Synthesis, Light-Harvesting and Energy-Transfer Properties of Regioregular Silylene-Spaced Alternating [(Donor-$SiMe_2$-)$_{n=1-3}$-(Acceptor-$SiMe_2$)] Copolymers

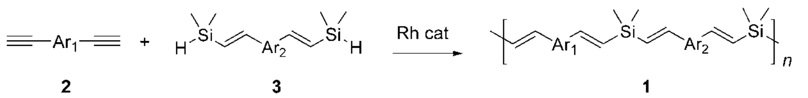
Yen-Ju Cheng and Tien-Yau Luh*[a]

Abstract: A series of silylene-spaced alternating [(donor-$SiMe_2$)$_{n=1-3}$-(acceptor-$SiMe_2$)] copolymers **4–6** was synthesized by rhodium-catalyzed hydrosilylation of bisalkynes with bissilyl hydrides. Monomeric reference compounds **7–10** with similar chromophore components were prepared for comparison. The ratio of donor to acceptor groups is well-controlled by the precise regiochemistry and nature of the repeat units. The silylene moieties serve as insulating spacers between chromophores. The polymers exhibit light-harvesting abilities, for which the intensity of the emission enhanced with larger donor-to-acceptor ratios. No emission originating from the donors was observed in fluorescence spectra, illustrating that intrachain energy transfer is highly efficient along the polymer chain.

Keywords: chromophores • energy transfer • hydrosilylation • inorganic polymers • light harvesting

Introduction

There has been ever-burgeoning interest in artificial light-harvesting systems capable of converting solar radiation into a useful source of energy.[1] Intramolecular energy transfer in supramolecular,[2,3] polymeric,[4] and dendritic[5] systems has been studied extensively. Conjugated copolymers with alternating donor–acceptor repeat units have received much attention because intramolecular charge transfer within the chain may result in concomitant changes in band gaps, and electrochemical and optical properties.[6] Linear polymer backbones with pendant chromophores provide alternative models for the investigation of energy-transfer or light-harvesting phenomena. Occasionally, moderate energy-transfer efficiencies are obtained and aggregation, resulting in quenching of the fluorescence, may occur. It is known that well-designed interruptions of the conjugation along the conjugated polymer backbone by insulating spacers may allow for tuning of the emission properties of the polymers.[7] The silylene moiety has been used extensively as an insulating spacer.[8] It is known that the intramolecular photoinduced charge transfer between donor and acceptor chromophores, separated by a silylene moiety, can occur readily.[9] The silylene-spaced copolymers **1** are readily accessible by rhodium-catalyzed hydrosilylation of bisalkynes **2** with bissilyl hydrides **3** [Eq. 1].[10] In this regard, two different chromophores, separated by a silylene group in the polymeric chain, are regioregularly positioned. It is envisaged that such a strategy may generate a useful variety of fascinating polymers that have different regioselective combinations of donors and acceptors along the polymer chain.



(1)

When the Ar groups in Equation (1) have relatively long conjugation lengths, the emission profiles of these copolymers appear to be similar to those of the corresponding monomers (having the same chromophores); no excimer-like emission is observed in their fluorescence spectra. It is thus believed that through-spaced interactions between chromophores along these polymeric chains may not take place.[11] We envision that silylene-spaced copolymers may serve as a useful model for the study of light harvesting and energy transfer along the polymeric backbone.[12] By adopt-

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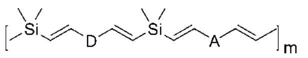
ing a strategy similar to that shown in Equation (1), different ratios of donor-to-acceptor chromophores can be regioselectively incorporated into the copolymers. Herein we report the unprecedented synthesis and photophysical properties of a series of silylene-spaced alternating [(donor-$SiMe_2)_n$-(acceptor-$SiMe_2$)]$_m$ copolymers **4–6**, where $n = 1–3$.



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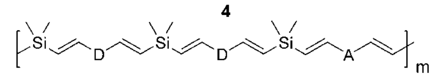

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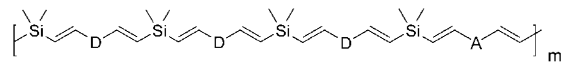

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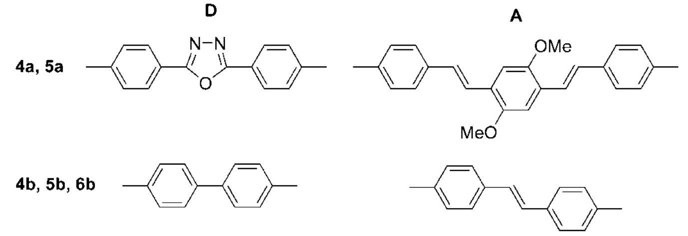
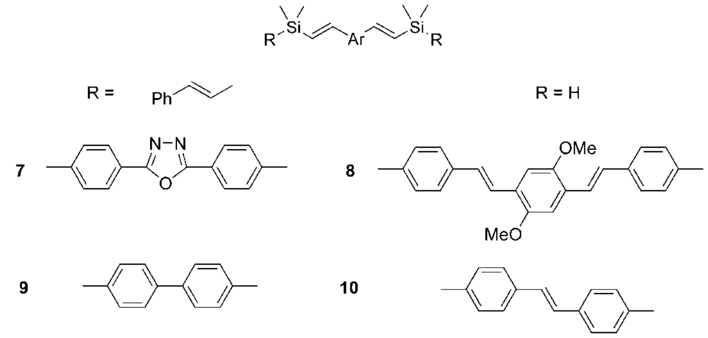




Results and Discussion

The synthesis of copolymers **4–6** was based on the strategy shown in Equation (1). The donor and acceptor chromophores were chosen on the basis of their absorption and emission profiles. The absorption and fluorescence spectra of the corresponding monomers **7–10** are shown in Figure 1. In general, the absorption of the acceptor chromophore should overlap with the emission maximum of the donor chromophore.

Accordingly, the divinyldiphenyl oxadiazole chromophore was paired with the dimethoxyterphenylene tetravinylene chromophore. Similarly, the divinylbiphenyl chromophore was used with the diphenylene tervinylene chromophore.

The acceptor chromophore was designed by incorporation of the silylhydride substituent at the olefinic termini (for example **8** and **10**). Nickel-catalyzed silyl olefination of the corresponding dithioacetals with (iPrO)Me_2SiCH_2MgCl, followed by the reduction of the corresponding Si–O bond, was employed for the synthesis of **8** and **10**.[13]

Silylene-spaced diynes **12** and **13** having different numbers of donor chromophores were prepared according to Scheme 1–3.

