JOC Article

Synthesis and Self-Association, Absorption, and Fluorescence Properties of Differentially Functionalized Hexakis(*p*-substituted-phenylethynyl)benzenes

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The dual Sonogashira coupling reactions of 1,3,5-tribromo-2,4,6-triiodobenzene with *p*-X-phenylacetylene followed by another *p*-Y-phenylacetylene (X, Y = $OSiMe_2Bu$-*t* or CO_2Et) produced a series of differentially functionalized hexakis(*p*-substituted-phenylethynyl)benzenes with D_{3h} symmetry (**3h**: 1,3,5-X-2,4,6-Y) and C_{2v} symmetry (**3g**,**i**: 1,2,3,5-X-4,6-Y; **3f**,**j**: 1-X-2,3,4,5,6-Y). In a similar manner, 1,3,5-tris(*p*-X-phenylethynyl)-2,4,6-tris(*p*-Y-phenylethynyl)benzenes and 1,2,3,5-tetrakis(*p*-X-phenylethynyl)-4,6-bis(*p*-Y-phenylethynyl)benzenes (**3l**: X = $OSiMe_2Bu$-*t*, Y = NO_2; **3m**,**n**: X = N(*n*-octyl)$_2$, Y = NO_2; **3o**,**p**: X = N(*n*-octyl)$_2$, Y = $CH(OCH_2CH_2O)$; **3q**,**r**: X = N(*n*-octyl)$_2$, Y = CHO; **3s**,**t**: X = N(*n*-octyl)$_2$, Y = $CH{=}C(CN)_2$) were prepared. Compounds **3** with electron-withdrawing groups self-aggregated by a $\pi-\pi$ stacking interaction and solvophobic effect. In the absorption and fluorescence spectra of **3**, λ_{max}(abs) and λ_{max}(em) showed red shifts as the donor−acceptor dipole at the end functional groups of the para position was increased. In the absorption spectra, λ_{max}(abs) showed red shifts upon increasing the number of combination of electron-donating and -withdrawing groups on the diagonal line in a molecule, whereas λ_{max}(em) in the fluorescence spectra exhibited red shifts upon decreasing the molecular symmetry.

Introduction

Hexaethynylbenzene derivatives with D_{6h} or D_{3h} symmetry have attracted considerable attention in the field of materials science because of their divergent and extended π-conjugated system. They have potential as a building block for hypothetical 2-D carbon allotropes such as graphyne and graphdiyne,[1−4] and serve as core structures for dendritic materials[5] and for discotic liquid crystals.[6] Differentially functionalized D_{3h} symmetry hexakis(*p*-substituted-phenylethynyl)benzenes with electron-donating and -withdrawing groups at the 1,3,5- and 2,4,6-positions, respectively, would also have potential as second-order nonlinear optical materials.[7−10] Kondo and co-workers reported the third-order optical nonlinearity of hexa(phenylethynyl)benzene.[11] The Sonogashira coupling reaction is a powerful method for the synthesis of D_{6h} symmetry hexaethynylbenzenes from hexabromobenzene and terminal acetylenes.[1,12,13] Differentially substituted D_{3h} symmetry hexaethynylbenzenes have been synthesized effectively by the Sonogashira coupling reac-

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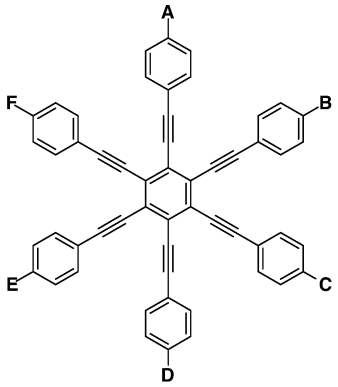
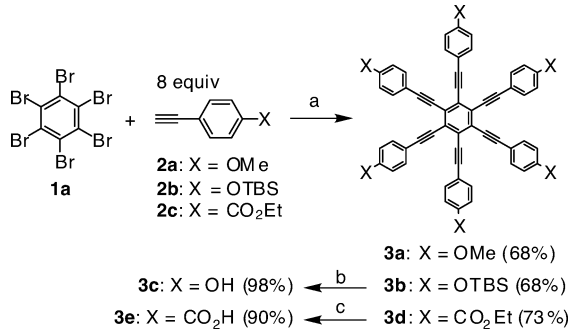
CHART 1



3a: A ~ F = OMe
3b: A ~ F = $OSiMe_2Bu$-*t*
3c: A ~ F = OH
3d: A ~ F = CO_2Et
3e: A ~ F = CO_2H
3f: A, B, C, D, E = $OSiMe_2Bu$-*t*; F = CO_2Et
3g: A, B, C, E = $OSiMe_2Bu$-*t*; D, F = CO_2Et
3h: A, C, E = $OSiMe_2Bu$-*t*; B, D, F = CO_2Et
3i: A, C = $OSiMe_2Bu$-*t*; B, D, E, F = CO_2Et
3j: A = $OSiMe_2Bu$-*t*; B, C, D, E, F = CO_2Et
3k: A, C, E = OH; B, D, F = CO_2H
3l: A, C, E = $OSiMe_2Bu$-*t*; B, D, F = NO_2
3m: A, C, E = $N(Oct\text{-}n)_2$; B, D, F = NO_2
3n: A, B, C, E = $N(Oct\text{-}n)_2$; D, F = NO_2
3o: A, C, E = $N(Oct\text{-}n)_2$; B, D, F = $CH(OCH_2CH_2O)$
3p: A, B, C, E = $N(Oct\text{-}n)_2$; D, F = $CH(OCH_2CH_2O)$
3q: A, C, E = $N(Oct\text{-}n)_2$; B, D, F = CHO
3r: A, B, C, E = $N(Oct\text{-}n)_2$; D, F = CHO
3s: A, C, E = $N(Oct\text{-}n)_2$; B, D, F = $CH{=}C(CN)_2$
3t: A, B, C, E = $N(Oct\text{-}n)_2$; D, F = $CH{=}C(CN)_2$

tion of 1,3,5-tribromo-2,4,6-triformylbenzene with terminal acetylenes followed by the Corey−Fuchs dibromoolefination and then treatment with LDA (Rubin's method),[3] or by the Sonogashira coupling reaction of 1,3,5-trichloro-2,4,6-triiodobenzene followed by the Negishi coupling reaction (Sonoda−Tobe's method).[14] However, the properties of *differentially functionalized* hexakis(*p*-substituted-phenylethynyl)benzenes have not been systematically studied so far. As a part of our project on the construction of hydrogen-bonded or metal-coordinated porous networks in the solid state of host molecules with extended π-conjugated system,[15] we have chosen the dual Sonogashira coupling reactions using 1,3,5-tribromo-2,4,6-triiodobenzene because the Sonogashira coupling reaction is tolerant of functional groups such as ester and cyano groups.[12] Here, we report the synthesis of a series of differentially functionalized hexakis(*p*-substituted-phenylethynyl)benzenes **3** with D_{6h}, D_{3h} (1,3,5-X-2,4,6-Y), and C_{2v} (1-X-2,3,4,5,6-Y or 1,2,3,5-X-4,6-Y) symmetries (Chart 1), and their self-association, absorption, and fluorescence properties.

SCHEME 1[a]



[a] Reagents and conditions: (a) $PdCl_2(PPh_3)_2$ (10 mol %), CuI (20 mol %), PPh_3 (20 mol %), Et_3N, reflux, 50−112 h; (b) KOH (12 equiv), MeOH−THF−H_2O, rt, 28 h; (c) KOH (60 equiv), THF−H_2O, 70 °C, 46 h.

Results and Discussion

Synthesis of Functionalized Hexakis(*p*-substituted-phenylethynyl)benzenes with D_{6h} Symmetry. The Sonogashira coupling reaction of hexabromobenzene **1a** with 8 equiv of *p*-methoxyphenylacetylene **2a**, *p*-(*tert*-butyldimethylsilyloxy)phenylacetylene **2b**, or *p*-(ethoxycarbonyl)phenylacetylene **2c** in the presence of $PdCl_2(PPh_3)_2$ (10 mol %), CuI (20 mol %), and PPh_3 (20 mol %) in Et_3N at refluxing temperature gave hexakis(*p*-methoxyphenylethynyl)benzene **3a**, hexakis[*p*-(*tert*-butyldimethylsilyloxy)phenylethynyl]benzene **3b**, or hexakis[*p*-(ethoxycarbonyl)phenylethynyl]benzene **3d** in 68%, 68%, or 73% yield, respectively (Scheme 1). The deprotection of **3b** or **3d** by KOH quantitatively produced hexakis(4-hydroxyphenylethynyl)benzene **3c** or hexakis(4-carboxyphenylethynyl)benzene **3e**, respectively.

Synthesis of Differentially Functionalized Hexakis(*p*-substituted-phenylethynyl)benzenes with D_{3h} and C_{2v} Symmetries. To synthesize differentially functionalized hexakis(*p*-substituted-phenylethynyl)benzenes with D_{3h} (1,3,5-X-2,4,6-Y) and C_{2v} (1-X-2,3,4,5,6-Y or 1,2,3,5-X-4,6-Y) symmetries, we chose the dual Sonogashira coupling reactions of 1,3,5-tribromo-2,4,6-triiodobenzene **1b** with *p*-X-phenylacetylene followed by another *p*-Y-phenylacetylene because the Sonogashira coupling reaction is tolerant of functional groups such as ester and cyano groups.[12] The compound **1b**[16] was synthesized by the reaction of 1,3,5-tribromobenzene with H_5IO_6 and KI in H_2SO_4.[17]

The Sonogashira coupling reaction of **1b** with **2b**−**d** (**2b**: X = $OSiMe_2Bu$-*t*, **2c**: X = CO_2Et, **2d**: X = $N(n\text{-octyl})_2$) was carried out in the presence of $PdCl_2(PPh_3)_2$ (3 mol %), CuI (6 mol %), and PPh_3 (6 mol %) in Et_3N. The results and the structures of products are summarized in Table 1 and Chart 2, respectively. The reaction of **1b** with 4 equiv of **2c** at refluxing temperature gave 1,3,5-tribromo-2,4-bis[*p*-(ethoxycarbonyl)phenylethynyl]-6-iodobenzene **4**, 1,3,5-tribromo-2,4,6-tris[*p*-(ethoxycarbonyl)phenylethynyl]benzene **5**, and 1,3-dibromo-2,4,5,6-tetrakis[*p*-(ethoxycarbonyl)phenylethynyl]-benzene **6** in 10%, 21%, and 20% yields, respectively (entry 1). The reaction of **1b** with 2.8 equiv of **2b** at

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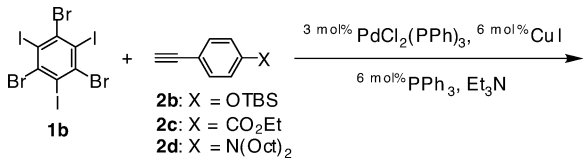
TABLE 1. The Sonogashira Coupling Reaction of 1b with 2b−d

