

Bis-Phosphoryl-Bridged Stilbenes Synthesized by an Intramolecular Cascade Cyclization

Aiko Fukazawa,[†] Masanao Hara,[†] Toshihiro Okamoto,[†] Eun-Cheol Son,[‡] Caihong Xu,[§] Kohei Tamao,^{‡,||} and Shigehiro Yamaguchi^{*,†,§}

Department of Chemistry, Graduate School of Science, Nagoya University, and SORST, Japan Science and Technology Agency (JST), Chikusa, Nagoya 464-8602, Japan, and Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

yamaguchi@chem.nagoya-u.ac.jp

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ABSTRACT



Bis-phosphoryl-bridged stilbenes have been synthesized using an intramolecular cascade cyclization. They show intense blue fluorescences at longer wavelengths with higher quantum yields compared to those of the known element-bridged stilbenes. In addition, they have much lower reduction potentials due to the inductive effect of phosphoryl groups. The incorporation of the phosphoryl moiety is an effective way for the construction of highly electron-accepting π -conjugated systems.

Ladder-type π -conjugated molecules having fully ring-fused structure represent an important class of fundamental materials in the current organic electronics.¹ Their rigid coplanar frameworks endow them with a set of superior properties, such as an intense luminescence and a high charge carrier mobility. For further design to modulate their inherent electronic and structural characteristics, one promising way is the incorporation of main group elements into the ladder framework.² A series of ladder molecules with various elements, such as B,³ Si,⁴ N,⁵ and S,^{6,7} have been synthesized,

some of which indeed show a high performance in organic light-emitting diodes and transistors. Among the elements, the incorporation of phosphorus atoms is of particular interest, because of the facile functionalization of the phosphorus atom, that is, oxidation to phosphine oxides or sulfides, or complexation with Lewis acids or transition

[†] Nagoya University.

[‡] Kyoto University.

[§] JST.

^{||} Present address: RIKEN, 2–1 Hirosawa, Wako, Saitama 351–0198, Japan.

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metals, which allows the electronic and thus properties tuning. This advantage has been well demonstrated in various π -conjugated systems consisting of phosphole,⁸ dibenzophosphole,⁹ or dithienophosphole¹⁰ as a building unit. Among the phosphole skeletons, we now focus our attention on the oxidized form, phosphole oxide, and designed bis-phosphoryl (P(=O)R)-bridged stilbenes **1** (Figure 1) as a new entity of

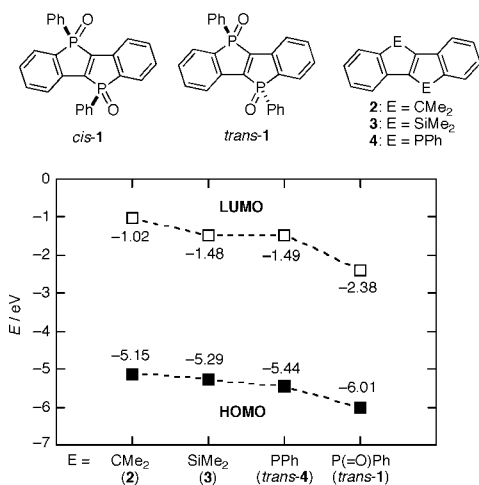


Figure 1. Kohn–Sham HOMO and LUMO energy levels of bridged stilbenes based on the calculations at the B3LYP/6-31G(d) level.

the ladder materials. In this skeleton, a fused phospholo[3,2-*b*]phosphole dioxide substructure would provide several attractive features. First, the double substitution with the strong electron-withdrawing phosphoryl group would lower the LUMO level and provides a highly electron-accepting nature. According to the molecular orbital calculations (Figure 1), the bis-phosphoryl-bridged stilbene **1** has the lowest-lying LUMO among a series of bridged stilbenes having carbon (**2**), silicon (**3**), and phosphorus (**4**) bridges. Second, the incorporation of two phosphoryl bridges gives rise to two geometrical isomers with respect to the directions of the P=O bonds, which would be different from each other

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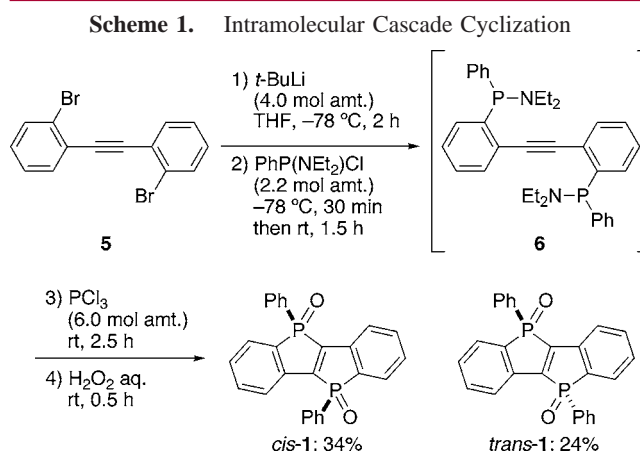
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in terms of dipole moment. Third, the high chemical stability of the phosphoryl functionality affords facile handling as a stable material. Herein we report the efficient synthesis of the bis-phosphoryl-bridged stilbenes based on a new intramolecular cascade cyclization. Throughout the study of their fundamental properties, we also show the potential utility of this skeleton as a building unit for π -electron materials.

