Thorpe–Ingold effect on the conformation and photophysical properties of dialkylsilylene-spaced divinylarene copolymers†

Mei-Yu Yeh,[a] Hsin-Chieh Lin,[a] Shern-Long Lee,[a] Chun-hsien Chen,‡[a] Tsong-Shin Lim,[b] Wunshain Fann[b] and Tien-Yau Luh*[a]

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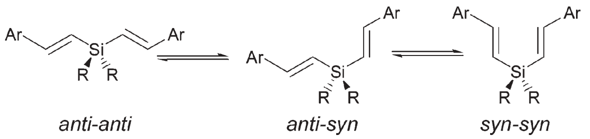
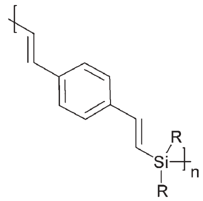
Geminal disubstitution on silicon in dialkylsilylene-spaced divinylarene copolymers may dictate the conformation and photophysical properties of the copolymers, bulky ^{i}Pr substituted copolymers being more folded than Me substituent analogues.

When two geminal hydrogen atoms on a carbon tethering chain connecting two reacting centers are replaced by two alkyl substituents, a change in conformational equilibrium populations by such substitutions would bring these two reacting centers into closer proximity such that the reactivity is enhanced.[1] This geminal disubstitution effect, known as the Thorpe–Ingold effect, has been extensively applied in organic[1] and organometallic chemistry.[2] Applications of this concept for the conformational investigations of polymers, other than peptides,[3] have not been explored. Alternating silylene-conjugated chromophore copolymers are well documented.[4] The copolymers have been used for conductivity studies,[5] electroluminescent devices,[6] and photovoltaic applications.[7] The silylene moiety in these copolymers can be considered as an insulating tetrahedral spacer to render polymers somewhat folded. A range of interesting photophysical studies on intrachain chromophore–chromophore aggregations, light harvesting and transfer of fluorescence resonance energy (FRET), electron and chiroptical properties have been explored.[8]

It is envisaged that the relative population of different conformations of divinylsilanes would depend on the size of the substituent R on silicon (eqn (1)). The bulkier substituent(s) may likely favor the *syn-syn* conformation over other conformations. Accordingly, the folding of silicon-containing copolymers may be enhanced when the methyl substituents on silicon are replaced by bulkier substituents. Intrachain interactions between chromophores may thus be affected by the modification of the substituent on silicon. We now wish to report the influence of the substituents at silicon on the morphology and photophysical properties of dialkylsilylene-spaced divinylbenzene copolymers **1**.



(1)



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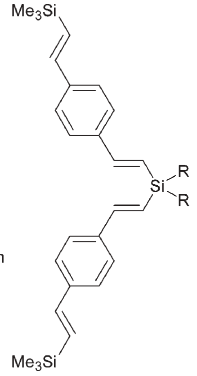

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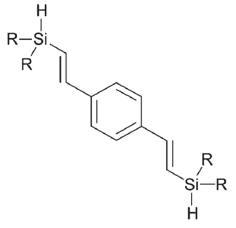
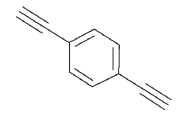


3

a R = Me; **b** R = ^{i}Pr



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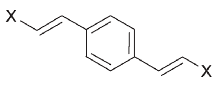

5 X = Br
6 X = Li

Copolymer **1b** was synthesised in a similar manner as that described for the preparation of **1a**,[8] by rhodium-catalyzed hydrosilylation of bisalkyne **4** with bis(silyl hydride) **3b**. Different degrees of polymerisation of **1** were obtained under different conditions. Higher temperatures and longer reaction times favored the formation of larger polymers. Silyl hydride **3b** was obtained from the displacement of (^{i}Pr)$_2$HSiCl with **6**.[9] The details for the preparation of dimers **2** and monomers **3** are described in the ESI†. The vicinal coupling constants between the proton on silicon and the vicinal vinylic proton in **3a** and **3b** were 2.7 and 4.7 Hz, respectively. Similar to those for the carbon analogues,[10] the larger coupling constant for **3b** suggested that the bulkier isopropyl substituent on silicon in **3b** may favor *syn* conformation **B** (eqn (2)). These results may imply that similar behavior may occur in **1b** and **2b**, the *syn-syn* conformation being favored by the presence of the bulkier isopropyl substituent (*cf.* eqn (1)).

