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Photoreaction of anthracenyl phosphine oxides: Usual reversible photo- and heat-induced emission switching, and unusual oxidative P—C bond cleavage

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ABSTRACT

Anthracenyl(diphenyl)phosphine oxide and dianthracenylphenylphosphine oxide as photoactive compounds have been synthesized. Anthracenyl group of these compounds indicate the multi-functional roles such as an emission component, a photodimerization component, and a leaving group. When the light irradiation was performed under an oxygen atmosphere, photo-oxidative P—C bond cleavage to leave the antharacenyl group was observed. Moreover, phosphonyl radical was produced and then P—P bond formation to form diphosphane was observed.

Introduction

Photoactive organic molecules such as dithienylethene, azobenzene and anthracene have exhibited reversible emission and structural changes induced by light irradiation and heating. Considerable attention has been focused on these molecules, mainly concerning the intriguing photocyclization of the dithienylethene unit [1], *E*/*Z* isomerization of the azobenzene unit [2], and [4π + 4 π] photodimerization [3–6] and photo-oxidation reactions of the anthracene unit [7]. Combining these photoactive units with polymers [8–11], complexes [12–16], supramolecular polymers [17] and supramolecules [18–20], is very interesting, as the resultant materials have the potential to show important stimuli-responsive behaviors. In particular, functionalized anthracenes and materials containing anthracene have been extensively reported as anthracene is easily functionalized. Furthermore, the molecular stacking modes such as π / π and CH/ π interactions, which play a key role in obtaining the desired luminescent properties, can be regulated. For example, an anthracene derivative with an imidazole displays three different packing structures, which show significantly different solid-state luminescence behaviors. Supramolecular interactions in these crystals can be reversibly changed by grinding and heating [21]. Anthracene-based nanocages such as anthraphane contain reactive packings in the crystal, and the photoreactivity of anthraphane crystals by [4 π + 4 π] photodimerization has been demonstrated [22]. Moreover, the luminescence behavior of a photoactive anthracene-based ligand and its Ir(III) complexes can be switched by photo-oxidation [23]. Recently, non-covalent interactions such as charge transfer (CT) in have been used to achieve various tailor-made molecular organic co-crystals with tunable fluorescence, with wide applications in optoelectronics [24–26]. Binary-component CT complexes which use anthracene derivatives as donors and 1,2,4,5-tetracyanobenzene (TCNB) as an acceptor have been reported [27]. In these materials, emission color changes are due to the regulation of the intermolecular interactions, such as π/π stacking between the anthracene moieties by grinding and heating. However, it is unclear whether it is optimal to use a grinding/heating process to regulate the intermolecular interactions in materials containing anthracene moieties and to control the luminescence behavior. Therefore, more anthracene derivatives must be designed and synthesized to understand the relationship between the molecular stacking mode and the grinding-/heating-responsive emission. Meanwhile, phosphorus compounds are well known and widely used as ligands for catalysts [28–30], ligands for coordination polymers [31,32], and Lewis base catalysts [33–35] because of the features that govern P(III)/P(V) chemistry, the potential to be connected to three-, four-, or five-connected building blocks and Lewis basicity. We have previously been interested in the development of novel luminescent phosphine materials [36]. Hence, it is a natural extension to create the phosphorus compounds with an

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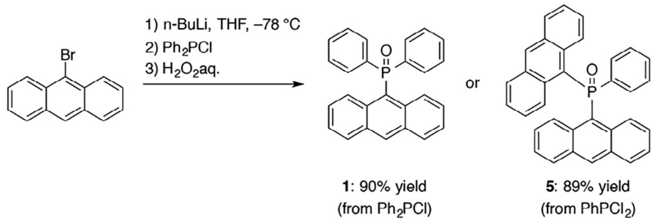
anthracenyl group as a stimuli-responsive luminescent material. In this paper, we have designed and synthesized an anthracenyl (diphenyl)phosphine oxide (**1**) and a dianthracenylphenylphosphine oxide (**5**) as photoactive organic compounds. The anthracenyl group in **1** and **5** plays the role of the luminescent unit, the quenching unit via [4 π + 4 π] and [4 π + 2 π] photodimerization, and the elimination group to demonstrate unusual P—C bond cleavage and P—P bond formation.

