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Disilylphenylene and Tetrasilylphenylene as a New Building Unit for Highly Fluorescent Poly(aryleneethynylene)s

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Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: We report the synthesis and photophysical properties of poly(aryleneethynylene)s (PAEs) containing disilyl- or tetrasilyl-substituted phenylene as the key building unit. The fluorescence spectra of one of the PAEs, consisting of the diethynylbis(trimethylsilyl)phenylene and fluorenylene units, shows an intense blue emission with the maximum at 428 nm. The absolute quantum yield (Φ_F) and the fluorescence lifetime (τ_s) are 0.92 and 0.39 ns, respectively. The calculated radiative decay rate constant (k_r) from the singlet excited state, based on Φ_F and τ_s, is 2.4×10^9 s^{-1}, which is extremely large for organic molecules. A series of silyl-substituted PAEs, including a tricyclic tetrasilylphenylene-containing polymer, also show intense emissions with large k_r values. Theoretical calculations of the model systems with the bis(phenylethynyl)benzene skeleton reveal the general substituent effect of the silyl groups attached to the PAE skeleton.

Keywords: conjugation • density functional calculations • fluorescence • polymers • silicon

Introduction

Poly(aryleneethynylene)s (PAEs) are one of the fundamental π-conjugated polymers and have long been the subject of extensive research since the first synthesis reported by Yamamoto and coworkers in 1984.[1] In the past two decades, a number of PAEs possessing various arylene units have been designed and studied.[2] Their intense absorption and fluorescence of various colors convinced researchers of their promising applications in light-emitting diodes,[3] photovoltaic cells,[4] and sensors.[5] For gaining their optimal properties and functions, the crucial issue is how to sterically and electronically modify the PAE skeletons. For example, the introduction of bulky substituents, such as the dendritic side chains[6] or structurally rigid three-dimensional skeleton like pentiptycene,[7] can effectively insulate the PAE main chain, resulting in an intense fluorescence even in a highly concentrated solution or in the solid state. The electronic perturbation by the substituents based on the inductive effect[8] or resonance effect[9] also modulates the electronic structure, and thus, the properties. In this context, we are now interested in exploiting a silyl group as a side chain for the PAEs. We envision that the trialkylsilyl group simply works as a bulky tertiary group to prevent the detrimental aggregation leading to the fluorescence quenching. Moreover, the silyl groups attached to π-conjugated systems are known to provide perturbations on the electronic structure through a σ–π or σ*–π* interaction, which is responsible for the bathochromic shifts in the absorption and fluorescence spectra, and enhancement of the fluorescence intensity.[10] The silyl group can also stabilize the anionic π-system through the hyperconjugative effects.[11]

In this study, we designed disilyl- and tetrasilyl-substituted phenylenes as a new building unit for PAEs, as shown in Figure 1. For the disilylphenylene unit, we employed a series of trialkylsilyl groups to elucidate the effect of the alkyl groups. In the case of the tetrasilylphenylene unit, we introduced four silyl groups onto one benzene ring with a fused tricyclic structure in order to minimize the steric congestion of the bulky trialkylsilyl groups. We also envisioned that the cyclic structure can effectively fix the exocyclic Si–C bonds so as to cause the efficient σ–π or σ*–π* interaction. To confirm the effect of the tricyclic structure, we also examined the acyclic tetrakis(trimethylsilyl)benzene as a reference skeleton. We synthesized a series of PAEs **1**–**3** consisting of

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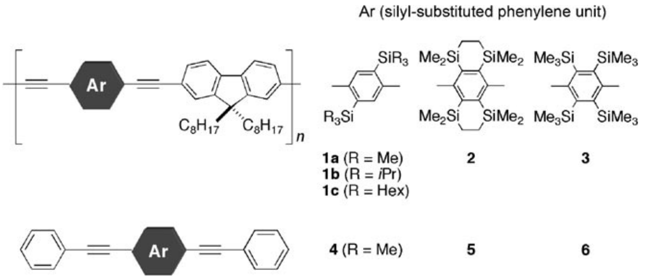


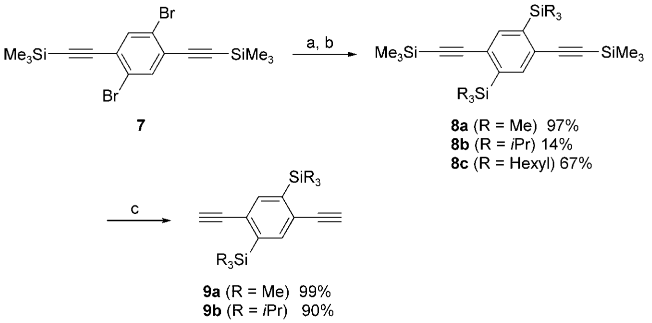
Figure 1. Chemical structures of silyl-substituted PAEs **1**–**3** and their model compounds **4**–**6**.

the disilyl- or tetrasilyl-substituted phenylene units and fluorene unit, as shown in Figure 1. The PAEs consisting of a fluorene unit generally have superior fluorescent properties.[12] Indeed, we now found that the produced polymers showed an intense fluorescence with very narrow emission bands. Furthermore, one of our polymers showed an extremely large radiative decay rate constant for the decay from the singlet excited state. Notably, a large radiative decay rate constant is one requirement for attaining an efficient amplified spontaneous emission (ASE) with a low threshold.[13] We also synthesized bis(phenylethynyl)benzene derivatives **4**–**6** as the models of the PAEs (Figure 1) in order to elucidate the structural and electronic effects of the silyl groups. The details of the synthesis and properties of the polymers, as well as the structural and electronic elucidation of the model systems are described in this article.

Results and Discussion

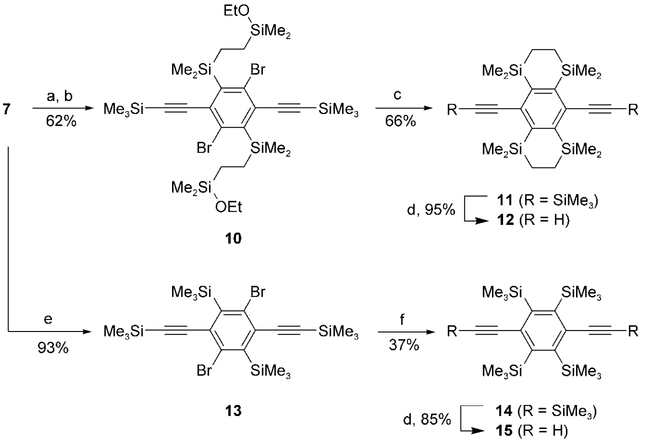
Monomer Synthesis

PAEs **1a**–**c** were synthesized from the key starting materials **9a**–**c**, which were prepared from 1,4-dibromo-2,5-bis(trimethylsilylethynyl)benzene (**7**) in two steps, as shown in Scheme 1. The lithium-halogen exchange reaction of **7** with *n* or *t*BuLi followed by treatment with trialkylsilyl chlorides or triflates produced the tetrasilylated compounds **8a**–**c**. The alkaline desilylation of the terminal trimethylsilyl groups produced the disilylbenzenes **9a**–**c**.



Scheme 1. Synthesis of diethynyldisilylbenzenes. Reaction conditions: a) *n* or *t*BuLi, THF, −78 °C; b) Me_3SiCl, Hex_3SiCl, or iPr_3SiOTf, −78 °C to RT; c) K_2CO_3, MeOH/THF, RT.

