

Selected Paper

Synthesis and Optical Properties, Including Two-Photon Absorption Cross-Sections, of Differentially Functionalized Starburst-Type π-Conjugated Molecules#

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Differentially functionalized hexakis(*p*-substituted-phenylethynyl)benzene and hexakis[4-(*p*-substituted-styryl)-phenylethynyl]benzene derivatives with various (D_{6h}, D_{3h}, D_{2h}, and C_{2v}) symmetries were synthesized by Sonogashira cross-coupling reactions. The optical properties of this starburst-type π-conjugated system were investigated. Among them, hexakis[4-(*p*-dioctylaminostyryl)phenylethynyl]benzene (**5**) showed the largest two-photon absorption cross-section of $\delta = 818$ GM at 800 nm, which was determined by open aperture *Z*-scan with 120 fs laser pulses in toluene solution.

Organic chromophores with large two-photon absorption (TPA) cross-sections have potential applications in new technologies,[1] including three-dimensional (3-D) optical data storage,[2] two-photon optical power limiting,[3] two-photon 3-D microfabrication,[2b,4] photodynamic therapy,[5] and 3-D fluorescence imaging.[6] The concept that intramolecular charge-transfer, from the ends of a π-conjugated system to the center or vice versa, upon excitation is correlated with enhanced TPA properties has been widely accepted for the design of molecules with large TPA cross-sections.[1] Molecular systems that have been intensively investigated so far include quasilinear D–π–A dipolar molecules,[7] and quasilinear D–π–D, A–π–A, and D–A–D quadrupolar molecules,[1a,8] where D is a donor group, A is an acceptor group, and π is a π-conjugated bridge. As extended systems, quasilinear D–π–A–π–D,[9] D–A–π–A–D, D–A–D–A–D, and D–D–A–D–D systems,[10] tri-branched-octupolar systems,[11] and tetra-branched-cruciform systems[12] have also been developed. It has been pointed out that expansion of π-conjugation, as well as multichromophore systems, lead to enhanced TPA abilities.

Hexa(phenylethynyl)benzene and 1,3,5-tris(*p*-dihexylamino-phenylethynyl)-2,4,6-tris(*p*-nitrophenylethynyl)benzene are known to exhibit third-order and second-order nonlinear optical properties, respectively.[13] A multiannulene molecule with D_{3h} symmetry shows a large TPA cross-section.[14] Previously, we have reported the synthesis of differentially functionalized hexakis(*p*-substituted-phenylethynyl)benzene derivatives with D_{6h}, D_{3h}, and C_{2v} symmetries by the Sonogashira cross-coupling reaction of 1,3,5-tribromo-2,4,6-triiodobenzene with one or two kinds of *p*-substituted-phenylacetylene(s).[15] Major advantages of the hexa(arylethynyl)benzene system are 1) the ease of introducing six chromophores onto the benzene core with various symmetries and 2) the high planarity of the molecule efficiently forming the fully π-conjugated starburst system. We are interested in learning whether the presence of additional donors and/or acceptors with various symmetries and extended π-conjugation would significantly influence optical properties in the starburst-type hexa(arylethynyl)-benzene system. Here, we report the synthesis and optical properties, including TPA cross-sections, of differentially functionalized hexakis(*p*-substituted-phenylethynyl)benzene derivatives **1**–**4** and hexakis[4-(*p*-substituted-styryl)phenyl-ethynyl]benzene derivatives **5**–**13** (Chart 1). Among them, hexakis[4-(*p*-dioctylaminostyryl)phenylethynyl]benzene (**5**) showed the largest TPA cross-section of $\delta = 818$ GM at 800 nm, which was determined by open aperture *Z*-scan with 120 fs laser pulses in toluene solution.

Results and Discussion

Synthesis. The synthesis of hexakis(*p*-substituted-phenyl-ethynyl)benzenes **2** and **3** with C_{2v} and D_{3h} symmetries, respectively, has already been reported.[15] Hexakis(*p*-dioctyl-aminophenylethynyl)benzene (**1**), hexakis[4-(*p*-dioctylamino-styryl)phenylethynyl]benzene (**5**), hexakis[4-(*p*-octylstyryl)-phenylethynyl]benzene (**6**), and hexakis{4-[*p*-bis(*p*-octyl-phenyl)aminostyryl]phenylethynyl}benzene (**13**) with D_{6h} symmetry were synthesized by the Sonogashira cross-coupling reactions of hexabromobenzene with *p*-dioctylaminophenyl-acetylene (**14**), 4-(*p*-dioctylaminostyryl)phenylacetylene (**15**), 4-(*p*-octylstyryl)phenylacetylene (**16**), and 4-[*p*-bis(*p*-octylphenyl)aminostyryl]phenylacetylene (**17**), respectively (Schemes 1a and 1b). 1,3,5-Tris(*p*-dioctylaminophenyl-ethynyl)-2,4,6-tris[4-(*p*-octylstyryl)phenylethynyl]benzene (**4**) with D_{3h} symmetry was prepared by the Sonogashira coupling reaction of 1,3,5-tribromo-2,4,6-tris(*p*-dioctylaminophenyl-ethynyl)benzene[15] with **16** (Scheme 1c).

The Sonogashira coupling reaction of 1,3,5-tribromo-2,4,6-triiodobenzene[15] with 3 equiv of **15** gave 1,3,5-tribromo-2,4,6-tris[4-(*p*-dioctylaminostyryl)phenylethynyl]benzene (**18**) and 1,3-dibromo-2,4,5,6-tetrakis[4-(*p*-dioctylaminostyryl)-

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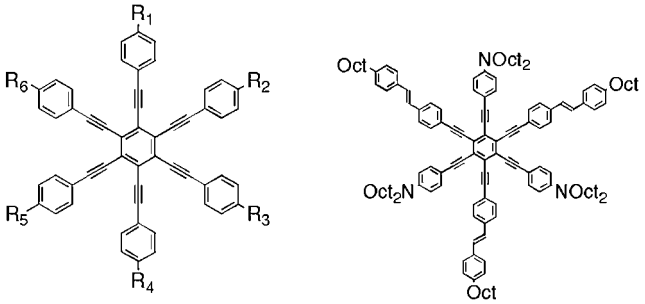
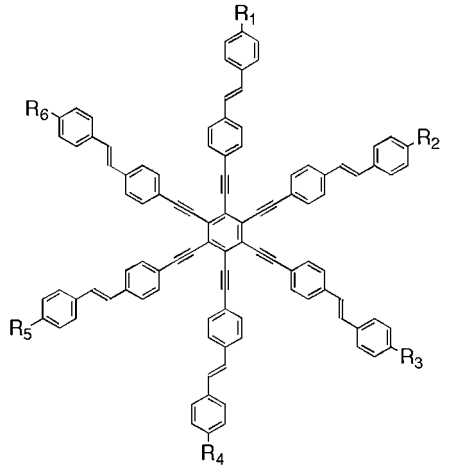


1: $R_1 \sim R_6 = NOct_2$
2: R_1, R_2, R_3, $R_5 = NOct_2$; R_4, $R_6 = NO_2$
3: R_1, R_3, $R_5 = NOct_2$; R_2, R_4, $R_6 = NO_2$

4

Oct = n-C_8H_{17}



5: $R_1 \sim R_6 = NOct_2$
6: $R_1 \sim R_6 = Oct$
7: $R_1 \sim R_5 = NOct_2$; $R_6 = NO_2$
8: R_1, R_2, R_3, $R_5 = NOct_2$; R_4, $R_6 = NO_2$
9: R_1, R_3, $R_5 = NOct_2$; R_2, R_4, $R_6 = NO_2$
10: R_1, R_2, R_4, $R_5 = NOct_2$; R_3, $R_6 = NO_2$
11: R_1, R_2, R_3, $R_5 = NOct_2$; R_4, $R_6 = CH{=}C(CN)_2$
12: R_1, R_3, $R_5 = NOct_2$; R_2, R_4, $R_6 = CH{=}C(CN)_2$
13: $R_1 \sim R_6 = N(C_6H_4\text{-}p\text{-}Oct)_2$

Chart 1. Structures of **1**–**13**.

phenylethynyl]benzene (**19**) in 48% and 14% yields, respectively (Scheme 2a). When 4 equiv of **15** was used under the same conditions, **18**, **19**, and 1-bromo-2,3,4,5,6-pentakis[4-(*p*-dioctylaminostyryl)phenylethynyl]benzene (**20**) were obtained in 25%, 42%, and 6% yields, respectively. The Sonogashira coupling reaction of building blocks **18** (D_{3h} symmetry), **19** (C_{2v} symmetry), and **20** (C_{2v} symmetry) with 4-(*p*-nitrostyryl)-phenylacetylene (**21**) produced 1,3,5-tris[4-(*p*-dioctylaminostyryl)phenylethynyl]-2,4,6-tris[4-(*p*-nitrostyryl)phenylethynyl]-benzene (**9**), 1,2,3,5-tetrakis[4-(*p*-dioctylaminostyryl)phenylethynyl]-4,6-bis[4-(*p*-nitrostyryl)phenylethynyl]benzene (**8**), and 1,2,3,4,5-pentakis[4-(*p*-dioctylaminostyryl)phenylethynyl]-6-[4-(*p*-nitrostyryl)phenylethynyl]benzene (**7**), respectively (Scheme 2b). 1,3,5-Tris{4-[*p*-(2,2-dicyanoethenyl)styryl]phenylethynyl}-2,4,6-tris[4-(*p*-dioctylaminostyryl)phenylethynyl]-benzene (**12**) and 1,3-bis{4-[*p*-(2,2-dicyanoethenyl)styryl]-phenylethynyl}-2,4,5,6-tetrakis[4-(*p*-dioctylaminostyryl)phenylethynyl]benzene (**11**) were prepared by the Sonogashira coupling reaction of 4-[*p*-(1,3-dioxolan-2-yl)styryl]phenylacetylene (**22**) with **18** and **19**, respectively, followed by hydrolysis of the acetal moiety of the resulting coupling products, and subsequent reaction of the resulting aldehyde moiety with malononitrile (Scheme 2c).

