

## Influence of polymer conformations on the aggregation behaviour of alternating dialkylsilylene-[4,4'-divinyl(cyanostilbene)] copolymers†

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Received 8th June 2011, Accepted 2nd September 2011

DOI: 10.1039/c1py00259g

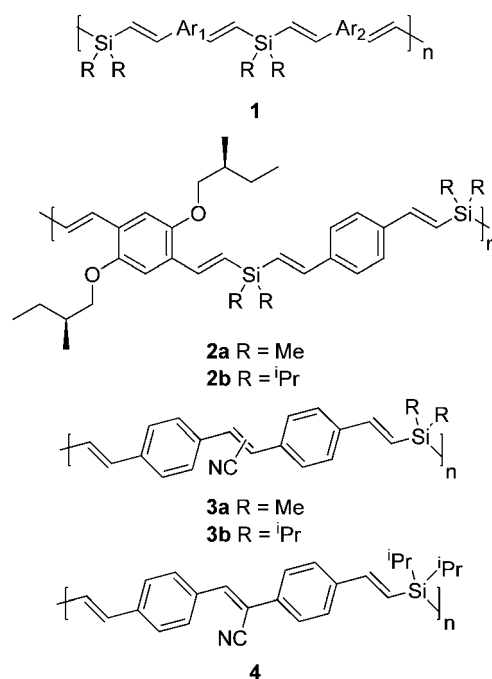
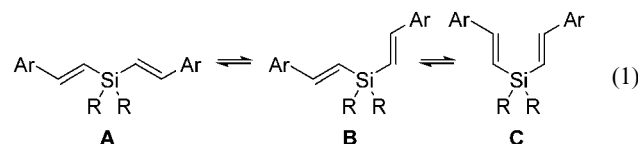
The influence of the substituents at silicon on the aggregation enhanced emission (AEE) of alternating dialkylsilylene-[4,4'-divinyl(cyanostilbene)] copolymers **3** and **4** is examined. The presence of the bulky isopropyl group in **3b** significantly enhances the quantum yield upon aggregation. On the other hand, the emission intensity of the methyl-substituted polymer **3a** is only slightly enhanced under the same conditions. The bulky isopropyl substituents on silicon may exert the Thorpe–Ingold effect on these copolymers resulting in conformation difference, which may dictate the nature of the aggregation between polymers, and hence, the photophysical behaviour of these polymers.

## Introduction

The conformation of a polymer chain and the feature of its interchain interactions should be closely related, and an ensemble of these factors, *inter alia*, will determine the macroscopic properties of polymers and nanomaterials.<sup>1</sup> Direct correlation of the polymer conformation with the aggregation properties, in general, is a nontrivial problem.<sup>1</sup> Interrelationship between the conformation of poly(*p*-phenylene-ethynylene)s, substituted with well-designed hydrophobic and hydrophilic moieties, and interchain interactions has been explored.<sup>2</sup> Substituents on poly(*p*-phenylene-vinylene)s have been shown to control the interchain interactions, hence the mode of aggregation can be adjusted.<sup>3</sup> It is known that a change of medium,<sup>4</sup> ionic strength,<sup>5</sup> temperature,<sup>6</sup> irradiation,<sup>7</sup> and other relevant factors may affect the polymer conformation and the aggregation nature of polymers. Circular dichroic (CD) properties of certain silicon-containing polymers are enhanced upon aggregation.<sup>8,9</sup> In this regard, the nature of the substituents on silicon may play an important role in the conformation of the polymers and hence the aggregated form.

We recently found that the photophysical properties of alternating dialkylsilylene-divinylarene copolymers **1** depend on the size of the substituent *R* on silicon, which may exert the Thorpe–Ingold effect on the conformation of these copolymers.<sup>9–11</sup> The

advantage of using polymer **1** is that the chromophores Ar<sup>1</sup> and Ar<sup>2</sup> as well as the alkyl substituent *R* can readily be modified. The conformational equilibrium of the distyrylsilane subunit in **1** may



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† Electronic supplementary information (ESI) available: XRD patterns of **3a** and **3b**, differential scanning calorimetry curves of **3a** and **3b**, <sup>1</sup>H and <sup>13</sup>C NMR spectra of **5**, **8**, **9**, and **12**, <sup>1</sup>H NMR spectra of polymers **3a**, **3b**, and **4**, the crystallographic data for **5**, and crystal size estimation. CCDC reference numbers 842709. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1py00259g

dictate the overall morphology of the polymer, and hence, the distance between the two adjacent chromophores in these polymers can be tuned (eqn (1)). Indeed, the STM images of **1** ( $\text{Ar}^1 = \text{Ar}^2 = 1,4\text{-C}_6\text{H}_4$ ,  $R = \text{Me}$ ) exhibit a fluffy morphology, whereas those of **1** with same chromophores and  $R = i\text{Pr}$  show a coil-like structure.<sup>11a</sup> The emission wavelength of methyl substituted **2a** appears at much shorter wavelengths than that of isopropyl-substituted **2b**, presumably due to the different folding nature of these two polymers. In addition, **2a** is CD inactive in dilute solution ( $10 \text{ mg L}^{-1}$ ) and becomes active only in the aggregated state at a high concentration ( $1 \text{ g L}^{-1}$ ), whereas **2b** shows CD response at dilute conditions.