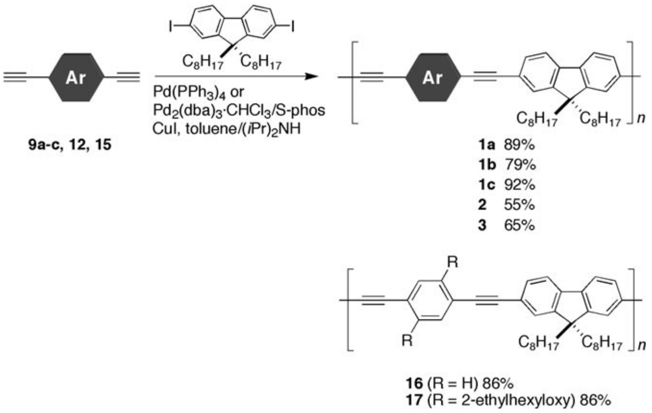
The synthetic routes of the 1,4-diethynyl-2,3,5,6-tetrasilylbenzenes are shown in Scheme 2. The key step in constructing the tetrasilylphenylene skeleton is the consecutive ortho-lithiation/silylation reaction at the *ortho* positions of the bromine, which was originally reported by Lulinski and Serwatowski.[14] The treatment of **7** with LDA in the presence of 1,2-bis(chlorodimethylsilyl)ethane gave a 1,4-dibromo-2,5-disilylbenzene intermediate, which was further converted to the ethoxysilyl-substituted **10** by treatment with EtOH and triethylamine. The dilithiation of **10** with *t*BuLi was followed by the intramolecular cyclization by nucleophilic substitution at the silicon atoms to produce the tricyclic compound **11**. Desilylation of the terminal trimethylsilyl groups with K_2CO_3 gave the tricyclic tetrasilylbenzene **12**. On the basis of this method, the acyclic tetrakis(trimethylsilyl)-substituted derivative **15** was also synthesized.



Scheme 2. Synthesis of diethynyltetrasilylbenzenes. Reaction conditions: a) 1,2-bis(chlorodimethylsilyl)ethane, LDA, THF, −78 °C to RT; b) EtOH, Et_3N, 0 °C to RT; c) *t*BuLi, THF, −78 °C to RT; d) K_2CO_3, MeOH/THF, RT; e) Me_3SiCl, LDA, THF, −78 °C to RT; f) i, LDA, THF, −78 °C; ii, Me_3SiCl, −78 °C to RT.

Synthesis of Copolymers with Fluorene

With the starting materials **9a**–**c** in hand, the Sonogashira reactions were conducted using 2,7-diiodo-9,9-dioctylfluorene. The reactions using $Pd(PPh_3)_4$ and CuI as the cocatalysts in toluene/$(i\mathrm{Pr})_2NH$ smoothly proceeded. After treatment of the reaction mixture with an aqueous solution of NH_4Cl, repeated reprecipitation from poor solvents, such as MeOH, *i*PrOH, and hexane, gave the spectroscopically pure PAEs **1a**–**1c** in good yields (Scheme 3). This condition, however, was not applicable to the synthesis of the tetrasilylphenylene-containing polymers, which resulted only in unidentified brown solids. Instead, using a $Pd_2(dba)_3 \cdot CHCl_3$/S-phos[15] catalyst system, the polymerization proceeded well to yield the desired polymers **2** and **3** in moderate yields. All of the obtained polymers are stable in air and moisture, and



Scheme 3. Synthesis of polymers.

soluble in common organic solvents, such as THF, $CHCl_3$, and CH_2Cl_2. As reference polymers, polymers **16** and **17**, containing unsubstituted phenylene and 2,5-bis(2-ethylhexyloxy)-1,4-phenylene, respectively, were also prepared in a similar manner.

The molecular weights of the polymers obtained by the reprecipitation were estimated by the GPC measurements using polystyrene standards. The number-average molecular weights (M_n) of the polymers varied from 8.8×10^3 to 1.02×10^5, and the degree of polymerizaton (DP) was from 11 to 180 (Table 1). For evaluation of their photophysical properties (Table 2), the high-molecular-weight samples were fractionated by the preparative GPC to minimize the effect of the terminal groups. The estimated molecular weights of those samples are summarized in Table 1.

Table 1. Estimated Molecular Weights of PAEs.[a]

	As-synthesized			Fractionated		
Cmpd	M_n	PDI[b]	DP[c]	M_n	PDI[b]	DP[c]
1a	102000	4.7	180	236000	1.9	360
1b	36000	3.7	43	50500	2.8	61
1c	15000	2.6	14	33500	1.7	31
2	8800	2.0	11	36900	1.1	46
3	11800	2.3	15	45400	1.4	57
16	21200	3.7	41	115000	1.5	220
17	52000	2.2	68	57700	1.7	75

[a] Determined by GPC in THF, using polystyrene standards. [b] Polydispersity index: M_w/M_n. [c] Degree of polymerization.

Table 2. Photophyiscal Properties of **1-5**, **16**, and **17.**[a]

	Absorption		Fluorescence				
Cmpd[b]	λ_{max} [nm][c]	log ε	λ_{max} [nm][c]	Φ_F[d]	τ_s [ns][e]	k_r [s^{-1}][f]	k_{nr} [s^{-1}][g]
1a	418	4.96[h]	428	0.92	0.39	2.4×10^9	2.1×10^8
1b	392	4.81[h]	428	0.58	0.43	1.4×10^9	9.8×10^8
1c	412	4.84[h]	430	0.65	0.44	1.5×10^9	8.0×10^8
2	427	4.75[h]	439	0.84	0.44	1.9×10^9	3.6×10^8
3	410	4.53[h]	445	0.45	0.45	1.0×10^9	1.2×10^9
4	350	4.68	360	0.79	0.79	1.0×10^9	2.7×10^8
5	360	4.66	369	0.31	0.52	6.0×10^8	1.3×10^9
16	406	4.91[h]	417	0.67	0.33	2.0×10^9	1.0×10^9
17	435	4.90[h]	448	0.65	0.46	1.4×10^9	7.6×10^8

[a] In THF. [b] The high molecular weight samples (see Table 1) fractionated by a preparative GPC were used for the measurements. [c] Only the longest absorption and shortest emission maximum wavelengths are given. [d] Absolute fluorescence quantum yield, determined by a calibrated integral sphere system. [e] Lifetime of the singlet excited state. [f] Radiative decay rate constant: $k_r = \Phi_F/\tau_s$. [g] Nonradiative decay rate constant: $k_{nr} = (1-\Phi_F)/\tau_s$. [h] Per repeating unit.

Structures of Tetrasilylphenylene Units

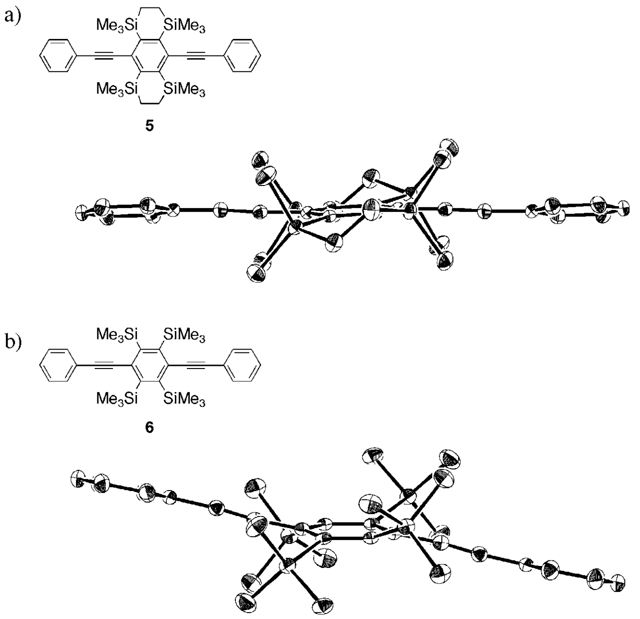


Figure 2. ORTEP drawings of bis(phenylethynyl)tetrasilylbenzenes a) **5** and b) **6**. Thermal ellipsoids are drawn at the 50 % probability. Hydrogen atoms are omitted for clarity.