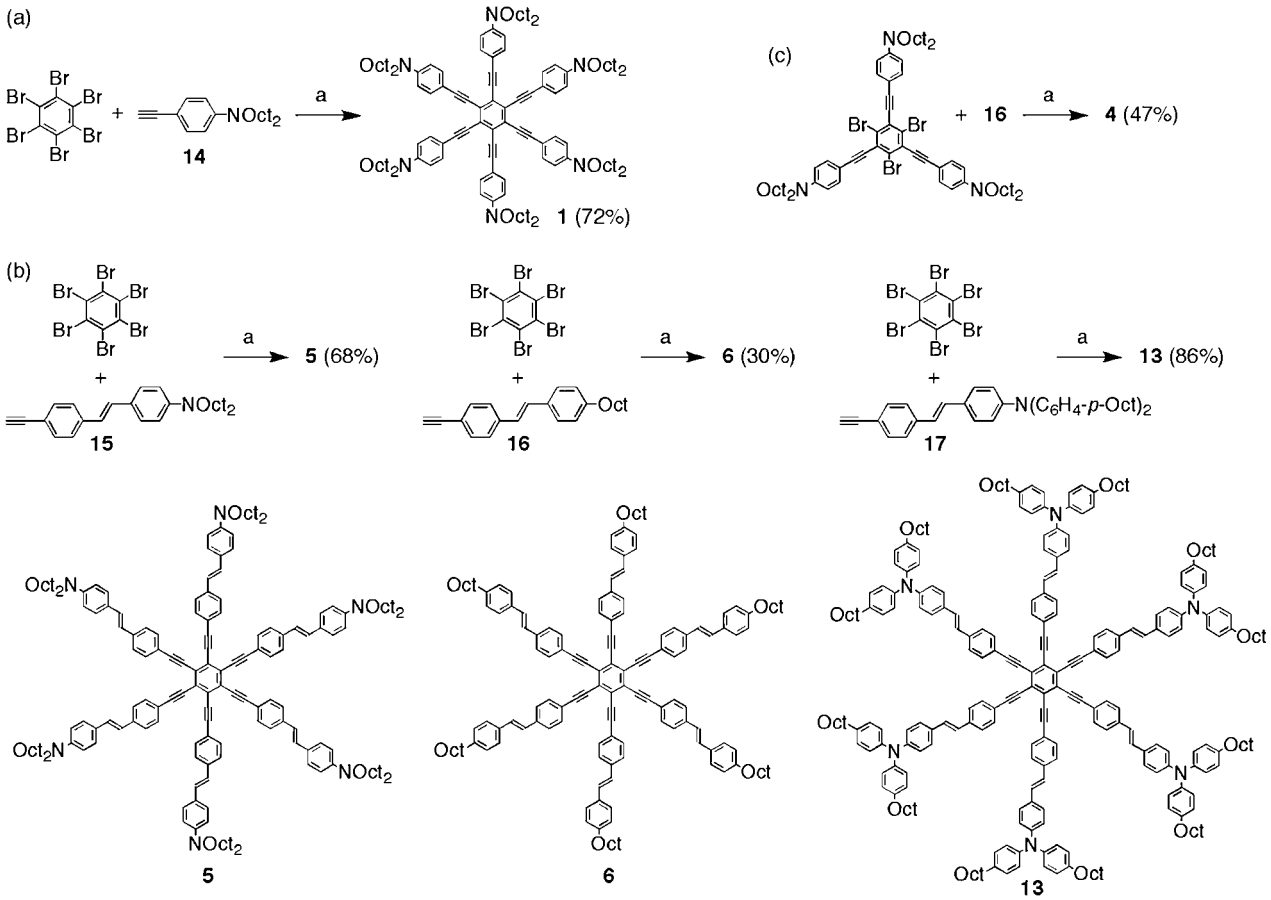
1,2,4,5-Tetrakis[4-(*p*-dioctylaminostyryl)phenylethynyl]-3,6-bis[4-(*p*-nitrostyryl)phenylethynyl]benzene (**10**) with D_{2h} symmetry as a counterpart of **8** with C_{2v} symmetry was synthesized by the Sonogashira coupling reaction of 1,2,4,5-tetrabromo-3,6-bis(trimethylsilylethynyl)benzene (**27**)[16] with **15**, followed by desilylation, and subsequent coupling reaction with 4-bromo-4′-nitrostilbene (Scheme 3).

One-Photon Absorption Properties. The one-photon absorption spectral data of **1**–**13** and representative absorption spectra are summarized in Table 1 and Figure 1, respectively. The absorption maxima ($\lambda^{(1)}_{max}$) were in the range from 399 to 464 nm in $CHCl_3$. In a series of hexakis(*p*-substituted-phenylethynyl)benzene derivatives **1**–**3**, $\lambda^{(1)}_{max}$ was red-shifted as the number of end nitro groups was increased:[15,17] **1** (D_{6h}) < **2** (C_{2v}) < **3** (D_{3h}).

By extension of the π-conjugation with a styryl group, $\lambda^{(1)}_{max}$ of hexakis[4-(*p*-dioctylaminostyryl)phenylethynyl]-benzene (**5**) was red-shifted by ca. 30 nm relative to that of hexakis(*p*-dioctylaminophenylethynyl)benzene (**1**).[8a,12a] In a series of hexakis[4-(*p*-substituted-styryl)phenylethynyl]-benzene derivatives with D_{6h} symmetry, $\lambda^{(1)}_{max}$ showed red shifts upon increasing the electron-donating ability of the end functional groups: **6** (octyl) < **13** (bis(*p*-octylphenyl)amino) < **5** (dioctylamino).[8a,15] The $\lambda^{(1)}_{max}$ of **4** showed a red shift relative to **1** and **6**, resulting from a combination of π-conjugation extension and electron-donating effect of the end functional group. In marked contrast to a series of hexakis-(*p*-substituted-phenylethynyl)benzene derivatives, $\lambda^{(1)}_{max}$ of hexakis[4-(*p*-substituted-styryl)phenylethynyl]benzene derivatives was slightly blue-shifted as the number of strong electron-withdrawing groups was increased: **5** (D_{6h}) ≥ **7** (C_{2v}) ≥ **8** (C_{2v}) > **10** (D_{2h}) > **9** (D_{3h}) in the combination of dioctylamino and nitro groups, and **5** (D_{6h}) > **11** (C_{2v}) > **12** (D_{3h}) in the combination of dioctylamino and 2,2-dicyanoethenyl groups. At this stage, the reason for this unusual result is not clear. In all cases, no notable solvatochromism of $\lambda^{(1)}_{max}$ was observed, although a slight red shift was observed as the dielectric constant of the solvents was increased.[18] For **5**, $\lambda^{(1)}_{max}$ was changed as follows: hexane (425 nm) < toluene (440 nm) < $CHCl_3$ (443 nm) < THF (447 nm) < CH_2Cl_2 (450 nm).

One-Photon Fluorescence Properties. The one-photon fluorescence spectral data of **1**–**13** and representative fluorescence spectra are summarized in Table 1 and Figure 2, respectively. In both series of **1**–**4** and **5**–**13**, derivatives with nitro or 2,2-dicyanoethenyl groups were scarcely fluorescent,[15] whereas the other derivatives were highly fluorescent. The emission maxima (λ^{em}_{max}) of these derivatives were in the range from 482 to 548 nm and showed relatively large Stokes shifts in the range from 4040 to 4690 cm^{-1} in $CHCl_3$.

By extension of π-conjugation with a styryl group, λ^{em}_{max} of **5** was red-shifted by 45 nm relative to that of **1**. In a series of hexakis[4-(*p*-substituted-styryl)phenylethynyl]benzene derivatives with D_{6h} symmetry, λ^{em}_{max} showed red shifts upon increasing the electron-donating ability of the end functional groups: **6** (octyl) < **13** (bis(*p*-octylphenyl)amino) < **5** (dioctylamino). Thus, a combination of π-conjugation extension and electron-donating effect of the end functional group provides enhanced Stokes shifts except for **4**. The fluorescence quantum



Scheme 1. Synthesis of **1**, **4**, **5**, **6**, and **13**. Reagents and conditions: (a) arylacetylenes (9–12 equiv), $PdCl_2(PPh_3)_2$ (7–10 mol %), CuI (14–20 mol %), PPh_3 (14–20 mol %), Et_3N, reflux.

yield (Φ_f) was also increased by extension of π-conjugation with a styryl group (**1** < **5**) and electron-donating effect of the end functional group (**7** ≪ **6** < **13** < **5**). Among **1**–**13**, compound **5** showed the largest fluorescence quantum yield of 0.91 in toluene. In marked contrast to the absorption spectra, the derivatives bearing dioctylamino or bis(*p*-octylphenyl)amino groups showed a notable solvatochromism of the emission as the dielectric constant of the solvents was increased (**5**, **13** vs. **6**), indicative of a polar excited state that is stabilized by polar solvents.[17] The solvatochromism was especially notable on extension of π-conjugation with a styryl group (**5** vs. **1**). For **5**, λ^{em}_{max} and Stokes shift were changed as follows: hexane ($\lambda^{em}_{max} = 483$ nm, Stokes shift = 2830 cm^{-1}) < toluene (514 nm, 3270 cm^{-1}) < $CHCl_3$ (548 nm, 4330 cm^{-1}) < THF (594 nm, 5540 cm^{-1}) < CH_2Cl_2 (602 nm, 5610 cm^{-1}), as shown in Figure 3.[18,19]

Two-Photon Absorption Cross-Sections. The two-photon absorption (TPA) cross-sections of **1**–**13** at 800 nm were determined by open aperture *Z*-scan with 120 fs laser pulses in toluene solution.[11f,20,21] The results are summarized in Table 1. *N*,*N*-Diphenyl-7-[2-(4-pyridyl)ethenyl]-9,9-didecyl-9*H*-fluoren-2-amine (AF-50) was used as a TPA benchmark.[7] In contrast to two-photon fluorescence method,[22] the open aperture *Z*-scan technique is applicable to the TPA-measurement of nonfluorescent compounds. All compounds studied in this work have different absorption maxima, and would exhibit the maximum TPA at different wavelengths. Although detailed discussion of the structure–TPA properties cannot be made at this stage because of no measurements at wavelengths other than 800 nm, the following four items seem to be noteworthy concerning TPA cross-sections in a series of hexakis(*p*-substituted-phenylethynyl)benzene derivatives **1**–**4** and hexakis[4-(*p*-substituted-styryl)phenylethynyl]benzene derivatives **5**–**13**.

Item 1: Among **1**–**13**, hexakis[4-(*p*-dioctylaminostyryl)-phenylethynyl]benzene (**5**) showed the largest TPA cross-section of $\delta = 818$ GM at 800 nm.[23] The power density dependence of transmittance of **5** is shown in Figure 4.

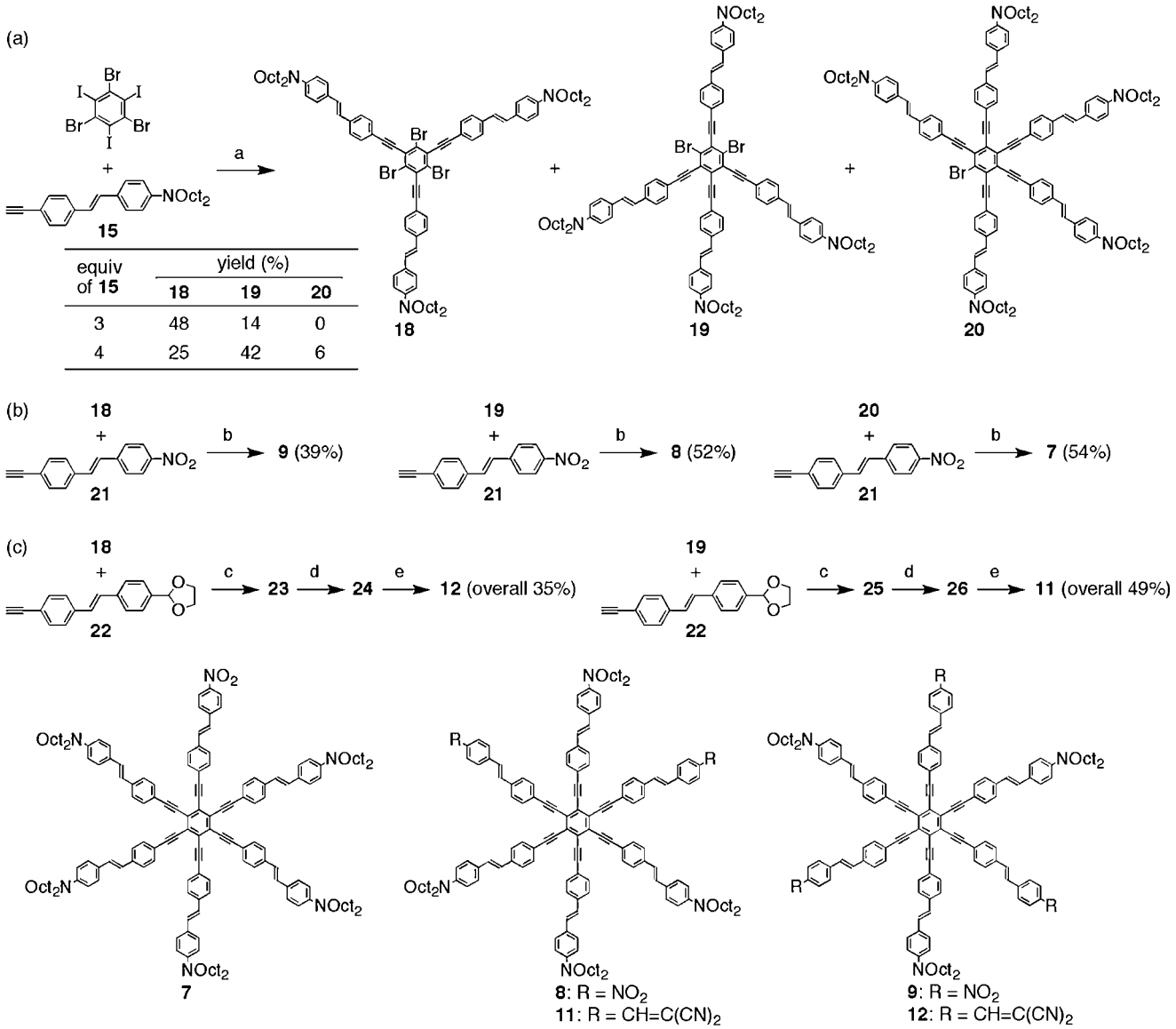
Item 2: TPA cross-sections would be enhanced as the result of π-conjugation extension with a styryl group:[8a] **1** ($\delta = 111$ GM) < **5** (818 GM); **2** (175 GM) < **8** (396 GM); and **3** (135 GM) < **9** (275 GM).