R = Me or ^{i}Pr (2)

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[a] *Department of Chemistry National Taiwan University, Taipei, Taiwan 106 E-mail: tyluh@ntu.edu; chhchen@ntu.edu.tw; Fax: +886-2-2364-4971; Tel: +886-2-2363-6288*
[b] *Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan 106*

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‡ To whom correspondence concerning STM should be addressed.

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The photophysical properties of **2** are summarised in Table 1 and the fluorescence spectra of **2** and **3** are compared in Fig. 1. It is noteworthy that the emission maxima (356, 374, 393 nm) for **2** appeared at longer wavelengths than those for **3**. Furthermore, the relative intensities of the emissions for **2b** were much higher at longer wavelengths (393, 417 nm) than those for **2a**. Presumably, interactions between neighboring chromophores would prevail in **2b** over **2a**. These results suggested that the bulky isopropyl substituent on silicon might bring the two divinylbenzene chromophores in **2b** into closer proximity.

The absorption and emission spectra of **1** are compared with those of the corresponding monomers **3** (Fig. 2 and 3) and the selected photophysical properties are also summarised in Table 1. Both absorption and emission profiles remained essentially unchanged with concentration (1–100 fold) and the fluorescence maxima exhibited not much alteration with solvents (<6 nm, in cyclohexane, benzene, $CHCl_3$ or EtOAc). Copolymers **1** exhibited strong absorptions around 300 nm due to the π–π^* transition of the divinylbenzene moiety and the extinction coefficients decreased with increasing degree of polymerisation due to intrachain interactions between chromophores.[11] There was a weak absorption in the region of 340–400 nm for **1** and the intensity slightly increases with the degree of polymerisation of **1**. Relatively speaking, the extinction coefficients at 360 nm for **1b** were somewhat larger than that for **1a**.

As shown in Fig. 2 and 3, polymers **1** exhibited dual fluorescence spectra. The higher energy emissions at *ca.* 340 nm for **1** are comparable with those for the corresponding monomers **3**. The relative intensity of the emission in the blue light region increased with M_n of **1** and typical vibronic fine structures (Δv around 1500 cm^{-1}) were observed. It is interesting to note that the quantum yields of **1b** appeared to be somewhat larger than those of **1a**. In addition, the curve obtained from a plot of the relative intensities of the longer wavelength emission (420 nm) to that of emission at shorter wavelengths (340 nm) against the number average degree of polymerisation is somewhat steeper for **1b** than that for **1a** (ESI†).

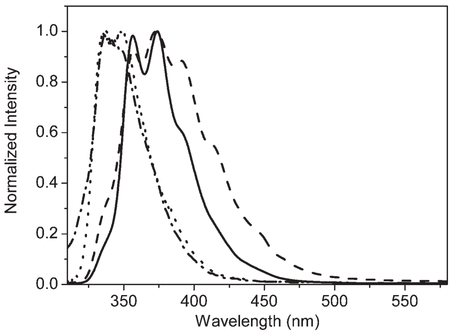

Fig. 1 Emission profiles of **2a** (solid line), **2b** (dashed line), **3a** (dotted line) and **3b** (dash-dotted line) in $CHCl_3$ (1×10^{-5} M) upon excitation at 300 nm.

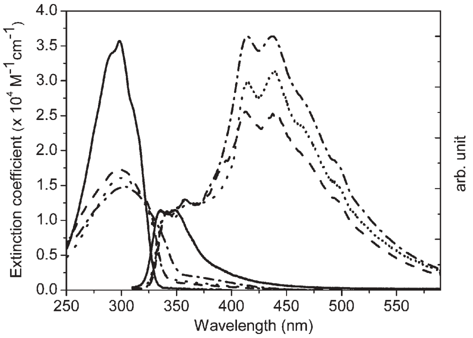

Fig. 2 Absorption and emission spectra of $\mathbf{1a_1}$ (dashed line), $\mathbf{1a_2}$ (dotted line), $\mathbf{1a_3}$ (dash-dotted line) and **3a** (solid line). Concentration: 1×10^{-5} M in $CHCl_3$.