To elucidate the structural difference between the cyclic and acyclic tetrasilylphenylene units, the bis(phenylethynyl)benzene derivatives **5** and **6** were prepared by the Sonogashira reactions of **12** and **15** with iodobenzene. The crystal structures of these compounds were determined by X-ray crystallographic analysis. Their ORTEP drawings are shown in Figure 2. The cyclic compound **5** has a fairly coplanar π-conjugated framework. The dihedral angle between the terminal benzene and the inner silyl-substituted benzene is 12.84(0.12)° (Figure 2a). The torsion angle between the two adjacent Si–C bonds attached to the central phenylene is 10.2(3)°, demonstrating that the four silicon atoms lie in the plane of the central phenylene. In contrast, the acyclic compound **6** has a highly distorted structure (Figure 2b). The central benzene ring has a chair conformation like cyclohexane. The torsion angle of the Si–C–C–Si on the central phenylene is as large as 42.70(16)°, and the four silicon atoms are significantly deviated from the central benzene plane. This structure is clearly a result of the steric repulsion between the adjacent bulky trimethylsilyl groups. These results demonstrate the importance of the cyclic structure for maintaining the high coplanarity.

UV/Vis Absorption and Fluorescence Spectra

The UV/Vis absorption and fluorescence spectra of the PAEs **1**–**3** in THF are shown in Figure 3. The data are summarized in Table 2, together with those of PAEs **16** and **17** for comparison. In the absorption spectra, PAEs **1a**–**c** have the longest wavelength absorption maxima in the range of 392–418 nm. The cyclic teterasilylphenylene-containing **2** has an absorption maximum at 427 nm, which is slightly longer than those of **1a**–**c**, arising from the effect of the silyl groups. In the fluorescence spectra, polymers **1a**–**c** show sharp emission bands with the maxima around 428–430 nm, together with broad weak vibronic bands. The cyclic-tetrasilylated derivative **2** again showed a slightly longer emission maximum at 439 nm. The acyclic one **3** also has a longer emission maximum at 445 nm. This is presumably a result of the highly distorted structure of the tetrasilylphenylene skeleton in **3**, which may induce the large structural relaxation in the excited state.

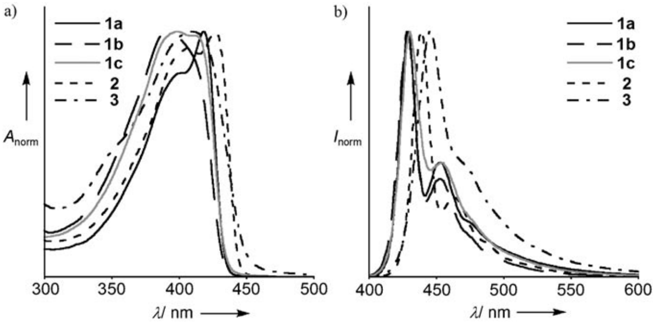


Figure 3. Normalized a) UV/Vis absorption and b) fluorescence spectra of **1**–**3** in THF.

To gain a deeper insight into the photophysical properties of the polymers, the fluorescence quantum yields (Φ_F) were determined using a calibrated integral sphere system, and the fluorescence lifetimes (τ_s) were measured by time-resolved photoluminescence spectroscopy. The data are included in Table 2. The radiative and nonradiative decay rate constants, k_r and k_{nr}, for all the polymers are calculated from Φ_F and τ_s, which are compared in Figure 4. Among the polymers **1**–**3**, the bis(trimethylsilyl)-substituted **1a** has superior properties, that is, the highest Φ_F of 0.92 with a rather short lifetime of 0.39 ns. These data are noteworthy because the resulting k_r, of $2.4\times10^9\,s^{-1}$ is significantly large, which is 20 % and 70 % greater, compared with those of the unsubstituted **16** and alkoxy-substituted **17**, respectively. This may be close to the maximum value for organic molecules.[16] A comparison among **1a**–**c**, however, shows that the large k_r observed for **1a** is not simply from the effect of the silyl groups, but may be special for the trimethylsilyl group. As for the tetrasilylphenylene derivatives, the cyclic derivative **2** also has a fairly large k_r ($1.9\times10^9\,s^{-1}$) comparable to that of **16**, whereas the acyclic tetrasilylphenylene-containing **3** has only a moderate k_r value of $1.0\times10^9\,s^{-1}$. A common feature of **1a** and **2** is their small nonradiative rate constants k_{nr}. Their relatively rigid-coplanar structures[17] may play an important role in these superior excited-state dynamics.

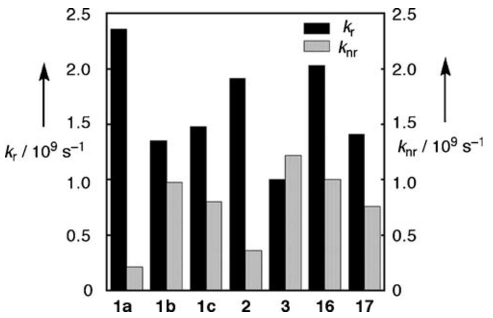


Figure 4. Radiative (k_r, black) and nonradiative (k_{nr}, gray) decay rate constants of **1**–**3**, **16**, and **17** in THF.

Theoretical Studies of the Silyl Effects

To study the electronic effects of the silyl groups, we carried out theoretical calculations of the model compounds, 1,4--bis(phenylethynyl)benzene **18**, the disilyl-substituted **4**, and the tetrasilyl-substituted **5**.

The calculations at the B3LYP/6-31G(d) level of theory revealed how the silyl groups affect the energy levels of the relevant molecular orbitals, as shown in Figure 5. The three compounds, **18**, **4**, and **5**, have similar HOMOs and LUMOs, both of which are delocalized over the entire π-conjugated skeleton, and the silyl groups provide trivial contribution to these frontier orbitals without changing their energy levels. Instead, the silyl groups affect the HOMO−2 and LUMO+2 in the disilyl-substituted **4**, through the σ-π and σ*-π* interaction, respectively. The effect of silyl becomes more significant in the tetrasilylated **5**, and further shifts the corresponding molecular orbitals to the HOMO−1 and LUMO+1, respectively. The insignificant contribution of the silyl groups to the HOMO and LUMO is presumably a result of the large differences in energy between the σ/σ* orbitals of the silyl group and the relevant π/π* orbitals of the bis(phenylethynyl)benzene skeleton.

