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Synthesis and Optical Properties of Bis(oligophenyleneethynylenes)

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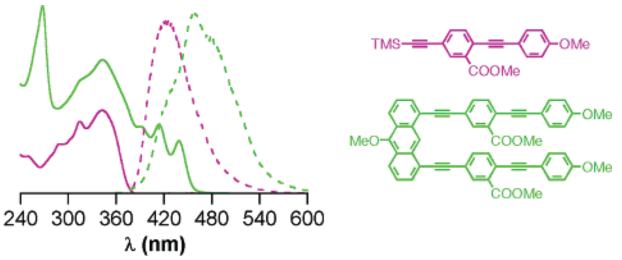

Bis(oligophenyleneethynylenes) **1−4** were prepared as representative members of a new class of potential nonlinear optical materials. The optical properties of **1−4** were examined for evidence of restricted rotation of the aryl rings when compared to their single-strand precursors, which could potentially increase their nonlinear response through more effective conjugation. The effect of altering the electron density of the terminating functional group of these compounds on their properties was also investigated.

Introduction

Materials which possess high second- and third-order optical susceptibilities ($\chi^{(2)}$ and $\chi^{(3)}$) have the ability to alter the properties of incident light and are required for potential applications in the computing, imaging, and telecommunications industries.[1] Organic compounds have some of the highest known $\chi^{(2)}$ and $\chi^{(3)}$ reported[2] and provide many advantages compared to inorganic materials, including processability and the opportunity to fine-tune the properties of the material by functional group manipulation.

While widely studied in their capacity to act as molecular wires,[3,4] oligo(phenyleneethynylene)s (OPEs) have not been extensively investigated for nonlinear optical (NLO) activity relative to their double-bond analogues, oligo(phenylenevinylene)s (OPVs). When direct comparisons of OPEs and OPVs have been reported,[5] the OPEs have decreased NLO responses due to the less effective conjugation[6] induced by the negligible barrier to rotation of the aryl rings.[7]

As part of our studies into the optical properties of OPEs and the effects of coplanarity of arylalkyne oligomers on increasing conjugation throughout the OPE chain,[8] we recently

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[1] For a general overview of NLO physics, basic design principles, and application of NLO materials, see: *Materials for Nonlinear Optics: Chemical Perspectives*; Marder, S. R., Sohn, J. E., Stucky, G. D., Eds.; ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991.

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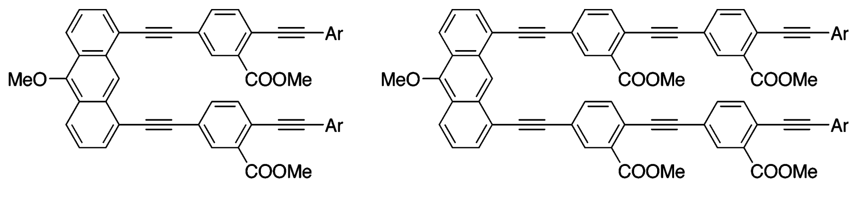
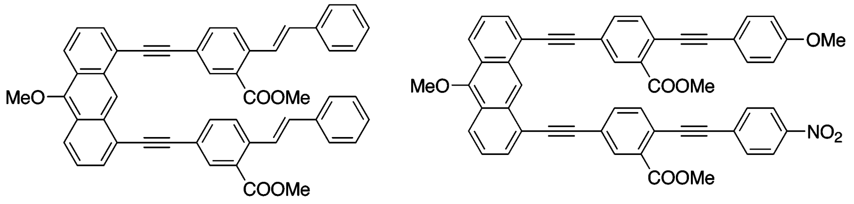
10.1021/jo052242t CCC: $33.50

CHART 1



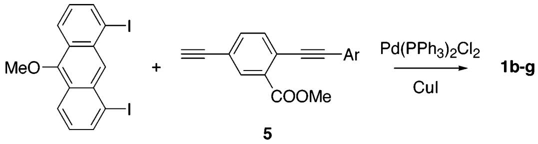
1 **2**

a: Ar = Ph; **b:** Ar = 4-$NO_2C_6H_4$; **c:** Ar = 4-$MeOC_6H_4$; **d:** Ar = 4-$BocNHC_6H_4$; **e:** Ar = 2-thienyl;
f: Ar = 4-BrC_6H_4; **g:** Ar = 4-$(TMSCH_2CH_2S)C_6H_4$.



