

Electronic structure of light-induced lophyl radical derived from a novel hexaarylbiimidazole with π -conjugated chromophore

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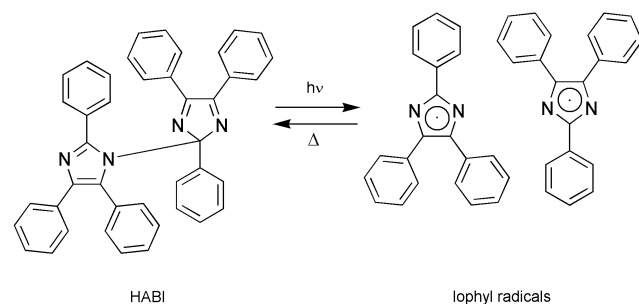
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A novel photochromic hexaarylbiimidazole with a bithienyl group as an extended π -conjugation unit was synthesized and the light-induced lophyl radical was found to be stabilized due to the delocalization of an unpaired electron, and to strongly absorb near-infrared light.

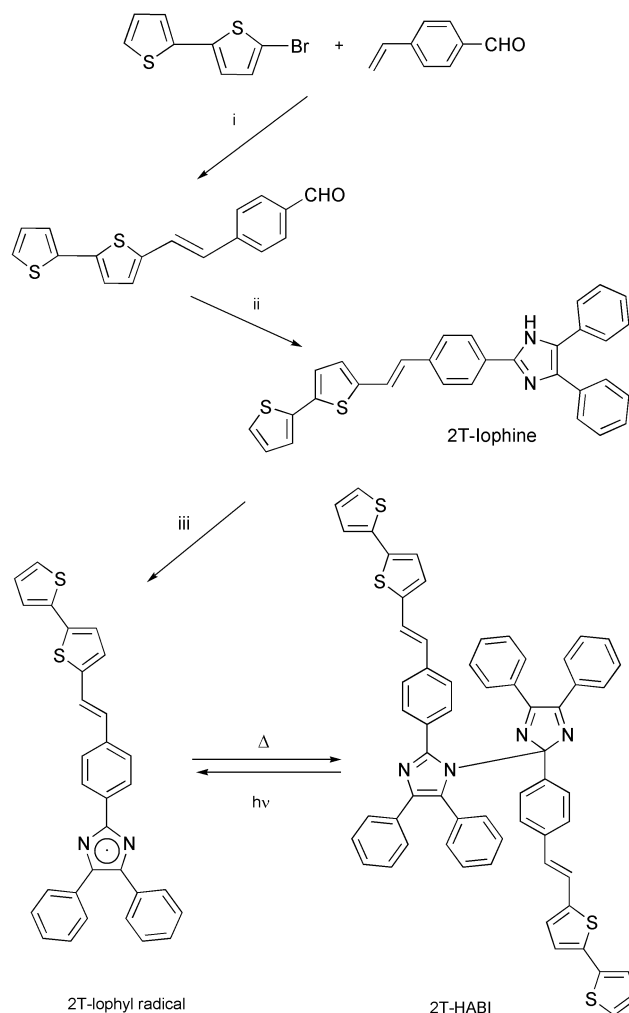
Hexaarylbiimidazole (HABI) was first synthesized by Hayashi and Maeda in 1960.¹ HABIs are readily cleaved, both thermally and photochemically, into a pair of triarylimidazolyl radicals called lophyl radicals that can recombine to form the lophine dimer. The high yield of lophyl radicals in solid matrices and their low sensitivity to the presence of oxygen stimulated industrial interest in the use of HABI as a photoinitiator and photosensitizer for a wide variety of imaging materials and resulted in extensive investigations of substituted HABIs.² Especially, 2-chlorohexaarylbiimidazole (*o*-Cl-HABI) has been used as a free radical initiator in photopolymer imaging for more than three decades. Although the photochromic behavior of HABI and its derivatives in solution and solid matrices has been extensively studied by spectroscopic methods, there is practically no knowledge of the molecular and electronic structures of the lophyl radicals and the pair of lophyl radicals with an extended π -conjugation unit.³ We have recently reported an unprecedented example of the *in situ* direct observation of a light-induced radical pair (RP) in a crystal of *o*-Cl-HABI by X-ray diffraction,⁴ and described the first example of the measurement of intermolecular exchange coupling for the light-induced RP by ESR measurement.⁵ Moreover, we have investigated the electronic structures for the RP by density functional theory.⁵ The spin density of the lophyl radical is found to be mainly delocalized over the imidazolyl ring. These studies could reveal both the molecular and electronic structures for the RP, and would lead to a better understanding of HABI chemistry and radical-pair chemistry. In this report we describe the synthesis of a family of a novel HABI with a bithienyl chromophore as an extended π -conjugation unit, and investigate the electronic structures of both the lophyl radical and the light-induced RP. This represents the first photochemical properties for the novel HABI system with a π -conjugated chromophore, which provides a new type of lophyl radicals which strongly absorb near-infrared light.

