

Unprecedented Radical–Radical Reaction of a [2.2]Paracyclophane Derivative Containing an Imidazolyl Radical Moiety

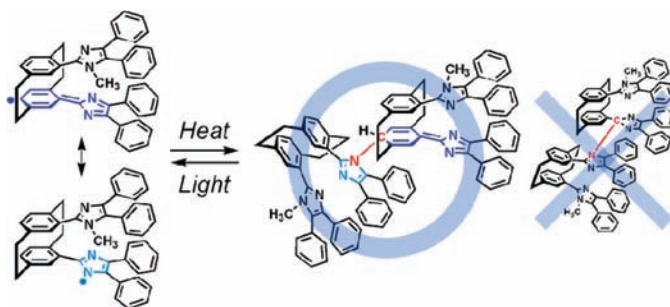
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ABSTRACT



Pseudogem-DPIM-DPI[2.2]PC dimer (**3**), with a C–N bond between the [2.2]paracyclophane ([2.2]PC) moiety and the imidazole ring, was synthesized. This is the first crystallographic observation of a highly sterically constrained 1-ene-2,5-cyclohexadiene structure for a [2.2]PC derivative. Compound **3** shows a photochromic behavior, exhibiting a color change from pale yellow to green upon either UV or visible light irradiation, both in the solid state and in solution at room temperature.

The photochromism of a hexaarylbiimidazole (HABI), formed by the radical–radical reaction of the oxidation product of 2,4,5-triphenylimidazole (TPI), was first discovered by Hayashi and Maeda.^{1a} Since then, a large number of HABI derivatives have been synthesized, and their photochromic behaviors have been extensively investigated.¹ In general, HABI derivatives are readily cleaved, both thermally and photochemically, into a pair of triphenylimidazolyl radicals (TPIRs) that can be recombined to afford the parent HABI derivatives. The characteristic feature of TPIR lies in their diversity of bond formation^{1f,g} between two TPIRs due to delocalization of an unpaired electron over

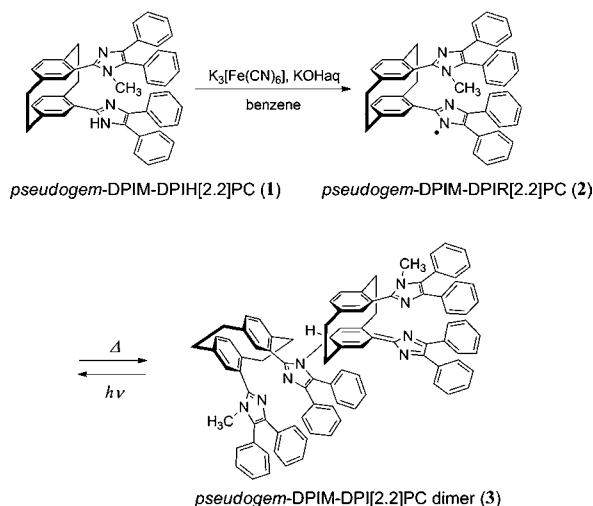
the whole molecule. We recently developed a photochromic [2.2]PC-bridged imidazole dimer, with a [2.2]paracyclophane ([2.2]PC) moiety that couples two diphenylimidazole (DPI) groups, that shows instantaneous coloration upon exposure to UV light and rapid fading in the dark.² The [2.2]PC-bridged imidazole dimer shows photoinduced homolytic bond cleavage of the C–N bond connecting the two imidazole rings and successive fast intramolecular C–N bond formation, which can be well correlated with the behaviors observed for HABI derivatives. In this study, we investigate the radical–radical reaction of an analogous monoradical containing a [2.2]PC moiety that sterically precludes the intermolecular radical–radical reaction between the imidazolyl radicals.

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Upon oxidation of *pseudogem*-DPIM-DPIH[2.2]PC (**1**) with potassium ferricyanide under basic conditions, the color of the solution changed from pale yellow to green. By analogy to the oxidation product of TPI, the green-colored species, ascribable to an imidazolyl radical, *pseudogem*-DPIM-DPIR[2.2]PC (**2**) (Scheme 1), was formed. The

Scheme 1. Synthesis of the *Pseudogem*-DPIM-DPI[2.2]PC Dimer



organic phase was separated from the mixture of benzene and water, washed with water, and concentrated in vacuo to afford a reddish orange powder. Recrystallization of the compound from a mixture of dichloromethane and acetonitrile with exclusion of light gave orange plates. The X-ray crystallographic analysis revealed an unprecedented *pseudogem*-DPIM-DPI[2.2]PC dimer (**3**) (Figure 1) as a result of the intermolecular radical–radical reaction of **2**. This radical–radical reaction of **2** is analogous to that of the triphenylmethyl radical. The structure of the dimer of the triphenylmethyl radical was determined to be the quinoid