Item 3: TPA cross-sections would be enhanced upon increasing the electron-donating ability of the end functional groups in a series of hexakis[4-(*p*-substituted-styryl)phenylethynyl]benzene derivatives with D_{6h} symmetry:[8a] **6** (octyl, $\delta = 84$ GM) < **13** (bis(*p*-octylphenyl)amino, 532 GM) < **5** (dioctylamino, 818 GM).

Item 4: Although compounds **2**, **3**, and **7**–**12** with nitro or 2,2-dicyanoethenyl groups were scarcely fluorescent, they showed moderate or good TPA cross-sections.

Conclusion

We have demonstrated the synthesis of differentially functionalized hexakis(*p*-substituted-phenylethynyl)benzene



equiv of **15**	yield (%)		
	18	**19**	**20**
3	48	14	0
4	25	42	6

Scheme 2. Synthesis of **7**, **8**, **9**, **11**, **12**, **18**, **19**, and **20**. Reagents and conditions: (a) **15** (3–4 equiv), $PdCl_2(PPh_3)_2$ (2 mol %), CuI (4 mol %), PPh_3 (4 mol %), Et_3N, reflux; (b) **21** (3–6 equiv), $PdCl_2(PPh_3)_2$ (3–9 mol %), CuI (6–18 mol %), PPh_3 (6–18 mol %), Et_3N–THF, reflux; (c) **22** (4–4.5 equiv), $PdCl_2(PPh_3)_2$ (6–9 mol %), CuI (12–18 mol %), PPh_3 (12–18 mol %), Et_3N, reflux; (d) 1 M HCl (12 equiv), THF, rt; (e) $CH_2(CN)_2$ (12 equiv), Et_3N (25 mol %), $PhCO_2H$ (20 mol %), CH_2Cl_2, rt.

and hexakis[4-(*p*-substituted-styryl)phenylethynyl]benzene derivatives with various (D_{6h}, D_{3h}, D_{2h}, and C_{2v}) symmetries, and presented a systematic approach to structure–optical property investigations in this starburst-type π-conjugated system. The one-photon absorption and fluorescence properties and two-photon absorption (TPA) cross-sections were significantly affected by the combination of π-conjugation extension and electron-donating effect of the end functional groups,[8a] as well as by the donor number of them.[14b] In this system, hexakis[4-(*p*-dioctylaminostyryl)phenylethynyl]benzene (**5**) showed the largest fluorescence quantum yield of 0.91 in toluene, and the largest TPA cross-section of $\delta = 818$ GM at 800 nm, which was determined by the open aperture *Z*-scan technique with 120 fs laser pulses in toluene solution. Study on more detailed TPA properties of this starburst-type π-conjugated system is currently underway in our laboratory.

Experimental

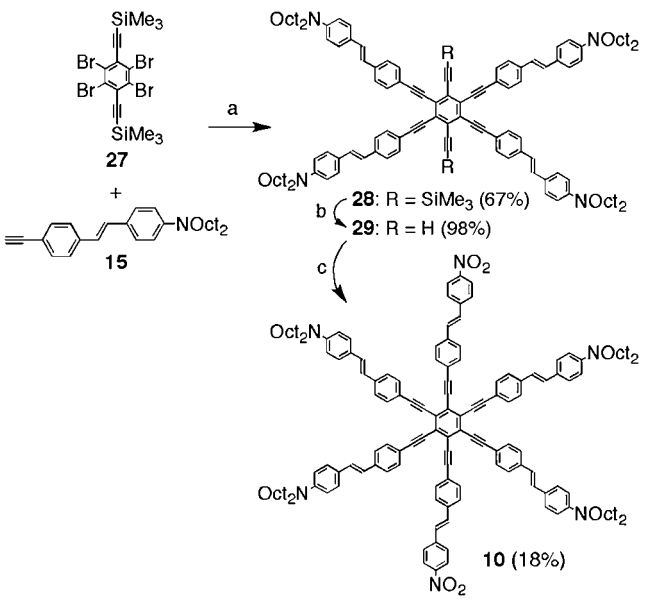
General. Compounds **2** and **3** were synthesized according to the literature.[15] Et_3N and THF were distilled from CaH_2 and sodium–benzophenone ketyl, respectively, under an argon atmosphere. The other solvents and all commercially available reagents were used without any further purification. ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, on a JEOL JNM-AL400 spectrometer. UV–vis spectra were measured on a Shimadzu UV-2450. Fluorescence spectra were measured on a JASCO FP-6300. Recycle preparative GPC was performed on a Japan Analytical Industry LC-9204 with polystyrene gel columns (JAIGEL 1H-40 and 2H-40).

Hexakis(*p*-dioctylaminophenylethynyl)benzene (1). To a mixture of hexabromobenzene (88.2 mg, 0.160 mmol), $PdCl_2(PPh_3)_2$ (11.2 mg, 0.016 mmol), CuI (6.1 mg, 0.032 mmol), and PPh_3 (8.4 mg, 0.032 mmol) under an argon atmosphere were added

Table 1. One- and Two-Photon Properties of **1**–**13** and AF-50

Compd	$\lambda^{(1)}_{max}$/nm (log ε)		λ^{em}_{max}/nm (Φ_f)[a]		Stokes shift[b]/cm^{-1}		δ[c]/GM[d]
	Toluene	$CHCl_3$	Toluene	$CHCl_3$	Toluene	$CHCl_3$	
1	408 (5.11)	415 (5.24)	489 (0.57)	503 (0.49)	4060	4220	111
2	429 (4.98)	433 (5.01)	na[e]	na	na	na	175
3	453 (4.96)	464 (4.97)	na	na	na	na	135
4	419 (5.18)	425 (5.14)	498	513 (0.41)	3790	4040	123
5	440 (5.35)	443 (5.37)	514 (0.91)	548, 578	3270	4330	818
6	398 (5.37)	399 (5.40)	479 (0.39)	482 (0.44)	4250	4320	84
7	440 (5.34)	441 (5.29)	523 (0.03)	na	3610	na	516
8	402, 439 (5.14, 5.14)	406, 434 (5.27, 5.26)	na	na	na	na	396
9	398 (5.15)	401 (5.24)	na	na	na	na	275
10	425 (5.23)	426 (5.30)	531 (0.02)	na	4700	na	357
11	436 (5.20)	439 (5.36)	na	na	na	na	371
12	426 (5.02)	433 (5.29)	na	na	na	na	365
13	433 (5.23)	434 (5.32)	506 (0.83)	545, 572	3330	4690	532
AF-50	394						45

a) Fluorescence quantum yield relative to 9,10-bis(phenylethynyl)anthracene in cyclohexane ($\Phi_f = 1.00$). b) $\Delta E = 1/\lambda^{(1)}_{max} - 1/\lambda^{em}_{max}$. c) Two-photon absorption cross-section at 800 nm which was determined by open aperture *Z*-scan with 120 fs laser pulses in toluene solution. The experimental uncertainty of δ value amounts to ±12%. d) 1 GM = 1×10^{-50} cm^4 s photon^{-1} molecule^{-1}. e) na: Not available.



Scheme 3. Synthesis of **10**. Reagents and conditions: (a) **15** (7 equiv), $PdCl_2(PPh_3)_2$ (10 mol %), CuI (20 mol %), PPh_3 (20 mol %), Et_3N, reflux; (b) *n*-Bu_4NF (2 equiv), THF, rt; (c) 4-bromo-4′-nitrostilbene (12 equiv), $Pd(PPh_3)_4$ (10 mol %), CuI (20 mol %), Et_3N–THF, reflux.

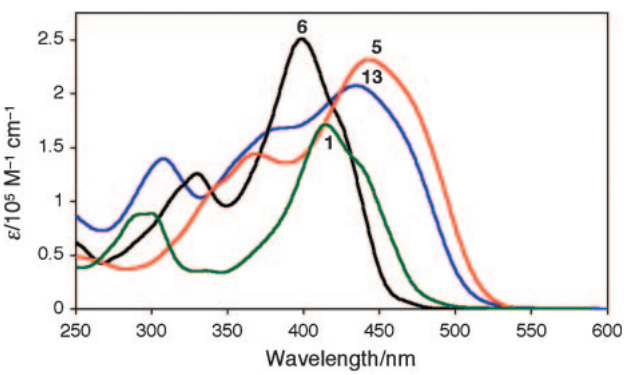


Figure 1. One-photon absorption spectra of **1**, **5**, **6**, and **13** in $CHCl_3$ at 1×10^{-5} M.

Et_3N (10 mL) and then a solution of *p*-dioctylaminophenylacetylene (**14**)[15] (492 mg, 1.44 mmol) in Et_3N (3 mL). The resulting mixture was stirred at refluxing temperature for 24 h. After evaporation of Et_3N, the residue was triturated with hexane and filtered. After evaporation of the filtrate, the residue was subjected to short-pass column chromatography on Al_2O_3 eluted with $CHCl_3$ followed by recycle preparative GPC to give **1** (243 mg, 72% yield). Deep red solid; mp <40 °C; ^{1}H NMR ($CDCl_3$): δ 7.53 (d, $J = 8.8$ Hz, 12H), 6.61 (d, $J = 8.8$ Hz, 12H), 3.32 (t, $J = 7.0$ Hz, 24H), 1.68–1.58 (m, 24H), 1.41–1.29 (m,

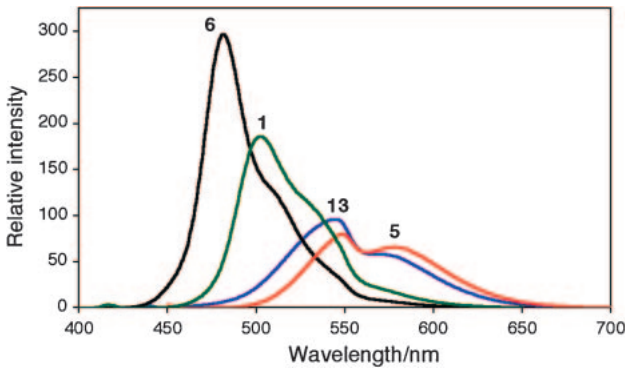


Figure 2. One-photon fluorescence spectra of **1**, **5**, **6**, and **13** in $CHCl_3$ at 1×10^{-6} M.