As shown in Fig. 1–3, the emission profiles of polymers **1** were very different from those of dimers **2**. It seems likely that, in addition to the interactions between neighboring divinylbenzene chromophores, the non-neighboring divinylbenzene chromophores in **1** may also be in close proximity due to folding, so that significant interactions between these chromophores may readily take place. The fluorescence lifetimes for $\mathbf{1a_1}$, $\mathbf{1b_1}$, **2** and **3** are also outlined in Table 1. It is worthy to note that the mode of non-neighboring interactions between divinylbenzene moieties in $\mathbf{1a_1}$ and $\mathbf{1b_1}$ might be similar because the fluorescence lifetimes (1.2 ns each for $\mathbf{1a_1}$ and $\mathbf{1b_1}$) at 420 nm were comparable. The shorter lifetimes (81–103 ps) for **1** and **2** may be assigned to the emission of the non-interacting monomeric divinylbenzene unit. The lifetimes monitored at 390 nm were 254 ps for **2a**, attributed to the neighboring interactions between two divinylbenzene moieties. A similar lifetime was also observed for $\mathbf{1a_1}$ (230 ps). These values were very much different from those for **2b** (502 ps) and $\mathbf{1b_1}$ (469 ps). The discrepancy between these photophysical behaviors

Table 1 Photophysical properties of **1**–**3**

Subt.	M_n (PDI)	n^a	λ_{max}/nm ($\varepsilon \times 10^{-4}$/M^{-1} cm^{-1})^{b,c}	λ_{em}/nm^b	$I_{420}/I_{340}{}^d$	Φ^e	τ/ps^{b,f}
3a			291 (3.40), 298 (3.56), 312 (sh)	334, 351		0.01	21^g
2a			299 (2.77), 315 (sh), 350 (0.06)	356, 374, 393		0.01	81(0.72), 254(0.28)^h
$\mathbf{1a_1}$	3800 (2.0)	20	299 (1.73), 360 (0.09)	341, 414, 441	2.1	0.02	85(0.58), 230(0.08), 1246(0.34)^i
$\mathbf{1a_2}$	8400 (1.8)	45	301 (1.62), 360 (0.16)	341, 414, 441	2.8	0.02	
$\mathbf{1a_3}$	13000 (2.0)	69	303 (1.46), 360 (0.20)	341, 414, 441	3.6	0.03	
3b			291 (3.56), 298 (3.40), 312 (sh)	338, 355		0.01	22^g
2b			294 (3.11), 315 (sh), 350 (0.13)	358, 374, 393, 417		0.02	93(0.56), 502(0.44)^h
$\mathbf{1b_1}$	4000 (1.5)	17	294 (1.88), 360 (0.42)	348, 417, 444	4.4	0.07	103(0.31), 469(0.21), 1182(0.45)^i
$\mathbf{1b_2}$	5900 (1.6)	24	295 (1.54), 360 (0.51)	348, 417, 444	5.5	0.07	
$\mathbf{1b_3}$	8700 (1.8)	36	296 (1.28), 360 (0.56)	348, 417, 444	6.8	0.07	

[a] Number average degree of polymerisation. [b] Measured in $CHCl_3$ (1×10^{-5} M), λ_{ex} = 300 nm at ambient temperature. [c] The extinction coefficients of polymers **1** were calculated based on molecular weight of monomeric unit. [d] Relative ratio of intensities of the emission spectra at 340 nm (I_{340}) and at 420 nm (I_{420}). [e] Using coumarin 1 in EtOAc (Φ = 0.99) as the standard. [f] Numbers in parentheses are relative weighting. [g] Monitored at 340 nm. [h] Monitored at 390 nm. [i] Monitored at 420 nm.