We also carried out the TD-DFT calculations of **18**, **4**, and **5** to understand the details of the transitions. According to the results, the longest absorption band is assigned to the HOMO→LUMO transition without any contribution by the other electronic configuration. The radiative rate constant, k_r, has a relationship with the wavenumber, ν, of the absorption maximum and the oscillator strength, f, as shown in Equation (1).[18]

$$k_r \propto \nu^2 f \tag{1}$$

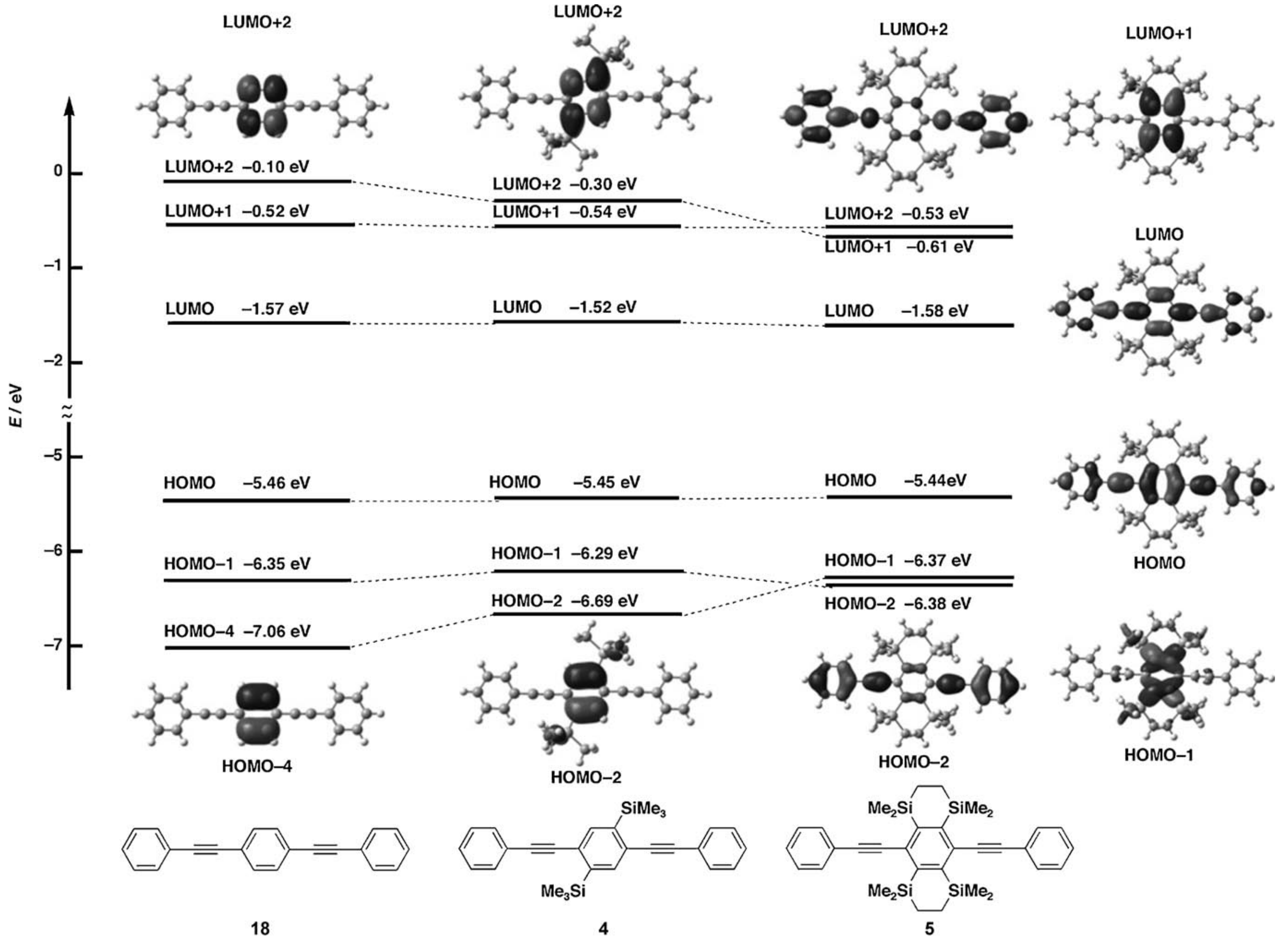


Figure 5. Molecular orbital energy diagram for **18**, **4**, and **5**, calculated at the B3LYP/6-31G(d) level of theory and pictorial representation of the relevant molecular orbitals.

We now paid attention to the effect of the silyl groups on the oscillator strength, *f*, since the differences in the absorption maxima among these three compounds are not significant. The TD-DFT calculations revealed that the *f* value tends to decrease in the order of **18**, **4**, and **5**. This trend was also experimentally confirmed. Thus, the oscillator strength, *f*, is experimentally detemined using Equation (2):[18]

$$f = \left(\frac{4m_e c\varepsilon_0}{N_A e^2}\ln 10\right) \times A = 1.44 \times 10^{-19} \times A \qquad (2)$$

where m_e is the electron mass, c is the velocity of light, ε_0 is the vacuum permittivity, N_A is Avogadro's number, and e is the elementary charge. A is the integral extinction coefficient defined by the Equation (3):[18]

$$A = \int \varepsilon(v)dv \qquad (3)$$

where ε is the extinction coefficient and v is the wavenumber. The oscillator strength, f_obs, was calculated using the observed absorption spectra shown in Figure 6. As summarized in Table 3, the f_obs decreased as the number of silyl groups increased. We can thus conclude that the incorporation of the silyl groups to the present π-conjugated skeleton results in a decrease in the oscillator strength of the transition.[19]

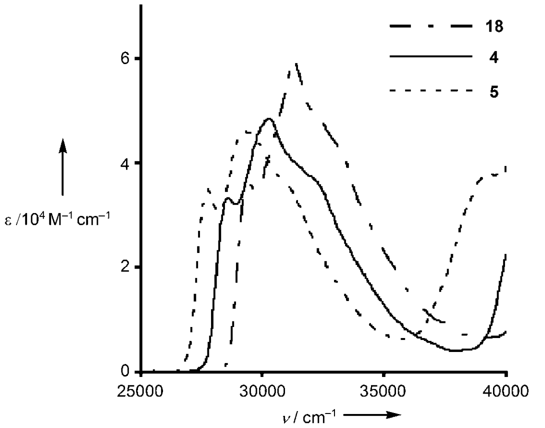


Figure 6. Absorption spectra of model compounds **18**, **4**, and **5** in THF.

Table 3. Observed and Calculated Transition Energies and Oscillator Strengths of **18**, **4** and **5**.

	Observed[a]			Calculated[b]	
Cmpd	λ_{abs} [nm][c] (eV)	ε_{max} (log ε_{max})	f_{obs}[d]	λ_{abs} [nm] (eV)	f_{calc}[d,e]
18	319 (3.78)	59800 (4.78)	1.31	344 (3.61)	1.83
4	331 (3.75)	48500 (4.68)	1.03	344 (3.61)	1.36
5	342 (3.64)	45900 (4.66)	0.97	352 (3.52)	1.21

[a] In THF. [b] Calculated at the B3LYP/6-31G(d) level of theory. Crystal structures determined by X-ray crystallography were used for the single point TD-DFT calculations. [c] Only the strongest absorption wavelengths are given. [d] Oscillator strength. [e] In all the compounds, the absorption bands are assigned to the HOMO→LUMO transition.

This finding of the silyl effect raises two new questions. One is how the silyl groups affect the oscillator strength of the HOMO→LUMO transition despite the trivial contribution of the silyl groups to the HOMO and LUMO. The careful inspection of the composition of these frontier orbitals in terms of the eigenvalue of each atomic orbital revealed that although the contribution of the silyl groups to the HOMO is indeed neglegible, the p orbitals of the silicon atoms, namely the σ* orbitals of the exocylcic Si–C bonds, slightly participate in the LUMO. This subtle contribution may be responsible for the silyl effect on *f*. The other question is the discrepancy between the trends in the oscillator strength, *f*, and k_r. Even in the case of these model systems, the k_r of **4** ($k_r = 1.0 \times 10^9\ s^{-1}$) and **5** ($6.0 \times 10^8\ s^{-1}$; Table 2) are much greater than that of the unsubstituted **18** ($1.95 \times 10^8\ s^{-1}$).[20] This is not consistent with the trend in the oscillator strength, *f* and this discrepancy is still to be understood at this moment.

