Solid-State Photoreaction of Stilbene Dicarboxylate Salts with Alkylammonium

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Photodimerization reaction of C=C double bonds in solid state has been firstly reported by Schmidt in 1971,[1] and such solid state photoreaction system has been developed by using crystal engineering technique. Herein, we focused on the simple electrostatic hydrogen-bonding interaction to control the molecular arrangement of photoreactive molecule of stilbene π-cores. A systematic change in the carbon number (n) of alkylammonium cations ($C_nH_{2n+1}NH_3^+$) for dianionic 4,4'-stilbenedicarboxylate (SDC^{2-}) can modulate the packing structures of SDC^{2-} in single-crystals, which realizes a suitable molecular arrangement of the formation of dimer molecule (Fig. 1).

Molecular salts between dianionic 4,4'-stilbenedicarboxylate (SDC^{2-}) and two molar alkylammonium ($C_nH_{2n+1}NH_3^+$) were prepared to control the molecular arrangement of SDC^{2-} in single-crystals, which enabled to design a possible photo-reactive intermolecular interaction. In salts of $(C_nH_{2n+1}NH_3^+)_2(SDC^{2-})$, change in the carbon number (n) can modulate the packing structures of the photo-reactive SDC^{2-} dianions. When the carbon–carbon distance at the central C=C bonds of two stilbene units is less than 4.2 Å,[1] the photo-dimerization reaction occurs by a UV-irradiation in solids. In this study, six single-crystals were obtained by the recrystallization of $(C_nH_{2n+1}NH_3^+)_2(SDC^{2-})$ from MeOH. All proton-transferred salts had 2:1 formula. A suitable π-dimer formation was observed at only the single-crystal of $(C_3H_7NH_3^+)_2(SDC^{2-})$, which central C=C bond distance was 3.64 Å. Although the intermolecular interactions between SDC^{2-} were observed in the other salts, there were insufficient condition for the photodimerization reaction. After the UV-irradiation to the powder $(C_3H_7NH_3^+)_2(SDC^{2-})$, ^{1}H NMR spectra in $CDCl_3$ showed the photo-dimer formation at cyclobutane structure of δ = 4.58 ppm. The photoreaction yield was reached at 89% after 30 min photo-irradiation.

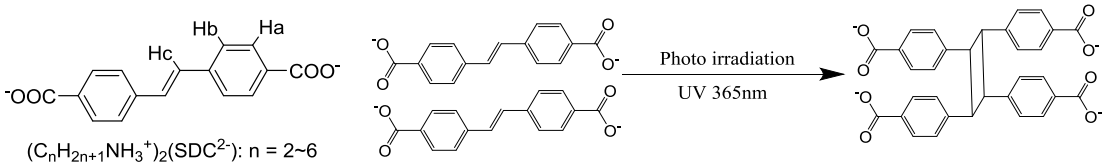

Fig. 1. Molecular structure of $(C_nH_{2n+1}NH_3^+)_2(SDC^{2-})$ salts and the formation of photo-irradiated dimer formation at the central C=C bonds.

1) Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, *27*, 647–678.