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Phenanthrene-Tethered Furan-Containing Cyclophenes: Synthesis and Photophysical Properties

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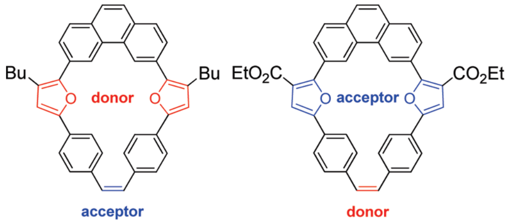

Two phenanthrene-fused furan-containing teraryl cyclophenes **5** and **6** are synthesized. These cyclophenes exhibit charge transfer band in the absorption spectra, unusually large Stokes shifts in the emission spectra, and exceptionally high $\mu\beta$ values in the electric-field-induced second-harmonic generation (EFISH) experiments. The $\mu\beta_{1.91}$ values for **5** and **6** are 438 and 777×10^{-48} esu, respectively. The bridging double bond in **5** and **6** can serve as either an electron donor or acceptor depending on the nature of the substituent on furan rings. DFT calculations at the B3LYP/6-31G** level indicate that the electron density distributions in HOMO and LUMO are very different. Interaction between the oligoaryl systems and the double bond may account for the significant enhancement in hyperpolarizability.

Introduction

Cyclophenes **1** incorporated with electron-rich heteroaromatic-containing oligoaryls (e.g., furan or thiophene) have recently been shown to furnish a unique structural feature rendering unusual photophysical properties.[1] To illustrate this, cyclophenes **1** exhibit monomeric oligoaryl-like absorption spectra but large Stokes shift in the emission spectra and unusual second-rder nonlinear optical (NLO) properties with β_o values comparable to that of 4-dimethylamino-4′-nitrostilbene (DANS, **2**).[1] The five-membered heteroaromatic rings in **1** may serve as an electron-donating group, whereas the bridged double bond may be viewed as an electron acceptor. The contribution of the resonance structure like **1a** resulting in charge-transfer interactions between two twisted π-systems may be responsible for these extraordinary properties.[1,2] The electron delocalization may take place in their respective hemisphere where the electron–vibration interaction may be strong enough to induce the polar character of **1**. This kind of resonance contribution has been shown to lead to symmetry breaking of centrosymmetric cyclophandienes **3** and **4** so that the similar remarkable second-order optical nonlinearity is observed.[3] It is known that the dihedral angle between two twisted π-systems significantly dictates the second-order nonlinear optical properties.[1,2] It is envisaged that when one of the *cis*-stilbene moieties in **4** is changed by a phenanthrene skeleton as in **5** the system would be more strained and the dihedral angle between the remaining bridging double bond and the adjacent benzene ring would also increase. As such, the two π systems would be more twisted, and the second-order NLO might therefore be enhanced. In this paper, we wish to report

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[1] (a) Lin, H.-C.; Lin, W.-Y.; Bai, H.-T.; Chen, J.-H.; Jin, B.-Y.; Luh, T.-Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 897–900. (b) Tseng, J.-C.; Lin, H.-C.; Huang, S.-L.; Lin, C.-L.; Jin, B.-Y.; Chen, C.-Y.; Yu, J.-K.; Chou, P.-T.; Luh, T.-Y. *Org. Lett.* **2003**, *5*, 4381–4384.

[2] (a) Albert, I. D. L.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 11174–11181. (b) Kang, H.; Facchetti, A.; Zhu, P.; Jiang, H.; Yang, Y.; Cariati, E.; Righetto, S.; Ugo, R.; Zuccaccia, C.; Macchioni, A.; Stern, C. L.; Liu, Z.; Ho, S.-T.; Marks, T. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 7922–7925. (c) Isborn, C. M.; Davidson, E. R.; Robinson, B. H. *J. Phys. Chem. A* **2006**, *110*, 7189–7196. (d) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195–242. (e) Di Bella, S.; Lanza, G.; Fragalà, I.; Yitzchaik, S.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 3003–3006.

[3] Lin, H.-C.; Hsu, J.-H.; Lee, C.-K.; Tai, O. Y.-H.; Wang, C.-H.; Chou, C.-M.; Chen, K.-Y.; Wu, Y.-L.; Luh, T.-Y. *Chem.—Eur. J.* **2009**, *15*, 13201–13209.

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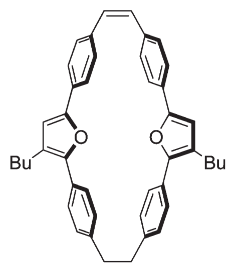
the synthesis and photophysical properties of phenanthrene-tethered furan-containing cyclophenes **5** and **6**.



