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Synthesis, Crystal Structure and Electrochemical Property of 3a,4,5,8,9,9a,10,11-Octahydro-2*H*,3*H*-1,6,7,12-tetrathiaperylene (H_{10}TTPR)

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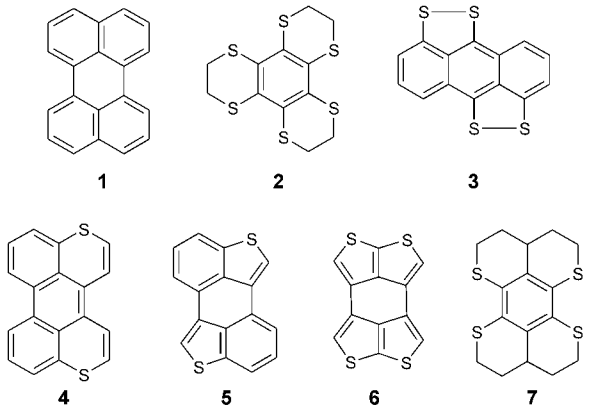
H_{10}TTPR was prepared starting from terephthalaldehyde and characterized. Crystal structure of H_{10}TTPR and an intermediate compound **11** were determined by X-ray diffraction analysis. A quasi-reversible redox wave at 1.15 V (vs. SCE) was observed for H_{10}TTPR, indicating that it is a weak electron donor.

Keywords synthesis, crystal structure, electron donor, oxidation potential

Introduction

Most of the charge-transfer (CT) complexes with high electrical conductivity are formed from the donor molecules based on tetrathiafulvalene (TTF) skeleton.[1] One way to develop the chemistry and physics in this area is to explore a new class of donors which do not contain such dichalcogenole rings so as to extend the range of molecular conductors.[2,3] It was found that the CT complex of perylene iodine showed high conductivity,[4] and since then many chemical modification of perylene (**1**) and its arene analogues were made. These included introducing sulfur atoms into the periphery of simple arenes such as compound **2**,[5] syntheses of dichalcogenole-bridged acenaphthylenes such as compound **3** and its close analogues,[6] replacing sp^2 carbon atoms or carbon-carbon bonds by polarizable elements containing a lone pair of electrons such as compounds **4**—**6** and their close analogues.[3,7] Our molecular design strategy for a new organic electron donor is the replacement of the four sp^2 carbon atoms linked to the central benzene ring in perylene by four sulfur atoms (TTPR). This might produce a novel electron donor with good electron donating ability and improve the intrastack interaction through the intermolecular S···S contacts. We now report the synthesis of 3a,4,5,8,9,9a,10,11-octahydro-2*H*,3*H*-1,6,7,12-tetrathia-perylene (H_{10}TTPR) (**7**), the key precursor of the 1,6,7,12-tetrathia-perylene (TTPR). Apart from the synthesis, the redox potential and crystal structure of **7** are also reported.



Results and discussion

Synthesis of H_{10}TTPR

In our retrosynthetic analysis, which is shown in Scheme 1, it was envisioned that the desired heterocyclic compound **7** could be synthesized from compound **13** by intramolecular Friedel-Crafts reaction.[8] Compound **13** could be obtained from the tetrabromide **12**,[9] which could be prepared from **10** in two steps.

Two synthetic approaches to **10** were designed and investigated. The first one started with terephthalaldehyde, which reacted with ethyl bromoacetate in pres-

