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Photochromic Phospholes

Tunable Photochromism in Air-Stable, Robust Dithienylethene-Containing Phospholes through Modifications at the Phosphorus Center**

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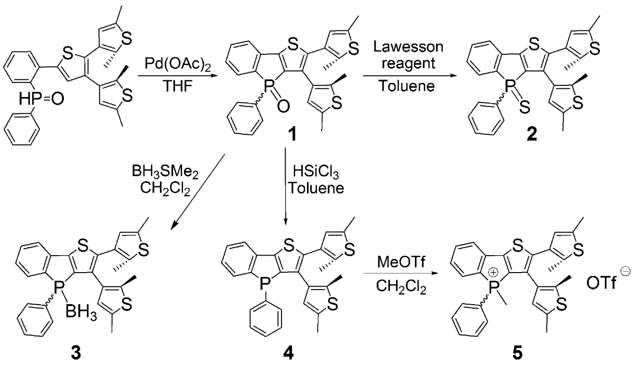
Research on photochromic diarylethene compounds has received much attention in the past two decades because of their excellent thermal reversibility, fatigue resistance, distinguishable absorption spectra of the open form and the closed form, and possible future applications including optical memory storage systems and photoswitchable molecular devices.[1] Recently, there has been substantial effort to functionalize photochromic diarylethenes to tune the electronic absorption properties and photochromic behavior, by using different aromatic systems or metal coordination.[2–4]

On the other hand, there has been an increasing interest in the study of phosphole-containing materials due to their capability to serve as organic light-emitting diodes (OLEDs) and electron transport materials in organic devices.[5–7] The trivalent phosphorus center in the phosphole adopts a pyramidal geometry and the lone pair of phosphorus displays a high degree of s character, which cannot be efficiently delocalized in the butadiene moiety of the phosphole.[5,8] So it provides a reactive phosphorus center that can be functionalized by various chemical modifications.[9–11] Since the phosphole system exhibits a unique electronic structure resulting from the interaction between the endocyclic π system of the conjugated 1,3-diene and the exocyclic P–R σ bond,[5] the electronic properties of the phosphole can be readily tuned, leading to a significant change in the photophysical properties. Such effective tuning by simple modification is less readily attainable in other non-phosphole-containing organic systems. As an extension of our continuing interests in designing various functionalized photochromic materials and in tuning the photochromism,[2] we hypothesized that, by utilizing this unique characteristic of phospholes, the electrochemistry, photophysics, and photochromism of the diarylethenes could be controlled through the rational design of the phosphole moiety without tedious modification of the diarylethene framework. To the best of our knowledge, although phosphole-containing materials have attracted growing interest and have been studied by a number of groups,[5–7,9–11] the integration of the phosphole moiety in the photochromic dithienylethene backbone has not been reported. Herein, we report the syntheses and photochromic properties of a series of dithienylethene-containing phospholes.

The target compounds were prepared as shown in Scheme 1. Phenyl{2-[2,2″,5,5″-tetramethyl(3,2′:3′,3″-terthiophen)-5′-yl]phenyl}phosphine oxide was synthesized by the Suzuki cross-coupling reaction[12] of 4,4,5,5-tetramethyl-2-[2,2″,5,5″-tetramethyl(3,2′:3′,3″-terthiophen)-5′-yl]-1,3,2-dioxaborolane[2i] and 1,2-dibromobenzene, followed by lithiation and reaction with $PhPCl_2$ to afford the hydrophosphine oxide according to modification of a literature method.[13] Finally, air-stable phosphole oxide was obtained by dehydrogenation in the presence of a catalytic amount of palladium(II) acetate in THF.[13] Further functionalization afforded compounds **2**–**5**.[9–11] All compounds have been characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, mass spectrometry, and elemental analysis. The $^{31}P\{^1H\}$ NMR signals of **1**–**5** are found



Scheme 1. Synthesis of **1**–**5**.

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at $\delta = 26.0$, 33.4, 21.6, -15.6, and 18.2 ppm, respectively, values typical of the corresponding phosphole derivatives.[5–7,9–11] The ^{11}B NMR signal at $\delta = -36.1$ ppm was further indicative of the formation of **3**.[9]

Single crystals suitable for X-ray crystallography were obtained for **1**, **2**, and **5**. The crystals selected for structure determination contain both enantiomers and are racemic mixtures, as shown in the packing diagram (Figures S1 and S2), suggesting that the reactions are not stereospecific. In addition, different conformations with respect to the orientation of the two peripheral thiophene rings were found for the compounds. For **1** and **2**, the two peripheral thiophene rings are arranged in an antiparallel configuration (Figure S3), while they are in a parallel configuration for **5** (Figure 1).