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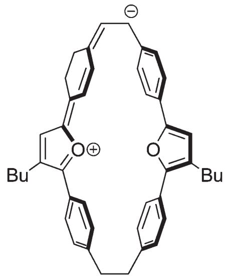

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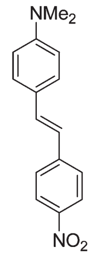

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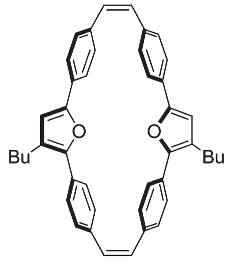

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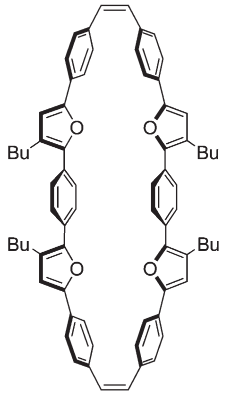

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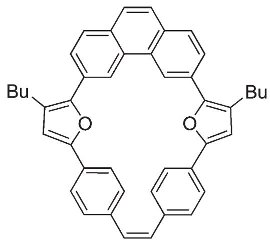

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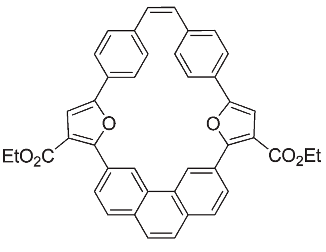
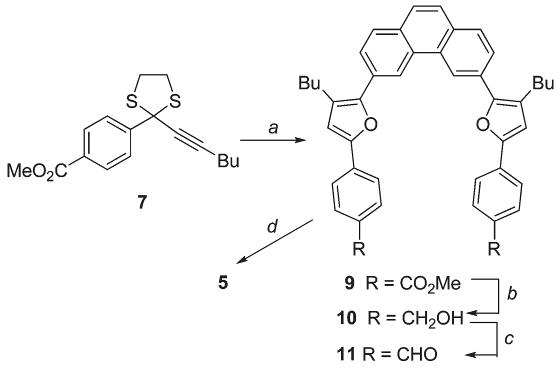


6

Results and Discussion

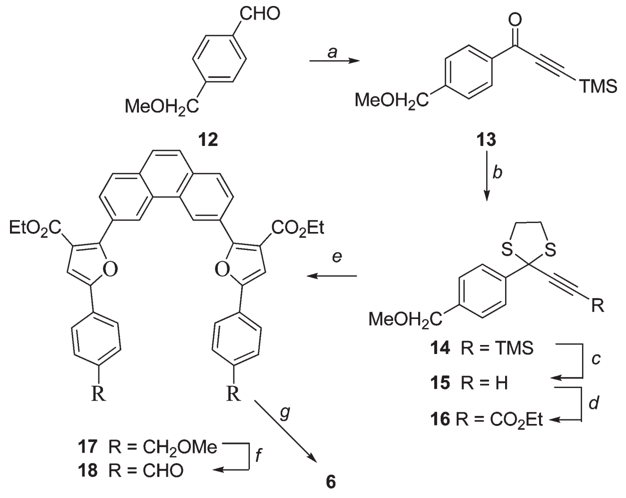
Synthesis. The synthesis of **5** and **6** are shown in Schemes 1 and 2. In a manner similar to those described previously,[1,3] annulation protocol starting from propargylic dithioacetals **7** was the key step to furnish the furan heterocycles.[4,5] Intramolecular McMurry coupling reactions of bis-aldehydes **11** and **18** afforded the bridging double bond in **5** and **6**, respectively.[6] The details are described in the Experimental Section.

SCHEME 1[a]



[a] Key: (a) (1) 1 equiv of ^{n}BuLi, THF, −78 °C, (2) phenanthrene-3,6-dicarboxaldehyde, **8**, −78 °C, (3) TFA, 45%; (b) DIBAL, THF, 94%; (c) MnO_2, 80%; (d) $TiCl_4$, Zn, pyridine, 10%.

SCHEME 2[a]



[a] Key: (a) (1) TMSC≡CLi, (2) MnO_2, 95%; (b) $HSCH_2CH_2SH$, $BF_3 \cdot OEt_2$, 90%; (c) K_2CO_3; (d) MeMgI, $ClCO_2Et$, 76%; (e) (1) 1 equiv of ^{n}BuLi, THF, −78 °C, (2) phenanthrene-3,6-dicarboxaldehyde, **8**, −78 °C, (3) TFA, 40%; (f) DDQ, 85%; (g) $TiCl_4$, Zn, pyridine, 30%.

Variable-temperature ^{1}H NMR spectra of **5** and **6** showed only slight changes in chemical shifts.[7] No broadening of signals was observed, indicating these cyclophenes would be relatively rigid.

