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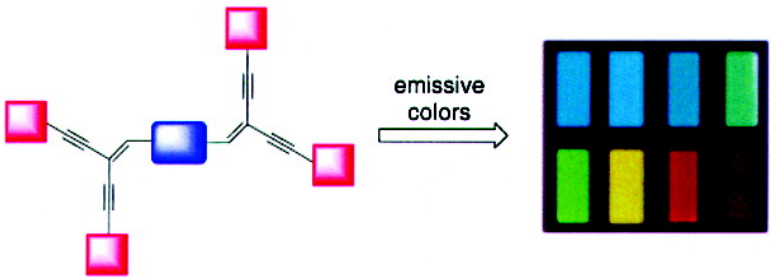

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Synthesis and Photophysical Studies of Bis-enediynes as Tunable Fluorophores

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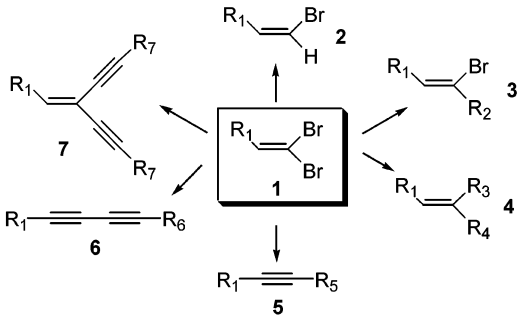
Abstract: We have synthesized a family of bis-enediynes by two complementary Pd/Cu-catalyzed Sonogashira cross-coupling methods. One is a modified Sonogashira reaction between the TMS-protected tetraalkyne **20** (or **21)** and various aromatic bromides to afford bis-enediynes **22a**−**d** and **23a**−**d** bearing different peripheral aryl units. The other, the reaction of bifunctional 1,1-dibromo-1-alkenes with phenylacetylene, afforded a series of bis-enediynes **24**−**32** bearing various core aryl groups. These chemical modifications to the core and periphery of bis-enediynes induce dramatic changes in absorption and emission spectra. Bis-enediynes **22** and **23** show a large Stokes shift of about 50−110 nm when compared to the less-conjugated bis-enediynes **20** and **21**. Absorptions and emissions of bis-enediynes **25**, **27**−**29**, and **31** were red-shifted relative to those of enediyne **35**. Substantial increases in fluorescence quantum yields are observed as a result of extending the π-conjugation. The emission wavelength of bis-enediynes was tailored from indigo blue to reddish-orange, suggesting that the color of emission can be tunable by modification of the core and/or peripheral units.

Introduction

The development of simple synthetic routes to wavelength-tunable fluorophores[1] is of great interest, with promising potential applications such as electronic and photonic devices. The ideal fluorophores should have high molar extinction coefficients, large differences in absorption and fluorescence frequencies (so-called 'Stokes shifts'), and high quantum efficiencies. Thus, it is important to synthesize efficiently classes of fluorophores that are amenable to further chemical functionalization or modification, which in turn are essential for obtaining materials with tunable optoelectronic properties.

1,1-Dibromo-1-alkenes **1**, which can be conveniently prepared by the procedure of Corey and Fuchs,[2] can be converted to (*Z*)-1-bromo-1-alkenes[3] **2**, (*Z*)-1-aryl(alkenyl)-1-bromo-1-alkenes[4] **3**, 1,1-diaryl(alkenyl)-1-alkenes[4c] **4**, 1-aryl(alkenyl)-1-alkynes[2,4c] **5**, and 1,3-diynes[5] **6** (Scheme 1). Sonogashira reactions[6] of 1,1-dibromo-1-alkenes **1**, however, have been ignored to some extent. Although there are examples of di- or tetra-ethynylethenes to be found in the literature,[7] only few reports on the synthesis of cross-conjugated mono-enediynes[8] and bis-enediynes[9] by this approach have been published. Recently, we have found it advantageous to exploit 1,1-dibromo-1-alkenes **1** as precursors for wavelength-tunable fluorophores.[9] Herein, we report syntheses of a family of cross-conjugated bis-enediynes[10] as an ideal class of tunable fluorophores through core and/or peripheral unit modifications of bis-enediynes, as well as their photophysical properties.

Scheme 1. Reactions of 1,1-Dibromo-1-alkenes **1**



(R: aliphatic or aromatic groups)

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10.1021/ja0349148 CCC: $25.00

