

# Alternating dialkylsilylene-divinylarene copolymers\*

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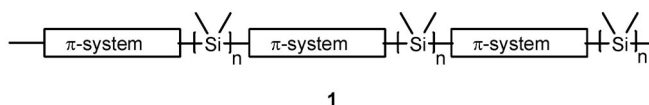
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**Abstract:** A summary of recent advances in the chemistry and photophysics of alternating dialkylsilylene-divinylarene copolymers is presented. The silicon moieties are considered to be insulating tetrahedral spacers in these copolymers. The substituents on silicon can readily be tuned, and the steric environment of these substituents around the silicon may dictate the conformation (or helicity) of the copolymers (the Thorpe–Ingold effect) and hence their photophysical properties. Because different chromophores can be regioregularly introduced into the polymeric chain, these copolymers have been used as models to study energy transfer and photoinduced electron transfer (PET), as well as chiroptical transfer.

**Keywords:** copolymers; dialkylsilylene; divinylarene; fluorescence resonance energy transfer; helical; photoinduced electron transfer; Thorpe–Ingold effect.

## INTRODUCTION

Linear polymers containing alternating silylene and  $\pi$ -conjugated moieties **1** [1] have been shown to have potential as ceramic precursor [2], heat-resistant materials [3], conducting materials [4], electroluminescent materials [5], and models for light-harvesting investigations [6]. Extensive studies on the  $\sigma$ – $\pi$  conjugation suggest that conjugative interactions only take place in  $\pi$ -conjugated systems with disilylene or higher homologous oligosilylene spacers **1** ( $n \geq 2$ ) [7–10].



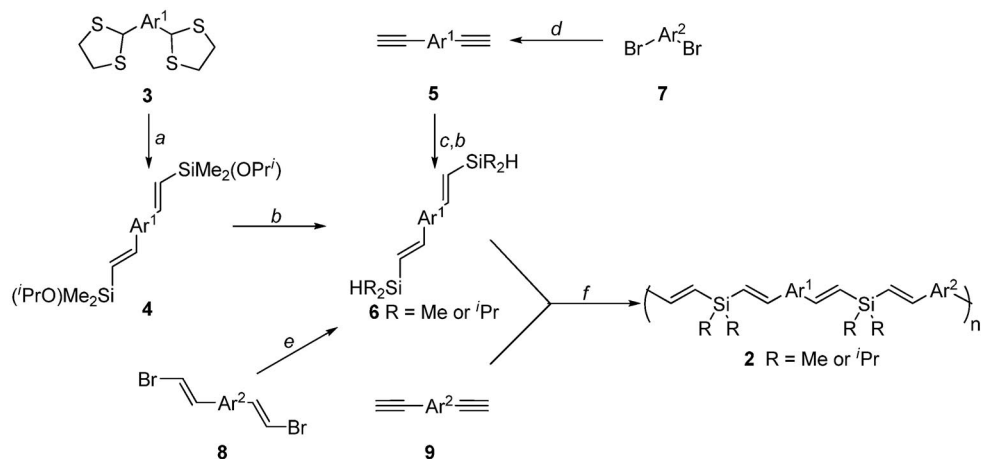
On the other hand, the  $\sigma$ – $\pi$  interaction may be too weak to be characterized in monosilylene-spaced copolymers and the monosilylene moieties are, in general, considered to be insulating tetrahedral spacers [7b,c,10]. In particular, when other photophysical processes prevail, the characteristics of  $\sigma$ – $\pi$  interaction, if any, may be buried in the overall spectroscopic properties and therefore cannot be unambiguously identified [9,11–17]. Consequently, incorporation of a monosilylene group into a polymeric chain as a spacer between well-defined chromophores (**1**,  $n = 1$ ) offers much scope to influence the properties of polymers. First, they interrupt overextended conjugation so that the photophysical properties of polymers can be well adjusted and readily tuned. Secondly, the presence of alkyl substituents on silicon which may increase the chain flexibility, and the resultant higher solubility of the