Photophysical Properties. The absorption and emission spectra of **5** and **6** are shown in Figure 1, and these properties are compared with those of **1** and **3** and related compounds in Table 1. Like those of **1** and **3**, both **5** and **6** exhibit similar absorption maxima at ca. 330−335 nm, which is very different from those of the oligoaryl precursors **9** and **17**. These results indicate that the conjugation lengths in **5** and **6** would be very different from those of **9** and **17**. In other words, little contribution from the phenanthrene moiety in **5** and **6** to the electronic transition in these cyclophenes would be expected. In addition to the λ_{max} in the region of 330 nm, the longer wavelengths absorption around 400 nm for **5** and **6** could be assigned to a symmetry-forbidden transition attributed to electron-vibration interactions, which may have charge-transfer character.[8]

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[4] (a) Lee, C.-F.; Yang, L.-M.; Hwu, T.-Y.; Feng, A.-H.; Tseng, J.-C.; Luh, T.-Y. *J. Am. Chem. Soc.* **2000**, *122*, 4992–4993. (b) Lee, C.-F.; Liu, C.-Y.; Song, H.-C.; Luo, S.-J.; Tseng, J.-C.; Tso, H.-H.; Luh, T.-Y. *Chem. Commun.* **2002**, 2824–2825. (c) Chou, C.-M.; Chen, W.-Q.; Chen, J.-H.; Lin, C.-L.; Tseng, J.-C.; Lee, C.-F.; Luh, T.-Y. *Chem. Asian J.* **2006**, *1*, 46–55. (d) For a review, see: Luh, T.-Y.; Lee, C.-F. *Eur. J. Org. Chem.* **2005**, 3875–3885.

[5] It is worthy noting that the ester group in **7** and **16** were stable at −78 °C upon treatment with BuLi under the reaction conditions.

[6] For a review, see: McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513–1524.

[7] See the Supporting Information.

[8] Walser, D.; Zumofen, G.; Plakhotnik, T. *J. Chem. Phys.* **2000**, *113*, 8047–8058.

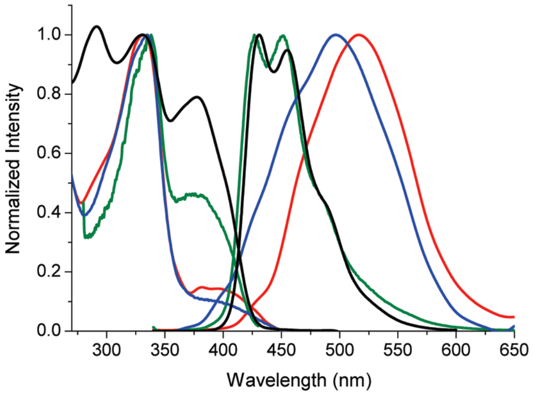

FIGURE 1. Absorption and emission spectra of **5** (blue), **6** (red), **9** (green), and **17** (black) in $CHCl_3$.

TABLE 1. Linear and Nonlinear Optical Properties of Cyclophenes and Related Compounds in $CHCl_3$

compd	λ_{max} (nm)	λ_{em} (nm)	Φ^a	μ^b	$\mu\beta_{1.91}{}^c$	$\beta_{1.32}{}^d$
1	325	501	0.28	1.12	232	220
3	330	550	0.01	0.27		208
5	335	479	0.01	0.50	438	
6	331	516	0.03	2.80	777	
9	335, 376	426, 451	0.90			
17	290, 330, 378	430, 456	0.75			

[a]Using coumarin I in EtOAc (Φ = 0.99) as reference. [b]Calculated by DFT at the 6-31G** level. [c]In 10^{-48} esu. [d]In 10^{-30} esu.

As shown in Figure 1, the emission profiles for **5** and **6** are very different from those of **9** and **17**, respectively. Both **5** and **6** exhibit large Stokes shift (>160 nm) in their emission spectra, and the quantum yields of **5** and **6**, like **1** and **3**, are much smaller than those of **9** and **17**. The bridging double bond and the remaining oligoaryl moiety would be nonplanar, and interactions between the two π-systems in **5** and in **6** may be different in the ground and the excited states resulting in large Stokes Shift.

As described previously,[1a,3] the furan moiety in **5** can be considered as an electron-donating group with a $\sigma_p{}^+$ value of -0.39,[9] and the bridging double bonds in **5** can serve as an electron acceptor. On the other hand, the presence of an ester substituent on the furan ring may change the electronic structure of **6**. In other words, the ethoxycarbonyl-substituted furan moiety in **6** is an electron donating group no more. Nevertheless, the absorption and emission profiles for **6** were similar to those of **5**, indicating that the importance of the twist π-interactions on the photophysical behavior of these cyclophenes.