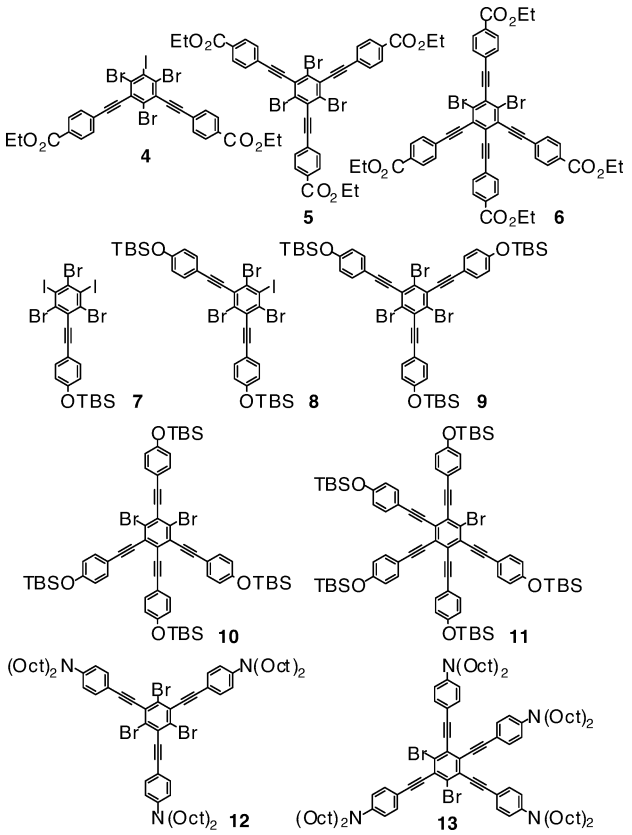


entry	acetylene	conditions	products, yield (%) 4	5	6
1	**2c**	4.0 equiv, reflux, 24 h	10	21	20
2	**2c**	2.5 equiv, reflux, 14 h and then 1.4 equiv, 55 °C, 24 h	32	17	32

entry	acetylene	conditions	products, yield (%) 7	8	9	10	11
3	**2b**	2.8 equiv, reflux, 40 h	14	37	12	3	0
4	**2b**	3.7 equiv, reflux, 40 h	0	0	17	36	5
5	**2b**	3.7 equiv, 55 °C, 150 h and then 0.75 equiv, 55 °C, 90 h	0	20	47	13	0

entry	acetylene	conditions	products, yield (%) 12	13
6	**2d**	3.7 equiv, reflux, 43 h	57	9

CHART 2

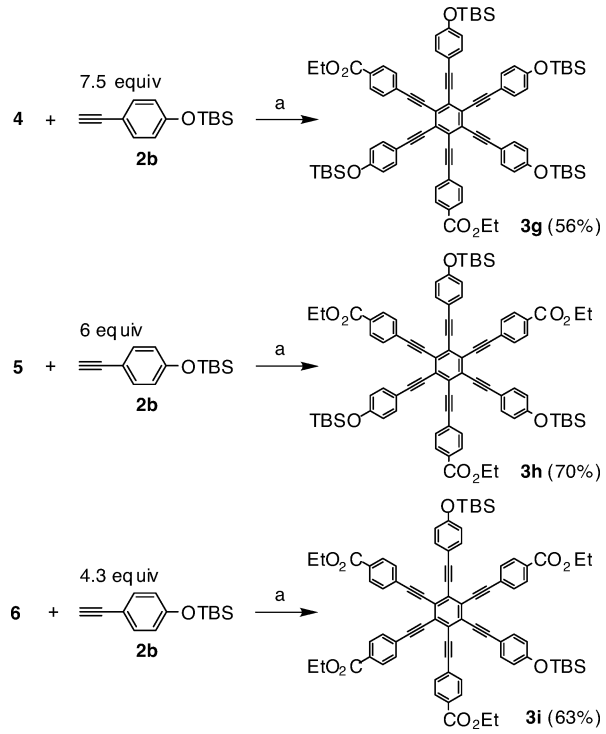


refluxing temperature produced 1,3,5-tribromo-2-[*p*-(*tert*-butyldimethylsilyloxy)phenylethynyl]-4,6-diiodobenzene **7**, 1,3,5-tribromo-2,4-bis[*p*-(*tert*-butyldimethylsilyloxy)-phenylethynyl]-6-iodobenzene **8**, 1,3,5-tribromo-2,4,6-tris-[*p*-(*tert*-butyldimethylsilyloxy)phenylethynyl]benzene **9**, and 1,3-dibromo-2,4,5,6-tetrakis[*p*-(*tert*-butyldimethylsilyloxy)phenylethynyl]benzene **10** in 14%, 37%, 12%, and 3% yields, respectively (entry 3), whereas **9**, **10**, and 1-bromo-2,3,4,5,6-pentakis[*p*-(*tert*-butyldimethylsilyloxy)-phenylethynyl]benzene **11** were obtained in 17%, 36%, and 5% yields, respectively, when 3.7 equiv of **2b** was used under the same conditions (entry 4). The reaction **1b** with 3.7 equiv of **2b** at 55 °C followed by the additional reaction using 0.75 equiv of **2b** gave **8**, **9**, and **10** in 20%, 47%, and 13% yields, respectively (entry 5). The reaction of **1b** with 3.7 equiv of *p*-(*N*,*N*-di-*n*-octylamino)phenylacetylene **2d** at refluxing temperature produced 1,3,5-tribromo-2,4,6-tris[*p*-(*N*,*N*-di-*n*-octylamino)phenylethynyl]-benzene **12** and 1,3-dibromo-2,4,5,6-tetrakis[*p*-(*N*,*N*-di-*n*-octylamino)phenylethynyl]benzene **13** in 57% and 9% yields, respectively (entry 6). Thus, the product ratio for the Sonogashira coupling reaction of **1b** with the *p*-substituted-phenylacetylenes **2b**−**d** strongly depends on the nature and the stoichiometry of **2b**−**d** and the reaction temperature.

Subsequently, the Sonogashira coupling reactions of halides of mono-, bis-, tris-, tetrakis-, or pentakis(*p*-X-phenylethynyl)benzenes **4**−**13** with *p*-Y-phenylacetylenes **2b**−**f** were conducted. The Sonogashira coupling reaction of **4**, **5**, or **6** with 7.5−4.3 equiv of **2b** in the presence of $PdCl_2(PPh_3)_2$ (8−6.5 mol %), CuI (16−13 mol %), and PPh_3 (16−13 mol %) in Et_3N at refluxing temperature gave 1,2,3,5-tetrakis[*p*-(*tert*-butyldimethylsilyloxy)phenylethynyl]-4,6-bis[*p*-(ethoxycarbonyl)phenylethynyl]-benzene **3g**, 1,3,5-tris[*p*-(*tert*-butyldimethylsilyloxy)phenylethynyl]-2,4,6-tris[*p*-(ethoxycarbonyl)phenylethynyl]-benzene **3h**, or 1,3-bis[*p*-(*tert*-butyldimethylsilyloxy)phenylethynyl]-2,4,5,6-tetrakis[*p*-(ethoxycarbonyl)phenylethynyl]benzene **3i** in 56%, 70%, or 63% yield, respectively (Scheme 2). The reaction of **7** or **11** with **2c** under similar conditions produced 1-[*p*-(*tert*-butyldimethylsilyloxy)-phenylethynyl]-2,3,4,5,6-pentakis[*p*-(ethoxycarbonyl)-phenylethynyl]benzene **3j** or 1,2,3,4,5-pentakis[*p*-(*tert*-butyldimethylsilyloxy)phenylethynyl]-6-[*p*-(ethoxycarbonyl)phenylethynyl]benzene **3f** in 86% or 61% yield, respectively (Scheme 3). The reaction of **9** with *p*-nitrophenylacetylene **2e** under similar conditions produced 1,3,5-tris[*p*-(*tert*-butyldimethylsilyloxy)phenylethynyl]-2,4,6-tris(*p*-nitrophenylethynyl)benzene **3l** in 54% yield (Scheme 4). The reaction of **12** or **13** with **2e** under similar conditions produced 1,3,5-tris[*p*-(*N*,*N*-di-*n*-octylamino)phenylethynyl]-2,4,6-tris(*p*-nitrophenylethynyl)benzene **3m** or 1,2,3,5-tetrakis[*p*-(*N*,*N*-di-*n*-octylamino)phenylethynyl]-4,6-bis(*p*-nitrophenylethynyl)benzene **3n** in 50% or 8% yield, respectively. The hydrolysis of **3h** by KOH in THF−H_2O quantitatively produced 1,3,5-tris(*p*-carboxyphenylethynyl)-2,4,6-tris(*p*-hydroxyphenylethynyl)benzene **3k**.

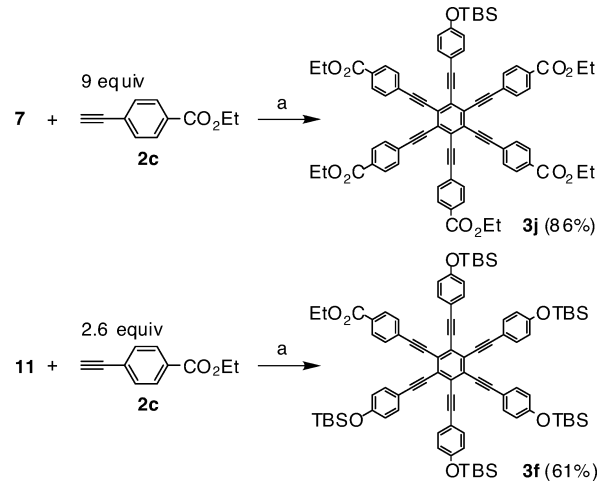
The Sonogashira coupling reaction of **12** or **13** with *p*-(1,3-dioxolan-2-yl)phenylacetylene **2f** under similar conditions gave 1,3,5-tris[*p*-(*N*,*N*-di-*n*-octylamino)phenylethynyl]-2,4,6-tris[*p*-(1,3-dioxolan-2-yl)phenylethynyl]-benzene **3o** or 1,2,3,5-tetrakis[*p*-(*N*,*N*-di-*n*-octylamino)-phenylethynyl]-4,6-bis[*p*-(1,3-dioxolan-2-yl)phenylethynyl]-benzene **3p** in 23% or 36% yield, respectively (Scheme 5). The hydrolysis of **3o** or **3p** by 1 M HCl in THF produced 1,3,5-tris[*p*-(*N*,*N*-di-*n*-octylamino)phenylethynyl]-2,4,6-tris(*p*-formylphenylethynyl)benzene **3q** or 1,2,3,5-tetrakis[*p*-(*N*,*N*-di-*n*-octylamino)phenylethynyl]-4,6-bis(*p*-

SCHEME 2[a]



[a] Reagents and conditions: (a) $PdCl_2(PPh_3)_2$ (6.5−8 mol %), CuI (13−16 mol %), PPh_3 (13−16 mol %), Et_3N, reflux, 43−65 h.

SCHEME 3[a]

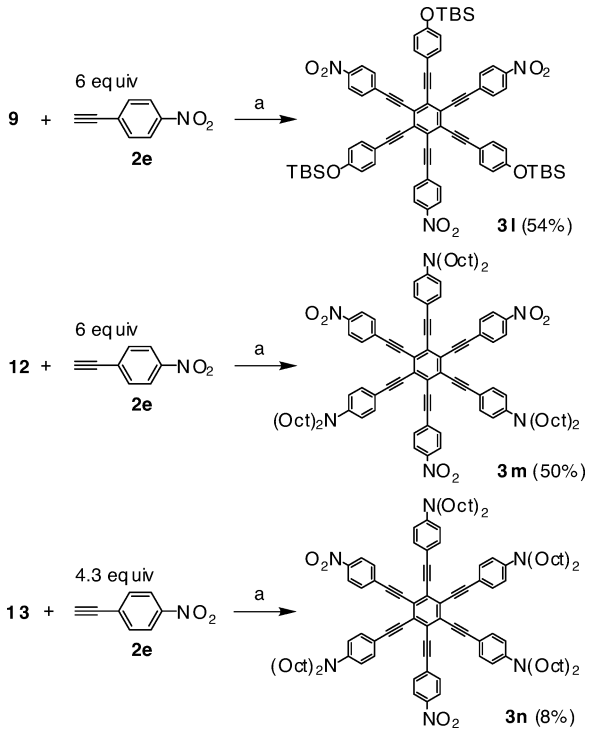


[a] Reagents and conditions: (a) $PdCl_2(PPh_3)_2$ (6.5−8 mol %), CuI (13−16 mol %), PPh_3 (13−16 mol %), Et_3N, reflux, 48−91 h.

formylphenylethynyl)benzene **3r** in 82% or 74% yield, respectively, which were converted, by the reaction of 3 equiv of malononitrile in $CHCl_3$ in the presence of Et_3N and benzoic acid (30 mol % each), into 1,3,5-tris[*p*-(2,2-dicyanoethenyl)phenylethynyl]-2,4,6-tris[*p*-(*N*,*N*-di-*n*-octylamino)phenylethynyl]benzene **3s** or 1,3-bis[*p*-(2,2-dicyanoethenyl)phenylethynyl]-2,4,5,6-tetrakis[*p*-(*N*,*N*-di-*n*-octylamino)phenylethynyl]benzene **3t** in 67% or 62% yield, respectively.