Scheme 2. Synthesis of Bifunctional 1,1-Dibromo-1-alkenes **8**−**19**

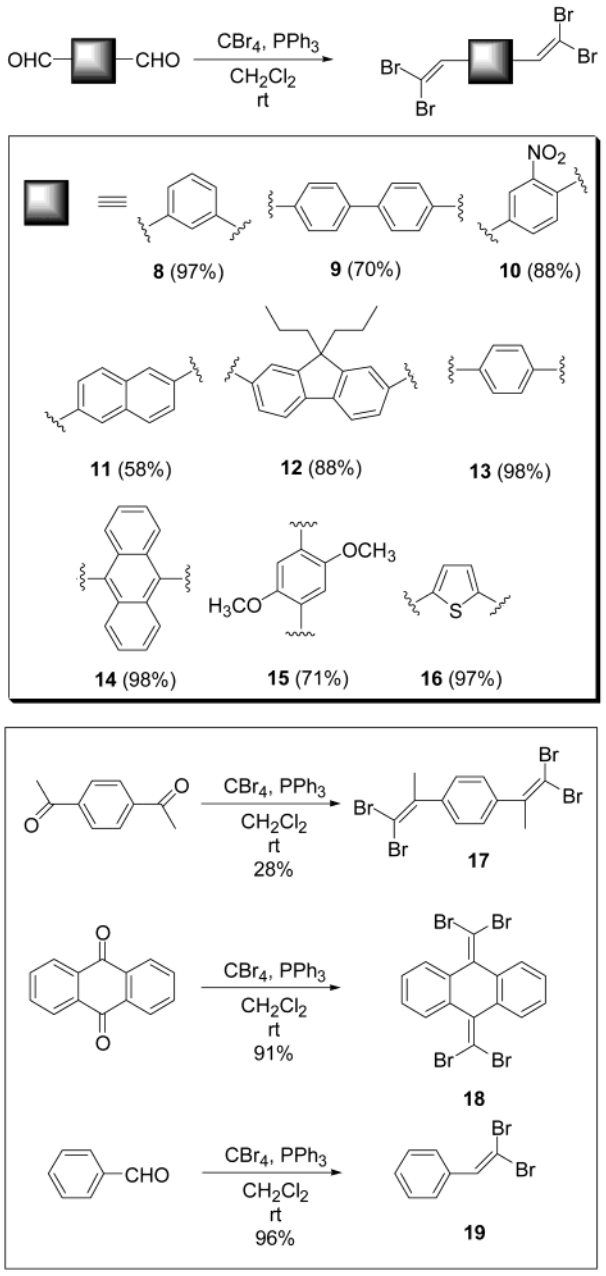


Table 1. Photophysical Data of **20**−**35** in $CHCl_3$

compd	λ_{abs}/nm[a]	ϵ/mol^{-1}cm^{-1}	λ_{em}/nm[b]	ϕ_F[c]	τ_s/ns[d]
20	412	47000	426, 463	0.03	0.6
21	458	48000	475, 503	0.01	0.3
22a	438	60000	498, 532	0.25	1.6
22b	450	45000	518, 551	0.16	0.6
22c	456	28000	533, 566	0.16	0.8
22d[e]	420	9400	472, 502	n.d.	n.d.
23a	486	51000	550, 587	0.07	0.7
23b	516	14000	577, 618	0.03	0.4
23c	524	40000	595, 628	0.03	0.5
23d[e]	522	11000	587, 612	n.d.	n.d.
24	349	49000	413, 431	0.06	0.3
25	394	86000	461, 490	0.39	0.7
26[e]	413	32000	560	n.d.	n.d.
27	418	61000	473, 498	0.49	1.1
28	422	53000	473, 501	0.31	0.6
29	416	55000	475, 506	0.35	1.2
30[e]	432	28000	n.d.	n.d.	n.d.
31	455	32000	522, 549	0.34	1.4
32	468	39000	528, 561	0.08	0.4
33	360	31000	454, 471	0.03	n.d.
34[e]	540	49000	n.d.	n.d.	n.d.
35[e]	340	23000	392	n.d.	n.d.

[a] Only the largest absorption maxima are listed. [b] Wavelength of emission maximum when excited at the absorption maximum. [c] Quantum efficiencies using fluorescein in 0.1 N NaOH as a standard, $\lambda_{ex} = 436$ nm. [d] Excited-state lifetime at the emission maximum. [e] Quantum yields were too low to be measured.

Results and Discussion

(I) Synthesis of Bifunctional 1,1-Dibromo-1-alkenes. A series of bifunctional 1,1-dibromo-1-alkenes **8**−**19** were prepared easily by the Corey and Fuchs method[2] from corresponding dialdehydes (Scheme 2).[11] 1,4-Bis(1,1-dibromo-2-methylvinyl)benzene **17**, bis(1,1-dibromovinyl)anthraquinone **18**, and mono-1,1-dibromovinylbenzene **19** were also prepared for the sake of comparison.

(II) Bis-enediynes: Modification on Peripheral Units. Two complementary methods were used for the synthesis of bis-enediynes. One is the modified Sonogashira reaction between the TMS-protected tetraalkyne **20** (or **21**)—with the liberation of the alkyne in situ using KF—and aromatic bromides (Scheme 3). This method is suitable for modifying the peripheral units of bis-enediynes. Because this approach avoids the TMS deprotection and purification steps, it is highly suitable for the coupling of unstable or volatile alkynes. Bis-enediynes **22a**−**d** and **23a**−**d** were synthesized by this method.

(III) Bis-enediynes: Modification of Core Units. The second method we used successfully for the preparation of bis-enediynes was Pd/Cu-catalyzed cross-couplings of **8**−**16** with phenylacetylene, which afforded a series of bis-enediynes **24**−**32** bearing different core aryl groups (Scheme 4). For comparison, bis-enediynes **33**, **34**, and enediyne **35** were synthesized from 1,4-bis(1,1-dibromo-2-methylvinyl)benzene **17**, bis(1,1-dibromovinyl)anthraquinone **18**, and mono-1,1-dibromovinylbenzene **19**, respectively. The structures of all bis-enediynes **20**−**34** were confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis. All of the bis-enediynes **20**−**34** are quite stable toward air and commonly used organic solvents.

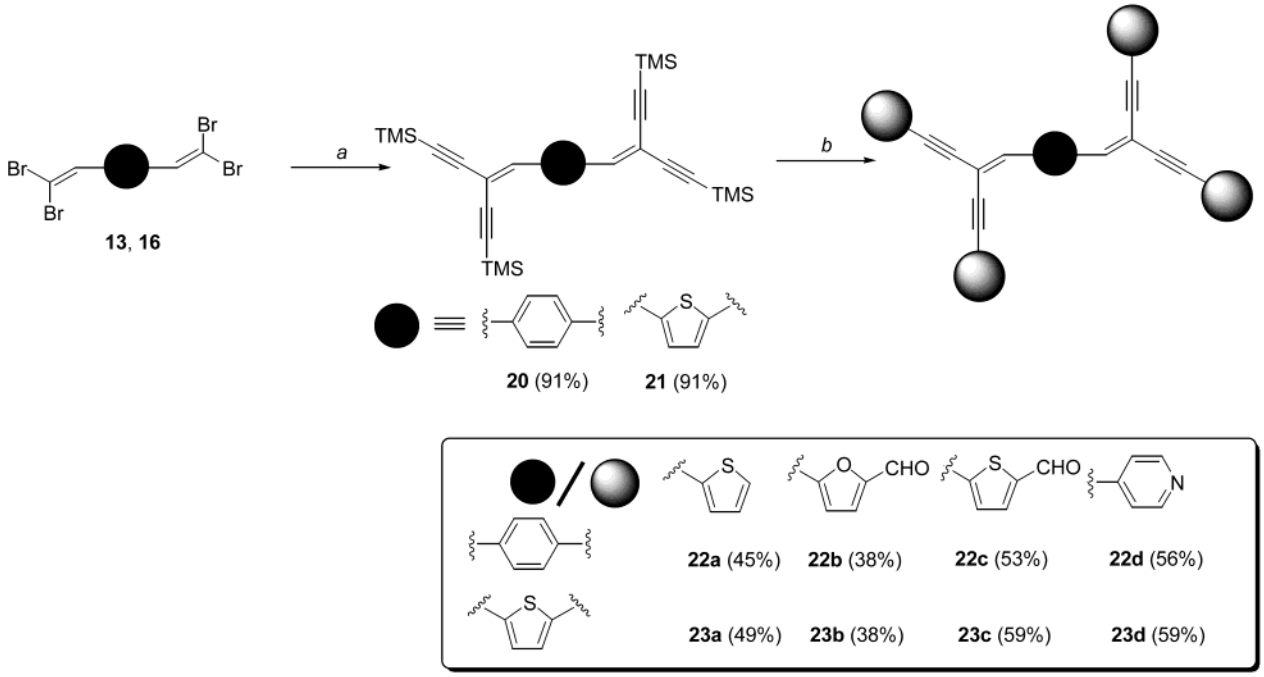
(IV) Photophysical Studies. Table 1 summarizes the photophysical properties of **20**−**35** in $CHCl_3$ solutions. The fluorescence quantum yields (ϕ_F) of fluorophores were determined in $CHCl_3$, using a 0.1-N aqueous NaOH solution of fluorescein as a standard, and the emission lifetimes (τ_s) were determined at each emission maximum and have error bars of $\pm$10%.[12]

There are some noteworthy features: (1) In the UV−visible absorption spectra, the wavelength of the absorption maxima, ascribed to $\pi-\pi^*$ transitions in the bis-enediynes, depend significantly on the nature of the core unit of the bis-enediynes. The absorption maxima of bis-enediynes **23a-23d**, which contain thiophene units as cores, show substantial red shifts relative to those of bis-enediynes **22a-22d**, which contain benzene units as cores. (2) The fluorescence spectra of almost all bis-enediynes show two strong emission bands in the visible region, with colors spanning from *the indigo blue to the reddish-orange*

(11) See Supporting Information.