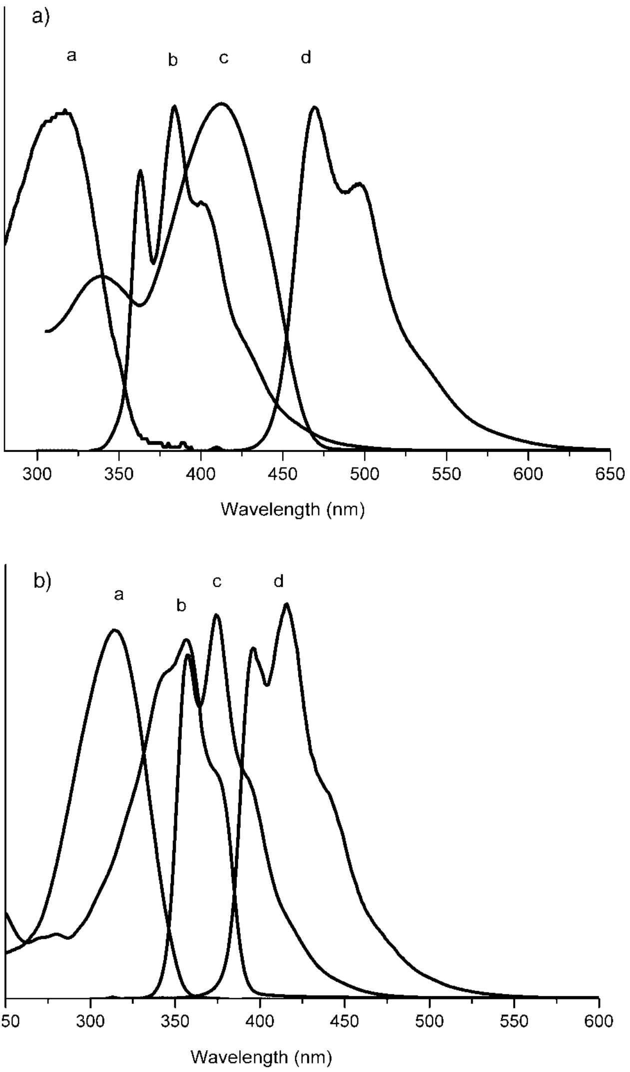
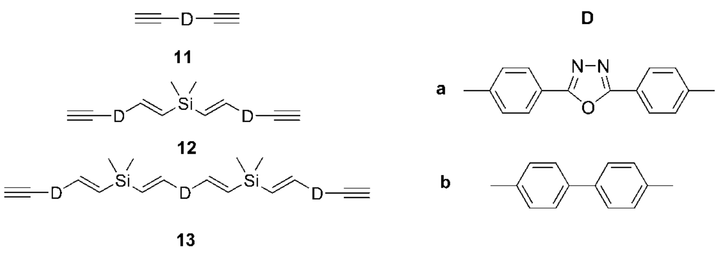


Figure 1. Top: absorption (a) and emission spectra (b) of **7**, absorption (c) and emission spectra (d) of **8** in $CHCl_3$. Bottom: absorption spectra of **9** (a) and **10** (b); emission spectra of **9** (c) and **10** (d) in $CHCl_3$.



Synthesis of the two-donor diyne 12a: Treatment of 4-bromobenzoylhydrazide (**15**) with 4-iodobenzoyl chloride (**14**) afforded the corresponding hydrazine **16** in 81% yield. Ring closure of **16** ($POCl_3$) furnished oxadiazole **17** in 82% yield. A double Heck reaction of **17** with **18** gave the corresponding dibromide **19** (46% yield).[14] Unfortunately, we were unable to couple **19** with trimethylsilylacetylene under various Sonogashira reaction conditions. Instead, the [$Pd_2(dba)_3$]/PPh_3-catalyzed Kumada–Corriu reaction of **19**

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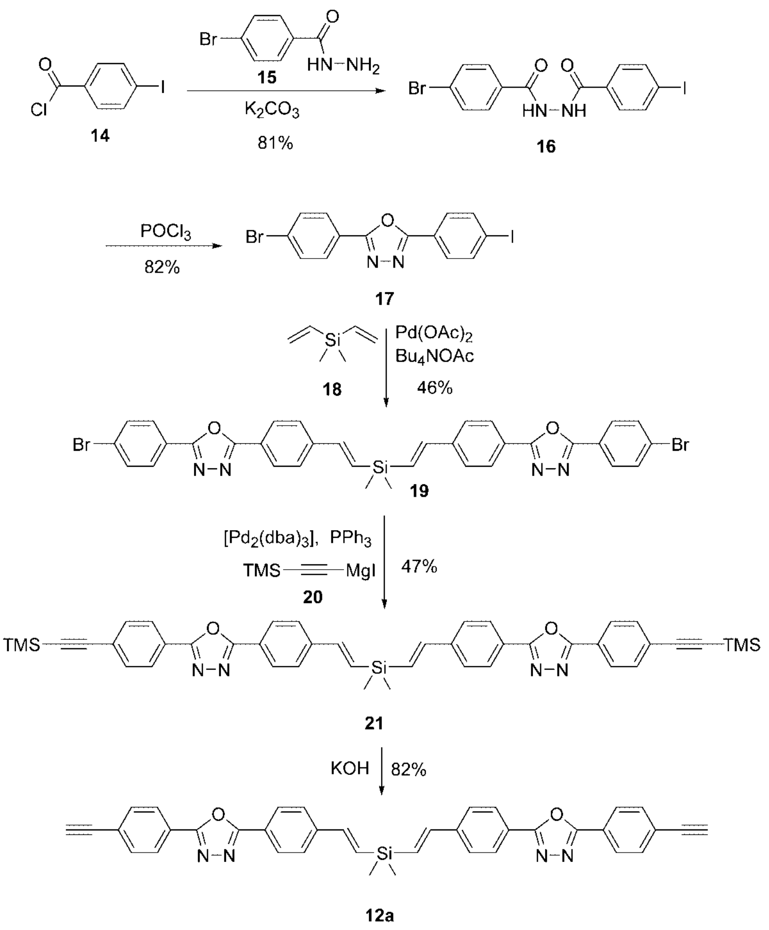
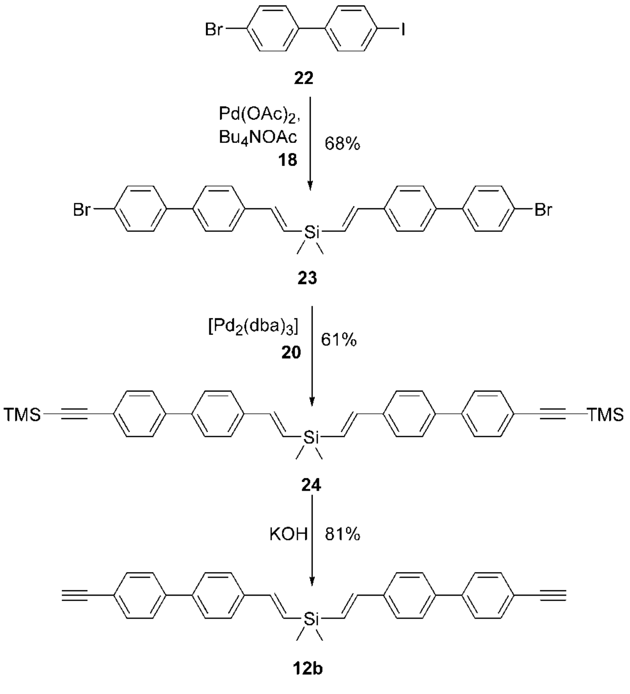
with the Grignard reagent **20**, prepared from trimethylacetylene and MeMgI, afforded the corresponding bisalkyne **21** in 47% yield.[15] Removal of the TMS group from **21** under basic conditions (KOH, MeOH) afforded **12a** in 82% yield (Scheme 1).

