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Communication: Time-resolved fluorescence of highly single crystalline molecular wires of azobenzene

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We report the enhanced fluorescence with the remarkably long lifetime (1.17 ns) in the first excited state (S_1) of highly crystalline molecular wires of azobenzene at the excitation wavelength of 467 nm for the first time. This observation suggests that *trans-cis* photoisomerization through the rotation or inversion mechanism may not be a favorable pathway after excitation to the S_1 state in highly single crystalline molecular wires of azobenzene due to the hindered motion within densely packed crystal structure. We also measured the fluorescence lifetime image of a single crystalline molecular wire of azobenzene, indicating that the lifetime was remarkably uniform and that there was only a very minor variation within the crystal. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3701733]

The photoisomerization and the fluorescence decay dynamics of the excited states of azobenzene upon photoexcitation have been extensively studied owing to its unique applications toward light driven switches,[1] molecular machines,[2] image storage devices,[3] and materials[4] for the liquid crystal. From the viewpoint of fundamental photochemistry, particularly, *trans-cis* photoisomerization mechanism and excited state decay dynamics of azobenzene are still a long standing issue to be much debated between theoretical calculations and experiments because of very fast isomerization process.[5–11] Recent ultrafast time-resolved spectroscopic results from probing short-lived azobenzene excited states propose that the isomerization pathways are rather complicated processes involving multiple relaxation channels.[12] In principle, azobenzene undergoes *trans-cis* photoisomerization by the excitation of the S_1 ($n \rightarrow \pi^*$) and the S_2 ($\pi \rightarrow \pi^*$) states in the UV and visible region.[5] Two pathways have been thus proposed to explain the intramolecular mechanism of the isomerization process: a twisting around the nitrogen–nitrogen double bond (rotational mechanism) and an increase in the C–N–N bending angles with an exchange in the position of the lone pair of one of the nitrogen atoms (inversion mechanism).[5]

According to previous results, the average lifetime of the S_1 state of *trans* azobenzene and *cis* azobenzene were estimated by a few picoseconds (~2.6 ps for *trans* and ~0.2 ps for *cis*) in solution and decayed monomodally or bimodally depending on the solvent viscosity and excitation wavelength.[12,13] As reported previously, azobenzene exhibits very weak fluorescence emission from the S_1 excited state with low quantum yield of $\sim 1 \times 10^{-6}$ due to deactivation of the first excited state by photoisomerization.[6] On the other hand, several attempts to enhance fluorescence emission of azobenzene derivatives have been recently reported by inducing the inhibition of the isomerization process via conformationally locked structural considerations.[14–16] Interestingly, Uchimoto *et al.*[17] reported reversible mechanical bending motion of plate-like microcrystals of *trans*-4-(dimethylamino)azobenzene upon UV irradiation (365 nm) and then they claimed that the planar *trans*-4-(dimethylamino)azobenzene undergo photoisomerization to *cis*-4-(dimethylamino)azobenzene on only the (001) crystal surface. However, *trans-cis* photoisomerization of pure azobenzene has not been observed in the crystalline state due to the geometric restrictions of the molecular motion under densely packed crystal lattices. As long as pure azobenzene in the crystalline state is concerned, to the best of our knowledge, there is no report for the fluorescence emission as well as the lifetime of the S_1 excited state yet. Thus, it is an interesting subject to explore photochemical dynamics of azobenzene molecular crystals in the crystalline state. In this communication, we report the synthesis of single crystalline azobenzene molecular wires as well as the fluorescence decay dynamics in the first excited state (S_1) for the first time.

