Alternating divinylarene–silylene copolymers

Tien-Yau Luh* and Yen-Ju Cheng

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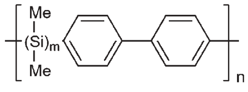
A summary of recent advances on the chemistry and photophysics of silylene-spaced divinylarene copolymers is presented. The silicon moieties have been shown to serve as an insulating spacer in these copolymers. The photophysical studies have provided useful insights into how chromophores in polymers interact intramolecularly. Because different chromophores can be regioregularly introduced into the polymeric chain, these copolymers have been extensively used as models for studying energy transfer, light harvesting as well as chiroptical transfer.

Introduction

Since the discovery of σ conjugation and conductivity in polysilanes,[1] numerous investigations have been directed towards linear polymers containing alternating arrangements of silylene and π-conjugated moieties.[2] These polymers have been shown to have potential as ceramic precursors,[3] heat-resistant materials,[4] conducting materials,[5] electroluminescent materials,[6] and models for light-harvesting investigations.[7] Delocalisation between Si-containing σ-bonds and conjugated systems may dictate the electrical and optical properties associated with these materials.[8–13] The nature of the σ–π conjugation has been extensively studied. Interaction of the high-lying Si–Si σ-bonding orbital with the π*-orbital of the conjugated chromophore may readily occur. Indeed, oligomers **1** with $m \geqslant 2$ exhibit a broad emission in the longer wavelengths and the vibronic structures gradually diminish as the silylene chain length increases. This observation is rationalized by an intramolecular charge transfer between the Si–Si bond and the π-conjugated block.[8,9]



m = 1-6

1

The photophysical properties of alternating monosilylene–chromophore copolymers or oligomeric analogues appear to be structure dependent. For example, oligomer **1** with $m = 1$ shows a vibronically structured emission attributed to the π–π* locally excited state from biphenylene unit.[8] In other words, the σ–π conjugation would be negligible in **1** when $m = 1$. Presumably, the energy difference between the Si–C bonding orbital and π*-orbital of the conjugated chromophore may be relatively large and, therefore, such interaction may be too weak to detect. Although there are reports on possible intramolecular charge transfer from conjugated chromophores to monosilylene species,[11,12] the details will be compared later in this feature article. It is noteworthy that, when the conjugation length is increased, σ–π interaction between the silylene group and the π-chromophore may become less important.[13] The monosilylene moiety can thus be considered

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Department of Chemistry, National Taiwan University, Taipei, Taiwan, 106

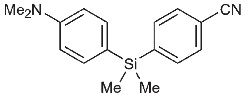
Tien-Yau Luh

Tien-Yau Luh obtained his PhD degree from the University of Chicago (with L. M. Stock) in 1974. After spending two years of postdoctoral research at the University of Minnesota (with P. G. Gassman), he began his independent research at the Chinese University of Hong Kong in 1976. He moved back in 1988 to his alma mater, National Taiwan University where he is currently University Chair Professor. He has published over 210 papers and has received numerous awards in Taiwan. His current research interests include OMCOS, polymers and materials chemistry.

Yen-Ju Cheng

Yen-Ju Cheng received his PhD degree in Organic Chemistry from the National Taiwan University in 2004 under supervision of Professor Tien-Yau Luh. After spending another year as a postdoc with Prof. Luh at NTU, he joined Prof. Alex K.-Y. Jen's group as a postdoctoral researcher at the University of Washington in 2005. During his tenure at the NTU, he has extensively engaged in the synthesis and photophysics of silylene-spaced copolymers. His current research interest is focused on the design, synthesis and characterization of organic functional materials for optoelectronic applications.

to serve as an insulating tetrahedral spacer.[10] Introduction of a monosilylene group into a polymeric chain as a spacer between well-defined chromophores has provided several interesting features on the properties of polymers. First, they can prevent over-extended conjugation so that the emission wavelength can be well-adjusted and the photophysical properties of polymers can be readily tuned.[6,10] Secondly, because of the presence of alkyl substituents on silicon which may increase the chain flexibility, the polymers may be more soluble in organic solvents and therefore more processable. Since the silylene moiety has tetrahedral structure, the silylene–chromophore copolymer may be highly folded. Intrachain through-space interactions between chromophores may result in unusual photophysical behavior. The distance between two neighboring chromophores separated by a silylene moiety (*e.g.* **2**) would be relatively short so that the photo-induced electron transfer between these chromophores can readily take place.[14] Such interactions may also be found in silylene–chromophore copolymers. This feature article summarizes recent development on chemistry of a range of silicon-containing copolymers. Particular emphasis is focused on the synthesis and photophysical studies of silylene–divinylarene copolymers **3** developed recently in the author's laboratory.