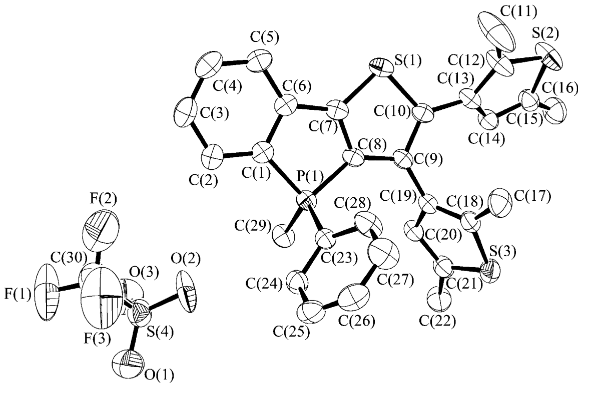

Figure 1. Perspective view of one enantiomer of **5** with atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

Crystal and structure determination data, selected bond lengths and angles, and intermolecular parameters are summarized in Tables S1–S3, respectively. As shown in Figure 1 and Figure S3, each phosphorus center adopts a distorted tetrahedral geometry with a small endocyclic C(1)–P(1)–C(8) angle in the range of 91.90–93.73°.[14] The endocyclic P–C bonds [P(1)–C(1) = 1.795(4) Å and P(1)–C(8) = 1.776(4) Å] in phosphonium compound **5** are shorter than those for the phosphorus oxide **1** and sulfide **2**, which is due to the cationic nature of the phosphorus center (Figure 1). The interplanar distance between molecules of the compounds is around 3.5 Å (Figures S1 and S2), indicating that weak π–π stacking interactions are present in the solid state.

Compound **4** shows an irreversible oxidation wave at +1.22 V vs. SCE, but no reduction wave was observed within the solvent window in THF. Compared with **4**, the σ^4-phosphole derivatives **1**–**3** and **5** show anodic shifts varying from +1.36 to +1.67 V vs. SCE for the first oxidation (Figure S4 and Table S4), attributed to the increase in electron deficiency of the phosphorus center. More importantly, the σ^4-phosphole compounds **1**–**3** show one quasi-reversible reduction couple in THF from -1.79 V to -1.96 V vs. SCE. The phosphonium compound **5** shows two less negative reduction waves at -1.33 and -1.77 V vs. SCE, probably due to the stronger electron-accepting ability of the phosphorus center arising from the presence of the cationic charge. Thus the first irreversible oxidation of **1**–**5** has been assigned to the oxidation of the aryl-fused phosphole, which is probably mixed with some peripheral thiophene character, while the reduction for the σ^4-phosphole compounds is mainly localized on the aryl-fused phosphole (vide infra).

All compounds were found to dissolve in benzene to give colorless to pale yellow solutions. In general, the electronic absorption spectra of **1**–**5** in benzene at 298 K show intense absorption bands at about 304–376 nm. The photophysical data of the compounds are summarized in Table S5 and the corresponding electronic absorption spectra are depicted in Figure 2a. Compared with σ^3-phosphole compounds, the neutral σ^4-phosphole derivatives **1**–**3** exhibit a red shift in the lower-energy absorption band, in which the oxide **1** and sulfide **2** show a comparable shift. A larger bathochromic shift was observed for the cationic σ^4-phosphole compound **5**, which is in line with other earlier studies.[9,10] The red shift is attributed to the increase in the electron-accepting ability of the phosphorus center which reduces both the HOMO and LUMO energy levels, with the LUMO being lowered to a greater extent (vide infra). Upon photoexcitation at room temperature, **1**–**5** in benzene solution display intense blue to yellow luminescence at about 415–507 nm (Figure 2b).[15] The effect of the phosphorus moiety on the emission maxima is similar to the trend observed in the electronic absorption studies. The luminescence quantum yields of the compounds are found to vary from 0.005 to 0.359 (Table 1).

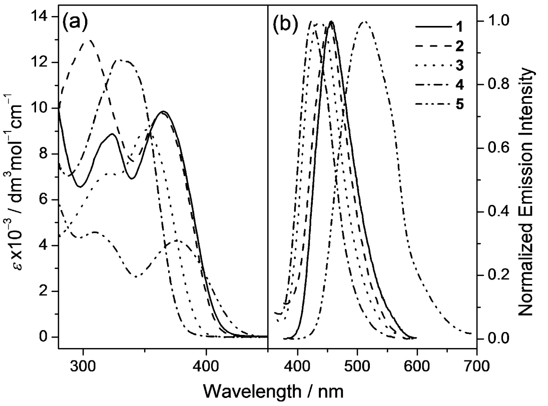

Figure 2. a) Electronic absorption spectra and b) normalized emission spectra of the open form of compounds **1**–**5** in benzene at 298 K.