Our new cyclization employs a simple bis(2-bromophenyl)acetylene **5** as the starting material and comprises of four-step sequential procedures, as shown in Scheme 1. Thus,

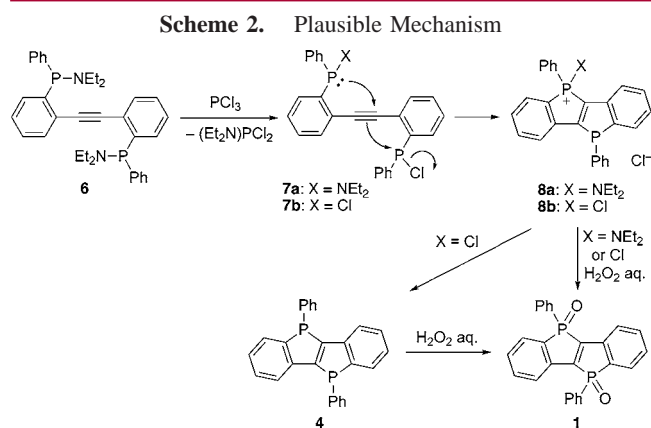


compound **5** was first dilithiated with *t*-BuLi in THF, followed by treatment with PhP(NEt₂)Cl to produce bis-(aminophosphanyl) derivative **6** *in situ*. An excess amount of PCl₃ (6 mol amounts) was then added to the reaction mixture at room temperature. The final step was the oxidation with H₂O₂, which afforded the bis-phosphoryl-bridged stilbenes **1** as a mixture of *cis* and *trans* isomers. Notably, these isomers could be easily separated from each other by silica gel column chromatography, due to the significant difference in their polarity, and were obtained in 34 and 24% yields, respectively. Their structures were verified by NMR spectroscopy as well as mass spectrometry and finally by X-ray crystallographic analyses.¹¹ For this cyclization, the addition of excess PCl₃ is crucial. Decreasing the amount of PCl₃ as well as the replacement with HCl resulted in much lower yields.

A plausible mechanism for the cyclization is shown in Scheme 2. Because the bis(aminophosphanyl) intermediate **6** does not undergo cyclization at ambient temperature, the initial step is likely the chlorination of one or both amino groups with PCl₃. The ³¹P NMR spectrum of the reaction mixture indeed confirms the formation of (Et₂N)PCl₂. In the produced **7a** or **7b**, one phosphanyl group acts as a nucleophile¹² and the other acts as an electrophile, and a nucleophilic cascade cyclization proceeds to produce a doubly cyclized phosphonium intermediate **8a** or **8b**. Butters and Winter reported a similar monocyclization from 2-(amino-

(11) See Supporting Information for detail.

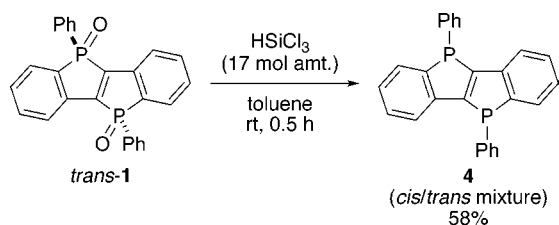
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phosphanyl)phenylacetylene mediated by treatment with HCl, which gives the corresponding benzophosphole.¹³ Notably, whereas their monocyclization required harsh condition (heating at 90 °C in neat condition), our double cyclization proceeds smoothly even at room temperature. These results demonstrate that the presence of two phosphanyl groups facilitates the cyclization and reflects the ambiphilic nature of the chloro-substituted phosphanyl group. Finally, the direct oxidation of **8** with H₂O₂ or a stepwise elimination-oxidation process via **4**¹⁴ gives the bis-phosphoryl-bridged stilbenes **1**.

Bis-phosphanyl-bridged stilbene **4** was also prepared for the sake of comparison with **1**, as shown in Scheme 3. Thus,

Scheme 3. Synthesis of Bis-Phosphanyl-Bridged Stilbene 4



the reduction of the pure *trans* isomer of **1** with an excess amount of HSiCl₃ afforded **4** in 58% yield as a mixture of *cis* and *trans* isomers.¹⁵ All attempts to separate these isomers from each other by chromatography failed due to their negligible difference in polarity.

