

# Ladderphanes

# Excimer Formation in a Confined Space: Photophysics of Ladderphanes with Tetraarylethylene Linkers

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Dedicated to Professor Armin de Meijere on the occasion of his 75th birthday

**Abstract:** Communication between chromophores is vital for both natural and non-natural photophysical processes. Spatial confinements offer unique conditions to scrutinize such interactions. Polynorbornene- and polycyclobutenebased ladderphanes are ideal model compounds in which all tetraarylethylene (TAE) linkers are aligned coherently. The spans for each of the monomeric units in these ladderphanes are 4.5–5.5 Å. Monomers do not exhibit emission, because bond rotation in TAE can quench the excited-state energy. However, polymers emit at 493 nm ( $\Phi$ =0.015) with large Stokes shift under ambient conditions and exhibit dual emission at 450 and 493 nm at 150 K. When the temperature is lowered, the emission intensity at 450 nm increases, whereas that at 493 nm decreases. At 100 K, both monomers and polymers emit only at 450 nm. This shorter-wavelength emission arises from the intrinsic emission of TAE chromophore, and the emission at 493 nm could be attributed to the excimer emission in the confined space of ladderphanes. The fast kinetics suggest diffusion-controlled formation of the excimer.

# Introduction

Electronic communication between chromophores is crucial for artificial optoelectronic applications<sup>[1,2]</sup> and for natural photosynthesis systems.<sup>[3]</sup> Intrachain exciton and electron migrations between chromophores appended to a polymeric backbone<sup>[4-7]</sup> or associated in a supramolecular scaffold<sup>[8]</sup> have offered a powerful arsenal to understand various natural light-harvesting processes. The excitonic effect between chlorophylls has been proposed to rationalize extremely efficient energy- and electron-transfer processes in photosynthesis.<sup>[3]</sup> Relative orientation and distance among these photophysically active modules would influence the electronic delocalization and thus bulk materials properties.<sup>[9]</sup> The interactions between chromophores would be more efficient if they could be better aligned along the polymeric backbone. This consideration has led to substantial efforts in the design and syntheses of chromophore arrays within supramolecular structures that may provide a confined spatial environment. The paracyclophane framework has been demonstrated to bring two chromophores into close proximity

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201403806. so that electron delocalization between chromophores can readily take place.<sup>[10-12]</sup> Long-range charge-carrier transport and electronic coupling have been found in polynorbornene-based macromolecular arrays.<sup>[6]</sup> Excimer formation has been facilitated between two chromophores bridged by oligo-nucleotides,<sup>[13a]</sup> cyclodextrins,<sup>[13b]</sup> cyclohexasilanes,<sup>[13c]</sup> carbazol-phanes,<sup>[13d]</sup> and xanthenes.<sup>[13e]</sup>

We recently reported a new class of polynorbornene-based double-stranded ladderphanes.<sup>[7,14]</sup> This kind of polymer can also be considered as a linear array of cofacially arranged arenes in a polymer matrix. Depending on the nature of the polymeric backbones in 1, the spacing between arene linkers would be 5.5 Å for double-stranded polynorbornenes<sup>[15]</sup> and around 4.5 Å for polycyclobutene-based ladderphanes.<sup>[16]</sup> Significant perturbation of photophysical properties has been observed in these ladderphanes in comparison with those of corresponding monomers, although these distances are somewhat longer than those in typical  $\pi$ - $\pi$  interactions between aromatic layers, such as those in DNA molecules<sup>[17]</sup> and in graphite.<sup>[18]</sup> To illustrate this, the Soret band splitting with porphyrin linkers, excimer emission with diethynylene-terphenylene linkers, and fluorescence quenching with a range of oligoaryl linkers are frequently observed in 1.<sup>[14]</sup> However, when  $16-\pi$ -electron antiaromatic metallacycles are employed as linkers in 1, the photophysical and electrochemical properties of 1 remain unchanged in comparison with those of the corresponding monomer.<sup>[19]</sup> Since the linkers in 1 are connected to the polymeric backbones through a benzylic or an ester group, certain flexibilities might be expected. These experiments are carried out at ambient temperature, so that thermally induced mo-

Chem. Eur. J. 2015, 21, 800-807

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Scheme 1. a) Br<sub>2</sub>, 71%; b) [Pd(PPh<sub>3</sub>)<sub>4</sub>], K<sub>2</sub>CO<sub>3</sub>, **7**, 15%; c) LAH, 85%; d) **10a**: **8**b, DMAP, Et<sub>3</sub>N, 56%; **10b**: **9b**, DMAP, Et<sub>3</sub>N, 50%.

tions can take place to enable interactions between adjacent chromophores. It is envisioned that the photophysical behavior may be different if the molecular motion can be frozen at low temperature. In this regard, the intrinsic photophysical properties of individual chromophores in **1** might be observed.