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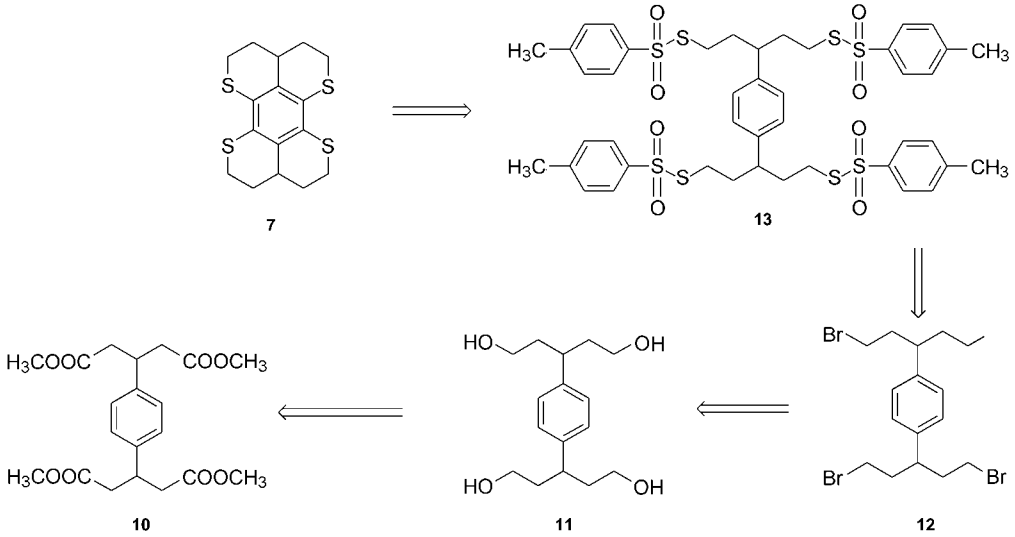
ence of zinc powder in THF (the Reformatsky reaction condition), followed by bromination, substitution, decarboxylation to give compound **10**. But the yield of this approach was very low (totally under 5%). In the second approach, as shown in Scheme 2, terephthalaldehyde was also used as starting material, which reacted with cyanoacetic acid in pyridine to afford compound **8**. It was reported[10] that benzaldehyde and only a few of its analogues reacted with 3 equiv. of cyanoacetic acid in pyridine to give 3-aryl-1,5-pentanedinitrile. Whereas in our synthesis the reaction was completed only when 10 equiv. of cyanoacetic acid was used to afford the desired product **8** in 69% yield. Compounds **9** and **10** were prepared with common procedures in yields of 96% and 95%, respectively.

The reduction of compound **10** was carried out with $LiAlH_4$ in THF, but the yield was moderate (60%), which was mainly attributed to the poor solubility of it in THF. When the reduction reaction was carried out in 1,4-dioxane, the yield was slightly improved (about 65%). The bromination of compound **11** was tried in several ways, such as using PBr_3, PPh_3/CBr_4, or first conversion to *p*-toluenesulfonate ester followed by the treatment with NaBr, but all failed. It was maybe owing to the formation of intermolecular hydrogen bonds in aprotic solvents, which may reduce the reactivity of hydroxyl groups. Hydrogen bonds can be seen clearly in the X-ray crystal structure of compound **11** as discussed below. Finally, conversion of compound **11** to compound **12** was achieved by treating with HBr (48% in water) and concentrated H_2SO_4 according to a traditional method.[11] The synthesis of compound **7** was performed according to Kloosterziel's method,[8] whereas we used *p*-toluenethiolsulfonate instead of methanethiolsulfonate. Because compound **13** was not dissolved well in nitromethane, the $CHCl_3$ solution of it was added dropwise into the solution of $AlCl_3$ in nitromethane. The optimized reaction could be realized at the temperature of 40—45 ℃ with a yield of 20%. The structure of compound **7** was characterized by ^{1}H NMR, IR, mass spectra as well as X-ray crystallographic analysis.

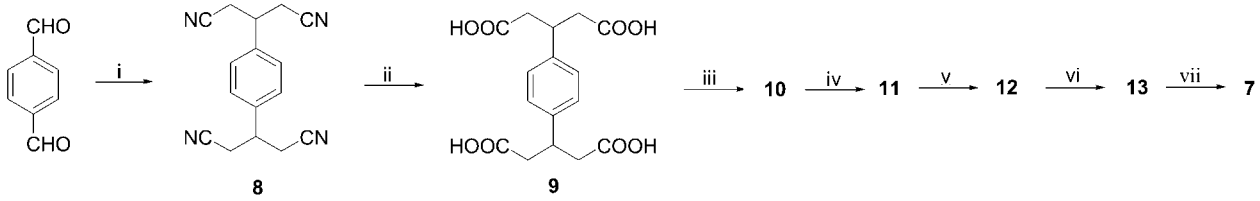
Electrochemical property

The redox potential of **7** was determined by cyclic voltammetry. The measurement was carried out in dichloromethane at room temperature with tetrabutylammonium hexafluorophosphate as supporting electrolyte. Its redox potential was listed in Table 1 together with those of compounds **1, 2, 4, 6** for comparison. H_{10}TTPR exhibited one quasi-reversible redox wave. Compared to

