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Heteroatom-Substituted Expanded Radialenes: One-Pot Synthesis and Characterization of Expanded 1,3-Dithiolane[*n*]radialenes

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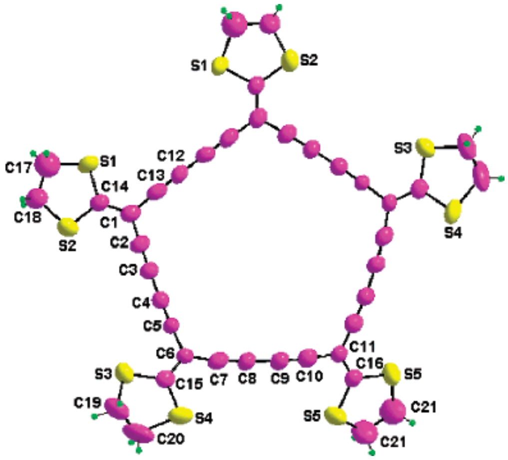
Received May 19, 2005



The one-pot synthesis, crystal structure, and electronic absorption properties of expanded 1,3-dithiolan[5]radialene (**6a**), the first heteroatom-substituted expanded radialene molecule with dithiolanylidene groups as strongly donor termini, has been developed. Catalyzed by $Ni(PPh_3)_2Cl_2-PdCl_2-CuI$, radialene **6a** was assembled by a highly efficient one-pot and protection-free oxidative coupling reaction of five α-enediyne units starting from the ready available α,α-diethynyl ketene dithioacetal (**13**) under mild conditions. The crystal of **6a**, obtained by slow evaporation of DMSO and acetone solutions, shows that the inclusion complex of DMSO molecules in the cavity of radialene **6a** molecule is formed. More importantly, owing to the introduction of the strong electron-donating alkylthio groups, per(alkylthiolated) expanded radialene **6a** shows an extremely strong intramolecular push−pull interaction and enhanced macrocyclic cross-conjugation.

Introduction

Carbon-rich materials are currently of extreme interest to researchers in many fields and have become the subject of an increasing number of experimental and theoretical studies. Expanded radialenes are a family of macrocycles derived from radialenes[1] by formal insertion of ethynediyl or buta-1,3-diynediyl moieties into the cyclic framework between each pair or a pairs of vicinal *exo*-methylene units[2−7] and have attracted increasing attention for their unusual and intriguing optoelectronic properties.[2−11] The first members of the expanded radialenes of type **1** (R = substituted ethynyl) was reported by Diederich and Boldi in 1994,[3] and subsequently an expanded radialene of type **2** (n = 3) was reported by

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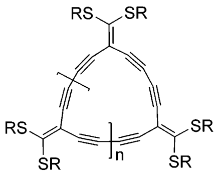
10.1021/jo050993p CCC: $30.25

Tykwinski and Eisler in 1999.[4] Very recently, expanded radialenes of type **1** with bicyclo[4.3.1]decatriene units and polyenyne macrocycles with π-extended [9]- and [12]-radialene frameworks were synthesized by Tobe and co-workers[5] and Iyoda and co-workers,[6] respectively. Since the all-C core in expanded radialenes, regardless of the ring size, is shown to comprise strong electron acceptors in similar strength within each type,[2−11] the donor strength of expanded radialenes has been focused on studying their electronic and intramolecular charge-transfer properties.[7−11] It is reasonable to expect that the hitherto unprecedented expanded 1,3-dithiol[*n*]radialenes **4** and **5**, which can be derived formally from 1,3-dithiol[*n*]radialenes **3**[12] by formal insertion of ethynediyl or buta-1,3-diynediyl moieties into the cyclic framework of **3** as mentioned above,[2−7] and their derivatives, such as **6**, could be a class of novel and interesting expanded radialenes. This is because on one hand the degree of macrocyclic cross-conjugation[2−11] involved is likely enhanced by the introduction of the strong electron-donating alkylthio functionality and on the other hand these radialenes possess the structural characters of both the expanded radialenes and the alkyne-extended tetrathiafulvalenes.[13]

Herein we wish to report the one-pot synthesis, characterizations, and crystal structure of the first heteroatom-substituted expanded radialene, expanded 1,3-dithiolan[5]radialene **6a**.



