Cooperative Conformational Change and Excitation Migration of Biphenyl-PMO Amorphous Film, as Revealed by Femtosecond Time-resolved Spectroscopy

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Supporting Information
5 pages

1. Fluorescence time profiles of Bp-PMO amorphous film.

Fluorescence time profiles were measured by using a time-correlated single photon counting system. As an excitation laser pulse, the third harmonic (266 nm) of a femtosecond broad band Ti: Sapphire laser (Tsunami, Spectra-Physics) pumped by the SHG of a cw Nd^{3+}:YVO_4 laser (Millennia Pro, Spectra-Physics) was employed with the repetition rate of 8 MHz. The emission was detected at the magic angle configuration utilizing a polarizer and a half-wave plate. A photomultiplier tube (R3809U-50, Hamamatsu) with an amplifier (C5594, Hamamatsu) and a counting board (PicoHarp 300, PicoQuanta) were used for the signal detection. A monochromator (77250, Oriel) was placed in front of the photomultiplier tube. The instrumental response time was 32 ps, which was determined by the FWHM of a scattered light from a colloidal solution.

Figure S1 shows time-resolved fluorescence spectra of (a)Bp-Et-PMO film and
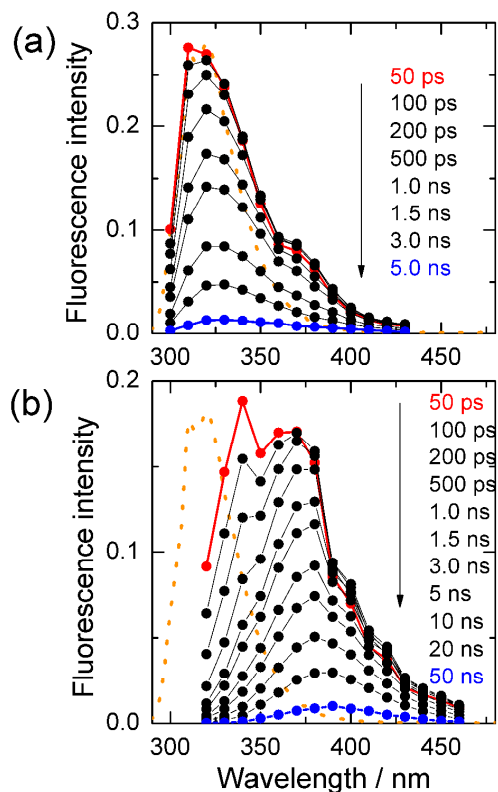
Figure S1 Time-resolved fluorescence spectra of (a)Bp-Et-PMO film and (b)Bp-PMO amorphous films, which were constructed from time profiles of the fluorescence under the excitation with a 266 nm laser pulse.

(b)Bp-PMO amorphous films, which were constructed from time profiles of the fluorescence under the excitation with a 266 nm laser pulse.

For Bp-Et-PMO film, immediately after the excitation, the spectra at 0-0.1 ns was similar to the steady-state fluorescence spectrum of BTEBp in cyclohexane. With an increase in the delay time after the excitation, the fluorescence maximum red-shifts and the spectral band evolves into broadened shape. On the other hand, for the Bp-PMO film, spectra at 0 - 0.1 ns after the excitation shows a peak at 340 nm, which locates in the wavelength region longer than the steady-state fluorescence of the Bp-Et-PMO film and BTEBp in cyclohexane. This result indicates that a part of excimer states was produced within the instrumental response function. In addition, the contribution from the excimer state is much larger than that observed in Bp-Et-PMO system.