Density Functional Theory (DFT) Calculations. DFT calculations at B3LYP/6-31G** level of **5** with full geometric optimization showed that the electron-density distribution shifted from the furan moieties in HOMO to the double bond in LUMO (Figure 2). Such electron distributions in HOMO and LUMO of **5** may resemble π(D) and π*(A), respectively.[10]

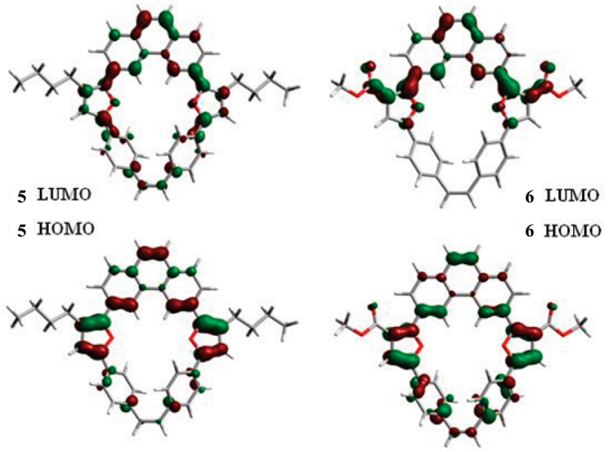

FIGURE 2. Contour plots of the frontier molecular orbitals obtained by DFT calculations at the B3LYP/6-31G** level (upper: LUMO, lower: HOMO) of **5** (left) and **6** (right).

This observation is similar to those found in **1**,[1a] where the electron delocalization from furan ring to the bridging double bond might take place. As such, the dipolar character like **1a** might contribute to the ground-state structures of **5**.

Because of the presence of an electron-withdrawing group on the furan moiety, the electron distribution in **6** would be very different. DFT calculations shown in Figure 2 indicate the electron flow from the bridging double bond in HOMO to the ester moieties in LUMO. Owing to different electron demand, the bridging double bond in **6** may serve as an electron donating group.

Electric-Field-Induced Second-Harmonic Generation (EFISH) Studies. As described above, both **5** and **6** exhibit unusual photophysical behavior. Like **1** and **3**, it seems likely that these cyclophenes may also exhibit second order NLO properties. As shown in Table 1, the $\mu\beta$ value for **5** (438×10^{-48} esu) measured by the EFISH method was comparable with that of **2** (450×10^{-48} esu, μ = 6.6 D) and almost twice of that of **1** (232×10^{-48} esu). It is noteworthy that the $\beta_{1.32}$ values for **1** and **3** are comparable (Table 1). Both **3** and **5** were relatively nonpolar as revealed by their calculated dipole moments (Table 1). Nevertheless, the presence of the phenanthrene moiety in **5** may slightly change the polarity so that the second-order nonlinearity for **5** is somewhat enhanced. In addition, **5** would be more strained than **3**, and the dihedral angle between the bridging double bond and the carbon−carbon bond of the immediate adjacent benzene ring in **5** would be somewhat larger than that of **3**. The two π systems would be more twisted in **5**, and the second-order optical nonlinearity might therefore be perturbed.

The presence of the ester substituent on the furan ring in **6** would significantly change the polarity of the molecule, and the calculated dipole moment for **6** was 2.8 D. The $\mu\beta$ value was 777×10^{-48} esu, which is also larger than that for **5**. The observation of second-order NLO properties for **6** indicates that interaction between the two twisted π-systems would be similar to those in **1**, **3**, and **5**.

Conclusions

We have depicted that phenanthrene-incorporated furan-containing cyclophanenes **5** and **6** exhibited extraordinarily

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(9) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165–195.

(10) (a) Nalwa, H. S., Miyata, S. Eds. *Nonlinear Optics of Organic Molecules and Polymers*; CRC Press: Boca Raton, FL, 1997. (b) Torre, G. D. L.; Vázquez, P.; Agulló-López, F.; Torres, T. *Chem. Rev.* **2004**, *104*, 3723–3750. (c) Delaire, J. A.; Nakatani, K. *Chem. Rev.* **2000**, *100*, 1817–1846. (d) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195–242. (e) Marder, S. *Chem. Commun.* **2006**, *131*, 131–134. (f) Ahlheim, M.; Barzoukas, M.; Bedworth, P. V.; Blanchard-Desce, M.; Fort, A.; Hu, Z.-Y.; Marder, S. R.; Perry, J. W.; Runser, C.; Staehelin, M.; Zysset, B. *Science* **1996**, *271*, 335–337.

large Stokes shifts and second-order nonlinear optical $\mu\beta$ values which were comparable to those of parent cyclophene **1** and cyclophanediene **3**. The substituents on furan rings in **5** and **6** may only perturb the polarity of these cyclophenes. Interactions between two twisted π-systems (oligoaryl and bridging double bond) would be the unique structural feature responsible for this unusual photophysical behavior.

