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Intrachain energy transfer in silylene-spaced alternating donor–acceptor divinylarene copolymers†

Yen-Ju Cheng, Tsyr-Yuan Hwu, Jui-Hung Hsu and Tien-Yau Luh*
Department of Chemistry, National Taiwan University, Taipei, Taiwan 106
Institute of Chemistry, Academia Sinica, Taipei, Taiwan 115. E-mail: tyluh@chem.sinica.edu.tw;
Fax: +886-2-2651-1488; Tel: +886-2-2789-8500

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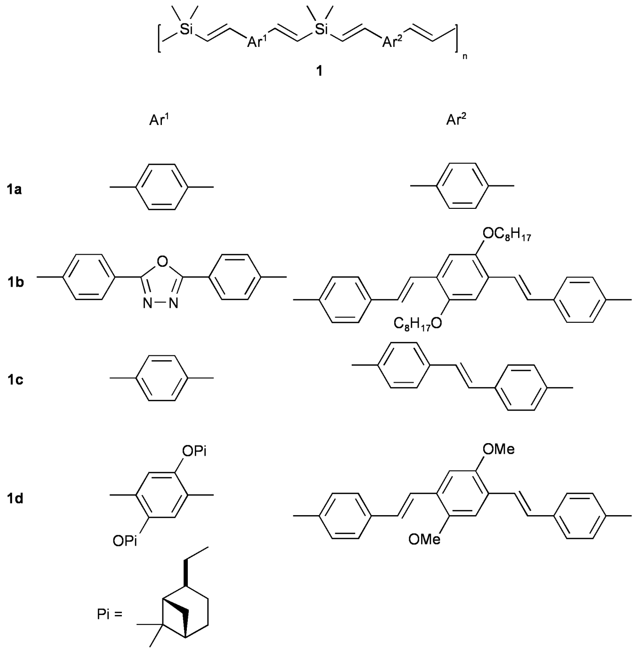
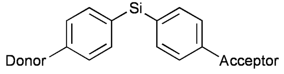
Silylene-spaced donor–acceptor divinylarene copolymers are synthesized by hydrosilylation of bisalkynes 7 with bisvinylsilanes 3; efficient intrachain energy transfer between donor–acceptor chromophores is observed.

Conjugated copolymers with alternating donor/acceptor repeating units have received much attention because the intramolecular charge transfer within the chain may result in concomitant changes in band gaps, electrochemical and optical properties.[1] Alternatively, intramolecular energy transfer along a non-conjugated supramolecular system or a polymer chain has been extensively investigated because it may serve as a useful model to mimic the natural light harvesting process.[2] We and others found that the silicon moiety in silylene spaced divinylarene copolymers **1** may serve as an insulating tetrahedral spacer so that there is no conjugation along the polymeric backbone.[3,4] Intrachain chromophore interaction due to folding of the polymer has been observed in silylene–divinylbenzene copolymers **1a**.[3] It is known that photoinduced through-space charge transfer may occur in 4-donor-4′-acceptor substituted diphenyldimethylsilanes **2**.[5] Since **1** is synthesized by the hydrosilylation of bisalkynes **7** with bisvinylsilanes **3**,[3] the two neighboring chromophores in **1** can be different and alternating. It is envisaged that interaction between the neighboring chromphores may also take place leading to transfer of energy. We now describe the first example on the synthesis and photophysics of silylene-spaced alternating donor–acceptor copolymers **1**.





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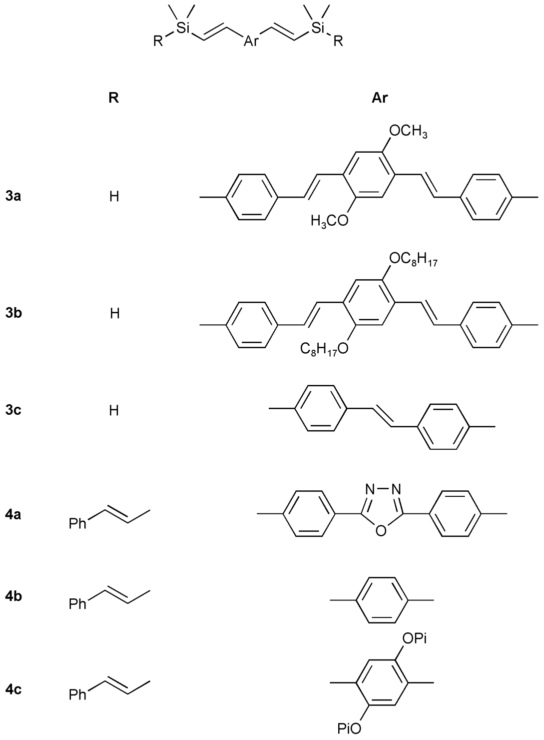
Our strategy was to synthesize a series of monomeric silyl-substituted divinylarenes **3**. Based on the absorption and emission properties of these monomers (Table 1), a series of polymers **1** was designed so that the absorption of one chromophore (Ar²) can overlap with the emission of the other chromophore (Ar¹). The synthesis of vinylsilanes **3** was based on the nickel-catalyzed silylolefination of the corresponding dithioacetals **5** followed by the reduction of the corresponding Si–O bond in **6**,[3] whereas a Sonogashira reaction was employed for the synthesis of bisalkynes **7**. Hydrosilylation of **7** with **3** afforded the corresponding copolymers **1**. Monomers **4** were obtained similarly from **7** and **8**.‡