3 **4**

SCHEME 1



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6

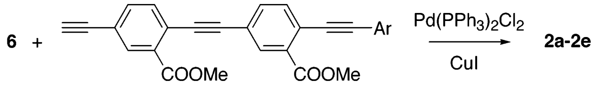
b: Ar = 4-$NO_2C_6H_4$; **c:** Ar = 4-$MeOC_6H_4$; **d:** Ar = 4-$BocNHC_6H_4$;
e: Ar = 2-thienyl; **f:** Ar = 4-BrC_6H_4; **g:** Ar = 4-$(TMSCH_2CH_2S)C_6H_4$

TABLE 1. Bis-coupling of Dimers to Anthracene 6[a]

dimer	product	Ar	yield (%)
5b[b]	**1b**	4-$NO_2C_6H_4$	29
5c	**1c**	4-$MeOC_6H_4$	41
5d	**1d**	4-$BocNHC_6H_4$	73
5e	**1e**	2-thienyl	79
5f	**1f**	4-BrC_6H_4	80
5g	**1g**	4-$(TMSCH_2CH_2S)C_6H_4$	55

[a] 1.0 equiv of **6**, 2.2 equiv of **5b**−**g**, 0.1 equiv of $Pd(PPh_3)_2Cl_2$, 0.1 equiv of CuI, Et_3N, DMF, 20 °C, 18 h. [b] Reaction performed at 60 °C.

SCHEME 2



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b: Ar = 4-$NO_2C_6H_4$; **c:** Ar = 4-$MeOC_6H_4$; **d:** Ar = 4-$BocNHC_6H_4$; **e:** 2-thienyl

TABLE 2. Bis-coupling of Trimers to Anthracene 6[a]

trimer	product	Ar	yield (%)
7b	**2b**	4-$NO_2C_6H_4$	11
7c	**2c**	4-$MeOC_6H_4$	41
7d	**2d**	4-$BocNHC_6H_4$	27
7e	**2e**	2-thienyl	32

[a] 1.0 equiv of **6**, 2.2 equiv **7b**−**e**, 0.1 equiv of $Pd(PPh_3)_2Cl_2$, 0.1 equiv of CuI, Et_3N, DMF, 60 °C, 18 h.

reported the synthesis of bis(OPEs) **1a** and **2a**.[9,10] We now discuss the preparation of more functionalized bis(OPEs) **1b**−**g**, **2b**−**e**, and **3**, as well as the asymmetric bis(dimer) **4** (Chart 1), and examine their spectroscopic properties.

Results and Discussion

The syntheses of the OPE fragments was reported previously.[9] Coupling of the dimers **5b**−**g** to the anthracene template **6**[11] proceeded in moderate to good yields under mild conditions (Scheme 1, Table 1). The reaction of nitro dimer **5b** required warming to 60 °C to promote the coupling of the second OPE unit as the monoadduct was almost completely insoluble in the reaction medium at room temperature. Similarly, trimers **7b**−**e** were coupled to **6** (Scheme 2, Table 2), except that all of the reactions were performed at 60 °C to improve the solubility of the intermediates; however, the isolated yields were much lower than for the bis(dimers) **1a**−**e**.

The nitro-substituted compounds **1b** and **2b** precipitated from the reaction mixture and were only sparingly soluble in a few solvents; **2b** was so insoluble that a satisfactory ^{13}C NMR spectrum could not be obtained, even at elevated temperatures. The other bis(OPEs) could only be completely separated from small amounts (<10%) of impurities by repeated chromatography. The impurities were identified as the corresponding 1,3-butadiynes, formed by copper-catalyzed oxidative dimerization of the terminal alkynes as indicated by their ^1H NMR spectra. In many cases, however, analytical samples were obtained by judicious pooling of fractions. The exceptions were the Boc-protected bis(OPEs) **1d** and **2d**, whose solutions in several solvents darkened considerably after just a few minutes at moderate concentrations. NMR spectra of these compounds revealed a mixture of components, some of which appeared to have free amino groups. Decomposition of the NMR samples was confirmed by TLC; however, the more dilute UV and fluorescence solutions showed no evidence of degradation.

The cinnamate **8a** and stilbene **8b**[9] were deprotected under the usual mild conditions (potassium carbonate−methanol) to

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[9] Armitt, D. J.; Crisp, G. T. *Tetrahedron* **2006**, *62*, 1485.

[10] Similar structures have been previously reported as candidates for molecular tweezers and molecular electronic devices, in addition to those in ref 8. See: (a) Vögtle, F.; Koch, H.; Rissanen, K. *Chem. Ber.* **1992**, *125*, 2129. (b) Maya, F.; Flatt, A. K.; Stewart, M. P.; Shen, D. E.; Tour, J. M. *Chem. Mater.* **2004**, *16*, 2987.