HABI derivative **2T-HABI** was prepared by oxidation of the corresponding lophine derivative, **2T-lophine**, according to



Scheme 1 Reversible photodissociation of HABI into two lophyl radicals.

known procedure (Scheme 2).¹ **2T-HABI** exhibited the expected reversible photochromic behavior, which showed low sensitivity to the presence of oxygen, both in solution and in solid state. The yellow benzene solution of **2T-HABI** showed the absorption at 393 nm corresponding to the bithienyl chromophore. On irradiation of the benzene solution with 340 nm light, the yellow solution quickly turned to dark violet and gave rise to two maxima at 534 nm and 862 nm (Fig. 1). The absorption spectrum has a characteristic broad band in the near-infrared region as well as a second band. This is the first example of a lophyl radical absorbing light in the near-infrared region. On standing in the dark, the dark violet color gradually faded with the decrease in these absorbances showing isosbestic points. Thermal reversion to the original spectrum was observed over the course of approximately 2 hours at 293 K in the dark, suggesting a relatively high stability for the lophyl radical even



Scheme 2 i. $\text{Pd}(\text{OAc})_2$, PPh_3 , $\text{N}(\text{C}_2\text{H}_5)_3\text{-CH}_3\text{CN}$, 120 °C, 7 days, yield (30%); ii. benzyl, $\text{CH}_3\text{COO-NH}_4^+\text{-CH}_3\text{COOH}$, 130 °C, 1 day, (30%); iii. $\text{K}_3[\text{Fe}(\text{CN})_6]$, KOH/benzene, rt, 1 day, (96%).

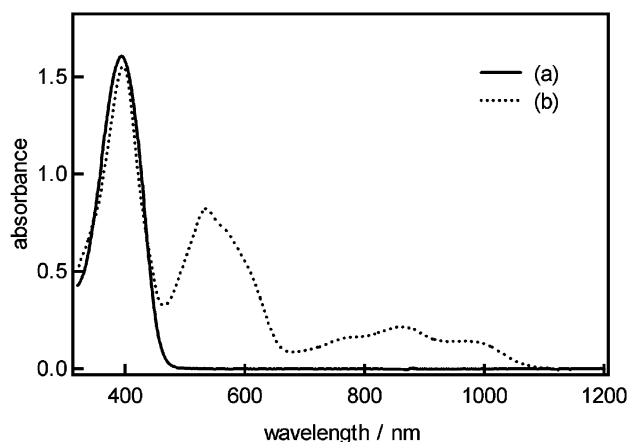


Fig. 1 Absorption spectra of **2T-HABI** in benzene (a) before irradiation (b) immediately after irradiation with 340 nm light at room temperature. Concentration of **2T-HABI**: $2.50 \times 10^{-5} \text{ mol l}^{-1}$.

in solution at room temperature. The absorption bands of HABI lie in the UV region at 278 nm in benzene, while the absorption bands of the lophyl radical are in the visible region at 351 nm and 574 nm.³ Thus, the extensively π -conjugated HABI system shows a large bathochromic shift of the absorption band, indicating an increase in the degree of delocalization of an unpaired electron of the lophyl radical derived from **2T-HABI**. As shown in Fig. 2, the spin-density distributions calculated by the DFT unrestricted Becke3LYP/6-31G(d) method clearly indicate the penetration of the unpaired electron over the bithienyl chromophore.[†]