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polymers in organic solvents is expected to render them more processable. In addition, the size of the alkyl substituent(s) on silicon may tune the relative conformation around the silicon atom so that the folding characteristics of the polymers can be adjusted [16]. Since the silylene moiety has tetrahedral structure, the copolymers are expected to be highly folded. Intrachain interactions between neighboring [12–15] and non-neighboring [11,16] chromophores may result in unusual photophysical behavior. During the past decade, alternating silylene-conjugated chromophore copolymers such as **2** have been shown to exhibit a range of fascinating photophysical properties, such as intrachain chromophore-chromophore aggregation [11], fluorescence resonance energy transfer (FRET) [12] between neighboring chromophores, and electroluminescent [18] as well as photovoltaic [19] applications. This account summarizes recent developments in the chemistry of a range of silicon-containing copolymers. Particular emphasis is focused on synthesis and photophysical studies of silylene-divinylarene copolymers **2** developed recently in the author's laboratory.

## SYNTHESIS

The rhodium-catalyzed hydrosilylation involving bis-silyl hydrides **6** with bisalkynes **8** has been used throughout this study for the synthesis of copolymers **2** having two or more than two different kinds of chromophores **2** in a regioregular manner (Scheme 1) [7b,c,11–17]. The vinylic silyl hydrides **6** are prepared from the nickel-catalyzed olefination [20] of benzylic dithioacetals **3** with  $\text{Me}_2(^i\text{PrO})\text{SiCH}_2\text{MgCl}$  followed by the reduction of the Si–O bonds [7b,c,11–17]. Alternatively, vinylsilanes **6** can be obtained from the hydrosilylation of the corresponding alkynes **5** (or **9**) [21] which are available from the Sonogashira reaction [22] of aryl dihalides **7** with trimethylsilylacetylene followed by desilylation of the trimethylsilyl group [7b,c,11–17]. Displacement of  $\text{R}_2\text{SiHCl}$  with vinylolithium generated in situ from **9** also gives the corresponding silyl hydride **6**.



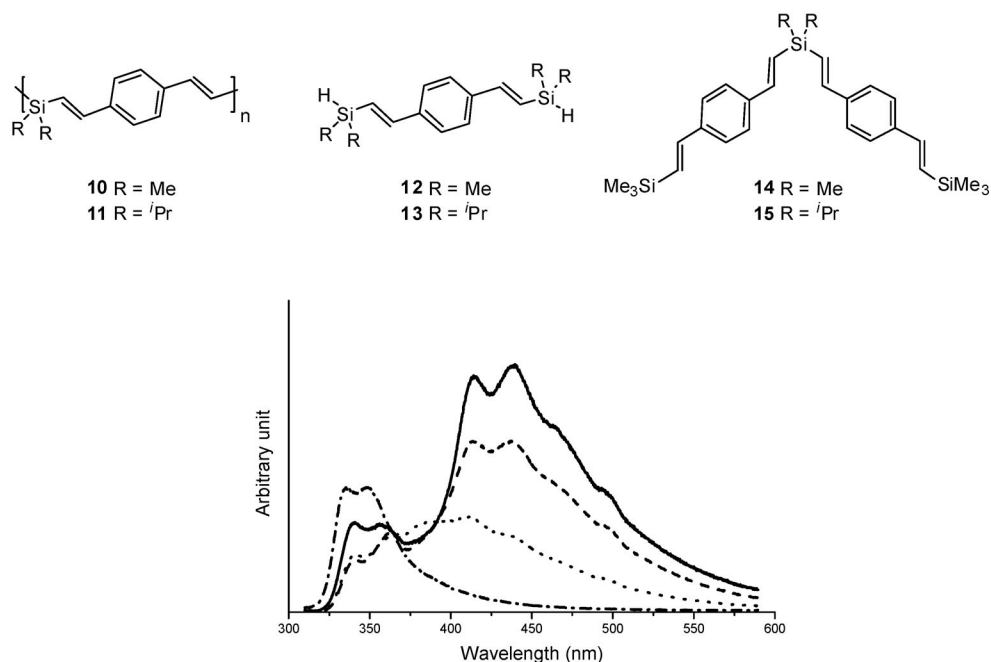
**Scheme 1** (a)  $\text{Me}_2(^i\text{PrO})\text{SiCH}_2\text{MgCl}$ ,  $\text{NiCl}_2(\text{PPh}_3)_2$ ; (b)  $\text{LiAlH}_4$ ; (c)  $\text{ClR}_2\text{SiH}$ ,  $\text{ClRh}(\text{PPh}_3)_3$ ; (d) i.  $\text{Pd}(\text{PPh}_3)_4$ ,  $\text{CuI}$ ,  $\text{TMSC CH}$ , ii.  $\text{KOH}$ ; (e) i.  $^t\text{BuLi}$ ,  $-78^\circ\text{C}$ , ii.  $\text{R}_2\text{SiHCl}$ ; (f)  $\text{ClRh}(\text{PPh}_3)_3$ .