Synthesis of the two-donor diyne 12b: In a similar manner (Scheme 2), a double Heck reaction of **22** with **18** gave **23** in 68% yield.[16] The palladium-catalyzed cross-coupling reaction of **23** with **20** yielded **24**. This was followed by desilylation to give **12b** in 49% yield (two steps).

Synthesis of the three-donor diyne 13: In a sequential Sonogashira reaction, **22** was first treated with one equivalent of triisopropylsilylacetylene to yield **25**, which was then allowed to react with trimethylacetylene to afford **26** (overall 84%). Selective removal of the TMS group in **26** (NaOH, MeOH) led to **27** (85%). Rhodium-catalyzed hydrosilylation of **28** with two equivalents of **27** resulted in the formation of **29** in 89% yield. Desilylation of the TIPS group in **29** with TBAF afforded **13** in 82% yield (Scheme 3).



Scheme 1. Synthesis of the two-donor diyne **12a**.

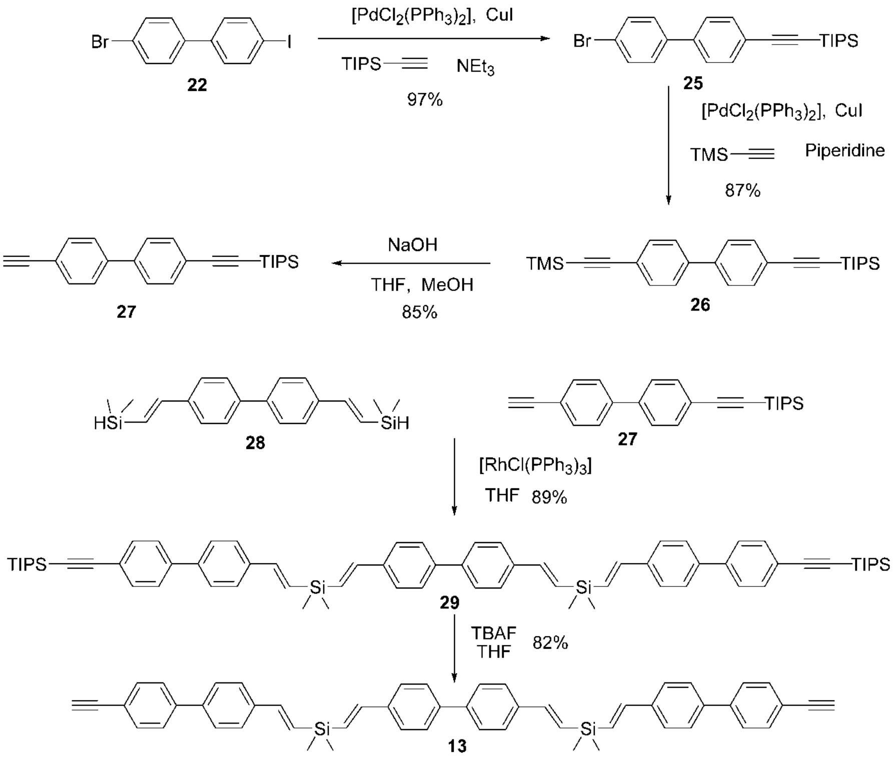


Scheme 2. Synthesis of the two-donor diyne **12b**.

Synthesis of polymers 4–6: A range of silylene-spaced copolymers **4–6** was synthesized by rhodium-catalyzed hydrosilylation of bisalkynes **11–13** with bissilyl hydride **8** and **10** according to Equation (1). The results are summarized in Table 1. The fluorescence quantum yields (Φ) of the polymers measured in $CHCl_3$ are also summarized in Table 1

Absorption and fluorescence properties: In the beginning of this investigation, a 1:1 mixture of the monomeric donor **7** and acceptor **8** chromophores was dissolved at different concentrations in chloroform. As can be seen from the fluorescence spectra in Figure 2, emission profiles from both **7** and **8** were observed upon excitation of **7** at 310 nm. The fluorescence spectrum for polymer **4a** is also included in Figure 2 for comparison. In contrast, when the solution was excited at 310 nm, the emission from the donor in **4a** was completely quenched; only fluorescence from the acceptor was observed at 467 nm and 490 nm. The photophysical properties of polymer **4a** were unaffected when the polarity of the solvent was changed (benzene, THF, EtOAc, and $CHCl_3$).[18] These results suggested that efficient intrachain energy transfer from the divinyldiphenyl oxadiazole donor moiety to the terphenylene tetravinylene chromophore can occur in polymer **4a** and that no photoinduced electron transfer takes place. The excitation spectrum, recorded at the λ_{em} of the acceptor (490 nm), and the absorption spectrum of **4a** are shown in Figure 3. When these two spectra are normalized at the λ_{max} value of the donor (405 nm), the efficiency of the energy transfer is estimated to be 87%.

Figure 4 shows the absorption spectra of the polymers **4a** and **5a** in chloroform. Two separate absorption bands, which correspond to the absorptions of the donor and acceptor, can be differentiated. Apparently, the spectrum of polymer **5a** is the summation of the individual absorptions of the donor and the acceptor chromophores. This observation again not only illustrates that the silylene moiety



Scheme 3. Synthesis of the three-donor diyne **13**.

Table 1. Reaction of donor with acceptor monomers by $[RhCl(PPh_3)_3]$ leading to silylene-spaced copolymers **4–6**.

Donor	Acceptor	Polymer	M_n (PDI)[a]	Φ[b]
11a	**8**	**4a**	7800(2.8)	0.58
11b	**10**	**4b**	8600(3.1)	0.66
12a	**8**	**5a**	6700(2.9)	0.52
12b	**10**	**5b**	9800(3.3)	0.59
13	**10**	**6b**	12100 (3.0)	0.51

[a] The M_n and PDI values were determined by GPC using polystyrenes as standard.[17] [b] Measured in $CHCl_3$ using coumarin 1 in EtOAc (Φ = 0.99) as the standard.