Conclusions

We have succeeded in synthesizing a series of poly(aryleneethynylene)s containing disilyl- and tetrasilyl-phenylenes as a key building unit. The incorporation of the silyl groups effectively produced superior fluorescence properties. Some of the produced polymers, such as **1a** and **2**, exhibit an intense fluorescence (Φ_F 0.92 for **1a** and 0.84 for **2**) with large k_r values of 2.4×10^9 and $1.9 \times 10^9\ s^{-1}$, respectively. The development of materials having high fluorescence quantum yields with large k_r values is one way of exploring the promising materials for organic lasers, as it is reported that the k_r is in inverse proportion to the lasing threshold.[13] Further investigations are now in progress on the synthesis of various π-conjugated polymers using disilyl- and tetrasilyl-substituted phenylene, as well as the rationalization of the effect of the silyl groups attached to the π-conjugated frameworks.

Experimental Section

General

Melting points (m.p.) were measured on a Stanford Research System OptiMelt MPA100. ^1H and ^{13}C NMR spectra were recorded with a JEOL A-400 spectrometer in $CDCl_3$, C_6D_6, or [D_8]toluene (400 MHz for ^1H and 100 MHz for ^{13}C). UV/Vis absorption spectra and fluorescence spectra measurements were performed with a Shimadzu UV-3150 spectrometer and a Hitachi F-4500 spectrometer, respectively, in spectral grade solvents. Quantum yields were determined with a Hamamatsu C9920-02 calibrated integral sphere system. Fluorescence lifetimes were measured with a Hamamatsu C4780 measurement system equipped with a picosecond light pulser PLP-10 (LED wavelength: 375 nm or 405 nm). Thin-layer chromatography (TLC) was performed on plates coated with 0.25 mm thick silica gel 60F-254 or Aluminum oxide 150 F-254 (Merck). Column chromatography was performed with a PSQ 60B (Fuji Silysia) or Aluminum oxide 150 (type T) (Merck). Preparative gel-permeation chromatography (GPC) was performed with a JAI LC-918 chromatograph equipped with JAIGEL 1H and 2H columns. The analytical GPC measurements were performed with a Shimadzu LC-10AD liquid chromatograph equipped with Shimadzu Shim-pack GPC-801, GPC-8025, GPC-803, GPC-805 columns using THF as an eluent. The molecular weights were calculated using the polystyrene standards. Compounds **7**,[21] **8b**,[22] **9b**,[22] and 2,7-diiodo-9,9-dioctylfluorene[23] were prepared according to the literature. All reactions were carried out under argon atmosphere.

Synthesis of Starting Materials

8a: 1,4-Bis(trimethylsilyl)-2,5-bis(trimethylsilylethynyl)benzene: To a solution of **7** (6.00 g, 14.0 mmol) in ether (35 mL) was added a hexane solution of *n*BuLi (1.6 M, 21.8 mL, 34.9 mmol) dropwise at −78 °C. The mixture was stirred at the same temperature for 10 h. Trimethylsilyl chloride (4.30 mL, 33.6 mmol) was added to the reaction mixture using a syringe. The reaction mixture was gradually warmed to room temperature and stirred for 19 h and concentrated under reduced pressure. The resulting mixture was purified by silica-gel column chromatography (hexane, $R_f = 0.60$) to afford a colorless solid (**8a**, 5.63 g, 13.6 mmol, 97 % yield): m.p. 118 °C (subl); ^1H NMR ($CDCl_3$): $\delta = 7.56$ (s, 2H), 0.36 (s, 18H), 0.25 ppm (s, 18H); ^{13}C NMR ($CDCl_3$): $\delta = 142.9$, 137.9, 127.2, 106.7, 98.9, −0.3, −1.4 ppm; HRMS (EI): *m/z* (%) calcd for $C_{22}H_{38}Si_2$: 414.2051 [M^+]; found: 414.2055.

8c: 1,4-Bis(trihexylsilyl)-2,5-bis(trimethylsilylethynyl)benzene: To a solution of **7** (1.50 g, 3.50 mmol) in ether (20 mL) was added a hexane solution of *n*BuLi (1.6 M, 5.42 mL, 8.66 mmol) dropwise at −78 °C. The mixture was stirred at the same temperature for 5 h. Trihexylsilyl chloride (2.82 mL, 7.70 mmol) was added to the reaction mixture using a syringe. The reaction mixture was gradually warmed to room temperature and stirred for 18 h and concentrated under reduced pressure. The resulting mixture was purified by silica-gel column chromatography (hexane, $R_f = 0.83$) to afford a colorless oil (**8c**, 2.53 g, 3.03 mmol, 67 % yield): ^1H NMR ($CDCl_3$): $\delta = 7.47$ (s, 2H), 1.35–1.18 (m, 48H), 0.95–0.83 (m, 30H), 0.26 ppm (s, 18H); ^{13}C NMR (CDCl3): $\delta = 141.0$, 139.6, 127.6, 107.5, 98.4, 33.8, 31.8, 24.1, 22.9, 14.4, 12.1 0.1 ppm; HRMS (FAB): *m/z* (%) calcd for $C_{52}H_{98}Si_4$: 834.6746 [M^+]; found: 834.6758.

9a: 1,4-Diethynyl-2,5-bis(trimethylsilyl)benzene: To a mixture of **8a** (5.63 g, 13.6 mmol) and K_2CO_3 (394 mg, 2.85 mmol) was added a THF/MeOH (1:1, 50 mL) mixed solvent and stirred at room temperature for 22 h. The reaction mixture was concentrated under reduced pressure and purified by silica-gel column chromatography (hexane, $R_f = 0.60$) to give a colorless solid (**9a**, 3.66 g, 13.5 mmol, 99 % yield): m.p. 99 °C (subl); ^1H NMR ($CDCl_3$): $\delta = 7.61$ (s, 2H), 3.31 (s, 2H), 0.36 (s, 18H); ^{13}C NMR ($CDCl_3$): δ 143.2, 138.5, 126.6, 85.1, 81.7 ppm, −1.3; HRMS (FAB): *m/z* (%) calcd for $C_{16}H_{22}Si_2$: 270.1260 [M^+]; found: 270.1264.

9c: 1,4-Diethynyl-2,5-bis(trihexylsilyl)benzene: To a mixture of **8c** (2.52 g, 3.03 mmol) and K_2CO_3 (88.7 mg, 0.64 mmol) was added a THF/MeOH (1/1, 20 mL) mixed solvent and stirred at room temperature for 20 h. After addition of an aqueous solution of HCl (1 M), the organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting product was purified by silica-gel column chromatography (hexane, $R_f = 0.83$) to give a yellow oil (**9c**, 1.37 g, 1.99 mmol, 66 % yield): ^1H NMR ($CDCl_3$): $\delta = 7.53$ (s, 2H), 3.27 (s, 2H), 1.35–1.15 (m, 48H), 0.98–0.80 ppm (m, 30H); ^{13}C NMR ($CDCl_3$): $\delta = 141.2$, 139.6, 126.7, 85.5, 81.1, 33.3, 31.4, 23.8, 22.6, 14.1, 11.9 ppm; HRMS (EI): *m/z* (%) calcd for $C_{46}H_{82}Si_2$: 690.5955 [M^+]; found: 690.5974.

