.52, 137.48, 137.46, 137.40, 137.38, 137.31, 137.30, 137.28, 137.26, 137.25, 137.21, 137.18, 137.14, 137.06, 137.03, 136.98, 136.93, 136.84, 136.82, 134.98, 134.96, 132.25, 132.08, 132.05, 132.03, 127.29, 127.26, 127.22, 127.20, 127.18, 127.12, 127.10, 127.09, 127.06, 126.99, 126.69, 126.66, 126.58, 126.54, 126.51, 126.50, 126.49, 0.04. HRMS (MALDI(P)) m/z calcd for $[\text{C}_{182}\text{H}_{194}\text{S}_{32}\text{Si}_{18}]$ 3912.2085, found 3912.2082. IR (KBr): 2956, 2924, 2854 (C–H) cm^{-1} .

2. NMR and HRMS spectra

NMR and HRMS spectra of COTh-3Br

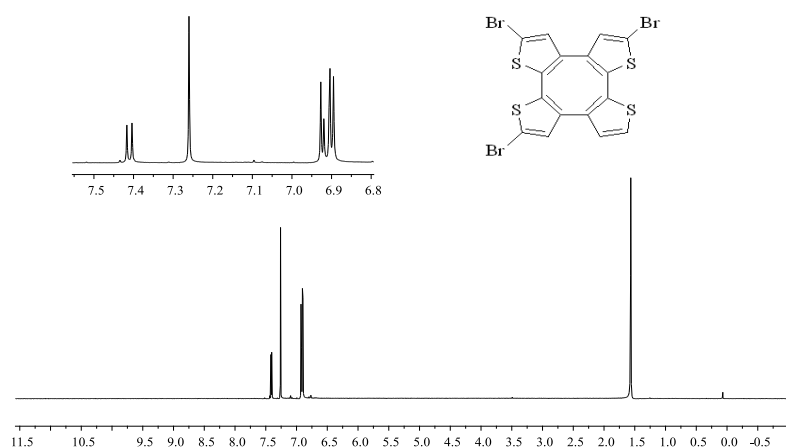


Figure S1. ^1H NMR (400 MHz, CDCl_3) spectra of COTh-3Br

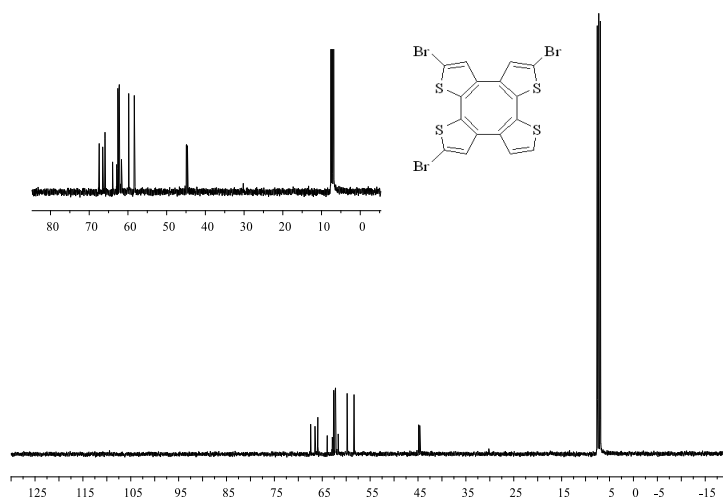


Figure S2. ^{13}C NMR (100 MHz, CDCl_3) spectra of COTh-3Br

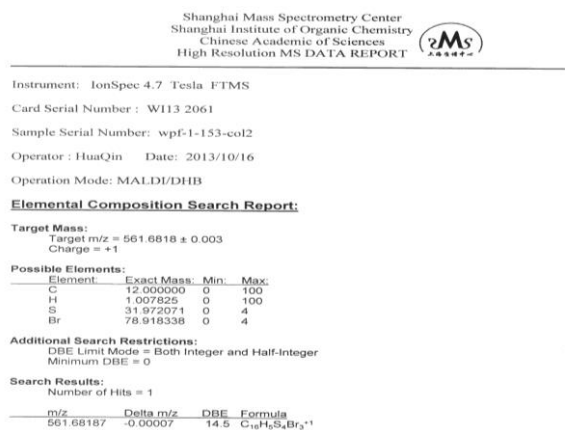


Figure S3. HRMS data of COTh-3Br

NMR and HRMS spectra of COTh-B3TMS

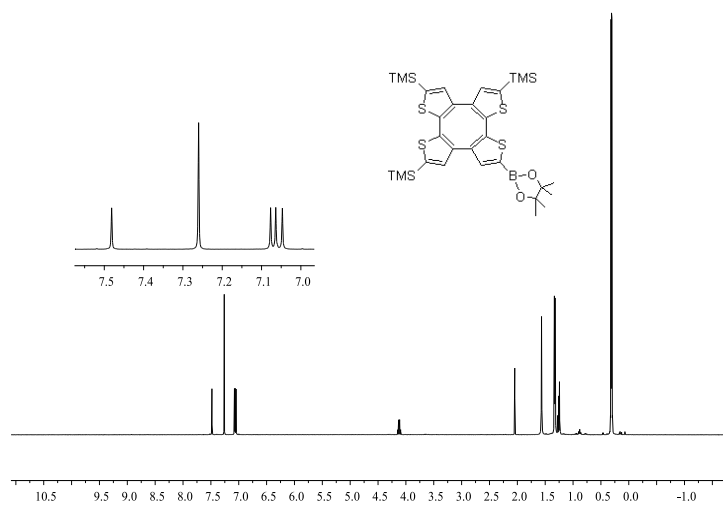


Figure S4. ^1H NMR (400 MHz, CDCl_3) spectra of COTh-B3TMS

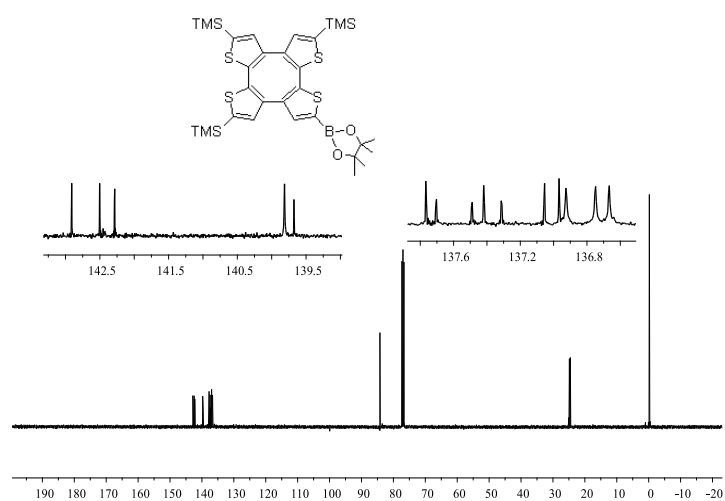


Figure S5. ^{13}C NMR (100 MHz, CDCl_3) spectra of **COTh-B3TMS**