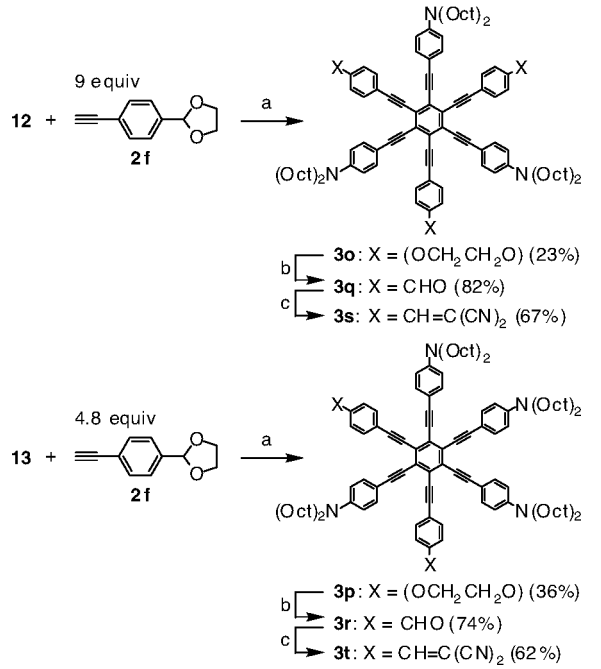
Self-Association Behavior. It is known that *m*-phenylacetylene macrocycles, as well as *m*-diethynylbenzene macrocycles, with electron-withdrawing groups at the peripheral positions self-aggregate by a $\pi-\pi$ stacking

SCHEME 4[a]



[a] Reagents and conditions: (a) $PdCl_2(PPh_3)_2$ (7−8 mol %), CuI (14−16 mol %), PPh_3 (14−16 mol %), Et_3N, reflux, 40−74 h.

SCHEME 5[a]



[a] Reagents and conditions: (a) $PdCl_2(PPh_3)_2$ (6−9 mol %), CuI (12−18 mol %), PPh_3 (12−18 mol %), Et_3N, reflux, 31−87 h; (b) 1 M HCl (10−12 equiv), THF, rt, 16 h; (c) malononitrile (3 equiv), Et_3N (30 mol %), $PhCO_2H$ (30 mol %), $CHCl_3$, rt, 24 h to 50 °C, 100 h.

interaction and solvophobic effect.[18] It was found that this behavior is also the case for hexa(arylethynyl)benzene derivatives with electron-withdrawing groups. In the ^1H NMR spectra of **3d** with the ethoxycarbonyl group in

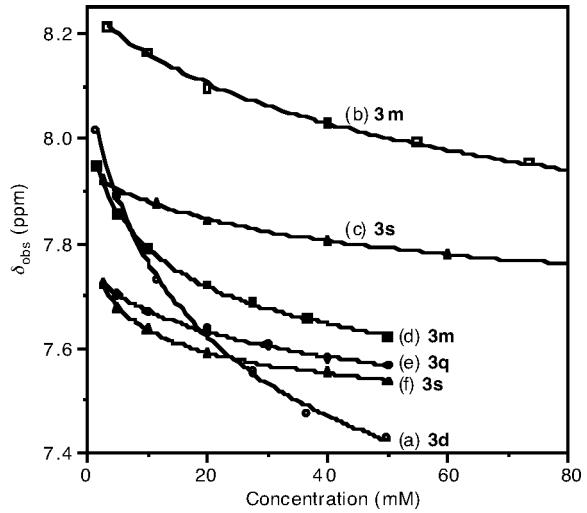


FIGURE 1. Concentration dependence of ^{1}H NMR chemical shifts for the aromatic ortho protons with respect to the ethoxycarbonyl, nitro, formyl, and 2,2-dicyanoethenyl groups of **3d**, **3m**, **3q**, and **3s**, respectively: (a) **3d**, (b) **3m**, and (c) **3s** in $CDCl_3$ at 23 °C; (d) **3m**, (e) **3q**, and (f) **3s** in a 1:4 mixture of acetone-d_6 and $CDCl_3$ at 23 °C.

TABLE 2. Calculated Indefinite-Association Constants (K_E) and Saturation Chemical Shift Changes ($\Delta\delta_{sat}$) of 3a, 3d, 3m, 3q, and 3s in $CDCl_3$ or a 1:4 Mixture of Acetone-d_6 and $CDCl_3$ at 23 °C[a]

compd	solvent	K_E (M^{-1})	$\Delta\delta_{sat}$ (ppm)
3a	$CDCl_3$	~0	NA
	acetone-d_6/$CDCl_3$ = 1/4	~0	NA
3d	$CDCl_3$	55.0 ± 6.0	−1.26 ± 0.02
	acetone-d_6/$CDCl_3$ = 1/4	449.2 ± 23.0	−1.54 ± 0.05
3m	$CDCl_3$	14.4 ± 0.7	−0.97 ± 0.02
	acetone-d_6/$CDCl_3$ = 1/4	93.0 ± 3.6	−0.62 ± 0.01
3q	acetone-d_6/$CDCl_3$ = 1/4	23.6 ± 1.2	−0.44 ± 0.01
3s	$CDCl_3$	20.5 ± 3.3	−0.37 ± 0.03
	acetone-d_6/$CDCl_3$ = 1/4	126.3 ± 11.4	−0.37 ± 0.01

[a] Determined on the basis of the indefinite-association model by nonlinear least-squares fitting of chemical shift data.[18] All correlation coefficients were $r > 0.99$.

$CDCl_3$, the signals of the aromatic protons were shifted upfield upon increasing the concentration (Figure 1), indicating that **3d** self-aggregates by a $\pi-\pi$ stacking interaction. When the chemical shift changes for the aromatic protons of **3d** as a function of the concentration were analyzed by the π-stacked infinite (isodesmic) association model,[18] the indefinite-association constant (K_E) of n aggregates of **3d** was estimated to be $K_E = 55.0$ M^{-1} in $CDCl_3$ at 23 °C (Table 2). Compounds **3m** and **3s**, which possess alternately the electron-donating dioctylamino group and the electron-withdrawing nitro or 2,2-dicyanoethenyl group, also self-aggregated by a $\pi-\pi$ stacking interaction, with K_E = 14.4 and 20.5 M^{-1}, respectively. On the other hand, the ^{1}H NMR spectra of **3a** with the methoxy group did not show any chemical shift changes even at higher concentration, indicating no association.

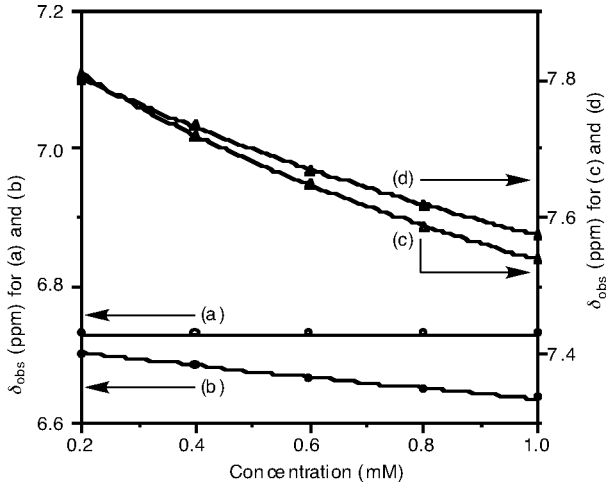


FIGURE 2. Concentration dependence of ^{1}H NMR chemical shifts for the aromatic ortho protons with respect to the methoxy group of **3a** and ethoxycarbonyl group of **3d** in a 1:4 mixture of acetone-d_6 and $CDCl_3$ at 23 °C: (a) **3a** alone, (b) the **3a** unit in a 1:1 mixture of **3a** and **3d**, (c) **3d** alone, and (d) the **3d** unit in a 1:1 mixture of **3a** and **3d**.

A solvophobic effect was also observed in the association of hexa(arylethynyl)benzene derivatives. In a 1:4 mixture of acetone-d_6 and $CDCl_3$ at 23 °C, the K_E was increased to 449.2 M^{-1} for **3d**, 93.0 M^{-1} for **3m**, and 126.3 M^{-1} for **3s**, the values of which are approximately seven times greater than those in $CDCl_3$. Compound **3q** with alternate dioctylamino and formyl groups also self-aggregated with $K_E = 23.6$ M^{-1}. Thus, the K_E increased in the order **3q** < **3m** < **3s** < **3d** with increasing the electron-withdrawing ability of functional groups at the para position (Table 2). For **3a**, no association was detected. These results clearly indicate the electron-withdrawing effect for the self-association of hexa(arylethynyl)benzene derivatives.[18] However, in the ^{1}H NMR spectra of a 1:1 mixture of **3a** and **3d** in a 1:4 mixture of acetone-d_6 and $CDCl_3$, the signals of the aromatic protons for the **3a** unit were undoubtedly shifted upfield upon increasing the concentration. In this mixture, the upfield chemical shift changes of the aromatic protons for the **3d** unit were unambiguously smaller than those for **3d** alone over the same concentration range (Figure 2). This result suggests, in a 1:1 mixture of **3a** and **3d**, coexistence of self-association of **3d** and a hetero-association between donor **3a** and acceptor **3d**.[18a]

Absorption and Fluorescence Properties. The selected absorption and fluorescence spectral data of the differentially functionalized hexakis(*p*-substituted-phenylethynyl)benzenes **3a**−**t** are summarized in Table 3.[19]

In the absorption spectra, for all compounds λ_{max}(abs), the absorption maximum, and $\lambda_{cut-off}$, the wavelength at which the transmittance is 95%, are in the range from 360 to 481 nm and from 410 to 601 nm in $CHCl_3$, respectively, depending on the nature of the end functional groups.[19] A notable solvatochromism was not observed, although a slight red shift of λ_{max}(abs) was observed as the dielectric constant of solvents was increased.[20] λ_{max}(abs) for all of **3a**−**t** in $CHCl_3$ were red-

(18) (a) Shetty, A. S.; Zhang, J.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 1019−1027. (b) Lahiri, S.; Thompson, J. L.; Moore, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 11315−11319. (c) Tobe, Y.; Utsumi, N.; Kawabata, K.; Nagano, A.; Adachi, K.; Araki, S.; Sonoda, M.; Hirose, K.; Naemura, K. *J. Am. Chem. Soc.* **2002**, *124*, 5350−5364.

(19) For all absorption and fluorescence spectra and their data for the individual derivatives **3**, see the Supporting Information (Figures S1−S17 and Table S1).

