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Chemical Communications

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Nanosecond Photochromic Molecular Switching of a Biphenyl-Bridged Imidazole Dimer Revealed by Wide Range Transient Absorption Spectroscopy

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We demonstrate that a biphenyl-bridged imidazole dimer exhibits fast photochromism with a thermal recovery time constant of ~100 ns, which is the fastest thermal back reaction in all reported imidazole dimers. Sub-ps transient absorption spectroscopy reveals that the generation process of the colored species occurs within 1 ps.

Microsecond time scales cover various phenomena such as electronic relaxation processes of triplets and charge transfer states, molecular diffusion, enzyme reactions, folding of proteins, etc. To trigger and precisely control these phenomena by external stimuli, switches are necessary that respond faster than these time scales. Photochromic molecules are the best candidates for such switch molecules because they can modulate various properties such as color, conductivity,[1,2] chirality,[3,4] intermolecular interaction,[5] etc. As compared to the structural changes during the electronic relaxation pathways from the Franck-Condon state to the lowest excited state (S_1), photochromic reactions induce drastic structural changes repeatedly. Therefore, photochromic molecular switches have a potential to produce mechanical work[6–8] and to act as optical logic gate systems to control electronic relaxation processes such as charge transfer and coupling.[9–13] There are some reports on photochromic compounds whose switch cycles at ambient temperature are completed on sub-μs time scales such as certain oxazine and azo derivatives.[14,15] The switching materials that show fast photochromism on the ns time scale offer novel applications such as high speed optical actuators[16,17] with MHz repetition frequencies.

We have developed a series of bridged imidazole dimers which act as sub-second to μs fast molecular switches.[18–22] However, there are few compounds which act as sub-μs photochromic switches in bridged imidazole dimers.[23] In our previous study,[24] we reported that bisDMDPI-BP (Figs. 1a and b) did not give any photochromic signals later than the μs time
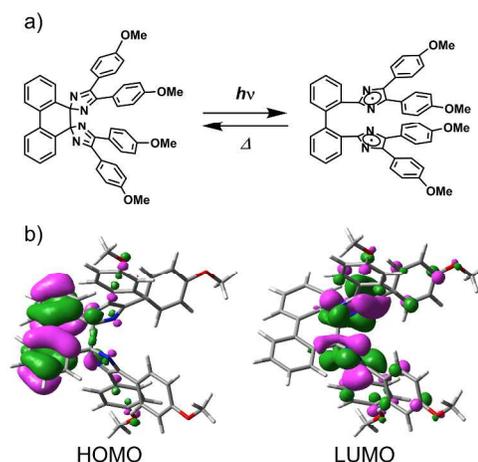

Fig. 1 (a) Photochromism and (b) the relevant molecular orbitals of bisDMDPI-BP obtained by the MPW1PW91/6-31G(d) level of the theory.

scale while other similar derivatives were reported to exhibit the characteristic negative photochromism. On the other hand, quantum chemical calculations of bisDMDPI-BP suggest a similarity of bisDMDPI-BP to the reported photochromic imidazole dimers. Quantum chemical calculations of the reported photochromic imidazole dimers suggest that the C–N bond between the two imidazole rings has anti-bonding character in the LUMO (Fig. 1b, DFT MPW1PW91/6-31G(d) level).[25] The calculations of bisDMDPI-BP also suggest that the C–C bond between the two imidazole rings has anti-bonding character in the LUMO. This similarity implicitly suggest that bisDMDPI-BP is very likely to show photoinduced bond cleavage of the C–C bond between the two imidazole rings as similar processes as the reported photochromic imidazole dimers.

In this study, we apply sub-ps and sub-μs transient absorption spectroscopy to reveal the photochromism of
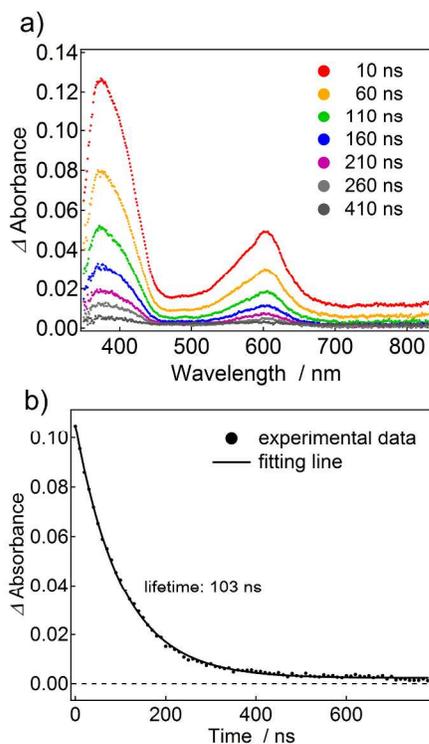
Fig. 2 (a) Transient absorption spectra on the ns time scale and (b) decay profile of the colored species of bisDMDPI-BP observed at 400 nm in degassed benzene (1.1×10^{-4} M, excitation wavelength: 305 nm, pulse duration: 5 ns, excitation intensity: 1.8 mJ).

bisDMDPI-BP. We found that bisDMDPI-BP indeed undergoes the expected ring opening (Fig. 1a) and is one of the fastest photochromic compounds, with a ring opening within 1 ps and thermal lifetime of the open form of ~100 ns. The fast and large conformational change of bisDMDPI-BP offers great potential for a molecular device to produce a large mechanical work and for a trigger to induce a local conformational change to macromolecular and biological organizations.