10: 1,4-Dibromo-2,5-bis{[2-(ethoxydimethylsilyl)ethyl]dimethylsilyl}-3,6-(trimethylsilylethynyl)benzene: To a mixture of **7** (8.57 g, 20.0 mmol) and 1,2-bis(chlorodimethylsilyl)ethane (21.5 g, 100 mmol) in THF (150 mL) was added a solution of lithium diisopropylamide (LDA) that was freshly prepared from (*i*Pr)$_2$NH (6.20 mL, 44.0 mmol), and a hexane solution of *n*BuLi (1.6 M, 27.5 mL, 44.0 mmol) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 14.5 h. Et_3N (34.0 mL, 244 mmol) and EtOH (14.3 mL, 244 mmol) were added to the mixture at 0 °C followed by stirring for an additional 1 h. The reaction mixture was filtered by celite® and the filtrate was concentrated under reduced pressure. The resulting product was purified by aluminum column chromatography (50:1 hexane/ethyl acetate, $R_f = 0.55$) to give a yellow oil (**10**, 9.91 g, 12.3 mmol, 62 % yield): ^{1}H NMR(C_6D_6) $\delta = 3.49$ (q, $^3J_{HH} = 7.1$ Hz, 4 H), 1.19–1.14 (m, 4 H), 1.09 (t, $^3J_{HH} = 7.1$ Hz, 6 H) , 0.66–0.64 (m, 4 H), 0.62 (s, 12 H) , 0.22 (s, 18 H) , 0.07 ppm (s, 12 H); ^{13}C NMR (C_6D_6) $\delta = 142.8$, 131.8, 129.3, 104.8, 102.3, 54.6, 15.3, 5.7, 5.6, −1.5, −4.1, −6.1 ppm; HRMS (APCI): *m/z* (%) calcd for $C_{32}H_{61}Br_2O_2Si_6$: 803.1654 [$M+H$]$^+$; found: 803.1648.

11: 1,1,4,4,5,5,8,8-Octamethyl-9,10-bis(trimethylsilylethynyl)-1,2,3,4,5,6,7,8-octahydro-1,4,5,8-tetrasilaanthracene: To a solution of **10** (9.50 g, 11.8 mmol) in THF (100 mL) was added a pentane solution of *t*BuLi (1.58 M, 31.5 mL, 49.8 mmol) dropwise at −78 °C. The mixture was allowed to warm to room temperature and stirred for 45 h. After addition of an aqueous solution of NH_4Cl (5 %) to the mixture, the organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude product was added to hexane and the soluble impurity was removed by filtration. The collected insoluble mixture was purified by recrystallization from ethyl acetate to givea colorless solid (**11**, 4.31 g, 7.77 mmol, 66 % yield): m.p. 220.7–220.9 °C; ^{1}H NMR($CDCl_3$) $\delta = 0.40$ (s, 36 H), 0.24 ppm (s, 18 H); ^{13}C NMR ($CDCl_3$) $\delta = 149.0$, 133.9, 109.0, 105.1, 8.7, −0.6, −1.5 ppm; HRMS (FAB): *m/z* (%) calcd for $C_{28}H_{50}Si_6$: 554.2528 [M^+]; found: 554.2515.

12: 9,10-Diethynyl-1,1,4,4,5,5,8,8-octamethyl-1,2,3,4,5,6,7,8-octahydro-1,4,5,8-tetrasilaanthracene: To a mixture of **11** (223 mg, 0.40 mmol) and K_2CO_3 (11.0 mg, 0.080 mmol) was added a MeOH/THF (3:4, 14 mL) mixed solvent. The mixture was stirred at room temperature for 21 h, then concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography (hexane, $R_f = 0.63$) to afford a colorless solid (**12**, 157 mg, 0.38 mmol, 95 % yield): m.p. 234.9–238.0 °C (dec); ^{1}H NMR($CDCl_3$) $\delta = 3.54$ (s, 2 H), 0.91 (s, 8 H), 0.41 ppm (s, 24 H); ^{13}C NMR ($CDCl_3$) $\delta = 149.5$, 133.2, 88.2, 87.4, 8.7, −1.3 ppm; HRMS (FAB): *m/z* (%) calcd for $C_{22}H_{34}Si_4$: 410.1738 [M^+]; found: 410.1725.

13: 1,4-Dibromo-2,5-bis(trimethylsilyl)-3,6-(trimethylsilylethynyl)benzene: To a mixture of **7** (1.50 g, 3.50 mmol) and trimethylsilyl chloride (1.80 mL, 14.0 mmol) in THF (7 mL), was added a THF solution of LDA that was freshly prepared from (*i*Pr)$_2$NH (1.10 mL, 7.70 mmol) and a hexane solution of *n*BuLi (1.6 M, 4.83 mL, 7.70 mmol) at −78 °C. The reaction mixture was stirred at the same temperature for 3 h and was allowed to warm to room temperature over 4 h. After addition of Et_3N (1 mL) and ethanol (0.5 mL) to quench the excess silyl chloride, an aqueous solution of NH_4Cl (5 %) was added. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting mixture was purified by silica-gel column chromatography (hexane, $R_f = 0.55$). The crude product was purified by recrystallization from ethyl acetate to afford a colorless solid (**13**, 1.88 g, 3.26 mmol, 93 % yield): m.p. 176.3–177.1 °C; ^{1}H NMR ($CDCl_3$) $\delta = 0.53$ (s, 18 H), 0.26 ppm (s, 18 H); ^{13}C NMR ($CDCl_3$) $\delta = 146.1$, 134.4, 131.9, 108.1, 105.0, 3.3, −0.6 ppm; HRMS (FAB): *m/z* (%) calcd for $C_{22}H_{36}Si_4Br_4$: 570.0261 [M^+]; found: 570.0256 .

14: 1,2,4,5-Tetrakis(trimethylsilyl)-3,6-bis(trimethylsilylethynyl)benzene: To a solution of **13** (859 mg, 1.50 mmol) in THF (3 mL) was added a pentane solution of *t*BuLi (1.58 M, 4. 0 mL, 6.32 mmol) dropwise at −78 °C. The mixture was stirred at the same temperature for 1.5 h. Trimethylsilyl chloride (571 µL, 4.50 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature followed by stirring for 21 h. After addition of Et_3N (0.5 mL) and ethanol (0.25 mL) to quench the excess silyl chloride, an aqueous solution of NH_4Cl (5 %) was added. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting mixture was purified by silica-gel column chromatography (hexane, $R_f = 0.55$). The crude product was purified by recrystallization from ethyl acetate to afford a colorless solid (**14**, 205 mg, 0.37 mmol, 37 % yield): m.p. 160.3–160.6 °C; ^{1}H NMR ($CDCl_3$) $\delta = 0.40$ (s, 36 H), 0.24 ppm (s, 18 H); ^{13}C NMR ($CDCl_3$) $\delta = 150.7$, 132.7, 109.0, 103.8, 2.7, −0.5 ppm; HRMS (FAB): *m/z* (%) calcd for $C_{28}H_{54}Si_6$: 558.2841 [M^+]; found: 558.2831.

15: 1,4-Diethynyl-2,3,5,6-tetrakis(trimethylsilyl)benzene: To a mixture of **14** (183 mg, 0.327 mmol) and K_2CO_3 (10.0 mg, 0.072 mmol) was added a MeOH/THF (1:2, 3 mL) mixed solvent. The mixture was stirred at room temperature for 20 h. After being concentrated under reduced pressure, the resulting mixture was purified by silica-gel column chromatography (hexane, $R_f = 0.48$) to afford a colorless solid (**15**, 115 mg, 0.28 mmol, 85 % yield): m.p. 156 °C (dec); ^{1}H NMR ($CDCl_3$) $\delta = 3.50$ (s, 2 H), 0.40 ppm (s, 36 H); ^{13}C NMR ($CDCl_3$) $\delta = 151.1$, 131.8, 87.3, 87.0, 2.7 ppm; HRMS (FAB): *m/z* (%) calcd for $C_{22}H_{38}Si_4$: 414.2051 [M^+]; found: 414.2060.

