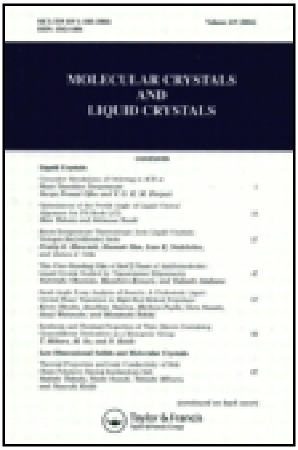

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Vibrational Coherence of Bis-imidazole Derivative, BDPI-2Y, Observed by Ultrafast Spectroscopy

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Ultrafast pump-probe measurement was applied to investigate the excited state deactivation dynamics of bisimidazolyl radical, 1,4-bis-(4,5-diphenylimidazol-2-ylidene)cyclohexa-2,5-diene (BDPI-2Y). BDPI-2Y is non-fluorescent and the recovery of the ground state took place in the time scale of femtoseconds to picoseconds, indicating a direct ultrafast nonradiative decay from the excited state. Coherent intermolecular vibrations were also observed and the low-frequency mode at $150\,cm^{-1}$ *and* $128\,cm^{-1}$ *had a phase shift of* $\sim\pi$ *compared to the mode at* $290\,cm^{-1}$.

Keywords: biradical; coherent vibration; photochromism; ultrafast spectroscopy

INTRODUCTION

Hexaarylbiimidazoles (HABIs) are known to exhibit photochromism, i.e. reversible photochemical cleavage of imidazole dimer into a pair of triarylimidazolyl (lophyl) radicals (Scheme 1a) [1,2]. On the other

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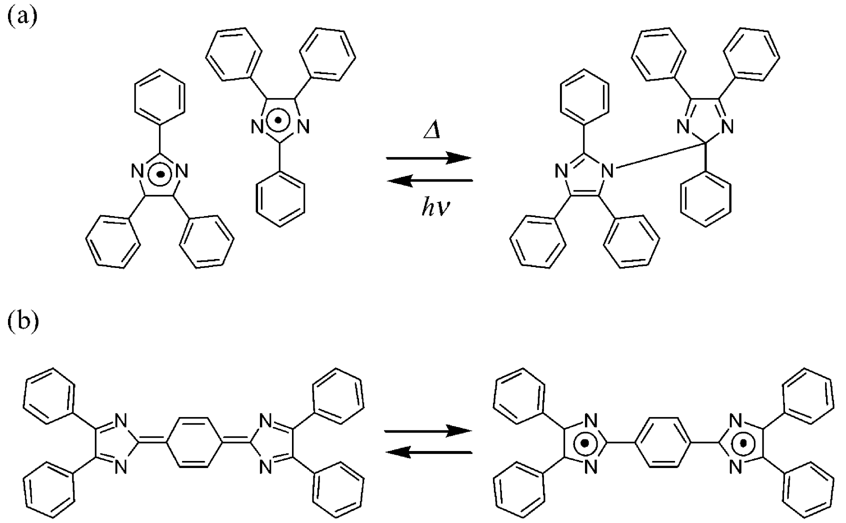

SCHEME 1 (a) Thermally reversible photochemical cleavage of Hexaarylbiimidazoles (HABIs) into a pair of triarylimidazolyl (lophyl) radicals. (b) Quinoid and biradical form of BDPI-2Y.

hand, the bisimidazolyl radical, 1,4-bis-(4,5-diphenylimidazol-2-ylidene)cyclohexa-2,5-diene (BDPI-2Y), exists only as a monomer and does not show dimerization or photochromism. The energy gap between the diamagnetic quinoid ground state and the thermally excited paramagnetic biradical state was considered to be responsible for the absence of the dimerization (Scheme 1b). Combined Studies of UV and ESR measurements revealed that only 0.1% of the BDPI-2Y molecules are in the paramagnetic state in the solution at room temperature [3]. The DFT (B3LYP/6-31G*) studies also indicated that the total energy of the open-shell triplet–biradical state is 7.54 kcal/mol higher than that of the closed-shell quinoid state [3]. Moreover, the presence of a stable solution for an open-shell singlet-biradical state was suggested by the DFT calculations. It was shown that substitution of the four hydrogen atoms on the central phenylene ring by fluorine atoms can lead to dimerization and photochromism by decreasing the energy gap and efficiently populating the triplet–biradical state [3].

Although, the presence of singlet–biradical state was suggested by the DFT calculations, not like triplet biradical, it cannot be detected by ESR measurement, which makes the research in this field extremely challenging. Application of ultrafast laser spectroscopy may resolve the complicated structure of such an electronic state and may provide a new insight to the field of π-conjugated delocalized biradical chemistry. In this report, femtosecond pump-probe (PP) spectroscopy utilizing laser pulses with duration of $\sim$30 fs fwhm was carried out on the solution of BDPI-2Y to investigate the electronic excited state deactivation dynamics.