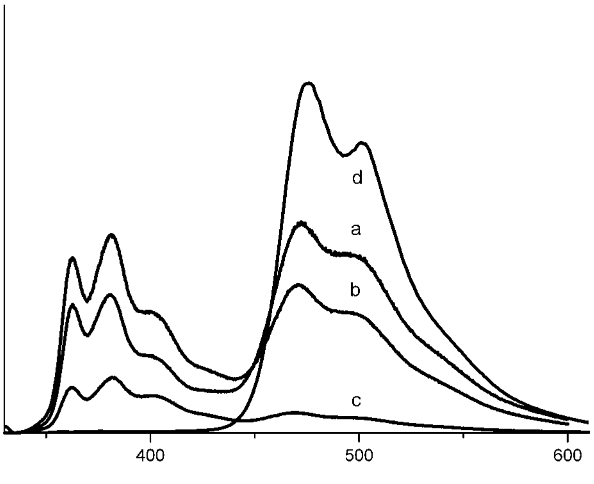


Figure 2. Concentration-dependent fluorescence spectra (λ_{ex}: 310 nm) of an equal molar mixture of **7** and **8** in $CHCl_3$ (a: 1×10^{-1} g mL^{-1}; b: 1×10^{-2} g mL^{-1}; c: 1×10^{-3} g mL^{-1}) and fluorescence spectrum (d: λ_{ex}: 310 nm) of **4a** in $CHCl_3$.

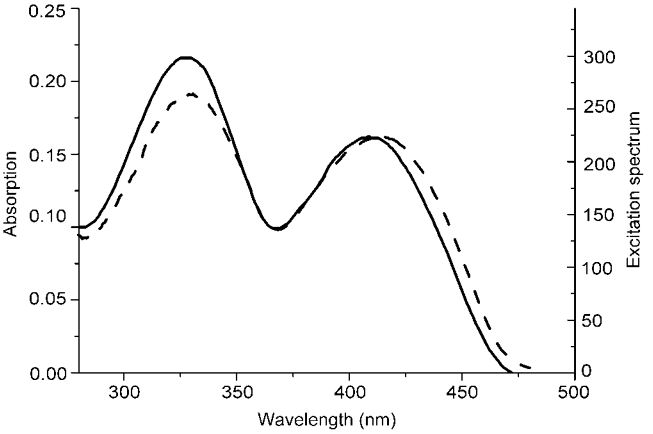


Figure 3. Comparison of the absorption spectrum (solid line) with the excitation spectrum (dashed line) of **4a** in $CHCl_3$, monitored at 490 nm.

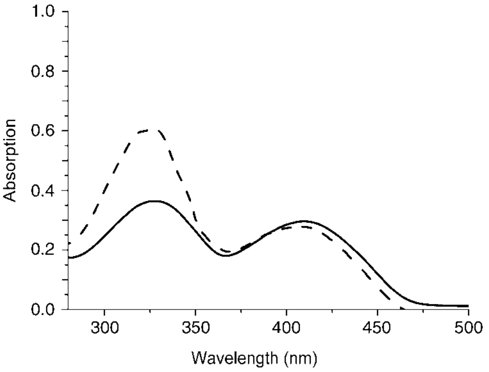


Figure 4. Absorption spectra of polymer **5a** (dashed line) and **4a** (solid line) in $CHCl_3$.

in these copolymers serves as insulating spacer, but also demonstrates that there is no interaction in the ground state between donors and acceptors. As the molar fraction of the donor in the polymers increases from 50% in **4a** to 67% in **5a**, the absorbance around 300–350 nm, corresponding to that of the donor chromophore, is also doubled. As shown in Figure 5, excitation of the donor chromophores at 310 nm in polymer **4a** and **5a** resulted in fluorescence from the acceptor exclusively. It is noteworthy that the emission intensity of **5a** is approximately doubled in comparison with that of **4a** when the intensity of acceptor absorption was kept the same in both polymers. These results indicated that the light-harvesting capability is significantly enhanced in **5a**. Again, a comparison of the excitation spectrum with the absorption spectrum of **5a** suggested that the energy-transfer efficiency is 86%.[18]

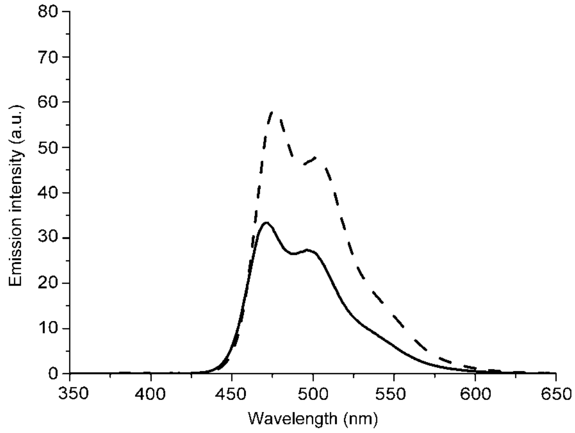


Figure 5. Emission spectra of **5a** (dashed line) and **4a** (solid line) in $CHCl_3$ (excitation at 310 nm).

The photophysical properties of **4b**, **5b**, and **6b** were also examined. The normalized absorption spectra of these polymers (normalized at the λ_{max} = 355 nm) are shown in Figure 6. This maximum originates from the absorption of the acceptor chromophores in these polymers. The increase of the absorption from divinylbiphenyl in **5b** and **6b** was due to the higher molar fraction of this donor chromophore. The emission spectra of these polymers upon excitation at 300 nm are shown in Figure 7.

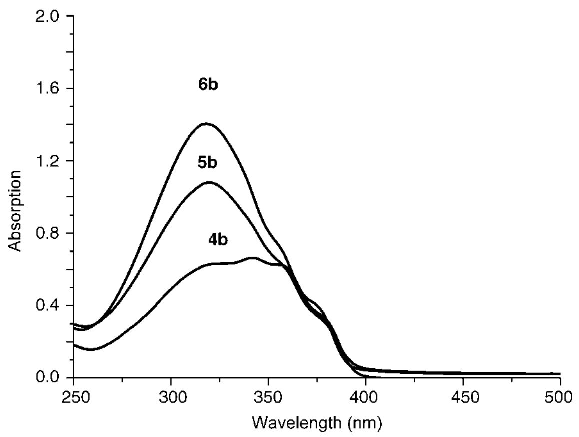


Figure 6. Absorption spectra of polymer **4b**, **5b**, and **6b** in $CHCl_3$.

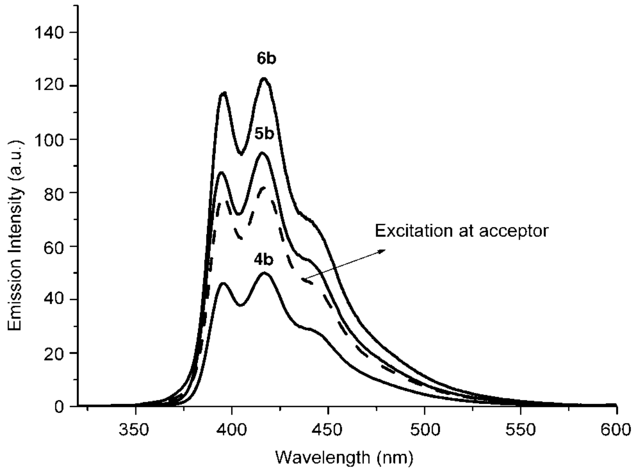


Figure 7. Emission spectra of **4b**, **5b**, and **6b** in $CHCl_3$ (excitation at 300 nm) and **6b** (directly excitation at 360 nm of the acceptor chromophore, dashed line).

