

Articles

Synthesis and Efficient Energy Transfer in a Three-Chromophore Energy Gradient of Regioregular Silylene-Spaced Divinylarene Copolymers

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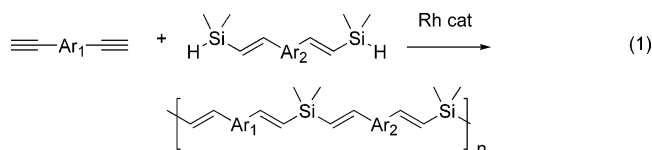
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ABSTRACT: Regioregular silylene-spaced copolymers **1** composed of an energy gradient with three different chromophores have been achieved by rhodium-catalyzed hydrosilylation of bis-vinylsilanes **3** and bis-alkynes **4**. Monomeric reference compounds **2** were prepared for comparison. The ratio of three chromophores is 1:2:1, corresponding to D₁, D₂, and A chromophores, respectively. The dimethylsilylene (SiMe₂) moiety serves as an insulating bridge between chromophores. Upon excitation of the donor chromophore (D₁), only emission from the acceptor (A) was observed. Efficient and sequential energy transfer across three different chromophores along the polymeric backbone may proceed smoothly in these silylene-spaced copolymers.

Introduction

In photosynthesis, energy is harvested by antenna pigments and transferred into a reaction center where redox reactions take place.¹ Morphologically, different antenna chromophores surrounding the reaction center are arranged in an order of energy gradient.^{2–4} Accordingly, energy can be sequentially transferred and efficiently funneled to the reaction center over nanometer distances in the direction of decreasing band gaps. Much effort has been directed toward the development of sequential multistep energy-transfer systems not only for mimicking the natural light-harvesting process^{2,3} but also for the potential applications in biological systems⁴ and optoelectronic applications.⁵ A conjugated polymeric backbone with well-designed interruptions of conjugation by insulating spacers may allow for tuning of the emission properties and provide an alternative model.⁶ The silylene moiety has been used extensively as an insulating spacer.⁷ In general, when the silylene spacer contains only one silicon atom, no conjugative interactions between the π systems and the silicon moiety is observed.⁸ The silylene-spaced divinylarene copolymers are readily accessible by rhodium-catalyzed hydrosilylation of bis-alkynes with bis-vinylsilanes (eq 1).⁹



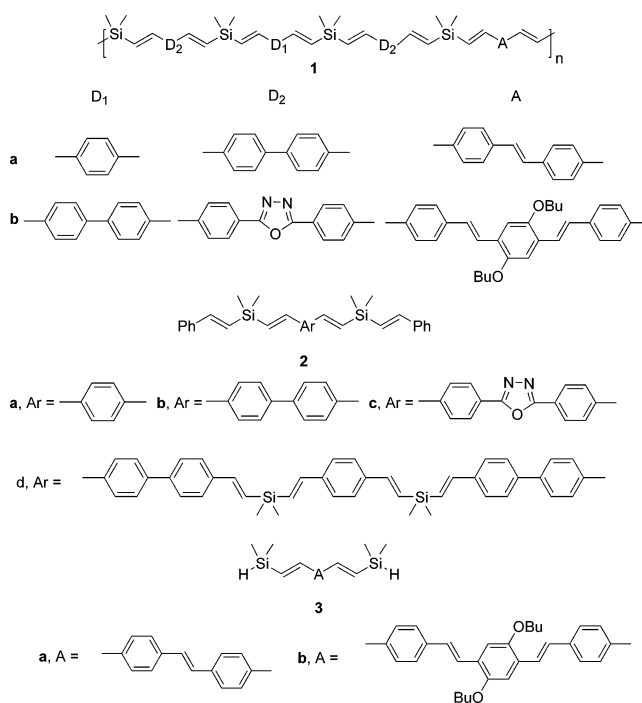
Such a protocol may furnish a range of fascinating polymers that have different regioselective combinations