Imidazole dimers are categorized into several isomers depending on the binding manner between two imidazole rings. BisDMDPI-BP is the 2,2'-isomer, in which the C–C bond is formed between the 2-position of an imidazole ring and the 2'-position of the other imidazole ring,[24] while almost all reported bridged imidazole dimers are the 1,2'- or the 1,4'-isomers, in which a C–N bond is formed between the two imidazole rings.[18,20,21,26] While there are several reports on the 2,2'-isomers of hexaarylbiimidazole (HABI) derivatives,[27,28] they are sensitive to temperature and pressure, and easily converted to the photochromic 1,2'-isomers via the imidazolyl radical formed by thermochromism or piezochromism. Therefore, the stable 2,2'-isomer of bisDMDPI-BP offers a unique opportunity to reveal the photochromism of a representative 2,2'-isomer.

BisDMDPI-BP was synthesized according to our previous report.[24] The steady-state absorption spectrum of bisDMDPI-BP is shown in Fig. S1 (Electronic supplementary information: ESI).

The absorbance of bisDMDPI-BP increases rapidly at wavelengths longer than ~370 nm. Prior to time-resolved experiments, we examined the durability of bisDMDPI-BP by repetitive exposures to ns laser pulses (See supporting information for detail). The absorption spectra and HPLC analyses reveal that bisDMDPI-BP almost does not decompose even after 10000 laser shots under O_2 atmosphere (Figs. S2 and S3 in ESI). It shows that bisDMDPI-BP has high durability and the decomposition during the laser experiments is negligible. We set the excitation wavelength to 305 nm in ns and 310 nm in fs transient absorption measurements. The details of the experimental setup were reported previously[29,30] and are briefly shown in the supporting information.

Fig. 2a shows ns transient absorption spectra of bisDMDPI-BP at different time delays at room temperature (~20 ºC). We observed two absorption bands at ~380 and 595 nm superimposed on a broad background, and the whole spectrum decays exponentially. The transient spectrum is very similar to those of the radical species of bridged imidazole dimers reported previously.[21,24] The quantum chemical calculations suggest that the absorption band at 550-650 nm can be attributed to the π-π* like transition (Figs. S13 and S14 in ESI). In addition, the calculations suggest that the dihedral angle of the biphenyl moiety changes from 20 to 91° by the photochromic reaction (Figs. S11 and S12 in ESI). The ns transient absorption experiment shows that the colored species of bisDMDPI-BP has a weak and broad background at >700 nm, where the absorption band due to the radical-radical interaction was observed in the previously studied bridged imidazole dimers.[20,21,26] Our previous work has demonstrated that the absorption band due to the radical-radical interaction decreases, becomes broad, and shifts to longer wavelengths with decreasing radical-radical interactions.[21] Since bisDMDPI-BP has little transient absorption at >700 nm as compared to that of reported bridged imidazole dimers,[20,21] it indicates that the radical-radical interaction of the colored species of bisDMDPI-BP is weak because of the large dihedral angle of the bridging biphenyl. The calculations and experimental results show that the photochromism of bisDMDPI-BP induces a large conformational change due to the rotation of the biphenyl moiety.

Fig. 2b shows the decay profile of the colored species of bisDMDPI-BP observed at 400 nm at room temperature. The decay is fitted with a single exponential function and the lifetime and the rate constant are 103 ns and 9.7×10^6 s^{-1} at room temperature, respectively. This lifetime shows that bisDMDPI-BP exhibits the fastest thermal back reaction in all reported imidazole dimers. The decays at other wavelengths are quite similar (see Fig. S4 in ESI), indicating that there is a single transient species that decays with first order kinetics, as expected for the biradical.

To reveal the detail of the bond cleavage process of bisDMDPI-BP, we conducted sub-ps transient absorption spectroscopy in which the sample was excited at 310 nm with a pulse duration of ~200 fs. Figs. 3a and b show the transient absorption spectra and dynamics of bisDMDPI-BP at different time delays. The grey dots and solid red curves show the

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experimental data and fitted spectra (and dynamics) obtained by the global analyses as explained later. We found that the transient absorption spectra until 1 ps are quite broadened and the spectra after 3 ps look very similar to those in the ns transient absorption experiments (Fig. 2a). Interestingly, although the spectral width earlier than 1 ps is quite broadened, the peak positions are almost identical, which indicates that the radical component is already generated on sub-ps time scales. We apply global analyses to reveal the multi-wavelength kinetics of bisDMDPI-BP. These analyses were done by using the TIMP package with the graphical interface program Glotaran, version 1.0.1 (http://glotaran.org).[31] The details of the analyses are shown in the supporting information. We propose that the kinetics follows a sequential model because the initial relaxation pathways of HABI derivatives can be expected as follows (Fig. S6 in ESI):[32,33] After the photoexcitation, the photogenerated Franck-Condon state relaxes to the S_1 state. Then, the S_1 state relaxes to the hot state of the colored species. Finally, the colored species is formed via vibrational cooling. In addition to the transition from the S_1 state to the higher vibrational state of the colored species, the higher excited state of the colored species may also contribute to the bond cleavage process through the coupling with the S_1 state of the colorless species. Therefore, we apply sequential kinetic models for the global analyses.