It is known that the emission of small molecules such as substituted cyano-substituted stilbenes can be enhanced upon aggregation.<sup>12,13</sup> Planisation of chromophore and restriction of excimer formation in the presence of the cyano substituent may account for this unusual photophysical behaviour.<sup>12b</sup> Siloles and other related systems behave similarly. The aggregation enhanced emission (AEE) has also been found in polymers such as polysiloles,<sup>14</sup> poly(*p*-phenylene-ethynylene)s,<sup>15</sup> poly(1,4-bis( $\beta$ -cyano-4'-methylstyryl)benzene)s,<sup>16</sup> polyacetylenes,<sup>17</sup> and poly(quinoline)s.<sup>18</sup> It is therefore envisaged that a variation of the substituent  $R$  on silicon in **1** may offer a useful probe to elucidate the relationship between the conformation of the individual polymer and the aggregation nature of these polymers. 4,4'-Divinyl-cyanostilbene chromophore was chosen because similar monomers with related chromophores are known to exhibit aggregation induced emission (AIE).<sup>12b</sup> We now wish to report the synthesis and photophysics of alternating dialkylsilylene-[divinyl(cyanostilbene)] copolymers **3** and **4**.

## Results and discussion

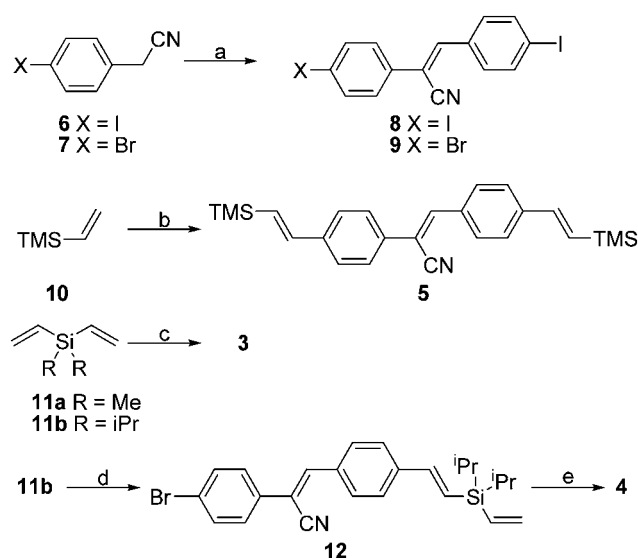
### Synthesis

The synthesis of monomer **5** and copolymers **3** and **4** are summarised in Scheme 1. The Heck reaction of aryl halides with vinylsilanes is the key protocol for the synthesis of **3–5** and the details are described in the Experimental section. It is noteworthy that the orientations of the cyano substituents in **3b** are random, while those in **4** are unidirectional.

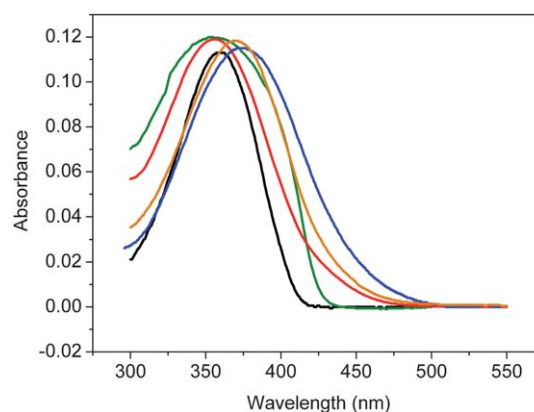
### Steady state photophysical properties of 3–5

The absorption spectra of monomer **5** are compared with those of polymers **3** and **4** in Fig. 1 and the relevant photophysical properties are summarised in Table 1. The absorption maximum ( $\lambda_{\text{max}}$ ) of **5** in THF appeared at 360 nm, whereas the absorption of the thin film of **5**, prepared by thermal evaporation on a quartz substrate, exhibited broader full width at half maximum (fwhm) at the similar wavelength than that in solution. The  $\lambda_{\text{max}}$  for **3a**, with methyl substituents on silicon, was observed at the similar wavelength. On the other hand, the  $\lambda_{\text{max}}$  for **3b** and **4**, having isopropyl groups on silicon, exhibited bathochromic shifts relative to those of **3a** and **5**. It is worth noting that the fwhm for polymers **3** and **4** was also broader than that for **5**.