Figure S6. HRMS spectrum of **COTh-B3TMS**

NMR and HRMS spectra of **2COTh**

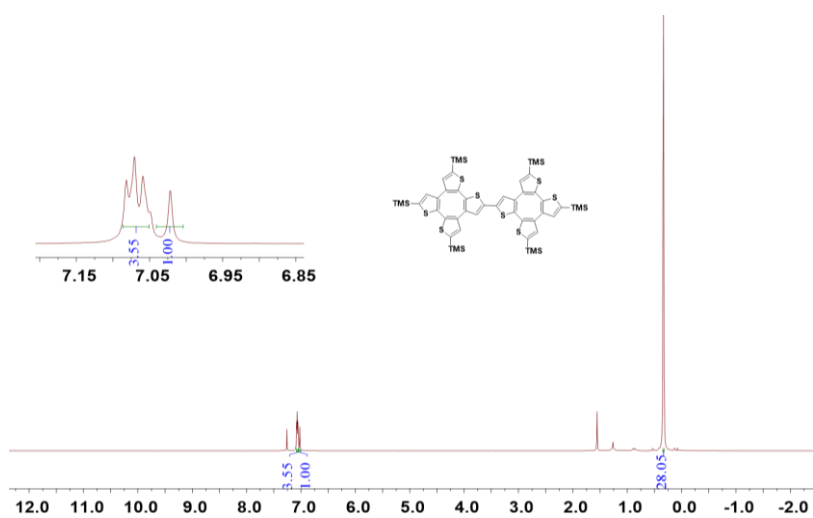


Figure S7. ^1H NMR (400 MHz, CDCl_3) spectra of **2COTh**

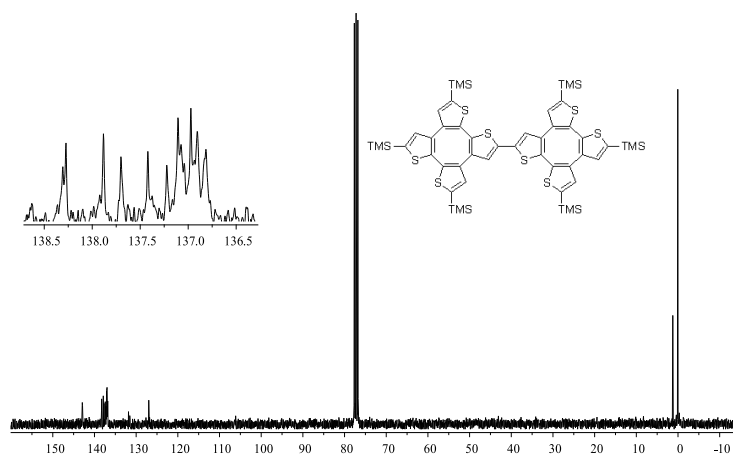


Figure S8. ^{13}C NMR (75 MHz, CDCl_3) spectra of **2COTh**

National Center for Organic Mass Spectrometry in Shanghai
 Shanghai Institute of Organic Chemistry
 Chinese Academic of Sciences
 High Resolution MS DATA REPORT



Instrument: Thermo Fisher Scientific LTQ FT Ultra

Card Serial Number : M151233

Sample Serial Number: WPF-3-197-COL2

Operator : HUAQIN Date: 2015/04/22

Operation Mode: DART Postive

Elemental composition search on mass 1087.13

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1087.1288	1087.1285	0.26	55.5	$\text{C}_{70}\text{H}_{32}\text{S}_4\text{Si}_4$
	1087.1272	1.52	30.5	$\text{C}_{52}\text{H}_{56}\text{S}_7\text{Si}_6$
	1087.1306	-1.58	25.5	$\text{C}_{50}\text{H}_{56}\text{S}_6\text{Si}_6$
	1087.1319	-2.84	50.5	$\text{C}_{47}\text{H}_{44}\text{S}_4\text{Si}_4$
	1087.1238	4.62	35.5	$\text{C}_{56}\text{H}_{58}\text{S}_6\text{Si}_6$