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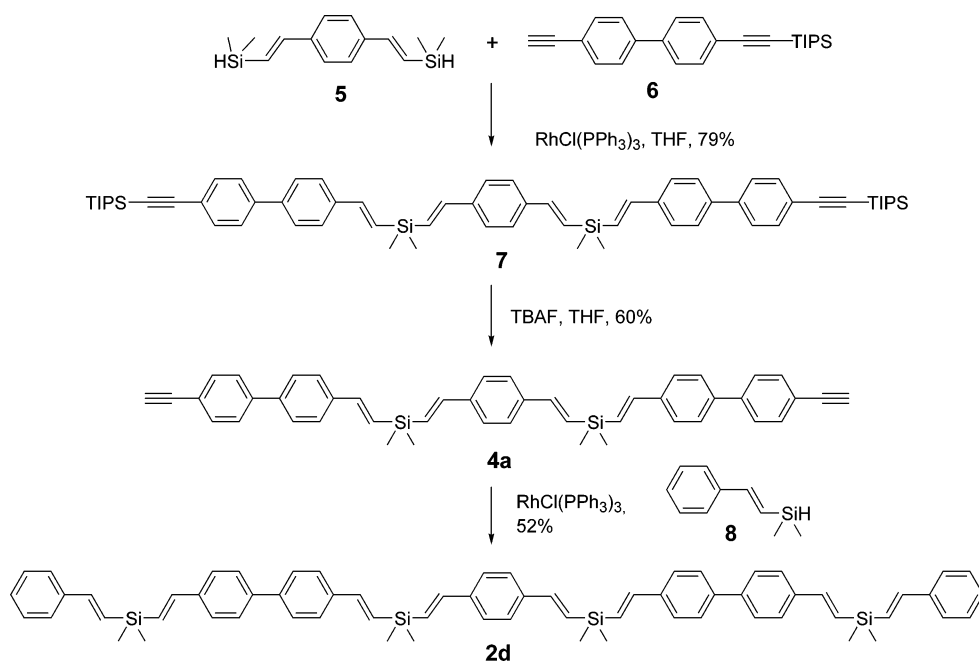
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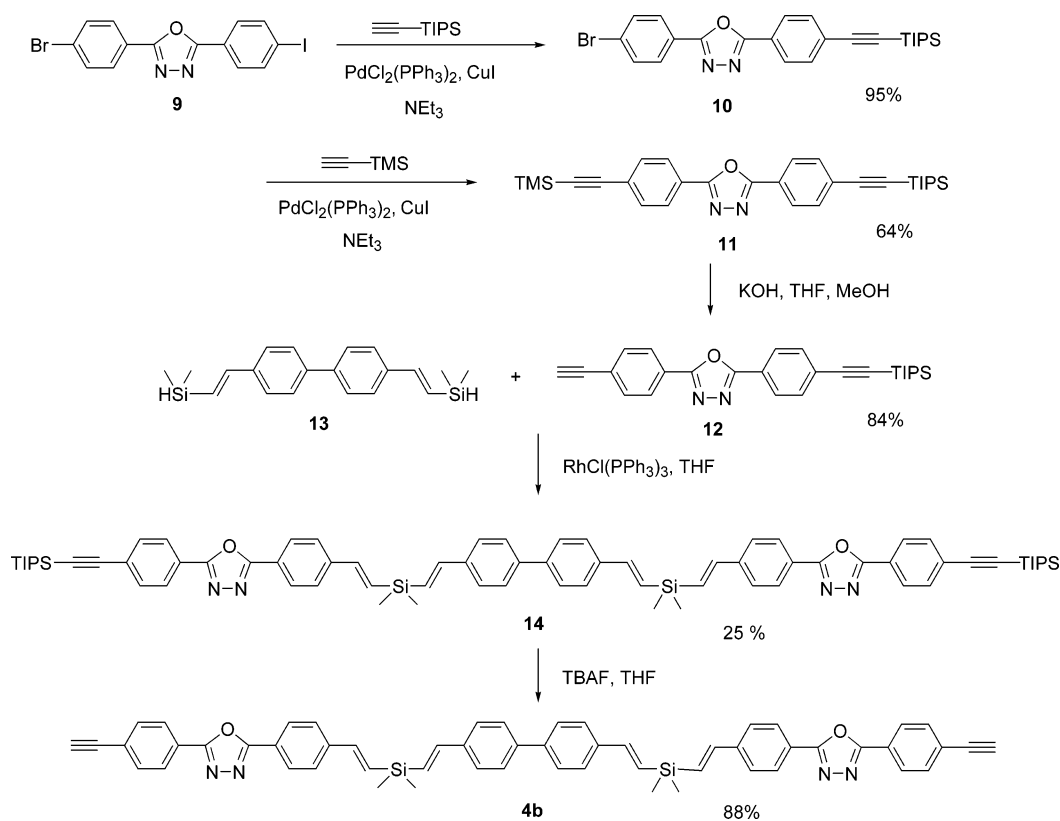
of donors and acceptors along the polymeric chain.^{9–12} Recently, we disclosed that a series of silylene-spaced copolymers can serve as an ideal architecture for efficient intrachain energy transfer^{10,12} and the light-harvesting ability is enhanced with the increasing ratio of donor to acceptor chromophore along the polymeric backbone.¹⁰ It is envisaged that introduction of an energy gradient with three well-designed chromophores into a silylene-spaced polymeric chain may lead to sequential energy transfer. Herein, we present the unprecedented synthesis and photophysical studies of silylene-spaced regioregular polymers **1** composed of a