Results and discussion

The synthesis of **1** and **5** are shown in Scheme 1. After the halogen/lithium exchange reaction of 9-bromoanthracene, chloro (diphenyl)phosphine or dichlorophenylphosphine was added and the resulting product was oxidized with aq. H_2O_2. The product **1** and **5** were afforded as yellow solid and were characterized by ^{1}H NMR and ^{31}P NMR. Recrystallization of **1** or **5** from CH_3CN yielded yellow crystals suitable for single crystal X-ray diffraction (SCXRD) analysis. The material **1** crystallized as a monoclinic system with space group $P2_1/n$, and each unit cell included 16 molecules of **1**. As shown in Fig. 1, the anthracenyl group was almost vertical against the P=O bond (the torsion angle of O—P—C—C is ca. 26.9°). The material **5** crystallized as a monoclinic system with space group $P2_1/n$, and each unit cell included 4 molecules of **5** (Fig. 1b). In the packing diagram of crystals **1** and **5**, the anthracenyl group was not aligned in face-to-face type stacking (Figs. S34 and S40).



Scheme 1. Synthesis of anthracenyl(diphenyl)phosphine oxide **1** or dianthracenylphenylphosphine oxide **5**.

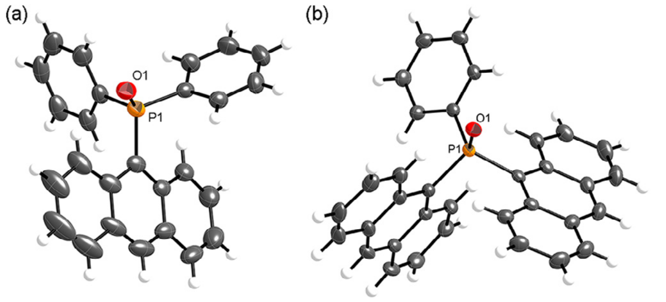
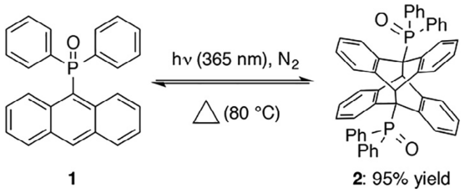


Fig. 1. Crystal structure of **1** (a) and **5** (b) in the thermal ellipsoid model. The ellipsoids of all non-hydrogen atoms have been drawn at 50% probability.

Although several organocrystals containing the anthracenyl group revealed that single-crystal-to-single-crystal (SCSC) dimerization reaction between face-to-face stacked anthracenes occurred, phosphine oxide **1** and **5** did not react to construct a photodimer in the solid state. No color or shape change was observed upon light irradiation of the yellow solid of **1** and **5**. In contrast, after light irradiation (365 nm) with N_2 bubbling through a chloroform or acetonitrile solution of **1,** the solution color changed from yellow to light yellow. ^{1}H NMR was performed in CD_3CN to observe any structural changes (Fig. S22). Although the proton signals of the phenyl groups were not shifted, remarkable upfield shifts of the anthracenyl proton signals were observed. The spectra were reversibly returned to the original by heating at 80 °C. This evidence suggests that a structural change between monomer **1** and photodimer **2** by [4 π + 4 π] photodimerization of the anthracene unit of **1** had occurred (Scheme 2). Recrystallization of an irradiated solution of **1** from CH_3CN yielded colorless crystals suitable for SCXRD analysis. The material crystallized as a triclinic system with space group *P*-1, and each unit cell included two molecules of photodimer **2**. The crystal structure of centrosymmetric photodimer **2** is shown in Fig. 2. One of the 9- and 10-positions of one anthracene unit is linked to the 9- and 10-positions of the other anthracene. After the heating the light yellow solution of **2**, the solution color returned to yellow. ^{1}H NMR and single crystal X-ray diffraction analysis revealed that the monomer **1** was obtained under these conditions. Moreover, to study the emission behavior of the solution, the UV/vis absorption and fluorescence spectral studies in CH_3CN solutions (*ca.* 1×10^{-5} M) were measured. The absorption and emission spectra of compounds **1** and **2** are shown in Fig. 3. Characteristic absorption bands and emission bands of the anthracene moieties (350–400 nm and 450–500 nm, respectively) were observed for **1**, and photodimerization of the anthracenyl group led to the disappearance of these bands.