Slow recombination of the lophyl radical favors the observation of radical pairs by ESR measurement under moderate experimental conditions. As described before, we have estimated the zero-field splitting (zfs) parameters for the light-induced RP of known structure in a crystal of *o*-Cl-HABI.⁵ The zfs parameters for a triplet RP are an extremely sensitive probe of RPs since they are inversely proportional to the cube of the distance separating the radical centers. Therefore, the ESR spectrum for the light-induced RP was measured in order to investigate the effect of the π -conjugated chromophore on the electronic and molecular arrangement for the RP derived from **2T-HABI**. The ESR spectrum of the UV-irradiated toluene solution of **2T-HABI** at 77 K shows a randomly oriented triplet pattern with an overlapping doublet signal derived from a trace of free radicals at $g = 2.003$ (Fig. 3). The detection of a forbidden weak transition ($\Delta M_s = 2$) at half field indicates the presence of a triplet-state species, which can be assigned to the light-induced triplet RP. The zfs parameters for the triplet RP are estimated to be $|D/hc| = 0.0099 \text{ cm}^{-1}$ and $|E/hc| = 0.0011 \text{ cm}^{-1}$ by simulation of the spectral line shape by the eigenfield method.⁶ These values are comparable to the values estimated for the light-induced RP in a crystal of *o*-Cl-HABI, $|D/hc| = 0.0103 \text{ cm}^{-1}$ and $|E/hc| = 0.0007 \text{ cm}^{-1}$. The average distances between the two radical centers of the light-induced RP derived from **2T-HABI** and *o*-Cl-HABI, as derived from the point dipole approximation, correspond to 6.40 Å and 6.26 Å,

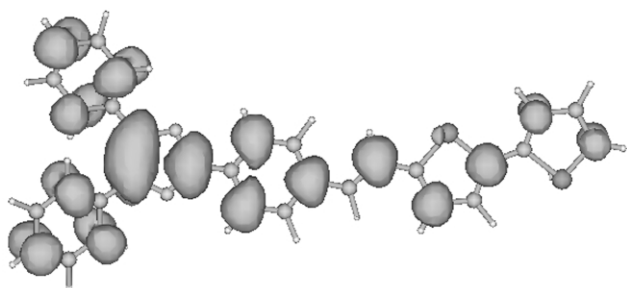


Fig. 2 Spin-density distribution calculated by the DFT B3LYP/6-31G(d) method.

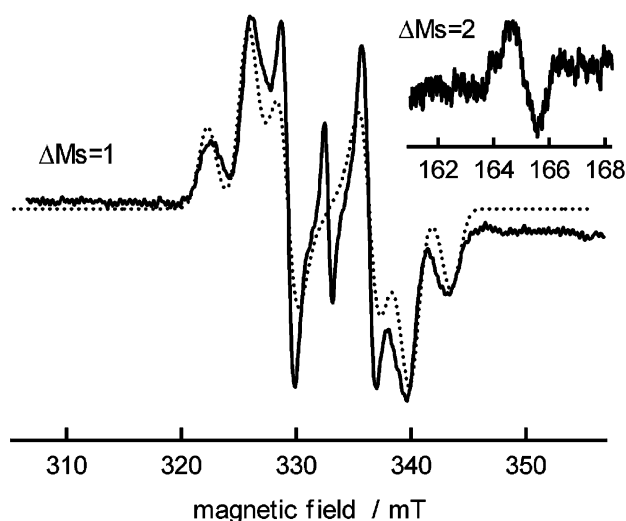


Fig. 3 ESR spectra of a UV-irradiated toluene solution of **2T-HABI** at 77 K. The top spectrum is the detection of a forbidden weak transition at half-field. The dotted curve shows spectral simulation. The simulation used $g_{\text{iso}} = 2.003$ and Gaussian line shapes with varying line widths.

respectively. These analyses suggest a similarity in the molecular arrangement between them, and could give valuable information about the effect of the π -conjugated chromophore. Though the π -conjugated chromophore enlarges the region of spin distribution, this effect is too small to induce the change in the molecular interaction between the radicals.

The present result clearly demonstrates that HABI derivatives with a π -conjugated chromophore show photochromic behavior affording stable lophyl radicals with a large bathochromic shift of the absorption band. Sensitization by introducing an ambient π -conjugated chromophore could be developed to increase the photospeed and extend the sensitivity range of the HABI initiator system in free-radical-initiated photoimaging systems.

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Notes and references

[†] Preparation of **2T-Iophine**: A mixture of 1.0 g (3.37 mmol) of 4-(2-[2,2'-bithienyl-5-ylvinyl]benzaldehyde, 708 mg (3.37 mmol) of benzyl and 2.60 g (33.7 mmol) of ammonium acetate in acetic acid (40 ml) was stirred. After stirring, the mixture was refluxed for an additional 1 day. After this reaction period, aqueous ammonia was added until the solution was neutral. After filtering, the residue was washed with hexane and purified by column chromatography packed with silica gel in chloroform eluent and recrystallized from chloroform to give the product as yellow powder in 30% yield.

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