Figure S9. HRMS data of **2COTh**

NMR and HRMS spectra of **4COTh**

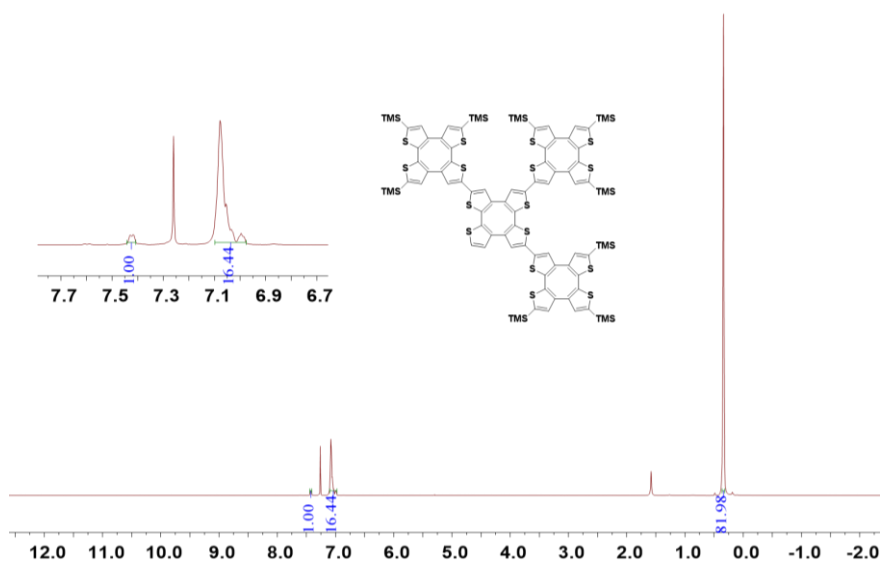


Figure S10. ^1H NMR (400 MHz, CDCl_3) spectra of **4COTh**

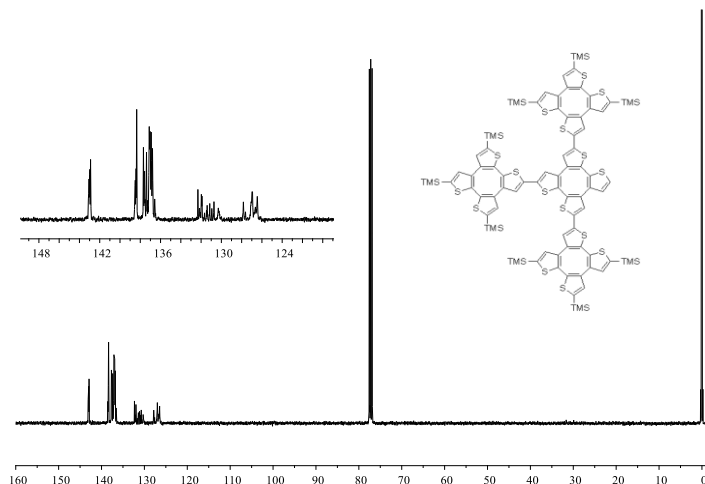


Figure S11. ^{13}C NMR (100 MHz, CDCl_3) spectra of **4COTh**

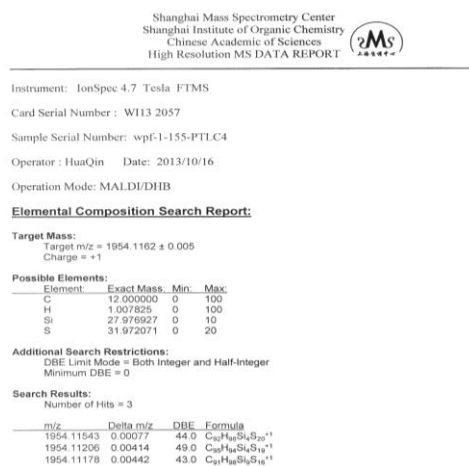


Figure S12. HRMS data of **4COTh**

NMR and HRMS spectra of **8COTh**