Scheme 2. Photodimerization reaction of **1** and heating under N_2 atmosphere.

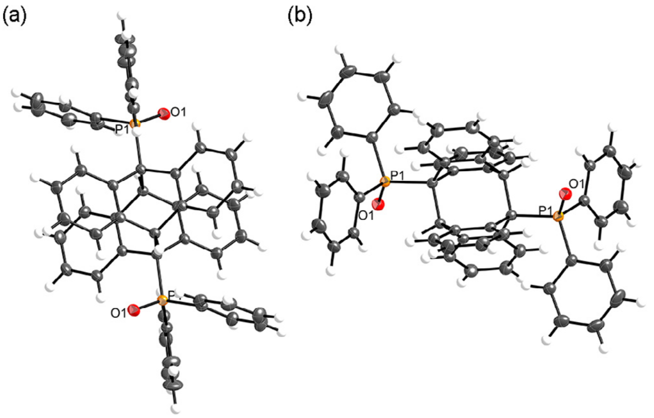


Fig. 2. Crystal structure of photodimer **2** in the thermal ellipsoid model. The ellipsoids of all non-hydrogen atoms have been drawn at 50% probability. (a) Top view. (b) Side view.

When the $CHCl_3$ or CH_3CN solution of dianthracenylphenylphosphine oxide (**5**) was irradiated at 365 nm with N_2 bubbling, the solution color changed from yellow to colorless. However, usual intermolecular [4 π + 4 π] photodimerization was not observed, and the proton signals of anthracenyl groups were changed to complex. Although the pure products were not isolated, colorless crystals suitable for SCXRD were obtained by recrystallization of an irradiated solution of **5** from CH_3CN. As shown in Fig. 4, one of the 9- and 10-positions of an anthracene unit is linked to the 1- and 2-positions of the other anthracene unit in the same molecule. This fact suggested that the intramolecular [4 π + 2 π] photoreaction was occurred instead of [4 π + 4 π] photodimerization reaction (Scheme 3). Generally, [4 π + 2 π] cyclization is recog-

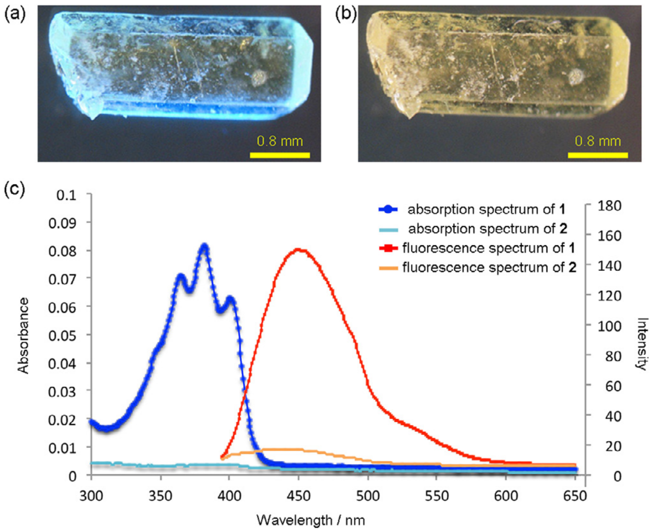


Fig. 3. (a) Photograph of irradiated crystal **1** under lamp with 365 nm wavelength light. (b) Photograph of crystal **1**. (c) Absorption and emission spectra (λ = 382 nm) of **1** and **2** in CH_3CN solutions (ca. 1 × 10^{-5} M).