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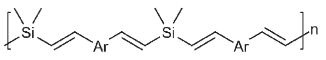

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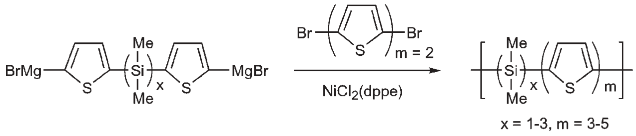
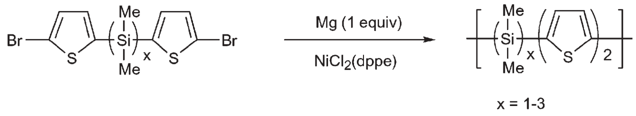
Synthesis

Silylene–chromophore copolymers are commonly prepared by two different approaches. The first method involves the condensation–polymerisation of substrates which already contain the silylene linker. The key step in these protocols involves carbon–carbon bond formation leading to conjugated systems. Thus, nickel-catalysed Kumada–Corriu cross-coupling reactions of Grignard reagents having a silylene linker with dibromoarenes furnish the corresponding polymers (eqn (1) and (2)).[10l]



(1)



(2)

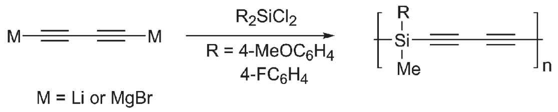
A Heck reaction provides an alternative route for the synthesis of silicon-based alternating copolymers (eqn (3)).[6d]

A Wittig reaction between the appropriate silicon-containing diphosphonium salts and a dialdehyde monomer also furnishes a useful route towards silylene–chromophore copolymers (eqn (4)).[6c]

Zirconocene-mediated coupling of silylene-linked alkynes followed by protonolysis yielded the corresponding silylene-spaced copolymers.[10m] The reaction occurs *via* a zircocyclopentadiene copolymer and the carbon–zirconium bond is decomposed by protonolysis.

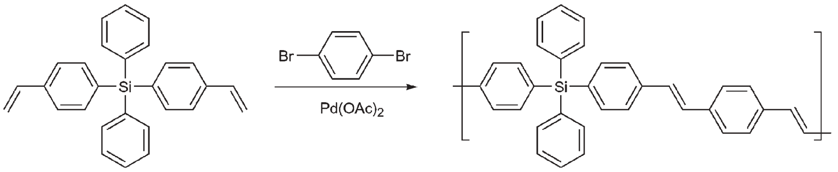
In general, these procedures can produce polymers having one type of chromophore separated by a silylene moiety.

The second protocol involves direct formation of silicon–carbon bonds during the course of polymerisation. Thus, nucleophilic displacement of dihalosilanes provides a convenient route for the synthesis of homo-copolymers (eqn (6)).[10b] A range of alkyne–silylene copolymers has been prepared by this procedure.



(6)

Pt-catalysed hydrosilylation of alkynylsilanes has been used to synthesize poly(vinylsilanes) (eqn (7)).[10a] An extension to this reaction involving bis-silyl hydrides with bisalkynes affords the corresponding sillylene–space copolymers



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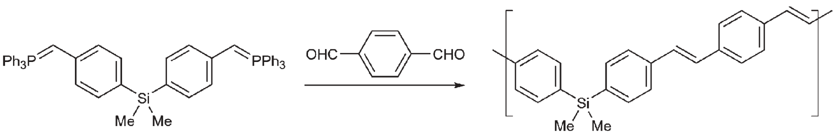

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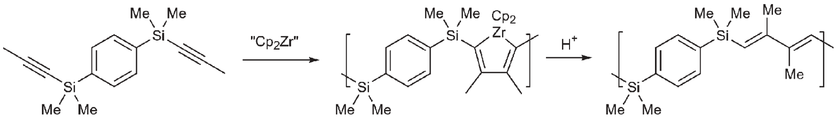

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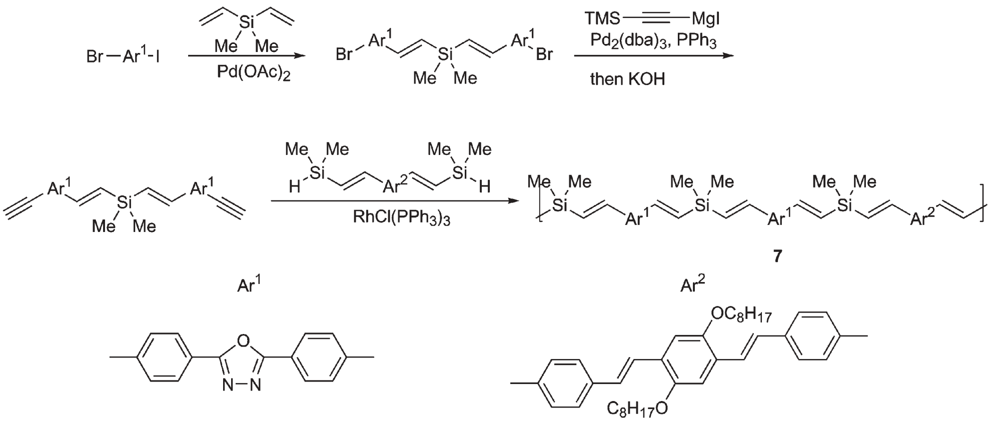
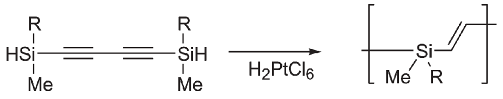


Scheme 1

(eqn (8)).[10h] Silyl hydride starting materials can readily be available by nucleophilic displacement reaction.