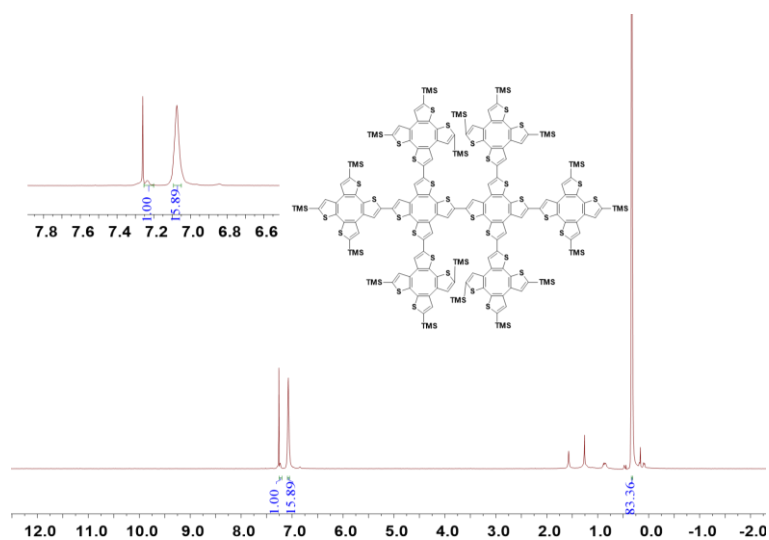


Figure S13. ^1H NMR (400 MHz, CDCl_3) spectra of **8COTh**

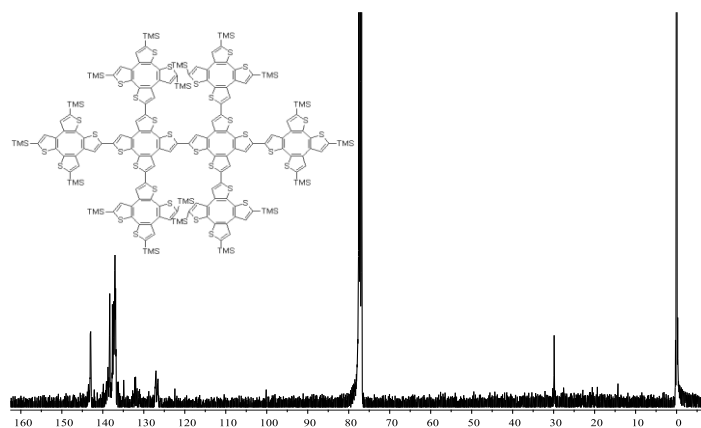


Figure S14. ^{13}C NMR (100 MHz, CDCl_3) spectrum of **8COTh** MALDI(P),20141117

Analysis Info		Acquisition Date	
Analysis Name	D:\Data\MALDI\2014\1117\wpf-3-11_0_01_000005.d	11/17/2014 2:35:37 PM	
Method	MALDI_P_100-3000	Operator	
Sample Name		Instrument	solarix
Comment			