Synthesis of Reference Compounds

5: 1,1,4,4,5,5,8,8-Octamethyl-9,10-bis(phenylethynyl)-1,2,3,4,5,6,7,8-octahydro-1,4,5,8-tetrasilaanthracene: To a mixture of **12** (125 mg, 0.304 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (5.1 mg, 4.9 µmol), CuI (1.9 mg, 10 µmol), and 2-(dicyclohexylphosphanyl)biphenyl (3.5 mg, 10 µmol) was added a toluene/(*i*Pr)$_2$NH (3:1, 2.4 mL) degassed mixed solvent and iodobenzene (72.0 µL, 0.638 mmol). The mixture was stirred at 100 °C for 72 h. After cooling to room temperature, an aqueous solution of NH_4Cl (5 %) was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting mixture was purified by silica-gel column chromatography (50:1 hexane/toluene, $R_f = 0.33$) to afford a colorless solid (**5**, 111 mg, 0.20 mmol, 64 % yield): m.p. 242.4 °C (dec); ^{1}H NMR ($CDCl_3$) $\delta = 7.54$–7.52 (m, 4 H,), 7.40–7.36 (m, 6 H), 0.98 (s, 8 H), 0.50 ppm (s, 24 H); ^{13}C NMR ($CDCl_3$) $\delta = 148.9$, 133.8, 130.8, 128.6, 128.3, 12.7, 98.7, 94.2, 8.8, −1.4 ppm; HRMS (FAB): *m/z* (%) calcd for $C_{34}H_{42}Si_4$: 562.2364 [M^+]; found: 562.2352.

6: 1,4-Bis(phenylethynyl)-2,3,5,6-tetrakis(trimethylsilyl)benzene: This compound was prepared essentially in the same manner as described for **5**. Using **15** (127 mg, 0.305 mmol), iodobenzene (80 µL, 0.72 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (3.3 mg, 3.2 µmol), CuI (1.3 mg, 6.8 µmol), and 2-(dicyclohexylphosphanyl)biphenyl (2.1 mg, 6.1 µmol), afforded a yellow solid (**6**, 111 mg,0.20 mmol, 64 % yield): m.p. 192.6–193.6 °C; ^{1}H NMR ($CDCl_3$) $\delta = 7.55$–7.52 (m, 4 H), 7.41–7.35 (m, 6 H), 0.48 ppm (s, 36 H); ^{13}C NMR ($CDCl_3$) $\delta = 150.5$, 132.8, 130.7, 128.5, 128.1, 124.0, 97.8, 94.1, 2.8 ppm; HRMS (FAB): *m/z* (%) calcd for $C_{34}H_{46}Si_4$: 566.2677 [M^+]; found: 566.2695.

Synthesis of PAEs

Polymer 1a: To a mixture of **9a** (50.0 mg, 0.185 mmol), 2,7-diiodo-9,9-dioctylfluorene (118.7 mg, 0.185 mmol), $Pd(PPh_3)_4$ (2.3 mg, 2.0 µmol), and CuI (1.2 mg, 6.3 µmol) was added a toluene/(*i*Pr)$_2$NH (3:1, 2 mL) degassed mixed solvent. The reaction mixture was stirred at 100 °C for 24 h. After cooling to room temperature, an aqueous solution of NH_4Cl (5 %) was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$. The combined organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting mixture was dissolved into a small amount of THF and poured into a vigorously stirred MeOH solution to form a precipitate. The reprecipitation was repeated using hexane as the poor solvent to afford a yellow solid (**1a**, 108 mg, 89 % yield): ^{1}H NMR ($CDCl_3$): $\delta =$ 7.77–7.67 (m, 4 H), 7.54–7.46 (m, 4 H), 1.30–0.95 (m, 24 H), 0.82 (t, $^3J_{HH} =$ 6.8 Hz, 6 H), 0.60–0.25 ppm (m, 22 H); ^{13}C NMR ($CDCl_3$): $\delta = 151.6$, 143.1, 141.0, 138.0, 130.6, 127.5, 126.1, 122.4, 120.5, 95.1, 92.3, 55.6, 40.6, 32.1, 30.3, 29.6, 29.5, 24.1, 23.0, 14.4, −0.7 ppm; $M_n = 1.02\times10^5$, $M_w = 4.78\times10^5$, $M_w/M_n = 4.68$.

Polymer 1b: This polymer was prepared essentially in the same manner as described for **1a** using **9b** (53.2 mg, 0.121 mmol), 2,7-diiodo-9,9-dioctylfluorene (77.9 mg, 0.121 mmol), $Pd(PPh_3)_4$ (1.8 mg, 1.6 μmol), CuI (1.2 mg, 6.3 μmol), and toluene/$(i\text{Pr})_2$NH (3:1, 2 mL). The obtained crude product was purified by repeated reprecipitation from MeOH and then from *i*PrOH to give a yellow solid (**1b**, 81 mg, 79 % yield): ^{1}H NMR ($CDCl_3$): $\delta = 7.76$ (s, 2H), 7.74–7.66 (m, 2H), 7.55–7.45 (m, 4H), 1.83 (7, $^3J_{HH} = 7.6$ Hz, 6H), 1.35–0.99 (m, 64H), 0.82 ppm (t, $^3J_{HH} = 6.8$ Hz, 6H); ^{13}C NMR ($CDCl_3$): $\delta = 151.1$, 140.6, 138.3, 131.1, 130.1, 127.9, 125.6, 122.3, 120.1, 93.5, 92.9, 55.1, 40.3, 31.8, 30.1, 29.3, 29.2, 23.9, 22.6, 19.1, 14.1, 12.1 ppm; $M_n = 3.60\times10^4$, $M_w = 1.33\times10^5$, $M_w/M_n = 3.70$.

Polymer 1c: This polymer was prepared essentially in the same manner as described for **1a** using **9c** (70.1 mg, 0.101 mmol), 2,7-diiodo-9,9-dioctylfluorene (65.1 mg, 0.101 mmol), $Pd(PPh_3)_4$ (1.3 mg, 1.1 μmol), CuI (2.0 mg, 11 μmol), and toluene/$(i\text{Pr})_2$NH (3:1, 2 mL). The obtained crude product was purified by repeated reprecipitation from MeOH and then from *i*PrOH to give a yellow solid (**1c**, 100 mg, 92 % yield): $\delta = 7.74$–7.68 (m, 2H), 7.66 (s, 2H), 7.56–7.50 (m, 4H), 1.42–0.98 (m, 88H), 0.92–0.80 ppm (m, 24H); ^{13}C NMR ($CDCl_3$): $\delta = 151.2$, 140.7, 138.9, 131.3, 130.3, 127.3, 125.7, 122.2, 120.0, 94.1, 92.3, 55.2, 40.4, 33.5, 31.8, 31.5, 30.2, 29.4, 29.3, 23.9, 23.8, 22.6, 22.5, 14.2, 14.1, 12.1 ppm; $M_n = 1.50\times10^4$, $M_w = 3.87\times10^4$, $M_w/M_n = 2.57$.