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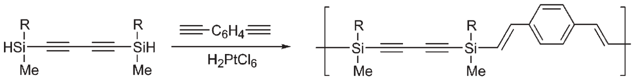
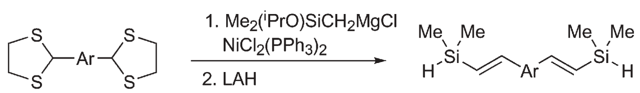


(8)

The hydrosilylation protocol turns out to be very useful for the synthesis of copolymers having more than two different types of chromophores in a regioregular manner. The vinylic silyl hydrides are accessible from the reaction sequences shown in eqn (9).[15] Nickel-catalyzed olefination[16] of benzylic dithioacetals with $Me_2(^iPrO)SiCH_2MgCl$ afforded the corresponding vinylsilanes.[15,17–21] The silylhydrides are obtained from the reduction of the Si–O bonds.[16–21] Vinylsilanes can also be accessible from the hydrosilylation of the corresponding alkynes[22] which are available from the Sonogashira reaction[23] of aryl dihalides with trimethylsilylacetylene followed by desilylation of the trimethylsilyl group (eqn (10)).



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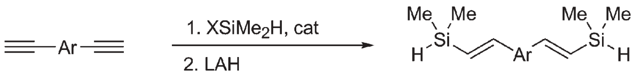

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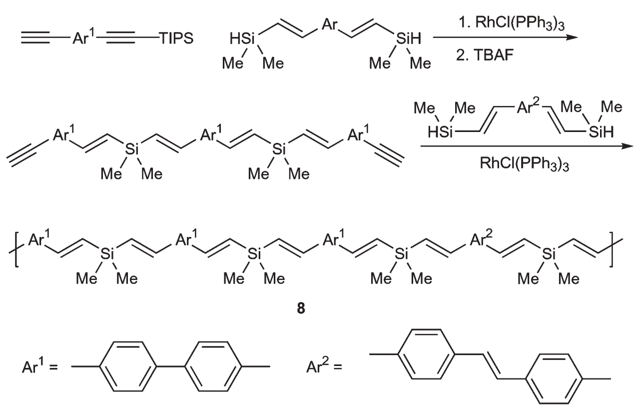
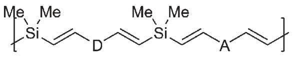


Scheme 2

By adopting a strategy similar to that shown in eqn (8), different ratios of donor-to-acceptor chromophores (**4–6**) can be regioselectively incorporated along the polymer chain.[17–21] Representative syntheses are shown in Schemes 1 and 2. The donor and acceptor chromophores are chosen on the basis of their absorption and emission profiles. Chiral auxiliaries can also be incorporated.[21]

Role of monosilylene moiety on photophysical properties of monosilylene–chromophore copolymers

The photophysics of alternating silylene–chromophore copolymers is rich. The interaction between the silylene group and the conjugated π-chromophore, if any, would be very weak.[11–13] For example, the very weak absorption at 310 nm for thiophene–dimethylsilylene co-oligomers **9** may arise from the transition involving charge transfer from the thiophene moiety to the dimethylsilylene group.[11] In addition, the weak



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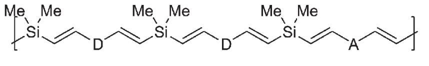

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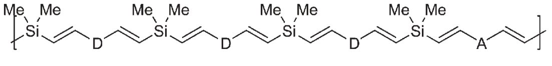

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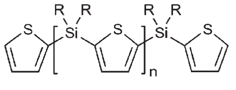
absorption around 345 nm and structureless emission in a series of diphenylacetylene–dialkylsilylene copolymers **10** may be attributed to possible intramolecular charge transfer.[12] As mentioned earlier, when the conjugation length is increased, the σ–π interaction between the silylene group and the oligothiophene moiety may become less important.[13] In particular, when other photophysical processes prevail, the characteristics of such weak interaction, if any, may be buried in the overall spectroscopic properties and therefore cannot be unambiguously identified.[10,15,17–21,24] In the following sections, the photophysical properties of a range of monosilylene–chromophore copolymers are discussed in detail. In general, the σ–π interaction, if any, may be too weak to be characterized in these polymers. Accordingly, the monosilylene moiety may be considered essentially as an insulating spacer.



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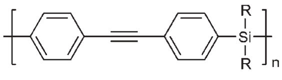

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Mononuclear divinylarene-dimethylsilylene copolymers

Three different types of mononuclear divinylbenzene–silylene copolymers **11–13** are compared.[15] Polymer **11** has a *p*-divinylbenzene chromophore, and polymer **12** contains a *m*-divinylbenzene moiety, whereas polymer **13** consists of alternating *p*- and *m*-divinylbenzene groups separated by the monosilylene moiety. Besides the strong absorptions due to localized transitions of the divinylbenzene moiety, there appeared a tailing weak absorption in the region of 340–400 nm. Fig. 1 shows the absorption spectra of **11** and the corresponding monomer **17**. Polymer **11** exhibited dual fluorescence spectra (Fig. 2). The higher energy emission at *ca*. 340 and 360 nm for **11** is compatible with those for **17**. The relative intensity of the emission in the blue light region increases with the degree of polymerisation of **11** and vibronic fine structures were observed in this region. The emission profiles remained unchanged with concentration (up to 100-fold) and with solvents (<8 nm, in methylcyclohexane, benzene or $CHCl_3$). Consequently, the interaction between chromophores, if any, should occur intramolecularly at these concentrations. When both methyl substituents at silicon atom in polymer **11** are changed to the more bulky phenyl group, the photophysical properties remain similar.