(12) Parker, C. A. In *Photoluminescence of Solutions*; Elsevier: Amsterdam, 1968.

Scheme 3. Synthesis of Bis-enediynes **20**−**23**



[a] Trimethylsilylacetylene, $(PPh_3)_2PdCl_2$, CuX (CuCl for **22b** and **23b**, CuI for all others), Et_3N/MeOH, 45−50 °C; [b] ArBr, KF, $(PPh_3)_2PdCl_2$, CuI, Et_2NH/MeOH, 45−50 °C for **22a** and **23a**, and Et_3N/MeOH, 45−50 °C for all others.

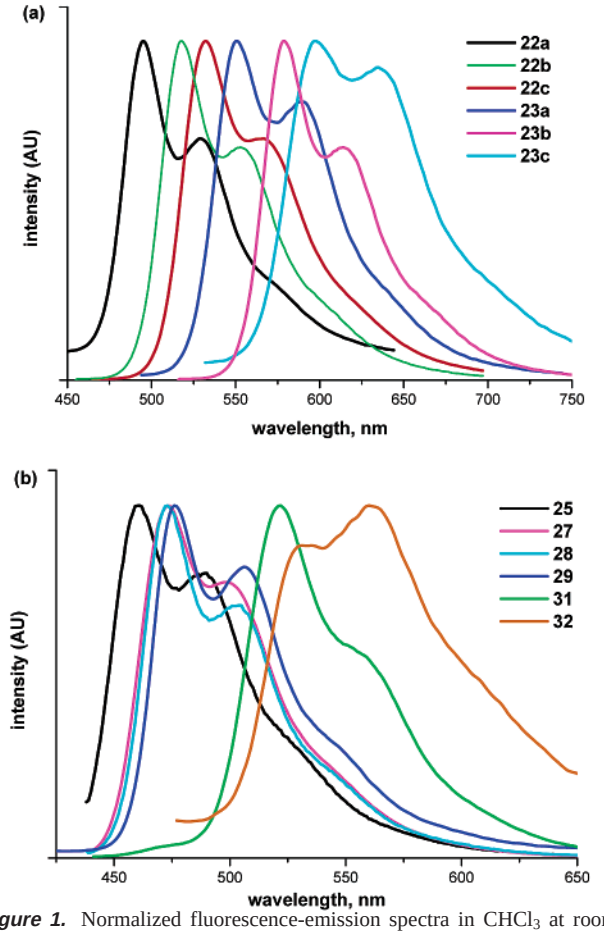


Figure 1. Normalized fluorescence-emission spectra in $CHCl_3$ at room temperature: (a) peripheral unit-modified bis-enediynes and (b) core unit-modified bis-enediynes. Emission spectra were obtained upon excitation at the absorption maxima.

region. (3) Bis-enediynes **22** and **23** show large Stokes shifts of ca. 50−110 nm relative to those of less-conjugated bis-

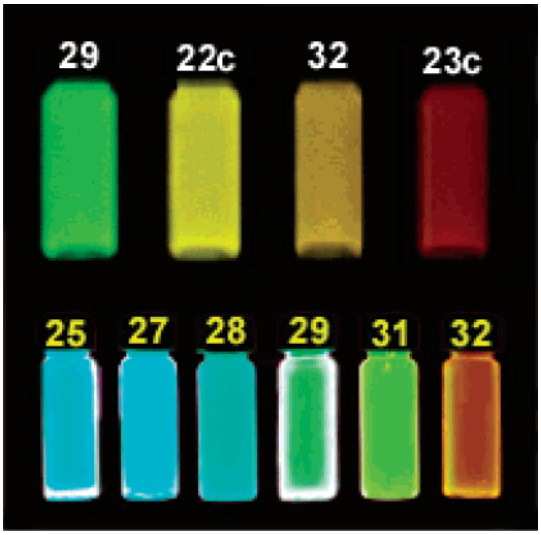
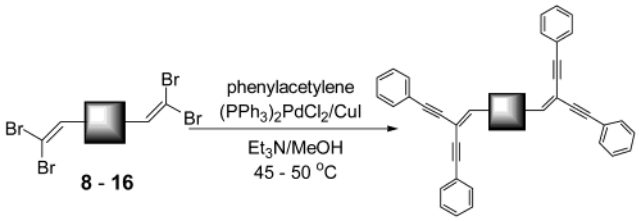
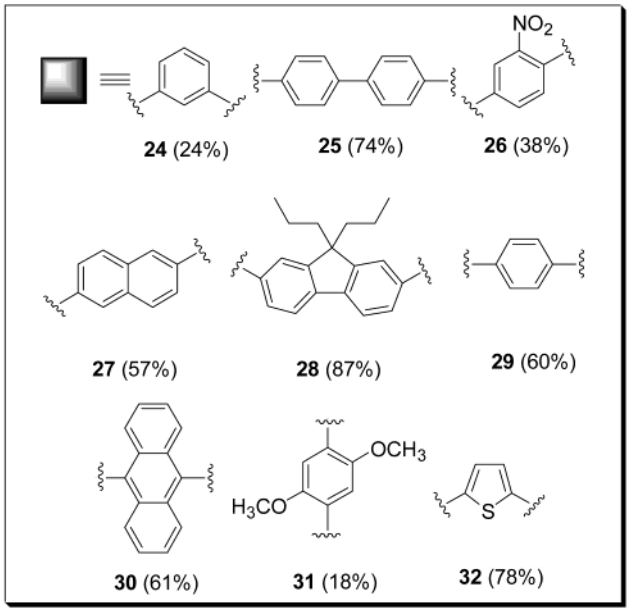


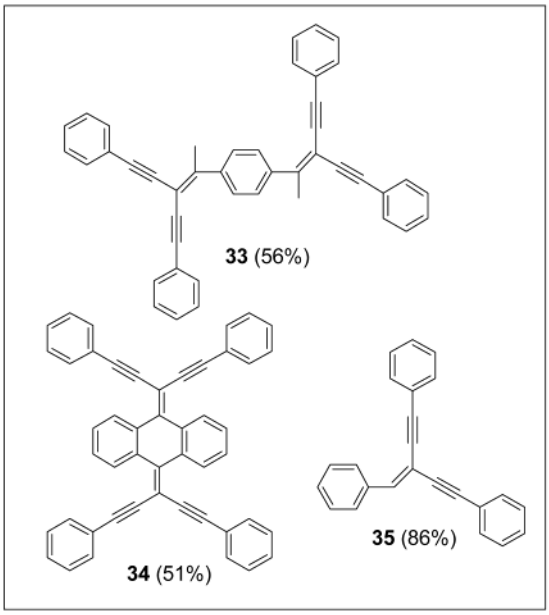
Figure 2. Photograph of the emissive behavior of bis-enediynes upon irradiation with light at 365 nm.