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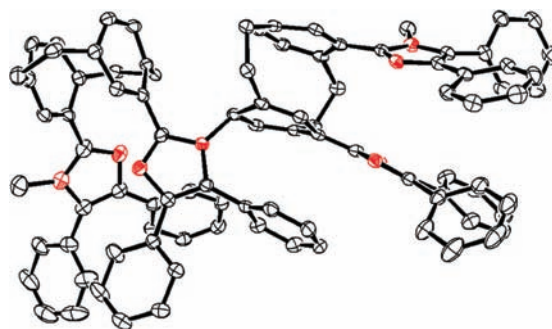


Figure 1. ORTEP representation of the molecular structure of **3** with thermal ellipsoids (50% probability), where nitrogen atoms are highlighted in red. [2.2]Paracyclophane groups are disordered over two sites, one of which is shown in this figure for clarity. Hydrogen atoms and solvent molecules are omitted for clarity.

structure with a 1-ene-2,5-cyclohexadiene moiety but not the tetraphenylethane structure.³ The most remarkable structural feature of **3** is that the dimeric structure is given by a C–N bond between the [2.2]PC moiety and the imidazole ring, in which one of the benzene rings of the [2.2]PC moiety of a monomer converted into a 1-ene-2,5-cyclohexadiene moiety.⁴ This is the first crystallographic observation of a highly sterically constrained 1-ene-2,5-cyclohexadiene structure for the [2.2]PC derivatives, even though the dimeric structure involving a 1,4-cyclohexadiene moiety was previously reported for the fluorinated 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane.⁵ The C–N bond connecting the [2.2]PC moiety and the imidazole ring in **3** (1.485(3) Å) has a length quite consistent with that connecting the two imidazole rings of HABI (1.482(2) Å).^{1j}

3 shows a photochromic behavior, exhibiting a color change from pale yellow to green upon either UV or visible light irradiation, both in the solid state and in solution, at room temperature. The vis-NIR absorption spectrum of **3** in benzene is shown in Figure 2, along with that of the colored species formed upon UV light irradiation (365 nm; a Keyence UV-400 series UV-LED).

While both HABI derivatives and [2.2]PC-bridged imidazole dimers have no absorption band at wavelengths longer than 400 nm, **3** shows an absorption maximum at 420 nm, which can be assigned to the π – π^* transition localized at the 2-(2,5-cyclohexadienylidene)-4,5-diphenyl-2H-imidazole unit on the basis of the TD-DFT calculation (Figure S14, Supporting Information), in addition to that at 360 nm. Thus,

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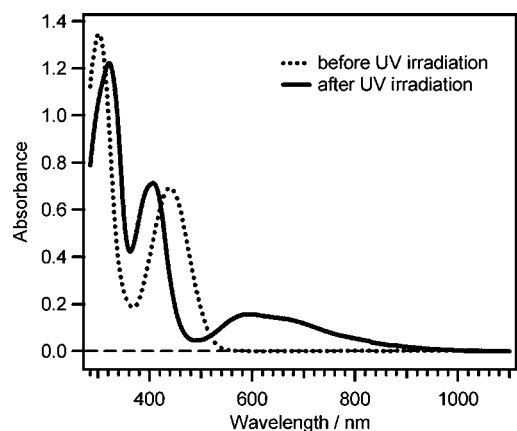


Figure 2. Vis-NIR absorption spectra of **3** in degassed benzene (2.6×10^{-5} M, light-path length: 10 mm) measured at 298 K before UV light irradiation (dashed line) and immediately after UV light irradiation (solid line).

the photochromic color change of **3** can be realized under visible light irradiation (at wavelengths shorter than 540 nm). The light-induced color change gives rise to a sharp absorption band at 400 nm and a broad absorption band ranging from 500 to 900 nm. Obviously, the appearance of these bands must be attributed to the photoinduced homolytic cleavage of the C–N bond connecting the [2.2]PC moiety and the imidazole ring, which was confirmed by the presence of ESR-active species. The ESR signal intensities of the toluene solution of **3** and the reference compound, DPPH (diphenylpicrylhydrazyl), were recorded at 298 K to estimate the degree of photodissociation in the photostationary state upon UV light irradiation. By comparing the ESR signal intensity of the sample solution with that of the DPPH solution, the degree of photodissociation of **3** was estimated to be 96%. The ESR spectra were also measured for the toluene solution of **3** after light irradiation at 78 K. As shown in Figure 3, a randomly oriented triplet pattern with an overlapping doublet signal derived from a trace of free radicals was observed for the UV-irradiated toluene solution. The same spectrum was also observed under visible light (450 nm) irradiation. The detection of a forbidden weak transition ($\Delta M_s = 2$) at half field shown in the inset of Figure 3 indicates the formation of a triplet-state species, which can be assigned to the light-induced triplet radical pair. Therefore, the colored species can be identified as a monoradical **2**.