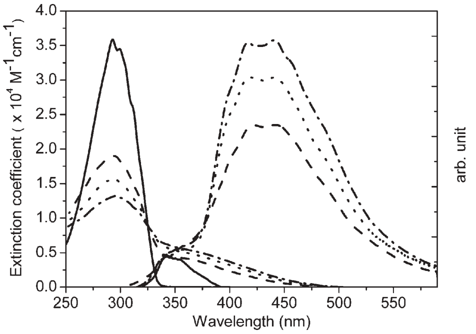

Fig. 3 Absorption and emission spectra of **$1b_1$** (dashed line), **$1b_2$** (dotted line), **$1b_3$** (dash-dotted line) and **3b** (solid line). Concentration: 1×10^{-5} M in $CHCl_3$.

of the methyl- *versus* isopropyl-substituted substrates could thus be rationalized within the framework of conformational changes shown in eqn (1).

To unveil the steric effect of the substituent R on the conformation of the silylene polymers, scanning tunnelling microscopy (STM) was employed to examine the morphology of **1** drop-cast on HOPG (highly oriented pyrolytic graphite). Panels a and b of Fig. 4 are typical STM images for **$1a_1$** and **$1b_1$**, respectively. The methyl-substituted **$1a_1$** exhibits a relatively loose and elongated feature with a nominal dimension of 4.5 × 2.0 nm, apparently different from the dense **$1b_1$** whose average diameter is 2.7 nm. The images of **$1a_1$** are fuzzier than those of **$1b_1$**, presumably due to the more fluxional conformation of **$1a_1$** than **$1b_1$**.

Images with a higher resolution (*e.g.* inset of Fig. 4b) indicate that each polymer may have 17–20 bright spots which may be attributed to the divinylbenzene moieties. These results are consistent with the GPC results (number average degree of polymerisation = 17) in **$1b_1$**. The distance between two non-neighboring divinylbenzene chromophores in space in **$1b_1$** could be as close as 3.5 Å. Strong interactions between these chromophores might be expected. Apparently, the isopropyl group may provide a bulky environment to impose more *syn-syn* conformations for the divinylsilane moieties (eqn (1)). A more rigid conformation for **$1b_1$** might therefore be expected, resulting in a highly coiled structure. In other words, these results may imply that **1b** would be more folded than **1a** on the HOPG surface. Accordingly, the chances for two chromophores meeting with each other would be higher in **1b** than in **1a**. The STM results appeared to be consistent with our photophysical data described above.

In summary, we have demonstrated the first example using the concept of the Thorpe–Ingold effect to direct the conformation and maybe the softness of silylene-spaced divinylarene copolymers. The results from the STM images are consistent with the outcome of photophysical studies on these polymers. Copolymers with bulky isopropyl substituents are more folded, bringing the chromophores into closer proximity so that intrachain interactions between these chromophores will become more prominent, leading to enhancement in aggregation emission. Since distance is known to play an important role in the FRET and photo-induced electron transfer processes, the present investigation would pave the way for further investigations of the Thorpe–Ingold effect on the photophysics of silicon-containing polymers and related systems.

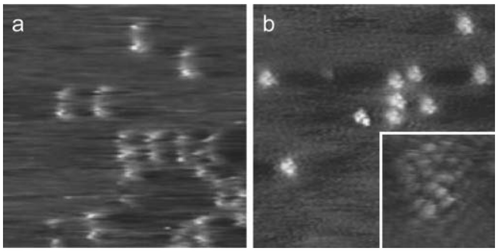

Fig. 4 STM image of (a) **$1a_1$** and (b) **$1b_1$**. Inset: high resolution image of **$1b_1$**. Conditions: (a) image size, 27 × 27 nm; E_{bias} 0.85 V, $i_{tunnelling}$ 20 pA; (b) image size, 27 × 27 nm; E_{bias} 0.50 V, $i_{tunnelling}$ 10 pA; inset: image size, 3 × 3 nm; E_{bias} 0.50 V, $i_{tunnelling}$ 33 pA.

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