Scheme 1



Scheme 2



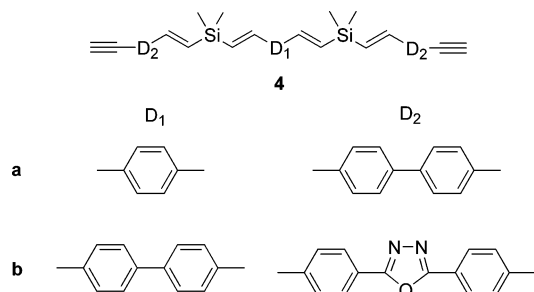
well-designed energy gradient of three-chromophore systems.

Results and Discussion

Synthesis. By adopting rhodium-catalyzed hydrosilylation of bis-alkynes with bis-vinylsilanes as shown in eq 1, a combination of three different chromophores separated by dimethylsilylene moieties (SiMe_2) can be regioregularly incorporated into the polymeric chain. The molar fraction of each chromophore in polymer **1** is 1:2:1, corresponding to D_1 , D_2 , and A, respectively.

Monomeric reference compounds **2a–d** were also prepared. Polymer **1a** was designed in accordance with the conjugation length of three chromophores. The divinylbenzene chromophore was chosen as the donor with highest band gap and the divinylstilbene chromophore acted as the acceptor with lowest band gap, whereas divinylbiphenyl chromophore served as the intermediate gradient. Polymer **2b**, consisting of a combination of three chromophores, divinylbiphenyl, divinyl-diphenyl oxadiazole, and dibutoxyterphenylene tetravinylene, was also designed and synthesized.

The synthesis of acceptor (A) monomers **3** with dimethylsilyl substituents at the olefinic termini was based on the nickel-catalyzed silylolefination of the corresponding dithioacetals with $(i\text{PrO})\text{Me}_2\text{SiCH}_2\text{MgCl}$, followed by reduction of the corresponding Si–O bond,^{9–13} whereas silylene-spaced diyne monomers **4**, which are readily comprised of two chromophores (D₁ and D₂), were prepared according to Schemes 1 and 2.



Rhodium-catalyzed hydrosilylation of **5** with 2 equiv of **6** resulted in the formation of **7** in 79% yield. Removal of the triisopropylsilyl (TIPS) group in **7** by TBAF afforded diyne **4a** in 60% yield. Hydrosilylation of **4a** with 2 equiv of **8** led to the corresponding monomeric reference **2d** containing divinylbenzene and divinylbiphenyl chromophores (Scheme 1) in 52% yield. In a sequential Sonogashira reaction, **9** was first treated with 1 equiv of triisopropylsilylacetylene to yield **10**, which was then allowed to react with trimethylsilylacetylene to afford **11** in 64% yield. Selective removal of the trimethylsilyl (TMS) group in **11** (NaOH/MeOH) led to **12** in 84% yield. Rhodium-catalyzed hydrosilylation of **13** with 2 equiv of **12** resulted in the formation of **14** in 25% yield. Desilylation of the TIPS group in **14** with TBAF furnished **4b** in 88% yield. (Scheme 2).

Hydrosilylation of **4a** with **3a** (**4b** with **3b**) afforded the first example of silylene-spaced polymers **1** consisting of an energy gradient with three chromophores in a regioregular arrangement. (Table 1).