UV–vis absorption and fluorescence spectra of the bis-phosphoryl-bridged stilbenes *cis*- and *trans*-**1** are shown in Figure 2. Their photophysical data are summarized in Table 1, together with those of carbon- (**2**), silicon- (**3**), and phosphanyl-bridged stilbenes (**4**),¹⁶ and fused phosphole oxides (dibenzophosphole oxides **9** and dithienophosphole oxide **10**) for comparison. Several features are summarized

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(14) The formation of *cis*- and *trans*-**4** as the intermediates was confirmed by the ³¹P NMR spectrum of the reaction mixture.

(15) The ratio of two isomers was found to be 1/1.1, which was estimated by the integral ratio of the ¹H NMR and ³¹P NMR spectra.

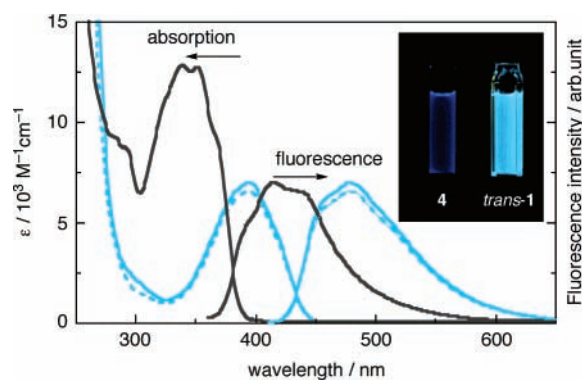


Figure 2. UV–vis absorption and fluorescence spectra of *cis*-**1** (blue broken line), *trans*-**1** (blue solid line), and **4** (black solid line) in CH₂Cl₂ at rt. The photographs of **4** and *trans*-**1** under irradiation of a black light at 365 nm are given in inset.

as follows: (1) In the UV–visible absorption spectra, both *cis*- and *trans*-**1** have absorption maxima at 395 nm, which are the longest wavelengths among those of the bridged stilbenes. Notably, the absorption spectra of the *cis* and *trans* isomers are almost identical to each other. This indicates that the configuration of the phosphoryl group does not affect the absorption properties.¹⁶ In addition, λ_{abs} of the bis-phosphoryl-bridged stilbenes **1** are significantly red-shifted compared to those of the known diaryl-fused phosphole oxides **9** and **10** due to the effective extension of the π -conjugation. (2) The bis-phosphoryl-bridged stilbenes **1** exhibit intense blue emissions with the fluorescence quantum yield Φ_{F} of almost unity, whereas they have large Stokes shifts of 85 nm (4500 cm⁻¹). This is in contrast to the faint fluorescence of the phosphanyl counterpart **4** ($\Phi_{\text{F}} = 0.07$). It is also noteworthy that the λ_{em} of **1** is more than 110 nm longer than that of the carbon analogue **2**, demonstrating the considerable effect of the phosphoryl groups. The Φ_{F} values of *cis*- and *trans*-**1** are extremely higher even compared to

Table 1. Photophysical Data for the Bridged Stilbenes and Related Compounds

compd	UV–vis absorption		fluorescence		
	λ_{abs}^a (nm)	$\epsilon/10^3$ (M ⁻¹ cm ⁻¹)	λ_{em}^b (nm)	Φ_{F}	τ_{s}^c (ns)
<i>cis</i> - 1 ^e	395	6.60	480	0.99 ^d	15.7
<i>trans</i> - 1 ^e	395	6.92	480	0.98 ^d	15.7
2 ^{f,g}	322	28.2	367	0.92	1.6
3 ^{f,g}	360	12.0	426	0.58	5.5
4 ^{e,h}	351	13	415	0.07 ^d	1.4, 9.8
9 ^{e,i}	332	3.01	366	0.042	–
10 ^{e,j}	366	2.14	453	0.57	–

^a Only the longest absorption maxima are shown. ^b Emission maxima upon excitation at the absorption maximum wavelengths. ^c Fluorescence lifetimes within ± 0.5 ns error. ^d Absolute fluorescence quantum yields determined by a calibrated integrating sphere system within $\pm 3\%$ errors. ^e In CH₂Cl₂. ^f In THF. ^g Ref 4a. ^h Mixture of *cis* and *trans* isomers. ⁱ Ref 9b. ^j Ref 10a.

those of the hitherto known phosphole oxide derivatives.^{8–10}
 (3) Both *cis*- and *trans*-**1** have fluorescence lifetime τ_s of 15.7 ns, which is significantly longer than those of **2–4**. Figure 3 shows a comparison of the radiative rate constant