Scheme 1



Scheme 2



i) piperidine, cyanoacetic acid, pyridine, refluxed; ii) KOH (10 mol•L^{-1}), refluxed for 10 h, then acidified with 3 mol•L^{-1} HCl; iii) *p*-toluenesulfonic acid monohydrate, MeOH, refluxed for 12 h; iv) $LiAlH_4$ (6 equiv.), THF, r.t.; v) H_2SO_4 (conc.), HBr (48% in water), stirred at 0 ℃, then refluxed for 12 h; vi) *p*-toluenethiosulfonic acid potassium salt (6 equiv.), DMF, stirred at 40—45 ℃ for 24 h; vii) $AlCl_3$, $CHCl_3/CH_3NO_2$, stirred at 40—45 ℃ for 8 h.

those of compounds **1** and **6**, the redox potential of **7** was shifted anodically about 0.1 V, but it was similar to that of compound **2**. It indicates that compound **7** possesses weak electron donating ability compared with perylene.

Table 1 Redox potentials of compounds **1**, **2**, **4** and **6**, **7**[a]

Compound	**1**	**2**[b]	**4**[c]	**6**[d]	**7**
$E_1^{1/2}$/V	1.00	1.14	0.42	1.01	1.15
$E_2^{1/2}$/V			0.76		

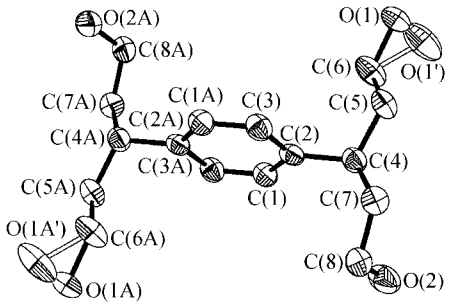
[a] V vs. SCE. [b] see Ref. 5. [c] see Ref. 7a. [d] see Ref. 7d.

Cation radicals of **7** can be generated by dissolving it in concentrated sulfuric acid at room temperature, resulting in a dark blue solution (λ_{max}=320, 600 nm). The color of the cation radical solution does not change at least several weeks at room temperature.

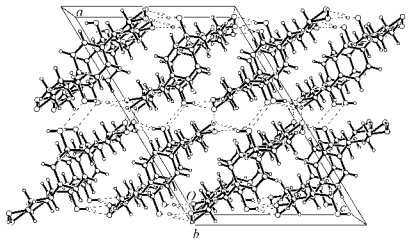
Crystal structures of 11 and 7

The crystallographic data of **7** and **11** are summarized in Table 2.

Figure 1 shows the molecular structure of compound **11** together with stacking pattern in the lattice viewed along axes *a* and *b*. The molecule has a symmetric center (Figure 1a). The oxygen atoms of two hydroxyl groups were disordered in two positions O(1) and O(1') with occupancies of 60% and 40% respectively. The selected bond lengths were summarized in Table 3. It can be seen that these molecules are packed into layer-structure along *bc* plane (Figure 1b). Intra-layer short contacts (O(1)···O(2)^i =0.2693(4) nm, O(1')···O(2)^i =0.2591(7) nm, O(1)···H(2A)^i =0.1882 nm, O(1')···H(2A)^i=0.1799 nm; *i*: *x*, 1−*y*, 0.5+*z*) and



(a)



(b)

Figure 1 (a) Molecular structure of compound **11** with 50% probability ellipsoids. (b) Packing arrangement of **11** viewed along *b*-axis.