Table 1. RhCl(PPh₃)₃-Catalyzed Reactions of Bis-alkyne **4** and Bis-vinylsilanes **3**

| bis-alkynes | bis-vinylsilanes | polymer | Mn (PDI) | Φ |
|-------------|------------------|-----------|-------------|------|
| 4a | 3a | 1a | 7900 (2.8) | 0.45 |
| 4b | 3b | 1b | 16300 (3.1) | 0.49 |

Photophysical Properties of Polymers. The absorption and emission properties of monomeric references **2** and **3** in chloroform are given in Table 2. Figure

Table 2. Absorption and Emission Properties of **2** and **3** in Chloroform

| substrate | λ_{max} (nm), ϵ_{max} (M ⁻¹ cm ⁻¹) | λ_{em} (nm) |
|-----------|--|----------------------------|
| 2a | 290 (35900) | 334, 347 |
| 2b | 312 (32300) | 361, 375 |
| 2c | 324 (35100) | 363, 384, 401 |
| 3a | 355 (55800) | 392, 411 |
| 3b | 411 (37000) | 467, 490 |

1 illustrates the emission spectra of monomeric references, **2a**, **2b**, and **3a**, corresponding to component chromophores in polymer **1a**.

Figure 2 shows the concentration-dependent emission spectra of an equal molar mixture of two-chromophore monomer **2d** and its corresponding acceptor **3a** upon excitation of divinylbenzene chromophore at 280 nm. It is apparent that the intramolecular energy transfer

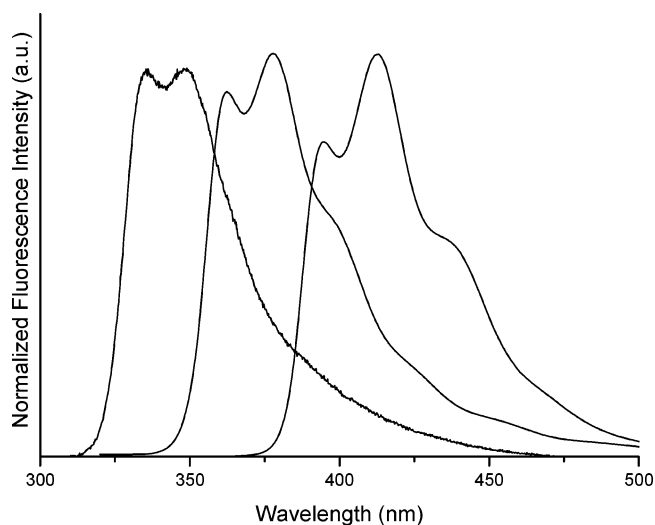


Figure 1. Fluorescence spectra of **2a** ($\lambda_{\text{ex}} = 280$ nm), **2b** ($\lambda_{\text{ex}} = 310$ nm) and **3a** ($\lambda_{\text{ex}} = 355$ nm) in CHCl₃.

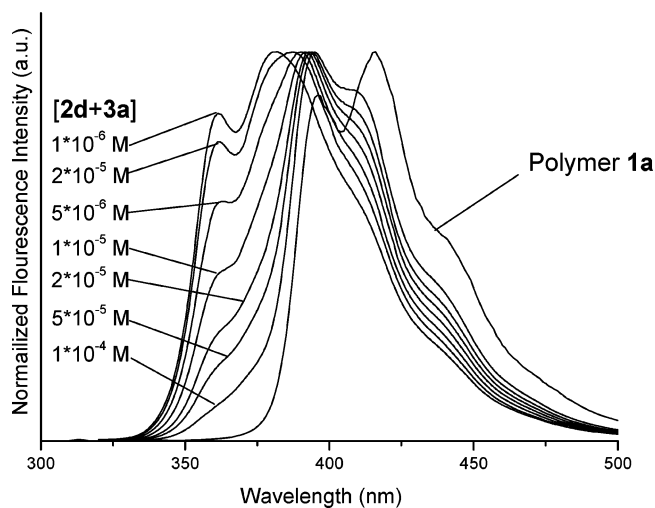


Figure 2. Concentration-dependent fluorescence spectra ($\lambda_{\text{ex}} = 280$ nm) of an equal molar mixture of **2d** and **3a** in CHCl₃ (from 10⁻⁴ M to 10⁻⁶ M) and fluorescence spectrum ($\lambda_{\text{ex}} = 280$ nm) of polymer **1a** in CHCl₃ (10⁻⁵ M).