Azobenzene molecular wires were directly grown on a cover glass through atmospheric pressure chemical vapor deposition[18] shown in Figure 1. Specifically, the growth of molecular wires was carried out in a single zone horizontal quartz tube furnace, 2.5 cm in diameter and 60 cm long. First, 1.0 mg fine-meshed azobenzene (1.0 mg) powder was loaded at the center of a 6 cm long quartz boat without further purification. The cover glass was placed approximately 15 cm downstream from the azobenzene powder. The azobenzene powder on the quartz boat and the cover glass in the quartz tube were heated at 65 °C under high-purity He (99.999%) carrier gas flowing for 2 h at a gas flow rate of 300 sccm. The molecular wires of azobenzene were then grown at a temperature of about 40 °C while the temperature of the furnace was kept at 65 °C. When the growth was complete, the furnace was allowed to cool down to room temperature while maintaining

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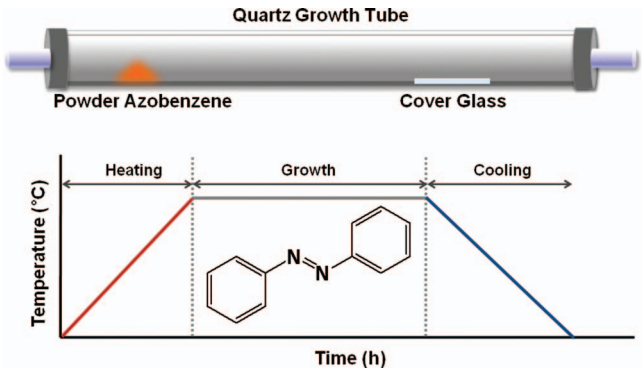

FIG. 1. Schematic diagrams of crystal growth apparatus for the vapor transport method, and temperature gradient in the experiment.

the flow of He. The structure and morphology of azobenzene wire were examined through scanning electron microscopy (SEM) and x-ray diffraction (XRD), respectively. The XRD patterns were recorded on a small angle x-ray diffractometer (Rigaku SWRD series) with Cu K_α radiation as the x-ray source ($\lambda = 1.5418$ Å). Electron micrographs were acquired using a field-emission scanning electron microscope (JSM-6700F, JEOL).

The fluorescence lifetime of azobenzene was measured by time-correlated single photon counting (TCSPC).[19] The light source used for excitation of the sample was a picosecond diode laser operating at a wavelength of 467 nm at 10 MHz (Picoquant, PDL 800-B). For sample excitation, a single-mode fiber was used to introduce the laser beam into a confocal microscope (Nikon, TE2000-S). The fluorescence from the sample excited by randomly polarized light was passed through a 488 nm long pass filter (Semrock) and detected using a microchannel plate photomultiplier tube. The fluorescence signal was detected by a microchannel plate photomultiplier tube and a fast TCSPC board (Becker-Hickl, SPC-830). The instrument response function (IRF) of the system was about 150 ps. The fluorescence lifetimes were calculated from the measured decay curves using a nonlinear least-squares fit procedure with the deconvolution of the IRF. For fluorescence lifetime imaging microscopy (FLIM) measurement, a single crystalline azobenzene wire was captured in a 256 × 256 pixel image with 1 Hz scan rate.

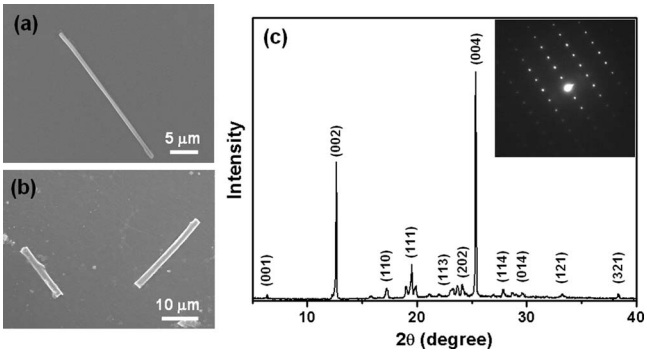

FIG. 2. SEM images of highly single crystalline azobenzene molecular wires (a) and (b), and XRD pattern (c). Inset represents a selective area electron diffraction pattern of a single azobenzene molecular wire.