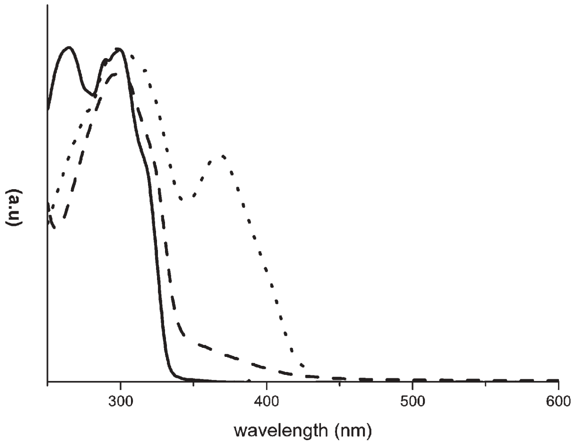
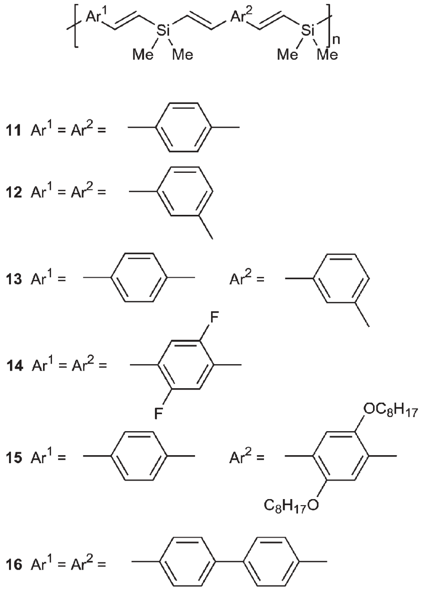
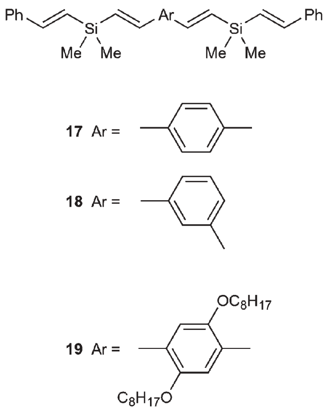


Fig. 1 Absorption spectra for **11** (M_n = 10 700, dashed line), **17** (solid line) and excitation spectrum for **11** (dotted line) in $CHCl_3$ monitored at 414 nm.

The excitation spectrum for **11** monitored at 414 nm is also compared in Fig. 1 and the intensity at 375 nm was substantially enhanced in comparison with that in the absorption spectrum. This observation indicates that significant intrachain interactions between chromophores in **11** both at the ground and at the excited states might occur and such interaction seems to be more important as the number of repetitive units in **11** increases. In other words, the opportunity for one chromophore unit in **11** located proximal to the other in space would increase with the molecular weight. MM2 force field calculations suggested that **11** with a chain length greater





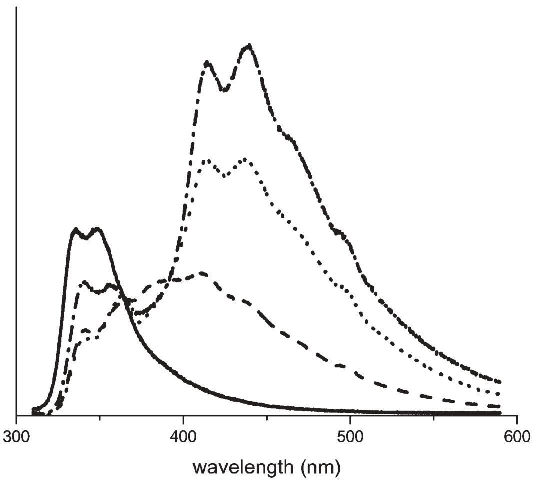


Fig. 2 The emission spectra of polymer **11** with different molecular weight (M_n = 2200; dashed line, M_n = 7500; dotted line, M_n = 10 700; dashed dotted line) and its corresponding monomer **17** (solid line).

than eight repetitive units can form a loop. The two chromophores at both ends are in close proximity and the distance between two proximal chromophores would be less than 3.5 Å.

Similar photophysical behaviors were observed for polymers **12** and **13**. A comparison of the emission profiles of **11–13** is shown in Fig. 3. Like the photoluminescence spectra for **11**, the emissions at 393 nm for **12** and at 393 and 414 nm and beyond for **17** may be attributed to the intrachain interactions between chromophores. Time-resolved fluorescence spectra of **11** (M_n = 10 700) and **17** in $CHCl_3$ were monitored at 341 and 414 nm. The fluorescence of **11** at 414 nm showed a slow decay with τ = 1.1 ns. On the other hand, both **11** and **17** exhibited a fast fluorescent decay (τ = 0.1 ns) at 341 nm. It is important to note that, when the fluorescence spectrum of **11** was monitored at 1 ns delay time after laser excitation, only low energy emission was observed. These data suggested that the emission of **11** at these two wavelengths might arise from different species. The *m*-divinylbenzene chromophore has a shorter conjugation length, therefore, both the absorption maximum and the emission wavelength for monomers **18** and polymer **12** appeared expectedly at shorter wavelength. The longer wavelength emission for **12** occurred at 393 nm with the fluorescence lifetime τ = 0.9 ns. It is noteworthy that the fluorescence lifetime at 414 nm for **13** (τ = 1.1 ns) is comparable with that for **11** at the same wavelength (τ = 1.1 ns). However, there is an additional emission at 393 nm for **13** and the lifetime 0.8 ns is similar to that for the all-*meta* isomer **12** (τ = 0.9 ns). The difference in lifetimes for the emission at 414 and 393 nm for **13** indicates that they arise from different species. As mentioned earlier, the emission in this region is ascribed to the strong intrachain interaction between two chromophores at both ground and excited states. The similarities in lifetimes for **13** to those for **11** and **12** at respective wavelengths suggest that the interaction pattern might be alike. Presumably, chromophores in **12** having comparable energy would interact preferentially.