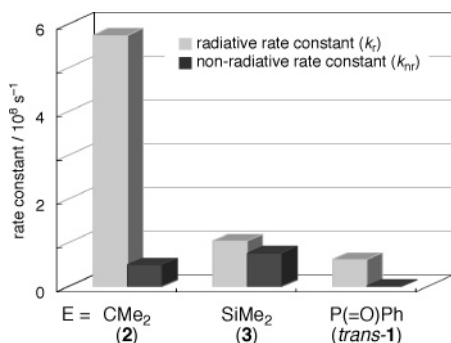
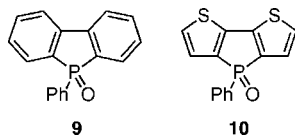


Figure 3. Comparison of radiative rate constant (k_r) and non-radiative rate constant (k_{nr}) among various element-bridged stilbenes in solutions. Rate constants were calculated with Φ_F and τ_s according to the formula of $k_r = \Phi_F/\tau_s$ and $k_{nr} = (1-\Phi_F)/\tau_s$.

k_r and nonradiative rate constant k_{nr} , calculated from Φ_F and τ_s , for the series of bridged stilbenes. Two trends are noted. First, the replacement of the bridging element from carbon to the heavier main group element, such as silicon or phosphorus, causes a dramatic decrease in the k_r value (5.8×10^8 , 1.1×10^8 , and $6.2 \times 10^7 \text{ s}^{-1}$ for **2**, **3**, and *trans*-**1**, respectively). This trend is consistent with a decrease in the oscillator strength for the lowest-energy transition, which is confirmed by the TD-DFT calculations.¹¹ Second, the bis-phosphoryl-bridged derivatives **1** also have extremely smaller nonradiative rate constant k_{nr} ($1.3 \times 10^6 \text{ s}^{-1}$) compared to other derivatives such as **2** ($5.0 \times 10^7 \text{ s}^{-1}$) and **3** ($7.6 \times 10^7 \text{ s}^{-1}$). The phosphoryl-bridge significantly impedes the non-radiative decay process, despite the large Stokes shift.



We also evaluated the electrochemical properties of the bis-phosphoryl-bridged stilbenes **1** by means of cyclic voltammetry. The cyclic voltammograms of *cis*- and *trans*-**1** and carbon-bridged stilbene **2** are shown in Figure 4. The *cis*- and *trans*-isomers of bis-phosphoryl-bridged stilbenes

(16) TD-DFT calculations for compounds **1** and **4** demonstrated that the transition energies for the lowest-energy excited state are nearly identical to each other between the *cis* and *trans* isomers. See Supporting Information for detail.

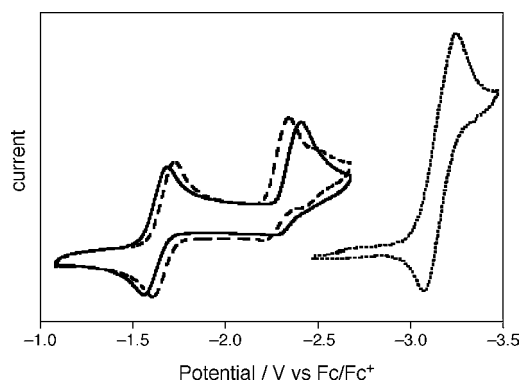


Figure 4. Cyclic voltammograms of *cis*-**1** (solid line), *trans*-**1** (broken line), and **2** (dotted line) in THF (1 mM) containing $\text{Bu}_4\text{N}^+\text{PF}_6^-$ (0.1 M) with a scan rate of 50 mV s^{-1} .

1 show the first reversible reduction waves with reduction potentials of -1.63 and -1.67 V (vs Fc/Fc^+) and the second irreversible reduction waves with peak potentials of -2.14 and -2.35 V , respectively. The first reduction potentials of the bis-phosphoryl-bridged stilbenes **1** are approximately 1.5 V more positive compared to that of the carbon-bridged one **2** (-3.17 V). These observations demonstrate that the phosphoryl-bridges substantially alter the nature of the stilbene to be highly electron-accepting. These results are consistent with the results of the molecular orbital calculations as shown in Figure 1.

In summary, the bis-phosphoryl-bridged stilbenes **1**, efficiently synthesized by a newly developed intramolecular cascade cyclization, show unusual photophysical properties as well as a high electron-accepting ability, which are totally different from the known bridged stilbenes. These results demonstrate not only the potential utility of this skeleton as a building unit but also the effectiveness of the incorporation of the phosphoryl moiety for construction of highly electron-accepting π -conjugated systems. Further study of the synthesis of a variety of phosphoryl-bridged ladder molecules based on the present methodology is now in progress.

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Supporting Information Available: Experimental details, spectral data for all new compounds, crystallographic data, and ORTEP drawings of *cis*- and *trans*-**1**, photophysical data, electrochemical data, and results of theoretical calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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