The emission profiles of **3–5** in dilute THF solution ( $1 \times 10^{-5} \text{ M}$ ) are shown in Fig. 2 and the quantum yields of these substrates are outlined in Table 1. Like the related monomer **13**,<sup>12b</sup> the quantum yield of **5** was extremely low ( $<0.001$ ). The emission



**Scheme 1** a: 4-Iodobenzaldehyde, NaOH, EtOH, **8**: 90%, **9**: 89%; b: **8** (0.5 equiv.), Pd(OAc)<sub>2</sub>, Bu<sub>4</sub>NOAc, **5**: 20%; c: **8** (1 equiv.), Pd(OAc)<sub>2</sub>, Bu<sub>4</sub>NOAc, **3a**: 75% ( $M_n = 5100$ , PDI = 1.85); **3b**: 70% ( $M_n = 5600$ , PDI = 1.97); d: **9** (1 equiv.), Pd(OAc)<sub>2</sub>, Bu<sub>4</sub>NOAc, **12**: 12%; e: Pd(OAc)<sub>2</sub>, P(*o*-tol)<sub>3</sub>, 65% ( $M_n = 5800$ , PDI = 2.11).



**Fig. 1** Absorption spectra of (a) **5** in THF ( $1.0 \times 10^{-5} \text{ M}$ , black), (b) thin film of **5** (green, arbitrary unit), (c) **3a** in THF ( $3.2 \text{ mg L}^{-1}$ , red), (d) **3b** in THF ( $3.7 \text{ mg L}^{-1}$ , blue), and (e) **4** in THF ( $3.7 \text{ mg L}^{-1}$ , brown).

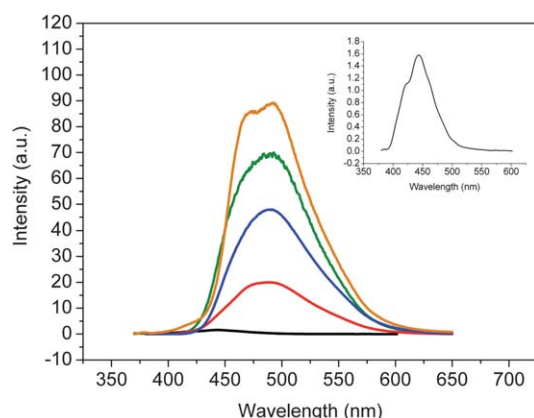
band of **5** in solid showed a significant bathochromic shift without the vibronic fine structure (Fig. 2) and the quantum yield was 0.48. An increase of quantum yield in solid for **5** could be rationalised by the synergetic planarisation and J-type aggregation resulting in AIE.<sup>12b</sup> Indeed, the crystal structure of **5** showed that the molecule in solid was essentially planar with a dihedral angle between two benzene rings around  $20^\circ$ . In addition, the packing pattern also suggests that **5** might be oriented in a J-type aggregation (Fig. 3). As shown in Fig. 2, the emission maxima ( $\lambda_{\text{em}}$ ) of **3** and **4** appeared at much longer wavelengths than that of **5** in THF but close to that of **5** in solid state. Moreover, the fluorescence intensities of **3** and **4** were much enhanced and the quantum yields for **3a**, **3b** and **4** in THF were 0.02, 0.05, and 0.11, respectively.

The monosilylene spacer in alternating dialkylsilylene-divinylarene copolymers **1** is known to be an insulator, and the possible

**Table 1** Photophysical parameters of **3a**, **3b**, and **4** in mixed *n*-hexane–THF solutions

<i>n</i> -Hexane/THF	<b>3a</b>				<b>3b</b>				<b>4</b>			
	$\lambda_{\text{max}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$\Phi^a$	$\tau^b/\text{ps}$	$\lambda_{\text{max}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$\Phi^a$	$\tau^b/\text{ps}$	$\lambda_{\text{max}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$\Phi^a$	$\tau^b/\text{ps}$
0	358	489	0.02	190	372	488	0.05	180	370	493	0.10	200
1	360	485	0.05	190	370	478	0.29	260	363	465	0.32	290
2	360	472	0.06	190	370	471	0.45	310	363	464	0.47	310
3	358	470	0.06	200	370	466	0.51	330	362	461	0.50	330
4	359	467	0.06	190	370	466	0.52	350	360	460	0.50	340

<sup>a</sup> Quantum yields,  $\Phi$ , were estimated by using coumarin-1 ( $\Phi = 0.99$  in ethyl acetate) as the standard. <sup>b</sup> Fluorescence lifetimes,  $\tau$ , were obtained by using single exponential fitting of fluorescence decay profiles.



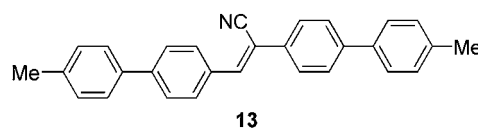
**Fig. 2** Emission spectra of (a) **5** in THF ( $1.0 \times 10^{-5}$  M, black), (b) thin film of **5** (green, arbitrary unit), (c) **3a** in THF ( $3.2 \text{ mg L}^{-1}$ , red), (d) **3b** in THF ( $3.7 \text{ mg L}^{-1}$ , blue), and (e) **4** in THF ( $3.7 \text{ mg L}^{-1}$ , brown). Inset: expanded emission spectrum of **5** in THF.