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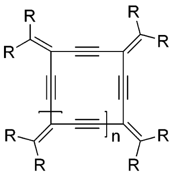

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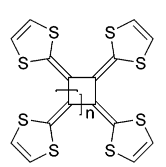

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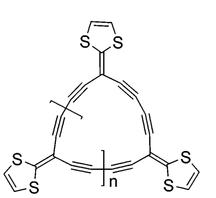

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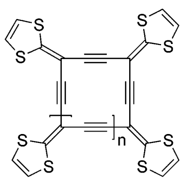

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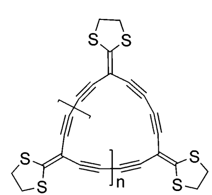


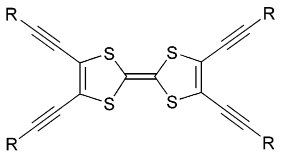
6

6a: n = 3

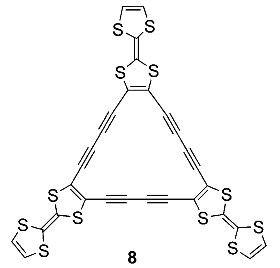
Results and Discussion

Synthesis of Expanded 1,3-Dithiolan[5]radialene 6a.

In 1998, Rubin and co-workers prepared the first tetraethynyl tetrathiafulvalenes **7**. In that report, they described the trimeric macrocycle **8**, which based on the PM3 calculation would be the important competent of a new class of organic superconductors due to the existence of the in-plane alkyne π-orbitals interacting through the bond with σ-orbitals on sulfur atoms.[14] Very recently, Iyoda et. al. reported the synthesis of mono- and bis-(tetrathiafulvaleno)hexadehydro[12]annulenes **9** and **10** and showed that the introduction of TTF unit(s) would enhance the cyclic conjugation of the annulene ring.[15]



7a: R = TMS
7b: R = SiMe$_2$t-Bu



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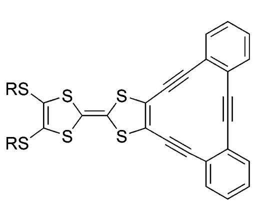
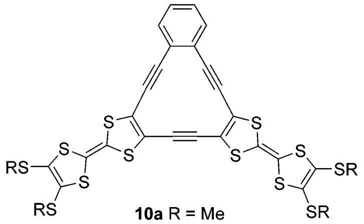


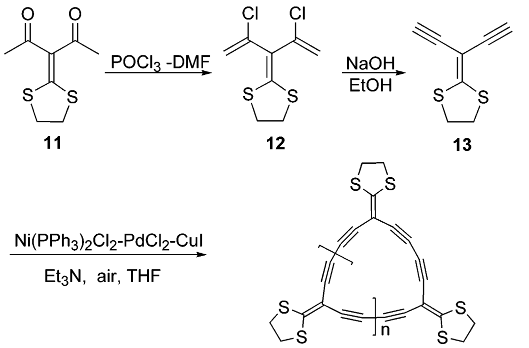
9 R = Bu^n



10a R = Me
10b R = Bu^n

Tetraethynylethene (TEE) and their derivatives[2] are versatile scaffolds and have been widely used for the assembly of expanded radialenes[2,3,7,10] through oxidative acetylenic coupling.[16] In our recent research on the synthetic applications of α-acetyl ketene-*S*,*S*-acetals and analogues,[17] a series of α-ethynyl ketene-*S*,*S*-acetals, such as α,α-diethynyl ketene-*S*,*S*-acetal **13** (Scheme 1), α-mo-

SCHEME 1. Synthesis of Expanded [5]Radialenes 6a



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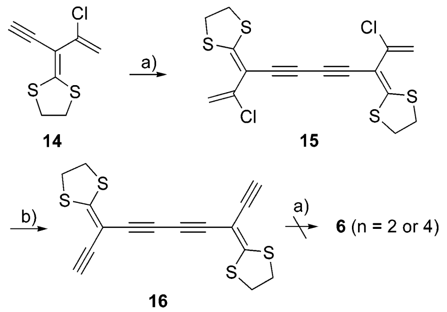
SCHEME 2. Synthesis of Alkyne-Extended Tetrahydro-tetrathiafulvalene 16[a]