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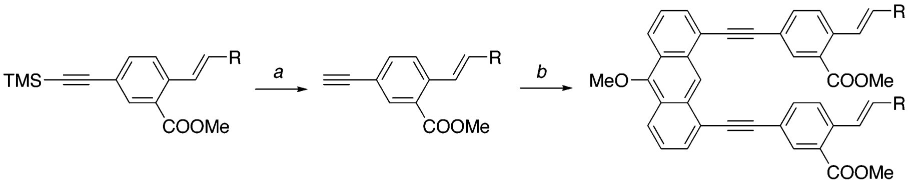
SCHEME 3 [a]



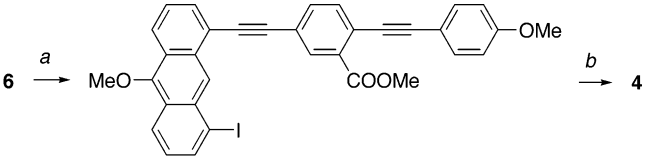
8a (R = COOMe)
8b (R = Ph)

9a (R = COOMe)
9b (R = Ph)

10 (R = COOMe) 58%
3 (R = Ph) 100%

[a] Conditions: (a) K_2CO_3, MeOH; (b) **6**, $Pd(PPh_3)_2Cl_2$, CuI.

SCHEME 4 [a]



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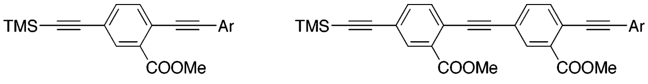
[a] Conditions: (a) **5c**, $Pd(PPh_3)_2Cl_2$, CuI, 41%; (b) **5b**, $Pd(PPh_3)_2Cl_2$, CuI, 51%.

CHART 2



12 **13**

a: Ar = Ph, **b**: Ar = 4-$NO_2C_6H_4$, **c**: Ar = 4-$MeOC_6H_4$, **d**: Ar = 4-$BocNHC_6H_4$
e: Ar = 2-thienyl, **f**: Ar = 4-BrC_6H_4, **g**: Ar = 4-$(TMSCH_2CH_2S)C_6H_4$

TABLE 3. UV Absorption and Fluorescence Emission Data of OPEs and Bis(OPEs)

entry	compd	$\lambda_{abs}{}^a$ (nm)	ϵ ($L{\cdot}mol^{-1}{\cdot}cm^{-1}$)	$\lambda_{em}{}^b$ (nm)	Stokes shift (nm)^c
1	**12a**	330	43900	367	37
2	**12b**	345	36000	459	114
3	**12c**	342	30300	405	63
4	**12d**	350	38400	416	66
5	**12e**	346	20100	394	48
6	**12f**	333	37300	368	35
7	**12g**	348	32500	424	76
8	**8b**	327	14100	398	71
9	**13a**	351	60800	388	37
10	**13b**	362	64200	470	108
11	**13c**	361	55900	427	66
12	**13d**	365	55200	445	80
13	**13e**	360	49000	416	56
14	**1a**	331	51900	457	126
15	**1b**	342	52200	460	118
16	**1c**	343	48700	461	118
17	**1d**	352	74000	424	72
18	**1e**	344	53800	461	117
19	**1f**	323	63300	461	138
20	**1g**	349	65600	432	83
21	**2a**	351	101900	465	115
22	**2b**	373	80100	471	98
23	**2c**	363	102900	457	94
24	**2d**	367	62500	456	89
25	**2e**	362	93300	465	103
26	**3**	331	51100	455	124
27	**4**	343	39200	460	118
28	**11**	356	30300	410	54

[a] Wavelength of lowest energy absorption for the OPE fragment in bis(OPEs). [b] Wavelength of highest energy emission maximum. [c] $\lambda_{em} - \lambda_{abs}$.

give the terminal alkynes **9a** and **9b**, and these were coupled with the anthracene **6** (Scheme 3). The resulting products **10** and **3** possess elements common to both OPE and the related oligo(phenylenevinylene) (OPV) classes of NLO materials. Using a combination of OPE and OPV motifs potentially allows for fine-tuning of desired NLO properties.[12]

An unsymmetrical bis(OPE) was also prepared (Scheme 4). The reaction of **6** with 1.1 equiv of **5c** gave a statistical mixture of unreacted **6**, the desired monocoupled product **11**, and the bis(dimer) **1c**, which were separated by flash chromatography. Further coupling of **11** to **5b** afforded the mixed bis(dimer) **4**, which possesses both electron-rich and electron-poor OPE chains.

Unfortunately none of the compounds could be induced to crystallize in a form suitable for X-ray analysis. ^1H NMR spectra of the bis(OPEs) did not reveal any evidence of restricted rotation at room temperature; only one set of sharply defined signals was observed for each compound.

The UV absorption and fluorescence emission spectra of the bis(OPEs) **1a**−**g**, **2a**−**e**, **3**, **4**, and their trimethylsilyl-protected precursors, **12a**−**g** and **13a**−**e** (Chart 2),[9] were recorded as dilute THF solutions and are summarized in Table 3. Spectra of selected compounds are shown in Figures 1 and 2.