enediynes **20** and **21**. (4) Absorptions and emissions of bis-enediynes **25**, **27**−**29**, and **31** were red-shifted relative to those of enediyne **35**, and a substantial increase in fluorescence quantum yield is observed because of the extension of π conjugation. Similarly, the wavelengths of the absorption and emission maxima of **24**, which lacks extensive π conjugation because of the chosen *meta* linkage, are shorter than those of **25**, **27**−**29**, and **31**. (5) The presence of an electron-accepting substituent in the core moiety of bis-enediyne **26** diminishes its fluorescence yield drastically when compared with **29**. The incorporation of electron donors, however, in the core moiety in bis-enediyne **31** does not affect its fluorescence quantum yield or emission lifetime. Moreover, these units result in significant red shifts in the absorption and emission wavelength maxima of **31**, and a slight increase in emission lifetime, compared to

Scheme 4. Synthesis of **24**−**35**







those of bis-enediyne **29**. (6) As seen in the data for bis-enediyne **33**, methylation at the 2-position of the 1,1-dibromo-olefin results in a decrease in fluorescence intensity. (7) Bis-enediynes **25** and **27**−**29** display similar bright-blue emissions and reasonably good quantum yields. In particular, bis-enediynes **25** and **27** have the highest quantum efficiencies (39% for **25**; 49% for **27**) and molar extinction coefficients (86 000 $mol^{-1}cm^{-1}$ for **25**; 61 000 $mol^{-1}cm^{-1}$ for **27**) among all the fluorophores in this study. Apparently, increasing the length of conjugation in the π system increases the quantum yield of fluorescence. On the other hand, substantial red shifts are observed in the absorption maxima of bis-enediynes **30** and **34**, which have more-highly π-conjugated core units, relative to those of bis-enediynes **25** and **27**−**29**. The fluorescence of bis-enediynes **30** and **34** is quenched, however, even at low concentrations, because of intermolecular stacking interactions. We observed red shifts in the absorption maxima of bis-enediynes **30** and **34** in $CHCl_3$ as their concentrations increased, which indicates that **30** and **34** self-associate.[8b,13] (8) The fluorescence lifetimes of bis-enediynes are on the order of nanoseconds (ns). Bis-enediynes **22a**, **29**, and **31**, which contain benzene-based core units, have higher fluorescence lifetimes (1.2−1.6 ns) than the other bis-enediynes.

These features suggest that modifying the core and periphery units of bis-enediynes provides novel tunable fluorophores with high quantum efficiencies. Figure 1 displays the normalized fluorescence spectra and emission patterns of representative bis-enediynes in $CHCl_3$ under irradiation at their absorption maxima. The dramatic range of emissions of representative bis-enediynes can be visualized in Figure 2.

Conclusions

We have prepared a series of bis-enediynes by two complementary Pd/Cu-catalyzed cross-coupling methods: modified Sonogashira reactions between TMS-protected tetraalkynes and various aromatic bromides allowed modifications to the peripheral units, whereas Sonogashira reactions of bifunctional 1,1-dibromo-1-alkenes with phenylacetylene allowed modifications of the core units. These chemical modifications in the core and periphery of bis-enediynes induce dramatic changes in their absorption and emission spectra, with the fluorescence colors spanning the regions from indigo blue to reddish-orange. These results demonstrate that core and side-unit modifications of bis-enediynes are efficient synthetic strategies for preparing tunable fluorophores. A deeper understanding of how the photophysical properties relate to chemical structures may allow for the design of ideal organic materials for the preparation of photonic devices.

Experimental Section

General. All commercially available chemicals were used without further purification and solvents were carefully dried and distilled prior to use. All reactions were carried out with dry glassware under argon atmospheres. Analytical TLC was carried out on Merck 60 F_{254} silica gel plate and column chromatography was performed on Merck 60 silica gel (230−400 mesh). Melting points were determined on an Electrothermal IA 9000 series melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Bruker Vector 22 spectrometer. ^1H and ^{13}C NMR spectra were taken on a Bruker NMR spectrometer (Aspect 300 MHz). FAB mass spectra were measured on a JEOL four sector tandem mass spectrometer (JMS−HX/HX110A). Elemental analyses were measured by the Center for Integrated Molecular Systems (CIMS), POSTECH, Korea. Ultraviolet (UV) spectra were obtained on an HP 8452A diode array spectrometer using 10 mm path quarts cell versus a pure-solvent reference. Fluorescence (FL) spectra were obtained on a PTI model D-104 microscope photometer. The syntheses of dialdehyde compounds, 1,1-dibromo-1-alkenes **8**, **18**, and **19** have already been described.[14]

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General Procedure for the Synthesis of Bifunctional 1,1-Dibromo-1-alkenes: The synthesis of **13** is representative: Terephthaldicarboxaldehyde (584 mg, 4.35 mmol) was added to a solution of CBr_4 (5.78 g, 17.4 mmol) and PPh_3 (9.14 g, 34.8 mmol) in CH_2Cl_2 (80 mL). After stirring at room temperature for 1 h, the solution was extracted with H_2O and dried. Column chromatography (SiO_2; hexane) gave **13** (1.90 g, 98%) as a solid.

4,4′-Bis(2,2-dibromoethenyl)biphenyl (9). Column chromatography (SiO_2; hexane), yield: 70%. M.p. 129−131 °C; IR (film): 3039, 1601, 1493, 1399, 1289, 1214, 1142, 863, 807, 761 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.76−7.59 (m, 8H, ArH), 7.52 (s, 2H, C═CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.2, 136.3, 134.5, 128.9, 126.9, 89.7.

1,4-Bis(2,2-dibromoethenyl)-2-nitrobenzene (10). Column chromatography (SiO_2; hexane/CH_2Cl_2, 30:1), yield: 88%. M.p. 78−79 °C; IR (film): 3029, 1597, 1527, 1488, 1401, 1350, 1260, 905, 884, 842, 800, 765 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.33 (d, 1H, J = 1.7 Hz, ArH), 7.82 (dd, 1H, J = 8.1, 1.8 Hz, ArH), 7.74 (s, 1H, C═CH), 7.63 (d, 1H, J = 8.1 Hz, ArH), 7.51 (s, 1H, C═CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.6, 136.6, 133.9, 133.4, 132.9, 131.7, 124.5, 124.4, 93.8, 93.8.

2,6-Bis(2,2-dibromoethenyl)naphthalene (11). Column chromatography (SiO_2; hexane/CH_2Cl_2, 20:1), yield: 58%. M.p. 154−156 °C; IR (film): 3041, 1650, 1514, 1462, 1264, 902, 836, 759 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.99 (s, 2H, ArH), 7.83 (d, 2H, J = 8.5 Hz, ArH), 7.64 (d, 2H, J = 8.5 Hz, ArH), 7.63 (s, 2H, C═CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.7, 133.6, 132.6, 128.4, 127.8, 126.4, 90.4.