TABLE 3. Selected Absorption and Fluorescence Spectral Data for 3[a]

compd	solvent	λ_{max}(abs) (nm)	log ϵ	$\lambda_{cut-off}$ (nm)	λ_{max}(em) (nm)[b]	Stokes shift (nm)
3a	$CHCl_3$	363.8	5.19	416.0	459.0	95.2
3b	$CHCl_3$	362.3	5.22	414.3	458.0	95.7
3d	$CHCl_3$	360.2	5.28	409.8	456.0	95.8
3f	$CHCl_3$	364.5	5.19	422.7	466.0	101.5
3g	$CHCl_3$	367.6	5.20	426.2	466.8	99.2
3h	$CHCl_3$	368.8	5.20	425.6	462.6	93.8
		332.6	5.17			
		316.6	5.16			
	1,4-dioxane	364.5	5.19	420.3	460.0	95.5
		308.9	4.65			
3i	$CHCl_3$	367.4	5.17	425.2	466.6	99.2
3j	$CHCl_3$	364.0	5.16	421.4	466.8	102.8
3l	$CHCl_3$	378.3	5.09	458.6	NA	NA
		318.1	4.80			
	1,4-dioxane	380.0	5.11	443.2	469.6	89.6
		316.8	4.75			
3m	$CHCl_3$	464.0	4.97	558.2	NA	NA
		340.2	4.95			
3n	$CHCl_3$	433.2	5.01	566.6	NA	NA
		332.0	4.85			
3o	$CHCl_3$	428.6	5.08	485.0	504.8	76.2
		319.8	4.89			
	hexane	418.6	5.12	455.8	472.2	53.6
		401.2	5.12		501.8	100.6
		321.0	4.90			
	1,4-dioxane	423.8	5.08	477.0	492.6	68.8
		318.6	4.88			
	CH_2Cl_2	434.2	5.15	496.6	530.8	96.6
		318.8	4.98			
	CH_3CN	434.0	5.11	514.6	569.6	135.6
		315.2	5.03			
3p	$CHCl_3$	418.6	5.07	508.4	515.1	96.5
	hexane	398.0	5.12	479.2	479.2	81.2
	1,4-dioxane	411.0	5.05	497.4	500.6	89.6
3q	$CHCl_3$	448.6	5.02	527.8	555.6	107.0
		329.0	5.00			
	benzene	440.8	5.03	510.1	527.2	86.4
		325.3	4.99			
	1,4-dioxane	440.4	5.05	512.4	541.2	100.8
		323.8	4.99			
	CH_2Cl_2	452.4	5.03	533.2	575.2	122.8
		328.6	5.00			
3r	$CHCl_3$	434.8	5.01	547.0	563.8	129.0
		323.4	4.91			
	hexane	415.8	5.07	512.0	508.4	92.6
		316.2	4.90			
	benzene	427.4	5.02	529.6	533.6	106.2
		319.4	4.90			
	1,4-dioxane	426.0	5.04	529.6	540.4	114.4
		317.4	4.92			
3s	$CHCl_3$	480.8	4.92	595.6	NA	NA
		375.2	5.08			
3t	$CHCl_3$	436.0	5.04	601.0	NA	NA
		384.8	5.05			

[a] Absorption and fluorescence spectra were measured at [**3**] = 1.0×10^{-5} M and [**3**] = 1.0×10^{-6} M, respectively, at room temperature. For all data in various solvents, see the Supporting Information. [b] The excitation wavelength is almost the same as λ_{max}(abs) in each case because the excitation spectrum of each **3** almost matched the absorption spectrum.

shifted by 10−131 nm relative to λ_{max}(abs) = 350 nm of the parent hexa(phenylethynyl)benzene,[11] which is probably due to the electron-donating and electron-withdrawing effects.[7f,g,10a] In a series of the D_{3h} symmetry derivatives **3h**, **3l**, **3m**, **3o**, **3q**, and **3s** in $CHCl_3$, λ_{max}(abs) at a longer wavelength was noticeably red-shifted as the donor−acceptor dipole at the end functional groups of the para position was increased (Table 3 and Figure 3). λ_{max}(abs) of **3s**, which has the combination of *N*,*N*-dioctylamino and 2,2-dicyanoethenyl groups, reached 481 nm.[21,22] This result reflects the π-electron delocalization over the *p*- and *o*-bis(*p*-substituted-phenylethynyl)benzene units in **3**. In a series of derivatives with *tert*-butyldimethylsilyloxy and ethoxycarbonyl groups **3b**, **3d**, and **3f**−**j** in $CHCl_3$, λ_{max}(abs) showed slight red shifts upon increasing the number of combination of the electron-donating and -withdrawing groups on the diagonal line in a molecule (λ_{max}(abs): **3b**,**d** < **3f**,**j** < **3g**,**i** < **3h**), as shown in Figure 4.[10a] This phenomenon was also observed, and more distinctively, for other combinations of the end functional groups: **3m** vs **3n** ($\Delta\lambda_{max}$(abs) = 31 nm), **3o** vs **3p** ($\Delta\lambda_{max}$(abs) = 10 nm), **3q** vs **3r** ($\Delta\lambda_{max}$(abs) = 14 nm), and **3s** vs **3t** ($\Delta\lambda_{max}$(abs) = 45 nm) in $CHCl_3$. The difference in the $\Delta\lambda_{max}$(abs) was increased upon increasing the donor−acceptor dipole at the end functional groups of the para position. These results also reflect the π-electron delocalization.

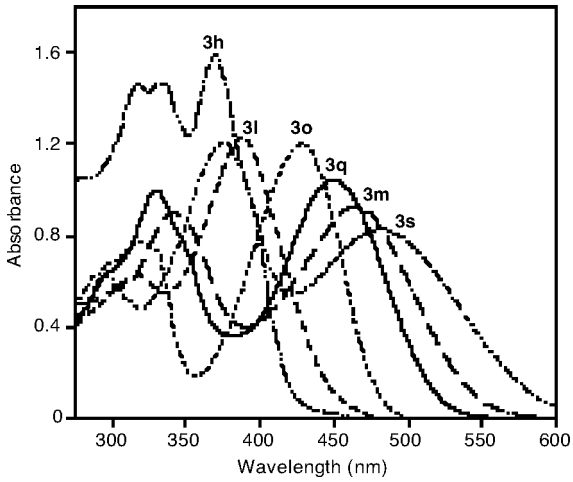


FIGURE 3. Absorption spectra of **3h**, **3l**, **3m**, **3o**, **3q**, and **3s** (1×10^{-5} M) in $CHCl_3$.

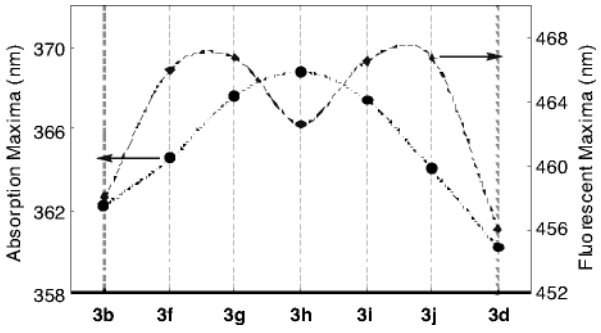


FIGURE 4. Diagram for λ_{max}(abs) and λ_{max}(em) of **3b**, **3d**, and **3f**−**j** in $CHCl_3$.

(20) The dielectric constants of solvents used here are as follows: hexane 1.89; 1,4-dioxane 2.21; benzene 2.28; $CHCl_3$ 4.81; CH_2Cl_2 8.9; CH_3CN 37.5.

(21) For nonlinear optical materials with the 2,2-dicyanoethenyl group, see: Katz, H. E.; Singer, K. D.; Sohn, J. E.; Dirk, C. W.; King, L. A.; Gordon, H. M. *J. Am. Chem. Soc.* **1987**, *109*, 6561−6563.

(22) For photoluminescent materials with the 2,2-dicyanoethenyl group, see: Ogura, K.; Zhao, R.; Yanai, H.; Maeda, K.; Tozawa, R.; Matsumoto, S.; Akazome, M. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 2359−2370.

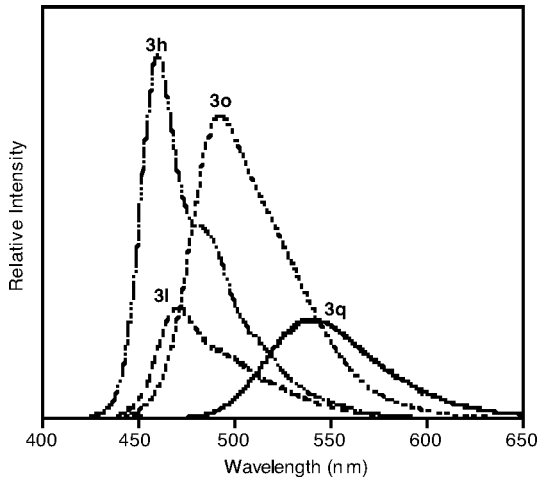


FIGURE 5. Emission spectra of **3h**, **3l**, **3o**, and **3q** (1×10^{-6} M) in 1,4-dioxane. The excitation wavelength is almost the same as λ_{max}(abs) in each case.

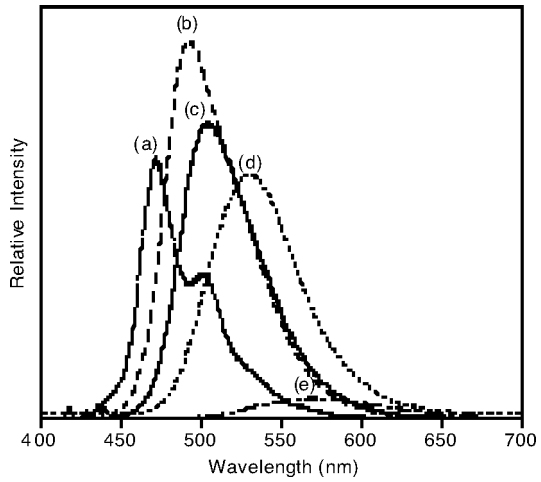


FIGURE 6. Emission spectra of **3o** (1×10^{-6} M) in (a) hexane, (b) 1,4-dioxane, (c) $CHCl_3$, (d) CH_2Cl_2, and (e) CH_3CN. The excitation wavelength is almost the same as λ_{max}(abs) in each case.

The differentially functionalized hexakis(*p*-substituted-phenylethynyl)benzenes **3**, except for **3l** in $CHCl_3$ and **3m**, **3n**, **3s**, and **3t** in all solvents, are highly fluorescent, λ_{max}(em) being in the range from 456 to 564 nm (Table 3).[19] The excitation spectra of **3** almost matched the absorption spectra, except for **3h** in which the excitation spectrum matched only the region of λ_{max}(abs) at a longer wavelength. In the majority of cases, the emission showed a relatively large Stokes shift in the range from 81 to 129 nm, except for **3o**. The large Stokes shift value is consistent with a nuclear reorganization taking place after excitation, prior to emission, as a result of electronic redistribution.[7f] In a series of the D_{3h} symmetry derivatives **3h**, **3l**, **3o**, and **3q** in $CHCl_3$ or 1,4-dioxane, λ_{max}(em) was red-shifted as the donor−acceptor dipole at the end functional groups of the para position was increased (Table 3 and Figure 5). λ_{max}(em) of **3q** in $CHCl_3$, which has the combination of *N*,*N*-dioctylamino and formyl groups, reached 556 nm. In a series of derivatives with *tert*-butyldimethylsilyloxy and ethoxycarbonyl groups **3b**, **3d**, and **3f**−**j** in $CHCl_3$, λ_{max}(em) exhibited modest red shifts upon decreasing the symmetry of a molecule (λ_{max}(em): D_{6h} (**3b**,**d**) < D_{3h} (**3h**) < C_{2v} (**3f**,**g**,**i**,**j**), as shown in Figure 4. This behavior was also observed with other combinations of the end functional groups: **3o** vs **3p** ($\Delta\lambda_{max}$(em) = −10 nm) and **3q** vs **3r** ($\Delta\lambda_{max}$(em) = −8 nm) in $CHCl_3$. These results would arise from a greater stabilization of the charge redistribution by the dipole orientation.[10a] In contrast to **3b**, **3d**, and **3h**, the derivatives bearing *N*,*N*-dioctylamino group **3o**−**r** showed a modest solvatochromic shift as the dielectric constant of the solvents was increased (Table 3), indicative of a polar excited state.[7f,10a,20] In the case of **3o**, λ_{max}(em) in CH_3CN was red-shifted by 98 nm relative to that in hexane (Figure 6).

Conclusion

We have demonstrated the synthesis of a series of differentially functionalized hexakis(*p*-substituted-phenylethynyl)benzenes **3** with D_{6h} symmetry by the Sonogashira coupling reaction of **1a** with **2**, or with D_{3h} and C_{2v} symmetries by the dual Sonogashira coupling reactions of **1b** with two kinds of **2**. Compounds **3** with electron-withdrawing groups were found to self-aggregate by a $\pi-\pi$ stacking interaction and solvophobic effect, wherein the K_E increased with increasing the electron-withdrawing ability of functional groups at the para position. In the absorption spectra of **3**, λ_{max}(abs) showed red shifts when the donor−acceptor dipole at the end functional groups of the para position or the number of combinations of these was increased. In the fluorescence spectra of **3**, λ_{max}(em) exhibited red shifts upon increasing the donor−acceptor dipole at the end functional groups of the para position or upon decreasing the symmetry of a molecule. The introduction of differentially functional groups into hexa(phenylethynyl)benzene would endow it with potential as a building block for molecular devices.[3,6,11] Studies are in progress to explore the nonlinear optical properties in **3**, as well as the application of **3c**, **3e**, and **3k** directed toward a 2-D hydrogen-bonded or metal-coordinated porous network with an asymmetric substituent.