$\sigma$ – $\pi$  conjugation, if any, could be neglected when other photophysical properties prevail.<sup>9–11,19–23</sup> Accordingly, the conjugation length of the chromophore in **3** and **4** would be the same as that in **5**. In general, the photophysical properties of **1** are quite similar to those of the corresponding monomers, when the conjugation length of the chromophore is long enough for the exciton delocalisation.<sup>20</sup> On the other hand, interactions between adjacent chromophores or through space interactions in certain silicon containing copolymers **1** (e.g.  $\text{Ar} = \text{Ar}' = 1,4\text{-C}_6\text{H}_4$ ) are known to lead to new emission at longer wavelengths.<sup>11a,20</sup> It is noteworthy that the fluorescence resonance energy transfer<sup>21</sup> and photoinduced electron transfer<sup>11b,22,23</sup> between neighbouring chromophores are common in this type of copolymers **1**. Moreover, interactions between these adjacent chromophores



**Fig. 3** X-Ray packing structures of **5** (a) front view and (b) side view.

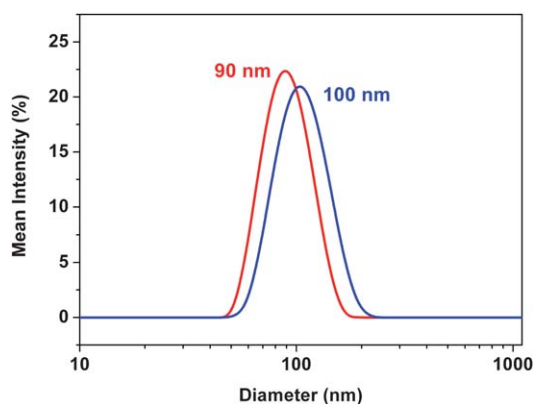
are closely related to the distance separating these two chromophores. Indeed, the steric bulkiness of the substituents on silicon would control the relative separation between the adjacent conjugated moieties, known as the Thorpe–Ingold effect in organosilicon chemistry.<sup>10</sup> As shown in Table 1, the quantum yields of **3b** and **4** were indeed higher than that of **3a**.



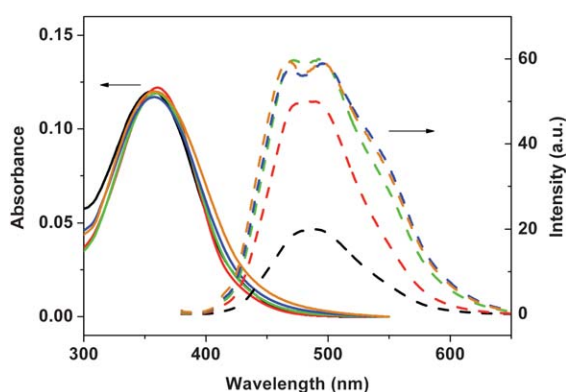
### Solvent-induced aggregation of polymers

The aggregation behaviour of polymers was studied in a mixed solvent of *n*-hexane and THF. Polymers **3** and **4** are highly soluble in THF but sparingly soluble in *n*-hexane. It is interesting to note that these polymers gave clear solutions in 80% *n*-hexane and 20% THF without precipitation. Dynamic light scattering investigations revealed that the average particle sizes of **3a** and **3b** were 90 and 100 nm, respectively, under these conditions (Fig. 4). These results indicate that **3** may exist in an aggregated state in mixed *n*-hexane–THF co-solvents. The photophysical properties of **3** and **4** in these mixed solvents at different ratios are tabulated in Table 1 and the spectra are shown in Fig. 5–7. The quantum yields for **3a** were only slightly increased in these mixed solvent systems. It is particularly noteworthy that the quantum yields of **3b** and **4** were significantly enhanced as the ratio of *n*-hexane increased under the same conditions. The orientations of chromophores in **3b** are random, while those in **4** are unidirectional. However, there was little discrepancy in photophysical properties between these two isomeric polymers in aggregated states.

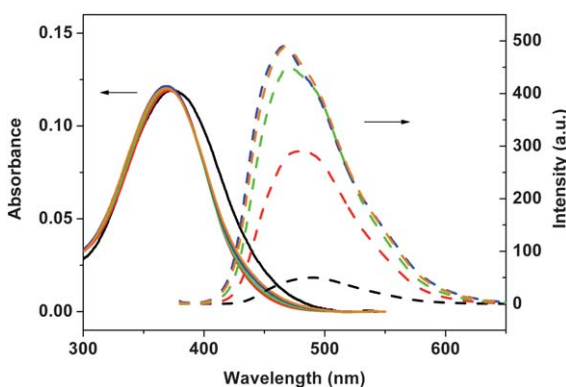
As shown in Fig. 5, little changes in Stokes shifts for **3a** were observed for the solvent dependent photophysical behaviour. On the other hand, the Stokes shifts for **3b** and **4** decreased with increasing *n*-hexane content in these mixed solvents. A decrease in Stokes shifts implies that the chromophore may become more rigid as the polarity of the mixed solvent decreased. As shown in Table 1, quantum yields of **3b** and **4** significantly increased with the increasing *n*-hexane content in mixed solvents. The only structural difference between **3a** and **3b** is the size of the substituents on silicon (Me vs. <sup>i</sup>Pr) in these polymers. It seems