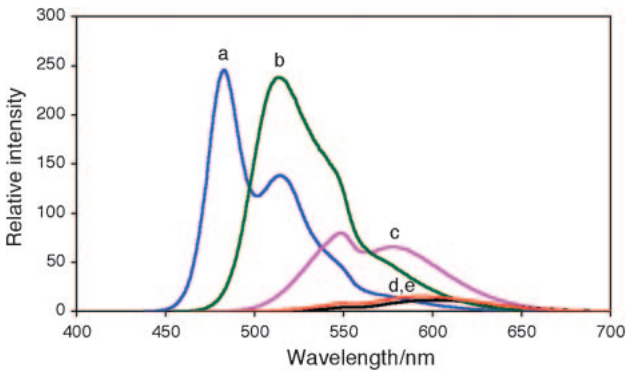


Figure 3. One-photon fluorescence spectra of **5** (1×10^{-6} M) in (a) hexane, (b) toluene, (c) $CHCl_3$, (d) THF, and (e) CH_2Cl_2.

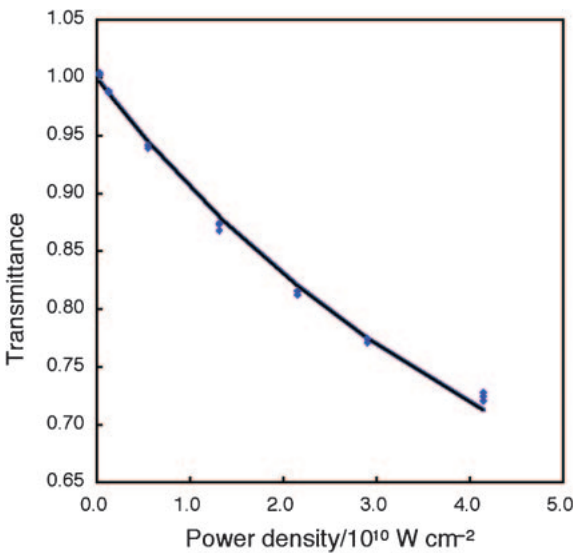


Figure 4. Power density dependence of transmittance of **5** (1×10^{-4} M) in toluene. The line is curve fitted by $T_i = \{\ln(1 + I_0 L\beta)\}/I_0 L\beta$.[21]

120H), 0.92 (t, $J = 7.0$ Hz, 36H); ^{13}C NMR ($CDCl_3$): δ 148.0, 133.2, 126.2, 111.2, 109.9, 99.7, 86.8, 51.0, 31.8, 29.5, 29.3, 27.3, 27.2, 22.7, 14.1. Anal. Calcd for $C_{150}H_{228}N_6$: C, 85.16; H, 10.86; N, 3.97%. Found: C, 84.95; H, 10.98; N, 3.88%.

Typical Procedure for the Synthesis of 4-(*p*-Substituted-styryl)phenylacetylenes: 4-(*p*-Dioctylaminostyryl)phenylacetylene (15). To a mixture of NaH (60% in mineral oil, 0.910 g, 22.7 mmol) and 15-crown-5 (0.39 mL, 2.0 mmol) in THF (60 mL) at 0 °C under an argon atmosphere was added a mixture of *p*-(dioctylamino)benzaldehyde (5.24 g, 15.4 mmol) and diethyl *p*-bromobenzylphosphonate[24] (2.85 g, 15.4 mmol) in THF (30 mL) at 0 °C.[25] The resulting mixture was stirred at 0 °C to room temperature for 24 h. After quenching with H_2O at 0 °C, the reaction mixture was 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–$CHCl_3$ (4:1) to give *trans*-4-bromo-4′-(dioctylamino)stilbene (9.42 g, 96% yield). Pale yellow solid; ^{1}H NMR ($CDCl_3$): δ 7.43 (d, $J = 8.5$ Hz, 2H), 7.37 (d, $J = 8.8$ Hz, 2H), 7.33 (d, $J = 8.5$ Hz, 2H), 7.02 (d, $J = 16.2$ Hz, 1H), 6.80 (d, $J = 16.2$ Hz, 1H), 6.62 (d, $J = 8.8$ Hz, 2H), 3.28 (t, $J = 7.6$ Hz, 4H), 1.65–1.55 (m, 4H), 1.35–1.20 (m, 20H), 0.90 (t, $J = 6.6$ Hz, 6H); ^{13}C NMR ($CDCl_3$): δ 148.0, 137.3, 131.6, 129.6, 127.8, 127.4, 124.0, 122.2, 119.9, 111.6, 51.0, 31.8, 29.5, 29.3, 27.3, 27.2, 22.6, 14.1.

To a mixture of *trans*-4-bromo-4′-(dioctylamino)stilbene (7.50 g, 15.0 mmol), $PdCl_2(PPh_3)_2$ (95 mg, 0.23 mmol), CuI (43 mg, 0.45 mmol), and PPh_3 (118 mg, 0.45 mmol) under an argon atmosphere were added Et_3N (40 mL), THF (40 mL), and trimethylsilylacetylene (3.4 mL, 24 mmol). The resulting mixture was stirred at 50 °C for 15 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. 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–$CHCl_3$ (5:1) to give *trans*-4-dioctylamino-4′-(trimethylsilylethynyl)stilbene (7.41 g, 96% yield). Yellow solid; mp <40 °C; ^{1}H NMR ($CDCl_3$): δ 7.43 (d, $J = 8.7$ Hz, 2H), 7.39 (d, $J = 8.7$ Hz, 2H), 7.38 (d, $J = 8.8$ Hz, 2H), 7.06 (d, $J = 16.2$ Hz, 1H), 6.84 (d, $J = 16.2$ Hz, 1H), 6.62 (d, $J = 8.8$ Hz, 2H), 3.29 (t, $J = 7.6$ Hz, 4H), 1.60–1.56 (m, 4H), 1.33–1.31 (m, 20H), 0.92 (t, $J = 6.6$ Hz, 6H), 0.27 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 148.0, 138.6, 132.1, 129.9, 127.9, 125.6, 124.1, 122.7, 120.7, 111.5, 105.6, 94.3, 51.0, 31.8, 29.5, 29.3, 27.3, 27.2, 22.6, 14.1, 0.20.

To a mixture of *trans*-4-dioctylamino-4′-(trimethylsilylethynyl)-stilbene (7.41 g, 14.4 mmol) and K_2CO_3 (1.98 g, 14.4 mmol) were added MeOH (50 mL) and THF (100 mL). The resulting mixture was stirred for 1 h at room temperature, and then 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 recrystallized from EtOH to give **15** (5.24 g, 82% yield). Pale yellow solid; mp <40 °C; ^{1}H NMR ($CDCl_3$): δ 7.46–7.40 (m, 4H), 7.38 (d, $J = 8.9$ Hz, 2H), 7.06 (d, $J = 16.2$ Hz, 1H), 6.65 (d, $J = 16.2$ Hz, 1H), 6.63 (d, $J = 8.5$ Hz, 2H), 3.29 (t, $J = 7.6$ Hz, 4H), 3.12 (s, 1H), 1.65–1.55 (m, 4H), 1.33–1.30 (m, 20H), 0.90 (t, $J = 6.1$ Hz, 6H); ^{13}C NMR ($CDCl_3$): δ 148.0, 139.0, 132.3, 130.2, 128.0, 125.7, 124.0, 122.6, 120.7, 111.5, 84.1, 77.3, 51.0, 31.8, 29.5, 29.3, 27.3, 27.2, 22.6, 14.1.

4-(*p*-Octylstyryl)phenylacetylene (16): When *p*-octylbenzaldehyde was used under similar conditions, **16** was obtained in overall 58% yield. Pale yellow solid; mp 140 °C; ^{1}H NMR ($CDCl_3$): δ 7.51–7.43 (m, 4H), 7.44 (d, $J = 8.1$ Hz, 2H), 7.19 (d, $J = 8.1$ Hz, 2H), 7.13 (d, $J = 16.3$ Hz, 1H), 7.04 (d, $J = 16.3$ Hz, 1H), 3.14 (s, 1H), 2.63 (t, $J = 7.7$ Hz, 2H), 1.66–1.61 (m, 2H), 1.33–1.29 (m, 10H), 0.90 (t, $J = 6.7$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 143.1, 138.1, 134.4, 132.4, 129.9, 128.8, 126.8, 126.6, 126.2, 120.8, 83.8, 77.7, 35.8, 31.9, 31.4, 29.5, 29.31, 29.25, 22.7, 14.1.

4-[*p*-Bis(*p*-octylphenyl)aminostyryl]phenylacetylene (17): When *p*-bis(*p*-octylphenyl)aminobenzaldehyde was used under similar conditions, **17** was obtained in overall 42% yield. Yellow viscous oil; ^{1}H NMR ($CDCl_3$): δ 7.47 (d, $J = 8.5$ Hz, 2H), 7.43 (d, $J = 8.5$ Hz, 2H), 7.35 (d, $J = 8.7$ Hz, 2H), 7.10–6.99 (m, 11H), 6.93 (d, $J = 16.3$ Hz, 1H), 3.12 (s, 1H), 2.57 (t, $J = 7.7$ Hz, 4H), 1.64–1.59 (m, 4H), 1.33–1.29 (m, 20H), 0.90 (t, $J = 6.7$ Hz, 6H); ^{13}C NMR ($CDCl_3$): δ 148.2, 145.0, 138.3, 138.0, 132.4, 130.0, 129.6, 129.2, 127.4, 126.0, 125.4, 124.7, 122.2, 120.4, 83.9, 77.7, 35.4, 31.9, 31.5, 29.5, 29.4, 29.3, 22.7, 14.1.

4-(*p*-Nitrostyryl)phenylacetylene (21): When *p*-nitrobenzaldehyde was used under similar conditions, **21** was obtained in overall 69% yield. Yellow solid; mp 210–212 °C; ^{1}H NMR ($CDCl_3$): δ 8.24 (d, $J = 8.8$ Hz, 2H), 7.64 (d, $J = 8.8$ Hz, 2H), 7.52 (s-like, 4H), 7.25 (d, $J = 16.3$ Hz, 1H), 7.16 (d, $J = 16.3$ Hz, 1H), 3.19 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 146.9, 143.4, 136.6, 132.6, 127.4, 127.0, 126.8, 126.6, 124.1, 122.3, 83.4, 78.7.

4-[*p*-(1,3-Dioxolan-2-yl)styryl]phenylacetylene (22): When *p*-(1,3-dioxolan-2-yl)benzaldehyde was used under similar conditions, **22** was obtained in overall 65% yield. Yellow solid; mp 176–179 °C; ^{1}H NMR ($CDCl_3$): δ 7.54 (d, $J = 8.3$ Hz, 2H), 7.51–7.45 (m, 6H), 7.15 (d, $J = 16.4$ Hz, 1H), 7.09 (d, $J = 16.4$ Hz, 1H), 5.84 (s, 1H), 4.18–4.11 (m, 2H), 4.10–4.03 (m, 2H), 3.14 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 137.8, 137.6, 137.4, 132.4, 129.3, 128.3, 126.9, 126.6, 126.4, 121.1, 103.5, 83.7, 78.0, 65.3.