2,7-Bis(2,2-dibromoethenyl)-9,9-dipropylfluorene (12). Column chromatography (SiO_2; hexane), yield: 88%. M.p. 99−100 °C; IR (film): 3044, 2955, 2869, 1647, 1462, 1267, 1007, 900, 820, 755, 722 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.68 (d, 2H, J = 7.9 Hz, ArH), 7.58 (s, 2H, ArH), 7.57 (s, 2H, C═CH), 7.52 (d, 2H, J = 7.9 Hz, ArH), 1.96 (t, 4H, J = 5.9 Hz, CCH_2), 0.69−0.65 (m, 10H, CH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.2, 140.8, 137.2, 134.3, 127.4, 123.0, 119.8, 89.0, 55.4, 17.2, 14.5.

1,4-Bis(2,2-dibromoethenyl)benzene (13). Column chromatography (SiO_2; hexane), yield: 98%. M.p. 98−99 °C; IR (film): 3057, 1593, 1405, 1262, 1112, 881, 835, 739 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.54 (s, 4H, ArH), 7.43 (s, 2H, C═CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.1, 135.2, 128.4, 90.3.

9,10-Bis(2,2-dibromoethenyl)anthracene (14). Column chromatography (SiO_2; hexane), yield: 98%. M.p. 214−216 °C; IR (film): 3064, 1646, 1517, 1442, 1374, 1245, 1027, 861, 803, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.14−8.08 (m, 6H, ArH and C═CH), 7.61−7.58 (m, 4H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.3, 131.5, 128.3, 126.4, 125.9, 95.7.

1,4-Bis(2,2-dibromoethenyl)-2,5-dimethoxybenzene (15). Column chromatography (SiO_2; hexane/EtOAc, 20:1), yield: 71%. M.p. 191−192 °C; IR (film): 3041, 1638, 1490, 1398, 1301, 1253, 1206, 1116, 1038, 907, 866, 835, 795 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.62 (s, 2H, ArH), 7.33 (s, 2H, C═CH), 3.82 (s, 6H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.2, 132.1, 125.0, 111.3, 90.1, 56.2.

2,5-Bis(2,2-dibromoethenyl)thiophene (16). Column chromatography (SiO_2; hexane), yield: 97%. M.p. 126−128 °C; IR (film): 3057, 1650, 1513, 1460, 1204, 1058, 852, 794, 742 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.57 (s, 2H, ArH), 7.13 (s, 2H, C═CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.0, 130.7, 129.3, 88.3.

1,4-Bis(2,2-dibromo-1-methylethenyl)benzene (17). Column chromatography (SiO_2; hexane), yield: 28%. M.p. 117−118 °C; IR (film): 3051, 2915, 1597, 1497, 1432, 1214, 1077, 1017, 840, 812, 749 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.23 (s, 4H, ArH), 2.22 (s, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.5, 141.3, 127.5, 87.9, 26.1.

General Procedure for the Synthesis of Bis-enediynes: Procedure A. The synthesis of **29** is representative: $(PPh_3)_2PdCl_2$ (76.0 mg, 0.108 mmol) and CuI (21.0 mg, 0.108 mmol) were added to a solution of **13** (322 mg, 0.722 mmol) and phenylacetylene (1.2 mL, 11.6 mmol) in Et_3N (2 mL) and MeOH (8 mL). Argon was bubbled through the mixture for 2 min, the mixture was subjected 10 times to a pump/purge cycle, and then it was stirred at 45−50 °C for 3 h. After evaporation of solvent in vacuo, the residue was subjected to chromatography on a silica gel column with hexane as eluent to give **29** (299 mg, 60%). Recrystallization from $CHCl_3$/MeOH (1:1) gave pure **29**.

Procedure B. The synthesis of **22a** is representative: A mixture of **20** (111 mg, 0.216 mmol), 2-bromothiophene (0.3 mL, 3.10 mmol), KF (141 mg, 2.51 mmol), $(PPh_3)_2PdCl_2$ (44 mg, 0.0627 mmol), and of CuI (12 mg, 0.063 mmol) was dissolved in Et_2NH (25 mL) and MeOH (6.3 mL). Argon was bubbled through the mixture for 2 min, the mixture was subjected 10 times to a pump/purge cycle, and then it was stirred at 45−50 °C for 4 h. The solvent was evaporated and column chromatography (SiO_2; hexane/EtOAc, 20:1) yielded of **22a** (54.5 mg, 45%) as a solid. Recrystallization from $CHCl_3$/MeOH (1:1) gave pure **22a**.

1,4-Bis[4-trimethylsilyl-2-(trimethylsilylethynyl)but-1-en-3-ynyl]benzene (20). Prepared according to Procedure A. Column chromatography (SiO_2; hexane), yield: 91%. M.p. 118−120 °C; IR (film): 3039, 2960, 2900, 2148, 1613, 1512, 1460, 1413, 1364, 1303, 1250, 1175, 918, 846, 756 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.86 (s, 4H, ArH), 7.04 (s, 2H, C═CH), 0.27 and 0.24 (2 s, 36H, $SiCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.1, 136.2, 128.9, 104.2, 103.8, 102.2, 101.7, 94.2, −0.2, −0.3; MS (FAB) m/z 514.3 [M^+]; Anal. Calcd. for $C_{30}H_{42}Si_4 \cdot H_2O$: C, 67.60; H, 8.32. Found: C, 67.30; H, 8.19.

1,4-Bis[4-trimethylsilyl-2-(trimethylsilylethynyl)but-1-en-3-ynyl]thiophene (21). Prepared according to procedure A. Column chromatography (SiO_2; hexane), yield: 91%. M.p. 146−148 °C; IR (film): 3031, 2960, 2900, 2068, 1601, 1410, 1360, 1302, 1250, 1174, 917, 845, 758 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.62 (s, 2H, ArH), 7.07 (s, 2H, C═CH), 0.26

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and 0.19 (2 s, 36H, $SiCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.4, 136.8, 130.0, 104.9, 103.7, 102.0, 101.9, 95.4, −0.2, −0.4; MS (FAB) *m/z* 520.2 [M^+]; Anal. Calcd. for $C_{28}H_{40}S_1Si_4$: C, 64.55; H, 7.74. Found: C, 64.20; H, 7.99.

1,4-Bis[4-(2-thienyl)-2-(2-thienylethynyl)but-1-en-3-ynyl]benzene (22a). Prepared according to procedure B. Column chromatography (SiO_2; hexane/EtOAc, 20:1), yield: 45%. M.p. 190−191 °C; IR (film): 3051, 2188, 1631, 1513, 1460, 1376, 1265, 1209, 1096, 1026, 844, 749, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.92 (s, 4H, ArH), 7.33−7.29 (m, 8H, $Ar_{Th}H$), 7.11 (s, 2H, C═CH), 7.03−6.99 (m, 4H, $Ar_{Th}H$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.1, 136.4, 132.7, 132.5, 129.1, 128.4, 127.8, 127.3, 127.2, 122.7, 103.4, 92.5, 90.7, 89.2, 82.7; MS (FAB) *m/z* 553.9 [M^+]; Anal. Calcd. for $C_{34}H_{18}S_4$: C, 73.61; H, 3.27. Found: C, 73.95; H, 3.13.