The photophysics of tetraarylethylenes (TAEs) is rich and strongly influenced by the environment.<sup>[20]</sup> In particular, this class of conjugated systems exhibits aggregation-induced emission in metal–organic frameworks<sup>[21]</sup> and modified DNA strands.<sup>[22]</sup> It seems likely that some kinds of interactions between these chromophores might take place on aggregation. As mentioned above, the spacing between adjacent chromophores in ladderphanes **1** is around 4.5–5.5 Å. We therefore envisaged that incorporation of TAE moieties as linkers in **1** would offer a useful model to understand the photophysical behavior of the interactions between these chromophores. We now wish to report the synthesis and photophysical properties of ladderphanes **2a** and **2b** with TAE linkers.

# **Results and Discussion**

## **Synthesis**

Diarylethyne  $\mathbf{3}^{[23]}$  was prepared by Sonogashira reaction of methyl 4-bromobenzoate and methyl 4-ethynylbenzoate. With an excess of bromide ions, *trans* bromination of **3** took place to afford tetrasubstituted alkene **4** (Scheme 1),<sup>[24]</sup> the single-

crystal X-ray structure of which was determined to confirm the stereochemistry (Figure S1 in the Supporting Information).<sup>[25]</sup> A Suzuki–Miyaura cross-coupling reaction was utilized to afford tetraarylethene **5**. The benzoate groups in **5** were reduced by lithium aluminum hydride (LAH) to give **6**. Treatment of **6** with **8b** afforded the corresponding monomer **10a**. Cyclobutene analogue **10b** was prepared from **6** and **9b**. Ring-opening metathesis polymerization (ROMP) of **10a** with the first-generation Grubbs catalyst **12**<sup>[26]</sup> gave the corresponding polynorbornene-based ladderphanes with *E* double bonds **2a**. On treatment with **11**, *N*-arylpyrrolidine-fused cyclobutene derivative **10b** underwent ROMP stereoselectively to give **2b** with all double bonds in *Z*-configuration.<sup>[27]</sup>

## Photophysical properties of ladderphane 2 a

The absorption spectrum of monomer **10a** is essentially the sum of the absorptions of tetraarylethylene **6** and aminobenzoate **8c** (Figure 1).<sup>[25]</sup> Like other single- and double-stranded polynorbornenes,<sup>[7,14–16,19]</sup> the absorption due to the aminobenzoate chromophores in ladderphane **2a** ( $\lambda_{max}$ =314 nm) exhibited a hypsochromic shift in comparison with that of **10a** ( $\lambda_{max}$ =320 nm, Figure 1), which may be due to release of strain from the norbornene moiety.<sup>[28]</sup> On excitation at 350 nm, no emission was observed from solutions of **10a**, **6**, and **8c** in CH<sub>2</sub>Cl<sub>2</sub> (1.0×10<sup>-5</sup> to 1.0×10<sup>-3</sup> M). In contrast, **2a** showed emission at  $\lambda_{em}$ =493 nm in CH<sub>2</sub>Cl<sub>2</sub> with quantum yield of  $\Phi$ =1.5% (Figure 1, Table 1). This unusually large Stokes shift<sup>[25]</sup> suggests that the structure of the excited state could be very different from that of the ground state (Table 1).<sup>[29]</sup> In addition, the ab-



Figure 1. Absorption (black) and emission (gray) spectra of 10 a (solid), 2 a (dashes), 8 c (dots), and 6 (dash/dots) in  $CH_2CI_2$  at ambient temperature.

**Table 1.** Number-average molecular weight  $M_{n'}$  polydispersity index (PDI), and photophysical properties (absorption maximum  $\lambda_{max'}$  emission maximum  $\lambda_{em'}$  quantum yield  $\Phi$ , Stokes shift for TAE) of monomers and polymers measured at ambient temperature.