Experimental Section

p-Substituted-phenylacetylenes **2a**−**f** were prepared according to the literature.[12a]

1,3,5-Tribromo-2,4,6-triiodobenzene (1b). The compound **1b**[16] was prepared by the modified procedure of the literature.[17] To concentrated H_2SO_4 (410 mL) at room temperature was added periodic acid (27.36 g, 120 mmol) in small portions over 15 min. After dissolution of the periodic acid, crushed KI (59.78 g, 360 mmol) was added in small portions at 0 °C over 1 h. To the resulting deep purple solution at 0 °C was added 1,3,5-tribromobenzene (12.59 g, 40.0 mmol) in small portions over 25 min. After the solution was stirred at room temperature for 62 h, the resulting thick mixture was poured onto ice. The resulting precipitate was filtered and washed with H_2O and then MeOH. The solid was triturated with MeOH, filtered, and recrystallized from pyridine−EtOH to give **1b** (18.46 g, 66% yield) in four crops as pale yellow needle crystals. Mp 268 °C; ^{13}C NMR (DMSO-d_6) δ 138.6, 108.2.

Typical Procedure for the Sonogashira Coupling Reaction of 1a with 2: Hexakis[*p*-(*tert*-butyldimethylsilyloxy)phenylethynyl]benzene (3b). To a mixture of **1a** (1.10 g, 2.00 mmol), $PdCl_2(PPh_3)_2$ (140 mg, 0.20 mmol), CuI (76.2 mg, 0.40 mmol), and PPh_3 (105 mg, 0.40 mmol) under

an argon atmosphere were added Et_3N (50 mL) and then a solution of **2b** (3.72 g, 16.0 mmol) in Et_3N (20 mL). The resulting mixture was stirred at refluxing temperature for 109 h. After evaporation of Et_3N, the residue was triturated with $CHCl_3$ and filtered. The filtrate was partitioned between $CHCl_3$ and H_2O, where the aqueous layer was neutralized with diluted HCl. The organic layer was washed with H_2O and brine and dried over Na_2SO_4. After evaporation of solvent, the residue was subjected to column chromatography on silica gel eluted with hexane−$CHCl_3$ (1.7:1) to give slightly crude **3b**, which was dissolved in a minimum amount of $CHCl_3$ and poured into hexane to give **3b** (2.00 g, 68% yield). Pale yellow solid; mp 275 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.52 (d, J = 8.6 Hz, 12H), 6.84 (d, J = 8.6 Hz, 12H), 1.02 (s, 54H), 0.24 (s, 36H); ^{13}C NMR ($CDCl_3$) δ 156.4, 133.3, 127.0, 120.3, 116.2, 99.1, 86.8, 25.6, 18.3, −4.4; IR (KBr) ν 2204, 1602, 1509, 1264 cm^{-1}. Anal. Calcd for $C_{90}H_{114}O_6Si_6$: C, 74.02; H, 7.87. Found: C, 73.80; H, 7.93.

Hexakis(*p*-methoxyphenylethynyl)benzene (3a). Reaction conditions: **1a** (1.10 g, 2.00 mmol), $PdCl_2(PPh_3)_2$ (140 mg, 0.20 mmol), CuI (76.2 mg, 0.40 mmol), PPh_3 (105 mg, 0.40 mmol), Et_3N (30 mL), and a solution of **2a** (2.12 g, 16.0 mmol) in Et_3N (15 mL) at refluxing temperature for 112 h. Purification: column chromatography on silica gel eluted with hexane−$CHCl_3$ (1:4.5) followed by reprecipitation with $CHCl_3$-hexane; 68% yield. Yellow solid; mp 320 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.58 (d, J = 8.8 Hz, 12H), 6.91 (d, J = 8.8 Hz, 12H), 3.86 (s, 18H); ^{13}C NMR ($CDCl_3$) δ 160.0, 133.3, 127.0, 115.6, 114.1, 99.0, 86.6, 55.4; IR (KBr) ν 2201, 1605, 1513, 1251 cm^{-1}. Anal. Calcd for $C_{60}H_{42}O_6$: C, 83.90; H, 4.93. Found: C, 83.90; H, 5.01.

Hexakis[*p*-(ethoxycarbonyl)phenylethynyl]benzene (3d). Reaction conditions: **1a** (1.10 g, 2.00 mmol), $PdCl_2(PPh_3)_2$ (140 mg, 0.20 mmol), CuI (76.2 mg, 0.40 mmol), PPh_3 (105 mg, 0.40 mmol), Et_3N (30 mL), and a solution of **2c** (2.79 g, 16.0 mmol) in Et_3N (15 mL) at refluxing temperature for 50 h. Purification: column chromatography on silica gel eluted with $CHCl_3$−EtOAc (1:1) followed by reprecipitation with $CHCl_3$-hexane. Yield 73%; yellow solid; mp 290 °C dec; ^{1}H NMR ($CDCl_3$, 5 mM) δ 7.89 (d, J = 8.3 Hz, 12H), 7.47 (d, J = 8.3 Hz, 12H), 4.41(q, J = 7.2 Hz, 12H), 1.44 (t, J = 7.2 Hz, 18H); ^{13}C NMR ($CDCl_3$) δ 165.5, 131.4, 130.4, 129.3, 127.6, 127.1, 99.0, 89.6, 61.2, 14.3; IR (KBr) ν 2210, 1723, 1605, 1290 cm^{-1}. Anal. Calcd for $C_{72}H_{54}O_{12}$: C, 77.82; H, 4.90. Found: C, 77.72; H, 4.94.

The Sonogashira Coupling Reaction of 1b with 2c (Table 1, Entry 1). To a mixture of **1b** (1.00 g, 1.44 mmol), $PdCl_2(PPh_3)_2$ (30.3 mg, 0.043 mmol), CuI (16.5 mg, 0.086 mmol), and PPh_3 (22.7 mg, 0.086 mmol) under an argon atmosphere were added Et_3N (40 mL) and then a solution of **2c** (1.00 g, 5.74 mmol) in Et_3N (15 mL). The resulting mixture was stirred at refluxing temperature for 24 h. After evaporation of Et_3N, the residue was triturated with $CHCl_3$ and filtered. The filtrate was partitioned between $CHCl_3$ and H_2O, where the aqueous layer was neutralized with diluted HCl. The organic layer was washed with H_2O and brine and dried over Na_2SO_4. After evaporation of solvent, the residue was subjected to column chromatography on silica gel eluted with hexane−$CHCl_3$ (1:3) to separate the fractions containing **4** and the fractions containing **5** and **6**. The crude **4** was purified by repeated recrystallization from $CHCl_3$−hexane to give **4** (115 mg, 10% yield). The mixture of **5** and **6** was separated and purified with recycle preparative GPC with $CHCl_3$ as an eluent to give **5** (247 mg, 21% yield) and **6** (267 mg, 20% yield).

On the other hand, the reaction of **1b** with 2.5 equiv of **2c** at refluxing temperature for 14 h followed by the additional reaction using 1.4 equiv of **2c** at 55 °C for 24 h gave **4**, **5**, and **6** in 32%, 17%, and 32% yields, respectively (Table 1, entry 2).

1,3,5-Tribromo-2,4-bis[*p*-(ethoxycarbonyl)phenylethynyl]-6-iodobenzene (4). White solid; mp 238 °C; ^{1}H NMR ($CDCl_3$) δ 8.08 (d, J = 8.2 Hz, 4H), 7.68 (d, J = 8.2 Hz, 4H), 4.42 (q, J = 7.1 Hz, 4H), 1.43 (t, J = 7.1 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 165.9, 134.0, 131.7, 130.9, 129.6, 129.1, 126.8, 126.4, 109.7, 98.2, 91.3, 61.3, 14.3; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 315.1 (4.87), 335.2 nm (4.81).

1,3,5-Tribromo-2,4,6-tris[*p*-(ethoxycarbonyl)phenylethynyl]benzene (5). Pale yellow solid; mp 232 °C; ^{1}H NMR ($CDCl_3$) δ 8.03 (d, J = 8.2 Hz, 6H), 7.66 (d, J = 8.2 Hz, 6H), 4.40 (q, J = 7.1 Hz, 6H), 1.42 (t, J = 7.1 Hz, 9H); ^{13}C NMR ($CDCl_3$) δ 165.9, 131.7, 130.9, 129.5, 128.9, 127.5, 126.6, 98.7, 89.9, 61.3, 14.3; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 316.3 (5.04), 337.3 nm (5.06).

1,3-Dibromo-2,4,5,6-tetrakis[*p*-(ethoxycarbonyl)phenylethynyl]benzene (6). Yellow solid; mp 209 °C; ^{1}H NMR ($CDCl_3$) δ 8.09−8.03 (m, 8H), 7.70 (d, J = 9.0 Hz, 2H), 7.67 (d, J = 8.5 Hz, 4H), 7.61 (d, J = 8.4 Hz, 2H), 4.42 (q, J = 7.1 Hz, 8H), 1.43 (t, J = 7.1 Hz, 12H); ^{13}C NMR ($CDCl_3$) δ 165.74, 165.67, 165.6, 131.8, 131.6, 131.1, 131.0, 130.9, 129.7, 129.6, 129.5, 128.9, 128.7, 128.2, 127.4, 126.93, 126.87, 126.7, 99.9, 99.7, 98.7, 89.54, 89.46, 89.4, 61.2, 14.3; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 329.8 nm (5.06).

The Sonogashira Coupling Reaction of 1b with 2b (Table 1, entry 4). To a mixture of **1b** (2.07 g, 3.00 mmol), $PdCl_2(PPh_3)_2$ (63.2 mg, 0.090 mmol), CuI (34.3 mg, 0.18 mmol), and PPh_3 (47.2 mg, 0.18 mmol) under an argon atmosphere were added Et_3N (35 mL) and then a solution of **2b** (2.58 g, 11.1 mmol; 3.7 equiv) in Et_3N (15 mL). The resulting mixture was stirred at refluxing temperature for 40 h. After the solution was cooled to room temperature, Et_2O was added to the reaction mixture, which was filtered. After evaporation of the filtrate, the residue was partitioned between $CHCl_3$ and H_2O, where the aqueous layer was neutralized with diluted HCl. The organic layer was washed with H_2O and brine and dried over Na_2SO_4. After evaporation of solvent, the residue was subjected to column chromatography on silica gel eluted with hexane−CH_2Cl_2 (7.5:1) to give **9** (524 mg, 17% yield), with hexane−CH_2Cl_2 (4:1) to separate crude **10**, and then with hexane−CH_2Cl_2 (3:1) to give **11** (182 mg, 5% yield). The crude **10** was purified by reprecipitation with $CHCl_3$−EtOH to give **10** (1.24 g, 36% yield).

When 2.8 equiv of **2b** was used under the same conditions, a mixture of **7**, **8**, **9**, and **10** was produced (Table 1, entry 3), which was subjected to column chromatography on silica gel eluted with hexane−CH_2Cl_2 (20:1) to give **7** (14% yield), with hexane−CH_2Cl_2 (10:1) to separated crude **8**, with hexane−CH_2Cl_2 (7.5:1) to give **9** (12% yield), and then with hexane−CH_2Cl_2 (4:1) to give **10** (3% yield). The crude **8** was purified by reprecipitation with hexane−EtOH to give **8** (37% yield). On the other hand, the reaction of **1b** with 3.7 equiv of **2b** at 55 °C for 150 h followed by the additional reaction using 0.75 equiv of **2b** at 55 °C for 90 h gave **8**, **9**, and **10** in 20%, 47%, and 13% yields, respectively (Table 1, entry 5).