As expected, polymer **6b** exhibits the highest emission intensity in comparison with those of **4b** and **5b**. In a similar manner, the intensity of the emission for **5b** is doubled in comparison with that of **4b**. However, the intensity of emission from **6b** (molar fraction = 0.75) was somewhat less than triple that from **4b**. Although increasing the donor number allows more light harvesting from donor to acceptor, the distance between donor and acceptor would not be the same. In other words, the distance between the donor chromophore at the center and the acceptor chromophore in **6b** would be different from the distance between the other donor and acceptor chromophores. Accordingly, the efficiencies for the energy transfer from different donor chromophores may not be identical.

The emission profile was recorded upon excitation at 360 nm (the λ_{max} of the acceptor chromophore in **6b**), and is also shown in Figure 7 (dashed line). Interestingly, the recorded intensity of this spectrum is much lower than that of **6b** when the excitation wavelength was 300 nm (the λ_{max} of the donor chromophore in **6b**). These results revealed that the acceptor can emit stronger through an energy-transfer mechanism from donors than when it is directly excited at the acceptor. The ability of the light-harvesting effect, along with subsequent energy transfer in these polymers, is very efficient (>88%).[18]

Conclusion

In summary, we have demonstrated efficient syntheses of three types of regioregular silylene-spaced copolymers **4**–**6**. The ratio of donor to acceptor can easily be controlled by appropriate design of the monomeric precursors. Unlike most copolymers, our strategy has provided a powerful arsenal for the construction of copolymers with precise regiochemistry and repeating units. In these polymers, the light-harvesting ability has been shown to increase with an increasing donor-to-acceptor ratio. No emission coming from the donor was observed in fluorescence spectra, illustrating that intrachain energy transfer is highly efficient along the polymer chain. These results suggest that the use of silylene linkers for the construction of donor–acceptor polymers has provided a new ideal architecture for light harvesting and energy transfer.

Experimental Section

4-Benzoic acid *N'*-4-iodobenzoylhydrazide (16): 4-iodobenzoic chloride **14** (13.3 g, 50 mmol) in THF (30 mL) was added dropwise over 30 min to a solution of 4-bromobenzoic acid hydrazide **15** (10.75 g, 50 mmol), sodium carbonate (5.3 g, 50 mmol) in THF (60 mL), and water (60 mL). The mixture was stirred at room temperature for 1 h. After removal of THF in vacuo, the solid was collected by filtration, washed with water, and dried in vacuo to give **16** as a white solid (18.02 g, 81 %): m.p. 320–321 °C; IR (KBr): $\tilde{\nu}$ 3183, 2997, 1594, 1554, 1498, 1453, 1256, 845, 743 cm^{-1}; ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 7.69$ (d, $J = 8.3$ Hz, 2 H), 7.74 (d, $J = 8.5$ Hz, 2 H), 7.85 (d, $J = 8.5$ Hz, 2 H), 7.91 (d, $J = 8.3$ Hz, 2 H), 10.59 ppm (s, 2 H); ^{13}C NMR (100 MHz, [D$_6$]DMSO): $\delta = 100.3$, 126.3, 129.9, 130.1, 132.2, 132.4, 138.0, 165.5, 165.8 ppm; HRMS (EI) ($C_{14}H_{10}BrIN_2O_4$): calcd: 443.8964; found: 443.8964; elemental analysis (%) calcd for $C_{14}H_{10}BrIN_2O_4$: C 37.78, H 2.26; found: C 37.92, H 2.34.

2-(4-Bromophenyl)-5-(4-iodophenyl)-[1,3,4]oxadiazole (17): A mixture of **16** (8.9 g, 20 mmol) and $POCl_3$ (100 mL) was refluxed for 16 h. Excess $POCl_3$ was removed by distillation. The residue was washed with water and collected by filtration and recrystallized from THF to afford **17** as a white solid (7 g, 82 %): m.p. 242–243 °C; IR (KBr): $\tilde{\nu}$ 3076, 1921, 1656, 1611, 1532, 1481, 1397, 833, 738 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.66 (d, $J = 8.4$ Hz, 2 H), 7.83 (d, $J = 8.4$ Hz, 2 H), 7.88 (d, $J = 8.4$ Hz, 2 H), 7.98 ppm (d, $J = 8.4$ Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 98.8$, 122.7, 123.2, 126.6, 128.3, 128.4, 132.5, 138.4, 164.1, 164.2 ppm; HRMS (FAB) (M^++H, $C_{14}H_9BrIN_2O$): calcd: 426.8943; found: 426.8940; elemental analysis (%) calcd for $C_{14}H_8BrIN_2O$: C 39.38, H 1.89; found: C 39.28, H 1.72.

Bis{2-[4-(2-[5-(4-bromophenyl)[1,3,4]oxadiazolyl])phenyl]vinyl}dimethylsilane (19): A mixture of **17** (4.27 g 10 mmol), **18** (0.67 g, 6 mmol), Pd(OAc)$_2$ (0.11 g, 0.5 mmol), Bu$_4$NOAc (6.03 g, 20 mmol), and molecular sieves (4 Å) in dry DMF (150 mL) was stirred at 80 °C for 24 h under argon. After filtration over celite, water was added, and the mixture was extracted with chloroform. The organic layer was washed with water and brine, and dried ($MgSO_4$). After removal of the solvent in vacuo, the crude product was separated on a flash silica gel column ($CHCl_3$) to afford **19** (1.63 g, 46 %): m.p. 247–248 °C; IR (KBr): $\tilde{\nu}$ 2985, 2952, 1926, 1605, 1577, 1543, 1481, 1076, 839, 738 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.37$ (s, 6 H), 6.68 (d, $J = 19.1$ Hz, 2 H), 7.01 (d, $J = 19.1$ Hz, 2 H), 7.60 (d, $J = 8.4$ Hz, 4 H), 7.67 (d, $J = 8.5$ Hz, 4 H), 8.00 (d, $J = 8.5$ Hz, 4 H), 8.09 ppm (d, $J = 8.4$ Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -2.7$, 122.8, 123.1, 126.4, 127.1, 127.3, 128.3, 130.4, 132.5, 141.4, 143.9, 163.9, 164.6 ppm; HRMS (FAB) (M^++H, $C_{34}H_{26}Br_2N_4O_2Si$): calcd: 709.0270; found: 709.0276; elemental analysis (%) calcd for $C_{34}H_{26}Br_2N_4O_2Si$: C 57.48, H 3.69; found: C 57.26, H 3.81.