[a] (a) $Ni(PPh_3)_2Cl_2$−$PdCl_2$−CuI, NEt_3, air, in THF, room temperature, 8−10 h; (b) NaOH, EtOH−DMF, 78 θ C, 10−12 h.

noethynyl ketene-*S*,*S*-acetal **14** (Scheme 2), and similar derivatives were prepared in high yields via a consecutive Vilsmeier−Haack reaction and dehydrohalogenation starting from the corresponding α-acetyl ketene-*S*,*S*-acetals under mild conditions.[18] With the consideration that compound **13**, a kind of enediyne carrying electron-donating alkylthio groups, could be a building block for the assembly of the representative per(alkylthiolated) expanded radialenes, we then focused our attention on the synthesis of the expanded [*n*]radialenes **6** to study the contribution of the electron-donating alkylthio substitutes on the macrocyclic cross-conjugation. As a result, 1,3-dithiolan[5]radialene **6a** was prepared successfully through sequential oxidative coupling of **13** in a one-pot and protection-free reaction (Scheme 1).

Initial experiments to prepare **6** by oxidative coupling under Hay conditions[16] in DMF (CuI, K_2CO_3, air) could not give the desired macrocycles but gave rather a black insoluble precipitate. With THF as the solvent, when the combination of $Ni(PPh_3)_2Cl_2$−CuI and NEt_3 or $PdCl_2$−CuI and NEt_3 were applied, however, no reaction was observed (TLC). Fortunately, under atmosphere, when enediyne **13** (2.0 mmol dissolved in 20 mL THF) was added dropwise over 2−3 h to a solution of $Ni(PPh_3)_2Cl_2$ (0.20 mmol), $PdCl_2$ (0.20 mmol), CuI (0.20 mmol), and Et_3N (6.0 mmol) in THF (180 mL) at room temperature and the resulted reaction mixture was stirred for another 5−6 h, the expanded 1,3-dithiolan[5]radialene **6a**, as a red solid, was isolated in 15% yield. In the preparation of **6a**, to our surprise, no other 1,3-dithiolan[*n*]radialenes **6** (Scheme 1, $n = 1, 2, 4$) could be observed under the above reaction conditions. As pure solids, **6a** is very stable at room temperature and can be stored in air for months. This compound is reasonably soluble in DMSO and DMF, less soluble in THF, and insoluble in solvents such as benzene, toluene, chloroform, acetonitrile, and acetone. The structure of expanded radialene **6a** is confirmed by means of ^1H NMR, ^{13}C NMR, IR, HRMS, and X-ray crystallography.

Synthesis of Alkyne-Extended Tetrahydro-tetrathiafulvalene 16. It has been found that within each expanded radialene series, independent of the ring size, the optical end-absorption remained almost constant.[2−5,7,9] These observations present a convenient way to obtain useful information for comparison of cross-conjugation

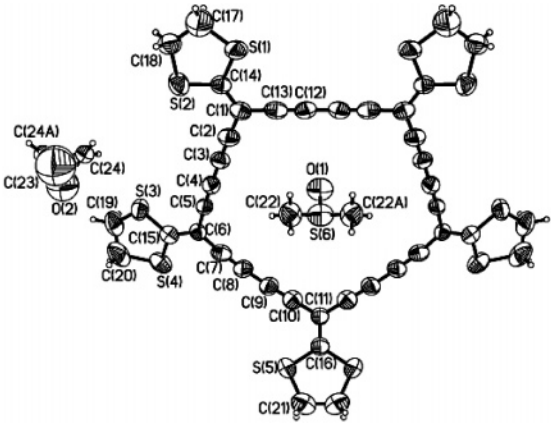


FIGURE 1. ORTEP representation of 1,3-dithiolan[5]radialene **6a** with solvents; thermal ellipsoids set at 50% probability (only unequal atoms are labeled).