Table 2 Crystallographic data for compounds **7** and **11**

Compound	**7**	**11**
Empirical formula	$C_{16}H_{18}S_4$	$C_{16}H_{26}O_4$
Formula weight	338.54	282.37
Temperature	293(2) K	293(2) K
Crystal system	orthorhombic	monoclinic
space group	*Pbca*	*C2/c*
Unit cell dimensions	a=0.9620 (1) nm	a=1.9258 (2) nm, α=90°
	b=0.9675 (1) nm	b=0.7438 (7) nm, β=121(4)°
	c=1.6399 (1) nm	c=1.3125 (1) nm, γ=90°
Volume	1.5264 (2) nm^3	1.6106 (3) nm^3
Z, Calculated density	4, 1.473 Mg/m^3	4, 1.165 Mg/m^3
F(000)	712	616
Crystal size	0.42 mm×0.32 mm×0.30 mm	0.58 mm×0.45 mm×0.43 mm
θ range	2.48° to 27.48°	3.00° to 27.30°
Limiting indices	−12≤h≤12, −12≤k≤12, −21≤l≤21	−24≤h≤24, −9≤k≤9, −16≤l≤16
Reflections, collected /unique	3199/1739 [R(int)=0.0219]	3191/1794 [R(int)=0.0191]
Goodness-of-fit on F^2	0.906	0.992
R, *wR*	0.0596, 0.1668	0.0534, 0.1572
Residual/(×10^3 e•nm^{-3})	0.413 and −0.305	0.208 and −0.155

inter-layer short contacts (O(1)···O(1)^{ii} =0.2730(7) nm, O(1)···O(1')^{ii} =0.2524(5) nm, O(1')···O(1')^{ii} =0.2623 nm, O(2)···O(2)^{iii} =0.2697 nm, O(1)···H(1A)^{ii}=0.1963 nm, O(1')···H(1A)^{i} =0.1708 nm; *ii*: 1−*x*, 2−*y*, 1−*z*; *iii*: 1−*x*, *y*, 0.5−*z*) clearly indicate the formation of hydrogen bonds.

Compound **7** is centrosymmtric with a peri-chair conformation as shown in Figure 2. The selected bond lengths of compound **7** are summarized in Table 4 and they are in normal range. Four sulfur atoms are coplanar with the center benzene ring. The six member rings C(1)-C(2)-S(1)-C(3)-C(5)-C(6) and C(7)-C(8)-S(2)-C(4)-C(5)-C(6) folded along the vector C(2)-C(6) and C(6)-C(8) with 50.7(4)° and 50.3(4)°, respectively. The molecule has two kinds of orientations in the lattice with a dihedral angle of 61.8° between the center aromatic planes. No short interaction could be observed in the lattice.

Conclusion

H_{10}TTPR was prepared in seven-step and characterized. It was a weak electron donor compared to compounds **1** and **6**. As we could expect the dehydrogenation product of H_{10}TTPR should lead to a novel electron donor and the further investigation on the dehydrogenation of compound **7** is in progress.

Experimental

General

Melting points were measured with a Büchi Melting Point B-500 microscope apparatus and uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker advance-300 spectrometer. Infrared spectra were re corded on a Perkin-Elmer System 2000 FT-IR spectrometer. Mass spectra were determined with an AEI-MS50 for EI-MS, a Beflex III for MALDI-TOF-MS; a Bruker Daltonics APEX II for FT-ICTMS, a GCT-MS micromass UK for HR-EI.Elemental analyses were performed on a Carlo-Erba-1106 instrument for C, H and barium titration for S. Cyclic voltammetric measurement was conducted on an EGDG PAR 370 System (0.1 mmol/L in CH_2Cl_2, Bu_4NPF_6 as supporting electrolyte, Pt electrode as working electrode, scan rate 100 mV/s, reported voltage vs. SCE).