Polymer 2: This polymer was prepared essentially in the same manner as described for **1a** using **12** (79.3 mg, 0.193 mmol), 2,7-diiodo-9,9-dioctylfluorene (124 mg, 0.193 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (2.0 mg, 1.9 μmol), CuI (0.8 mg, 4.2 μmol), 2-(dicyclohexylphosphanyl)biphenyl (1.4 mg, 4.0 μmol), and toluene/$(i\text{Pr})_2$NH (3:1, 2 mL). The obtained crude product was purified by repeated reprecipitation from MeOH and then *i*PrOH to give a yellow solid (**2**, 84 mg, 55 % yield): ^{1}H NMR ($CDCl_3$): $\delta = 7.76$–7.74 (m, 2H), 7.55–7.35 (m, 4H), 3.54 (s, terminal unit), 2.12–1.86 (m, 4H), 1.25–1.14 (m, 22H), 1.05–0.99 (m, 8H, containing terminal unit), 0.84 (t, $^3J_{HH} = 6.8$ Hz, 6H), 0.58–0.46 ppm (m, 24H, containing terminal unit); ^{13}C NMR ($CDCl_3$): $\delta = 151.5$, 148.9, 140.5, 133.8, 130.8, 129.7, 125.4, 122.4, 120.2, 99.8, 94.9, 55.0, 39.9, 31.8, 29.9, 29.2, 29.2, 23.9, 22.6, 14.1, 8.8, −1.3 ppm; $M_n = 8.77\times10^3$, $M_w = 1.76\times10^4$, $M_w/M_n = 2.01$.

Polymer 3: This polymer was prepared essentially in the same manner as described for **1a** using **15** (81.3 mg, 0.196 mmol), 2,7-diiodo-9,9-dioctylfluorene (126 mg, 0.196 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (2.1 mg, 2.0 μmol), CuI (0.8 mg, 4.2 μmol), 2-(dicyclohexylphosphanyl)biphenyl (1.4 mg, 4.0 μmol), and toluene/$(i\text{Pr})_2$NH (3:1, 2.4 mL). The obtained crude product was purified by reprecipitation from *i*PrOH to give a yellow solid (**3**, 102 mg, 65 % yield): ^{1}H NMR ($CDCl_3$): $\delta = 7.85$–7.65 (m, 2H), 7.60–7.45 (m, 4H), 3.54 (s, terminal unit), 2.14–1.82 (m, 4H), 1.30–0.95 (m, 22H), 0.83 (t, $^3J_{HH} = 7.1$ Hz, 6H), 0.55–0.35 ppm (m, 36H, containing terminal unit); ^{13}C NMR ($CDCl_3$): $\delta = 151.3$, 150.6, 140.3, 132.8, 129.6, 125.3, 122.7, 120.1, 98.9, 94.7, 55.0, 40.0, 31.8, 30.9, 29.2, 29.2, 23.9, 22.6, 14.1, 2.9, 1.7 (terminal unit), 1.3 ppm (terminal unit); $M_n = 1.18\times10^4$, $M_w = 2.78\times10^4$, $M_w/M_n = 2.35$.

Polymer 16: This polymer was prepared essentially in the same manner as described for **1a** using 1,4-diethynylbenzene (63.0 mg, 0.499 mmol), 2,7-diiodo-9,9-dioctylfluorene (320.9 mg, 0.499 mmol), $Pd(PPh_3)_4$ (5.4 mg, 4.7 μmol), CuI (2.2 mg, 12 μmol), and toluene/$(i\text{Pr})_2$NH (3:1, 40 mL). The obtained crude product was purified by reprecipitation from *i*PrOH to give a yellow solid (**16**, 229 mg, 86 % yield): ^{1}H NMR ($CDCl_3$): $\delta = 7.76$–7.65 (m, 2H), 7.65–7.45 (m, 8H), 1.98 (br, 2H), 1.30–0.98 (m, 22H), 0.89–0.77 (m, 8H), 0.62 ppm (br, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 150.8$, 140.5, 131.2, 130.5, 125.7, 122.8, 121.4, 119.7, 92.1, 89.3, 55.1, 40.0, 31.5, 29.7, 29.6, 28.9, 23.4, 22.3, 13.8 ppm; $M_n = 2.12\times10^4$, $M_w = 7.77\times10^4$, $M_w/M_n = 3.66$.

Polymer 17: This polymer was prepared essentially in the same manner as described for **1a** using 1,4-diethynyl-2,5-bis(2-ethylhexyloxy)benzene (52.5 mg, 0.137 mmol), 2,7-diiodo-9,9-dioctylfluorene (88.2 mg, 0.137 mmol), $Pd(PPh_3)_4$ (6.6 mg, 5.7 μmol), CuI (2.5 mg, 13 μmol), and toluene/$(i\text{Pr})_2$NH (3:1, 15 mL). The obtained crude product was purified by reprecipitation from MeOH to give a yellow solid (**17**, 91 mg, 86 % yield): ^{1}H NMR ($CDCl_3$): $\delta = 7.73$–7.65 (m, 2H), 7.58–7.48 (m, 4H), 7.07 (s, 2H), 4.02–3.91 (m, 4H), 1.92–0.78 ppm (m, 64H); ^{13}C NMR ($CDCl_3$): $\delta = 153.9$, 151.0, 140.7, 130.6, 125.9, 122.1, 119.9, 116.3, 113.8, 96.0, 86.6, 71.9, 55.1, 40.8, 39.6, 31.8, 30.7, 30.6, 30.1, 29.3, 29.1, 24.1, 23.7, 23.1, 22.6, 14.1, 14.0, 11.4 ppm; $M_n = 5.20\times10^4$, $M_w = 1.14\times10^5$, $M_w/M_n = 2.19$.

X-Ray Crystal Structure Analysis

5: Single crystals of **5** suitable for X-ray crystal analysis were obtained by recrystallization from ethyl acetate. Intensity data were collected at 123 K on a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with a $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å) and a graphite monochromator. A total of 21450 reflections were measured at a maximum 2θ angle of 50.0°, of which 2867 were independent reflections ($R_{int} = 0.01594$). The structure was solved by direct methods (SHELXS-97[24]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[24]). All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{34}H_{42}Si_4$; FW = 563.04, crystal size $0.15\times0.12\times0.10$ mm^3, tetragonal, $P4_2/n$ (#86), $a = 18.0686(5)$ Å, $b = 18.0686(5)$ Å, $c = 9.9689(4)$ Å, $V = 3254.59(18)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.149$ g cm^{-3}. The refinement converged to $R_1 = 0.0519$, $wR_2 = 0.1161$ ($I > 2\sigma(I)$), GOF = 1.126. CCDC 682412 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

6: Single crystals of **6** suitable for X-ray crystal analysis were obtained by recrystallization from ethyl acetate. Intensity data were collected at 173 K on a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with a $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å) and a graphite monochromator. A total of 11303 reflections were measured at a maximum 2θ angle of 51.0°, of which 3116 were independent reflections ($R_{int} = 0.0282$). The structure was solved by direct methods (SHELXS-97[24]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[24]). All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{34}H_{46}Si_4$; FW = 567.07, crystal size $0.20\times0.20\times0.10$ mm^3, monoclinic, $P2_1/c$ (#14), $a = 12.481(2)$ Å, $b = 10.1186(19)$ Å, $c = 13.259(3)$ Å, $\beta = 90.351(3)$°, $V = 1674.5(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.125$ g cm^{-3}. The refinement converged to $R_1 = 0.0337$, $wR_2 = 0.0885$ ($I > 2\sigma(I)$), $GOF = 1.052$. CCDC 682413 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

Theoretical Calculations

Molecular orbital calculations were performed using the Gaussian 98 program.[25] Single point calculations of **18**, **4**, and **5** at the B3LYP/6-31G(d) level of theory were carried out using the geometries derived from the crystal structures. The time-dependent density functional theory (TD-DFT) calculations were conducted at the B3LYP/6-31G(d) level of theory.

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