TABLE 1. Selected Bond Lengths (Å) and Bond Angles (deg) of Compound 6a

S(1)−C(14)	1.728(3)	C(1)−C(2)	1.397(4)
S(1)−C(17)	1.804(5)	C(1)−C(13)	1.449(5)
S(2)−C(14)	1.727(3)	C(2)−C(3)	1.212(4)
S(2)−C(18)	1.760(4)	C(3)−C(4)	1.366(4)
S(3)−C(15)	1.723(3)	C(4)−C(5)	1.200(4)
S(3)−C(19)	1.800(4)	C(5)−C(6)	1.429(4)
S(4)−C(15)	1.723(3)	C(6)−C(15)	1.377(4)
S(4)−C(20)	1.896(5)	C(6)−C(7)	1.398(4)
S(5)−C(21)	1.737(5)	C(7)−C(8)	1.203(4)
S(5)−C(16)	1.738(3)	C(8)−C(9)	1.385(5)
C(1)−C(14)	1.364(4)		
C(14)−S(1)−C(17)	97.74(19)	C(7)−C(8)−C(9)	177.5(4)
C(14)−S(2)−C(18)	97.07(16)	C(10)−C(9)−C(8)	173.4(3)
C(15)−S(3)−C(19)	96.79(17)	C(9)−C(10)−C(11)	175.2(4)
C(15)−S(4)−C(20)	91.94(18)	C(16)−C(11)−C(10)	120.7(2)
C(21)−S(5)−C(16)	98.5(2)	C(16)−C(11)−C(10′)	120.7(2)
C(14)−C(1)−C(2)	123.5(3)	C(10)−C(11)−C(10′)	118.2(4)
C(14)−C(1)−C(13)	120.8(3)	C(13)−C(12)−C(12′)	176.0(2)
C(2)−C(1)−C(13)	115.5(3)	C(12)−C(13)−C(1)	177.8(3)
C(3)−C(2)−C(1)	177.5(3)	C(1)−C(14)−S(2)	122.0(2)
C(2)−C(3)−C(4)	178.8(3)	C(1)−C(14)−S(1)	122.8(2)
C(5)−C(4)−C(3)	177.9(3)	S(2)−C(14)−S(1)	115.19(17)
C(4)−C(5)−C(6)	177.9(3)	C(6)−C(15)−S(4)	122.0(2)
C(15)−C(6)−C(7)	122.9(3)	C(6)−C(15)−S(3)	121.9(2)
C(15)−C(6)−C(5)	119.3(2)	S(4)−C(15)−S(3)	116.19(17)
C(7)−C(6)−C(5)	117.7(2)	C(11)−C(16)−S(5)	123.20(13)
C(8)−C(7)−C(6)	173.2(3)		

between expanded radialene and the model compound containing the longest linearly conjugated π-electron fragment as in the expanded radialenes. For this purpose, the related alkyne-extended tetrahydro-tetrathiafulvalene **16** was then prepared (Scheme 2) and served as the model for the longest linearly π-electron fragment as in **6a**. Interestingly, the attempt to synthesize expanded radialenes **6** (Scheme 1, $n = 2$ or 4) from **16** under the identical conditions as the preparation of **6a** could not give the desired results (Scheme 2).

X-ray Crystallography of 6a. The structure of **6a** in the crystal, grown by slow evaporation of DMSO and acetone solutions (10:1, v/v), is shown in Figure 1. Selected bond lengths and angles are listed as well (Table 1). The lengths for three unequal edges are C(1)−C(6) 6.596 Å, C(6)−C(11) 6.551 Å, C(1)−C(1′) 6.638 Å, respectively. One DMSO molecule locates at the center of **6a**; it has short contacts with $C(21)H_2$ and $C(21')H_2$ on the 1,3-dithiolan moiety of another **6a** in neighboring layer

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[18] Dong, D.; Liu, Y.; Zhao, Y.; Qi, Y.; Wang, Z.; Liu, Q. *Synthesis* **2005**, 85−91.