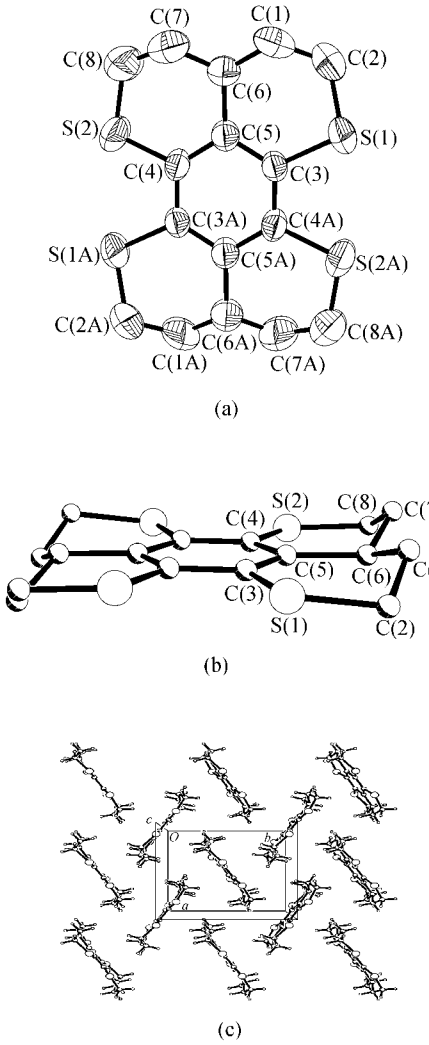


Figure 2 (a) Molecular structure of compound **7** with 50% probability ellipsoids. (b) Molecular structure of compound **7**. (c) Packing arrangement of **7** viewed along *c*-axis.

Table 3 Selected bond lengths (nm) of compound **11**

O(1)—C(6)	0.1430(4)	O(1')—C(6)	0.1501(7)	C(2)—C(3)	0.1383(2)
C(1—C(3)	0.1382(3)	C(1)—C(2)	0.1382(2)	C(4)—C(5)	0.1520(2)
C(2)—C(4)	0.1517(2)	C(5)—C(6)	0.1483(3)	C(7)—C(8)	0.1493(3)
C(4)—C(7)	0.1531(3)	O(2)—C(8)	0.1413(2)		

Table 4 Selected bond lengths (nm) of compound **7**

S(1)—C(3)	0.1766(3)	C(7)—C(8)	0.1455(7)	S(1)—C(2)	0.1772(5)
S(2)—C(4)	0.1758(3)	C(1)—C(2)	0.1441(7)	C(3)—C(4)	0.1407(5)
C(4)—C(5)	0.1402(5)	C(3)—C(5)	0.1397(5)	C(5)—C(6)	0.1534(5)
C(6)—C(7)	0.1449(6)	C(6)—C(1)	0.1486(7)	S(2)—C(8)	0.1743(5)

X-ray crystallography

The single crystals of **7** and **11** suitable for X-ray structural analyses were obtained by evaporating the solvent from chloroform and acetone respectively. Intensity data were collected on a Rigaku R-AXIS Rapid IP diffractometer with graphite monochromated Mo Kα radiation (λ=0.071073 nm). By using SHLEXL-97 programs,[12] the structure were solved by direct method and refined by full matrix least-squares method.

3-[4-(2-Cyano-1-cyanomethylethyl)phenyl]pentane-1,5-dinitrile (8): Piperidine (8 mL) was added to a stirred solution of cyanoacetic acid (37 g, 0.46 mol) in pyridine (60 mL). The solution was refluxed for 0.5 h, and then a solution of terephthalaldehyde (5.5 g, 0.042 mol) in pyridine (60 mL) was added dropwise. After addition, the solution was refluxed until there was no gas released. The mixture was cooled to room temperature after being concentrated to 40 mL under reduced pressure, leading to a pale yellow precipitate. The precipitate was collected with suction, washed with acetone, dried *in vacuo* to give **8** (7.8 g, 69%). m.p. 167.5—170.1 ℃(recrystallized from acetone); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.87 (d, J=6.9 Hz, 8H), 3.44—3.46 (m, 2H), 7.36 (s, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 138.6, 127.9, 116.6, 38.2, 23.4; IR (KBr) v: 2959, 2251, 1629, 1429, 1350 cm^{-1}; MS (70 eV) m/z (%): 262 (M^+, 12.8), 222 (100), 181 (71.1). Anal. calcd for $C_{16}H_{14}N_4$: C 73.28, H 5.34, N 21.38; found C 73.16, H 5.38, N 21.25.