**Fig. 4** Particle size distribution of **3a** (red) and **3b** (blue) in *n*-hexane/THF (80/20).

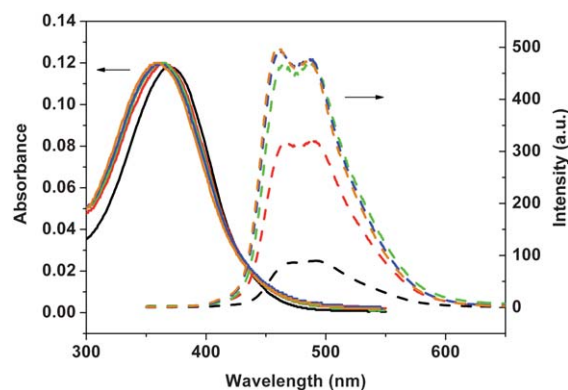


**Fig. 5** Absorption (solid lines) and emission spectra (dashed lines) of **3a** in different ratios of *n*-hexane/THF: 0/100 (black), 50/50 (red), 67/33 (green), 75/25 (blue), and 80/20 (brown).



**Fig. 6** Absorption (solid lines) and emission spectra (dashed lines) of **3b** in different ratios of *n*-hexane/THF: 0/100 (black), 50/50 (red), 67/33 (green), 75/25 (blue), and 80/20 (brown).

likely that the isopropyl substituents on silicon as in **3b** and **4** would exert the Thorpe–Ingold effect on the local conformation of the divinylsilane moiety, and hence the overall conformation of the polymer.<sup>9,10</sup> On the other hand, the methyl-substituted polymers such as in **3a** would be more fluxional.<sup>9,10</sup> Such conformational difference may affect the nature of the aggregation of these dialkylsilylene-divinylarene copolymers **3** and **4**.



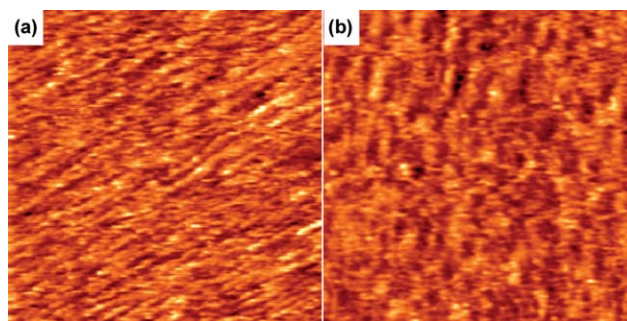
**Fig. 7** Absorption (solid lines) and emission spectra (dashed lines) of **4** in different ratios of *n*-hexane/THF: 0/100 (black), 50/50 (red), 67/33 (green), 75/25 (blue), and 80/20 (brown).

### Solid state properties

The glass transition temperature ( $T_g$ ) of **3b** (150 °C) is higher than that of **3a** (118 °C).<sup>†</sup> Powder X-ray diffraction (XRD) of both **3a** and **3b** showed three characteristic peaks at  $2\theta = 40$ , 46, and 68°.<sup>†</sup> However, the half widths of these peaks for **3a** were slightly broader than those of **3b**. The crystal sizes of **3a** and **3b**, calculated by Scherrer's formula,<sup>24</sup> were 9.9 and 11.5 nm, respectively.<sup>†</sup> These results suggest that **3a** and **3b** might exhibit a similar packing structure, but the range of the ordered orientation seems to be more extended in **3b** than in **3a**. The scanning tunneling microscopic (STM) images of **3a** and **3b** are shown in Fig. 8. It is interesting to note that the morphology for each of the polymeric molecules **3a** in aggregated form appears to be an elongated rod, whereas **3b** shows a coil-like molecular structure. This observation was similar to those reported earlier on related polymers.<sup>11,22c</sup> The discrepancy in solid state properties between **3a** and **3b** might correlate to the photophysical behaviour of the aggregation properties of these polymers in solution, although the actual mode of interactions remains to be solved.