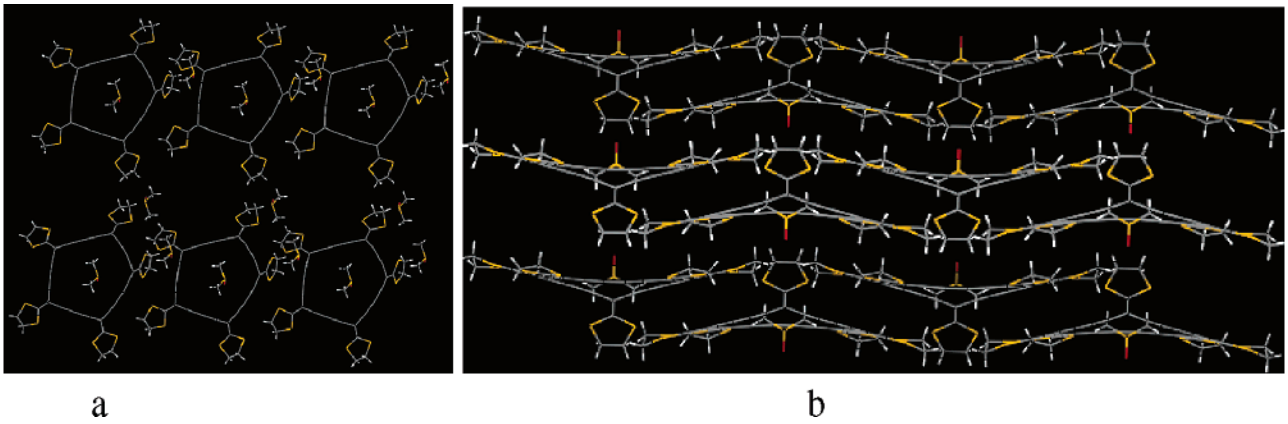

FIGURE 2. (a) Top view of a single layer of **6a** and (b) side view of 3D **6a** with solvents.

(O⋯H−CH, 2.635 Å). As a result, one 1,3-dithiolan ring (C(16), S(5), C(21)) and two edges (C(7)−C(11), C(7′)−C(11′)) tilt out of the plane of three edges (C(1)−C(6), C(1)−C(1′), C(1′)−C(6′)). Then S(4) and S(4′) forms short contacts with C(17)H_2 and C(17′)H_2 (S⋯H−CH, 2.934 Å), respectively, forming ribbons. Furthermore, neighboring ribbons interact each other through short contacts with solvents forming 2D layers (Figure 2a). As depicted in Figure 2b, the tilted parts of each **6a** always point to the neighboring layers, forming a condensed 3D structure.

Diederich and co-workers have described the first X-ray crystal structure of a perethynylated expanded [6]radialene. That molecule adopts a chairlike conformation in the solid state.[7] Determined by ^{1}H NMR and MALDI TOF-MS spectra, Iyoda and co-workers claimed that the small cavity of the π-expanded [9]radialene, the cyclic oligomer of a bis(ethynyl)[3]dendralene, can incorporate a silver cation.[6] In our work, the inclusion behavior[19] of **6a** is clear. In the solid state, the interaction[2020] between a **6a** molecule and a DMSO molecule occurs repeatedly and forms the crystal motif that suggests that an organic molecule can be recognized by the all-C core in expanded radialenes.

Electronic Absorption Spectroscopy. Comparing the UV−vis spectra of **6a** with the "dimer" **16** (Figure 3), there is some important information included about the molar extinction coefficients and especially the end-absorption.[2−5,7,9] For the end-absorption of **6a** at about 530 nm, a bathochromic shift of ~80 nm compared to "dimer" **16** appears and this bathochromic shift is almost to the same degree as with the per(anilinoethynylated) expanded radialenes, which show the largest bathochromic shift in the known expanded radialenes.[2,7] Additionally, comparing the UV−vis spectra in $CHCl_3$ of the expanded radialenes with bicyclo[4.3.1]decatriene units with compound **6a**, the optical end-absorption in **6a** appeared bathochromically shifted by approximately 130 nm, which might be caused by the introduction of the strong electron-donating alkylthio groups, although the solvent effects may be significant.[15] Similarly with the per(anilinoethynylated) expanded radialenes, the experimental results from **6a** may indicate that the per(alkylthiolated) expanded radialenes are also of major importance for inducing macrocyclic cross-conjugation. Moreover, it should be noticed that a bathochromic shift of the end-absorption in **6a** (~530 nm) is evident even when compared with the overall π-conjugated dehydrothieno[18]annulenes, for example, **17a** (~500 nm), **17b** (~450 nm), and **17c** (~410 nm).[2121]