The UV spectra of **1**−**4** all display characteristic peaks emanating from the anthracene portion of the molecules, with a narrow, intense primary absorption at around 265 nm and a series of less intense secondary bands from 360 to 440 nm, some of which are obscured by the OPE absorption. Significantly, **1**−**4** have negligible absorption at wavelengths >460 nm, resulting in good optical transparency in the visible region. There is remarkably little difference between the OPE region in the spectra of the bis(OPEs) and that of their precursors. They all have broad, almost featureless absorptions between 240 and 400 nm, with a maximum at ca. 345 nm, reflecting the conformational flexibility of the OPE chains. The shapes of the absorption spectra of **12** and **13** display the single-sided exponential broadening described for other OPEs,[13] but this effect is somewhat obscured by the intense anthracene absorbance in the bis(OPE) spectra.

Substitution of the parent OPE with electron-donating or -withdrawing groups appears to have a minimal effect on the wavelength of maximum UV absorptions, although a change in peak shape occurs as the absorbance at 340−350 nm becomes more dominant over that at 305−320 nm when strongly electron-donating or -withdrawing groups are appended. The trimeric substrates are red-shifted by 15−20 nm in comparison to their dimeric analogues as a result of increased conjugation length. Also noteworthy are the high extinction coefficients of the bis(trimers).

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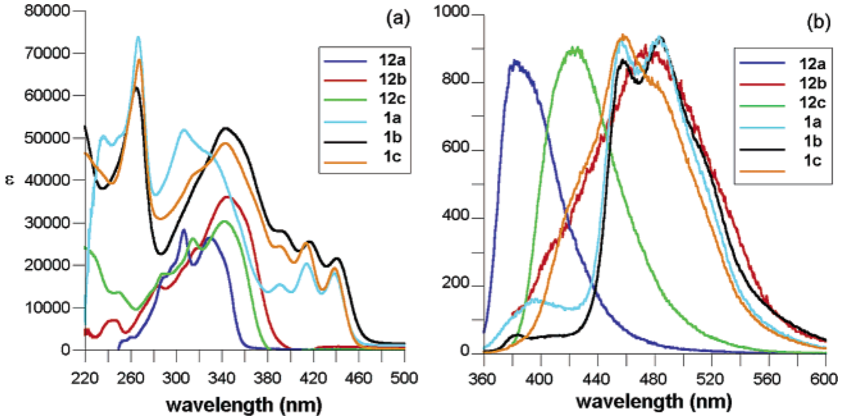


FIGURE 1. (a) UV absorption and (b) normalized fluorescence emission spectra of selected dimers and bis(dimers).

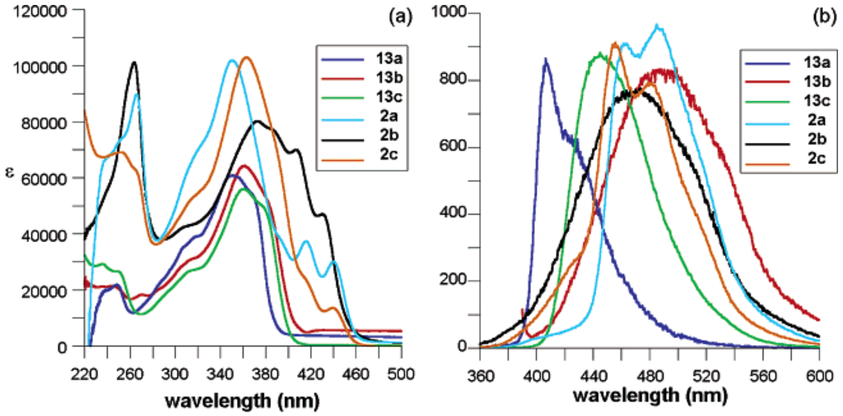
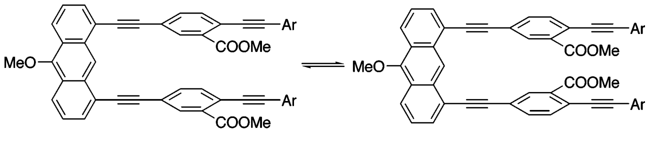


FIGURE 2. (a) UV absorption and (b) normalized fluorescence emission spectra of selected trimers and bis(trimers).

CHART 3



14 "*syn*" **15** "*anti*"

Restricting the rotational freedom of the arylalkyne groups reduces the number of available energy levels and increases effective conjugation; thus an increase in fine structure coupled with a bathochromic shift was expected for the bis(OPE) relative to the free dimer/trimer. The absence of these effects suggests the OPE chains still have significant torsional mobility in **1**−**4**, probably by flipping between "*syn*"- and "*anti*"-conformations, e.g., **14** and **15**, and that this motion happens rapidly on an NMR time scale (Chart 3). No concentration effect on the UV spectra of **1a** and **12a** was observed.