3-[4-(2-Carboxy-1-carboxymethylethyl)phenyl]-pentane-1,5-dioic acid (9): Compound **8** (10 g, 0.038 mol) was added to a solution of KOH (30 g) in water (80 mL). The suspension was refluxed for about 10 h, and then poured into 200 mL of ice water. The solution was acidified with 3 mol•L^{-1} hydrochloric acid to pH=1, leading to a white precipitate which was collected with suction, washed with water, dried *in vacuo* to give **9** (7.8 g, 96%). m.p. 261.2—262.5 ℃ (recrystallized from acetone); ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 2.87 (d, J=6.9 Hz, 8H), 3.38—3.46 (m, 2H), 7.16 (s, 4H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 173.2, 141.8, 127.6, 40.4, 37.7; IR (KBr) v: 1716, 3101 (broad), 1403, 1252 cm^{-1}; MS (70 eV) m/z: 262 (M^+, 12.8), 216 (93.8) 130 (100). Anal. calcd for $C_{16}H_{18}O_8$: C 56.81, H 5.25; found C 56.79, H 5.31.

3-[4-(2-Methoxycarbonyl-1-methoxycarbonylmethylethyl)phenyl]pentane-1,5-dioic acid dimethyl ester (10): A 500 mL bottle flask was charged with compound **9** (10 g, 25.4 mmol), methanol (350 mL) and a catalytic amount of *p*-toluenesulfonic acid monohydrate. After beibg refluxed for about 12 h, the mixture was cooled to room temperature to form white needle crystals, which were collected with suction, washed with methanol, dried *in vacuo* to give **10** (11.2 g, 95%). m.p. 132—133 ℃ (recrystallized from $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.60—2.77 (m, 8H), 3.60 (s, 12H), 3.58—3.68 (m, 2H), 7.16 (s, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 171.8, 140.9, 127.1, 51.4, 40.0, 37.6; IR (KBr) v: 1740, 2955,1438, 1266, 1226, 1158 cm^{-1}; MS (70 eV) m/z: 394 (M^+, 25). Anal. calcd for $C_{20}H_{26}O_8$: C 60.91, H 6.60; found C 61.15, H 6.70.

3-{4-[3-Hydroxy-1-(2-hydroxyethyl)propyl]phenyl}pentane-1,5-diol (11): To a suspension of $LiAlH_4$ (2.3 g, 60 mmol) in THF (80 mL) was added compound **10** (3 g, 7.6 mmol). The suspension was stirred for 12 h at room temperature followed by the addition of ethyl acetate (10 mL) and H_2O (5 mL). The mixture was washed with *t*-butanol/ethyl acetate (V : V, 3 : 1) by suction. The filtrate was dried with $MgSO_4$, concentrated and cooled to 0 ℃ for 24 h, then white micro crystals were separated out which were collected with suction, dried *in vacuo* to give **11** (1.2 g, 60%). m.p. 133.5—134.5 ℃ (recrystallized from acetone); ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 1.62—1.67 (m, 4H), 1.72—1.77 (m, 4H), 2.72—2.75 (m, 2H), 3.14—3.20 (m, 8H); 7.06 (s, 4H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 140.8, 125.8, 58.0, 37.6, 36.3; IR (KBr) v: 3263 (broad, OH), 2926, 2854, 1450, 1044 cm^{-1}; MS (70 eV) m/z (%): 282 (M^+, 7.9). Anal. calcd for $C_{16}H_{26}O_4$: C 68.08, H 9.22; found C 67.98, H 9.32.