1,3,5-Tribromo-2-[*p*-(*tert*-butyldimethylsilyloxy)phenylethynyl]-4,6-diiodobenzene (7). White solid; mp 153 °C; ^{1}H NMR ($CDCl_3$) δ 7.48 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 1.00 (s, 9H), 0.23 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 157.1, 137.6, 133.7, 133.5, 126.5, 120.4, 114.5, 107.4, 99.2, 90.1, 25.6, 18.2, −4.4; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 323.4 (4.45), 338.3 nm (4.42).

1,3,5-Tribromo-2,4-bis[*p*-(*tert*-butyldimethylsilyloxy)-phenylethynyl]-6-iodobenzene (8). White solid; mp 174 °C; ^{1}H NMR ($CDCl_3$) δ 7.51 (d, J = 8.6 Hz, 4H), 6.86 (d, J = 8.6 Hz, 4H), 1.00 (s, 18H), 0.23 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 157.0, 133.4, 132.4, 128.3, 127.4, 120.4, 114.8, 109.2, 99.6, 88.4, 25.6, 18.2, −4.4; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 324.1 (4.76), 335.6 nm (4.76).

1,3,5-Tribromo-2,4,6-tris[*p*-(*tert*-butyldimethylsilyloxy)phenylethynyl]benzene (9). White solid; mp 163 °C; ^{1}H NMR ($CDCl_3$) δ 7.55 (d, J = 8.6 Hz, 6H), 6.87 (d, J = 8.6 Hz, 6H), 1.00 (s, 27H), 0.24 (s, 18H); ^{13}C NMR ($CDCl_3$) δ 156.9, 133.4, 127.8, 127.2, 120.4, 115.1, 99.7, 87.1, 25.6, 18.2, −4.4; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 336.9 nm (5.00).

1,3-Dibromo-2,4,5,6-tetrakis[*p*-(*tert*-butyldimethylsilyloxy)phenylethynyl]benzene (10). Yellow solid; mp 218 °C; ^{1}H NMR ($CDCl_3$) δ 7.55 (d, J = 8.6 Hz, 2H), 7.53 (d, J = 8.6 Hz, 4H), 7.46 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 4H), 6.82 (d, J = 8.6 Hz, 2H), 1.00 (s, 36H), 0.24 (s, 24H); ^{13}C NMR ($CDCl_3$) δ 156.9, 156.69, 156.66, 133.44, 133.42, 133.3, 128.4, 127.6, 127.3, 127.0, 120.4, 115.7, 115.6, 115.3, 100.4, 100.1, 99.1, 87.6, 86.8, 86.5, 25.6, 18.2, −4.4; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 337.8 nm (5.02).

1-Bromo-2,3,4,5,6-pentakis[*p*-(*tert*-butyldimethylsilyloxy)phenylethynyl]benzene (11). Yellow solid; mp 233 °C; ^{1}H NMR ($CDCl_3$) δ 7.57−7.50 (m, 10H), 6.88−6.83 (m, 10H), 1.05 (s, 45H), 0.28 (s, 30H); ^{13}C NMR ($CDCl_3$) δ 156.6, 156.5, 156.4, 133.4, 133.3, 127.7, 127.2, 127.0, 126.7, 120.3, 116.2, 116.1, 115.8, 99.7, 99.6, 98.6, 87.2, 86.9, 86.3, 25.6, 18.2, −4.4; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 351.4 nm (5.12).

The Sonogashira Coupling Reaction of 1b with 2d (Table 1, Entry 6). To a mixture of **1b** (2.33 g, 3.40 mmol), $PdCl_2(PPh_3)_2$ (70.8 mg, 0.10 mmol), CuI (38.5 mg, 0.20 mmol), and PPh_3 (53.0 mg, 0.20 mmol) under an argon atmosphere were added Et_3N (40 mL) and then a solution of **2d** (4.25 g, 12.4 mmol) in Et_3N (15 mL). The resulting mixture was stirred at refluxing temperature for 43 h. After the solution was cooled to room temperature, Et_2O was added to the reaction mixture, which was filtered. After evaporation of the filtrate, the residue was partitioned between $CHCl_3$ and H_2O. The organic layer was washed with H_2O and brine and dried over Na_2SO_4. After evaporation of solvent, the residue was subjected to column chromatography on silica gel eluted with hexane−$CHCl_3$ (3.3:1) to give **12** (2.57 g, 57% yield) and then with hexane−$CHCl_3$ (2:1) to separate the fractions containing **13**. The crude **13** was purified with recycle preparative GPC with $CHCl_3$ as an eluent to give **13** (461 mg, 9% yield).

1,3,5-Tribromo-2,4,6-tris[*p*-(*N*,*N*-di-*n*-octylamino)phenylethynyl]benzene (12). Yellow solid; mp 59.4 °C; ^{1}H NMR ($CDCl_3$) δ 7.48 (d, J = 8.9 Hz, 6H), 6.60 (d, J = 8.9 Hz, 6H), 3.30 (t, J = 7.4 Hz, 12H), 1.60−1.50 (m, 12H), 1.35−1.25 (m, 60H), 0.90 (t, J = 6.9 Hz, 18H); ^{13}C NMR ($CDCl_3$) δ 148.6, 133.2, 128.1, 125.6, 111.2, 107.8, 101.3, 86.8, 51.0, 31.8, 29.5, 29.3, 27.2, 27.1, 22.6, 14.1; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 395.2 nm (5.09).

1,3-Dibromo-2,4,5,6-tetrakis[*p*-(*N*,*N*-di-*n*-octylamino)-phenylethynyl]benzene (13). Dark red solid; mp 53 °C; ^{1}H NMR ($CDCl_3$) δ 7.52−7.46 (m, 8H), 6.63−6.57 (m, 8H), 3.31 (t, J = 7.3 Hz, 16H), 1.65−1.55 (m, 16H), 1.36−1.29 (m, 80H), 0.92 (t, J = 6.6 Hz, 24H); ^{13}C NMR ($CDCl_3$) δ 148.5, 148.3, 133.4, 127.4, 127.3, 127.1, 125.7, 111.2, 109.0, 108.7, 108.2, 101.7, 101.3, 100.4, 87.4, 86.7, 86.3, 51.0, 31.8, 29.5, 29.3, 27.25, 27.16, 22.6, 14.1; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 393.2 nm (5.03).

Typical Procedure for the Sonogashira Coupling Reaction of Halides of Mono-, Bis-, Tris-, Tetrakis-, or Pentakis(*p*-substituted-phenylethynyl)benzenes 4−13 with 2: 1,3,5-Tris[*p*-(*tert*-butyldimethylsilyloxy)phenylethynyl]-2,4,6-tris[*p*-(ethoxycarbonyl)phenylethynyl]benzene (3h). To a mixture of **5** (233 mg, 0.28 mmol), $PdCl_2(PPh_3)_2$ (14.7 mg, 0.021 mmol), CuI (8.0 mg, 0.042 mmol), and PPh_3 (11.0 mg, 0.042 mmol) under an argon atmosphere were added Et_3N (25 mL) and then a solution of **2b** (391 mg, 1.68 mmol) in Et_3N (15 mL). The resulting mixture was stirred at refluxing temperature for 65 h. After evaporation of Et_3N, the residue was triturated with $CHCl_3$ and filtered. The filtrate was partitioned between $CHCl_3$ and H_2O, where the aqueous layer was neutralized with diluted HCl. The organic layer was washed with H_2O and brine and dried over Na_2SO_4. After evaporation of solvent, the residue was subjected to column chromatography on silica gel eluted with hexane−$CHCl_3$ (1:2.5) to separate the fractions containing **3h**. The crude **3h** was purified by reprecipitation with $CHCl_3$−hexane followed by recycle preparative GPC with $CHCl_3$ as an eluent to give **3h** (252 mg, 70% yield). Yellow solid; mp 312 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.06 (d, J = 8.3 Hz, 6H), 7.69 (d, J = 8.3 Hz, 6H), 7.50 (d, J = 8.6 Hz, 6H), 6.86 (d, J = 8.6 Hz, 6H), 4.42 (q, J = 7.1 Hz, 6H), 1.44 (t, J = 7.1 Hz, 9H), 1.02 (s, 27 H), 0.26 (s, 18H); ^{13}C NMR ($CDCl_3$) δ 166.0, 156.7, 133.4, 131.6, 130.1, 129.4, 128.7, 127.9, 126.0, 120.4, 115.8, 100.4, 97.9, 90.3, 86.4, 61.1, 25.6, 18.2, 14.3, −4.4; IR (KBr) ν 2209, 1719, 1602, 1509, 1274 cm^{-1}. Anal. Calcd for $C_{81}H_{84}O_9Si_3$: C, 75.66; H, 6.58. Found: C, 75.64; H, 6.65.

1,2,3,4,5-Pentakis[*p*-(*tert*-butyldimethylsilyloxy)phenylethynyl]-6-[*p*-(ethoxycarbonyl)phenylethynyl]benzene (3f). Reaction conditions: **11** (138 mg, 0.11 mmol), $PdCl_2(PPh_3)_2$ (5.2 mg, 0.0074 mmol), CuI (2.8 mg, 0.015 mmol), PPh_3 (3.9 mg, 0.015 mmol), Et_3N (10 mL), and a solution of **2c** (50.0 mg, 0.29 mmol) in Et_3N (5 mL) at refluxing temperature for 48 h. Purification: column chromatography on silica gel eluted with hexane−$CHCl_3$ (1:1.5) followed by recycle preparative GPC. Yield 61%; yellow solid; mp 255 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.53−7.49 (m, 10H), 6.85−6.82 (m, 10H), 4.42 (q, J = 7.1 Hz, 2H), 1.44 (t, J = 7.1 Hz, 3H), 1.02 (s, 45 H), 0.26 (s, 30H); ^{13}C NMR ($CDCl_3$) δ 166.0, 156.6, 156.50, 156.46, 133.4, 133.35, 133.31, 131.6, 130.1, 129.5, 128.0, 127.8, 127.4, 127.1, 125.8, 120.4, 120.3, 116.1, 116.0, 99.6, 99.5, 99.3, 97.5, 90.6, 86.7, 86.6, 86.5, 61.2, 25.6, 18.2, 14.3, −4.4; IR (KBr) ν 2206, 1719, 1602, 1509, 1272 cm^{-1}. Anal. Calcd for $C_{87}H_{104}O_7Si_5$: C, 74.52; H, 7.48. Found: C, 74.46; H, 7.56.

1,2,3,5-Tetrakis[*p*-(*tert*-butyldimethylsilyloxy)phenylethynyl]-4,6-bis[*p*-(ethoxycarbonyl)phenylethynyl]benzene (3g). Reaction conditions: **4** (164 mg, 0.21 mmol), $PdCl_2(PPh_3)_2$ (11.7 mg, 0.017 mmol), CuI (6.4 mg, 0.033 mmol), PPh_3 (8.8 mg, 0.033 mmol), Et_3N (20 mL), and a solution of **2b** (364 mg, 1.57 mmol) in Et_3N (10 mL) at refluxing temperature for 65 h. Purification: column chromatography on silica gel eluted with hexane−$CHCl_3$ (1:2.5) followed by recycle preparative GPC. Yield 56%; yellow solid; mp 295 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.05 (d, J = 8.2 Hz, 4H), 7.68 (d, J = 8.2 Hz, 4H), 7.51 (d, J = 8.7 Hz, 2H), 7.50 (d, J = 8.7 Hz, 4H), 7.49 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.7 Hz, 6H), 4.42 (q, J = 7.2 Hz, 4H), 1.43 (t, J = 7.2 Hz, 6H), 1.02 (s, 36H), 0.25 (s, 24H); ^{13}C NMR ($CDCl_3$) δ 166.1, 156.8, 156.7, 156.6, 133.4, 133.3, 131.6, 130.2, 129.6, 128.3, 127.9, 127.8, 127.2, 125.9, 120.5, 120.42, 120.36, 116.0, 115.8, 115.7, 100.1, 99.6, 97.7, 90.3, 86.5, 86.3, 61.2, 25.6, 18.3, 14.3, −4.4; IR (KBr) ν 2208, 1719, 1602, 1509, 1273 cm^{-1}. Anal. Calcd for $C_{84}H_{94}O_8Si_4$: C, 75.07; H, 7.05. Found: C, 75.20; H, 7.05.