	<i>M</i> <sub>n</sub> (PDI) <sup>[a]</sup>	$\lambda_{\max}$ [nm]	$\lambda_{_{em}}$ [nm]	$\Phi$ [%]	[cm <sup>-1</sup> ]			
10a		320	_[b]					
10b		318	_ <sup>[b]</sup>					
2a	13 700 (1.23)	314	493	1.5	10770			
2b	11100 (1.20)	309	495	1.4	10850			
[a] Determined by GPC with polystyrene references. [b] There is no emission for $10a$ and $10b$ in $CH_2CI_2$ .								

sorption and emission spectra do not overlap. Several photophysical processes, such as fluorescence resonance energy transfer (FRET),<sup>[30]</sup> photoinduced electron transfer (PET),<sup>[31]</sup> and other bimolecular interactions,<sup>[29,32]</sup> might result in large Stokes shift between absorption and emission spectra. FRET would not take place with excitation wavelength at 350 nm in **2 a**, because no other chromophore has lower excited energy.<sup>[33]</sup> On the other hand, PET between the aminobenzoate moiety and an acceptor chromophore linker in ladderphanes might be possible if their frontier orbitals matched. In this regard, emission from the corresponding charge-separated state has been occasionally observed, and the wavelength of this emission was solvent-dependent.<sup>[14f,34]</sup> However, the emission profile of ladderphane **2a** remains unchanged in different solvents on excitation at 350 nm (Figure 2). These observations suggest that the characteristic emission in **2a** does not arise from the PET process.



Figure 2. Emission spectra of  ${\bf 2a}$  in  $Et_2O$  (solid),  $CHCl_3$  (dots), and  $CH_2Cl_2$  (dashes).

As mentioned above, the separation between adjacent linkers in polynorbornene-based ladderphanes is about 5.5 Å.<sup>[15]</sup> Because of the flexibility of the benzylic moiety and the ester groups, the adjacent linkers may be brought into closer proximity, and thus bimolecular interactions would take place. Photoinduced bimolecular interactions such as exciton coupling,<sup>[35]</sup> charge-transfer complex formation<sup>[36,37]</sup> and excimer or exciplex formation<sup>[13]</sup> are known to take place readily and result in perturbation of absorption and/or emission properties.<sup>[29,32]</sup> As shown in Figure 1, the absorption band of **2a** was only slightly different ( $\Delta\lambda = 6$  nm) from that of **10a**. These results suggest that neither exciton coupling nor charge-transfer complex formation between adjacent linkers would take place.

The adjacent TAE chromophores in polymeric ladderphanes **2a** are relatively rigid. Unlike monomer **10a**, in which rotation about aryl-aryl bonds can more freely take place, such rotation in **2a** would be more restricted. Since the TAE chromophores in **2a** are in close proximity, a dynamic excimer could readily be formed, and the excited-state energy would be released as fluorescence with a large Stokes shift.

## Variable-temperature emission spectra of ladderphane 2 a

The absorption and emission spectra of **6** and **10a** were measured at 100 K (Figure 3). As mentioned above, neither **6** nor **10a** exhibited observable emission at ambient temperature. However, strong emission at 450 nm in methyltetrahydrofuran (MTHF) at 100 K was observed for both **6** and **10a** (Figure 3). A



Figure 3. Absorption (black) and emission (gray) spectra of 6 (dash dot) and 10a (solid) at 100 K in MTHF.

significant spectral overlap between this low-temperature emission and the absorption of these small molecules indicates that this new low-temperature emission at shorter wavelength may arise from the intrinsic emission of the TAE chromophore. At ambient temperature, nonradiative torsional deactivation<sup>[38]</sup> of aryl moieties in **6** and **10a** may quench the excited-state energy in TAE chromophores and lead to disappearance of this intrinsic emission. This molecular motion would be significantly reduced at low temperatures, and the intrinsic emission might be turned on.

As shown in Figure 4, the emission intensity of 2a at 493 nm gradually increased from 298 to 150 K. The enhancement of the emission intensity may be due to decreased thermal quenching. Below 150 K, a new emission band at shorter wavelength gradually emerged. The emission maximum of 2a was shifted to 450 nm at 100 K, and the profile is similar to those of 6 and 10a under the same conditions. Apparently, dual emission occurs from 2a. The emission at 450 nm could be observed only at low temperature, whereas the emission at 493 nm became dominant at higher temperature. At higher temperature, the decrease in emission intensity at 450 nm for 2a followed the same trend as observed for monomers 6 and 10a. The thermal energy would enhance molecular motions, and thus bond rotation in TAE might quench the excited-state



**Figure 4.** Temperature-dependent emission spectra of **2a** at different temperatures in MTHF (298 K: black solid; 250 K: gray solid; 200 K: black dashes; 150 K: gray dashes; 140 K: black dots; 130 K: gray dots; 120 K: black dash/dots; 110 K: gray dash/dots; 100 K: black dash/dot/dots). Excitation wavelength: 350 nm.

energy. On the other hand, the flexibility of benzylic or ester groups in **2a** might also be increased due to increasing thermal energy. These phenomena would offer the opportunity for the adjacent TAE linker in **2b** to move into closer proximity, so that direct interaction between these chromophores might take place during this photophysical process. Therefore, at higher temperature, the emission at longer wavelength (493 nm) in **2a** might be considered to result from the formation of an excimer between TAE chromophores.