1,4-Bis-[3-bromo-1-(2-bromoethyl)propyl]benzene (12): To a solution of compound **11** (1 g, 3.5 mmol) in 48% HBr (100 mL) was added concentrated H_2SO_4 (50 mL) in an ice water bath. The mixture was stirred for another 20 min at 0 ℃, then heated to 120 ℃. After stirring for 12 h at this temperature, the mixture was cooled to room temperature and poured into 200 mL of ice water. The mixture was extracted with CH_2Cl_2 (3× 100 mL). The combined organic layers were washed with water, 10% $NaHCO_3$, and brine, then dried over anhydrous Na_2SO_4. The solvent was removed and the resulting crude residue was purified by column chromatography on silica gel (eluted with 8:1 petroleum ether/CH_2Cl_2) to give **12** (1.51 g, 80%). m.p. 77.2—78.5 ℃ (recrystallized from petroleum); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.05—2.15 (m, 8H), 2.94—3.06 (m, 6H), 3.16—3.24 (m, 4H), 7.08 (s, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 140.3, 128.1, 42.2, 39.0, 31.4; IR (KBr) v: 2940, 1450, 1227 cm^{-1}; MS (70 eV) m/z (%): 538 (M^++8, 3.1), 536 (M^++6, 11.8), 534 (M^++4, 18.1), 532 (M^++2, 13.1), 530 (M^+, 3.9), 429 (34.0), 427 (95.5), 425 (100), 423 (35.8), 321 (24.8), 319 (51.4), 317 (27.8). Anal. calcd for $C_{16}H_{22}Br_4$: C 35.99, H 4.15, Br 59.86; found C 36.03, H 4.16, Br 60.02.

Toluene-4-thiosulfonic acid *S*-5-(toluene-4-sulfonylsfanyl)-3-{{4-[3-(toluene-4-sulfonylsulfanyl)-1-[2-(tulene-4-sulfonylsulfanyl)ethyl]propyl}phenyl}pentyl ester (13): To a three necked flask was added *p*-toluenethiosulfonic acid potassium salt (1.35 g, 6 mmol), a catalytic amount of KI and 40 mL of anhydrous DMF. The mixture was maintained at 40—45 ℃ and stirred at argon atmosphere, and a solution of compound **12** (0.53 g, 1 mmol) in DMF (20 mL) was added. After stirring for 24 h, water (50 mL) was added, followed with the addition of CH_2Cl_2 (80 mL). The organic layer was separated, washed successively with H_2O, 5% $NaHCO_3$, and dried over anhydrous Na_2SO_4. The solvent was evaporated and the resulting solid was washed

with ether, dried *in vacuo* to give **13** (0.86 g, 90%). m.p.: 88.2—89.6 ℃ (recrystallized from CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.86—1.90 (m, 8H), 2.44 (s, 12H), 2.60—2.75 (m, 10H), 6.95 (s, 4H), 7.31 (d, J=8.1 Hz, 8H), 7.85 (d, J=8.1 Hz, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 144.9, 141.7, 140.3, 129.8, 128.1, 126.8, 43.0, 35.3, 33.6, 21.6; IR (KBr) v: 2927, 1594, 1448, 1323, 1141 cm^{-1}; MS (FT-ICTMS) calcd for $C_{44}H_{50}O_8S_8Na$ 985.1169, found 985.1156.

3a,4,5,8,9,9a,10,11-Octahydro-2*H*,3*H*-1,6,7,12-tetrathiaperylene (7): To a solution of $AlCl_3$ (0.8 g, 6.1 mmol) in dry nitromethane (80 mL) was added a solution of compound **13** (0.962 g, 1 mmol) in chloroform (60 mL). After stirring at 40—45 ℃ for 8 h, the reaction was quenched by addition of 3 mol•L^{-1} hydrochloric acid. The organic layer was separated, washed successively with 10% sodium hydrogen carbonate solution and water, dried over anhydrous $MgSO_4$. The solvent was removed, and the resulting crude residue was purified by column chromatography on silica gel (eluted with 2∶1 petroleum ether/CH_2Cl_2) to give **7** (67 mg, 20%). m.p. up to 300 ℃ decomposed; UV-vis (CH_2Cl_2) λ_{max}: 295, 350 nm; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.80—1.82 (m, 4H), 2.26—2.31 (m, 4H), 2.72—2.75 (m, 2H), 2.87—2.91 (m, 4H), 3.02—3.06 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 132.4, 128.3, 35.1, 31.2, 26.9; IR (KBr) v: 2933, 2844, 1430, 1280, 1162 cm^{-1}; MS (HR-EI) calcd for $C_{16}H_{18}S_4$ 338.0291, found 338.0294.

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