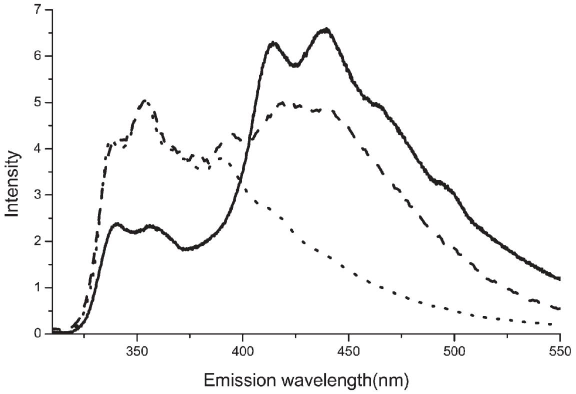
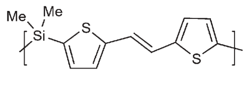


Fig. 3 A comparison of the emission spectra of polymers **11** (solid line), **12** (dotted line) and **13** (dashed line).

The presence of a fluoro substituent in polymer **14** does not cause significant steric hindrance.[25] Despite the electron-withdrawing character for the fluorine substituent, polymer **14** is observed to fold in a manner similar to that of **11** leading to similar spectroscopic characteristics.[16b] The introduction of a bulky substituent may, however, alter the situation.[16b] Therefore, the emission profiles for the polymer **15** are similar to that for the corresponding monomer **19**, no excimer-like emission being observed in the fluorescence spectrum. Presumably, the bulky alkoxy substituent prohibits the interaction between chromophores due to the steric hindrance. The biphenyl moiety has a longer persistent conjugation length and is non-planar. The relative intensity for the longer wavelength emission in **16** is only slightly affected by increasing the degree of polymerization. Vibronic fine splittings are found in these fluorescence spectra and the ground-state interaction between the divinylbiphenylene chromophores might still exist. As described in the next section, the through-space chromophore–chromophore interactions appear to be dependent on the conjugation length. It is therefore not surprising that the relative intensity at the longer wavelengths is not as prominent as those with mononuclear chromophores discussed above.

Similar π–π interactions between chromophores have been observed in the emission spectra of **20**[10g] and **21**.[24]



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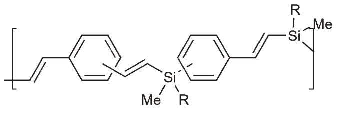

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Higher homologues of divinyloligoarylene–silylene copolymers

As described in the previous section, chromophores in silylene-spaced copolymers may interact with each other through space leading to extraordinary photophysical properties. Such interaction appears to be less prominent when the chromophore is changed from divinylbenzene to divinylbiphenyl. Theoretical and experimental studies on inter- or intra-chain interactions between chromophores suggest that the extent of such through-space interactions in the excited state to be dependent on the conjugation length of the chromophores.[26,27] As the conjugation length increases, the interactions between chromophores may be significantly reduced because the

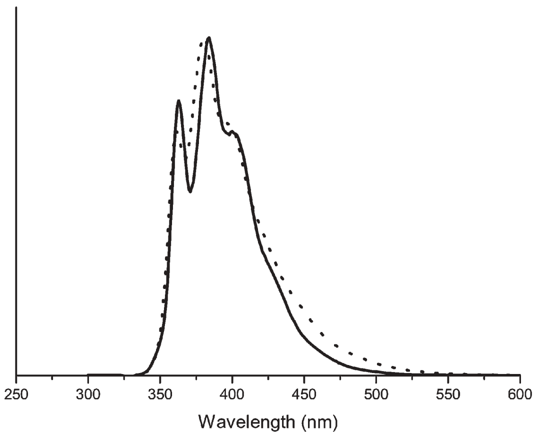
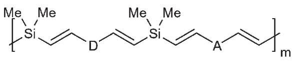


Fig. 4 Emission spectra (λ_{ex} = 325 nm) of **25** (solid line), **29** (dotted line) in $CHCl_3$.

geometry relaxation in the excited state of longer conjugated moieties may stabilize the localization of exciton in a single chromophore. Accordingly, polymers having chromophores such as teraryl (*e.g.* **22** and **23**) or ter(phenylene–vinylene) chromophores (*e.g.* **24**) or other oligoaryls (*e.g.* **25**) exhibit almost identical emission profiles as those of the corresponding monomers **26–29**, respectively.[17] Representative examples (**25** and **29**) are shown in Fig. 4. In these regards, the monosilylene group serves simply as an insulating spacer.