## INFLUENCE OF THE THORPE–INGOLD EFFECT ON CONFORMATION

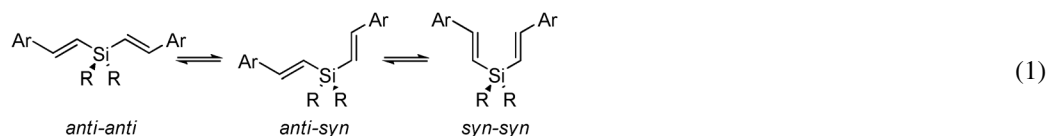
Replacement of two geminal hydrogen atoms on a tether connecting two reacting centers by two alkyl substituents has been shown to lead a change of conformational equilibrium which would bring these two reacting centers in close proximity such that the rate of reaction is enhanced [23]. This geminal disubstitution effect, known as the Thorpe–Ingold effect, has been extensively applied in organic

[23a–c] and organometallic chemistry [23d]. The use of this concept for the conformational investigations of polymers other than peptides [23e] has only sporadically been explored [24].

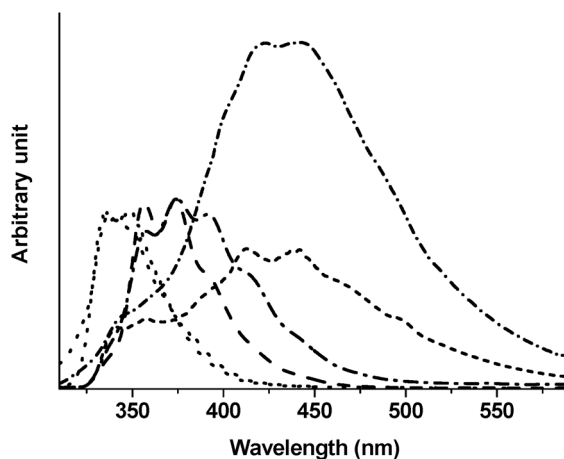
Divinylbenzene-dimethylsilylene copolymers **10** are known to exhibit unusual dual emission, at ca. 340 nm (comparable with that of the monomer **12**) and in the blue light region with vibronic fine structures (Fig. 1) [11a]. The relative intensity of the emission around 430 nm increases with the degree of polymerization of **10**. It is envisaged that the divinylsilane moieties in **10** may display a conformational equilibrium shown in eq. 1. Copolymer **10** would be highly folded and intrachain interactions between chromophores may readily take place at both ground and excited states leading to emission at 430 nm. More intrachain interactions between chromophores may take place as the number of repetitive units in **10** increases because the opportunity for one chromophore unit in **10** located proximal to the other in space would increase with the molecular weight.



**Fig. 1** Molecular-weight-dependent emission spectra (normalized at ca. 360 nm) of **10** (dot,  $M_n = 2200$ , dash,  $M_n = 7500$ , and solid,  $M_n = 10\,700$ ) and **12** (dash-dot).



The folding nature of **10** may depend on the relative contribution of the conformers of the divinylsilane moieties shown in eq. 1. By adopting the idea of the Thorpe–Ingold effect, it is envisaged that an introduction of bulkier substituent(s) R in divinylsilanes may likely favor the *syn-syn* conformation over the others. The folding of silicon-containing copolymers may thus be enhanced when the methyl substituent on the silicon are replaced by a bulkier substituent. In addition, the two styryl moieties shown in eq. 1 would be in closer proximity in the *syn-syn* conformation than the others. It seems likely that the interactions between these geminal distyryl groups would be different among these conformers. As such, the photophysical behavior may also reflect the relative contribution of these con-