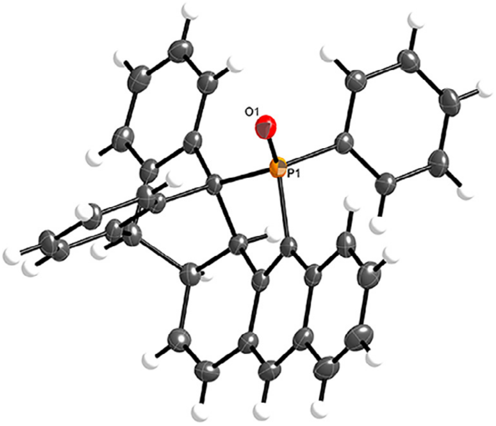
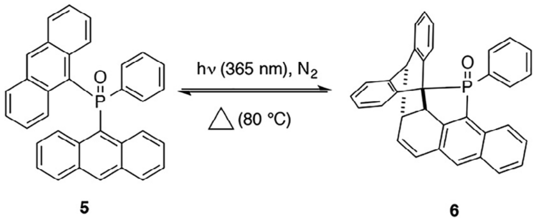


Fig. 4. Crystal structure of **6** in the thermal ellipsoid model. The ellipsoids of all non-hydrogen atoms have been drawn at 50% probability.

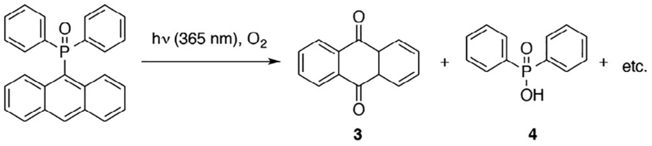


Scheme 3. Photoreaction of **5** and heating under N_2 atmosphere.

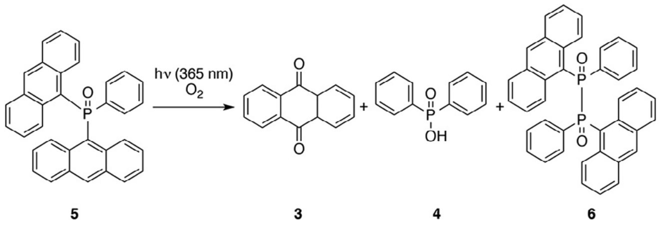
nized as photochemical forbidden [37–41]. As shown in Fig. 1, 9- and 10-positions of an anthracene and 1- and 2-positions of the other anthracene of compound **5** is located near each other. Usual [4 π + 4 π] photodimerization reaction was interrupted because of steric hinderence of anthracenyl groups. Therefore, photochemical forbidden [4 π + 2 π] cyclization reaction was allowed. Sakurai et al reported this type [4 π + 2 π] cyclization reaction of anthracenyl silane and anthracenyl german compounds [42].

When light irradiation without N_2 bubbling was performed, photodimerization was observed in a low yield, and anthraquinone (**3**) was obtained as a by-product. Positive mode ESI-MS measurement suggested the formation of the oxidative species by observation of the ion peaks corresponding to the oxygen linked $[\mathbf{1} + 2OH]^+$ at *m*/*z* of 412.9 (Fig. S26). This inspired us to attempt the reaction under oxidative conditions. Under an oxygen atmosphere, the anthracenyl group of **1** act as a leaving group to form the anthraquinone via P—C bond cleavage, and the phosphorus unit was transformed to diphenyl phosphinic acid (**4**) (Scheme 4). Similarly, photooxidation reaction of **5** under oxygen atmosphere also suggested P—C bond cleavage to afford the phosphinic acid and anthraquinone (Scheme 5) and some phosphine oxide compounds. Recrystallization of an irradiated solution of **5** from CH_3CN yielded colorless crystals suitable for SCXRD analysis. Interestingly, unusual P—P bond formation by the coupling reaction of phosphonyl radical to form the anthracenylphenyldiphosphane **7** was observed in this reaction (Fig. 5).