Bis{2-[4-(2-[5-(4-triisopropylethynylphenyl)[1,3,4]oxadiazolyl])phenyl]vinyl}dimethylsilane (21): A freshly prepared 2 M solution of methylmagnesium iodine (2.2 mL) was added to a solution of trimethylacetylene (0.64 mL, 4.48 mmol) in dry diethyl ether (5 mL) at room temperature and the mixture was stirred for 30 min under argon. THF (120 mL) was introduced, followed by the successive addition of [Pd$_2$(dba)$_3$] (0.08 g), PPh$_3$ (0.08 g), and **19** (0.8 g, 1.12 mmol). The reaction mixture was refluxed for a further 24 h, quenched with NH_4Cl, extracted with $CHCl_3$, and dried ($MgSO_4$). After removal of the solvent in vacuo, the crude product was purified by flash chromatography (chloroform) to afford **21** (0.39 g, 47 %): m.p. 286–288 °C; IR (KBr): $\tilde{\nu}$ 2952, 2157, 1611, 1566, 1538, 1487, 1397, 1250, 845 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.25 (s, 18 H), 0.36 (s, 6 H), 6.68 (d, $J = 19.1$ Hz, 2 H), 7.00 (d, $J = 19.1$ Hz, 2 H), 7.59–7.64 (m, 8 H), 8.06 (d, $J = 8.3$ Hz, 4 H), 8.09 ppm (d, $J = 8.3$ Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ −2.8, −0.2, 97.7, 103.9, 123.1, 123.4, 126.6, 127.1, 127.2, 128.3, 130.3, 132.5, 141.3, 143.8, 164.0, 164.5 ppm; HRMS (FAB) (M^++H, $C_{44}H_{44}N_4O_2Si_3$): calcd: 745.2850, found: 745.2863; elemental analysis (%) calcd for $C_{44}H_{44}N_4O_2Si_3$: C 70.93, H 5.95; found: C 70.56, H 5.61.

Bis{2-[4-(2-[5-(4-ethynylphenyl)[1,3,4]oxadiazolyl])phenyl]vinyl}dimethylsilane (12a): A solution of **21** (75 mg, 0.1 mmol) in MeOH (10 mL), THF (40 mL) and 0.1 M NaOH solution (2.2 mL) was stirred at room temperature for 1 h. After removal of the solvent in vacuo, water was added and the mixture was extracted with $CHCl_3$. The organic layer was dried ($MgSO_4$), evaporated in vacuo and the residue was purified on a flash silica gel column ($CHCl_3$) to yield **12a** (49 mg, 82 %): m.p. 312 °C (decomp); IR (KBr): $\tilde{\nu}$ 3295, 3273, 3042, 2952, 2912, 2101, 1926, 1612, 1577, 1543, 1481, 1245, 991, 833, 743 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.37$ (s, 6 H), 3.24 (s, 2 H), 6.68 (d, $J = 19.1$ Hz, 2 H), 7.01 (d, $J =$ 19.1 Hz, 2 H), 7.61 (d, $J = 8.5$ Hz, 4 H), 7.63 (d, $J = 8.5$ Hz, 4 H), 8.09 (d, $J = 8.5$ Hz, 4 H), 8.10 ppm (d, $J = 8.5$ Hz, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ −2.8, 80.1, 82.7, 123.1, 123.9, 125.6, 126.7, 127.1, 127.2, 130.4, 132.7, 141.4, 143.9, 164.0, 164.6 ppm; HRMS (FAB) (M^++H, $C_{38}H_{29}N_4O_2Si$): calcd: 601.2060, found: 601.2056; elemental analysis (%) calcd for $C_{38}H_{29}N_4O_2Si$: C 75.97, H 4.70; found: C 75.62, H 5.07.

Bis[2-(4'-bromobiphenyl-4-yl)vinyl]dimethylsilane (23): A mixture of **22** (3.59 g, 10 mmol), **18** (0.67 g, 6 mmol), Pd(OAc)$_2$ (0.11 g, 0.5 mmol), Bu$_4$NOAc (6.03 g, 20 mmol), and molecular sieves (4 Å) in dry DMF (100 mL) was stirred under argon at 80 °C for 16 h. After filtration over celite, the filtrate was extracted with $CHCl_3$ and washed with water and brine, and then dried ($MgSO_4$). After removal of the solvent in vacuo, the residue was purified by flash chromatography (hexane) to afford **23** (1.95 g, 68 %); m.p. 233–234 °C; IR (KBr): $\tilde{\nu}$ 3030, 2985, 2957, 1909, 1605, 1481, 1385 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.35$ (s, 6 H), 6.58 (d, $J = 19.1$ Hz, 2 H), 7.00 (d, $J = 19.1$ Hz, 2 H), 7.47 (d, $J = 8.4$ Hz, 4 H), 7.5–7.6 ppm (m, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -2.4$, 121.7, 127.1, 128.0, 128.6, 132.0, 137.8, 139.7, 144.4 ppm; HRMS (EI) ($C_{30}H_{26}Br_2Si$): calcd: 572.0171, found: 572.0161; elemental analysis (%) calcd for $C_{30}H_{26}Br_2Si$: C 62.73, H 4.56; found: C 62.91, H 4.37.

Bis{2-[4'-trimethylsilylethynyl-biphenyl-4-yl]vinyl}dimethylsilane (24): A freshly prepared 2 M solution of methylmagnesium iodine (0.7 mL) was added to a solution of trimethylacetylene (0.2 mL, 1.4 mmol) in diethyl ether (2 mL) at room temperature, and the mixture stirred under argon for 30 min. THF (30 mL) was introduced, followed by the successive addition of [Pd$_2$(dba)$_3$] (0.025 g), PPh$_3$ (0.025 g), and **23** (0.2 g, 0.35 mmol). The mixture was refluxed for 24 h, quenched with NH_4Cl, extracted with $CHCl_3$, and dried ($MgSO_4$). After removal of the solvent in vacuo, the residue was purified by flash chromatography (hexane) to afford **24** (0.13 g, 61 %): m.p. 249–250 °C; IR (KBr): $\tilde{\nu}$ 3036, 2946, 2918, 2839, 2152, 1605, 1487, 1245, 997, 833 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.24$ (s, 18 H), 0.3 (s, 6 H), 6.56 (d, $J = 19.1$ Hz, 2 H), 7.00 (d, $J = 19.1$ Hz, 2 H), 7.4–7.6 ppm (m, 16 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -2.4$, 0.1, 95.1, 105.1, 122.2, 126.8, 127.1, 127.2, 128.0, 132.5, 137.7, 140.0, 140.7, 144.4 ppm; HRMS (FAB) (M^++H, $C_{40}H_{45}Si_3$): calcd: 609.2829; found: 609.2823; elemental analysis (%) calcd for $C_{40}H_{44}Si_3$: C 78.88, H 7.28; found: C 79.14, H 7.45.