1,4-Bis[4-(5-formyl-2-furanyl)-2-[(5-formyl-2-furanyl)ethynyl]but-1-en-3-ynyl]benzene (22b). Prepared according to procedure B. Column chromatography (SiO_2; hexane/EtOAc, 1:1), yield: 38%. M.p. > 131 °C dec; IR (film): 3038, 2200, 1674, 1560, 1503, 1388, 1273, 1200, 1118, 1022, 966, 804, 753 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.66 (s, 4H, CHO), 7.96 (s, 4H, ArH), 7.31−7.25 (m, 10H, $Ar_{Fu}H$ and C═CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.2, 153.0, 152.8, 145.6, 141.1, 136.4, 129.7, 125.9, 121.3, 118.7, 118.0, 101.4, 94.6, 92.2, 87.2, 85.3; Anal. Calcd. for $C_{38}H_{18}O_8$: C, 75.75; H, 3.01. Found: C, 75.52; H, 3.00.

1,4-Bis[4-(5-formyl-2-thienyl)-2-[(5-formyl-2-thienyl)ethynyl]but-1-en-3-ynyl]benzene (22c). Prepared according to procedure B. Column chromatography (SiO_2; hexane/EtOAc, 1:1), yield: 53%. M.p. > 146 °C dec; IR (film): 3063, 2207, 1673, 1531, 1443, 1400, 1256, 1167, 1123, 1087, 1026, 797, 749 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.88 (s, 4H, CHO), 7.93 (s, 4H, ArH), 7.70 (br d, 4H, $Ar_{Th}H$), 7.38 (br d, 4H, $Ar_{Th}H$), 7.24 (s, 2H, C═CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.4, 182.3, 145.1, 144.7, 144.5, 136.5, 136.2, 135.9, 133.5, 133.2, 131.1, 129.5, 128.2, 102.6, 96.2, 94.0, 88.7, 82.7; MS (FAB) *m/z* 669.9 [M + H]$^+$; Anal. Calcd. for $C_{38}H_{18}O_4S_4 \cdot H_2O$: C, 66.45; H, 2.93. Found: C, 66.10; H, 2.64.

1,4-Bis[4-(4-pyridyl)-2-(4-pyridylethynyl)but-1-en-3-ynyl]benzene (22d). Prepared according to procedure B. Column chromatography (SiO_2; EtOAc/MeOH, 10:1), yield: 56%. M.p. > 380 °C dec; IR (film): 3041, 2201, 1646, 1555, 1473, 1394, 1172, 1075, 1034, 810 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.60 (br d, 8H, J = 4.7 Hz, $Ar_{Py}H$), 7.94 (s, 4H, ArH), 7.39−7.30 (m, 8H, $Ar_{Py}H$), 7.27 (s, 2H, C═CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.9, 149.8, 145.1, 136.4, 130.6, 130.4, 129.4, 125.5, 125.3, 120.9, 95.3, 92.6, 92.3, 90.3; MS (FAB) *m/z* 535.0 [M + H]$^+$; Anal. Calcd. for $C_{38}H_{22}N_4 \cdot 0.5H_2O$: C, 83.96; H, 4.26; N, 10.30. Found: C, 84.08; H, 4.09; N, 10.23.

2,5-Bis[4-(2-thienyl)-2-(2-thienylethynyl)but-1-en-3-ynyl]thiophene (23a). Prepared according to procedure B. Column chromatography (SiO_2; hexane/EtOAc, 10:1), yield: 49%. M.p. > 126 °C dec; IR (film): 3052, 2181, 1649, 1555, 1514, 1461, 1217, 832, 768, 701 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.35 (s, 2H, ArH), 7.25−7.20 (m, 10H, ArH and C═CH), 6.96 (t, 2H, J = 4.3 Hz, ArH), 6.84 (t, 2H, J = 4.3 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.1, 135.3, 132.6, 132.4, 130.7, 128.5, 127.8, 127.2, 122.8, 122.3, 101.2, 92.3, 92.0, 91.0, 83.7; MS (FAB) *m/z* 559.8 [M^+]; Anal. Calcd. for $C_{32}H_{16}S_5$: C, 68.54; H, 2.88. Found: C, 68.54; H, 3.03.

2,5-Bis[4-(5-formyl-2-furanyl)-2-[(5-formyl-2-furanyl)ethynyl]but-1-en-3-ynyl]thiophene (23b). Prepared according to procedure B. Column chromatography (SiO_2; hexane/EtOAc, 3:2), yield: 38%. M.p. > 133 °C dec; IR (film): 3046, 2192, 1728, 1675, 1504, 1388, 1270, 1023, 967, 801, 746 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.63 (s, 2H, CHO), 9.58 (s, 2H, CHO), 7.55−7.51 (2 d, 8H, J = 3.9 Hz, $Ar_{Fu}H$), 7.45 (s, 2H, $Ar_{Th}H$), 7.27 (s, 2H, C═CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.2 (d), 152.8, 138.7, 134.9, 132.9, 130.9, 130.4, 128.8, 128.0, 121.2, 118.4, 118.0, 101.2, 96.3, 93.1, 87.5, 85.8; MS (FAB) *m/z* 608.9 [M + H]$^+$; Anal. Calcd. for $C_{36}H_{16}O_8S_1$: C, 71.05; H, 2.65. Found: C, 71.28; H, 2.68.

2,5-Bis[4-(5-formyl-2-thienyl)-2-[(5-formyl-2-thienyl)ethynyl]but-1-en-3-ynyl]thiophene (23c). Prepared according to procedure B. Column chromatography (SiO_2; hexane/EtOAc, 1:1), yield: 59%. M.p. > 88 °C dec; IR (film): 3053, 2188, 1708, 1513, 1435, 1278, 1161, 1119, 832, 751 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.87 (s, 2H, CHO), 9.78 (s, 2H, CHO), 7.67 (d, 2H, J = 3.9 Hz, $Ar_{Th}H$), 7.47 (d, 2H, J = 3.9 Hz, $Ar_{Th}H$), 7.40 (br d, 4H, $Ar_{Th}H$), 7.34 (d, 2H, J = 3.9 Hz, $Ar_{Th}H$), 7.25 (s, 2H, C═CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.3, 182.2, 145.1, 144.5, 142.8, 138.0, 135.9, 135.7, 133.2, 132.5, 131.7, 131.1, 102.0, 100.4, 95.9, 94.6, 91.3; MS (FAB) *m/z* 672.9 [M + H]$^+$; Anal. Calcd. for $C_{36}H_{16}O_4S_5$: C, 64.26; H, 2.40. Found: C, 63.89; H, 2.27.