Scheme 6 shows a postulated mechanism for this reaction. When light irradiation under N_2 atmosphere was performed, photochemical allowed [4 π + 4 π] photodimerization reaction was occurred. In contrast, when light irradiation under O_2 atmosphere was performed, photo-oxidation such as oxygen addition via radical path was proceeded. After the homolysis of oxygen adducts,



Scheme 4. Photooxidation reaction of **1** under an O_2 atmosphere.



Scheme 5. Photooxidation reaction of **5** under an O_2 atmosphere.

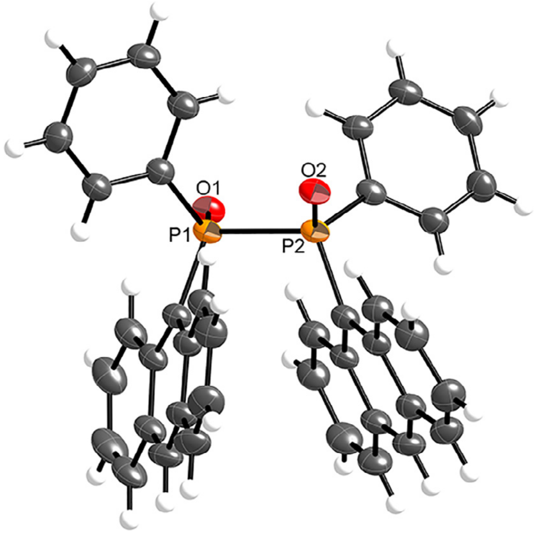
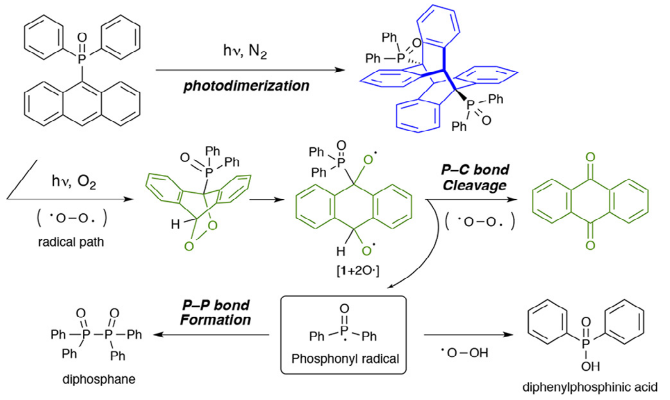


Fig. 5. Crystal structure of **7** in the thermal ellipsoid model. The ellipsoids of all non-hydrogen atoms have been drawn at 50% probability.



Scheme 6. Postulated mechanism of the photodimerization and photooxidation reaction.

P—C bond cleavage to form the anthraquinone occurred, and then a phosphonyl radical was produced. These easy switching between photodimerization and heating may be only occurred in the P—C (anthracenyl) bond because the photodimerization and photo-oxidation reactions of anthracenylphenyl(diphenyl)phosphine oxide **8** (Figs. S43 and S44) were not observed in solution- or solid-state.

Conclusion

We have synthesized phosphine oxide compounds with anthracenyl group such as anthracenyl(diphenyl)phosphine oxide (**1**) and dianthracenylphenylphosphine oxide (**5**), and have demonstrated the roles of the anthracenyl group. The emission behavior of phosphine oxide **1** and **5** can be reversibly switched by photoirradiation under a N_2 atmosphere with heating. Characteristic absorption and emission spectra of an anthracenyl group were observed in compound **1**. In contrast, [4 π + 4 π] photodimerization reaction of the anthracenyl groups lead to formation of photodimer **2** with no fluorescence. In compound **1**, the anthracenyl moiety plays the role of the photoresponsive group. Upon irradiation under an O_2 atmosphere, P—C bond cleavage was observed to form an anthraquinone. In this reaction, the anthracene fragment plays the specific role of a leaving group to form the diphosphane structure by P—P bond formation between the phosphonyl radicals. The presence of the P–anthracenyl bond is an important factor for the formation of the diphosphane. Our findings are expected to pave the way for the creation of new and more efficient photoresponsive materials based on phosphorus compounds containing an anthracenyl group.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tetlet.2019.06.063.

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