Upon photo-irradiation at $\lambda < 400$ nm, **1**–**5** undergo photocyclization and the solutions change in color (ranging from purple to green), with the emergence of low-energy absorption bands from 450 to 800 nm (Figures 3a and 4). The significant bathochromic shift in the absorption maxima of the closed forms relative to their open forms is mainly due to the extended π-conjugation across the 8a,8b-dimethyl-1,8-thia-as-indacene moiety. Interestingly, the closed form of compound **5** shows a very broad absorption band in its spectrum (Figure 4). The color of the closed form can be fine-tuned by simple modification at the phosphorus center (Figure 4). The emission intensity would decrease upon photocyclization of the phosphole compounds (Figure 3b),

Table 1: Luminescence quantum yields, photocyclization/photocycloreversion quantum yields, and the percentage conversion at the photostationary state (PSS) for **1**–**5**.

Compound	ϕ_{lum}[a]	Photochemical quantum yield/ϕ		Conversion at PSS [%]
		photocyclization[b,d]	photocycloreversion[c,d]	
1	0.024	0.28	0.031	49
2	0.005	0.37	0.026	69
3	0.011	0.34	0.027	46
4	0.008	0.43	0.021	53
5	0.359	0.17	0.048	37

[a] Luminescence quantum yields were recorded using a degassed solution of quinine sulfate in $0.5\,\text{M}$ H_2SO_4 ($\phi_{\text{lum}} = 0.577$, ex $= 350$ nm) as a standard at 298 K; see also Ref. [15]. [b] Data obtained using $\lambda = 334$ nm as the excitation source. [c] Data obtained using $\lambda = 509$ nm as the excitation source. [d] Data obtained with an uncentainty of $\pm 10\%$.

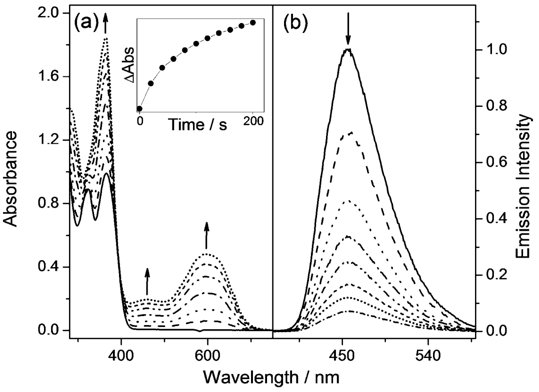

Figure 3. a) Changes in the UV/Vis absorption spectrum of compound **1** upon irradiation at $\lambda = 365$ nm; insert shows the plot of the absorbance change at $\lambda = 600$ nm as a function of irradiation time. b) Changes in the emission spectrum of compound **1** upon irradiation at $\lambda = 365$ nm.

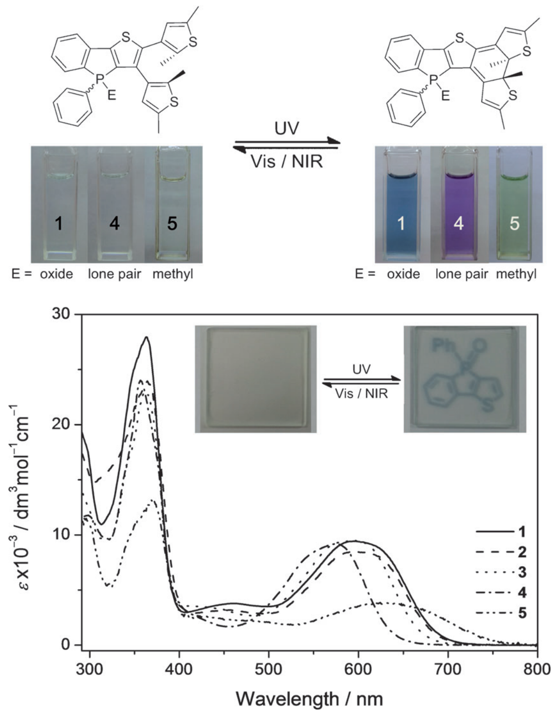

Figure 4. Top: Color change of **1**, **4**, and **5** in benzene upon photoirradiation at 298 K. Bottom: Electronic absorption spectra of the closed form of **1**–**5** in benzene at 298 K. Insert shows the color change of compound **1** in PMMA film.

rendering the dithiethylethene-containing phosphole moiety a possible photoswitchable material. The quantum yields for both photocyclization and photocycloreversion processes have been determined (Table 1). The photocyclization quantum yields for **1**–**4** are found to be in the range of 0.28 to 0.43, while that of **5** is determined to be only 0.17, probably as a result of the more effective competing radiative decay processes. The photocycloreversion quantum yields for the compounds vary from 0.021 to 0.048. The photocyclization conversion from the open form to the closed form for the compounds is found to be 37–69% at the photostationary state. These photochromic efficiencies are comparable to those of other dithienylethene-containing photochromic systems.[1a,2]