Figures 2(a) and 2(b) show the typical SEM images of azobenzene molecular wires. The size and length of as grown azobenzene molecular wires, as estimated from the SEM images, are from a few hundred nanometers to several micrometers and 15–20 μm, respectively. The XRD pattern of the azobenzene molecular wires in Figure 2(c) clearly indicates that all diffraction peaks can be perfectly indexed according to the monoclinic phase ($P2_1/a$), which is consistent with the standard value of a = 11.46 Å, b = 5.77 Å, c = 14.20 Å, and $\beta = 102.12°$ (JCPDS No. 30-1530).[20] X-ray diffraction measurement reveals two dominant sharp peaks, corresponding to (002) and (004) faces, respectively. To gain further insight into the fine crystal structure, we have tried transmission electron microscopy (TEM) measurement for a single azobenzene molecular wire. Particularly, it is very challenging to obtain TEM image since it easily decomposes within a few second exposure times due to very low melting point. Although we thus failed to obtain the detailed crystal structure from TEM, a selective area electron diffraction pattern observed for a single azobenzene molecular wire implies that as grown azobenzene molecular wires are highly single crystalline as shown in Figure 2(inset). The growth mechanism of azobenzene molecular wires resembles sublimation followed by recrystallization, a process referred to as vapor-solid growth.[21]

Figure 3(a) shows the absorption spectrum of azobenzene in solution and the fluorescence emission spectrum of azobenzene molecular wires at the excitation wavelength of 467 nm. According to previous works, the absorption band peaked at ~450 nm can be easily assigned as the $S_1 \leftarrow S_0$ (n-π*) transition, corresponding to the tail of the first excited state.[5] In principle, since the fluorescence from the S_1 excited state in solution is extremely weak even in the time-integrated spectrum due to its very short lifetime and its optically forbidden nature, it is hardly observed.[22] On the other hand, we clearly observed the steady state fluorescence emission in molecular crystal wires at the intensity maximum of 576 nm.[23] It is immediately apparent that the relaxation mechanism of the S_1 excited state in the crystalline state is quite different from that of solution. Furthermore, Figure 3(b) shows the time resolved fluorescence decay curves of azobenzene powder and single-crystalline azobenzene. None of these data show a single exponential, which may arise from sample heterogeneity, nonexponential population decays, surface effects, etc. Assigning individual contributions by the decay curve analysis is not possible at present. Therefore, the curves were simply fit to a double exponential form to obtain the average lifetime that represent a characteristic time constant. The average lifetime of azobenzene powder was 360 ps, and that of single-crystalline azobenzene was 1.17 ns. Consequently, the fluorescence decay of azobenzene molecular wires is remarkably longer than that of azobenzene in powder and in solution, implying that the relaxation process of the S_1 excited state effectively slows down in the crystalline state, consistent with the enhanced fluorescence emission spectrum of Figure 3(a). The present results strongly indicate that *trans-cis* photoisomerization process of azobenzene followed by the S_1 excitation may not occur in the crystalline state. The intermolecular interactions originated from the π-π orbital overlap of two adjacent phenyl rings of the planar structure generally results