2,5-Bis[4-(4-pyridyl)-2-(4-pyridylethynyl)but-1-en-3-ynyl]thiophene (23d). Prepared according to procedure B. Column chromatography (SiO_2; EtOAc/MeOH, 10:1), yield: 59%. M.p. 246−249 °C; IR (film): 3060, 2210, 1590, 1476, 1397, 1253, 1036, 884, 821, 741 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.49 (d, 4H, J = 4.7 Hz, $Ar_{Py}H$), 8.32 (d, 4H, J = 4.9 Hz, $Ar_{Py}H$), 7.35 (s, 2H, $Ar_{Th}H$), 7.29 (s, 2H, C═CH), 7.26 (d, 4H, J = 5.7 Hz, $Ar_{Py}H$), 7.25 (d, 4H, J = 5.6 Hz, $Ar_{Py}H$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.9 (d), 142.3, 138.7, 132.3, 130.4, 129.7, 125.2, 124.7, 100.2, 95.0, 92.1, 91.8, 90.6; MS (FAB) *m/z* 540.0 [M^+]; Anal. Calcd. for $C_{36}H_{20}N_4S_1$: C, 79.98; H, 3.73; N, 10.36. Found: C, 79.78; H, 3.85; N, 10.21.

1,3-Bis[4-phenyl-2-(phenylethynyl)but-1-en-3-ynyl]benzene (24). Prepared according to procedure A. Column chromatography (SiO_2; hexane/CH_2Cl_2, 30:1), yield: 24%. M.p. 95−97 °C; IR (film): 3054, 2196, 1644, 1489, 1442, 1379, 1289, 1023, 896, 819, 751 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.39 (s, 1H, ArH), 8.04 (dd, 2H, J = 7.9, 1.4 Hz, ArH), 7.59−7.55 (m, 9H, ArH), 7.40−7.37 (m, 12H, ArH), 7.21 (s, 2H, C═CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.6, 135.9, 131.7, 130.3, 129.2, 128.8, 128.5, 128.4, 128.3, 128.0, 126.6, 122.9, 122.7, 104.1, 94.9, 89.0, 88.6, 86.8; MS (FAB) *m/z* 530.0 [M^+].

4,4′-Bis[4-phenyl-2-(phenylethynyl)but-1-en-3-ynyl]-1,1′-biphenyl (25). Prepared according to procedure A. Column chromatography (SiO_2; hexane/CH_2Cl_2, 3:1), yield: 74%. M.p. 133−134 °C; IR (film): 3058, 2200, 1600, 1489, 1443, 1277, 1219, 1001, 887, 813, 754 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.08 (2 d, 4H, J = 8.4 Hz, ArH), 7.72 (d, 4H, J = 8.4 Hz, ArH), 7.63−7.57 (m, 8H, ArH), 7.44−7.37 (m, 12H, ArH), 7.23 (s, 2H, C═CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.5, 140.7, 135.2, 131.7, 131.7, 129.6, 128.8, 128.5, 128.3, 128.0, 126.8, 122.9, 122.8, 103.4, 95.0, 89.3, 88.7, 87.1; MS (FAB) *m/z* 606.2 [M^+]; Anal. Calcd. for $C_{48}H_{30}$: C, 95.02; H, 4.98. Found: C, 94.76; H, 5.03.

1,4-Bis[4-phenyl-2-(phenylethynyl)but-1-en-3-ynyl]-2-nitrobenzene (26). Prepared according to procedure A. Column chromatography (SiO_2; hexane/EtOAc, 30:1), yield: 38%. M.p. 136−137 °C; IR (film): 3061, 2196, 1645, 1601, 1528, 1490, 1344, 1098, 908, 876, 824, 753 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.96 (s, 1H, $Ar_{NO2}H$), 8.37 (d, 1H, J = 8.3 Hz, $Ar_{NO2}H$), 8.00 (d, 1H, J = 8.4 Hz, $Ar_{NO2}H$), 7.64−7.55 (m, 8H, ArH), 7.45−7.30 (m, 13H, ArH and C═CH), 7.16 (s, 1H, C═CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.9, 138.9, 136.9, 132.5, 131.9, 131.8, 131.7, 130.7, 129.3, 129.0, 128.8, 128.5, 128.4, 128.1, 124.1, 122.5, 122.2, 122.0, 108.1, 106.8; MS (FAB) m/z 575.1 [M^+]; Anal. Calcd. for $C_{42}H_{25}N_1O_2$: C, 87.63; H, 4.38; N, 2.43. Found: C, 87.55; H, 4.29; N, 2.27.

2,6-Bis[4-phenyl-2-(phenylethynyl)but-1-en-3-ynyl]naphthalene (27). Prepared according to procedure A. Column chromatography (SiO_2; hexane/EtOAc, 25:1), yield: 57%. M.p. 166−168 °C; IR (film): 3049, 2198, 1597, 1538, 1489, 1458, 1216, 1025, 907, 811, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.39 (s, 2H, $Ar_{naph}H$), 8.13 (dd, 2H, J = 8.6, 1.0 Hz, $Ar_{naph}H$), 7.84 (d, 2H, J = 8.6 Hz, $Ar_{naph}H$), 7.63−7.55 (m, 8H, ArH), 7.42−7.35 (m, 12H, ArH), 7.32 (s, 2H, C═CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.8, 134.3, 133.2, 131.7, 131.6, 128.8, 128.7, 128.5, 128.3, 128.0, 127.8, 126.7, 126.5, 122.9, 122.8, 103.8, 95.2, 89.4, 89.0, 87.3; MS (FAB) m/z 580.2 [M^+]; Anal. Calcd. for $C_{46}H_{28}$: C, 95.14; H, 4.86. Found: C, 94.88; H, 4.97.

2,7-Bis[4-phenyl-2-(phenylethynyl)but-1-en-3-ynyl]-9,9-dipropylfluorene (28). Prepared according to procedure A. Column chromatography (SiO_2; hexane/CH_2Cl_2, 10:1), yield: 87%. M.p. 96−98 °C; IR (film): 3042, 2957, 2869, 2206, 1600, 1490, 1456, 1216, 1171, 1098, 1025, 906, 818, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.11 (s, 2H, ArH), 7.95 (d, 2H, J = 7.9 Hz, ArH), 7.77 (d, 2H, J = 8.0 Hz, ArH), 7.67−7.60 (m, 8H, ArH), 7.45−7.39 (m, 12H, ArH), 7.33 (s, 2H, C═CH), 1.97 (t, 4H, J = 3.9 Hz, CCH_2), 0.75−0.66 (m, 10H, CH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.6, 143.7 (d), 141.6, 135.1, 131.8, 131.5, 128.8, 128.3, 128.0, 123.3, 123.0, 123.0, 122.9, 102.4, 95.0, 89.6, 88.5, 87.3, 42.6, 29.7, 17.2, 14.3; MS (FAB) m/z 702.2 [M^+]; Anal. Calcd. for $C_{55}H_{42}$: C, 93.98; H, 6.02. Found: C, 93.61; H, 6.18.