1,3,5-Tris(*p*-dioctylaminophenylethynyl)-2,4,6-tris[4-(*p*-octylstyryl)phenylethynyl]benzene (4). To a mixture of 1,3,5-tribromo-2,4,6-tris(*p*-dioctylaminophenylethynyl)benzene[15] (46.8 mg, 0.035 mmol), **16** (100 mg, 0.32 mmol), $PdCl_2(PPh_3)_2$ (2.2 mg, 0.003 mmol), CuI (1.2 mg, 0.006 mmol), and PPh_3 (1.7 mg, 0.006 mmol) under an argon atmosphere was added Et_3N (10 mL). The resulting mixture was stirred at 70 °C for 20 h. After evaporation of Et_3N, the residue was triturated with $CHCl_3$ and filtered. After evaporation of the filtrate, the residue was subjected to column chromatography on silica gel eluted with hexane–$CHCl_3$ (2:1) and then hexane–EtOAc (5:1) followed by recycle preparative GPC to give **4** (33.7 mg, 47% yield). Red solid; mp 117–121 °C; ^{1}H NMR ($CDCl_3$): δ 7.68 (d, $J = 8.3$ Hz, 6H), 7.53 (d, $J = 8.3$ Hz, 6H), 7.51 (d, $J = 8.9$ Hz, 6H), 7.49 (d, $J = 8.2$ Hz, 6H), 7.20 (d, $J = 8.2$ Hz, 6H), 7.17 (d, $J = 16.3$ Hz, 3H), 7.09 (d, $J = 16.3$ Hz, 3H), 6.61 (d, $J = 8.9$ Hz, 6H), 3.32 (t, $J = 7.9$ Hz, 12H), 2.63 (t, $J = 7.9$ Hz, 6H), 1.64–1.56 (m, 18H), 1.35–1.30 (m, 90H), 0.92–0.87 (m, 27H); ^{13}C NMR ($CDCl_3$): δ 148.4, 143.0, 137.5, 134.6, 133.3, 132.2, 129.5, 128.8, 128.4, 127.2, 126.5, 126.3, 125.0, 122.7, 111.3, 108.9, 101.5, 98.2, 89.3, 86.3, 51.0, 35.8, 31.9, 31.8, 31.4, 29.5, 29.33, 29.26, 27.3, 27.2, 22.7, 14.1. Anal. Calcd for $C_{150}H_{195}N_3$: C, 88.31; H, 9.63; N, 2.06%. Found: C, 88.06; H, 9.82; N, 1.92%.

Typical Procedure for the Synthesis of Hexakis[4-(*p*-substituted-styryl)phenylethynyl]benzenes with D_{6h} Symmetry: Hexakis[4-(*p*-dioctylaminostyryl)phenylethynyl]benzene (5). To a mixture of hexabromobenzene (168.4 mg, 0.305 mmol), **15** (1.64 g, 3.70 mmol), $PdCl_2(PPh_3)_2$ (15.0 mg, 0.021 mmol), CuI (8.1 mg, 0.043 mmol), and PPh_3 (11.2 mg, 0.043 mmol) under an argon atmosphere was added Et_3N (25 mL). The resulting mixture was stirred at refluxing temperature for 45 h. After evaporation of Et_3N, the residue was triturated with hexane and filtered. After evaporation of the filtrate, the residue was subjected to column chromatography on Al_2O_3 eluted with hexane–$CHCl_3$ (2:1) followed by recycle preparative GPC to give **5** (567 mg, 68% yield). Deep red solid; mp 93–96 °C; ^{1}H NMR ($CDCl_3$): δ 7.61 (d, $J = 8.3$ Hz, 12H), 7.47 (d, $J = 8.3$ Hz, 12H), 7.42 (d, $J = 8.7$ Hz, 12H), 7.12 (d, $J = 16.2$ Hz, 6H), 6.90 (d, $J = 16.2$ Hz, 6H), 6.64 (d, $J = 8.7$ Hz, 12H), 3.30 (t, $J = 7.4$ Hz, 24H), 1.62–1.56 (m, 24H), 1.34–1.31 (m, 120H), 0.91 (t, $J = 6.6$ Hz, 36H); ^{13}C NMR ($CDCl_3$): δ 148.0, 138.8, 132.2, 130.0, 128.1, 127.2, 125.9, 124.3, 123.0, 121.1, 111.6, 99.9, 88.5, 51.1, 31.9, 29.5, 29.4, 27.4, 27.2, 22.7, 14.1. Anal. Calcd for $C_{198}H_{264}N_6$: C, 87.17; H, 9.75; N, 3.08%. Found: C, 87.07; H, 9.72; N, 2.97%.

Hexakis[4-(*p*-octylstyryl)phenylethynyl]benzene (6): When **16** was used under similar conditions, **6** was obtained in 30% yield. Yellow solid; mp 140 °C; ^{1}H NMR ($CDCl_3$): δ 7.38 (d, $J = 8.2$ Hz, 12H), 7.34 (d, $J = 8.2$ Hz, 12H), 7.22 (d, $J = 8.3$ Hz, 12H), 7.07 (d, $J = 8.1$ Hz, 12H), 7.01 (d, $J = 16.3$ Hz, 6H), 6.92 (d, $J = 16.3$ Hz, 6H), 2.60 (t, $J = 7.7$ Hz, 12H), 1.64–1.60 (m, 12H), 1.36–1.27 (m, 60H), 0.93 (t, $J = 6.6$ Hz, 18H); ^{13}C NMR ($CDCl_3$): δ 142.6, 137.1, 134.6, 132.3, 129.0, 128.7, 127.3, 126.7, 126.3, 126.2, 122.7, 99.3, 89.3, 35.9, 32.0, 31.5, 29.6, 29.4, 22.7, 14.1. Anal. Calcd for $C_{150}H_{162}$: C, 91.69; H, 8.31%. Found: C, 91.43; H, 8.49%.

Hexakis{4-[*p*-bis(*p*-octylphenyl)aminostyryl]phenylethynyl}benzene (13): When **17** was used under similar conditions, **13** was obtained in 86% yield. Deep red solid; mp 75 °C; ^{1}H NMR ($CDCl_3$): δ 7.61 (d, $J = 8.3$ Hz, 12H), 7.48 (d, $J = 8.3$ Hz, 12H), 7.36 (d, $J = 8.8$ Hz, 12H), 7.13–6.95 (m, 72H), 2.58 (t, $J = 7.7$ Hz, 24H), 1.64–1.61 (m, 24H), 1.36–1.33 (m, 120H), 0.94 (t, $J = 6.6$ Hz, 36H); ^{13}C NMR ($CDCl_3$): δ 147.9, 145.1, 137.9, 137.7, 132.3, 130.2, 129.1, 127.5, 127.2, 126.2, 125.8, 124.7, 123.0, 122.4, 122.0, 99.6, 88.9, 35.4, 31.9, 31.6, 31.4, 29.5, 29.3, 22.7, 14.1. Anal. Calcd for $C_{270}H_{312}N_6$: C, 89.06; H, 8.64; N, 2.31%. Found: C, 89.24; H, 8.80; N, 2.17%.

The Sonogashira Coupling Reaction of 1,3,5-Tribromo-2,4,6-triiodobenzene with 15. To a mixture of 1,3,5-tribromo-2,4,6-triiodobenzene[15] (1.56 g, 2.25 mmol), **15** (4.00 g, 9.01 mmol; 4.0 equiv), $PdCl_2(PPh_3)_2$ (31.6 mg, 0.045 mmol), CuI (17.2 mg, 0.090 mmol), and PPh_3 (23.6 mg, 0.090 mmol) under an argon atmosphere was added Et_3N (80 mL). The resulting mixture was stirred at refluxing temperature for 48 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. 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 Al_2O_3 eluted with hexane–$CHCl_3$ (2.5:1) followed by recycle preparative GPC to give **18** (1.08 g, 25% yield), **19** (1.89 g, 42% yield), and **20** (0.31 g, 6% yield).

When 3.0 equiv of **15** was used under the same conditions, **18** and **19** were obtained in 48% and 14% yields, respectively.

1,3,5-Tribromo-2,4,6-tris[4-(*p*-dioctylaminostyryl)phenylethynyl]benzene (18): Red solid; mp <40 °C; ^{1}H NMR ($CDCl_3$): δ 7.60 (d, $J = 8.3$ Hz, 6H), 7.48 (d, $J = 8.3$ Hz, 6H), 7.40 (d, $J = 8.8$ Hz, 6H), 7.11 (d, $J = 16.1$ Hz, 3H), 6.88 (d, $J = 16.1$ Hz, 3H), 6.63 (d, $J = 8.8$ Hz, 6H), 3.30 (t, $J = 7.5$ Hz, 12H), 1.61–1.56 (m, 12H), 1.34–1.31 (m, 60H), 0.92 (t, $J = 6.7$ Hz, 18H); ^{13}C NMR ($CDCl_3$): δ 148.1, 139.5, 132.1, 130.5, 128.1, 127.8, 127.6, 125.9, 124.1, 123.0, 119.9, 111.6, 100.1, 88.6, 51.1, 31.9, 29.5, 29.4, 27.4, 27.2, 22.7, 14.1. Anal. Calcd for $C_{102}H_{132}Br_3N_3$: C, 74.71; H, 8.11; N, 2.56%. Found: C, 74.42; H, 7.92; N, 2.33%.

1,3-Dibromo-2,4,5,6-tetrakis[4-(*p*-dioctylaminostyryl)phenylethynyl]benzene (19): Deep red solid; mp <40 °C; ^{1}H NMR ($CDCl_3$): δ 7.63–7.56 (m, 8H), 7.50–7.41 (m, 16H), 7.13 (d, $J = 16.1$ Hz, 3H), 7.11 (d, $J = 16.1$ Hz, 1H), 6.91 (d, $J = 16.1$ Hz, 3H), 6.89 (d, $J = 16.1$ Hz, 1H), 6.65 (d, $J = 8.6$ Hz, 8H), 3.31 (t, $J = 7.3$ Hz, 16H), 1.63 (m, 16H), 1.36–1.33 (m, 80H), 0.94 (t, $J = 6.5$ Hz, 24H); ^{13}C NMR ($CDCl_3$): δ 148.0, 139.3, 139.2, 139.1,

132.1, 130.3, 130.2, 128.4, 128.0, 127.6, 127.4, 125.9, 125.8, 124.5, 124.2, 122.7, 120.5, 120.1, 111.6, 101.2, 100.6, 99.9, 89.2, 88.4, 88.1, 51.0, 31.8, 29.8, 29.7, 29.5, 29.3, 27.3, 27.2, 22.7, 14.1. Anal. Calcd for $C_{134}H_{176}Br_2N_4$: C, 80.36; H, 8.86; N, 2.80%. Found: C, 80.10; H, 8.81; N, 2.65%.

1-Bromo-2,3,4,5,6-pentakis[4-(*p*-dioctylaminostyryl)phenylethynyl]benzene (20): Deep red solid; mp <40 °C; ^{1}H NMR ($CDCl_3$): δ 7.61 (t, $J = 8.8$ Hz, 10H), 7.51–7.48 (m, 10H), 7.41 (d, $J = 8.8$ Hz, 10H), 7.10 (d, $J = 15.7$ Hz, 5H), 6.89 (d, $J = 15.7$ Hz, 5H), 6.63 (d, $J = 8.8$ Hz, 10H), 3.29 (t, $J = 7.6$ Hz, 20H), 1.61 (m, 20H), 1.34–1.31 (m, 100H), 0.90 (t, $J = 6.8$ Hz, 30H); ^{13}C NMR ($CDCl_3$): δ 147.9, 138.9, 138.8, 138.7, 132.4, 132.20, 132.18, 130.0, 129.9, 128.1, 127.7, 127.3, 127.2, 127.1, 125.9, 125.8, 124.3, 122.9, 121.1, 121.0, 120.8, 111.6, 100.4, 100.2, 99.2, 88.9, 88.6, 88.0, 51.1, 31.8, 31.7, 29.5, 29.3, 29.2, 27.4, 27.2, 22.6, 22.5, 14.1. Anal. Calcd for $C_{166}H_{220}BrN_5$: C, 84.29; H, 9.37; N, 2.96%. Found: C, 84.11; H, 9.55; N, 3.07%.