EXPERIMENTAL

The details of the femtosecond cavity-dumped Kerr lens mode-locked chromium-doped forsterite (Cr:F) laser and the setup for the PP measurement were reported elsewhere [4]. The repetition rate of the cavity-dumping was 100 kHz and the output was focused into a 4 mm LBO crystal to generate the second harmonic beam centered at 635 nm with a pulse duration of $\sim$30 fs. The arrival time of the probe pulse was varied relative to the pump pulse by introducing a computer-controlled optical delay stage. Both pump and probe pulses were focused into the sample by a lens with 10 cm focal length. Intensities of the pump and probe pulses were 900–700 pJ/pulse and 90–70 pJ/pulse, respectively. The samples were placed into a home-made high-speed rotating cuvette to avoid optical degradation and multiple excitation of the sample. The optical path length of the sample cuvette was 0.5 mm and absorbance of the sample was $\sim$1.0 at the peak absorption wavelength. Photodiode with a lock-in amplifier was utilized for the signal detection and the difference in the intensity of the transmitted probe beam ($\Delta trans$) was detected.

RESULTS AND DISCUSSION

The femtosecond PP signal of BDPI-2Y in benzene is shown in Figure 1a. The intensity of the transmitted beam suddenly increases at the time origin, due to the photo-bleaching of the ground state absorption by the pump beam. The stimulated emission can also contribute to the signal. The contribution from the transient absorption seems to be minor in this wavelength region (center wavelength: 635 nm, fwhm: $\sim$28 nm) because increase of the absorption should result as a decrease of the transmitted beam (negative signal).

The signal intensity decreases in a multi-exponential manner in the femtosecond to picosecond time range due to the recovery of the ground state. Three decay components were necessary to reproduce the experimental result by nonlinear least-square fitting. The obtained time constants were 130 fs (68%), 2.5 ps (24%) and 12.5 ps (8%), respectively. Such fast decays indicate direct ultrafast nonradiative deactivation of the excited state into the ground state. Generally

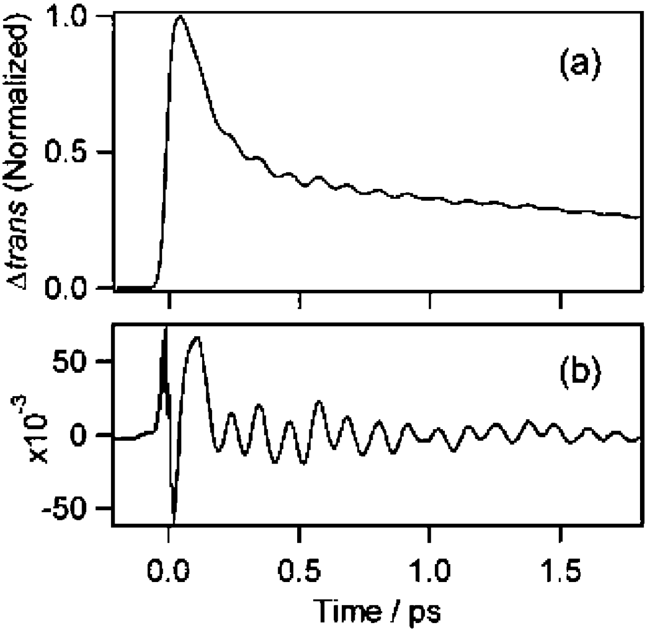

FIGURE 1 (a) The femtosecond PP signal of BDPI-2Y in benzene measured at a central wavelength of 635 nm with pulse duration of ~30 fs. (b) The oscillation of the signal remained after subtraction of the decay components.

speaking, the fastest component with time constant of 130 fs can be assigned to the thermal relaxation process (vibrational cooling) in the excited state, the second one (2.5 ps) to the nonradiative deactivation of the excited state to the ground state, and the third one (12.5 ps) to the thermal relaxation process of vibrationally hot molecules in the ground state, because these events take place in this order. However, the origin of each component must be considered carefully and confirmation is necessary by other observations.

The PP signal is also modulated by coherent intramolecular oscillations. Figure 1b shows the oscillation component obtained by subtracting the decay components from the experimental signal. The oscillations in Figure 1b was Fourier transformed into frequency domain spectrum as shown in Figure 2. These spectra are rather similar to the resonance Raman scattering spectrum of BDPI-2Y in benzene measured at 632.8 nm (Fig. 3). Interestingly, in the real part of the spectrum, some modes have opposite sign, i.e. the mode at 290 cm^{-1} is positive while the modes at 128 cm^{-1} and 150 cm^{-1} are negative. The real and imaginary parts of the spectrum are sensitive