1,3-Bis[*p*-(*tert*-butyldimethylsilyloxy)phenylethynyl]-2,4,5,6-tetrakis[*p*-(ethoxycarbonyl)phenylethynyl]benzene (3i). Reaction conditions: **6** (267 mg, 0.29 mmol), $PdCl_2(PPh_3)_2$ (13.6 mg, 0.019 mmol), CuI (7.3 mg, 0.039 mmol), PPh_3 (10.1 mg, 0.039 mmol), Et_3N (20 mL), and a solution of **2b** (287 mg, 1.24 mmol) in Et_3N (10 mL) at refluxing temperature for 43 h. Purification: column chromatography on silica gel eluted with $CHCl_3$ followed by reprecipitation with $CHCl_3$−hexane and then recycle preparative GPC. Yield 63%; yellow solid; mp 265 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 8H), 7.62 (d, J = 8.2 Hz, 8H), 7.46 (d, J = 8.5 Hz, 4H), 6.81 (d, J = 8.5 Hz, 4H), 4.42 (q, J = 7.2 Hz, 8H), 1.44 (t, J = 7.2 Hz, 12H), 1.02 (s, 18 H), 0.25 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 165.82, 165.75, 165.7, 156.6, 133.3, 131.6, 131.5, 130.1, 130.0, 129.34, 129.31, 128.7, 127.8, 127.7, 127.5, 127.4, 126.8, 126.3, 120.2, 115.7, 100.6, 98.5, 98.2, 98.1, 90.4, 90.2, 90.1, 86.5, 61.1, 25.6, 18.2, 14.3, −4.4; IR (KBr) ν 2207, 1719, 1603, 1509, 1275 cm^{-1}. Anal. Calcd for $C_{78}H_{74}O_{10}Si_2$: C, 76.32; H, 6.08. Found: C, 76.34; H, 6.17.

1-[*p*-(*tert*-Butyldimethylsilyloxy)phenylethynyl]-2,3,-4,5,6-pentakis[*p*-(ethoxycarbonyl)phenylethynyl]benzene (3j). Reaction conditions: **7** (206 mg, 0.26 mmol), $PdCl_2(PPh_3)_2$ (14.4 mg, 0.021 mmol), CuI (7.9 mg, 0.042 mmol), PPh_3 (10.8 mg, 0.041 mmol), Et_3N (20 mL), and a solution of **2c** (405 mg, 2.33 mmol) in Et_3N (10 mL) at refluxing temperature for 91 h. Purification: column chromatography on silica gel eluted with $CHCl_3$ followed by reprecipitation with $CHCl_3$−hexane and then recycle preparative GPC. Yield 86%; yellow solid; mp 240 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.99 (d, J = 8.1 Hz,

10H), 7.59 (d, J = 8.1 Hz, 10H), 7.43 (d, J = 8.5 Hz, 2H), 6.79 (d, J = 8.5 Hz, 2H), 4.42 (q, J = 7.1 Hz, 10H), 1.45 (t, J = 7.1 Hz, 15H), 1.02 (s, 9H), 0.25 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 165.62, 165.55, 165.5, 156.6, 133.3, 131.5, 131.41, 131.37, 130.1, 130.0, 129.2, 128.8, 127.5, 127.41, 127.35, 127.3, 127.1, 126.7, 120.1, 115.5, 100.8, 98.6, 98.5, 98.4, 90.1, 89.90, 89.86, 86.4, 61.1, 25.6, 18.2, 14.3, −4.4; IR (KBr) ν 2202, 1719, 1604, 1509, 1275 cm^{-1}. Anal. Calcd for $C_{75}H_{64}O_{11}Si$: C, 77.03; H, 5.52. Found: C, 76.91; H, 5.69.

1,3,5-Tris[*p*-(*tert*-butyldimethylsilyloxy)phenylethynyl]-2,4,6-tris(*p*-nitrophenylethynyl)benzene (3l). Reaction conditions: **9** (355 mg, 0.35 mmol), $PdCl_2(PPh_3)_2$ (18.6 mg, 0.027 mmol), CuI (10.1 mg, 0.053 mmol), PPh_3 (13.9 mg, 0.053 mmol), Et_3N (20 mL), and a solution of **2e** (322 mg, 2.20 mmol) in Et_3N (15 mL) at refluxing temperature for 74 h. Purification: column chromatography on silica gel eluted with hexane−$CHCl_3$ (1.2:1) followed by reprecipitation with $CHCl_3$−hexane. Yield 54%; yellow solid; mp 320 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.21 (d, J = 8.8 Hz, 6H), 7.70 (d, J = 8.8 Hz, 6H), 7.45 (d, J = 8.6 Hz, 6H), 6.85 (d, J = 8.6 Hz, 6H), 1.01 (s, 27H), 0.26 (s, 18 H); ^{13}C NMR ($CDCl_3$) δ 157.2, 147.4, 133.3, 132.4, 129.8, 129.4, 125.5, 123.8, 120.1, 115.1, 101.4, 96.7, 92.1, 85.9, 25.6, 18.3, −4.3; IR (KBr) ν 2206, 1599, 1521, 1342, 1267 cm^{-1}. Anal. Calcd for $C_{72}H_{69}N_3O_9Si_3$: C, 71.79; H, 5.77; N, 3.49. Found: C, 71.50; H, 5.75; N, 3.34.

1,3,5-Tris[*p*-(*N*,*N*-di-*n*-octylamino)phenylethynyl]-2,4,6-tris(*p*-nitrophenylethynyl)benzene (3m). Reaction conditions: **12** (1.68 g, 1.30 mmol), $PdCl_2(PPh_3)_2$ (66.5 mg, 0.095 mmol), CuI (36.0 mg, 0.19 mmol), PPh_3 (49.6 mg, 0.19 mmol), Et_3N (80 mL), and a solution of **2e** (1.15 g, 7.80 mmol) in Et_3N (30 mL) at refluxing temperature for 40 h. Purification: column chromatography on silica gel eluted with hexane−$CHCl_3$ (1.2:1) followed by reprecipitation with Et_2O−MeOH. Yield 50%; orange red solid; mp 61 °C; ^{1}H NMR ($CDCl_3$, 10 mM) δ 8.16 (d, J = 8.9 Hz, 6H), 7.71 (d, J = 8.9 Hz, 6H), 7.38 (d, J = 8.9 Hz, 6H), 6.56 (d, J = 8.9 Hz, 6H), 3.32 (t, J = 7.3 Hz, 12H), 1.67−1.55 (m, 12H), 1.36−1.29 (m, 60H), 0.90 (t, J = 6.9 Hz, 18H); ^{13}C NMR ($CDCl_3$) δ 148.7, 146.7, 133.3, 132.2, 130.7, 130.2, 123.6, 123.4, 111.0, 108.2, 103.1, 95.9, 93.8, 86.3, 50.9, 31.8, 29.5, 29.4, 27.3, 27.2, 22.7, 14.1; IR (KBr) ν 2193, 1604, 1522, 1337, 851, 813 cm^{-1}. Anal. Calcd for $C_{102}H_{126}N_6O_6$: C, 79.96; H, 8.29; N, 5.49. Found: C, 79.86; H, 8.26; N, 5.38.

1,2,3,5-Tetrakis[*p*-(*N*,*N*-di-*n*-octylamino)phenylethynyl]-4,6-bis(*p*-nitrophenylethynyl)benzene (3n). Reaction conditions: **13** (240 mg, 0.15 mmol), $PdCl_2(PPh_3)_2$ (8.4 mg, 0.012 mmol), CuI (3.4 mg, 0.018 mmol), PPh_3 (4.7 mg, 0.018 mmol), Et_3N (15 mL), and a solution of **2e** (95.2 mg, 0.65 mmol) in Et_3N (10 mL) at refluxing temperature for 60 h. Purification: column chromatography on silica gel eluted with hexane−$CHCl_3$ (1.5:1) followed by recycle preparative GPC. Yield 8%; red solid; mp 57 °C; ^{1}H NMR ($CDCl_3$) δ 8.23 (d, J = 8.9 Hz, 4H), 7.77 (d, J = 8.9 Hz, 4H), 7.51 (d, J = 8.9 Hz, 2H), 7.47 (d, J = 8.9 Hz, 4H), 7.43 (d, J = 8.9 Hz, 2H), 6.61 (d, J = 8.9 Hz, 8H), 3.32 (t, J = 7.4 Hz, 16H), 1.67−1.55 (m, 16H), 1.36−1.29 (m, 80H), 0.90 (t, J = 7.0 Hz, 24H); ^{13}C NMR ($CDCl_3$) δ 148.6, 148.5, 148.3, 146.9, 133.3, 133.1, 132.3, 130.8, 129.2, 128.1, 126.5, 123.7, 123.6, 111.2, 109.0, 108.6, 108.2, 102.4, 101.8, 101.3, 95.5, 93.7, 86.2, 86.1, 85.7, 51.0, 31.8, 29.5, 29.3, 27.3, 27.2, 22.6, 14.1; IR (KBr) ν 2192, 1604, 1521, 1338, 853, 810 cm^{-1}. Anal. Calcd for $C_{118}H_{160}N_6O_4$: C, 82.09; H, 9.34; N, 4.87. Found: C, 82.27; H, 9.52; N, 4.77.

1,3,5-Tris[*p*-(*N*,*N*-di-*n*-octylamino)phenylethynyl]-2,4,6-tris[*p*-(1,3-dioxolan-2-yl)phenylethynyl]benzene (3o). Reaction conditions: **12** (800 mg, 0.60 mmol), $PdCl_2(PPh_3)_2$ (37.9 mg, 0.054 mmol), CuI (20.6 mg, 0.11 mmol), PPh_3 (28.3 mg, 0.11 mmol), Et_3N (45 mL), and a solution of **2f** (941 mg, 5.40 mmol) in Et_3N (10 mL) at refluxing temperature for 87 h. Purification: column chromatography on silica gel eluted with hexane−$CHCl_3$ (3:7) and then hexane−EtOAc (5:1) followed by reprecipitation with EtOAc−MeOH and then recycle preparative GPC. Yield 23%; deep orange solid; mp 92 °C; ^{1}H NMR ($CDCl_3$) δ 7.73 (d, J = 8.2 Hz, 6H), 7.52 (d, J = 8.2 Hz, 6H), 7.46 (d, J = 8.8 Hz, 6H), 6.59 (d, J = 8.8 Hz, 6H), 5.87 (s, 3H), 4.21−4.14 (m, 6H), 4.13−4.04 (m, 6H), 3.31 (t, J = 7.3 Hz, 12H), 1.67−1.55 (m, 12H), 1.36−1.29 (m, 60H), 0.91 (t, J = 6.9 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.4, 137.8, 133.2, 131.8, 128.8, 126.5, 124.7, 124.6, 111.2, 108.6, 103.4, 101.7, 97.5, 88.7, 86.0, 65.3, 51.0, 31.8, 29.5, 29.3, 27.3, 27.2, 22.7, 14.1; IR (KBr) ν 2185, 1603, 1523, 812 cm^{-1}. Anal. Calcd for $C_{111}H_{141}N_3O_6$: C, 82.64; H, 8.81; N, 2.60. Found: C, 82.81; H, 8.71; N, 2.60.

