Photochromic behavior of diarylbenzene nanoparticles prepared by ball-milling and reprecipitation methods

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Photochromic molecules change their physicochemical properties in response to light stimulation and have many potential applications. In particular, the investigation of photochromic behavior in nanoparticles is essential for the development of novel functional materials.[1,2] Recently, we have developed diarylbenzene (DAB) molecules as a new family of T-type photochromic molecules.[3] DABs undergo 6π-electron photocyclization and thermal back reaction. Thus, DAB molecules have great potential as a photochromic molecule. However, the photochromic behavior of nanoparticles made from DABs has been unexplored. In this work, we report the preparation and characterization of nanoparticles composed of diarylbenzene **1a** (Figure 1) and investigated their photochromic behaviors.

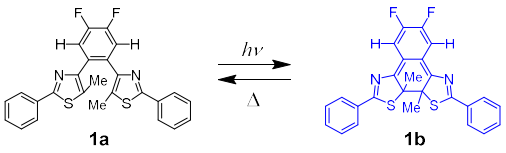

Fig. 1 Diarylbenzene investigated in this work.

First, nanoparticles were prepared by a ball-milling method. The single crystal of **1a** was finely crushed in water containing sodium dodecyl sulfate. After centrifugation, the supernatant of the solution was collected (**NP-ball**). Furthermore, nanoparticles were prepared by a reprecipitation method. A tiny amount of the ethanol solution of **1a** was injected in the vigorously stirred water by a micro-syringe. After further stirring, nanoparticles suspended in water could be obtained (**NP-rep**). From powder X-ray diffraction measurements, it was revealed that **NP-ball** is crystalline, whereas **NP-rep** is amorphous. Next, the photochromic behaviors of **NP-ball** and **NP-rep** were investigated. Both nanoparticles showed T-type photochromism, but the rate constants of the thermal back reaction were different from each other. From the detailed analysis, the kinetics of the thermal back reaction in nanoparticles were successfully interpreted by the difference in the environment around molecules. Thus, the different approaches for fabricating nanoparticles resulted in the different state nanoparticles and the rate constant of the thermal-back reaction depends on the state of the nanoparticles. This result provides a convenient and useful method for preparing nanoparticles with different thermochromic reactivity from one molecule.

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2) Y. Ishibashi *et al*., *Chem*. *Commun*, **2020**, *56*, 7088-7091.
3) D. Kitagawa *et al*., *J. Mater*. *Chem*. *C*, **2019**, *7*, 2865-2870.