1,3,5-Tris[4-(*p*-dioctylaminostyryl)phenylethynyl]-2,4,6-tris-[4-(*p*-nitrostyryl)phenylethynyl]benzene (9). To a mixture of **18** (561 mg, 0.342 mmol), **21** (511 mg, 2.05 mmol), $PdCl_2(PPh_3)_2$ (24.0 mg, 0.034 mmol), CuI (13.6 mg, 0.068 mmol), and PPh_3 (17.9 mg, 0.068 mmol) under an argon atmosphere were added Et_3N (15 mL) and THF (50 mL). The resulting mixture was stirred at 70 °C for 23 h. After evaporation of solvents, the residue was triturated with $CHCl_3$ and filtered. After evaporation of the filtrate, the residue was subjected to column chromatography on Al_2O_3 eluted with hexane–$CHCl_3$ (2:1) followed by recycle preparative GPC to give **9** (288 mg, 39% yield). Deep red solid; mp 190 °C; ^{1}H NMR ($CDCl_3$): δ 7.84 (d, $J = 8.2$ Hz, 6H), 7.22–7.07 (m, 30H), 6.96 (d, $J = 7.7$ Hz, 6H), 6.87–6.68 (m, 9H), 6.55 (d, $J = 16.1$ Hz, 3H), 6.42 (d, $J = 8.4$ Hz, 6H), 3.27–3.15 (m, 12H), 1.62–1.48 (m, 12H), 1.39–1.26 (m, 60H), 0.92 (t, $J = 6.6$ Hz, 18H); ^{13}C NMR ($CDCl_3$): δ 148.1, 146.3, 143.3, 137.8, 135.2, 132.5, 132.2, 132.1, 129.3, 127.9, 127.5, 126.7, 126.6, 126.1, 125.4, 124.3, 123.9, 123.5, 122.5, 121.7, 111.3, 99.3, 98.7, 90.1, 89.0, 50.8, 31.9, 29.5, 29.4, 29.3, 27.1, 22.7, 14.1. Anal. Calcd for $C_{150}H_{162}N_6O_6$: C, 83.99; H, 7.61; N, 3.92%. Found: C, 83.78; H, 7.87; N, 4.11%.

1,2,3,5-Tetrakis[4-(*p*-dioctylaminostyryl)phenylethynyl]-4,6-bis[4-(*p*-nitrostyryl)phenylethynyl]benzene (8): The reaction of **19** with 6 equiv of **21** under the same conditions gave **8** in 52% yield. Deep red solid; mp 165 °C; ^{1}H NMR ($CDCl_3$): δ 7.92 (d, $J = 8.6$ Hz, 4H), 7.39–7.16 (m, 32H), 7.08 (d, $J = 8.2$ Hz, 4H), 6.99–6.47 (m, 20H), 3.28–3.22 (m, 16H), 1.62 (m, 16H), 1.36–1.33 (m, 80H), 0.96–0.92 (m, 24H); ^{13}C NMR ($CDCl_3$): δ 147.9, 147.8, 146.2, 143.5, 137.8, 135.1, 132.7, 132.3, 129.3, 128.0, 127.5, 127.4, 127.0, 126.8, 126.7, 126.6, 125.9, 125.6, 124.4, 124.2, 124.1, 123.8, 123.0, 121.8, 111.5, 99.6, 99.4, 99.3, 98.7, 90.2, 89.2, 88.9, 50.9, 31.9, 29.6, 29.5, 29.4, 29.3, 27.4, 27.20, 27.15, 22.7, 14.1. Anal. Calcd for $C_{166}H_{196}N_6O_4$: C, 85.23; H, 8.44; N, 3.59%. Found: C, 85.05; H, 8.72; N, 3.82%.

1,2,3,4,5-Pentakis[4-(*p*-dioctylaminostyryl)phenylethynyl]-6-[4-(*p*-nitrostyryl)phenylethynyl]benzene (7): The reaction of **20** with 3 equiv of **21** under the same conditions gave **7** in 54% yield. Deep red solid; mp 117 °C; ^{1}H NMR ($CDCl_3$): δ 8.11 (d, $J = 8.3$ Hz, 2H), 7.56–7.52 (m, 14H), 7.41–7.39 (m, 22H), 7.18 (d, $J = 16.6$ Hz, 1H), 7.11–7.05 (m, 6H), 6.91–6.84 (m, 5H), 6.62–6.60 (m, 10H), 3.35–3.25 (m, 20H), 1.67–1.55 (m, 20H), 1.39–1.26 (m, 100H), 0.92 (t, $J = 6.8$ Hz, 30H); ^{13}C NMR ($CDCl_3$): δ 147.9, 146.5, 143.7, 138.4, 135.8, 132.8, 132.34, 132.30, 129.8, 129.7, 128.1, 127.3, 127.2, 126.93, 126.87, 126.5, 125.8, 124.3, 124.1, 124.0, 123.1, 121.5, 111.7, 99.8, 98.9, 88.9, 88.85, 88.79, 51.0, 31.9, 29.5, 29.4, 27.4, 27.2, 22.7, 14.1. Anal. Calcd for $C_{182}H_{230}N_6O_2$: C, 86.27; H, 9.15; N, 3.32%. Found: C, 86.22; H, 9.38; N, 3.19%.

1,3,5-Tris[4-(*p*-dioctylaminostyryl)phenylethynyl]-2,4,6-tris-{4-[*p*-(1,3-dioxolan-2-yl)styryl]phenylethynyl}benzene (23). To a mixture of **18** (819 mg, 0.499 mmol), **22** (621 mg, 2.25 mmol), $PdCl_2(PPh_3)_2$ (35.0 mg, 0.045 mmol), CuI (19.0 mg, 0.100 mmol), and PPh_3 (26.2 mg, 0.100 mmol) under an argon atmosphere was added Et_3N (100 mL). The resulting mixture was stirred at refluxing temperature for 42 h. After evaporation of Et_3N, the residue was triturated with $CHCl_3$ and filtered. After evaporation of the filtrate, the residue was subjected to column chromatography on silica gel eluted with hexane–$CHCl_3$ (1:7) followed by recycle preparative GPC to give **23** (656 mg, 59% yield). Deep red solid; mp 130 °C; ^{1}H NMR ($CDCl_3$): δ 7.60–7.52 (m, 18H), 7.48–7.38 (m, 24H), 7.17 (d, $J = 16.1$ Hz, 3H), 7.11 (d, $J = 16.1$ Hz, 3H), 7.09 (d, $J = 16.1$ Hz, 3H), 6.88 (d, $J = 16.1$ Hz, 3H), 6.62 (d, $J = 8.8$ Hz, 6H), 5.84 (s, 3H), 4.18–4.12 (m, 6H), 4.11–4.07 (m, 6H), 3.30 (t, $J = 7.6$ Hz, 12H), 1.61–1.57 (m, 12H), 1.35–1.30 (m, 60H), 0.91 (t, $J = 6.8$ Hz, 18H); ^{13}C NMR ($CDCl_3$): δ 148.0, 138.7, 138.1, 137.23, 137.17, 132.3, 132.2, 129.9, 128.9, 128.7, 128.1, 127.5, 127.0, 126.9, 126.7, 126.5, 125.8, 124.2, 123.0, 122.8, 121.2, 111.6, 103.6, 100.0, 99.3, 89.1, 88.6, 65.3, 51.0, 31.9, 29.5, 29.4, 27.4, 27.2, 22.7, 14.1. Anal. Calcd for $C_{159}H_{177}N_3O_6$: C, 85.79; H, 8.01; N, 1.89%. Found: C, 85.53; H, 8.29; N, 1.64%.

1,2,3,5-Tetrakis[4-(*p*-dioctylaminostyryl)phenylethynyl]-4,6-tris{4-[*p*-(1,3-dioxolan-2-yl)styryl]phenylethynyl}benzene (25): The reaction of **19** with 4 equiv of **22** under the same conditions gave **25** in 72% yield. Deep red solid; mp 80 °C; ^{1}H NMR ($CDCl_3$): δ 7.65–7.51 (m, 32H), 7.41 (d, $J = 8.2$ Hz, 8H), 7.20 (d, $J = 16.1$ Hz, 2H), 7.15 (d, $J = 16.1$ Hz, 2H), 7.12 (d, $J = 16.1$ Hz, 4H), 6.90 (d, $J = 16.1$ Hz, 4H), 6.63 (d, $J = 8.8$ Hz, 8H), 5.85 (s, 2H), 4.18–4.12 (m, 4H), 4.11–4.05 (m, 4H), 3.30 (t, $J = 7.6$ Hz, 16H), 1.63–1.53 (m, 16H), 1.34–1.30 (m, 80H), 0.91 (t, $J = 6.8$ Hz, 24H); ^{13}C NMR ($CDCl_3$): δ 147.9, 138.4, 138.1, 137.1, 136.9, 132.3, 129.7, 128.8, 128.6, 128.1, 127.4, 127.3, 126.9, 126.8, 126.7, 126.4, 125.8, 124.4, 123.1, 123.0, 121.4, 111.6, 103.6, 99.8, 99.2, 89.3, 88.8, 65.2, 51.0, 31.9, 29.5, 29.4, 27.4, 27.2, 22.7, 14.1. Anal. Calcd for $C_{172}H_{206}N_4O_4$: C, 86.31; H, 8.67; N, 2.34%. Found: C, 86.36; H, 8.96; N, 2.55%.

1,3,5-Tris[4-(*p*-dioctylaminostyryl)phenylethynyl]-2,4,6-tris-[4-(*p*-formylstyryl)phenylethynyl]benzene (24). To a solution of **23** (530 mg, 0.238 mmol) in THF (20 mL) under an argon atmosphere was added 1 M HCl (2.8 mL). After being stirred at room temperature for 17 h, the reaction mixture was neutralized with aqueous Na_2CO_3 and extracted with CH_2Cl_2. 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 Al_2O_3 eluted with CH_2Cl_2 followed by recycle preparative GPC to give **24** (338 mg, 68% yield). Deep red solid; mp 216–219 °C; ^{1}H NMR ($CDCl_3$): δ 9.89 (s, 3H), 7.71 (d, $J = 8.3$ Hz, 6H), 7.52–7.43 (m, 18H), 7.31–7.28 (m, 18H), 7.09 (d, $J = 16.1$ Hz, 3H), 7.01–6.96 (m, 6H), 6.76 (d, $J = 16.1$ Hz, 3H), 6.55 (d, $J = 8.8$ Hz, 6H), 3.27 (t, $J = 7.6$ Hz, 12H), 1.64–1.55 (m, 12H), 1.40–1.28 (m, 60H), 0.92 (t, $J = 6.8$ Hz, 18H); ^{13}C NMR ($CDCl_3$): δ 191.3, 148.0, 143.1, 138.2, 135.9, 135.1, 132.3, 131.6, 130.1, 129.5, 128.1, 127.6, 127.4, 126.95, 126.89, 126.7, 125.7, 124.0, 123.8, 122.9, 121.6, 111.5, 99.7, 98.9, 89.9, 88.9, 51.0, 31.9, 29.5, 29.4, 27.4, 27.2, 22.7, 14.1.