from divinylbenzene to divinylbiphenyl chromophore in **2d** is highly efficient, resulting in a complete quenching of the emission of divinylbenzene. At low concentration (10⁻⁶ M), the observed emission mainly originates from the divinylbiphenyl chromophore in **2d**, which indicates that energy transfer between **2d** and **3a** is negligibly weak. With gradually increasing concentration of the mixture, the intermolecular energy transfer from divinylbiphenyl in **2d** to divinylstilbene in **3a** becomes important, leading to a decreasing emission of divinylbiphenyl along with an increasing emission of divinylstilbene. Nevertheless, the energy transfer does not process completely even at a relatively higher concentration (10⁻⁴ M). In sharp contrast, when polymer **1a** was excited at 280 nm, complete energy transfer was observed, resulting in emission only from divinylstilbene exclusively. No emission arising from divinylbenzene itself or divinylbiphenyl was observed. Moreover, the emission profiles of polymer **1a** remain unchanged, with concentrations from 10⁻⁴ to 10⁻⁶ M,¹⁴ which not only indicates that the energy transfer may take place in an intramolecular manner but also reveals that undesired intrachain or interchain aggregation which will cause

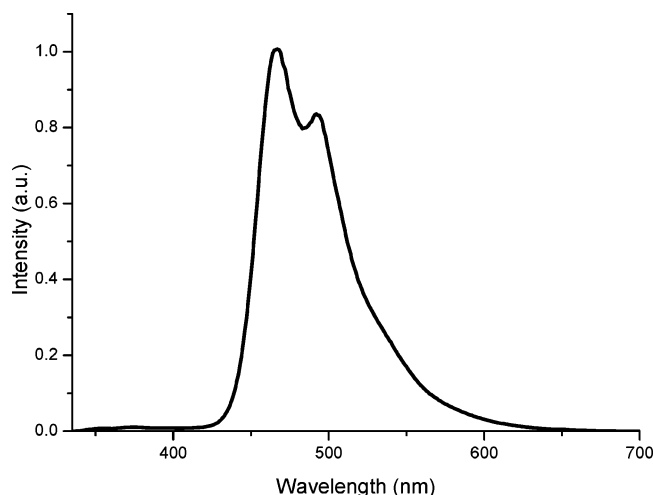


Figure 3. Fluorescence spectrum ($\lambda_{\text{ex}} = 300$ nm) of **1b** in chloroform.

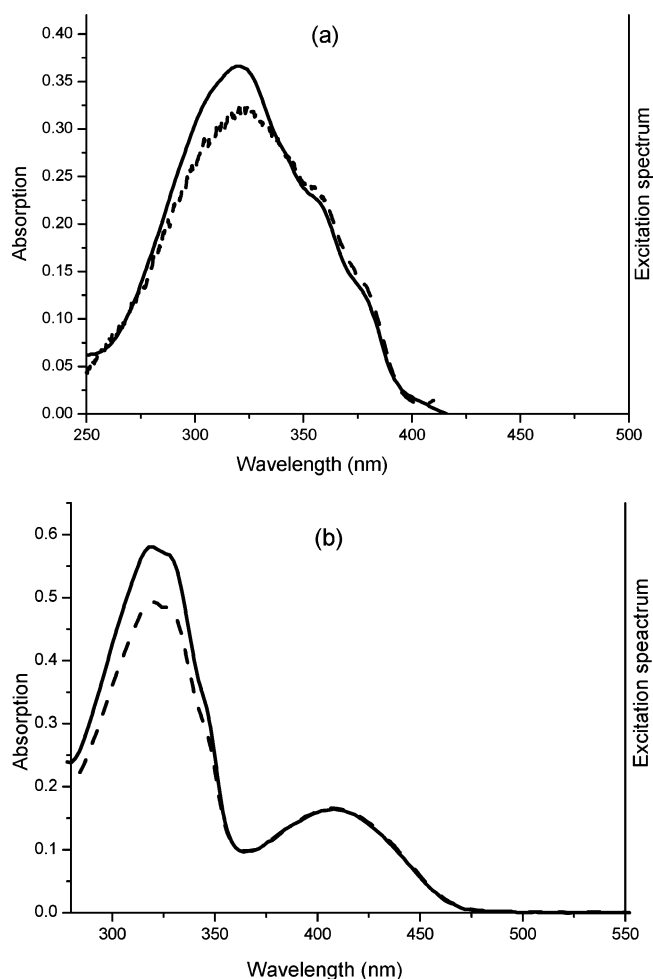


Figure 4. A comparison of the absorption spectra (solid line) of (a) **1a** and (b) **1b** in CHCl_3 with the corresponding excitation spectra (dashed line) monitored at (a) 411 nm and (b) 490 nm, respectively.

energy losses may not occur in **1a** under the conditions of measurements.