Efficient intrachain energy transfer (FRET) and light-harvesting properties in regioregular alternating [(donor–SiMe$_2$)$_n$–(acceptor)–SiMe$_2$]$_m$ copolymers

As shown in the previous section, the silylene moiety in these silylene-spaced copolymers is considered as an insulating spacer.[10] It is known that the intramolecular photoinduced charge transfer between donor and acceptor chromophores, separated by a silylene moiety, can readily occur (*e.g.* **2**).[14] Accordingly, intramolecular efficient fluorescence resonance energy transfer (FRET) might also be expected in these silylene-spaced copolymers. The donor and acceptor chromophores are chosen on the basis of their absorption and emission profiles.[18–20] Hence, the divinyldiphenyloxadiazole chromophore was paired with the dimethoxyterphenylene–tetravinylene chromophore. Similarly, the divinylbiphenyl chromophore was used with a diphenylene–tervinylene chromophore.



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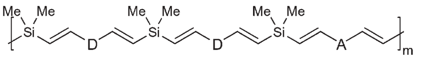

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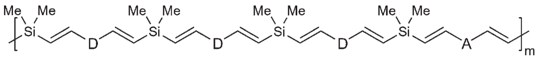

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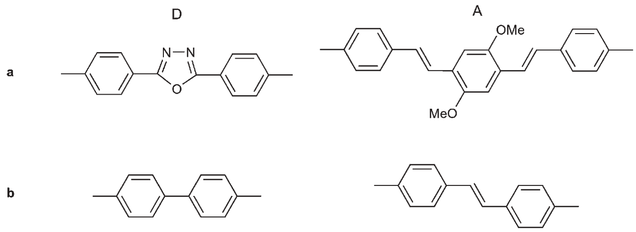
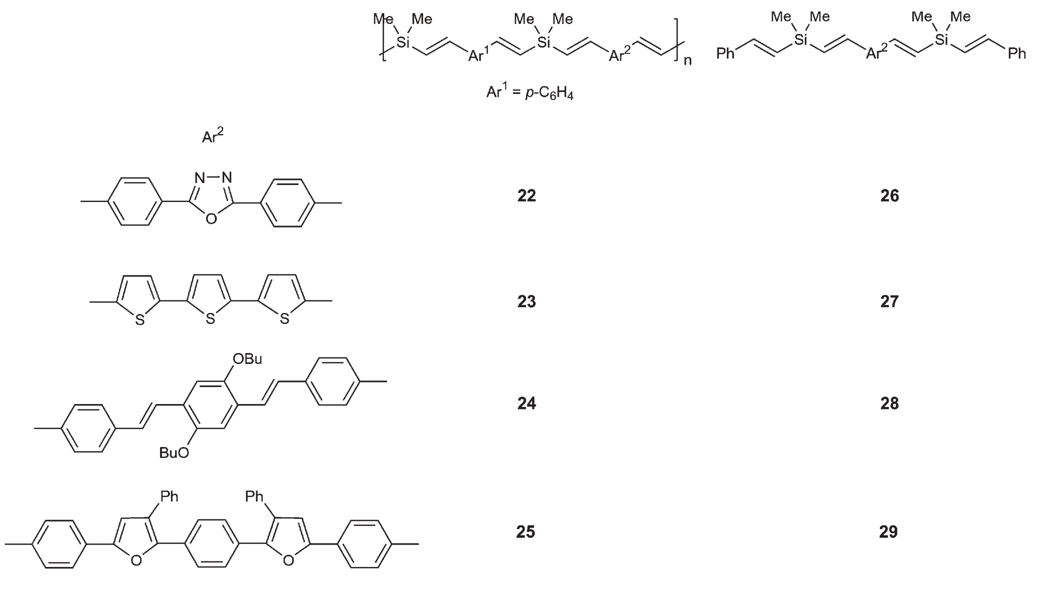


The fluorescence spectrum for polymer **30a** is shown in Fig. 5. When the solution was excited at 310 nm, the emission from donor in **30a** has been completely quenched, only fluorescence at 467 and 490 nm due to the acceptor being observed. The efficiency of such intrachain energy transfer was estimated to be 87%. As the molar fraction of the donor in polymers increases from 50% in **30a** to 67% in **31a**, the absorbance around 300–350 nm corresponding to the donor chromophore is also doubled; and excitation of donor chromophores at 310 nm in polymer **30a** and **31a** resulted in fluorescence exclusively from the acceptor. It is noteworthy that the emission intensity of **31a** is approximately doubled in comparison with that of **30a** when the intensity of acceptor



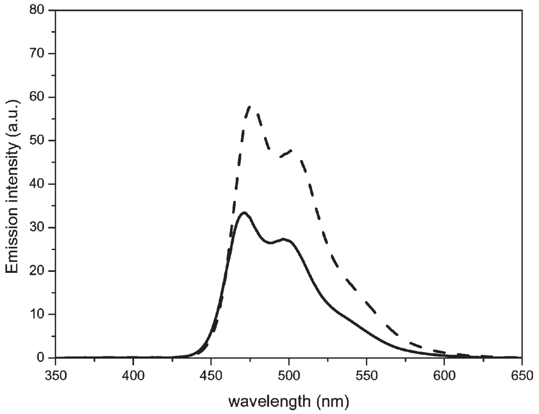


Fig. 5 Emission spectra (λ_{ex} = 310 nm) of **30a** (solid line) and **31a** (dashed line) in chloroform.