After the photoexcitation, the dynamics from 430 to 750 nm show a fast decay and a very slow decay. On the other hand, the transient absorption at 380 nm only shows a fast rise and a very slow decay. The slow decay is attributed to the colored photoproduct, which is almost stationary on this time scale. Firstly, we applied the two-state sequential model as follows:

$$[S_0] \overset{h\nu}{\to} [\text{Component 1}] \overset{\tau_1}{\to} [\text{Colored species}]$$
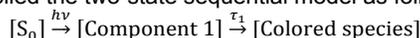
(1)

In this model, we assume that the precursor states of the colored species are not distinguishable and give a single transient signal (Component 1). This model qualitatively explains the transient spectra and decays, and the time constant of the generation process of the colored species (τ_1) is 760 fs (Fig. S7 in ESI). However, it is difficult to reproduce the small amount of another rise component appearing in the range 520-600 nm (Indicated as black arrows in Fig. S8, ESI). The rise component does not look like noise or an artifact. To give a better explanation to the transient signals, we introduce the three-state sequential model as follows.

$$[S_0] \overset{h\nu}{\to} [\text{Component 1}] \overset{\tau_1}{\to} [\text{Component 2}] \overset{\tau_2}{\to} [\text{Colored species}]$$　　(2)
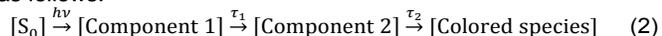
The model assumes that the precursor state of the colored species can be split into two states and they sequentially generate and decay. The model fits the transient spectra and decays very well and the time constants τ_1 and τ_2 are both found to be 420 fs. The fitted spectra and decay curves are shown as the red curves in Fig. 3. The fitted spectra of the individual species and time traces of their population are given in Fig. S9 (ESI). This well-fitted global analysis suggests that the bond cleavage process consists of at least two distinct processes. The second component in the spectral evolution looks like a somewhat shifted and broadened version of the spectrum of the
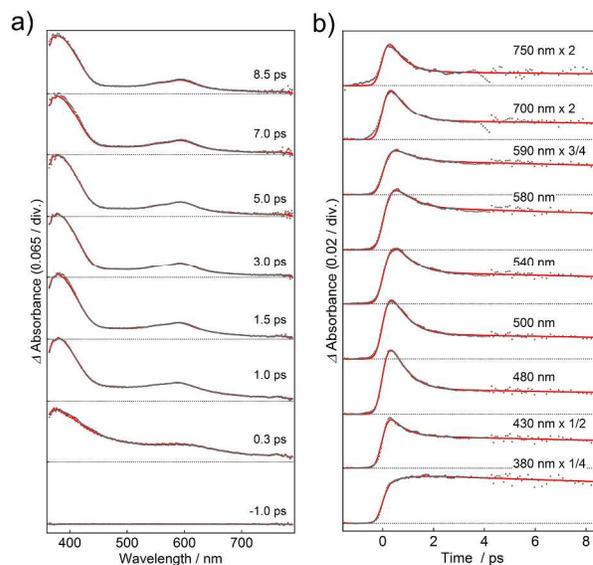

Fig. 3 (a) Transient absorption spectra at sub-ps to 8.5 ps and (b) transient absorption dynamics of bisDMDPI-BP in degassed benzene probed at different wavelength (5.5×10^{-4} M, excitation wavelength: 310 nm, pulse duration 200 fs, and laser intensity: 1.8 μJ). The red curves are the fitted spectra according to the model of eq. 2.

colored species (Fig. S9 in ESI). First and second transient species are therefore best assigned as the transient absorption of the S_1 state and the vibrationally hot electronic ground state of the colored species formed during the dissociation process, respectively.

In conclusion, sub-ps to sub-μs transient absorption spectroscopy reveals that bisDMDPI-BP exhibits extremely fast photochromism with a large conformational change. The colored species of bisDMDPI-BP forms within 1 ps after the excitation and the thermal back reaction of the colored species takes only ~100 ns. As compared to other ns-scale switching molecules, a merit for bisDMDPI-BP is an easy functionalization with sustained fast photochromic properties because the rates of the photochromic properties in bridged imidazole dimers are mostly dominated by the bridging unit: biphenyl in the present case. This property of the imidazole dimer supports the potential of bisDMDPI-BP for ns-time-scale photoswitch materials.

Notes and references

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