Experimental Section

Phenanthrene-Incorporated Oligoaryl 9. Under Ar atmosphere, to a solution of **7**[1a] (752 mg, 2.4 mmol) in THF (60 mL) at −78 °C was added dropwise ^{n}BuLi (1.1 mL, 2.5 M in hexane 2.8 mmol), and the mixture was stirred for 50 min. A solution of dialdehyde **8**[11] (250 mg, 1.1 mmol) in THF (30 mL) was then added at −78 °C. The mixture was stirred for 1 h, then gradually warmed to rt, and further stirred for 1 h. TFA (1.0 mL, 1.54 g/mL, 12.0 mmol) was added, the mixture was stirred at rt overnight, and the organic layer was separated. The aqueous layer was extracted with Et_2O (150 mL × 3). The combined organic layer was washed with saturated $NaHCO_3$ (100 mL × 2) and brine (100 mL), dried ($MgSO_4$), filtered, and evaporated in vacuo. The resulting residue was suspended in Et_2O, the solid was filtered and washed with a mixture of Et_2O/pentane (1:1), and **9** was collected as a fluorescent yellow powder (2.20 g, 40%): mp 177−179 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ0.92 (t, J = 7.5 Hz, 6 H), 1.44 −1.50 (sext, J = 7.5 Hz, 4 H), 1.76 (quint, J = 7.5 Hz, 4 H), 2.91 (t, J = 7.5 Hz, 4 H), 3.91 (s, 6 H), 6.89 (s, 2 H), 7.74 (s, 2 H), 7.83 (d, J = 8.4 Hz, 4 H), 7.92−7.98 (m, 4 H), 8.02 (d, J = 8.4 Hz, 4 H), 9.05 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ14.1, 22.7, 26.1, 32.1, 52.1, 111.7, 119.3, 123.0, 124.2, 124.9, 126.6, 128.1, 128.8, 129.4, 130.0, 130.2, 131.1, 134.4, 149.1, 150.9, 166.5; UV−vis ($CHCl_3$): 335 nm (ε = 5.0×10^4 $M^{-1}\,cm^{-1}$); IR (KBr) ν 3487, 2955, 2930, 2870, 1720, 1609, 1435, 1277, 1178, 1109, 1017, 934, 848, 771, 669 cm^{-1}; HRMS (FAB) (M^+) calcd for $C_{46}H_{42}O_6$ 690.2981, found 690.2993.

Diol 10. To a solution of diester **9** (1.30 g, 1.80 mmol) in THF (80 mL) under Ar atmosphere was added slowly a solution of DIBAL (17.0 mL, 1.0 M in hexane 17.0 mmol) at 0 °C, and the mixture was stirred at rt for 3 h. The reaction was quenched by pouring it into saturated NH_4Cl (100 mL), and the mixture was stirred for 30 min. The gel-like mixture was acidified with 6 M HCl (50 mL) and extracted with CH_2Cl_2 (200 mL × 3). The combined organic extracts were washed with saturated $NaHCO_3$ (200 mL × 2) and brine (200 mL), dried ($MgSO_4$), filtered, and evaporated in vacuo to afford the crude product, which was recrystallized from Et_2O/CH_2Cl_2 to give **10** as a fluorescent yellow solid (1.235 g, 95%): mp 177−178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, J = 7.6 Hz, 6 H), 1.46−1.51 (m, 4 H), 1.74−1.78 (m, 6 H), 2.87 (t, J = 7.6 Hz, 4 H), 4.68 (s, 4 H), 6.74 (s, 2 H), 7.32 (d, J = 8.2 Hz, 4 H), 7.71 (s, 2 H), 7.81 (d, J = 8.2 Hz, 4 H), 7.90−7.92 (AB q, J = 8.8 Hz, 4 H), 9.17 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 23.0, 26.4 32.4, 65.1, 109.1, 109.4, 119.1, 123.4, 123.6, 124.5, 126.2, 127.2, 128.4, 129.4, 129.8, 130.6, 139.3, 151,4; IR (KBr) ν 3391, 2956, 2927, 2870, 2854, 1667, 1650, 1615, 1463, 1262, 1015, 847, 804, 738 cm^{-1}; HRMS (FAB) (M^+) calcd for $C_{44}H_{42}O_4$ 634.3083, found 634.3088.

Dialdehyde 11. A solution of **10** (1.13 g, 1.71 mmol) in CH_2Cl_2 (20 mL) was added slowly to a suspension of activated MnO_2 (1.80 g, 20.52 mmol) in CH_2Cl_2 (30 mL) at rt. The reaction mixture was stirred for 6 h at rt. After being passed through a silica gel bed (2 cm) and washed with CH_2Cl_2 (120 mL × 3), the combined filtrate was evaporated in vacuo. The resulting residue was recrystallized from Et_2O/CH_2Cl_2, to afford **11** as a fluorescent yellow solid (1.11 g, 97%): mp 89−90 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 (t, J = 7.4 Hz, 6 H), 1.50 (quint, J = 7.4 Hz, 4 H), 1.79 (m, 4 H), 2.91 (t, J = 7.4 Hz, 4 H), 6.94 (s, 2 H), 7.75 (s, 2 H), 7.87 (d, J = 8.4 Hz, 4 H), 7.91 (d, J = 8.4 Hz, 4 H), 7.96 (br s, 4 H), 9.03 (s, 2 H), 9.96 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 26.0, 32.1, 112.6, 119.5, 123.6, 124.3, 125.1, 126.8, 128.9, 129.3, 130.2, 130.3, 131.3, 134.6, 135.8, 149.8, 150.6, 191.1; IR (KBr) ν 3411, 2955, 2927, 2870, 2816, 1707, 1605, 1502, 1411, 1381, 1253, 1097, 1017, 915, 845, 754 cm^{-1}; HRMS (FAB) ($M + H^+$) calcd for $C_{44}H_{39}O_4$ 631.2848, found 631.2848.