## **Kinetic measurements**

Time-resolved fluorescence spectroscopy with a femtosecond Ti:sapphire laser equipped with a streak camera was employed to determine the emission lifetimes of **2a** at various temperatures (Table 2). The observed excimer fluorescence decay life-

<b>Table 2.</b> Kinetic parameters of <b>2 a</b> : lifetimes $(\tau_{d1}, \tau_{d2'}, \text{and } \tau_r)$ and apparent rate constants $k_r$ at different temperatures.								
T [K]	$ au_{d1}{}^{[a]}$ [ns]	${\tau_{d2}}^{[c]}$ [ns]	$ au_{ m r}^{ m [a]}$ [ps]	$k_{\rm r}^{\rm [e]}  [10^9  {\rm s}^{-1}]$				
298	0.5	_[d]	_[d]					
200	1.0	_ <sup>[d]</sup>	_[d]					
150	1.8	0.4	104	9.62				
140	1.9	0.6	115	8.70				
130	2.0-10.0 <sup>[b]</sup>	1.0	172	5.81				
120	2.0-10.0 <sup>[b]</sup>	1.7	215	4.65				
100	2.0-10.0 <sup>[b]</sup>	2.0-10.0 <sup>[b]</sup>	_[d]					
[a] Detected at 520–540 nm. [b] The exact decay lifetimes could not be obtained due to instrumental limitations. [c] Detected at 440–460 nm. [d] No signal was detected. [e] The rate was estimated from $\tau_{\rm p}$								

times  $\tau_{d1}$  of **2a**, which were wavelength-independent, were 500 ps at 298 K and 1.0 ns at 200 K.<sup>[25]</sup> The increase of  $\tau_{d1}$  may be due to decreased thermal relaxation. When the temperature reached 150 K, on excitation, the features of the time-resolved fluorescence varied significantly with emission wavelength. Representative decay profiles are shown in Figure 5, and the details are described in the Supporting Information.<sup>[25]</sup> The fluorescence at 440-460 nm displays an instrument-limited rise followed by slow decay. However, the fluorescence at 520-540 nm shows a slow rise  $(\tau_r)$  followed by a slow decay from the excimer ( $\tau_{d1}$ ). These results suggested that at least two excited species were involved in 2a at 150 K, and this observation is consistent with the temperature-dependent emission spectra described above (Figure 4). The fluorescence decay  $\tau_{d2}$ at shorter wavelength (440-460 nm) may arise from the intrinsic emission of the TAE chromophore in **2a**. The lifetime  $\tau_{d1}$ , for the longer-wavelength (520-540 nm) emission of 2a at 150 K would be attributed to the excimer emission, in a manner similar to those described above for higher temperatures.

The  $\tau_r$  values gradually increase from 150 to 120 K (Table 2). These results suggest that  $\tau_r$  may be responsible for the formation of a dynamic excimer.<sup>[39]</sup> The estimated apparent rate constants  $k_r$  (=1/ $\tau_r$ ), including formation, dissociation, and decay

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**Figure 5.** Time-resolved fluorescence profiles of **2a** at 150 K with different detection wavelengths. a) 440–460 nm and b) 520–540 nm.

of the excimer in such processes, are listed in Table 2. When the temperature reached 100 K, the feature of the time-resolved fluorescence became independent of wavelength. This phenomenon indicates that excimer formation in **2a** would be significantly restricted, and these results are consistent with the observation in steady-state measurements, in which intrinsic emission becomes predominant.