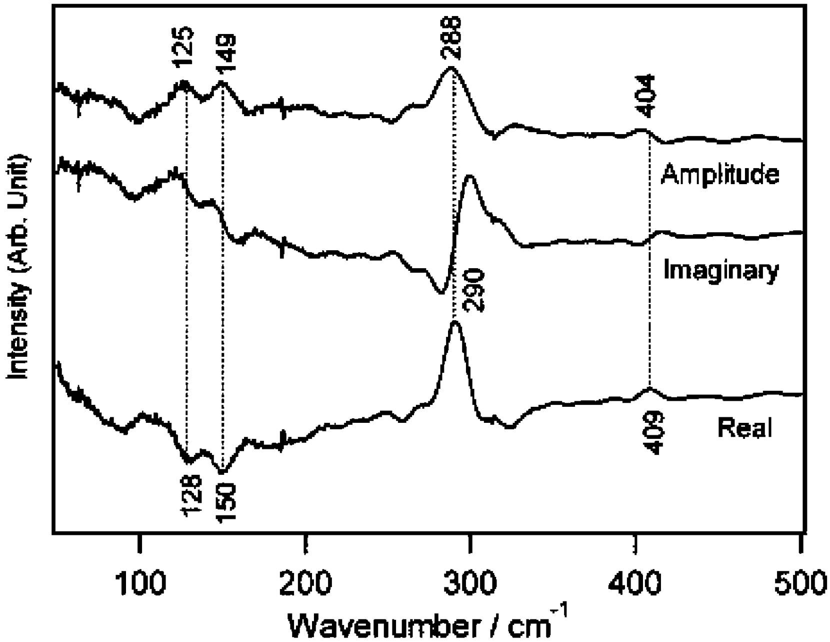

FIGURE 2 Real, imaginary, and amplitude of the Fourier transformed spectrum of the coherent oscillation. Fast Fourier transform method was applied.

to initial phase of the oscillation while the amplitude is not, thus these modes can be considered to have a phase-shift of $\sim\pi$. As mentioned before, ground state bleach and transient absorption have opposite sign in the PP signal, positive and negative, respectively. Analogically, oscillations in the ground state and in the excited state can have an opposite sign if the ground state bleach and the excited state absorption are overlapped at the probe wavelength. If the 150 cm^{-1} oscillation originates from the excited state, the shortest time constant of 130 fs should be excluded from the candidate for the excited state lifetime, because 130 fs, is as short as half the period of the 150 cm^{-1} oscillation, i.e. $\sim$220 fs. In this case, 130 fs will be the time constant for the relaxation in the excited state, 2.5 ps is the excited lifetime, and 12.5 ps is the time constant for the ground state relaxation as we expected. On the other hand, if the excited state lifetime is as short as 130 fs, the nonradiative deactivation process could be fast enough to generate coherent low-frequency oscillations in the ground state. Usually, coherent oscillation in the ground state is generated by instantaneous Raman process. The oscillation caused by the ultrafast nonradiative

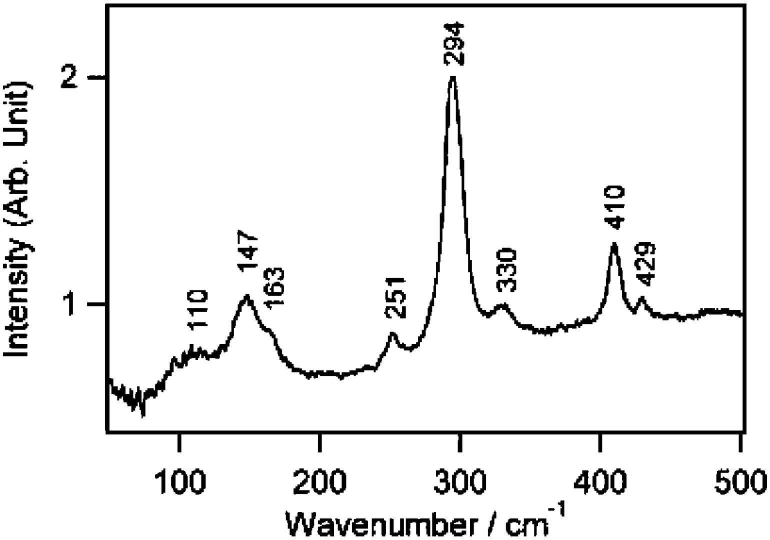

FIGURE 3 Steady-state resonance Raman spectrum of BDPI-2Y in benzene obtained by 632.8 nm excitation utilizing He-Ne laser.

deactivation could be delayed from the normal oscillations with some phase-shift. This point is interesting and we are planning to investigate in the future by determining the excited state lifetime accurately.

As a conclusion, the recovery of the ground state took place in the time scale of femtoseconds to picoseconds, which indicates an ultrafast nonradiative decay channel of the excited state. Coherent intermolecular vibrations were observed and the low-frequency mode at 150 cm^{-1} and 128 cm^{-1} had a negative sign in the real part of the Fourier transformed spectrum. These modes are likely to be the excited state vibrations coherently induced by the direct photo-excitation, although the possibility of the ground state vibrations induced by the ultrafast deactivation process cannot be excluded and we are planning to check this point in the near future.

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