Acquisition Parameter			
Acquisition Mode	Single MS	Acquired Scans	10
Polarity	Positive	No. of Cell Fills	1
Broadband Low Mass	202.1 m/z	No. of Laser Shots	25
Broadband High Mass	8000.0 m/z	Laser Power	20.2 lp
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec
Ion Accumulation Time	0.300 sec		
		Calibration Date	Thu Jun 26 09:51:13 2014
		Data Acquisition Size	1048576
		Data Processing Size	2097152
		Apodization	Sine-Bell Multiplication

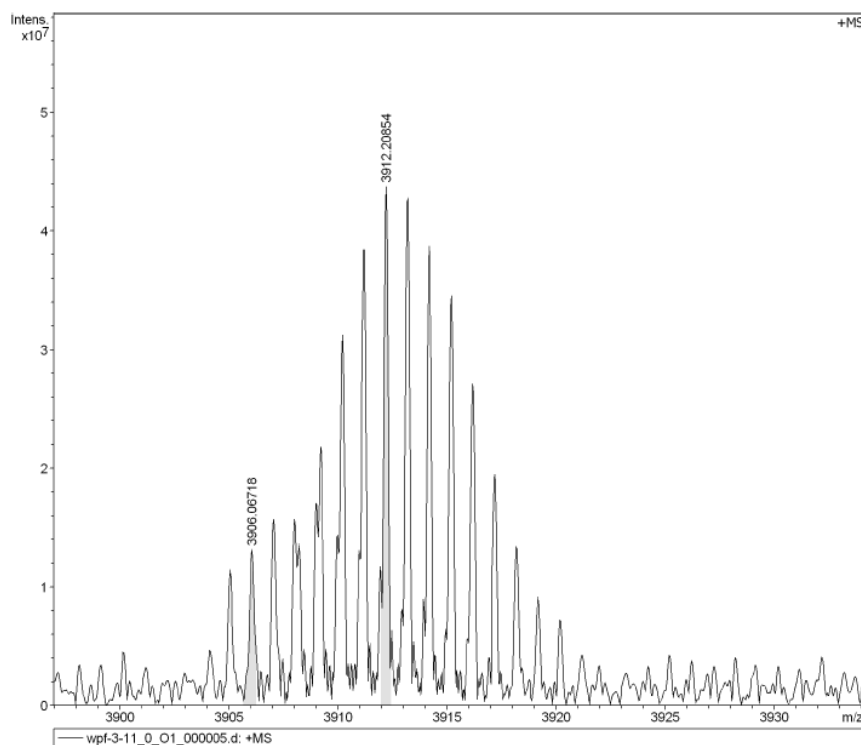


Figure S15. HRMS spectrum of **8COTh**

3. Theoretical calculation

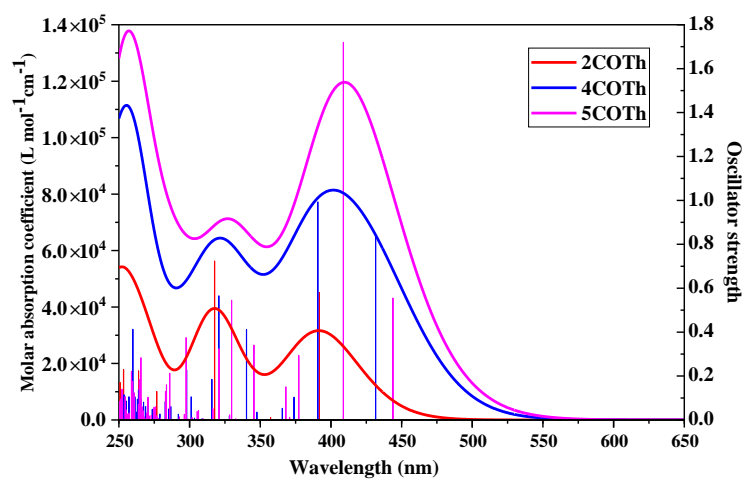
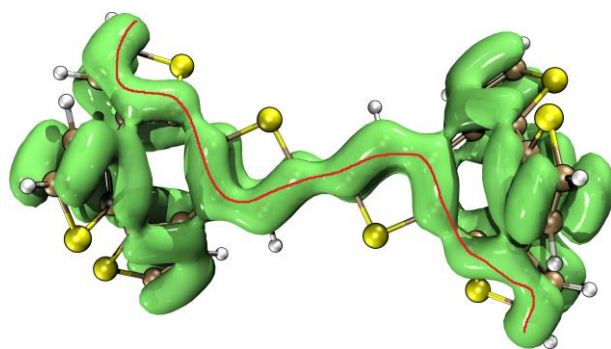
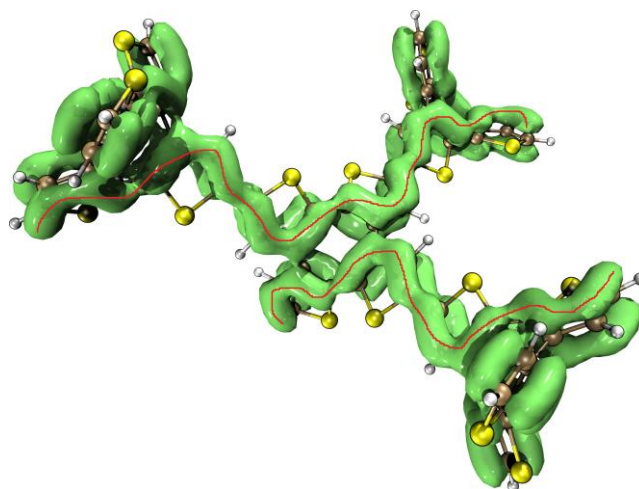