# Polynorbornene- versus polycyclobutene-based ladderphanes

At ambient temperature, the photophysical properties of **2b**, including absorption and emission profiles as well as quantum yield, were almost same as those of **2a** (Table 1, Figure S3 of the Supporting Information).<sup>[25]</sup> The temperature-dependent emission spectra of **2b** also showed similar behavior to those of **2a** (Supporting Information, Figure S4),<sup>[25]</sup> whereby the emission maxima gradually shifted from 495 to 450 nm on lowering the temperature. The kinetic properties of **2b** were also measured at different temperatures. Basically, the kinetic parameters of **2b** were similar to those of **2a** except that the  $k_r$  values of **2b** were slightly larger than those of **2b** at 120–150 K (Figure 6). It seems likely that the formation of excimer could more readily occur for **2b** than that for **2a**, and such



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Figure 6. Rate constant versus temperature for 2a (squares) and 2b (circles).

a difference might arise from the shorter span of the polycyclobutene skeleton.

#### TAE excimer formation in ladderphanes

Interactions between two chromophores can be reflected by photophysical processes.<sup>[29]</sup> In general, if the chromophores are in close proximity, such interactions may lead to ground-state interactions between chromophores provoking the formation of a charge-transfer complex or exciton delocalization, which may result in the appearance of a new absorption and/or emission at longer wavelength, if allowed. Occasionally, vibronic structure may be observed in the emission profiles.<sup>[39,40]</sup> Alternatively, fluorescence quenching and shortening of lifetimes are frequently found in various systems. Indeed, a number of ladderphanes with different aromatic linkers are known to show such behavior.<sup>[14d,e]</sup> The third possibility is the formation of an excited dimer, which may exhibit a new structureless emission at longer wavelength.<sup>[29]</sup> In particular, if the chromophores are in a confined space, such as anthracene appended in polynorbornene,<sup>[41]</sup> terphenylene–diethynylenelinked ladderphane,<sup>[14d]</sup> and surface attachment of pyrene on porous silica,<sup>[42]</sup> excimer emissions are observed.

As mentioned above, neither TAE core **6** nor monomers **10a** and **10b** exhibit any emission at ambient temperature. However, polymers **2a** and **2b** show fluorescence at 493 nm with quantum yields of 0.015, and 0.014, respectively. It is noteworthy that there are no spectral overlaps between the absorption and emission profiles of these polymers. In other words, the Stokes shifts appear to be fairly large. Apparently, the induction of fluorescence from the TAE chromophore should be attributed to the confined space in polymeric ladderphanes. As described above, the span between two adjacent chromophores in **2a** and **2b** would be 5.5 and 4.5 Å, respectively, and the benzylic ester linking groups would be quite flexible. Consequently, electronic interaction between adjacent chromophores would be feasible. It seems likely that excimers would be readily formed in **2a** and **2b**.

# Conclusion

We have demonstrated the design and synthesis of polynorbornene- and polycyclobutene-based ladderphanes with TAE

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linkers. Structurally, the TAE chromophores are aligned cofacially with interchromophoric distances of about 4.5–5.5 Å. The photophysical behaviors of these polymers were examined in detail. In contrast to monomeric species containing the same chromophore, excimer emission is observed at ambient temperature in these polymers. At low temperatures (< 150 K), a new intrinsic emission gradually emerged and became predominant at 100 K. Note that, even in concentrated solution at ambient temperature, the TAE excimer was not observed for monomers **6**, **10a**, and **10b**. The confined space in ladderphanes offers a useful platform to facilitate these interchromophore interactions resulting in intriguing photophysical properties that would otherwise not be feasible. Our results may offer a possible pathway for aggregation-induced emission involving TAE chromophores.

# **Experimental Section**

# General

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian 400 Unity Plus (400 MHz) at ambient temperature. Samples for <sup>1</sup>H and <sup>13</sup>C NMR measurements were dissolved in CDCl<sub>3</sub> and CHCl<sub>3</sub>. Residual proton signals of the deuterated solvents were used as internal standard. The chemical shift of  $\rm CHCl_3$  was calibrated at  $\delta\!=\!7.26\,\rm ppm$  in <sup>1</sup>H NMR spectra and  $\delta$  = 77.0 ppm in <sup>13</sup>C NMR spectra. All <sup>13</sup>C NMR spectra were recorded with complete proton decoupling. High-resolution mass spectra were obtained with a Jeol JMS-700 mass spectrometer by using the FAB method in 3-nitrobenzyl alcohol matrix. Gel permeation chromatography (GPC) was performed on a Waters GPC instrument by using an isocratic HPLC pump (1515) and a refractive-index detector (2414). THF was used as eluent (flow rate 1 mLmin<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  $(M_{\rm p})$ 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 by using a spectrophotometer with an integrating sphere (Hamamatsu C9920-02).