1-(4-(Methoxymethyl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-one (13). Under N_2, to a THF solution (200 L) of trimethylsilylacetylene (28.0 mL, 0.71 g/mL, 0.2 mol) was slowly added n-BuLi (82.0 mL, 2.5 M in hexane 0.21 mol) at −78 °C. The mixture was warmed to rt and stirred for 1 h. After the mixture was cooled to −78 °C, a THF (200 mL) solution of **12** (30.0 g, 0.2 mol) was added slowly, and the mixture was stirred for 10 min at −78 °C and then slowly warmed to rt and further stirred for 1 h. The mixture was quenched with saturated NH_4Cl (800 mL), and the organic layer was separated. The aqueous layer was extracted with Et_2O (200 mL × 2). The combined organic extracts were dried ($MgSO_4$), filtered, and evaporated in vacuo to afford the crude ynol. A solution of crude ynol in CH_2Cl_2 (250 mL) was added slowly to a suspension of activated MnO_2 (87.0 g, 1.0 mol) in CH_2Cl_2 (250 mL) at rt, and the mixture was stirred for 12 h at rt. After being passed through a silica gel bed (7 cm) and washed with EtOAc (200 mL × 2), the combined filtrate was evaporated in vacuo to give crude **13** (49.6 g, 97%) as a yellow liquid. Kugelrohr distillation (0.01 Torr, 80 °C) afforded pure **13** as colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.31 (s, 9 H), 3.40 (s, 3 H), 4.52 (s, 2 H), 7.41−7.44, 8.09−8.11 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.5, 58.5, 73.9, 100.4, 100.8, 127.1, 129.7, 135.6, 144.9, 177.1; IR (KBr) ν 2955, 2924, 2854, 2153, 1647, 1607, 1572, 1458, 1414, 1379, 1308, 1253, 1195, 1171, 1034, 1014, 971, 924, 847, 761, 740; HRMS (FAB) ($M + H^+$) calcd for $C_{14}H_{19}O_2Si$ 247.1154, found 247.1158.

[2-[2-(4-Methoxymethylphenyl)-1,3-dithiolan-2-yl]ethynyl]trimethylsilane (14). To a solution of **13** (22.1 g, 0.09 mol) in MeOH (400 mL) were added $BF_3 \cdot Et_2O$ (13.1 mL, 0.1 mol) and 1, 2-ethanedithiol (7.6 mL, 0.09 mol) at −78 °C. The reaction mixture was gradually warmed to rt and further stirred for 12 h. After quenching with 10% NaOH (400 mL), the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (100 mL × 3). The combined organic layer was washed with 10% NaOH (200 mL) and brine (100 mL) and dried ($MgSO_4$), filtered, and evaporated in vacuo to give **14** (27.5 g, 95%) as a yellow solid: mp 41−43 °C (Et_2O and CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.22 (s, 9 H), 3.37 (s, 3 H), 3.70−3.66 (m, 4 H), 4.44 (s, 2 H), 7.28−7.30, 7.89−7.91 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.49, 41.4, 58.2, 61.8, 74.1, 91.2, 106.3, 127.0, 127.3, 137.2, 137.9; IR (KBr) ν 2957, 2924, 2892, 2857, 2816, 2162, 1724, 1608, 1505, 1410, 1379, 1277, 1248, 1193, 1100, 1056, 1020, 837; HRMS (FAB) ($M + H^+$) calcd for $C_{16}H_{23}OSiS_2$ 323.0960, found 323.0964.

2-Ethynyl-2-(4-methoxymethylphenyl)-1,3-dithiolane (15). A mixture of **14** (2.80 g, 10.0 mmol) and K_2CO_3 (20.0 g, 0.15 mol) in MeOH (60.0 mL) was stirred at rt for 6 h, poured into water (100 mL), and extracted with Et_2O (20 mL × 3). The combined organic extracts were dried ($MgSO_4$), filtered, and evaporated in vacuo to afford the residue, which was purified by flash column chromatography (silica gel, hexane/EtOAc = 3/1) to afford **15** as oil (2.02 g, 98%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.04 (s, 1 H), 3.37 (s, 3 H), 3.73−3.68 (m, 4 H), 4.44 (s, 2 H), 7.29−7.31, 7.91−7.93 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.5, 58.3, 61.2, 74.1, 75.2, 85.7, 127.1, 127.2, 136.7, 138.2; IR (KBr) ν 3410, 3055, 3024, 2958, 2929, 2870, 2854, 1665, 1600, 1503, 1446, 1378,

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1316, 1261, 1201, 1177, 1072, 1023, 913, 800, 755, 696 cm^{-1}; HRMS (FAB) (M + H$^+$) calcd for $C_{13}H_{15}OS_2$ 251.0564, found 251.0563.