There is a stronger dependence of the fluorescence emission maxima of **12** and **13** on their substituents. Both strongly electron-donating (entries 3, 4, 7, and 10−12) and -withdrawing (entries 2 and 10) groups induce a red shift of 40−90 nm in comparison to the unsubstituted compounds (entries 1 and 9) and those bearing substituents with less influence on electronic structure (entry 6).[14] By contrast, the maxima of the bis(OPEs) all fall within a relatively narrow range (ca. 30 nm), regardless of substituents and chain length. This may suggest that inter- or intramolecular interactions between OPE chains are amplified in the excited states of **1**−**4**. It is assumed that the fluorescence of **1**−**4** arises through absorption of the OPE segments, as the fluorescence excitation spectrum of **1c** exhibited a maximum at 370 nm (Figure 3) when recorded at the emission maximum of this compound. In addition, the emission maximum was independent of the excitation wavelength used. Generally, the fluorescence spectra of bis(OPEs) displayed more vibronic fine structure than both the UV spectra and the emission spectra of

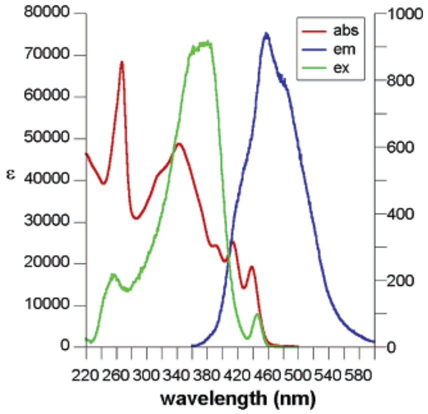


FIGURE 3. UV absorption, normalized fluorescence emission, and excitation spectra of bis(OPE) **1c**.

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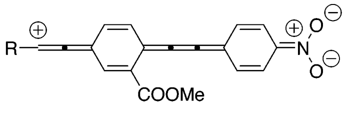
[14] Similar effects were reported for 2,7-bis(arylethynyl)-9,10-anthraquinones; see: Yang, J.; Dass, A.; Rawashdeh, A.-M. M.; Sotiriou-Leventis, C., Panzner, M. J.; Tyson, D. S.; Kinder, J. D.; Leventis, N. *Chem. Mater.* **2004**, *16*, 3457.

the dimers and trimers. This may be indicative of a more rigid and planar emitting state for the bis(OPEs).[15,16]

All compounds studied had moderately large Stokes shifts (35−138 nm), indicating a significant reordering of the surrounding solvent molecules upon excitation.[17] One explanation for this is the existence of a charge-separated excited state, such as **16**, with some quinoidal character.[13,18,19] The ester sidearms may also provide added stability for such an excited state when the OPE chains are electron rich, as shown in resonance structure **17**.

Interestingly, the emission maximum of the mono(OPE) **11** was almost unchanged from the value for the parent dimer **1c**, but the addition of a second OPE chain induced a red-shift of ca. 60 nm.



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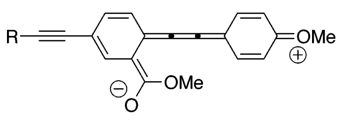

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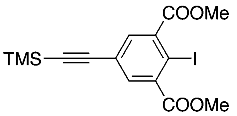

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Conclusions

In summary, several members of a new class of potential NLO materials, the bis(OPEs), were synthesized by double-palladium-catalyzed cross-coupling reactions. Spectroscopic comparisons of the bis(OPEs) with their silylated OPE precursors did not reveal any evidence of restricted rotation of the arylalkyne groups at room temperature. It may be possible to force coplanarity of the OPE strands, however, either by the use of more substituted monomer units, e.g., **18**, or through the introduction of sidearms capable of hydrogen bonding. The introduction of electron-donating and -withdrawing groups on the termini of the precursor OPEs resulted in an alteration of relative intensities, but not the wavelengths, of their UV absorptions. In contrast, substituents had a marked influence on the wavelength of fluorescence emission of these compounds. When two OPE chains are attached to an anthracene template, the UV characteristics of the parent are retained but substituent effects are less significant in their emission spectra, and are more unpredictable. In addition, the bis(OPEs) have significant optical transparency, an important characteristic for potential NLO materials.[20]

Experimental Section

Sonogashira Coupling of Terminal Alkynes to 6. A mixture of **6** (1.0 mmol), alkyne (2.2 mmol), and 1:2 Et_3N−DMF (6 mL) was degassed with a stream of N_2. $Pd(PPh_3)_4$ or $Pd(PPh_3)_2Cl_2$ (0.1 mmol) and CuI (0.1 mmol) were added, and the mixture was stirred at room temperature under N_2 for 18 h and then poured into saturated NH_4Cl (40 mL). The resulting suspension was extracted with a suitable solvent (3 × 30 mL), and the combined extracts were washed with water (5 × 30 mL) and brine (30 mL), dried (Na_2SO_4), filtered, and concentrated under vacuum.