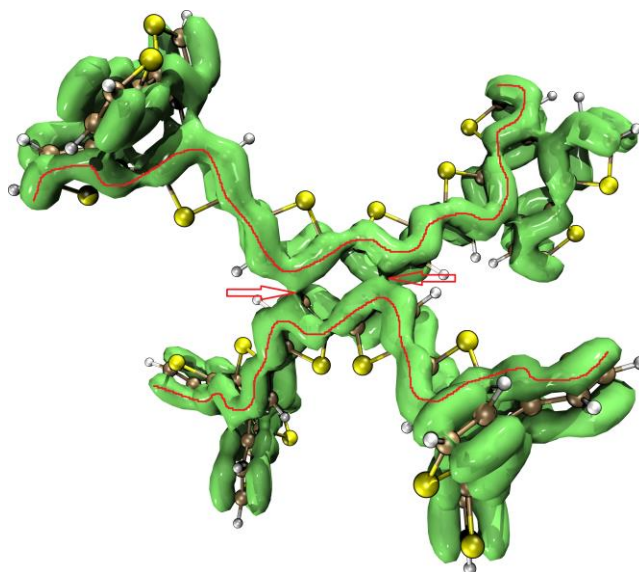
Figure S16. Simulated UV-Vis absorption spectra (curve) and oscillator strength (spikes) of the 2COTh, 4COTh and 5COTh.



2COTh



4COTh



5COTh

Figure S17. Isosurfaces maps of LOL- π of **2COTh**, **4COTh** and **5COTh**. The isovalues are set to 0.28 au.

4. Fluorescence spectra of **2COTh**, **4COTh**, **5COTh** and **8COTh**

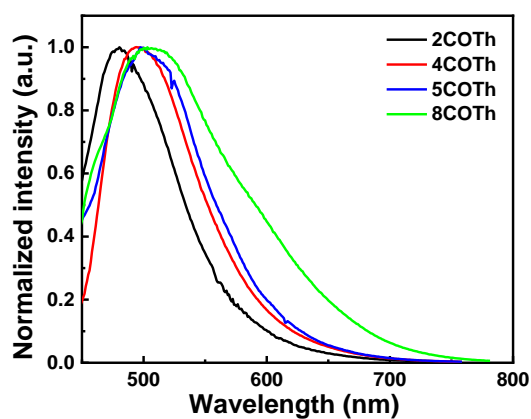


Figure S18. Fluorescence spectra of **2COTh**, **4COTh**, **5COTh** and **8COTh** in rigid state (77 K) in 2-MTHF ($\lambda_{\text{ex}} = 410$ nm, $[C] = 1\text{E-}5$ M).

5. References

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