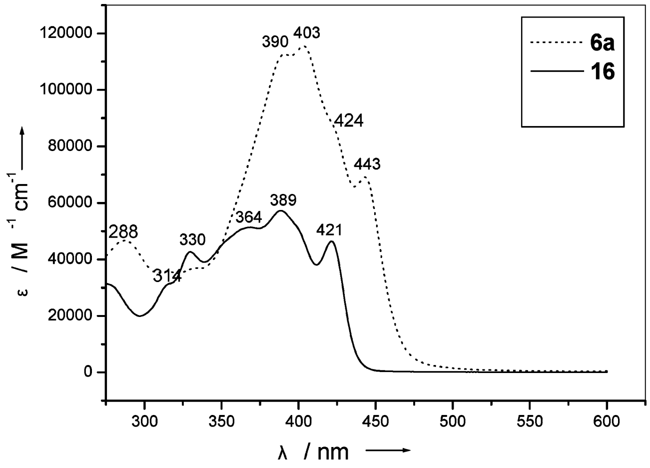

FIGURE 3. Electronic absorption spectra of **6a** and **16** in DMSO at room temperature.

TABLE 2. **^{13}C NMR Data of Compounds 11−13, 15, 16, and 6a**

compd	^{13}C NMR (125 MHz) δ
11	($CDCl_3$) 195.8, 175.1, 129.3, 37.3, 30.4.
12	($CDCl_3$) 148.9, 137.4, 122.1, 119.0, 38.2.
13	($CDCl_3$) 165.6, 87.8, 82.6, 80.7.
6a	(DMSO-d_6) 172.4, 85.2, 81.7, 79.1, 31.2.
15	($CDCl_3$) 37.7, 39.7, 81.0, 82.3, 106.0, 116.8, 136.3, 159.3.
16	($CDCl_3$) 167.5, 88.0, 82.7, 81.2, 79.7, 79.4, 39.4, 39.3.

Additionally, the ^{13}C NMR data of compounds **13**, **16**, and **6a** (summarized in Table 2) may be taken as further evidence to evaluate the difference of the cross-conjugation between acyclic and macrocyclic systems. The two signals (δ) of the sp^2 carbons for **13**, **16**, and **6a** are 165.6 and 87.8 ($\Delta\delta = 77.8$), 167.5 and 88.0 ($\Delta\delta = 79.5$), and 172.4 and 85.2 ($\Delta\delta = 87.2$), respectively. The significant downfield shift for the *exo*-methylene carbon atom and

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[19] Kawase, T.; Tanaka, K.; Shiono, N.; Seirai, Y.; Oda, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1722−1724.

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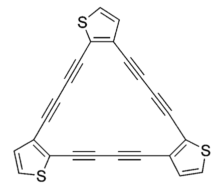
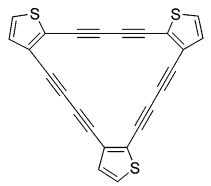
upfield shift for the sp^2 carbon atom on the macrocycle of **6a**, as well as the enlarged $\Delta\delta$ between expanded radialene **6a** and compounds **13** and **16**, are likely to be attributed to the increasing of bond polarization caused by the strong intramolecular push−pull interaction.

Conclusions

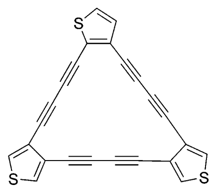
We have demonstrated the first representative heteroatom-substituted expanded radialene molecules, expanded 1,3-dithiolan[5]radialene **6a**. Compound **6a** can be obtained efficiently by means of the oxidative coupling of α-enediyne **13** with the catalyst system of $Ni(PPh_3)_2Cl_2-PdCl_2-CuI$ under mild conditions and without the need of a protection or deprotection step for the alkynyl group(s).[2] This one-pot oxidative coupling reaction proceeded selectively, and only the cyclic oligomer **6a** was obtained (a single ring size). Compared with the "dimer" of α-enediyne **13**, per(alkylthiolated) expanded radialene **6a** shows an extremely strong intramolecular push−pull interaction and enhanced macrocyclic cross-conjugation. Among these compounds, for example, radialene **6a**, dimer **16**, and dehydrothieno[18]annulenes **17**, **6a** gives the end-absorption at the longest wavelength according to their electronic absorption spectra. An inclusion complex by inserting a DMSO molecule into the cavity of radialene **6a** is formed.