1,8-Bis[3-(methoxycarbonyl)-4-(4-nitrophenylethynyl)phenylethynyl]-10-methoxyanthracene 1b. A mixture of **6** (0.20 g, 0.43 mmol), **5b** (0.29 g, 0.96 mmol), and 1:2 Et_3N−DMF (3 mL) was degassed with a stream of N_2. CuI (8 mg, 0.04 mmol) and $Pd(PPh_3)_2Cl_2$ (31 mg, 0.04 mmol) were added, and the mixture was stirred at 60 °C under N_2 for 18 h. After cooling, the mixture was diluted with CH_2Cl_2 (15 mL), and the precipitate was collected by filtration, washed with CH_2Cl_2 (10 mL), and dried to afford **1b** (0.10 g, 29%) as an orange solid: mp 198−207 °C dec; $C_{51}H_{30}N_2O_9Na$ requires 837.1849, found $(M + Na)^+$ 837.1836; δ_H (600 MHz, pyridine-d_5) 9.72 (1H, br s), 8.52 (2H, d, *J* 9.0), 8.44 (2H, d, *J* 1.8), 8.10−8.12 (6H, m), 7.84−7.86 (2H, m), 7.75−7.78 (4H, m), 7.64−7.67 (4H, m), 4.16 (3H, s), 3.97 (6H, s); δ_C (150 MHz, pyridine-d_5) 165.8, 154.9, 148.0, 135.7, 135.6, 135.4, 134.6, 133.4, 133.0, 132.4, 130.5, 126.3, 125.5, 125.0, 124.6, 123.6, 123.4, 121.8, 95.2, 95.1, 94.1, 91.9, 64.4, 53.0; ν_{max} 2198, 1737, 1717, 1594, 1512, 1350, 1248, 1078, 851 cm^{-1}; ESI-MS *m/z* 837 $(M + Na)^+$; UV λ_{abs} (log ϵ) 441 (4.33), 417 (4.41), 393 (4.45), 342 (4.72), 265 (4.79) nm; fluorescence λ_{em} 460, 486 nm.

1,8-Bis[3-(methoxycarbonyl)-4-(4-methoxyphenylethynyl)phenylethynyl]-10-methoxyanthracene 1c. The general procedure was followed using **6** (0.23 g, 0.49 mmol), **5c** (0.31 g, 1.08 mmol), CuI (9 mg, 0.05 mmol), and $Pd(PPh_3)_2Cl_2$ (34 mg, 0.05 mmol). After extraction with CH_2Cl_2, flash chromatography of the residue (1:2 acetone−hexane) afforded **1c** (0.16 g, 41%) as a yellow solid (R_f 0.15, 4:1 CH_2Cl_2−hexane): mp 85−97 °C dec; $C_{53}H_{36}O_7Na$ requires 807.2359, found $(M + Na)^+$ 807.2352; δ_H (200 MHz, $CDCl_3$) 9.36 (1H, br s), 8.34 (2H, dt, *J* 1.1, 8.8), 8.22 (2H, dd, *J* 0.6, 1.8), 7.82 (2H, dd, *J* 0.9, 7.0), 7.51−7.59 (4H, m), 7.45 (4H, m), 7.37 (2H, dd, *J* 0.4, 8.1), 6.73 (4H, m), 4.17 (3H, s), 3.92 (6H, s), 3.79 (6H, s); δ_C (75 MHz) 165.9, 159.9, 134.3, 133.9, 133.6, 133.5, 132.0, 131.7, 131.1, 125.0, 124.5, 124.1, 123.5, 122.4, 121.3, 119.6, 115.3, 113.9, 96.8, 94.0, 90.1, 87.2, 63.7, 55.2, 52.2; ν_{max} 2206, 1729, 1605, 1514, 1288, 1250, 1184, 1071, 1035, 926, 839 cm^{-1}; ESI-MS *m/z* 807 $(M + Na)^+$; UV λ_{abs} (log ϵ) 439 (4.28), 414 (4.40), 390 (4.39), 343 (4.69), 320 (4.63), 267 (4.83) nm; fluorescence λ_{em} 461 nm.

1,8-Bis{3-[methoxycarbonyl]-4-[3-(methoxycarbonyl)-4-(4-nitrophenylethynyl)phenylethynyl]phenylethynyl}-10-methoxyanthracene 2b. The procedure for **1b** was followed using **6** (65 mg, 0.14 mmol), **7b** (0.14 g, 0.31 mmol), CuI (3 mg, 0.01 mmol), and $Pd(PPh_3)_2Cl_2$ (10 mg, 0.01 mmol), except that the precipitated solid was rinsed with hexane (2 × 5 mL) to afford **2b** (18 mg, 11%) as an orange solid: mp 192−200 °C dec; $C_{71}H_{42}N_2O_{13}Na$ requires 1153.2585, found $(M + Na)^+$ 1153.2601; δ_H (600 MHz, pyridine-d_5) 9.55 (1H, br s), 8.43−8.46 (4H, m), 8.26−8.32 (4H, m), 8.13 (2H, dd, *J* 1.8, 7.8), 8.03 (2H, d, *J* 7.8), 7.94 (2H, dd, *J* 1.2, 7.2), 7.82−7.86 (8H, m), 7.62 (2H, dd, *J* 7.2, 9.0), 7.27−7.29 (2H, m), 4.12 (3H, s), 3.99 (6H, s), 3.97 (6H, s); ν_{max} 2198, 1737, 1591, 1520, 1342, 1243, 1073, 829 cm^{-1}; ESI-MS *m/z* 1153 $(M + Na)^+$; UV λ_{abs} (log ϵ) 430 (4.67), 407 (4.84), 373 (4.90), 264 (5.00) nm; fluorescence λ_{em} 471 nm.