Ethyl 3-[[2-(4-Methoxymethylphenyl)]-1,3-dithiolan-2-yl]propiolate (16). Under N_2, to **15** (2.5 g, 10.0 mmol) in THF (60 mL) was added MeMgI (15 mL, 1 M, 15 mmol). After the mixture was stirred for 30 min, $ClCO_2Et$ (1.25 mL, 14.1 mmol) was slowly introduced, and the mixture was stirred for 6 h, quenched with saturated NH_4Cl (100 mL), and extracted with ether (100 mL × 3). The combined organic layer was washed with brine (100 mL), dried ($MgSO_4$), filtered, and evaporated in vacuo to afford the residue which was chromatographed on silica gel (hexane/EtOAc = 4/1) to afford **16** as an oil (3.00 g, 94%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (t, J = 6.8 Hz, 3 H), 3.36 (s, 3 H), 3.71 (br s, 4 H), 4.25 (q, J = 6.8 Hz, 2 H), 4.44 (s, 2 H), 7.30−7.32, 7.84−7.86 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 41.4, 58.1, 60.4, 62.1, 73.9, 78.2, 87.4, 127.35, 127.43, 135.6, 138.9, 153.5; IR (KBr) ν 2982, 2925, 2820, 2223, 1745, 1708, 1448, 1412, 1365, 1251, 1194, 1098, 1017, 851, 755 cm^{-1}; HRMS (FAB) (M + H$^+$) calcd for $C_{16}H_{19}O_3S_2$ 323.0776, found 323.0766.

Bis-dimethoxy Ether 17. Under Ar atmosphere, a solution of ^{n}BuLi (0.95 mL, 2.5 M in hexane, 2.4 mmol) was introduced dropwise to a solution of **16** (757 mg, 2.4 mmol) in THF (70 mL) at −78 °C, the mixture was stirred for 1 h, and a solution of dialdehyde **8** (250 mg, 1.1 mmol) in THF (30 mL) was then added at −78 °C. The mixture was stirred for 1 h, gradually warmed to rt, and further stirred for 1 h. TFA (0.2 mL, 1.54 g/mL, 2.4 mmol) was added, the mixture was stirred at rt overnight and quenched with saturated $NaHCO_3$ (100 mL × 2), and the organic layer was separated. The aqueous layer was extracted with ether (150 mL × 3), and the combined organic layer was washed with brine (100 mL), dried ($MgSO_4$), filtered, and evaporated in vacuo to give the residue which was chromatographed on silica gel (hexane/EtOAc = 10/1) to afford **17** (300 mg, 40%) as a fluorescent yellow solid: mp 143−144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (t, J = 7.2 Hz, 6 H), 3.41 (s, 6 H), 4.35 (q, J = 7.2 Hz, 4 H), 4.48 (s, 4 H), 7.17 (s, 2 H), 7.38 (d, J = 8.2 Hz, 4 H), 7.80 (s, 2 H), 7.81 (d, J = 8.2 Hz, 4 H), 7.95 (d, J = 8.4 Hz, 2 H), 8.31 (dd, J = 8.4, 1.0 Hz, 2 H), 9.65 (d, J = 1.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 58.3, 60.9, 74.3, 108.1, 116.0, 122.9, 123.8, 126.0, 127.2, 127.6, 127.8, 127.9, 128.8, 129.9, 132.2, 137.7, 151.9, 155.8, 163.0; ε = 3.1 × 10^4 M^{-1} cm^{-1} (330 nm), log ε = 4.5 M^{-1} cm^{-1} in $CHCl_3$; IR (KBr) ν 3435, 2923, 2853, 1717, 1605, 1444, 1497, 1378, 1231, 1094, 1025, 850, 776 cm^{-1}; HRMS (FAB) (M$^+$) calcd for $C_{44}H_{38}O_8$ 694.2567, found 694.2556.

Bis-dialdehyde 18. A mixture of **17** (72 mg, 0.1 mmol) and DDQ (98 mg, 0.4 mmol) in CH_2Cl_2/H_2O (9:1, 1 mL) was stirred at rt. After beign stirred for 24 h, the mixture was passed through a silica gel bed (1 cm) and washed with CH_2Cl_2 (40 mL). The filtrate was washed with saturated $NaHCO_3$ (20 mL × 4) and brine (20 mL), dried ($MgSO_4$), and evaporated in vacuo to **18** (63 mg, 86%) as a yellow solid: mp 213-214 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, J = 7.2 Hz, 6 H), 4.24 (q, J = 7.2 Hz, 4 H), 7.63 (s, 2 H), 7.72−7.78 (m, 12 H), 8.17 (d, J = 8.8 Hz, 2 H), 9.50 (s, 2 H), 9.84 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 61.0, 111.2, 116.3, 122.9, 123.7, 125.8, 127.0, 127.3, 127.9, 129.7, 129.9, 132.3, 134.4, 134.8, 150.2, 156.9, 162.5, 190.4; IR (KBr) ν 3431, 2962, 2926, 2855, 1698, 1695, 1573, 1506, 1417, 1261, 1168, 1095, 1021, 800, 759, 667 cm^{-1}; HRMS (FAB) (M$^+$) calcd for $C_{42}H_{30}O_8$ 662.1941, found 662.1933.