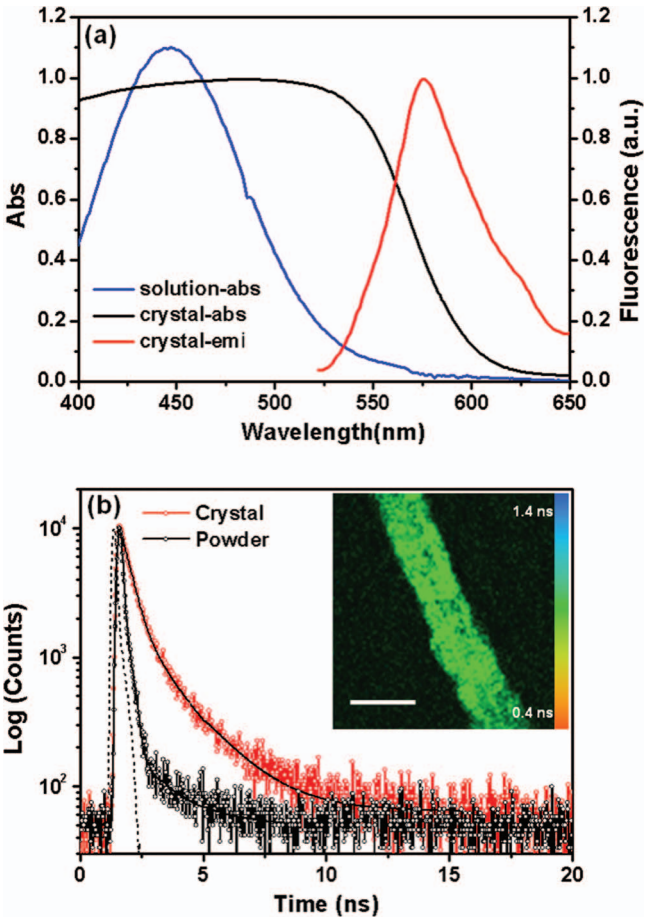

FIG. 3. (a) Absorption spectrum of azobenzene in solution and fluorescence emission spectrum of azobenzene molecular wires at the excited wavelength of 467 nm. (b) Fluorescence decay curves of azobenzene powder and azobenzene molecular wires. The dotted line represents the instrument response function. Note that the fluorescence spectra of power and crystal were normalized. Inset represents a FLIM image of a single crystalline wire. The image dimensions are 256 × 256 pixels at the scale bar of 2 μm.

in densely stacked crystal structure in the crystal lattice of azobenzene. Under such a restricted space within the crystal structure, the rotation relaxation or inversion relaxation process of azobenzene molecular wire upon photoexcitation may not be a favorable pathway due to the conformationally hindered motion. It can be thus suggested that any photoisomerization process through a twisting in the N=N double bond of azobenzene or an increase in the C–N–N bending angles could be significantly suppressed by the rigid structure in the crystalline state.[23] In other words, our observation can be rationalized that the suppression of the nonradiative relaxation like photoisomerization is responsible for its enhanced fluorescence emission and greatly long lifetime of the S_1 state compared with those of solution. In addition, the dramatic difference of the lifetime of the S_1 state between the powder and crystal can be partially attributed to the distinct crystallinity of azobenzene in the solid state. It is readily expected that molecular crystal wires of azobenzene obtained by the vapor phase transport has highly ordered crystallinity as shown in Figure 2 and then has more rigid crystal structure compared with the powder sample of that. For the crystal sample, therefore, *trans-cis* photoisomerization process could be more effectively blocked than that of powder sample. On the other hand, the random orientations of various crystal surfaces of azobenzene (in the polycrystalline form) in the powder sample might also affect the fluorescence decay dynamics by effectively allowing the photoisomerization process. Therefore, it would not be excluded that the favorable contribution of the surface decay dynamics in the powder sample can be responsible for much shorter average fluorescence lifetime of the S_1 excited state compared to highly crystalline molecular wires of azobenzene. Additionally, we obtained the FLIM of a single crystalline molecular wire (inset in Figure 3(b)). The homogeneity of the image indicates that the lifetime was remarkably uniform and that there was only a very minor variation within the crystal.

In summary, we briefly demonstrate the fluorescence decay dynamics of highly single crystalline azobenzene molecular wires in the crystalline state for the first time. We observed the enhanced fluorescence emission as well as the remarkably long lifetime (1.17 ns) of the first excited state (S_1) at the excitation wavelength of 467 nm in the crystalline state, implying that *trans-cis* photoisomerization process through the rotation or inversion around the N=N double bond of azobenzene could be effectively blocked due to the densely packed single crystalline molecular structure.

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