1,4-Bis[4-phenyl-2-(phenylethynyl)but-1-en-3-ynyl]benzene (29). Prepared according to procedure A. Column chromatography (SiO_2; hexane), yield: 60%. M.p. 182−185 °C; IR (film): 3062, 2195, 1599, 1489, 1442, 1287, 1069, 1024, 895, 817, 753 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.98 (s, 4H, ArH), 7.55−7.52 (m, 8H, ArH), 7.38 (m, 12H, ArH), 7.15 (s, 2H, C═CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.2, 136.5, 131.7, 131.6, 129.0, 128.8, 128.5, 128.3, 122.9, 122.8, 104.0, 95.4, 89.4, 89.1, 87.2; MS (FAB) m/z 530.2 [M^+]; Anal. Calcd. for $C_{42}H_{26}\cdot 0.5H_2O$: C, 93.48; H, 5.04. Found: C, 93.44; H, 4.87.

9,10-Bis[4-phenyl-2-(phenylethynyl)but-1-en-3-ynyl]anthracene (30). Prepared according to procedure A. Column chromatography (SiO_2; hexane/CH_2Cl_2, 6:1), yield: 61%. M.p. 177−179 °C; IR (film): 3063, 2202, 1650, 1490, 1444, 1372, 1270, 1101, 1025, 912, 802, 753 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.35 (2 d, 4H, J = 6.8 Hz, ArH), 8.16 (s, 2H, C═CH), 7.67 (2 d, 4H, J = 7.7 Hz, ArH), 7.56 (2 d, 4H, J = 6.8 Hz, ArH), 7.42−7.38 (m, 8H, ArH), 7.08−6.92 (m, 4H, ArH), 6.66 (d, 4H, J = 7.3 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.0, 131.9, 131.3, 131.1, 129.0, 128.7, 128.4, 128.3, 127.8, 126.8, 125.6, 122.8, 122.1, 110.9, 94.5, 88.8, 87.9, 86.3; MS (FAB) m/z 630.0 [M^+]; Anal. Calcd. for $C_{50}H_{30}$: C, 95.21; H, 4.79. Found: C, 94.85; H, 4.71.

1,4-Bis[4-phenyl-2-(phenylethynyl)but-1-en-3-ynyl]-2,5-dimethoxybenzene (31). Prepared according to procedure A. Column chromatography (SiO_2; hexane/EtOAc, 30:1), yield: 18%. M.p. 214−216 °C; IR (film): 3041, 2945, 2831, 2190, 1636, 1597, 1487, 1410, 1313, 1278, 1210, 1041, 896, 854, 758 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.20 (s, 2H, ArH), 7.59 (s, 2H, C═CH), 7.56−7.52 (m, 8H, ArH), 7.37−7.33 (m, 12H, ArH), 3.75 (s, 6H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.0, 136.6, 131.7, 131.5, 128.8, 128.5, 128.4, 128.3, 126.4, 123.0, 122.7, 110.2, 102.9, 95.3, 89.8, 87.3, 56.0; MS (FAB) m/z 590.2 [M^+]; Anal. Calcd. for $C_{44}H_{30}O_2$: C, 89.46; H, 5.12. Found: C, 89.15; H, 5.48.

2,5-Bis[4-phenyl-2-(phenylethynyl)but-1-en-3-ynyl]thiophene (32). Prepared according to procedure A. Column chromatography (SiO_2; hexane), yield: 78%. M.p. 134−136 °C; IR (film): 3060, 2193, 1655, 1559, 1490, 1252, 1024, 913, 876, 798, 753 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.62−7.56 (m, 8H, ArH), 7.48 (s, 2H, ArH), 7.43−7.39 (m, 6H, ArH), 7.37 (s, 2H, C═CH), 7.28−7.26 (m, 6H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.0, 135.6, 131.6, 131.5, 130.6, 128.6, 128.4, 128.3, 128.2, 122.8, 122.4, 101.7, 98.1, 90.0, 89.2, 87.5; MS (FAB) m/z 536.1 [M^+]; Anal. Calcd. for $C_{40}H_{24}S_1$: C, 89.52; H, 4.51. Found: C, 89.23; H, 4.64.

1,4-Bis[4-phenyl-2-(phenylethynyl)-1-methylbut-1-en-3-ynyl]benzene (33). Prepared according to procedure A. Column chromatography (SiO_2; hexane/EtOAc, 30:1), yield: 56%. M.p. 79−80 °C; IR (film): 3058, 2926, 2205, 1597, 1490, 1444, 1271, 1066, 1020, 916, 837, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.74 (s, 4H, ArH), 7.58−7.55 (m, 4H, ArH), 7.39−7.29 (m, 10H, ArH), 7.28−7.19 (m, 6H, ArH), 2.55 (s, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.5, 131.3, 128.6, 128.3, 128.1, 127.8, 127.6, 127.3, 127.2, 123.2, 123.1, 102.4, 93.8, 90.8, 87.7, 87.5, 22.4; MS (FAB) m/z 558.1 [M^+]; Anal. Calcd. for $C_{44}H_{30}$: C, 94.59; H, 5.41. Found: C, 94.51; H, 5.73.

9,10-Bis[3-phenyl-1-(phenylethynyl)prop-2-ynylidene]-9,-10-dihydroanthracene (34). Prepared according to procedure A. Column chromatography (SiO_2; hexane/EtOAc, 20:1), yield: 51%. M.p. 121−122 °C; IR (film): 3058, 2188, 1595, 1488, 1444, 1408, 1261, 1093, 1022, 866, 801, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.53 (q, 4H, J = 3.0 Hz, $Ar_{AQ}H$), 7.57−7.55 (m, 8H, ArH), 7.47 (q, 4H, J = 3.0 Hz, $Ar_{AQ}H$), 7.39−7.37 (m, 12H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.7, 134.6, 131.6, 128.5, 128.3, 127.4, 127.2, 123.1, 100.8, 93.7, 89.2; MS (FAB) m/z 604.1 [M^+]; Anal. Calcd. for $C_{48}H_{28}$: C, 95.33; H, 4.67. Found: C, 95.09; H, 4.74.

(4-Phenyl-2-phenylethynylbut-1-en-3-ynyl)benzene (35). Prepared according to procedure A. Column chromatography (SiO_2; hexane/EtOAc, 15:1), yield: 86%. M.p. 118−119 °C; IR (film): 3059, 2198, 1597, 1490, 1446, 1378, 1265, 1070, 1025, 918, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.99 (d, 2H, J = 6.9 Hz, ArH), 7.61−7.57 (m, 4H, ArH), 7.47−7.35 (m, 9H, ArH), 7.22 (s, 1H, C═CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.1, 135.6, 131.6, 129.1, 129.0, 128.7, 128.4, 128.3, 128.0, 126.5, 122.8, 122.7, 103.2, 94.6, 89.1, 88.3, 86.9; MS (FAB) m/z 304.0 [M^+].

Absorption and Fluorescence Measurements. Absorption and fluorescence spectra were recorded using 10^{-5}−10^{-6} M

solutions of bis-enediynes in $CHCl_3$. The excitation wavelengths were those of the wavelength of maximum absorption of each bis-enediyne.

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Supporting Information Available: Normalized absorption spectra of **20**−**35** and synthetic schemes of dialdehydes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org/.

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