1,8-Bis[3-(methoxycarbonyl)-4-E-(2-phenylethenyl)phenylethynyl]-10-methoxyanthracene 3. The general procedure was followed using **6** (66 mg, 0.14 mmol), **9b** (83 mg, 0.32 mmol), CuI (3 mg, 0.01 mmol), and $Pd(PPh_2)_2Cl_2$ (10 mg, 0.01 mmol). After extraction with CH_2Cl_2, flash chromatography of the residue (1:1 CH_2Cl_2−hexane) afforded **3** (45 mg, 44%) as a yellow solid (R_f 0.11): mp 155−167 °C dec; $C_{51}H_{36}O_5Na$ requires 751.2460, found $(M + Na)^+$ 751.2469; δ_H (200 MHz, $CDCl_3$) 9.44 (1H, br s), 8.35 (2H, br d, *J* 8.8), 8.20 (2H, d, *J* 1.5), 7.99 (2H, d, *J* 16.1), 7.83 (2H, dd, *J* 1.3, 7.0), 7.58−7.64 (4H, m), 7.53 (2H, dd, *J* 7.0, 8.8), 7.38−7.48 (6H, m), 7.20 (4H, m), 7.01 (2H, d, *J* 16.4), 4.19

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(3H, s), 3.86 (6H, s); δ_C (50 MHz, $CDCl_3$) 167.0, 153.5, 139.0, 139.0, 137.0, 134.9, 133.9, 132.5, 132.1, 130.8, 128.7, 128.6, 128.0, 127.0, 126.7, 126.2, 125.0, 124.5, 123.4, 122.0, 121.5, 119.8, 94.3, 89.2, 63.7, 52.2; ν_{max} 1721, 1440, 1243, 1188, 1072, 1036, 960 cm^{-1}; EI-MS *m/z* 728 ($M^{+\bullet}$), 713, 626, 611; UV λ_{abs} (log ϵ) 439 (4.35), 414 (4.39), 391 (4.25), 331 (4.71), 267 (4.96) nm; fluorescence λ_{em} 455, 483 nm.

1,8-Bis{3-[methoxycarbonyl]-4(*E*)-[2-(methoxycarbonyl)ethenyl]phenylethynyl}-10-methoxyanthracene 10. The general procedure was followed using **6** (94 mg, 0.20 mmol), **9a** (0.11 g, 0.45 mmol), CuI (4 mg, 0.02 mmol), and $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol). After extraction with $CHCl_2$, flash chromatography of the residue (3:7 EtOAc−hexane) afforded **10** (81 mg, 58%) as a yellow solid (R_f 0.16, 1:2 EtOAc−hexane): mp 125−140 °C dec; $C_{43}H_{32}O_9Na$ requires 715.1944, found $(M + Na)^+$ 715.1938; δ_H (200 MHz, $CDCl_3$) 9.35 (1H, br s), 8.37 (2H, d, *J* 16.0), 8.35 (2H, dt, *J* 0.9, 8.8), 8.15 (2H, d, *J* 1.6), 7.82 (2H, dd, *J* 0.9, 7.0), 7.48−7.61 (6H, m), 6.26 (2H, d, *J* 15.9), 4.17 (3H, s), 3.85 (6H, s), 3.83 (6H, s); δ_C (50 MHz, $CDCl_3$) 166.7, 166.3, 153.6, 142.4, 135.7, 134.9, 133.8, 132.0, 131.1, 130.3, 127.7, 125.0, 124.6, 124.5, 123.7, 121.4, 119.5, 107.9, 93.7, 90.4, 63.8, 52.5, 51.8; ν_{max} 1723, 1320, 1287, 1203, 1176, 1077 cm^{-1}; EI-MS *m/z* 692 ($M^{+\bullet}$), 677; UV λ_{abs} (log ϵ) 438 (4.09), 414 (4.13), 393 (3.97), 301 (4.57), 267 (4.83) nm; fluorescence λ_{em} 489, 687 nm.