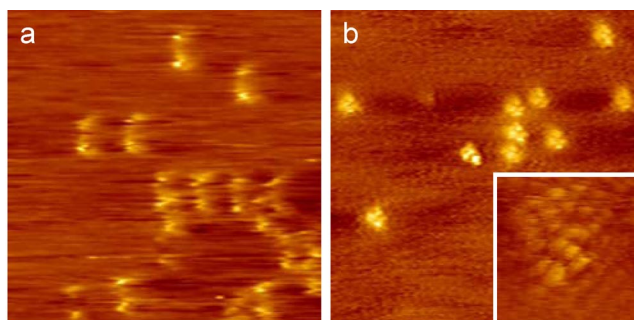
**Fig. 2** Emission spectra **10** (short dash, degree of polymerization = 57), **11** (short dash-dot, degree of polymerization = 54), **12** (solid), **13** (dot), **14** (dash), and **15** (dash-dot).

formers. This viewpoint has been tested by comparing the emission profiles of monomers **12** and **13**, dimers **14** and **15**, as well as polymers **10** and **11** (Fig. 2) [16].

As can be seen from Fig. 2, monomers **12** and **13** exhibit similar emission profiles. It is interesting to note that the emission intensity in the blue light region for **11** is much higher than that of **10**, whereas the degrees of polymerization of **10** and **11** are similar. Apparently, interactions between chromophores would be more prominent in **11** than those in **10**. The contribution of the *syn-syn* conformation for each of the individual divinylsilane modules in **11** would presumably be more prominent than that in **10** because of the Thorpe–Ingold effect, and thereby **11** would be more folded than **10**. Consequently, through-space interactions between the divinylbenzene chromophores in **11** would have better opportunity than those in **10**.

A red shift of the emission maxima for dimers **14** and **15** in comparison with those for monomers **12** and **13** is noteworthy. Interactions between the two geminal divinylbenzene chromophores may be responsible for this photophysical behavior. As shown in Fig. 2, the  $\lambda_{em}$  for **15** appears at even longer wavelength than that of **14**. Presumably, interactions between neighboring chromophores would prevail in **15** over **14**. These results suggest that the bulky isopropyl substituent on silicon might bring the two divinylbenzene chromophores in **15** to closer proximity due to the Thorpe–Ingold effect.

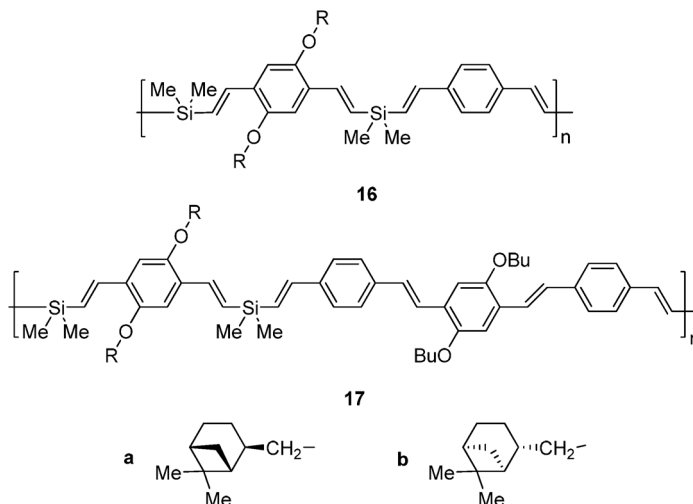
The scanning tunneling microscopy (STM) images of **10** and **11** are shown in Fig. 3 [16]. It is interesting to note that the images of **10** are fuzzier than those of **11**. Presumably, the conformation of **10** would be more fluxional than that of **11**. As shown in the inset of Fig. 3b, the image of **11** shows 17–20 bright spots which may be attributed to the divinylbenzene moieties. These results are consistent with the number average degree of polymerization (= 17) for **11**. The distance between two non-neighboring divinylbenzene chromophores in space in **11** could be as close as 3.5 Å. Strong interactions between these chromophores might be expected. Apparently, the isopropyl substituents on silicon may provide a bulky environment to impose more *syn-syn* conformation for the divinylsilane moieties (eq. 1). A more rigid conformation for **11** might, therefore, be expected, resulting in a highly coiled structure. The STM results appeared to be consistent with the photophysical properties described above.