17a



17b



17c

Experimental Section

Synthetic Procedure for Expanded 1,3-Dithiolan[5]-radialene (6a). Under atmosphere, to a solution of $Ni(PPh_3)_2Cl_2$ (0.20 mmol, 130.8 mg), $PdCl_2$ (0.20 mmol, 35.4 mg), CuI (0.20 mmol, 38.1 mg) and triethylamine (6.0 mmol, 0.83 mL) in THF (180 mL), enediyne **13** (2.0 mmol, 332 mg in 20 mL THF was added dropwise over 2−3 h. Then the reaction mixture was stirred for 5−6 h at room temperature. After the starting material **13** was consumed (monitored by TLC), the reaction mixture was poured into water (400 mL) and stirred. The crude solid was filtered, washed with water, and chromatographed over silica gel using diethyl acetone−hexanes−ethanol (1/1/0.1,v/v/v) as eluent to give compound **6a** (49.2 mg, 15% total yield): red solid; mp 260 °C (decomp); ^{1}H NMR (DMSO-d_6, 500 MHz) δ 3.34 (s, 20H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 31.2, 79.1, 81.7, 85.2, 172.4; IR (KBr, cm^{-1}) 1280, 1492, 1631, 2122; HRMS (EI) calcd for $C_{40}H_{20}S_{10}$ 819.8772, found 819.8903.

Synthetic Procedure for 2-(8-(1,3-Dithiolan-2-ylidene)-deca-1,4,6,9-tetrayn-3-ylidene)-1,3-dithiolane (16). To a solution of **15** (1.0 mmol, 403 mg) in DMF (3 mL) and C_2H_5OH (15 mL) were added NaOH (4.0 mmol, 160 mg) and H_2O (5 mL). Then the reaction mixture was refluxed for 10−12 h until compound **15** was consumed (monitored by TLC). Cooled down to room temperature, the reaction mixture was poured into water (80 mL) and extracted with diethyl ether (3 × 10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to yield the corresponding crude product, which was purified by column chromatography over silica gel using acetone−hexane (1/10, v/v) as eluent to give a 40% yield of compound **16** (0. 4.0 mmol, 132 mg): yellow solid; mp 146−148 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.42 (s, 2H), 3.55 (s, 8H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 39.3, 39.4, 79.4, 79.7, 81.2, 82.7, 88.0, 167.5; IR (KBr, cm^{-1}) 581, 676, 887, 1281, 1457, 1640, 2126, 3280; MS m/z 331 [M$^+$ + H]. Anal. Calcd (found) for $C_{16}H_{10}S_4$: C, 58.14 (58.19); H, 3.05 (3.11).

Synthetic Procedure for 2-(2,9-Dichloro-8-(1,3-dithiolan-2-ylidene)deca-1,9-dien-4,6-diyn-3-ylidene)-1,3-dithiolane (Compound 15). A solution of compound **14** (1.0 mmol, 202 mg), $Ni(PPh_3)_2Cl_2$ (0.050 mmol, 32.7 mg), $PdCl_2$ (0.050 mmol, 8.9 mg), CuI (0.050 mmol, 9.5 mg), and triethylamine (3.0 mmol, 0.42 mL) in THF (40 mL) was stirred for 8−10 h at room temperature. After the starting material **14** was consumed (monitored by TLC), the reaction mixture was poured into water (200 mL) and stirred. The crude solid was filtered, washed with water, and chromatographed using diethyl acetone−hexane = (1/2, v/v) as eluent to give a 80% yield of compound **15** (0. 4.0 mmol, 161 mg): yellow solid; mp 183−185 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.47−3.52 (m, 8H), 5.48 (d, J = 1.5 Hz, 2H), 5.55 (d, J = 1.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 37.7, 39.7, 81.0, 82.3, 106.0, 116.8, 136.3, 159.3; IR (KBr, cm^{-1}) 665, 887, 1087, 1206, 1273, 1480, 1617, 1727, 2112, 2171, 2860, 2927; MS m/z 403 [M$^+$ + H]. Anal. Calcd (found) for $C_{16}H_{12}Cl_2S_4$: C, 47.63 (47.70); H, 3.00 (3.09).

Acknowledgment. Financial support of this research by the NNSFC (20272008) and the Key Grant Project of Chinese Ministry of Education (10412) is gratefully acknowledged.

Supporting Information Available: Crystallographic data for **6a** in CIF format, general methods, a description of how X-ray data are collected and procured for **6a**, experimental procedures, NMR spectra, and characterization data for new compounds **6a**, **15**, and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO050993P