Figure S2 shows the wavelength dependence of pre-exponential factors for these four time constants. Here, a set of time profiles were analyzed by using a global fitting method on the basis of a quadruple exponential function with four time constants of 140 ps, 1.6 ns, 8.6 ns and 30 ns. These four time constants were obtained as averaged values for all the
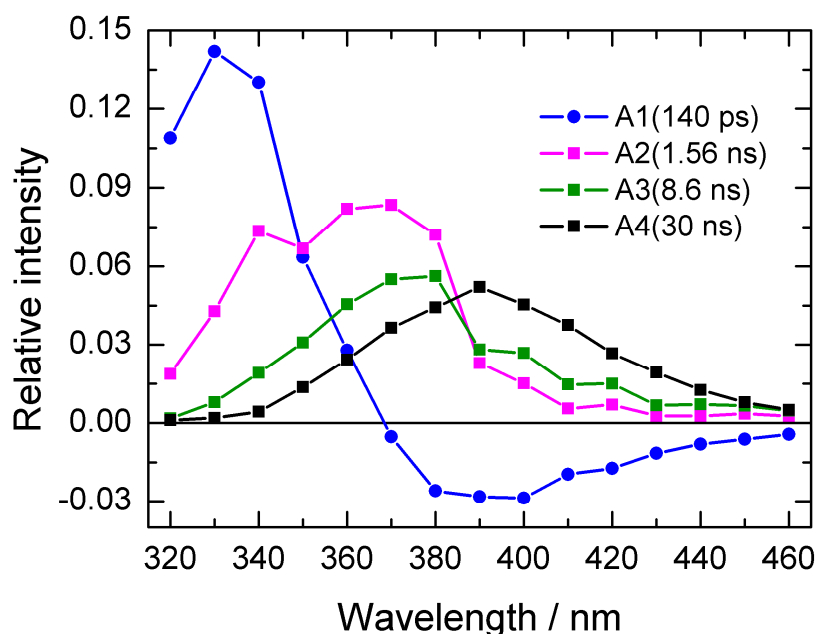

Figure S2. Wavelength dependence of the partial amplitudes of the decay times obtained by global analysis of the decays of the fluorescence decay curves of Bp-PMO film.

time profiles and were almost the same with those obtained for the Bp-PMO powder system[1]. The positive and negative signals respectively indicate the decaying and growing components for each time constant.

The spectrum for the 140-ps time constant shows positive signals around 325 nm and negative ones in the wavelength range longer than 360 nm. From these positive and negative signals depending on the monitoring wavelength, the 140-ps time constant was attributable to the excimer formation. That is, the excimer is formed with the 140-ps time constant in addition to the rapid process within the instrumental response.

The other three components of 1.6 (A2), 8.6 (A3) and 30 ns (A4) show only positive signals in the wavelength region. This result indicates that these three components were mainly produced with the time constant of 140 ps and decayed almost independently with each lifetime. It should be noted, however, that the spectra for A2 and A3 components show relatively smaller values in the wavelength region longer than 360 nm, compared to that for A4 which shows a symmetrical shape with the center of the fluorescence maximum at 380 nm. In the previous study of the Bp-PMO powder system with higher periodic alignments of Bp moieties, it was observed that each component corresponding to A2, A3, and A4 showed almost symmetrical spectral shapes[1]. This result suggests that some interconversion processes such as A2→A4 and A3→ A4 may take place in the present system. The yield of
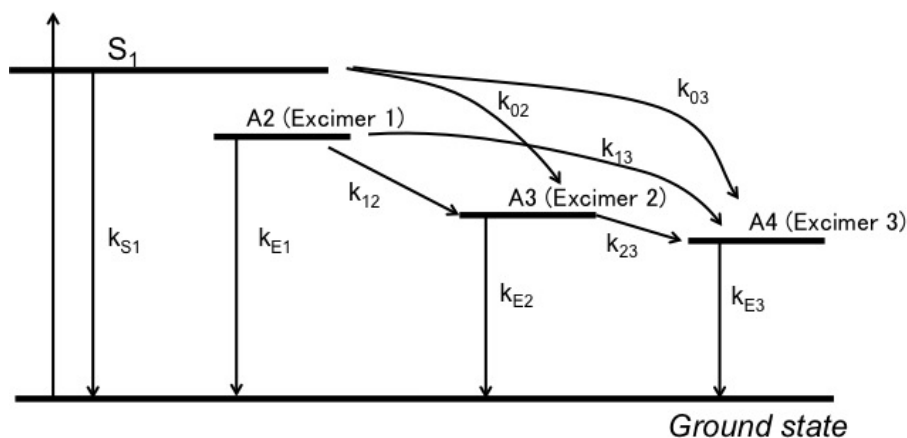