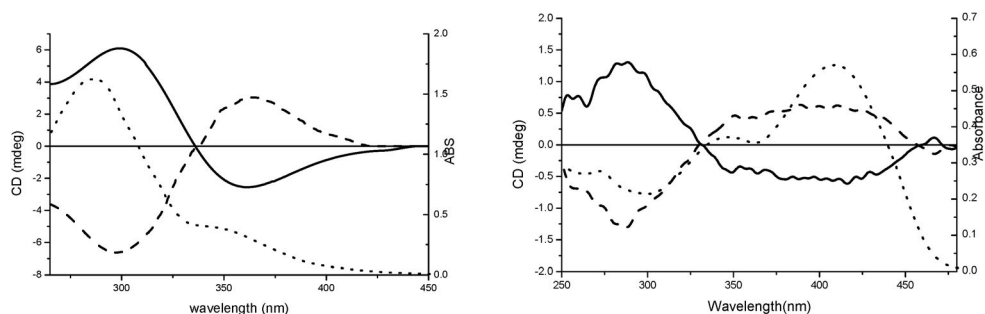
**Fig. 3** STM image of (a) **10** and (b) **11**. Inset, high-resolution image of **11**. Conditions: (a) image size,  $27 \times 27$  nm;  $E_{\text{bias}}$  0.85 V,  $i_{\text{tunnelling}}$  20 pA; (b) image size,  $27 \times 27$  nm;  $E_{\text{bias}}$  0.50 V,  $i_{\text{tunnelling}}$  10 pA; inset: image size,  $3 \times 3$  nm;  $E_{\text{bias}}$  0.50 V,  $i_{\text{tunnelling}}$  33 pA.

### INFLUENCE OF THE THORPE-INGOLD EFFECT ON HELICITY

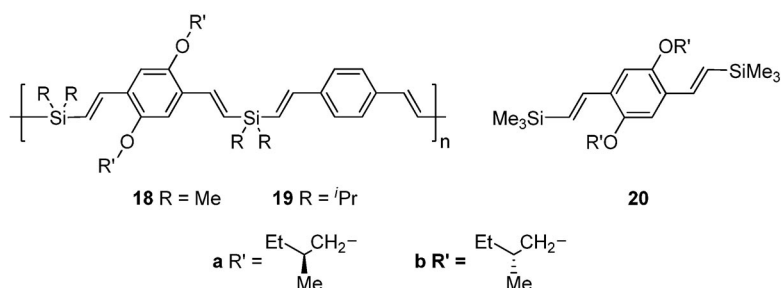
Incorporations of chiral auxiliary have been shown to induce the helical conformation of dimethylsilylene-spaced divinylarene copolymers **16** and **17** (Fig. 4) [14]. However, relatively high concentration (1 g/l) is required for the circular dichroic measurements. Presumably, aggregation of these dimethylsilyl-spaced copolymers may be responsible for the observation of the helical property. It is worth noting that the transfer of chiroptical properties from the dialkoxydivinylbenzene chromophore to terphenylene-tetravinylene chromophore is observed in **17** (Fig. 4b).



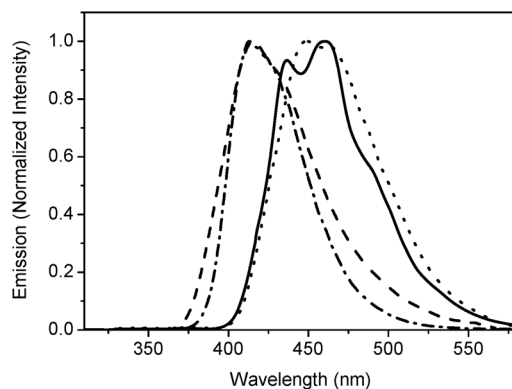
As mentioned in the previous section, replacements of dimethyl substituents by bulky isopropyl groups on silicon would increase the population of the *syn-syn* conformation of the divinylsilane moiety shown in eq. 1, and copolymers with diisopropylsilylene spacers (e.g., **11**) exhibit more coil-like conformation due to the Thorpe-Ingold effect (cf. Fig. 3b). Within this context, it is believed that an incorporation of bulky isopropyl substituent on silicon may also induce helicity of the silylene-spaced copolymers. This viewpoint has been tested by examining the photophysical and circular dichroism (CD) properties of copolymers **18** and **19**, and the corresponding monomers **20** [25].