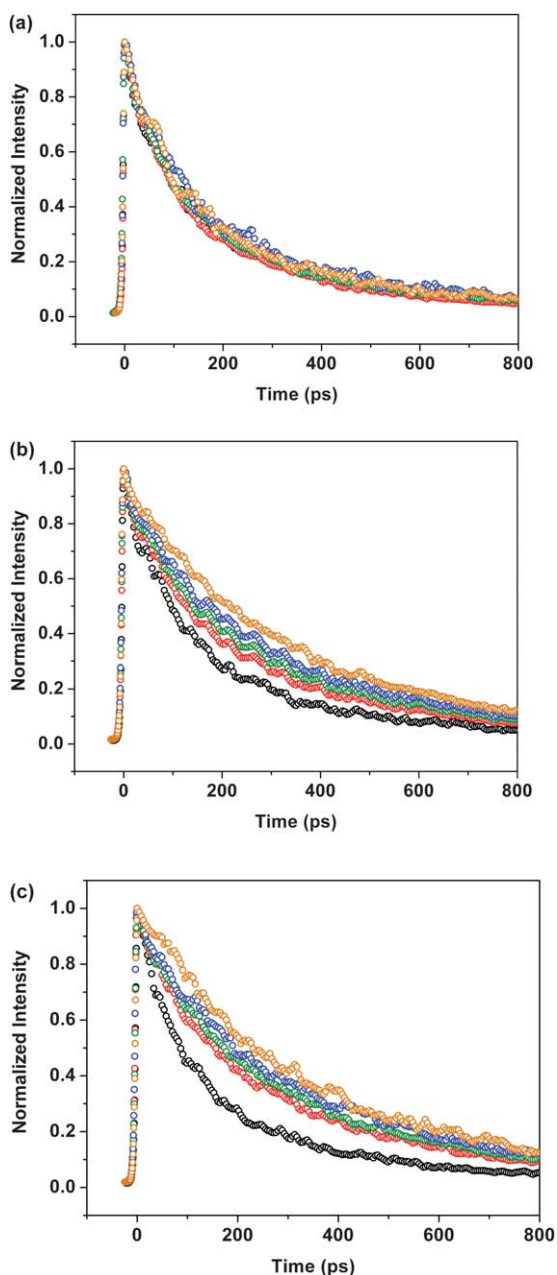
### Kinetic measurements

Time-resolved fluorescence spectroscopy using femto-second Ti-sapphire laser equipped with a streak camera was employed to give the fluorescence decay lifetimes by single exponential fitting. The decay profiles for **3a**, **3b** and **4** are shown in Fig. 9 and the results are also outlined in Table 1. The lifetimes for **3a** in



**Fig. 8** STM images of (a) **3a** and (b) **3b** on highly ordered pyrolytic graphite (HOPG). Imaging conditions:  $E_{\text{bias}}$ ,  $i_{\text{tunneling}}$ , and image sizes were 0.95 V, 90 pA, and  $50 \times 50$  nm.





**Fig. 9** Fluorescence decay profiles of (a) **3a**, (b) **3b**, and (c) **4** in different ratios of *n*-hexane/THF: 0/100 (black), 50/50 (red), 67/33 (green), 75/25 (blue), and 80/20 (brown).

different mixed *n*-hexane–THF solvents were around 190 ps, whereas those for **3b** and **4** were gradually increased from 180 to 350 ps under the same conditions. An increase of fluorescence lifetimes may be attributed to the lower contribution from other radiationless decay processes, and hence, a higher quantum yield would be expected. These kinetic results were consistent with the steady state measurement discussed above.

## Conclusions

In summary, we have demonstrated an interesting feature on the influence of the substituents at silicon on the AEE of alternating

dialkylsilylene[divinyl(cyanostilbene)] copolymers **3** and **4**. The presence of the bulky isopropyl group in **3b** significantly enhances the quantum yield upon aggregation. On the other hand, the emission intensity of the methyl-substituted polymer **3a** is only slightly enhanced under the same conditions. It is known that the substituents on silicon may exert the Thorpe–Ingold effect on silylene-spaced divinylarene copolymers.<sup>9–11</sup> Consequently, the conformation of **3b** may be very different from that of **3a** due to the steric effect. It seems likely that this conformation difference may dictate the nature of the aggregation between polymers, and hence, the photophysical behaviour of these polymers. The present study offers a preliminary platform to correlate the conformation of this silicon-containing polymer and the mode of interchain aggregation.

## Experimental section

### General

High-resolution mass spectrometric measurements were obtained from a Jeol-JMS-700 mass spectrometer using the FAB method in 3-nitrobenzyl alcohol matrix and the EI method was collected with a resolution of 8000(3000) (5% valley definition). Gel permeation chromatography (GPC) was performed on a Waters GPC machine using an isocratic HPLC pump (1515) and a refractive index detector (2414). THF was used as the eluent (flow rate = 1 mL min<sup>−1</sup>). Waters Styragel HR2, HR3, HR3, and HR4 (7.8 × 300 mm) columns were employed for molecular weight determination, and polystyrenes were used as the standard (*M<sub>n</sub>* values ranging from 375 to 3.5 × 10<sup>6</sup>). Absorption spectra were recorded on a Hitachi U-3310 spectrophotometer and emission spectra on a Hitachi F-4500 fluorescence spectrophotometer. The quantum yield was obtained using coumarin-I in EtOAc as reference ( $\Phi = 0.99$ ). Particle sizes of polymers in mixed co-solvent were measured on a Malvern Zetasizer Nano S90 using dynamic light scattering. X-Ray powder diffraction patterns were recorded on a PANalytical X' Pert PRO. The glass transition temperature was measured on a LT-Modulate DSC 2920 calorimeter.