1,2,3,5-Tris[4-(*p*-dioctylaminostyryl)phenylethynyl]-4,6-tris-[4-(*p*-formylstyryl)phenylethynyl]benzene (26): The hydrolysis of **25** under the same conditions gave **26** in 80% yield. Deep red

solid; mp 140–142; ^{1}H NMR ($CDCl_3$): δ 9.93 (s, 2H), 7.77 (d, $J = 8.3$ Hz, 4H), 7.57–7.46 (m, 16H), 7.38–7.34 (m, 20H), 7.16 (d, $J = 16.1$ Hz, 2H), 7.08–7.00 (m, 6H), 6.85 (d, $J = 16.1$ Hz, 3H), 6.82 (d, $J = 16.1$ Hz, 1H), 6.61–6.57 (m, 8H), 3.30 (t, $J = 7.3$ Hz, 16H), 1.64–1.55 (m, 16H), 1.35–1.31 (m, 80H), 0.92 (t, $J = 6.8$ Hz, 24H); ^{13}C NMR ($CDCl_3$): δ 191.4, 147.9, 143.2, 138.3, 136.1, 135.1, 132.34, 132.30, 131.7, 130.2, 129.7, 128.1, 127.5, 127.2, 127.0, 126.9, 126.8, 125.8, 124.3, 123.8, 123.0, 122.8, 121.5, 111.6, 99.8, 99.7, 99.0, 89.8, 88.9, 51.0, 31.9, 29.6, 29.4, 27.4, 27.2, 22.7, 14.1.

1,3,5-Tris{4-[*p*-(2,2-dicyanoethenyl)styryl]phenylethynyl}-2,4,6-tris[4-(*p*-dioctylaminostyryl)phenylethynyl]benzene (12). To a solution of **24** (100.6 mg, 0.045 mmol) in CH_2Cl_2 (2 mL) were added benzoic acid (1.1 mg, 0.009 mmol), Et_3N (1.6 μL, 0.011 mmol), and malononitrile (38.8 mg, 0.587 mmol). The resulting mixture was stirred at room temperature for 4 h. After evaporation of solvents, the residue was subjected to column chromatography on Al_2O_3 eluted with CH_2Cl_2 followed by recycle preparative GPC to give **12** (89 mg, 88% yield). Deep red solid; mp 195 °C; ^{1}H NMR ($CDCl_3$): δ 7.59 (d, $J = 8.3$ Hz, 6H), 7.37–7.33 (m, 21H), 7.17–7.12 (m, 18H), 6.93 (d, $J = 15.6$ Hz, 3H), 6.79 (d, $J = 16.1$ Hz, 3H), 6.76 (d, $J = 16.1$ Hz, 3H), 6.60 (d, $J = 15.6$ Hz, 3H), 6.48 (d, $J = 8.3$ Hz, 6H), 3.29–3.21 (m, 12H), 1.62–1.53 (m, 12H), 1.38–1.27 (m, 60H), 0.93 (t, $J = 6.8$ Hz, 18H); ^{13}C NMR ($CDCl_3$): δ 158.5, 148.1, 143.5, 138.3, 135.7, 132.4, 131.4, 129.8, 129.5, 128.2, 127.8, 127.3, 126.9, 126.8, 126.6, 125.8, 124.1, 122.6, 121.5, 114.3, 113.3, 111.6, 99.7, 98.9, 90.3, 89.1, 80.5, 51.0, 32.1, 29.7, 29.6, 27.5, 27.3, 22.9, 14.1. Anal. Calcd for $C_{162}H_{165}N_9$: C, 86.94; H, 7.43; N, 5.63%. Found: C, 86.65; H, 7.70; N, 5.85%.

1,3-Bis{4-[*p*-(2,2-dicyanoethenyl)styryl]phenylethynyl}-2,4,5,6-tetrakis[4-(*p*-dioctylaminostyryl)phenylethynyl]benzene (11). The reaction of **26** with 10 equiv of malononitrile under the same conditions gave **11** in 86% yield. Deep red solid; mp 160 °C; ^{1}H NMR ($CDCl_3$): δ 7.64 (d, $J = 8.3$ Hz, 4H), 7.48–7.38 (m, 18H), 7.35–7.21 (m, 22H), 7.10–6.67 (m, 10H), 6.61–6.56 (m, 6H), 6.50 (d, $J = 8.8$ Hz, 2H), 3.29–3.21 (m, 16H), 1.68–1.57 (m, 16H), 1.35–1.31 (m, 80H), 0.94–0.91 (m, 24H); ^{13}C NMR ($CDCl_3$): δ 158.4, 148.0, 147.8, 143.5, 138.3, 135.7, 132.6, 132.3, 131.4, 129.6, 128.1, 127.8, 127.4, 127.3, 126.92, 126.88, 126.7, 125.8, 124.2, 124.15, 124.10, 122.8, 121.4, 114.2, 113.1, 111.5, 99.6, 98.9, 90.0, 88.9, 88.7, 80.2, 51.0, 50.9, 31.9, 29.6, 29.4, 27.44, 27.39, 27.23, 27.19, 22.7, 14.1. Anal. Calcd for $C_{174}H_{198}N_8$: C, 87.02; H, 8.31; N, 4.67%. Found: C, 86.81; H, 8.55; N, 4.63%.

1,2,4,5-Tetrabromo-3,6-bis(trimethylsilylethynyl)benzene (27).[16a] To a solution of trimethylsilylacetylene (1.6 mL, 12 mmol) in THF (20 mL) at −78 °C under an argon atmosphere was added a hexane solution of *n*-BuLi (1.6 M, 6.8 mL, 11 mmol). After being stirred at −78 °C for 30 min and then at 0 °C for 15 min, to the resulting solution of lithium trimethylsilylacetylide at 0 °C was added a solution of *p*-bromanil (2.12 g, 5.00 mmol) in THF (30 mL). After being stirred at room temperature for 16 h, the reaction mixture was quenched with saturated NH_4Cl and then 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 (5:1 to 1:1) to give 2,3,5,6-tetrabromo-1,4-bis(trimethylsilylethynyl)-2,5-cyclohexadiene-1,4-diol (2.47 g, 80% yield). ^{1}H NMR ($CDCl_3$): δ 3.25 (s, 2H), 0.21 (s, 18H); ^{13}C NMR ($CDCl_3$): δ 127.6, 101.2, 93.6, 71.9, −0.6.

To a mixture of the diol (2.55 g, 4.11 mmol) and $SnCl_2 \cdot 2H_2O$ under an argon atmosphere were added CH_3CN (30 mL) and two drops of H_2O. The resulting mixture was stirred at refluxing temperature for 16 h. After evaporation of solvents, the residue was triturated with hexane and filtered through celite. After evaporation of the filtrate, the residue was reprecipitated with hexane–EtOH to give **27** (1.32 g, 55% yield). White solid; mp 164 °C; ^{1}H NMR ($CDCl_3$): δ 0.31 (s, 18H); ^{13}C NMR ($CDCl_3$): δ 128.9, 128.0, 108.3, 102.9, −0.4.

1,2,4,5-Tetrakis[4-(*p*-dioctylaminostyryl)phenylethynyl]-3,6-bis(trimethylsilylethynyl)benzene (28). To a mixture of **27** (113 mg, 0.193 mmol), **15** (600 mg, 1.35 mmol), $PdCl_2(PPh_3)_2$ (13.6 mg, 0.019 mmol), CuI (7.4 mg, 0.039 mmol), and PPh_3 (10.1 mg, 0.039 mmol) under an argon atmosphere was added 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 CH_2Cl_2 and filtered. After evaporation of the filtrate, the residue was subjected to column chromatography on Al_2O_3 eluted with CH_2Cl_2 followed by recycle preparative GPC to give **28** (265 mg, 67% yield). Red solid; mp 150 °C; ^{1}H NMR ($CDCl_3$): δ 7.60 (d, $J = 8.3$ Hz, 8H), 7.50 (d, $J = 8.3$ Hz, 8H), 7.42 (d, $J = 8.8$ Hz, 8H), 7.13 (d, $J = 16.1$ Hz, 4H), 6.90 (d, $J = 16.1$ Hz, 4H), 6.64 (d, $J = 8.8$ Hz, 8H), 3.30 (t, $J = 7.6$ Hz, 16H), 1.66–1.55 (m, 16H), 1.39–1.27 (m, 80H), 0.91 (t, $J = 6.6$ Hz, 24H), 0.39 (s, 18H); ^{13}C NMR ($CDCl_3$): δ 148.0, 139.0, 132.1, 130.2, 128.0, 127.6, 127.0, 125.8, 124.1, 122.7, 120.8, 111.5, 104.9, 101.7, 99.9, 88.0, 51.1, 31.8, 29.5, 29.3, 27.3, 27.2, 22.7, 14.1, 0.1. Anal. Calcd for $C_{144}H_{194}N_4Si_2$: C, 84.89; H, 9.60; N, 2.75%. Found: C, 85.16; H, 9.84; N, 2.86%.

1,2,4,5-Tetrakis[4-(*p*-dioctylaminostyryl)phenylethynyl]-3,6-diethynylbenzene (29). To a solution of **28** (202 mg, 0.099 mmol) in THF (10 mL) at room temperature under an argon atmosphere was added a THF solution of *n*-Bu_4NF (1.0 M, 200 μL, 0.200 mmol). After being stirred at room temperature for 40 min, the reaction mixture was partitioned between CH_2Cl_2 and H_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 Al_2O_3 eluted with CH_2Cl_2 to give **29** (184 mg, 98% yield). Red solid; mp <40 °C; ^{1}H NMR ($CDCl_3$): δ 7.60 (d, $J = 8.3$ Hz, 8H), 7.49 (d, $J = 8.3$ Hz, 8H), 7.42 (d, $J = 8.8$ Hz, 8H), 7.12 (d, $J = 16.1$ Hz, 4H), 6.90 (d, $J = 16.1$ Hz, 4H), 6.64 (d, $J = 8.8$ Hz, 8H), 3.79 (s, 2H), 3.30 (t, $J = 6.8$ Hz, 16H), 1.66–1.56 (m, 16H), 1.39–1.25 (m, 80H), 0.91 (t, $J = 6.6$ Hz, 24H); ^{13}C NMR ($CDCl_3$): δ 148.0, 139.1, 132.2, 130.2, 128.03, 127.99, 126.4, 125.8, 124.1, 122.8, 120.6, 111.6, 100.2, 87.7, 86.6, 80.6, 51.1, 31.8, 29.5, 29.3, 27.3, 27.2, 22.7, 14.1.

1,2,4,5-Tetrakis[4-(*p*-dioctylaminostyryl)phenylethynyl]-3,6-bis[4-(*p*-nitrostyryl)phenylethynyl]benzene (10). To a mixture of **29** (152 mg, 0.080 mmol), *trans*-4-bromo-4′-nitrostilbene (293 mg, 0.964 mmol), $Pd(PPh_3)_4$ (9.3 mg, 0.008 mmol), and CuI (3.1 mg, 0.016 mmol) under an argon atmosphere were added Et_3N (6 mL) and THF (9 mL). The resulting mixture was stirred at 70 °C for 44 h. After evaporation of solvents, the residue was triturated with CH_2Cl_2 and filtered. After evaporation of the filtrate, the residue was subjected to column chromatography on Al_2O_3 eluted with CH_2Cl_2 followed by recycle preparative GPC to give **10** (34 mg, 18% yield). Deep red solid; mp 70 °C; ^{1}H NMR ($CDCl_3$): δ 8.01 (d, $J = 8.8$ Hz, 4H), 7.44–7.38 (m, 16H), 7.33–7.29 (m, 16H), 7.23 (d, $J = 8.3$ Hz, 4H), 7.09 (d, $J = 16.1$ Hz, 2H), 6.99 (d, $J = 16.1$ Hz, 4H), 6.96 (d, $J = 16.1$ Hz, 2H), 6.79 (d, $J = 16.1$ Hz, 4H), 6.56 (d, $J = 8.8$ Hz, 8H), 3.28 (t, $J = 7.1$ Hz, 16H), 1.65–1.54 (m, 16H), 1.38–1.26 (m, 80H), 0.92 (t, $J = 6.6$ Hz, 24H); ^{13}C NMR ($CDCl_3$): δ 147.9, 146.4, 143.6, 138.1, 135.5, 132.7, 132.34, 132.30, 129.5, 128.1, 127.3, 127.0, 126.9, 126.8, 126.3, 125.7,

124.2, 124.1, 124.0, 123.0, 121.7, 111.5, 99.6, 98.8, 90.2, 89.0, 51.0, 31.9, 29.5, 29.4, 27.4, 27.2, 22.7, 14.1. Anal. Calcd for $C_{166}H_{196}N_6O_4$: C, 85.23; H, 8.44; N, 3.59%. Found: C, 84.98; H, 8.70; N, 3.41%.