Bis{2-[4'-ethynylbiphenyl-4-yl]vinyl}dimethylsilane (12b): A mixture of **22** (0.12 g, 0.2 mmol) in MeOH (10 mL) and THF (40 mL) and 0.1 M aqueous NaOH solution (4 mL) was stirred at room temperature for 1 h. After removal of the solvent in vacuo, water was added and the mixture was extracted with $CHCl_3$ and dried ($MgSO_4$). Removal of the solvent in vacuo afforded the residue which was purified on a flash silica gel ($CHCl_3$) to yield **12b** (0.075 g, 81 %): m.p. 241 °C (decomp); IR (KBr): $\tilde{\nu}$ 3267, 2969, 2912, 2107, 1909, 1600, 1492, 1397, 1256, 997, 833, 805 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.34$ (s, 6 H), 3.12 (s, 2 H), 6.57 (d, $J =$ 19.1 Hz, 2 H), 6.98 (d, $J = 19.1$ Hz, 2 H), 7.5–7.6 ppm (m, 16 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ −2.5, 77.9, 83.6, 121.0, 126.8, 127.0, 127.1, 128.0, 132.6, 137.7, 139.8, 141.0, 144.3 ppm; HRMS (EI) ($C_{34}H_{28}Si$): calcd: 464.1960; found: 464.1963; elemental analysis (%) calcd for $C_{34}H_{28}Si$: C 87.88, H 6.07; found: C 87.91, H 6.31.

4′-Bromo-4-[(triisopropylsilyl)ethynyl]biphenyl (25): A mixture of **22** (3.59 g, 10.0 mmol), (triisopropylsilyl)acetylene (2.5 mL, 11.0 mmol), $[Pd(PPh_3)_2Cl_2]$ (0.35 g, 0.5 mmol) and CuI (95 mg, 0.5 mmol) in NEt_3 (40 mL) was refluxed under argon for 8 h and then cooled to room temperature. The mixture was filtered and NEt_3 was evaporated. The crude product was purified by silica gel column chromatography (hexane) to give **25** as a white solid (4 g, 97 %): m.p. 37–38 °C; IR (KBr): $\tilde{\nu}$ 2942, 2850, 2154, 2064, 1893, 1588, 1481, 1462, 1380, 1221, 1075, 1002, 882, 836, 813, 742, 663 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$,): $\delta = 1.15$ (s, 21 H), 7.44 (d, $J = 8.3$ Hz, 2 H), 7.49 (d, $J = 7.7$ Hz, 2 H), 7.54 (d, $J = 7.7$ Hz, 2 H), 7.56 ppm (d, $J = 8.3$ Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 18.6, 91.7, 106.7, 121.9, 122.9, 126.6, 128.5, 131.9, 132.5, 139.3, 139.7 ppm; HRMS (FAB) (M^++H, $C_{23}H_{29}BrSi$): calcd: 413.1300; found: 413.1306; elemental analysis (%) calcd for $C_{23}H_{29}BrSi$: C 66.81, H 7.07; found: C 66.89; H 6.99.

(4′-Triisopropylsilylethynyl-4-trimethylsilylethnyl)biphenyl (26): To a mixture of trimethylsilylacetylene (1.5 mL, 7.2 mmol) and **25** (2.0 g, 4.8 mmol) in piperidine (40 mL) was added $[Pd(PPh_3)_2Cl_2]$ (0.1 g, 0.14 mmol) and CuI (30 mg, 0.15 mmol). The mixture was refluxed for 12 h under argon and then cooled to room temperature. After filtration, the solvent was evaporated in vacuo and the residue was purified on silica gel (hexane) to afford **26** as an oil (1.8 g, 87 %). IR (KBr): $\tilde{\nu}$ 3033, 2957, 2943, 2865, 2156, 1910, 1489, 1462, 1383, 1249, 1221, 995, 840, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.27$ (s, 9 H), 1.14 (s, 21 H), 7.52 ppm (s, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.03, 11.3, 18.7, 91.7, 95.2, 104.8, 106.8, 122.4, 122.9, 126.7, 132.4, 132.5, 140.1, 140.3 ppm; HRMS (FAB) (M^++H, $C_{28}H_{39}Si_2$): calcd: 430.2512; found: 430.2505; elemental analysis (%) calcd for $C_{28}H_{38}Si_2$: C 78.07, H 8.89; found: C 78.56; H 8.55.

(4′-Triisopropylsilylethynyl-4-ethnyl)biphenyl (27): A mixture of **26** (1.5 g, 3.5 mmol) and NaOH (0.14 g, 3.5 mmol) in MeOH (10 mL) and THF (10 mL) was stirred at room temperature for 1 h. After filtration, the solvent was evaporated in vacuo. The residue was purified by silica gel (hexane) to give **27** as a yellowish solid (1.07 g, 85 %): m.p. 41–42 °C; IR (KBr): $\tilde{\nu}$ 3301, 2942, 2864, 2153, 2101, 1910, 1488, 1463, 1230, 996, 822, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.16 (s, 21 H), 3.15 (s, 1 H), 7.5–7.6 ppm (m, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 11.3$, 18.6, 78.0, 83.4, 91.7, 106.7, 121.3, 122.9, 126.7, 126.8, 132.5, 132.6, 139.9, 140.7 ppm; HRMS (FAB) (M^++H, $C_{25}H_{31}Si$): calcd: 359.2195; found: 359.2200; elemental analysis (%) calcd for $C_{25}H_{30}Si$: C 83.74, H 8.43; found: C 83.43; H 8.31.

4,4′-Bis(2-{[2-(4′-trimethylpropylethynyl-biphenyl-4-yl)vinyl]dimethylsilyl}vinly)biphenyl (29): A mixture of **27** (0.66 g, 1.86 mmol), **28** (0.3 g, 0.93 mmol), and $[Rh(PPh_3)_3Cl]$ (8 mg) in THF (5 mL) was refluxed for 2 h under argon. After the mixture was cooled to room temperature, it was poured into MeOH. The precipitate was collected and recrystallized from $CHCl_3$ to give **29** (0.79 g, 82 %): m.p. 91–92 °C; IR (KBr): $\tilde{\nu}$ 3027, 2942, 2864, 2153, 1910, 1603, 1492, 1462, 1247, 987, 830, 795, 706, 676 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.37$ (s, 12 H), 1.17 (s, 42 H), 6.59 (d, $J = 19.1$ Hz, 2 H), 6.60 (d, $J = 19.1$ Hz, 2 H), 7.02 (d, $J = 19.1$ Hz, 4 H), 7.5–7.63 ppm (m, 24 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -2.6$, 11.3, 18.7, 91.4, 106.9, 122.5, 126.6, 126.7, 126.8, 126.91, 126.94, 126.98, 127.1, 127.5, 127.9, 132.4, 137.6, 139.9, 140.4, 144.3, 144.4 ppm; HRMS (FAB) (M^++H, $C_{70}H_{87}Si_4$): calcd: 1039.5885; found: 1039.5861; elemental analysis (%) calcd for $C_{70}H_{86}Si_4$: C 80.86, H 8.34; found: C 80.39; H 8.24.