**Fig. 4** Absorption spectra (dot) and CD curves of (a) **16** and (b) **17** (a, solid; b, dash).



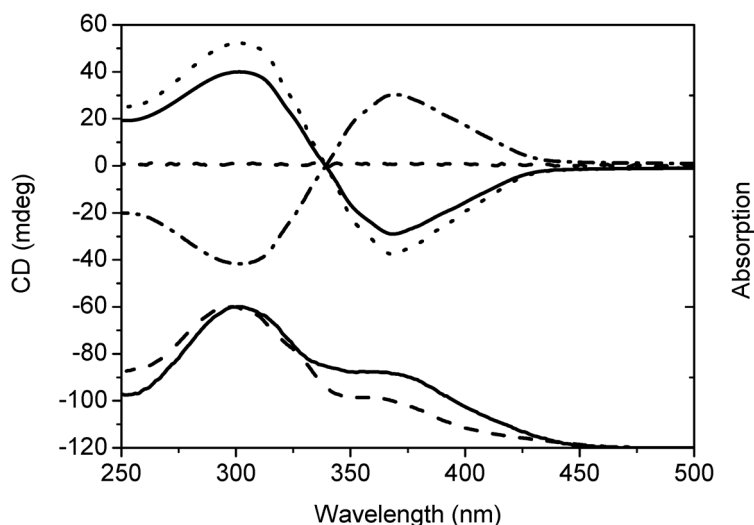
As shown in Fig. 5, the emission maximum of **19b** appears at longer wavelength in comparison with those of **18a** and monomer **20a** in dilute dodecane (10 mg/l). It is note worthy that the  $\lambda_{\text{em}}$  for **18a** is comparable to that of monomer **20a** under these conditions. This discrepancy indicates that there may be strong intrachain chromophore–chromophore interactions in **19**. Intriguingly, the emission spectrum of **18a** also shifts to the longer wavelength at high concentration (1 g/l), presumably, due to intermolecular aggregation.



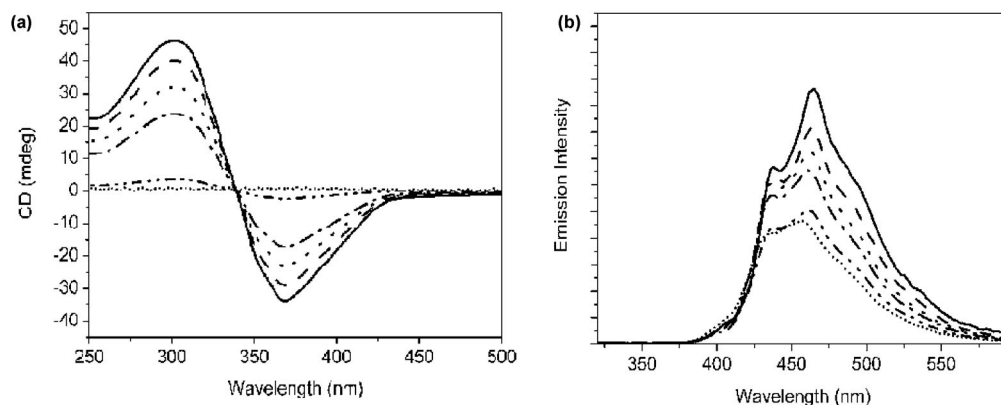
**Fig. 5** The emission spectra of **18a** (10 mg/l, dash; 1 g/l, dot), **19b** (10 mg/l, solid) and **20a** (dash-dot) in dodecane at ambient temperature.

The absorption and CD profiles of **18a** and **19** are shown in Fig. 6. Like **16** and **17**, **18a** is not CD active at low concentration (10 mg/l), but exhibits CD curve at high concentration (1 g/l) due to aggregation. On the other hand, **19a** and **19b** give mirror image CD profiles at low concentration (10 mg/l).

This observation suggests that **19** could be helical without intermolecular aggregation. Temperature-dependent emission spectra and CD curves of **19a** in dodecane are shown in Fig. 7. The CD signals disappear at 100 °C due to conformational changes and gradually appear again at lower temperatures, and completely recovered at 0 °C. These reversible CD profiles were reproducible after several thermal cycles. It is interesting to note that the emission profiles of **19a** are also significantly changed as the temperature increases. The conformational changes may provoke variations in chromophore–chromophore interactions in **19**. These results appear to be consistent with the temperature-dependent CD profiles of **19**.