1,2,3,5-Tetrakis[*p*-(*N*,*N*-di-*n*-octylamino)phenylethynyl]-4,6-bis[*p*-(1,3-dioxolan-2-yl)phenylethynyl]benzene (3p). Reaction conditions: **13** (299 mg, 0.19 mmol), $PdCl_2(PPh_3)_2$ (7.9 mg, 0.011 mmol), CuI (4.3 mg, 0.023 mmol), PPh_3 (5.9 mg, 0.023 mmol), Et_3N (15 mL), and a solution of **2f** (158 mg, 0.91 mmol) in Et_3N (10 mL) at refluxing temperature for 31 h. Purification: column chromatography on silica gel eluted with hexane−$CHCl_3$ (1:1.5) followed by recycle preparative GPC. Yield 36%; brown solid; mp 54.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.72 (d, J = 8.2 Hz, 4H), 7.54 (d, J = 8.7 Hz, 2H), 7.51 (d, J = 8.2 Hz, 4H), 7.49 (d, J = 8.8 Hz, 4H), 7.45 (d, J = 8.9 Hz, 2H), 6.63−6.57 (m, 8H), 5.87(s, 2H), 4.22−4.13 (m, 4H), 4.12−4.04 (m, 4H), 3.31 (t, J = 7.3 Hz, 16H), 1.67−1.55 (m, 16H), 1.36−1.29 (m, 80H), 0.91 (t, J = 6.9 Hz, 24H); ^{13}C NMR ($CDCl_3$) δ 148.3, 148.2, 148.1, 137.7, 133.3, 133.2, 131.8, 128.0, 127.6, 126.4, 126.1, 124.9, 124.7, 111.2, 109.5, 109.1, 108.9, 103.5, 101.1, 100.9, 100.4, 97.2, 89.0, 86.3, 86.1, 65.3, 51.0, 31.8, 29.5, 29.3, 27.3, 27.2, 22.6, 14.1; IR (KBr) ν 2187, 1604, 1523, 812 cm^{-1}. Anal. Calcd for $C_{124}H_{170}N_4O_4\cdot H_2O$: C, 82.80; H, 9.64; N, 3.11. Found: C, 82.71; H, 9.45; N, 3.07.

1,3,5-Tris[*p*-(*N*,*N*-di-*n*-octylamino)phenylethynyl]-2,4,6-tris(*p*-formylphenylethynyl)benzene (3q). To a solution of **3o** (170 mg, 0.11 mmol) in THF (4 mL) under an argon atmosphere was added 1 M HCl (1.3 mL). After being stirred at room temperature for 16 h, the reaction mixture was neutralized with aqueous Na_2CO_3 and extracted with Et_2O. The organic layer was washed with H_2O and brine and dried over Na_2SO_4. After evaporation of solvents, the residue was subjected to column chromatography on silica gel eluted with hexane−EtOAc (10:1) followed by recycle preparative GPC to give **3q** (128 mg, 82% yield). Deep orange solid; mp 84 °C; ^{1}H NMR ($CDCl_3$) δ 10.04 (s, 3H), 7.88 (d, J = 8.2 Hz, 6H), 7.80 (d, J = 8.2 Hz, 6H), 7.45 (d, J = 8.9 Hz, 6H), 6.59 (d, J = 8.9 Hz, 6H), 3.32 (t, J = 7.4 Hz, 12H), 1.67−1.55 (m, 12H), 1.36−1.29 (m, 60H), 0.90 (t, J = 6.9 Hz, 18H); ^{13}C NMR ($CDCl_3$) δ 191.4, 148.6, 135.4, 133.3, 132.2, 130.0, 129.8, 129.6, 124.0, 111.2, 108.1, 102.9, 97.0, 92.2, 85.9, 51.0, 31.8, 29.5, 29.3, 27.2, 27.1, 22.6, 14.1; IR (KBr) ν 2725, 2189, 1702, 1601, 1523 cm^{-1}. Anal. Calcd for $C_{105}H_{129}N_3O_3$: C, 85.14; H, 8.78; N, 2.84. Found: C, 84.91; H, 8.82; N, 2.69.

1,2,3,5-Tetrakis[*p*-(*N*,*N*-di-*n*-octylamino)phenylethynyl]-4,6-bis(*p*-formylphenylethynyl)benzene (3r). Yield 74%; deep red solid; mp 49.7 °C; ^{1}H NMR ($CDCl_3$) δ 10.05 (s, 2H), 7.90 (d, J = 8.3 Hz, 4H), 7.81 (d, J = 8.3 Hz, 4H), 7.55−7.43 (m, 8H), 6.62−6.58 (m, 8H), 3.31 (t, J = 7.2 Hz, 16H), 1.67−1.56 (m, 16H), 1.35−1.28 (m, 80H), 0.91 (t, J = 6.9 Hz, 24H); ^{13}C NMR ($CDCl_3$) δ 191.5, 148.5, 148.4, 148.2, 135.3, 133.3, 133.1, 132.2, 130.2, 129.6, 128.8, 127.9, 126.4, 123.9, 111.2, 109.1, 108.7, 108.4, 102.0, 101.5, 101.0, 96.5, 92.6, 86.3, 86.1, 85.9, 51.0, 31.8, 29.5, 29.3, 27.2, 27.1, 22.6, 14.1; IR (KBr) ν 2728, 2187, 1703, 1604, 1522, 811 cm^{-1}. Anal. Calcd for $C_{120}H_{162}N_4O_2$: C, 85.15; H, 9.65; N, 3.31. Found: C, 84.88; H, 9.65; N, 3.27.

1,3,5-Tris[*p*-(2,2-dicyanoethenyl)phenylethynyl]-2,4,6-tris[*p*-(*N*,*N*-di-*n*-octylamino)phenylethynyl]benzene (3s). To a solution of **3q** (73.6 mg, 0.050 mmol) in $CHCl_3$ (5 mL) were added benzoic acid (1.8 mg, 0.015 mmol), Et_3N (2.1 μL, 0.015 mmol), and malononitrile (10.5 mg, 0.16 mmol). The resulting mixture was stirred at room temperature for 24 h and then at 50 °C for 100 h. The mixture was washed with H_2O and brine and dried over Na_2SO_4. After evaporation of solvents, the residue was subjected to column chromatography

on Al_2O_3 eluted with hexane−$CHCl_3$ (1.1:0.9) to separate the fractions containing **3s**. The crude **3s** was purified by recycle preparative GPC with $CHCl_3$ as an eluent followed by reprecipitation with $CHCl_3$−hexane to give **3s** (54.0 mg, 67% yield). Dark red solid; mp 119 °C; ^{1}H NMR ($CDCl_3$, 10 mM) δ 7.88 (d, J = 8.5 Hz, 6H), 7.74 (d, J = 8.5 Hz, 6H), 7.72 (s, 3H), 7.42 (d, J = 8.8 Hz, 6H), 6.60 (d, J = 8.8 Hz, 6H), 3.32 (t, J = 7.3 Hz, 12H), 1.67−1.55 (m, 12H), 1.36−1.27 (m, 60H), 0.91 (t, J = 6.9 Hz, 18H); ^{13}C NMR ($CDCl_3$) δ 158.3, 148.7, 133.3, 132.5, 130.6, 130.32, 130.26, 130.2, 123.7, 113.7, 112.7, 111.2, 108.1, 103.5, 97.0, 94.1, 86.2, 82.3, 50.9, 31.8, 29.5, 29.3, 27.3, 27.1, 22.6, 14.1; IR (KBr) ν 2225, 2197, 1604, 1577, 1523, 814 cm^{-1}. Anal. Calcd for $C_{114}H_{139}N_9$: C, 84.24; H, 8.00; N, 7.76. Found: C, 84.07; H, 8.06; N, 7.50.

1,3-Bis[*p*-(2,2-dicyanoethenyl)phenylethynyl]-2,4,5,6-tetrakis[*p*-(*N*,*N*-di-*n*-octylamino)phenylethynyl]benzene (3t). Yield 62%; dark red solid; mp 37 °C; ^{1}H NMR ($CDCl_3$) δ 7.91 (d, J = 8.5 Hz, 4H), 7.77 (d, J = 8.5 Hz, 4H), 7.74 (s, 2H), 7.52−7.42 (m, 8H), 6.61 (d, J = 8.9 Hz, 8H), 3.31 (t, J = 7.4 Hz, 16H), 1.66−1.56 (m, 16H), 1.36−1.27 (m, 80H), 0.90 (t, J = 6.9 Hz, 24H); ^{13}C NMR ($CDCl_3$) δ 158.5, 148.63, 148.55, 148.3, 133.3, 133.1, 132.6, 130.7, 130.6, 130.2, 129.3, 126.6, 123.6, 113.8, 112.7, 111.3, 109.1, 108.6, 108.2, 102.6, 102.0, 101.3, 96.5, 94.5, 86.3, 86.1, 85.8, 82.3, 51.0, 31.8, 29.5, 29.3, 27.3, 27.2, 22.6, 14.1; IR (KBr) ν 2225, 2190, 1603, 1577, 1521, 812 cm^{-1}. Anal. Calcd for $C_{126}H_{162}N_8\cdot 2(H_2O)$: C, 82.94; H, 9.17; N, 6.14. Found: C, 82.94; H, 9.10; N, 5.79.

Hexakis(4-hydroxyphenylethynyl)benzene (3c). To a solution of **3b** (749 mg, 0.51 mmol) in MeOH (15 mL) and THF (15 mL) at 0 °C under an argon atmosphere was added a 2.2 M aqueous solution of KOH (2.8 mL, 6.2 mmol). After being stirred at room temperature for 28 h, the reaction mixture was diluted with H_2O (5 mL). After evaporation of organic solvents, the aqueous residue was acidified with 0.5 M HCl and extracted with EtOAc. The organic layer was washed with H_2O and brine and dried over Na_2SO_4. After evaporation of solvent, the residue was dissolved in a minimum amount of EtOAc and poured into hexane to give **3c** (388 mg, 98% yield). Yellow brown solid; mp 190 °C dec; ^{1}H NMR (DMSO-d_6) δ 10.13 (s, 6H), 7.42 (d, J = 8.5 Hz, 12H), 6.85 (d, J = 8.5 Hz, 12H); ^{13}C NMR (DMSO-d_6) δ 158.9, 133.2, 126.0, 116.2, 112.1, 100.0, 85.6; IR (KBr) ν 3500−3000, 2202, 1607, 1513, 1233 cm^{-1}. Anal. Calcd for $C_{54}H_{30}O_6\cdot 2.5(H_2O)$: C, 79.11; H, 4.30. Found: C, 79.22; H, 4.05.

Hexakis(4-carboxyphenylethynyl)benzene (3e). To a solution of **3d** (520 mg, 0.47 mmol) in THF (30 mL) under an argon atmosphere was added a solution of KOH (1.87 g, 28 mmol) in H_2O (30 mL). The resulting mixture was stirred at 70 °C for 46 h. After evaporation of THF, the aqueous residue was acidified with 2 M HCl. The resulting precipitate was filtered and washed with H_2O and then MeOH. The solid was triturated with MeOH−CH_2Cl_2 and filtered to give **3e** (396 mg, 90% yield). Yellow brown solid; mp 300 °C dec; ^{1}H NMR (DMSO-d_6) δ 7.62 (d, J = 7.8 Hz, 12H), 7.26 (d, J = 7.8 Hz, 12H); ^{13}C NMR (DMSO-d_6) δ 166.3, 131.2, 131.0, 129.2, 126.9, 125.8, 98.9, 88.9; IR (KBr) ν 3300−2700, 2205, 1685, 1604, 1280 cm^{-1}. Anal. Calcd for $C_{60}H_{30}O_{12}\cdot 1.5(H_2O)$: C, 74.30; H, 3.43. Found: C, 74.21; H, 3.64.

1,3,5-Tris(*p*-carboxyphenylethynyl)-2,4,6-tris(*p*-hydroxyphenylethynyl)benzene (3k). Yield 99%; yellow solid; mp 230 °C dec; ^{1}H NMR (DMSO-d_6) δ 10.16 (s, 3H), 8.00 (d, J = 8.3 Hz, 6H), 7.67 (d, J = 8.3 Hz, 6H), 7.41 (d, J = 8.5 Hz, 6H), 6.84 (d, J = 8.5 Hz, 6H); ^{13}C NMR (DMSO-d_6) δ 166.6, 158.6, 133.3, 131.3, 130.4, 129.1, 128.2, 126.9, 124.7, 115.5, 112.6, 101.0, 97.4, 90.2, 85.8; IR (KBr) ν 3600−2500, 2208, 1686, 1604, 1512, 1269 cm^{-1}. Anal. Calcd for $C_{57}H_{30}O_9\cdot 2(H_2O)$: C, 76.50; H, 3.83. Found: C, 76.43; H, 3.95.

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Supporting Information Available: Absorption and fluorescence spectra and their data for **3** and ^{1}H NMR spectra of **3**−**13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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