# **Time-resolved fluorescence experiments**

Light from a mode-locked Ti:sapphire laser (repetition rate: 76 MHz; pulse width: <200 fs) was passed through an optical parametric amplifier to produce the desired wavelength. The fluorescence of the sample was reflected by a grating (150 grooves/mm; 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 in cuvet. The signal was collected ten times to decrease signal-to-noise ratio.

# Synthesis

(*E*)-1,2-Dibromo-bis(4'-methoxycarbonyl)stilbene (4): A solution of bromine in CCl<sub>4</sub> (1 M, 12 mL, 12 mmol) was added dropwise to a slurry of **3** (2.98 g, 10.0 mmol) in CCl<sub>4</sub> (50 mL) at 0 °C. The reaction mixture was stirred for 1 h and then added to 10% aqueous sodium sulfite (50 mL). After extraction with Et<sub>2</sub>O, the organic layer was collected, dried (MgSO<sub>4</sub>), and the solvent removed in vacuo. The residue was recrystallized from ethanol to give **4** as a white

solid (3.22 g, 71%). M.p. 211–212 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 3.95 (s, 6H), 7.60 (d, *J*=8.4 Hz, 4H), 8.11 (d, *J*=8.4 Hz, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$ =52.5, 117.4, 128.8, 129.4, 130.2, 144.1, 165.7 ppm; IR (KBr):  $\tilde{\nu}$ =3026, 2948, 2848, 1724, 1603, 1507, 1434, 1403, 1276, 1109, 1019, 857, 823 cm<sup>-1</sup>.

## (E)-1,2-Bis(4-hexyloxyphenyl)-bis(4'-methoxycarbonyl)stilbene

(5): Under N<sub>2</sub>, a mixture of 2-(4-hexyloxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.28 g, 7.5 mmol), 4 (0.88 g, 3 mmol),  $Pd(PPh_{3})_{4}$  (30.0 mg,  $2.6 \times 10^{-2}$  mmol), and TBAB (0.10 g, 0.3 mmol) in toluene (30 mL) was mixed with  $K_2CO_3$  solution (2 m, 8 mL) and the mixture was heated to 90 °C for 24 h. The mixture was then poured into water (50 mL) and extracted with EtOAc (50 mL $\times$ 2). The combined organic layer was washed with brine (100 mL) and water (100 mL) and dried (MgSO<sub>4</sub>). The solvent was removed in vacuo to give a residue, which was purified by chromatography on silica gel (hexane/CH<sub>2</sub>Cl<sub>2</sub>, 2/1) to give **5** as a yellow solid (0.29 g, 15%). M.p. 102–103 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ =0.92 (t, J= 7.0 Hz, 6H), 1.30-1.50 (m, 16H), 1.70-1.80 (m, 4H), 3.87 (s, 6H), 3.90 (t, J=7.0 Hz, 4H), 6.66 (d, J=8.8 Hz, 4H), 6.90 (d, J=8.8 Hz, 4 H), 7.07 (d, J = 8.4 Hz, 4 H), 7.74 ppm (d, J = 8.4 Hz, 4 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 14.2$ , 22.7, 25.8, 29.3, 31.7, 52.0, 67.9, 113.7, 127.9, 128.9, 131.2, 132.3, 134.9, 139.9, 148.6, 157.8, 166.7 ppm; IR (KBr):  $\tilde{\nu} = 3035$ , 2928, 2856, 1723, 1603, 1506, 1434, 1276, 1244, 1176, 1103, 937, 833, 759 cm<sup>-1</sup>; HRMS (FAB): *m/z* calcd for C<sub>42</sub>H<sub>48</sub>O<sub>6</sub>: 648.3451; found: 648.3475.