**Fig. 6** The absorption spectra and CD profiles of polymers **18a** (10 mg/l, dash; 1 g/l, dot), **19a** (10 mg/l, solid line), and **19b** (10 mg/l, dash-dot) in dodecane at ambient temperature.

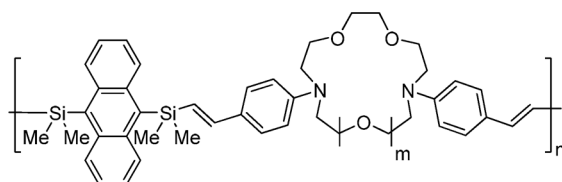


**Fig. 7** Variable temperature (a) CD and (b) emission profiles of **19a** in dodecane (0 °C: solid; 20 °C: dash; 40 °C: dot; 60 °C: dash-dot; 80 °C: dash-dot-dot; 100 °C: short dot).

### PHOTOINDUCED ELECTRON TRANSFER (PET)

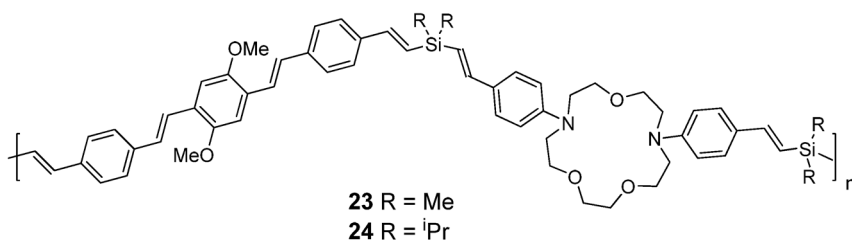
As mentioned in the previous sections, the synthetic protocol of dialkylsilylene-spaced divinylarene copolymers shown in Scheme 1 offers a useful entry for the synthesis of a series of the silylene-spaced

copolymers having alternating donor and acceptor chromophores. These polymers have been used as an ideal architecture for efficient intrachain energy transfer. Indeed, the light-harvesting ability is enhanced when the ratio of donor to acceptor chromophore along the polymeric backbone is increased [12]. The use of the silylene spacer to link donor and acceptor chromophores in diarylsilane for electron transfer has briefly been explored [26]. We have examined the silylene-spaced copolymers with alternating azacrown and anthracene moieties **21** and **22** for photoinduced electron-transfer investigations [15]. These polymers exhibited efficient intrachain PET with charge separation yield about 0.96–0.99. The corresponding charge-transfer rates are around  $10.8\text{--}32.2\text{ ns}^{-1}$  in different solvents. Intrachain interactions between chromophores may readily take place, leading to highly efficient electron-transfer processes. Metal cations have been shown to perturb the fluorescence intensity due to complexation with crown ether moieties in **21** and **22** [15,27].



**21**  $m = 1$   
**22**  $m = 2$

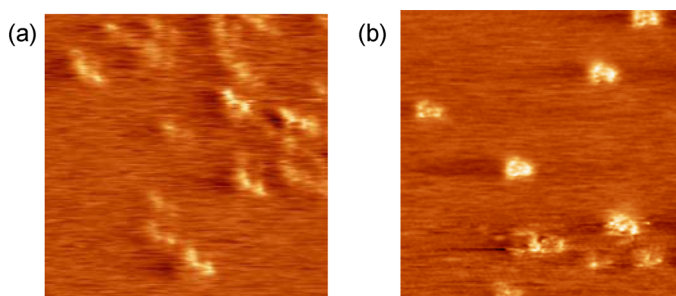
The rates of PET have also been shown to be dependent on the nature of the substituent on silicon. Thus, a replacement of the methyl substituent by the bulky isopropyl group has been shown to enhance the rate of PET (**23** vs. **24**) [15b]. The results are rationalized in terms of the Thorpe–Ingold effect (eq. 1) which would bring the neighboring donor and acceptor chromophores in closer proximity.