Scheme S1. Relaxation flow of Bp-PMO amorphous film. k **stands for a rate constant between states, and the inferior letters, for example, 02 and 13 means the relaxation from preplanar-excited state to excimer 2, and from excimer 1 to excimer 3, respectively.**

the interconversion process among the excimers was roughly estimated to be 0.04 in the present system on the basis of the rate equations of scheme S1 and fluorescence yield of each excimer state[1]. This result indicates that the interconversion among excimers states is a minor process also in the present amorphous Bp-PMO film.

2. Estimation of excitation density of Bp moeites in Bp-PMO.

We estimated the excitation density of Bp moieties by using molecular alignment in the Bp-PMO film as shown in Figure S3. On the basis of the excitation radius (170 μm), wavelength, and light intensity (μJ/pulse), the photon number under the higher excitation condition (1.0 μJ/pulse) is 2.3×10^{10} and Bp molecules in the excitation volume is 2.3×10^{10} and 1.9×10^{11} in 1-nm depth from the surface, indicating that 12% of Bp moieties are estimated to be excited as mentioned in text. Since the distance between Bp layers is 0.44 nm[1], the 1-nm depth corresponds to three layers including 27 Bp moieties (Figure S3). That is, three Bp molecules (27 molecules x 12%) are excited in 27 Bp molecules under higher excitation condition.   Since a Bp molecule (yellow marker) is excited by one photon, 2 in 26 molecules are certainly excited. Considering that there are four nearest Bp moieties (blue markers) around the yellow marker, the excitation probability of the nearest neighbor Bp moiety could be estimated to be ca. 30% (4 molecules x 1/26 x 2 photons).
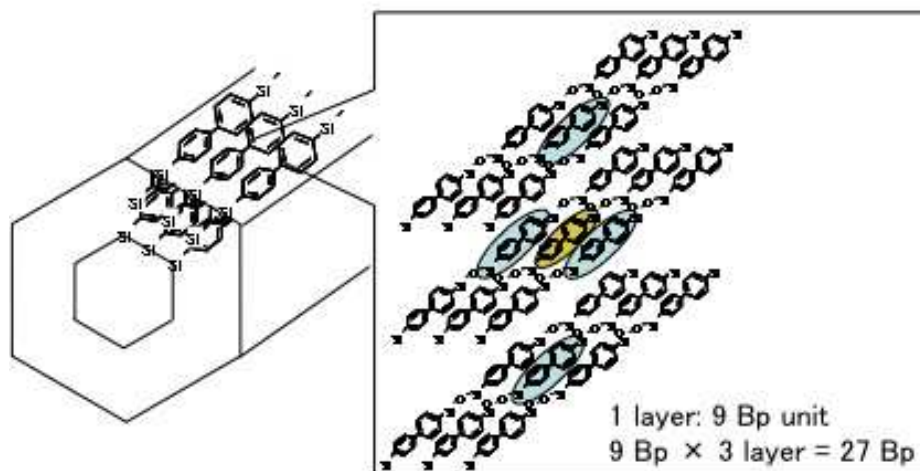
Figure S3. Molecular alignment of Bp moieties in Bp-PMO film, and three layer unit including 27 Bp molecules. Blue markers are the nearest excited Bp molecules neighboring a Bp molecule (yellow maker).

References

1. Yamanaka, K.; Okada, T.; Goto, Y.; Tani, T.; Inagaki, S. Dynamics in the Excited Electronic State of Periodic Mesoporous Biphenylylene-silica Studied by Time-resolved Diffuse Reflectance and Fluorescence Spectroscopy. *Phys Chem. Chem. Phys.*, **2010**, *12*, 11688-11696.