### (*Z*)-2,3-Bis(4-iodophenyl)acrylonitrile (**8**)

A solution of NaOH (50 mg) in ethanol (30 mL) was added dropwise to the mixture of **6** (2.43 g, 10.0 mmol) and 4-iodobenzaldehyde (2.32 g, 10.0 mmol) in ethanol (50 mL). The reaction mixture was stirred at rt for 1 h. The precipitate was collected as a white solid (4.11 g, 90%); mp 157–158 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.39 (d, *J* = 8.8 Hz, 2H), 7.44 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  95.4, 97.3, 111.4, 117.1, 127.4, 130.5, 132.6, 133.5, 138.08, 138.09, 141.0; IR (KBr)  $\nu$  3046, 2221, 1581, 1486, 1405, 1340, 1011, 992, 926, 832, 817 cm<sup>−1</sup>; HRMS (EI+) (*M*<sup>+</sup>) calcd for C<sub>15</sub>H<sub>9</sub>I<sub>2</sub>N: 456.8825. Found: 456.8826.

### (*Z*)-2-(4-Bromophenyl)-3-(4-iodophenyl)acrylonitrile (**9**)

A solution of NaOH (50.0 mg) in ethanol (30 mL) was added dropwise to the mixture of **7** (1.96 g, 10.0 mmol) and

4-iodobenzaldehyde (2.32 g, 10.0 mmol) in ethanol (50 mL). The reaction mixture was stirred at rt for 1 h. The precipitate was collected as a white solid (3.73 g, 91%); mp 135–136 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.42 (s, 1H), 7.52 (d,  $J$  = 8.8 Hz, 2H), 7.57 (d,  $J$  = 8.8 Hz, 2H), 7.59 (d,  $J$  = 8.4 Hz, 2H), 7.81 (d,  $J$  = 8.4 Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  97.3, 111.3, 117.2, 123.6, 127.3, 130.5, 132.1, 132.6, 132.9, 138.1, 141.0; IR (KBr)  $\nu$  3047, 2220, 1645, 1490, 1403, 1077, 1002, 919, 833, 820  $\text{cm}^{-1}$ ; HRMS (FAB+) ( $\text{M}^+$ ) calcd for  $\text{C}_{15}\text{H}_9^{79}\text{BrIN}$ : 408.8963. Found: 408.8964.

#### (Z)-2,3-Bis{4-[(E)-2-(trimethylsilyl)vinyl]phenyl}acrylonitrile (5)

A mixture of **8** (0.91 g, 2.0 mmol), **10** (0.20 g, 2.0 mmol), Pd(OAc) $_2$  (45.0 mg, 0.2 mmol), and Bu $_4$ NOAc (1.82 g, 6.0 mmol) in dry DMF (30 mL) was stirred at 80 °C for 24 h. After filtration over celite, the crude product was chromatographed on silica gel (10%  $\text{CH}_2\text{Cl}_2$ /hexane) to give **8** as a yellow solid (0.16 g, 20%); mp 128–129 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  0.18 (s, 18H), 6.57 (d,  $J$  = 19.2 Hz, 1H), 6.61 (d,  $J$  = 19.2 Hz, 1H), 6.89 (d,  $J$  = 19.2 Hz, 1H), 6.90 (d,  $J$  = 19.2 Hz, 1H), 7.45–7.55 (m, 5H), 7.64 (d,  $J$  = 8.4 Hz, 2H), 7.88 (d,  $J$  = 8.4 Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  -1.12, -1.11, 110.5, 118.0, 125.9, 126.7, 126.8, 129.5, 131.3, 132.30, 133.0, 133.7, 139.0, 140.2, 140.9, 142.2, 142.3; IR (KBr)  $\nu$  3056, 2993, 2955, 2894, 2217, 1600, 1511, 1416, 1251, 982, 868, 836  $\text{cm}^{-1}$ ; HRMS (FAB+) ( $\text{M}^+$ ) calcd for  $\text{C}_{25}\text{H}_{31}\text{NSi}_2$ : 401.1995. Found: 401.1989.

#### (Z)-2-(4-Bromophenyl)-3-(4-[(E)-2-(dimethyl(vinyl)silyl)vinyl]phenyl)acrylonitrile (12)

A mixture of **9** (0.82 g, 2.0 mmol), **11b** (0.34, 2.0 mmol), Pd(OAc) $_2$  (22.0 mg, 0.1 mmol), and Bu $_4$ NOAc (1.21 g, 4.0 mmol) in dry DMF (30 mL) was stirred at 80 °C for 24 h. After filtration over celite, the crude product was chromatographed on silica gel (10%  $\text{CH}_2\text{Cl}_2$ /hexane) to give **12** as a pale yellow solid (90.0 mg, 12%); mp 88–89 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  1.00–1.20 (m, 14H), 5.85 (dd,  $J$  = 7.8, 17.0 Hz, 1H), 6.15 (d,  $J$  = 17.0 Hz, 1H), 6.18 (d,  $J$  = 7.8 Hz, 2H), 6.56 (d,  $J$  = 19.2 Hz, 1H), 7.00 (d,  $J$  = 19.2 Hz, 1H), 7.50 (s, 1H), 7.53–7.59 (m, 6H), 7.88 (d,  $J$  = 8.4 Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  11.5, 18.3, 18.4, 109.7, 117.4, 123.0, 125.6, 126.5, 127.0, 129.3, 131.8, 132.48, 132.50, 133.1, 134.5, 140.1, 141.5, 145.0; IR (KBr)  $\nu$  3120, 3047, 2983, 2222, 1640, 1491, 1403, 1390, 1070, 998, 910, 818  $\text{cm}^{-1}$ ; HRMS (FAB+) ( $\text{M}^+$ ) calcd for  $\text{C}_{25}\text{H}_{28}\text{BrNSi}$ : 449.1174. Found: 449.1176.