Bis-4–4′-(2-{[2-(4′-ethynyl-biphenyl-4-yl)vinyl]dimethylsilyl}vinyl)biphenyl (13): A 1 M solution of TBAF (0.5 mL, 0.5 mmol) was added dropwise to a solution of **29** (0.208 g, 0.2 mmol) in THF (5 mL). The mixture was stirred at room temperature for 2.5 h, diluted with water, and extracted with $CHCl_3$. The organic layer was washed with brine and dried ($MgSO_4$). Solvent was removed in vacuo to give a brown solid which was recrystallized from $CHCl_3$ to yield **13** (0.78 g, 82 %): m.p. 321 °C (decomp); IR (KBr): $\tilde{\nu}$ 3295, 2982, 2944, 2097, 1918, 1603, 1491, 1246, 987, 830, 796, 642 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.35$ (s, 12 H), 3.12 (s, 2 H), 6.57 (d, $J = 19.1$ Hz, 2 H), 6.59 (d, $J = 19.1$ Hz, 2 H), 6.99 (d, $J = 19.1$ Hz, 4 H), 7.5–7.7 ppm (m, 24 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -2.62$, 77.7, 83.5, 121.0, 126.7, 126.86, 126.93, 127.0, 127.5, 128.0, 132.5, 137.4, 137.8, 139.8, 140.3, 141.0, 144.2, 144.4 ppm; HRMS (FAB) (M^++H, $C_{52}H_{47}Si_2$): calcd: 727.3216. found: 727.3226; elemental analysis (%) calcd for $C_{52}H_{46}Si_2$: C 85.90, H 6.38; found: C 85.52; H 6.11.

Polymer 4a: A mixture of **11a** (54 mg, 0.2 mmol), **8** (102 mg, 0.2 mmol) and $[Rh(PPh_3)_3Cl]$ (4.6 mg) in THF (5 mL) was refluxed for 4 h under argon. After the mixture was cooled to room temperature, it was poured into MeOH. The precipitate was collected and re-dissolved in THF, then reprecipitated with MeOH. The product **4a** was collected by filtration and washed with MeOH (0.12 g, 77 %): $M_n = 7800$, PDI = 2.8; IR (KBr): $\tilde{\nu}$ 2942, 2864, 1598, 1481, 1462,1410, 1209, 1045, 814, 668; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.28$ (s, 12 H), 3.93 (s, 6 H), 6.4–6.6 (m, 2 H), 6.4–6.8 (m, 2 H), 6.9–7.2 (m, 8 H), 7.3–7.7 (m, 14 H), 7.8–8.2 ppm (m, 4 H); elemental analysis (%) calcd for $C_{50}H_{48}N_2O_3Si_2$: C 76.88, H 6. 19; found: C 75.59; H 5.79.

Polymer 4b: A mixture of **11b** (0.061 g, 0.3 mmol), **10** (0.105 g, 0.3 mmol) and $[Rh(PPh_3)_3Cl]$ (6.9 mg) in THF (5 mL) was refluxed for 4 h under argon. After the mixture was cooled to room temperature, it was poured into MeOH. The precipitate was collected and re-dissolved in THF, then reprecipitated with MeOH. The product **4b** was collected by filtration and washed with MeOH (0.13 g, 78 %): $M_n = 8600$, PDI = 3.1; IR (KBr): $\tilde{\nu}$ 3023, 2982, 2952, 1914, 1693, 1600, 1492, 1413, 1040, 1247, 986, 839, 803; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.29$ (s, 12 H), 6.45–6.6 (m, 4 H), 6.85–7.03 (m, 4 H), 7.11 (s, 2 H), 7.35–7.65 ppm (m, 16 H); elemental analysis (%) calcd for $C_{38}H_{38}Si_2$: C 82.85, H 6.95; found: C 81.76; H 6.69.

Polymer 5a: A mixture of **12a** (42 mg, 0.07 mmol), **8** (35 mg, 0.07 mmol) and $[Rh(PPh_3)_3Cl]$ (2 mg) in THF (3 mL) was refluxed for 4 h under argon. After the mixture was cooled to room temperature, it was poured into MeOH. The precipitate was collected and re-dissolved in THF, then reprecipitated with MeOH. The product **5a** was collected by filtration and washed with MeOH (53 mg, 69 %): M_n = 6700, PDI = 2.9; IR (KBr): $\tilde{\nu}$ 2942, 2863, 1598, 1481, 1461, 1384, 1248, 1210, 1074, 1045, 838, 814; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.33$ (s, 18 H), 3.91 (s, 6 H), 6.4–6.6 (m, 2 H), 6.6–6.8 (m, 4 H), 6.9–7.05 (m, 6 H), 7.05–7.15 (m, 4 H), 7.35–7.55 (m, 10 H), 7.55–7.7 (m, 8 H), 8.00–8.15 ppm (m, 8 H); elemental analysis (%) calcd for $C_{70}H_{66}N_4Si_3$: C 75.64, H 5.98; found: C 74.51; H 5.57.

Polymer 5b: A mixture of **12b** (23.1 mg, 0.05 mmol), **10** (17.4 mg, 0.05 mmol) and $[Rh(PPh_3)_3Cl]$ (2 mg) in THF (3 mL) was refluxed for 4 h under argon. After the mixture was cooled to room temperature, it was poured into MeOH. The precipitate was collected and re-dissolved in THF, then reprecipitated with MeOH. The product was collected by filtration and washed with MeOH (33 mg, 81 %): $M_n = 9800$, PDI = 3.3; IR (KBr): $\tilde{\nu}$ 3023, 2954, 2919, 1905, 1684, 1600, 1492, 1396, 1248, 1045, 987, 838, 798; ^1H NMR (400 MHz, $CDCl_3$): δ 0.32 (s, 18 H), 6.45–6.65 (m, 6 H), 6.85–7.05 (m, 6 H), 7.11 (s, 2 H), 7.35–7.6 ppm (m, 24 H); elemental analysis (%) calcd for $C_{56}H_{56}Si_3$: C 82.70, H 6.94; found: C 81.44; H 6.72.

Polymer 6b: A mixture of **13** (0.121 g, 0.166 mmol), **10** (0.058 g, 0.166 mmol) and $[Rh(PPh_3)_3Cl]$ (3.8 mg) in THF (5 mL) was refluxed for 4 h under argon. After the mixture was cooled to room temperature, it was poured into MeOH. The precipitate was collected and re-dissolved in THF, then reprecipitated with MeOH. The product **6b** was collected by filtration and washed with MeOH (0.15 g, 84 %): $M_n = 12100$, PDI = 3.0; IR (KBr): $\tilde{\nu}$ 3023, 2986, 2954, 2890, 2954, 1905, 1601, 1492, 1400, 1330, 1247,1196, 1059, 986, 837, 793 cm^{-1}, ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.35$ (s, 24 H), 6.45–6.65 (m, 8 H), 6.9–7.05 (m, 8 H), 7.1 (s, 2 H), 7.4–7.65 ppm (m, 32 H); elemental analysis (%) calcd for $C_{74}H_{74}Si_4$: C 82.62, H 6.93; found: C 81.67; H 7.06.

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[17] 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 = 1.0 mL min^{-1}). Waters Styragel HR 2, HR 3 and HR 4 (7.8 × 300 mm) were employed using polystyrene as standard (M_n values range from 375 to 3.5×10^6).

[18] The spectra are shown in the supporting information.

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