(E)-1,2-Bis(4-hexyloxyphenyl)-bis(4'-hydroxymethyl)stilbene (6): Compound 5 (0.32 g, 0.5 mmol) was added to LAH (40 mg, 1.0 mmol) in Et<sub>2</sub>O (10 mL) at 0  $^{\circ}$ C under N<sub>2</sub>. The reaction mixture was stirred at RT for 4 h and quenched with water (1 mL).  $Et_2O$ (20 mL) was then added and the mixture was washed with brine (50 mL) and water (50 mL) and dried (NaSO<sub>4</sub>). The solvent was removed in vacuo to give a residue, which was purified by chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/EtOAc, 10/1) to give 6 as a white solid (0.27 g,90%). M.p. 178–179  $^{\circ}$ C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta =$ 0.92 (t, J=7.0 Hz, 6H), 1.30-1.50 (m, 16H), 1.70-1.80 (m, 4H), 3.89 (t, J = 6.6 Hz, 4H), 4.59 (s, 4H), 6.63 (d, J = 8.8 Hz, 4H), 6.91 (d, J =8.8 Hz, 4H), 6.97 (d, J=8.4 Hz, 4H), 7.08 ppm (d, J=8.4 Hz, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 14.2, 22.7, 25.9, 29.4, 31.7, 65.2, 67.8, 113.5, 126.2, 131.5, 132.3, 136.0, 138.4, 139.2, 143.6, 157.4 ppm; IR (KBr):  $\tilde{\nu} = 3229$ , 3041, 2926, 2862, 1604, 1507, 1466, 1439, 1410, 1239, 1172, 1110, 1014, 965, 825 cm<sup>-1</sup>; HRMS (FAB): *m/z* calcd for C<sub>40</sub>H<sub>48</sub>O<sub>4</sub>: 592.3552; found: 592.3567.

Monomer 10a: Compound 8b [freshly prepared from the corresponding carboxylic acid 8a (0.15 g, 0.60 mmol) and (COCl)<sub>2</sub>  $(0.1 \text{ mL}, d = 1.5 \text{ g mL}^{-1}, 1.20 \text{ mmol})]$  in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added to a stirred solution containing 6 (0.15 g, 0.25 mmol), 4-dimethylaminopyridine (one crystal), and  $Et_3N$  (1 mL) in  $CH_2Cl_2$  (15 mL) at 0 °C. The mixture was stirred at RT overnight. CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was then added and the mixture was washed with saturated NaHCO3 (30 mL) and water. The organic layer was dried (MgSO<sub>4</sub>). After filtration, the solvent was evaporated in vacuo to give a residue, which was purified by chromatography on Et<sub>3</sub>N-treated silica gel (hexane/ CH<sub>2</sub>Cl<sub>2</sub>, 1/1) to afford 10a as white solid (0.15 g, 56%). M.p. 119-120 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 0.92$  (t, J = 6.6 Hz, 6H), 1.30– 1.50 (m, 16H), 1.53 (d, J=7.8 Hz, 2H), 1.63 (d, J=7.8 Hz, 2H), 1.70-1.80 (m, 4H), 2.92-3.05 (m, 8H), 3.05-3.12 (m, 4H), 3.25-3.35 (m, 4 H), 3.89 (t, J = 6.4 Hz, 4 H), 5.22 (s, 4 H), 6.12 (s, 4 H), 6.37 (d, J =8.4 Hz, 4H), 6.64 (d, J=8.4 Hz, 4H), 6.93 (d, J=8.4 Hz, 4H), 7.01 (d, J=8.0 Hz, 4H), 7.14 (d, J=8.0 Hz, 4H), 7.88 ppm (d, J=8.4 Hz, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 14.2, 22.7, 25.8, 29.4, 31.7, 45.4, 46.7, 50.5, 52.1, 65.6, 67.8, 110.8, 113.5, 116.1, 126.9, 131.2, 131.3 132.3, 134.5, 135.6, 136.0, 139.2, 143.6, 150.2, 157.3, 166.6 ppm; IR (KBr):  $\tilde{\nu}\!=\!3055,\;2928,\;2850,\;1756,\;1700,\;1603,\;1508,\;1472,\;1377,\;1271,$ 

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1242, 1176, 1098, 1014, 972, 826 cm $^{-1}$ ; HRMS (FAB): m/z calcd for  $C_{72}H_{79}N_2O_6$  [ $M\!+\!H$ ]: 1067.5938; found: 1067.5978.