Butyl-Substituted Cyclophene 5. To a suspension of zinc dust (1.97 g, 30.2 mmol) in THF (50 mL) under nitrogen was added $TiCl_4$ (1.8 mL, 1.73 g/mL, 15.1 mmol) over a period of 30 min, and the suspension was refluxed for 1 h. A solution of dialdehyde **16** (1.00 g, 1.51 mmol) in THF (50 mL) was then syringed. After being refluxed for 16 h, the mixture was cooled to rt. Na_2CO_3 (10%, 100 mL) was carefully introduced with stirring, the mixture was filtered, and the filtrate was extracted with CH_2Cl_2 (2 × 100 mL). The organic solution was washed with water (2 × 100 mL), dried ($MgSO_4$), and evaporated in vacuo to give the residue, which was purified by flash column chromatography (silica gel, hexane/CH_2Cl_2 = 4/1) to afford **5** (238 mg, 25%) as a pale yellow solid: mp 236−238 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, J = 7.2 Hz, 6 H), 1.50 (sext, J = 7.2 Hz, 4 H), 1.70−1.74 (m, 4 H), 2.80 (t, J = 7.2 Hz, 4 H), 6.55 (s, 2 H), 6.71 (s, 2 H), 7.06−7.08, 7.61−7.64 (m, 8 H), 7.59 (s, 2 H), 7.76 (dd, J = 8.2, 1.2 Hz, 2 H), 7.80 (d, J = 8.2 Hz, 2 H), 9.51 (d, J = 1.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.8, 26.6, 32.3, 109.3, 119.6, 122.6, 125.0, 126.3, 128.5, 129.8, 129.9, 130.0, 130.8, 130.9, 131.2, 136.1, 148.0, 152.5; ε = 7.7 × 10^3 M^{-1} cm^{-1} (335 nm), log ε = 3.9 M^{-1} cm^{-1} in $CHCl_3$; IR (KBr) ν 3409, 2956, 2926, 2858, 1730, 1660, 1605, 1510, 1457, 1261, 1100, 1028, 798 cm^{-1}; HRMS (FAB) (M$^+$) calcd for $C_{44}H_{38}O_2$ 598.2872, found 598.2875.

Ethoxycarbonyl-Substituted Cyclophene 6. In a manner similar to that described for the preparation of **5**, **18** (211 mg, 0.32 mmol) was allowed to react with $TiCl_4$ (0.5 mL, 1.73 g/mL, 3.2 mmol) and zinc dust (420 mg, 6.4 mmol) in THF (200 mL) to give **6** (38 mg, 18%) as a pale yellow solid: mp > 290 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.42 (t, J = 7.2 Hz, 6 H), 4.39 (q, J = 7.2 Hz, 4 H), 6.77 (s, 2 H), 7.02 (s, 2 H), 7.05 (d, J = 8.0 Hz, 4 H), 7.61 (d, J = 8.0 Hz, 4 H), 7.70 (s, 2 H), 7.88 (d, J = 8.6 Hz, 2 H), 8.83 (d, J = 8.6 Hz, 2 H), 9.45 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.5, 60.8, 108.5, 116.5, 121.5, 125.3, 126.2, 127.5, 127.9, 128.4, 128.9, 130.0, 130.3, 131.3, 132.6, 136.9, 152.6, 155.9, 163.5; ε = 5.0 × 10^3 (330 nm), log ε = 3.7 in $CHCl_3$; IR (KBr) ν 3464, 2953, 2923, 2920, 2868, 2851, 1717, 1647, 1457, 1376, 1223, 1093, 668 cm^{-1}; ε = 5.6 × 10^3 M^{-1} cm^{-1} (330 nm), log ε = 3.7 M^{-1} cm^{-1} in $CHCl_3$; HRMS (EI) (M$^+$) calcd for $C_{42}H_{30}O_6$ 630.2042, found 630.2050.

DFT Calculations. The ground state structures of **5** and **6** were calculated by the DFT method which was implemented in Gaussian 98 package.[12] Geometry optimizations without any symmetry constraints have been performed. The dipole moments were calculated on the basis of optimized geometries. All DFT calculations were carried out with the 6-31G** split valence plus polarization basis set.[13] The B3LYP functional was employed where Becke's three-parameter hybrid exchange functional was combined with the Lee−Yang−Parr correlation functional.[14]

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of all new compounds and variable-temperature ^{1}H NMR spectra of **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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