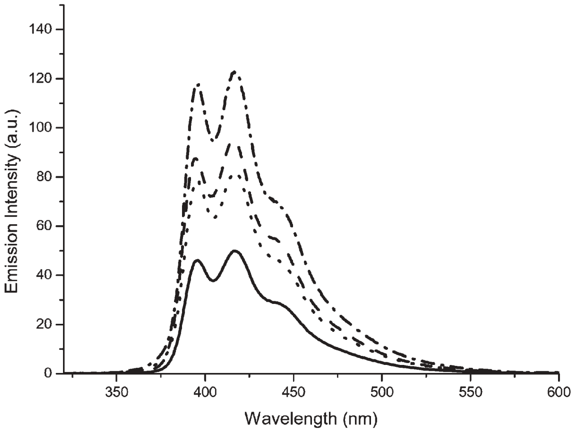


Fig. 6 Emission spectra of **30b** (solid line), **31b** (dashed line) and **32b** (dash-dotted line) in chloroform (λ_{ex} = 300 nm) and **32b** (direct excitation at 360 nm of acceptor, dotted line).

absorption was kept the same in both polymers. These results indicated that the light harvesting capability is significantly enhanced in **31a**. Again, a comparison of the excitation spectrum with absorption spectrum for **31a** suggested that the energy transfer efficiency is 86%.[19]

In a similar manner, the photophysical properties of **30b**, **31b** and **32b** were also examined. The increases of the intensities due to absorption of the divinylbiphenyl moiety in **31b** and **32b** were obvious due to the higher molar fraction of this donor chromophore. The emission spectra of these polymers upon excitation at 300 nm are shown in Fig. 6.[19]

As expected, polymer **32b** exhibits the highest emission intensity in comparison with those of **30b** and **31b**. In a similar manner, the intensity of the emission for **31b** is doubled by comparing with that of **30b**. However, the intensity of emission from **32b** (molar fraction = 0.75) was somewhat less than tripled in comparison with that of emission from **30b**. Although increasing the number of donor moieties allows more light-harvesting from donor to acceptor, the distance between donor and acceptor in **32b** would, however, not be the same. In other words, the distance between the donor chromophore at the center and the acceptor chromophore in **32b** would be different from the distance between the other donor and the acceptor chromophores in this copolymer. Accordingly, the efficiencies for the energy transfer from the donor chromophores in **32b** may not be identical.[19]

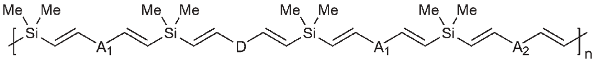
Upon excitation at 360 nm, the λ_{max} of the acceptor chromophore in **32b**, the emission profile is also shown in Fig. 6 (dotted line). It is interesting to note that the intensity of this spectrum is much lower than that of **32b** when the excitation wavelength was 300 nm, the λ_{max} of the donor chromophore in **32b**. These results reveal that the acceptor can emit stronger emission through fluorescence resonance energy transfer mechanism from donors than when it is directly excited at the acceptor. The ability of light-harvesting effect along with subsequent energy transfer is very efficient (>88%).[19]

Sequential energy transfer in a three-chromophore gradient system

Introduction of an energy gradient with three well-designed chromophores into a silylene-spaced polymeric chain may lead to sequential energy transfer. Thus, silylene-spaced regioregular polymers **33** composed of a well-designed energy gradient of three-chromophore systems was synthesized.[20] For example, efficient intrachain energy transfer from divinylbiphenyl *via* divinyldiphenyloxadiazole to terphenylene–tetravinylene chromophores was observed (Fig. 7).

Chiroptical properties transfer in chiral silylene-spaced divinylarene copolymers

It is known that the chirospectroscopic property is transferred from the chiral auxiliary to the polymeric backbone as witnessed by its circular dichroic (CD) properties.[28,29] Thus, in the presence of chiral substituents, conjugated polymers may adopt helical conformation and show characteristic



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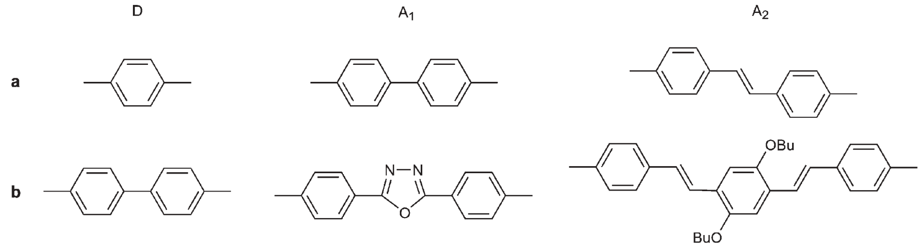


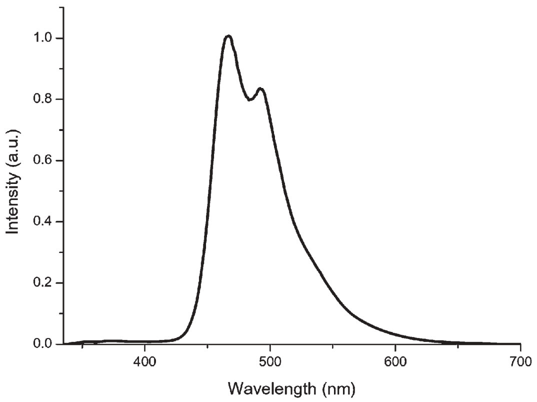


Fig. 7 Fluorescence spectrum (λ_{ex} = 300 nm) of **33b** in chloroform.

