

Stimuli-responsive Single Crystals of Pyrene-introduced Indanedione Dimers

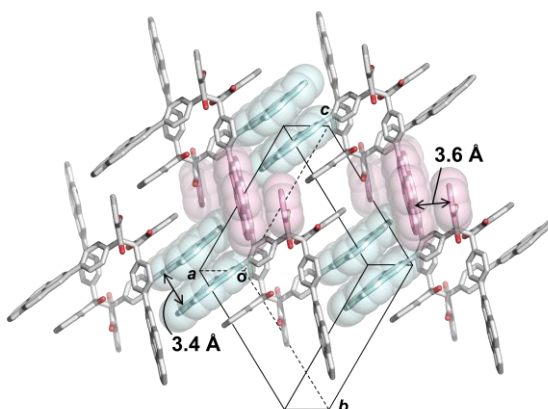
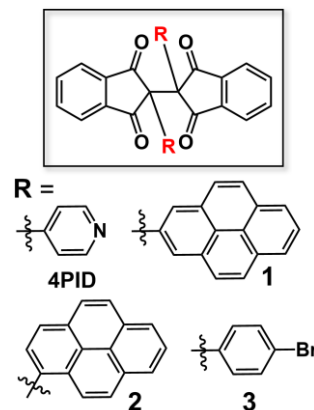
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In general, molecular crystals are constructed by weak intramolecular interactions and tend to have poor structural stability to external stimuli. However, in recent years, many examples of molecular crystals that flexibly change their structures and physical properties in response to the outer stimuli are reported. In this context, we also have great interest on the stimuli-responsive soft crystals and focused on X-shaped indanedione dimers as their building units.¹⁾ Their unique X-shape enables the solvent-included channel formation in the crystalline state and provides the flexibility to the framework. These features resulted in the preparation of sponge-like crystalline system of **4PID** in which two structures, 1D-channel holding **OPEN** form and tightly packed **CLOSE** form are interconvertible by the guest solvent adsorption/removal with keeping the crystallinity.^{1a)} On the basis of this result, here we designed and synthesized two new indanedione dimers **1** and **2** in which pyrene unit was introduced as the fluorophore.

The desired products **1** and **2** were prepared from bis(bromophenyl)indanedione dimer **3** by Suzuki-Miyaura cross coupling reaction with corresponding pyreneboronic acid. Both solution- and solid-state emission spectra of **1** showed emission band from pyrene monomer at around 400 nm. In addition to that, the solid sample also showed the emission attributable to pyrene excimer while the dense solution did not. On the other hand, diluted solution of **2** showed the emission band derived from pyrene monomer and the concentrated one gave pyrene excimer emission, though the solid sample did not show any emission. Single crystal X-ray analysis of **1** revealed the formation of two types of π - π interactions, between two pyrene skeletons (3.4 Å) and between the pyrene and indanedione skeletons (3.6 Å) (Figure). Interestingly, this crystal of **1** showed the phase transition by heating to show the structure and emission property changes.



1) a) Y. Yakiyama, T. Fujinaka, M. Nishimura, R. Seki, H. Sakurai, *Chem. Commun.* **2020**, 56, 9687.

b) Y. Yakiyama, T. Fujinaka, M. Nishimura, R. Seki, H. Sakurai, *Asian J. Org. Chem.* **2021**, 10, 2690.