Monomer 10b: Compound 9b [freshly prepared from the corresponding carboxylic acid **9a** (0.14 g, 0.60 mmol) and (COCl)<sub>2</sub>  $(0.1 \text{ mL}, d = 1.5 \text{ g mL}^{-1}, 1.20 \text{ mmol})]$  in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added to a stirred solution consisting of 6 (0.15 g, 0.25 mmol), DMAP (one crystal), Et\_3N (1 mL), and CH\_2Cl\_2 (15 mL) at 0  $^\circ\text{C}.$  The mixture was stirred at RT overnight. CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was then added and the mixture was washed with saturated NaHCO<sub>3</sub> (30 mL) and water. The organic layer was dried (MgSO<sub>4</sub>). After filtration, the solvent was evaporated in vacuo to give a residue, which was purified by chromatography on Et<sub>3</sub>N-treated silica gel (hexane/CH<sub>2</sub>Cl<sub>2</sub>, 1/1) to afford **10b** as white solid (0.12 g, 50%). M.p. 123–124°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 0.92$  (t, J = 7.0 Hz, 6H), 1.30–1.50 (m, 16H), 1.70-1.80 (m, 4H), 2.93 (dd, J=10.6, 6.4 Hz, 4H), 3.55 (d, J=6.4 Hz, 4H), 3.65 (d, J=10.6 Hz, 4H), 3.89 (t, J=6.4 Hz, 4H), 5.23 (s, 4H), 6.14 (s, 4H), 6.62 (d, J=8.8 Hz, 4H), 6.64 (d, J=8.4 Hz, 4H), 6.93 (d, J=8.8 Hz, 4H), 7.01 (d, J=8.4 Hz, 4H), 7.15 (d, J=8.4 Hz, 4H), 7.91 ppm (d, J = 8.4 Hz, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 14.2$ , 22.7, 25.9, 29.4, 31.7, 46.5, 48.9, 65.7, 67.8, 112.0, 113.5, 117.4, 127.0, 131.2, 131.3, 132.4, 134.3, 136.0, 139.2, 143.7, 153.1, 157.3, 166.5 ppm; IR (KBr):  $\tilde{\nu} = 3056$ , 2928, 2851, 1758, 1701, 1603, 1523, 1509, 1473, 1378, 1272, 1242, 1177, 1098, 1014, 972, 826 cm<sup>-1</sup>; HRMS (FAB): m/z calcd for  $C_{66}H_{71}N_2O_6$  [*M*+H]: 987.5312; found: 987.5339.

**Polymer 2a:** A solution of **12** (6.5 mg,  $8.0 \times 10^{-3}$  mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) was added to a solution of **10a** (43 mg,  $4 \times 10^{-2}$  mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL). The reaction mixture was stirred for 2 h at RT, after which ethyl vinyl ether (0.1 mL) was added and the mixture was stirred for 10 min. The mixture was concentrated and the residual solution was added to MeOH (15 mL). The precipitate was collected, rinsed with MeOH, and dried in vacuo to give **2a** as a pale gray powder (40 mg, 93%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 0.85-0.95$  (br, 6H), 1.20–2.50 (br, 24 H), 2.60–3.50 (br, 16 H), 3.80–4.00 (br, 4H), 5.00–5.60 (br, 8 H), 6.40–6.70 (br, 8 H), 6.80–7.20 (br, 12 H), 7.80–8.05 ppm (br, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 15.7$ , 22.6, 25.7, 29.3, 31.6, 39.2, 45.1, 46.9, 49.2, 49.9, 65.4, 67.8, 111.4, 113.6, 117.0, 126.1, 126.5, 128.6, 131.4, 132.5, 134.5, 136.4, 139.3, 143.7, 150.9, 157.5, 166.7 ppm; GPC:  $M_n = 13700$  (PDI=1.23).

**Polymer 2b.** In a manner similar to that described above for **2a**, reaction of **10b** (39 mg,  $4 \times 10^{-2}$  mmol) and **11** (6.8 mg,  $8 \times 10^{-3}$  mmol) yielded **2b** as a pale gray powder (35 mg, 91%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 0.80-1.00$  (br, 6H), 1.20–1.55 (br, 12H), 1.65–1.80 (br, 4H), 3.00–3.70 (br, 12H), 3.80–3.95 (br, 4H), 5.10–5.30 (br, 4H), 5.50–5.85 (br, 4H), 6.30–6.70 (br, 8H), 6.80–7.20 (br, 12H), 7.80–8.05 ppm (br, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 14.2$ , 22.7, 25.9, 29.4, 31.7, 40.7, 53.8, 65.8, 67.8, 110.5, 113.5, 117.4, 125.8, 126.8, 128.1, 131.4, 132.3, 133.9, 136.4, 139.1, 143.7, 150.0, 157.3, 166.3 ppm; GPC: *M*<sub>n</sub> = 11100 (PDI = 1.20).

# Acknowledgements

This work was supported by the Ministry of Science and Technology of the Republic of China and the National Taiwan University. We thank Professor Huan-Cheng Chang for allowing us to use their femtosecond laser facilities for kinetic measurements.

**Keywords:** confinement · excimers · ladderphanes · photophysics · ring-opening polymerization

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Received: June 4, 2014 Published online on October 24, 2014

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