As shown in Table 1, the emission maximum of **4a** matched well with the absorption maximum of **3b**. Fig. 1 shows the concentration dependent emission spectra (excitation at 324 nm) of an equal molar mixture of **3b** and **4a**. It is noteworthy that the intermolecular energy transfer between **4a** and **3b** does not proceed efficiently. The fluorescence spectrum (excitation at 324 nm) for polymer **1b** is also included in Fig. 1 for comparison, only emission from chromophore Ar² being observed. This result indicated that complete energy transfer from diphenyloxadiazole moiety to terphenylene-tetravinylene chromophore occurred in **1b**. In a similar manner, efficient energy transfer from divinylbenzene to divinylstilbene in **1c** and from divinyldialkoxybenzene to terphenylene-tetravinylene

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b2/b206308e/

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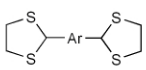

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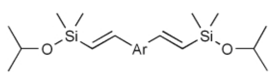

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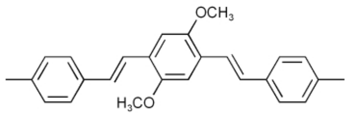
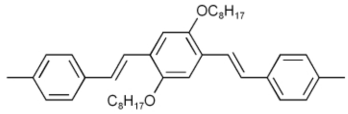
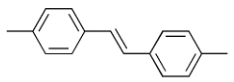
a Ar =

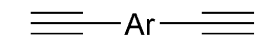


b Ar =



c Ar =





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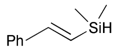

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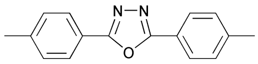
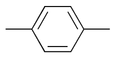
7a Ar =



7b Ar =



7c Ar =

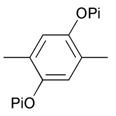


Table 1 Absorption and emission properties of polymers **1** and monomers **3** and **4**

Substrate	λ_{max}/nm	λ_{em}/nm	M_n (PDI)
1b	328, 411	471, 495	4100 (1.5)
1c	345, 355	396, 415	3200 (2.7)
1d	345, 408	468, 496	3990 (1.5)
3a	338, 411	467, 490	
3b	348, 413	467, 490	
3c	355	392, 411	
4a	324	363, 384, 401	
4b	263, 300	334, 347	
4c	262, 360	418	

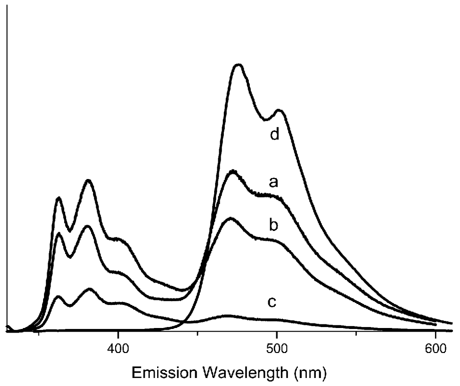


Fig. 1 Concentration dependent fluorescence spectra (excitation wavelength: 324 nm) of an equal molar mixture of **3b** and **4a** in $CHCl_3$ (a: 1×10^{-1} g mL^{-1}; b: 1×10^{-2} g mL^{-1}; c: 1×10^{-3} g mL^{-1}) and (d) fluorescence spectrum (excitation wavelength: 324 nm) of **1b** in $CHCl_3$.

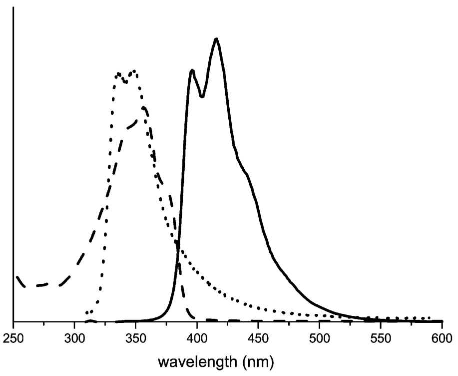


Fig. 2 Emission spectra (excitation wavelength: 300 nm) of **1c** (—), **4b** (···) and absorption spectrum of **3c** (**---**) in $CHCl_3$.

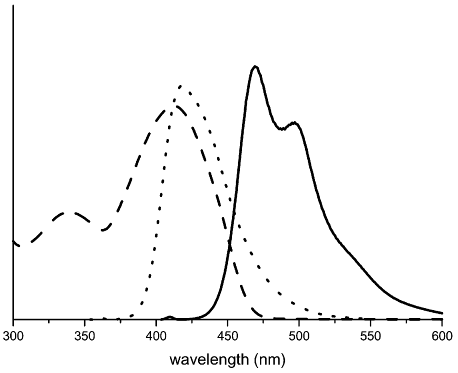


Fig. 3 Emission spectra (excitation wavelength: 360 nm) of **1d** (—), **4c** (···) and absorption spectrum of **3a** (**---**) in $CHCl_3$.

chromophore in **1d** was observed (Figs. 2 and 3). The emission profiles remained essentially unchanged with concentration (up to 100 fold) and with solvents (< 3 nm in benzene, $CHCl_3$, THF and EtOAc). Energy transfer therefore should occur within the polymer chain. Photoinduced charge transfer,[5] if any, would apparently play little role in these polymers.

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Notes and references

‡ All new compounds gave satisfactory spectroscopic and analytical data. The details are described in the ESI.†

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