Because the rate of energy transfer depends strongly on distance, being inversely proportional to r^6 , it seems likely that successive two-step energy transfer might be first transferred from divinylbenzene chromophores to the nearest divinylbiphenyl chromophores, then

subsequently to divinylstilbene chromophores.¹⁵ In a similar manner, upon excitation of divinylbiphenyl chromophore in polymer **1b** at 300 nm, the emissions from divinylbiphenyl or divinyl-diphenyloxadiazaole in polymer **1b** have been quenched so that a strong emission at 467 and 490 nm resulting from the acceptor chromophore was observed. This result indicates that efficient intrachain energy transfer may occur from divinylbiphenyl via divinyl-diphenyloxadiazaole to terphenylene tetravinylene chromophores (Figure 3). The energy transfer directly from divinylbiphenyl to terphenylene tetravinylene chromophore, if any, would be relatively unfavorable because of the much longer distance and poorer spectral overlap.

As shown in Figure 4, the absorption spectra of polymers **1a** and **1b** were compared with its excitation spectra monitored at 411 and 490 nm, respectively, and the energy-transfer efficiency in **1a** was estimated to be 89% and **1b** 86%.

Conclusions

In summary, the first successful example of regio-regular silylene-spaced polymers **1** composed of three different chromophores have been designed and synthesized by the rhodium-catalyzed hydrosilylation of bis-vinylsilanes **3** and bis-alkynes **4**. The ratio of three chromophores was $D_1/D_2/A = 1:2:1$. Our synthetic protocol has furnished a powerful arsenal for the construction of copolymers with precise regiochemistry and structural variety. In the polymeric segments of an energy gradient, the band gaps of three chromophores decrease by means of the increasing conjugation lengths. Upon excitation of the donor chromophores (D_1), only emission from the acceptor (A) was observed. Efficient and sequential energy transfer across three different chromophores along the polymeric backbone may proceed smoothly in these silylene-spaced copolymers.

Experimental Section

The absorption spectra were recorded on a Hitachi U-3310 spectrometer. The photoluminescence and excitation spectra were measured on a Hitachi F-4500 fluorescence spectrometer. Gel permeation chromatography (GPC) was performed on a Waters GPC machine using an isocratic HPLC pump (1515) and a refractive index detector (2414). THF was used as the eluent (flow rate = 1 mL/min). Waters Styragel HR2, HR3, HR3, and HR4 (7.8×300 mm) columns were employed for molecular weight determination, and polystyrenes were used as standard (M_n values ranging from 375 to 3.5×10^6). Quantum yield (Φ) of polymer **1** was measured in CHCl_3 using coumarin 1 in EtOAc ($\Phi = 0.99$) as the standard. The ionization method of HRMS for all compounds was FAB using 3-nitrobenzyl alcohol (NBA) matrix.

1,4-Bis{2-[2-[4-(tri-isopropylsilylethynyl)biphen-4-yl]-vinyl]dimethylsilylvinyl}benzene (7). Under argon, a mixture of **6**¹⁰ (1.08 g, 3 mmol), **5** (0.37 g, 1.5 mmol), and $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (14 mg, 0.5 mol %) in THF (5 mL) was refluxed for 2 h. After cooling to room temperature, the mixture was poured into MeOH. The precipitate was collected and recrystallized from CHCl_3 to give **7** (1.1 g, 79%): mp 90–91 °C; IR (KBr): ν 3019, 2942, 2863, 2153, 1910, 1602, 1491, 1462, 1247, 985, 832, 731, 706, 676 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 0.38 (s, 12 H), 1.19 (s, 42 H), 6.58 (d, $J = 19.1$ Hz, 2 H), 6.61 (d, $J = 19.1$ Hz, 2 H), 7.00 (d, $J = 19.1$ Hz, 2 H), 7.03 (d, $J = 19.1$ Hz, 2 H), 7.48 (s, 4 H), 7.55–7.65 (m, 16 H); ^{13}C NMR (100 MHz, CDCl_3): δ -2.4, 11.5, 18.8, 91.5, 107.1, 122.7, 126.8, 126.9, 127.1, 127.2, 127.5, 127.6, 128.0, 132.6, 137.8, 140.1, 140.6, 144.4, 144.7; HRMS (FAB) ($\text{C}_{64}\text{H}_{82}\text{Si}_4$) calcd: 962.5494; found: 962.5488. Anal. Calcd for $\text{C}_{64}\text{H}_{82}\text{Si}_4$: C 79.77, H 8.58; found: C 79.49, H 8.53.

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