Supporting Information

^{1}H NMR spectra and one-photon absorption and fluorescence spectra of **1**–**13**, and two-photon absorption measurement. This material is available free of charge on the Web at: http://www.csj.jp/journals/bcsj/.

References

Dedicated to the memory of the late Professor Yoshihiko Ito.

1 a) M. Albota, D. Beljonne, J.-L. Brédas, J. E. Ehrlich, J.-Y. Fu, A. A. Heikal, S. E. Hess, T. Kogej, M. D. Levin, S. R. Marder, D. McCord-Maughon, J. W. Perry, H. Röckel, M. Rumi, G. Subramaniam, W. W. Webb, X.-L. Wu, C. Xu, *Science* **1998**, *281*, 1653. b) T.-C. Lin, S.-J. Chung, K.-S. Kim, X. Wang, G. S. He, J. Swiatkiewicz, H. E. Pudavar, P. N. Prasad, *Adv. Polym. Sci.* **2003**, *161*, 157. c) M. Pawlicki, H. A. Collins, R. G. Denning, H. L. Anderson, *Angew. Chem., Int. Ed.* **2009**, *48*, 3244.

2 a) D. A. Parthenopoulos, P. M. Rentzepis, *Science* **1989**, *245*, 843. b) B. H. Cumpston, S. P. Ananthavel, S. Barlow, D. L. Dyer, J. E. Ehrlich, L. L. Erskine, A. A. Heikal, S. M. Kuebler, I.-Y. S. Lee, D. McCord-Maughon, J. Qin, H. Röckel, M. Rumi, X.-L. Wu, S. R. Marder, J. W. Perry, *Nature* **1999**, *398*, 51.

3 a) J. D. Bhawalkar, G. S. He, P. N. Prasad, *Rep. Prog. Phys.* **1996**, *59*, 1041. b) J. E. Ehrlich, X. L. Wu, I.-Y. S. Lee, Z.-Y. Hu, H. Röckel, S. R. Marder, J. W. Perry, *Opt. Lett.* **1997**, *22*, 1843.

4 a) J. H. Strickler, W. W. Webb, *Proc. SPIE—Int. Soc. Opt. Eng.* **1990**, *1398*, 107. b) S. Maruo, O. Nakamura, S. Kawata, *Opt. Lett.* **1997**, *22*, 132. c) S. Kawata, H.-B. Sun, T. Tanaka, K. Takada, *Nature* **2001**, *412*, 697. d) W. Zhou, S. M. Kuebler, K. L. Braun, T. Yu, J. K. Cammack, C. K. Ober, J. W. Perry, S. R. Marder, *Science* **2002**, *296*, 1106.

5 a) W. G. Fisher, W. P. Partridge, Jr., C. Dees, E. A. Wachter, *Photochem. Photobiol.* **1997**, *66*, 141. b) J. D. Bhawalkar, N. D. Kumar, C.-F. Zhao, P. N. Prasad, *J. Clin. Laser Med. Surg.* **1997**, *15*, 201.

6 a) W. Denk, J. H. Strickler, W. W. Webb, *Science* **1990**, *248*, 73. b) P. T. C. So, C. Y. Dong, B. R. Masters, K. M. Berland, *Annu. Rev. Biomed. Eng.* **2000**, *2*, 399.

7 B. A. Reinhardt, L. L. Brott, S. J. Clarson, A. G. Dillard, J. C. Bhatt, R. Kannan, L. Yuan, G. S. He, P. N. Prasad, *Chem. Mater.* **1998**, *10*, 1863.

8 a) M. Rumi, J. E. Ehrlich, A. A. Heikal, J. W. Perry, S. Barlow, Z. Hu, D. McCord-Maughon, T. C. Parker, H. Röckel, S. Thayumanavan, S. R. Marder, D. Beljonne, J.-L. Brédas, *J. Am. Chem. Soc.* **2000**, *122*, 9500. b) S. J. K. Pond, M. Rumi, M. D. Levin, T. C. Parker, D. Beljonne, M. W. Day, J.-L. Brédas, S. R. Marder, J. W. Perry, *J. Phys. Chem. A* **2002**, *106*, 11470. c) O. Mongin, L. Porrès, L. Moreaux, J. Mertz, M. Blanchard-Desce, *Org. Lett.* **2002**, *4*, 719. d) K. Kamada, K. Ohta, Y. Iwase, K. Kondo, *Chem. Phys. Lett.* **2003**, *372*, 386.

9 a) S. Kato, T. Matsumoto, T. Ishi-i, T. Thiemann, M. Shigeiwa, H. Gorohmaru, S. Maeda, Y. Yamashita, S. Mataka, *Chem. Commun.* **2004**, 2342. b) A. Hayek, J.-F. Nicoud, F. Bolze, C. Bourgogne, P. L. Baldeck, *Angew. Chem., Int. Ed.* **2006**, *45*, 6466.

10 a) S. K. Lee, W. J. Yang, J. J. Choi, C. H. Kim, S.-J. Jeon, B. R. Cho, *Org. Lett.* **2005**, *7*, 323. b) S.-J. Chung, M. Rumi, V. Alain, S. Barlow, J. W. Perry, S. R. Marder, *J. Am. Chem. Soc.* **2005**, *127*, 10844. c) S.-J. Chung, S. Zheng, T. Odani, L. Beverina, J. Fu, L. A. Padilha, A. Biesso, J. M. Hales, X. Zhan, K. Schmidt, A. Ye, E. Zojer, S. Barlow, D. J. Hagan, E. W. Van Stryland, Y. Yi, Z. Shuai, G. A. Pagani, J.-L. Brédas, J. W. Perry, S. R. Marder, *J. Am. Chem. Soc.* **2006**, *128*, 14444.

11 a) S.-J. Chung, K.-S. Kim, T.-C. Lin, G. S. He, J. Swiatkiewicz, P. N. Prasad, *J. Phys. Chem. B* **1999**, *103*, 10741. b) B. R. Cho, K. H. Son, S. H. Lee, Y.-S. Song, Y.-K. Lee, S.-J. Jeon, J. H. Choi, H. Lee, M. Cho, *J. Am. Chem. Soc.* **2001**, *123*, 10039. c) L. Porrès, O. Mongin, C. Katan, M. Charlot, T. Pons, J. Mertz, M. Blanchard-Desce, *Org. Lett.* **2004**, *6*, 47. d) R. Kannan, G. S. He, T.-C. Lin, P. N. Prasad, R. A. Vaia, L.-S. Tan, *Chem. Mater.* **2004**, *16*, 185. e) P. Wei, X. Bi, Z. Wu, Z. Xu, *Org. Lett.* **2005**, *7*, 3199. f) S. Kato, T. Matsumoto, M. Shigeiwa, H. Gorohmaru, S. Maeda, T. Ishi-i, S. Mataka, *Chem.—Eur. J.* **2006**, *12*, 2303. g) A. Bhaskar, G. Ramakrishna, Z. Lu, R. Twieg, J. M. Hales, D. J. Hagan, E. W. Van Stryland, T. Goodson, III, *J. Am. Chem. Soc.* **2006**, *128*, 11840.

12 a) G. P. Bartholomew, M. Rumi, S. J. K. Pond, J. W. Perry, S. Tretiak, G. C. Bazan, *J. Am. Chem. Soc.* **2004**, *126*, 11529. b) H. Y. Woo, J. W. Hong, B. Liu, A. Mikhailovsky, D. Korystov, G. C. Bazan, *J. Am. Chem. Soc.* **2005**, *127*, 820.

13 a) K. Kondo, S. Yasuda, T. Sakaguchi, M. Miya, *J. Chem. Soc., Chem. Commun.* **1995**, 55. b) B. Traber, J. J. Wolff, F. Rominger, T. Oeser, R. Gleiter, M. Goebel, R. Wortmann, *Chem.—Eur. J.* **2004**, *10*, 1227.

14 a) A. Bhaskar, R. Guda, M. M. Haley, T. Goodson, III, *J. Am. Chem. Soc.* **2006**, *128*, 13972. b) A. D. Slepkov, F. A. Hegmann, R. R. Tykwinski, K. Kamada, K. Ohta, J. A. Marsden, E. L. Spitler, J. J. Miller, M. M. Haley, *Opt. Lett.* **2006**, *31*, 3315. c) K. Kamada, L. Antonov, S. Yamada, K. Ohta, T. Yoshimura, K. Tahara, A. Inaba, M. Sonoda, Y. Tobe, *ChemPhysChem* **2007**, *8*, 2671. d) H. M. Kim, Y. O. Lee, C. S. Lim, J. S. Kim, B. R. Cho, *J. Org. Chem.* **2008**, *73*, 5127.

15 K. Kobayashi, N. Kobayashi, *J. Org. Chem.* **2004**, *69*, 2487.

16 a) D. M. Bowles, G. J. Palmer, C. A. Landis, J. L. Scott, J. E. Anthony, *Tetrahedron* **2001**, *57*, 3753. b) M. Sonoda, A. Inaba, K. Itahashi, Y. Tobe, *Org. Lett.* **2001**, *3*, 2419.

17 a) J. Brunel, I. Ledoux, J. Zyss, M. Blanchard-Desce, *Chem. Commun.* **2001**, 923. b) G. P. Bartholomew, G. C. Bazan, *J. Am. Chem. Soc.* **2002**, *124*, 5183.

18 The dielectric constants of solvents are as follows: hexane 1.89, toluene 2.38, $CHCl_3$ 4.81, THF 7.6, and CH_2Cl_2 9.08.

19 For **1**, $\lambda^{em}{}_{max}$ and Stokes shift were changed as follows: hexane ($\lambda^{em}{}_{max} = 478$ nm, Stokes shift $= 4330\ cm^{-1}$) < toluene (489 nm, $4060\ cm^{-1}$) < THF (499 nm, $4170\ cm^{-1}$) < $CHCl_3$ (503 nm, $4220\ cm^{-1}$) < H_2Cl_2 (512 nm, $4220\ cm^{-1}$).

20 G. S. He, L. Yuan, N. Cheng, J. D. Bhawalkar, P. N. Prasad, L. L. Brott, S. J. Clarson, B. A. Reinhardt, *J. Opt. Soc. Am. B* **1997**, *14*, 1079.

21 See the Supporting Information.

22 C. Xu, W. W. Webb, *J. Opt. Soc. Am. B* **1996**, *13*, 481.

23 For reference, the TPA cross-section of **5** determined by the two-photon fluorescence method was $\delta = 4211$ GM at 800 nm.

24 C. Bellucci, F. Gualtieri, A. Chiarini, *Eur. J. Med. Chem.* **1987**, *22*, 473.

25 Cf. R. Baker, R. J. Sims, *Synthesis* **1981**, 117.