induced CD curves.[29] For random coil polymers, the CD curves appeared to be relatively weak because of the cancellation of the transition dipole moments.[30] However, aggregation may play a pivotal role to enhance the CD properties.[29]

Introduction of a chiral auxilliary into silylene-spaced conjugated copolymers has shown intrachain transfer of chiroptical properties to the conjugated chromophores.[21] The CD curves shown in Fig. 8 suggested that the chiroptical properties have been transferred from the chiral auxiliary to the aromatic chromophore in copolymers **34** and **35**. It is noteworthy that the concentrations of copolymers **34** and **35** for the CD measurements were relatively high. At low concentration, the CD intensity was too weak to observe. Aggregation of copolymers **34** and **35** may occur as evidenced by shifts of emission maxima to longer wavelengths. It is of note that no CD curves were observed for the corresponding monomer **36**.

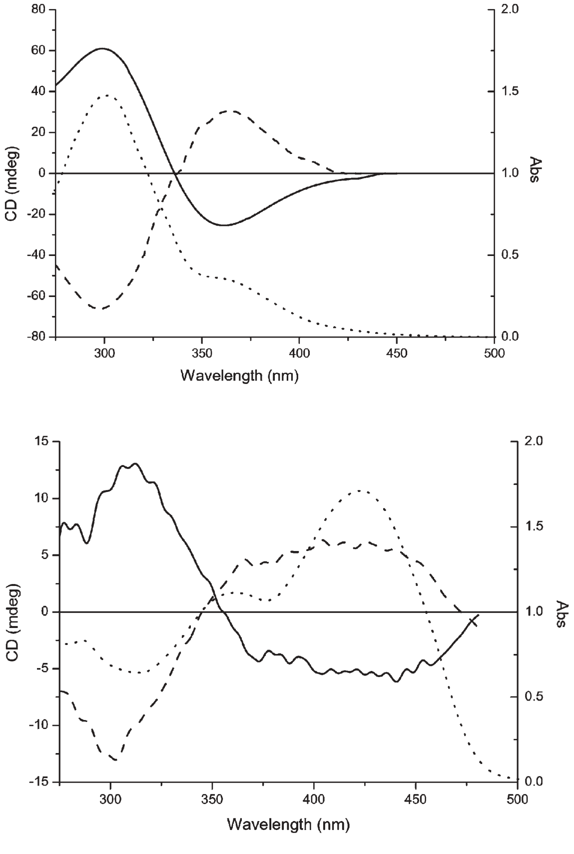
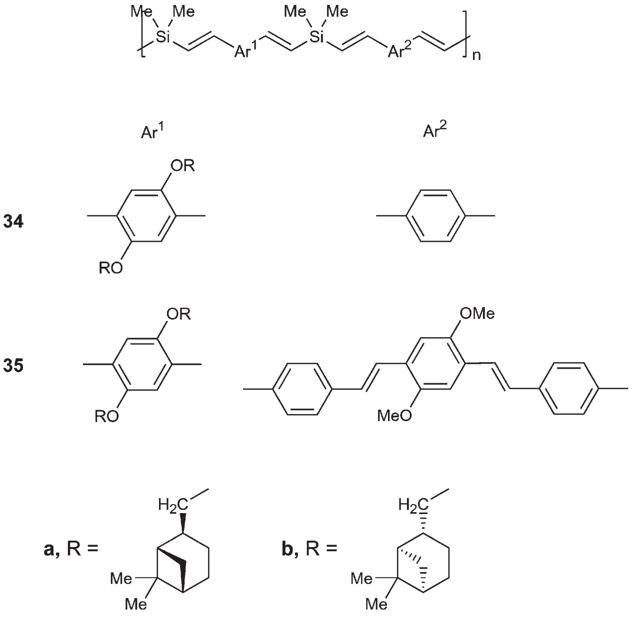


Fig. 8 CD curves of (a) **34a** (solid line), **34b** (dashed line) and UV spectrum of **34a** (dotted line) and (b) **34a** (solid line), **34b** (dashed line) and UV spectrum of **34a** (dotted line) in $CHCl_3$.



Conclusions

Our earlier work on nickel-catalysed silylolefination from the corresponding benzylic dithioacetals 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 ratio of donor to acceptor chromophore and the combination of three or more chromophores in a polymeric chain can be controlled by suitable design of bis-alkynes monomers. Our strategy has provided a powerful arsenal for the construction of copolymers with precise regiochemistry and repetitive units. The silicon moieties have been shown to serve as insulating spacers in these copolymers. The photophysical studies may provide useful insights into how chromophores in polymers interact intramolecularly. In addition, because different chromophores can be regioregularly introduced into the polymeric chain, these copolymers have been extensively used as models for studying energy transfer, light harvesting, as well as chiroptical transfer. Extension to other related systems has been shown feasible.[31] New applications such as photoinduced electron transfer,[32] electroluminescence,[33] or photovoltaic emanating from the present research abound.

Acknowledgements

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