**23**  $R = \text{Me}$   
**24**  $R = \text{iPr}$

Similar to that described earlier (Fig. 3), **23** exhibits a relatively loose and elongated feature with a length roughly about 4.3 nm in the STM images (Fig. 8). On the other hand, the morphology of **24** appears to be very different and the average diameter of **24** is 3.4 nm. In other words, the images of **23** are fuzzier than those of **24**, presumably due to the more fluxional conformation of **23** than that of **24**. Apparently, the isopropyl group may provide a bulky environment to render the divinylsilane moieties in **24** to adopt the *syn-syn* conformation (eq. 1). As a result, the conformation for **24** would be expected to be in highly coiled structure. Such kind of coiled structure may lead to strong interactions between chromophores in **24** and is consistent with the photophysical results described above [15b].

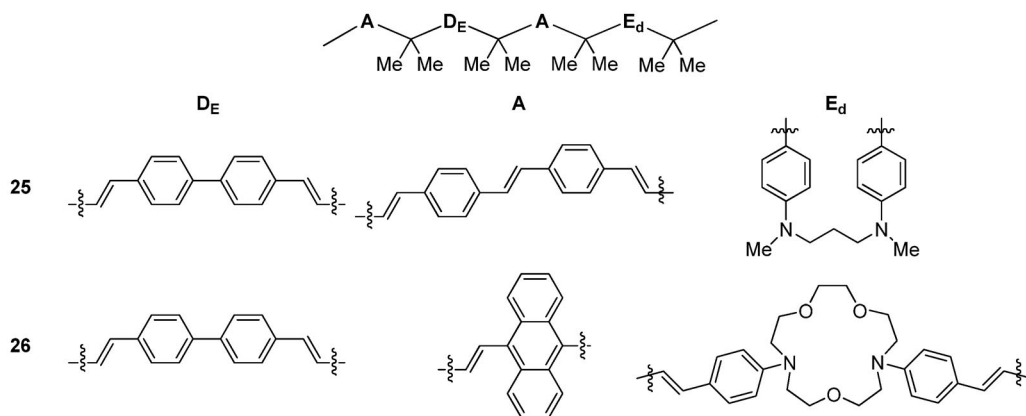




**Fig. 8** STM image of (a) **23** and (b) **24**. Conditions: (a) image size,  $27 \times 27$  nm;  $E_{\text{bias}}$  0.80 V,  $i_{\text{tunnelling}}$  20 pA; (b) image size,  $27 \times 27$  nm;  $E_{\text{bias}}$  0.50 V,  $i_{\text{tunnelling}}$  20 pA.

### COUPLING OF FRET AND PET IN REGIOREGULAR SILYLENE-SPACED COPOLYMERS

As described in the previous sections, efficient intra-chain FRET and PET can readily proceed in these silylene-spaced divinylarene copolymers. The advantage of using silylene-spaced divinylarene copolymers relies on the easy accessibility by regioselective hydrosilylation of a bisalkyne with a bis-silyl hydride (Scheme 1). Accordingly, regioselective ensemble of three-component systems having a chromophore as an antenna for absorbing light ( $D_E$ ), a FRET acceptor (A) and an electron donor for electron transfer ( $E_d$ ) gives the corresponding copolymers **25** and **26** as an integrated polymeric archetype for the light harvesting and electron transfer.



Since the distance between two neighboring chromophores separated by a silylene moiety in these copolymers would be relatively short, the chromophores in these polymers can exhibit light harvesting to collect light energy, energy transfer as well as efficient charge separation. The overall efficiencies involving both FRET and PET in these silylene-spaced vinylarene copolymers can be up to 96 % [28].

### CONCLUSIONS

Our earlier works on the nickel-catalyzed silylolefination from the corresponding benzylic dithioacetals [20] have provided a convenient entry to bis-vinylsilane monomers which can react with bis-alkynes in the presence of a rhodium catalyst to furnish a wide variety of regioregular and alternating silylene-spaced copolymers with different combinations of donor and acceptor chromophores. The silicon moieties have been shown to serve as insulating tetrahedral spacers in these copolymers. The substituents

on silicon can readily be tuned, and the steric environment of these substituents around the silicon atom may dictate the conformation (or helicity) of the copolymers (the Thorpe–Ingold effect) and hence the photophysical properties of these copolymers. The photophysical studies have provided useful insights into how chromophores in polymers interact intramolecularly. In addition, because different chromophores can regioregularly be introduced into the polymeric chain, these copolymers have extensively been used as models for studying FRET, PET, as well as chiroptical transfer.

## ACKNOWLEDGMENTS

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