#### General procedure for the preparation of 3

A mixture of dialkyldivinylsilane (0.2 mmol), **8** (82.0 mg, 0.2 mmol), Pd(OAc) $_2$  (3.0 mg), and Bu $_4$ NOAc (60.0 mg, 0.2 mmol) in dry DMF (3.0 mL) was refluxed under N $_2$  for 18 h. After cooling to rt, the mixture was poured into EtOAc. The precipitate was collected and dissolved in THF, and then reprecipitated with MeOH. The product was collected by filtration and washed with MeOH.

#### Polymer 3a

Yield: 75%;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  0.20–0.40 (br, 6H), 6.55–6.75 (br, 2H), 6.90–7.05 (br, 2H), 7.40–8.00 (m, 9H); IR (KBr)  $\nu$  3027, 2983, 2957, 2213, 1603, 1509, 1415, 1251, 1041, 986, 840, 804  $\text{cm}^{-1}$ ;  $M_n$  = 5100, PDI = 1.85.

#### Polymer 3b

Yield: 70%;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  1.00–1.40 (m, 14H), 6.50–6.70 (br, 2H), 7.00–7.15 (br, 2H), 7.50–8.00 (m, 9H); IR (KBr)  $\nu$  3027, 2939, 2806, 2214, 1603, 1508, 1460, 1416, 1024, 989, 794  $\text{cm}^{-1}$ ;  $M_n$  = 5600, PDI = 1.97.

#### Polymer 4

A mixture of **12** (90.0 mg, 0.2 mmol), Pd(OAc) $_2$  (3.0 mg), and P(*o*-tol) $_3$  (5.0 mg) in dry DMF (4.0 mL) was refluxed under N $_2$  for 24 h. After cooling to rt, the mixture was poured into EtOAc. The precipitate was collected and dissolved in THF, and then reprecipitated with MeOH. The product was collected by filtration and washed with MeOH to give product (49.0 mg, 65%);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  1.00–1.35 (m, 14H), 6.50–6.65 (br, 2H), 7.00–7.15 (br, 2H), 7.50–7.80 (m, 7H), 7.85–8.00 (m, 2H); IR (KBr)  $\nu$  3027, 2940, 2862, 2211, 1601, 1510, 1461, 1260, 1094, 1014, 989, 880, 759  $\text{cm}^{-1}$ ;  $M_n$  = 5800, PDI = 2.11.

#### Time-resolved fluorescence experiments

A mode-locked Ti:sapphire laser (wavelength: 740 nm; repetition rate: 76 MHz; pulse width: <200 fs) passed through an optical parametric amplifier to produce 370 nm pulse laser. The fluorescence of the sample was reflected by a grating (150 g  $\text{mm}^{-1}$ ; BLZ: 500 nm) and detected by an optically triggered streak camera (Hamamatsu C5680) with a time resolution of about 0.3 ps. The sample was prepared with  $1.0 \times 10^{-5}$  M concentration, and using ultra-micro cuvette with 1 mm pathlength to maintain the excitation at the same time. The signal was collected for ten times to decrease the signal to noise ratio.

#### STM imaging

An aliquot of polymer in solvent (*n*-hexane : THF = 1 : 1) was placed on HOPG (Advanced Ceramics, ZYH grade) followed by a treatment of shear flow.<sup>25</sup> STM imaging was carried out with a NanoScope IIIa controller (Veeco Metrology Group/Digital Instruments) at room temperature. The STM probes were commercially available Pt/Ir tips (PT, Nanotips, Veeco Metrology Group/Digital Instruments). Typical imaging conditions of bias voltage and tunneling current were about 0.95 V and 90 pA, respectively. The images were filtered with a first-order flattening to minimise noise and without further processing.

#### Preparation of aggregated polymer

THF solutions of polymer **3** or **4** were prepared and the concentrations were adjusted to be  $2.0 \times 10^{-5}$ ,  $3.0 \times 10^{-5}$ ,  $4.0 \times 10^{-5}$ , and  $5.0 \times 10^{-5}$  M. These aliquots (1.0 mL) were slowly added ( $1.0 \text{ mL min}^{-1}$ ), respectively, into different volumes of *n*-hexane (1.0 mL, 2.0 mL, 3.0 mL, and 4.0 mL) under ultrasound

irradiation to form the aggregates of polymers for photophysical measurements.

## Acknowledgements

We thank the National Science Council and the National Taiwan University for support. We thank Professor Huan-Cheng Chang for helpful discussion.

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