1-Iodo-8-[3-(methoxycarbonyl)-4-(4-methoxyphenylethynyl)phenylethynyl]-10-methoxyanthracene 11. A mixture of **6** (0.14 g, 0.30 mmol), **5c** (0.10 g, 0.33 mmol), and 1:2 Et_3N−DMF (3 mL) was degassed with a stream of N_2. CuI (3 mg, 0.02 mmol) and $Pd(PPh_3)_2Cl_2$ (11 mg, 0.02 mmol) were added, and the mixture was stirred at room temperature under N_2 for 1 h. The solution was poured into saturated NH_4Cl (20 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The combined extracts were washed with water (5 × 15 mL) and brine (15 mL), dried (Na_2SO_2), filtered, and concentrated under vacuum. Flash chromatography of the residue (2:1 CH_2Cl_2−hexane, then 9:1) afforded **11** (77 mg, 41%) as a yellow solid (R_f 0.63, 4:1 CH_2Cl_2-hexane): mp 72−83 °C dec; $C_{34}H_{23}IO_4$ requires 622.0641, found ($M^{+\bullet}$) 622.0648; δ_H (300 MHz, $CDCl_3$) 9.15 (1H, br s), 8.46 (1H, dd, *J* 0.6, 1.8), 8.32 (1H, dt, *J* 1.0, 6.9), 8.29 (1H, dt, *J* 1.1, 7.0), 8.15 (1H, dd, *J* 1.0, 7.0), 7.84 (1H, dd, *J* 1.8, 8.0), 7.79 (1H, dd, *J* 1.0, 7.0), 7.66 (1H, dd, *J* 0.5, 8.1), 7.54 (2H, m), 7.50 (1H, dd, *J* 6.9, 8.7), 7.20 (1H, dd, *J* 7.1, 8.8), 6.91 (2H, m), 4.14 (3H, s), 4.00 (3H, s), 3.84 (3H, s); ν_{max} 2207, 1731, 1672, 1606, 1514, 1304, 1288, 1249, 1175, 1076, 1032, 834 cm^{-1}; EI-MS *m/z* 622 ($M^{+\bullet}$), 607; UV λ_{abs} (log ϵ) 430 (4.10), 406 (4.17), 356 (4.48), 265 (4.67) nm; fluorescence λ_{em} 410, 437 nm.

1-[3-(Methoxycarbonyl)-4-(4-methoxyphenylethynyl)phenylethynyl]-8-[3-(methoxycarbonyl)-4-(4-nitrophenylethynyl)phenylethynyl]-10-methoxyanthracene 4. A mixture of **11** (65 mg, 0.10 mmol), **5b** (44 mg, 0.14 mmol), and 1:2 Et_3N−DMF (3 mL) was degassed with a stream of N_2. CuI (2 mg, 0.01 mmol) and $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol) were added, and the mixture was stirred at room temperature under N_2 for 18 h. The mixture was poured into saturated NH_4Cl (20 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The combined extracts were washed with water (5 × 15 mL) and brine (15 mL), dried (Na_2SO_2), filtered, and concentrated under vacuum. Flash chromatography of the residue (1:30:19 EtOAc−CH_2Cl_2−hexane) afforded **4** (41 mg, 51%) as an orange solid (R_f 0.31): mp 187−189 °C; $C_{52}H_{33}NO_8$ requires 799.2206, found ($M^{+\bullet}$) 799.2213; δ_H (200 MHz, $CDCl_3$) 9.35 (1H, br s), 8.36 (2H, app dq, *J* 1.1, 8.6), 8.22 (2H, app dd, *J* 1.3, 5.3), 7.93 (2H, m), 7.83 (2H, dt, *J* 0.9, 7.0), 7.49−7.60 (6H, m), 7.41 (2H, m), 7.26 (2H, dd, *J* 0.6, 7.9), 6.75 (2H, m), 4.18 (3H, s), 3.93 (3H, s), 3.91 (3H, s), 3.81 (3H, s); δ_C (50 MHz, $CDCl_3$) 165.8, 165.3, 160.2, 153.6, 147.0, 134.6, 134.4, 133.8, 133.7, 133.6, 133.4, 132.4, 132.1, 131.8, 131.1, 131.0, 130.0, 125.1, 125.0, 124.6, 124.5, 124.1, 123.9, 123.8, 123.6, 123.4, 122.4, 121.3, 121.1, 119.6, 115.1, 114.0, 96.9, 94.1, 93.9, 93.8, 93.1, 91.0, 90.1, 87.2, 63.8, 55.3, 52.4, 52.2; ν_{max} 2209, 1713, 1592, 1342, 1285, 1246, 1075, 831 cm^{-1}; LSIMS *m/z* 800 ($M^{+\bullet}$), 785; UV λ_{abs} (log ϵ) 440 (4.22), 415 (4.27), 392 (4.19), 342 (4.59), 267 (4.69) nm; fluorescence λ_{em} 405, 460, 485 nm.

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Supporting Information Available: General experimental details, characterization data for compounds **1d**−**g**, **2d**,**e**, and **9a**,**b**, and reproductions of selected ^{1}H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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