Crystal Structure and Electrochemical Properties of Octathio[8]circulene

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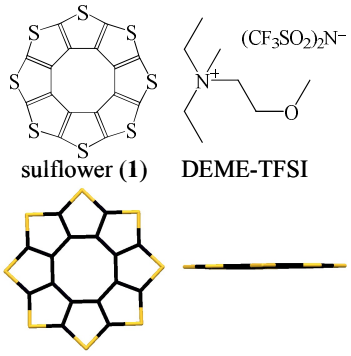

Carbon-sulfur compounds have been studied extensively as key materials in organic/molecular electronics. Octathio[8]circulene (**1**), called "sulflower," is a new molecule that is attracting much attention from various points of view: anti-aromaticity caused by molecular symmetry with the 8π electrons on the inner ring and orbital degeneracy, intermolecular packing caused by the sulfur atoms exposed to the outside of the molecular rings, and applications in organic electronics [1]. While the strong intermolecular interactions of **1** were expected in the solid state, no detailed structural data have been reported so far. In this work we carried out crystal growths, structural determination and electrochemistry of the thin films of **1**.

1 was prepared by the literature methods [1]. Single crystal of **1** was obtained as red needles by vacuum sublimation. The structural analyses revealed that there were the molecule **1** possesses a very planar structure, in which the structural distortion anticipated from the 8π anti-aromaticity is released. Since the compound **1** is insoluble in aqueous and organic solvents, we examined the electrochemistry of the thin films of **1**. Thin films were obtained by vacuum vapor deposition, and thin-film XRD indicated a lamellar structure in which the molecular planes are nearly perpendicular to the substrates [2]. Although the thin films of **1** easily peeled off during electrochemical reactions in organic solvents, they were stable enough to exhibit a repeatable redox process in ionic liquids such as DEME-TFSI. The compound **1** exhibited simultaneous two-electron oxidation in the oxidation scan and then stepwise reductions to the original neutral state, showing significant electrochromism. This color change, well-interpreted in terms of the allowed *n*-π transition by electrochemical oxidation, was a good experimental evidence for the nearly-degenerated HOMOs in **1** [3]. We will discuss the electrochemical thin-film field-effect transistor of **1**.

[1] V. G. Nenajdenko *et al*., Angew. Chem. Int. Ed. 45 (2006) 7367.
[2] T. Fujimoto *et al*., Chem. -Eur. J. 14 (2008) 6053.
[3] T. Fujimoto *et al*., J. Am. Chem. Soc. 130(47) (2008) 15790.