The reversibility of the photochromic behavior was studied on a representative sample of **1**. As shown in Figure S5, the compound shows good reversibility, with no apparent loss in its photochromic reactivities over at least seven repeating cycles. In addition, **1** was spin-coated on a polymethylmethacrylate (PMMA) film on a quartz plate to demonstrate the photochromic properties in rigid medium. The quartz plate was covered with a patterning mask and exposed to light; the uncovered area undergoes color change and the resulting patterns are stable in the dark for a period of time (Figure 4). Compound **1** was also used to demonstrate the thermal stability of the closed form of the phosphole compounds (Figure S6). The compound undergoes very slow thermal back reactions even at 333 K and the half-life for the closed form is about 442 days in benzene solution, which was determined by plotting $\ln k$ versus T^{-1} using the Arrhenius equation (Figure S7); this half-life is comparable to those of the thermally stable diarylperfluorocyclopentenes.[1a] The activation energy and the pre-exponential factor of the thermal cycloreversion of **1** were found to be $120.6\,\text{kJ}\,\text{mol}^{-1}$ and $1.01 \times 10^{13}\,\text{s}^{-1}$, respectively, indicating that the compound has a thermally stable closed form.[1a]

Computational studies were performed to gain a deeper insight into the nature of the low-energy absorptions in this class of compounds (see Computational Details in the Supporting Information). For the open forms of **1**–**5**, the HOMO corresponds to the π orbital of the aryl-fused phosphole mixed with the π orbital of the peripheral thiophene rings, while the LUMO corresponds to the π* orbital localized on the aryl-fused phosphole (Figure 5a and Figure S8). The HOMO has a node at the phosphorus atom, while a contribution from the σ* orbital of the exocyclic P−C bond to the LUMO is found. For the closed form, the HOMO of each compound is the π orbital localized on the condensed ring of the dithienylthiophene unit, while the LUMO is the π* orbital delocalized over the condensed ring phosphole system (Figure 5b and Figure S9).

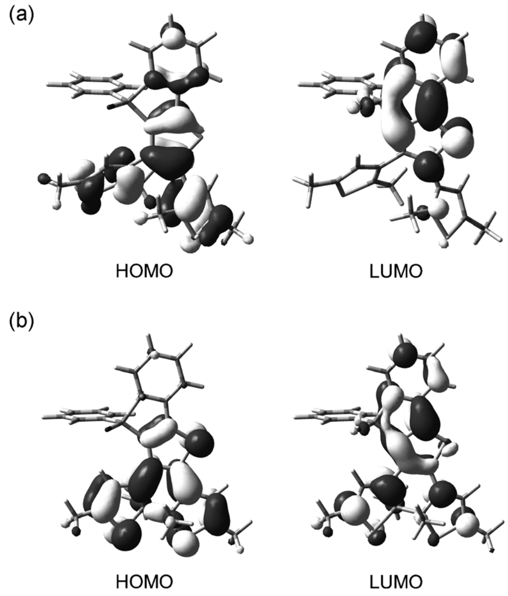

Figure 5. Spatial plots (isovalue = 0.03) of the HOMO and LUMO for the a) open form and b) closed form of **1**.

Both the HOMO and LUMO levels in the two forms of the σ^4-phosphole compounds are lower in energy than the analogous levels in the σ^3-phosphole compound **4**, because of an increase in electron deficiency of the phosphorus center. Since the LUMO shows a mixing of the σ^* orbital of the phosphorus moiety with the π^* orbital of the phosphole backbone, the energy of the LUMO decreases to a larger extent than that of the HOMO, leading to a decrease in the HOMO–LUMO separation (Table S6). The $S_0 \rightarrow S_1$ transitions for the open and closed forms mainly correspond to the HOMO→LUMO excitation and can be assigned as π–π^* transitions (Tables S7 and S8). The energies of the two forms are computed to be red-shifted in the order of $\mathbf{4} > \mathbf{3} > \mathbf{1} \approx \mathbf{2} > \mathbf{5}$, in agreement with the trend observed in the electronic absorption spectra.

In conclusion, a new series of photochromic phosphole compounds has been successfully synthesized and structurally characterized. Their photophysical, photochromic, and electrochemical properties have been studied, and can be readily modulated by functionalization at the phosphorus center without the need for tedious modification of the dithienylethene framework. The present work provides further insights for the future design of phosphole-containing photochromic materials.

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[15] A photochromic change was observed during the photo-excitation. However, the emission spectra were recorded at fast scan rates to minimize the photo-conversion of the compound, such that the conversion to the closed form can be considered to be negligible.