The back-reaction regenerating **3** is not accelerated by light irradiation, and the thermal bleaching process takes place over a day at 298 K in the dark because of the slow intermolecular radical–radical reaction of **2** (Figure S12, Supporting Information). Moreover, the back-reaction does not proceed in a quantitative fashion, due to the fact that the solution of **3** left to stand in the dark for a day after UV light irradiation does not show a vis-NIR absorption spectrum which entirely coincides with that observed for the solution before UV light irradiation (Figures S11 and S13, Supporting Information). This observation indicates the presence of a side reaction leading to the formation of a byproduct other

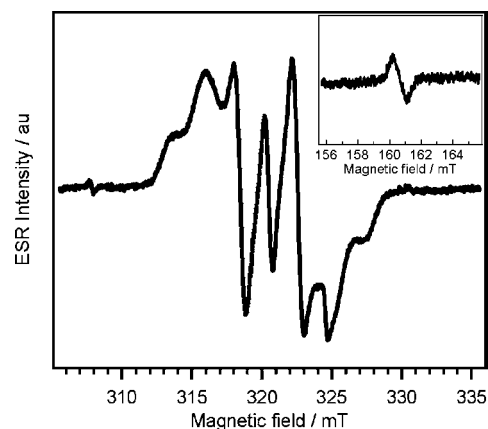


Figure 3. ESR spectra of a UV-irradiated toluene solution (2.3×10^{-4} M) of **3** at 78 K. The inset is the detection of a forbidden weak transition at half-field.

than **3**. Though the presence of another nonphotochromic dimer, given from the coupling of two molecules of **2**, could be considered, the details for such photoproducts of **3** are under investigation.

The significant feature of the formation of **3** from two molecules of **2** is in their unusual radical reaction on the [2.2]PC moiety. To the best of our knowledge, no reports have demonstrated such radical addition reactions at the [2.2]PC moiety in the literature. The radical substituent on the [2.2]PC moiety makes the radical–radical reaction realized in this work possible. The resonance structure shown in Figure 4a localizes the spin in the *para*-position to the

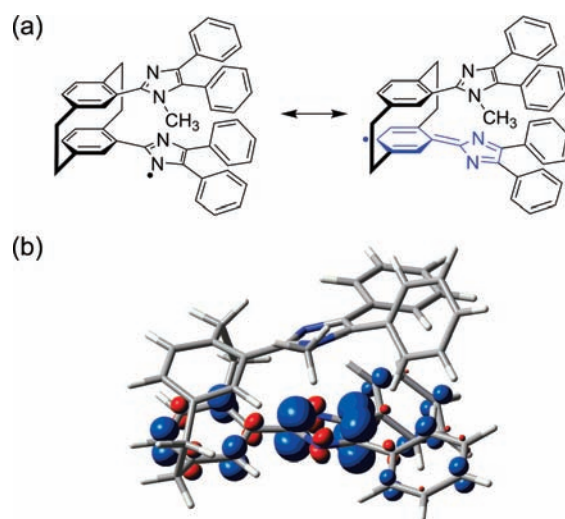


Figure 4. (a) Resonance structures of **2**. (b) The total spin-density distribution of **2** calculated by the DFT UMPW1PW91/6-31G(d).

DPIR group, which will make a large contribution to the radical–radical reaction on the [2.2]PC moiety. Indeed, the spin-density distribution of **2** calculated by the DFT

UMPW1PW91/6-31G(d) method (Figure 4b) clearly shows the delocalization of an unpaired electron over the [2.2]PC moiety. Although the spin-density in TPIR also delocalizes on the phenyl ring attached to the 2-position of the imidazole ring, the radical addition on the phenyl ring does not lead to formation of a bond between the imidazole ring and the phenyl ring.¹¹ This is due to the fact that the activation energy for the bond formation between two imidazole rings is different from that for the bond formation between the imidazole and the phenyl rings. However, the bond formation between the two imidazole rings of **2** seems unfavorable from the steric viewpoints; there is a strong steric repulsion between the DPI group and the methylated DPI group (DPIM) that are facing each other.

In conclusion, based on the radical–radical reaction of a [2.2]PC derivative containing an imidazolyl radical group, we have synthesized a novel photochromic compound **3**, with a C–N bond formed between the [2.2]PC moiety and the imidazole ring. This kind of bond formation is unusual and quite unique in view of their photochromic behaviors. This

finding will lead to the development of a new class of photochromic compounds based on imidazolyl radicals. We also find for the first time that the stable 1-ene-2,5-cyclohexadiene structure can be formed by such a radical addition reaction by employing the [2.2]PC moiety.

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Supporting Information Available: Synthesis of **3**, experimental details of spectroscopic measurement, crystallographic data in CIF format, and details of DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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