σ-Delocalized Orbitals and Charge-Transport Properties of Polyiodobenzenes

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The major focus of organic semiconductors has been on π-conjugated molecules, and the origin of charge transport has been the interaction between π-orbitals (Figure 1, left). However, the intermolecular interactions of these compounds are constrained by planar extended π-orbitals, and the molecular packings are restricted to one-dimensional or two-dimensional manner. These molecular packing results in an anisotropy of charge transport, which suppresses efficient charge transport. In order to expand the dimensional diversity of charge transport, we have focused on cyclic delocalized orbitals with σ-symmetry (Figure 1, right). We hypothesized that this type of an orbital would contribute to the multi-dimensional charge transport thanks to the σ-delocalized orbital orthogonal to the conventional π-orbitals.

In this work, we have designed polyiodobenzenes **1** and **2** bearing more than five iodine atoms on a benzene platform as the target molecules and investigated their charge transport properties. Calculated reorganization energies and transfer integrals of these molecules indicated that the polyiodobenzenes possess a three-dimensional pathway for charge transport. Time-resolved microwave conductivity (TRMC) measurements of these compounds revealed that a photoconductivity of the polyiodobenzenes (5.0×10^{-4} cm^2 V^{-1} s^{-1}, for **1**, 1.9×10^{-4} cm^2 V^{-1} s^{-1}, for **2**) is the same order as that of general organic semiconductors (e.g. 6.5×10^{-4} cm^2 V^{-1} s^{-1}, for rubrene)[1], suggesting that the molecules bearing σ-orbitals should have a high charge transport property.

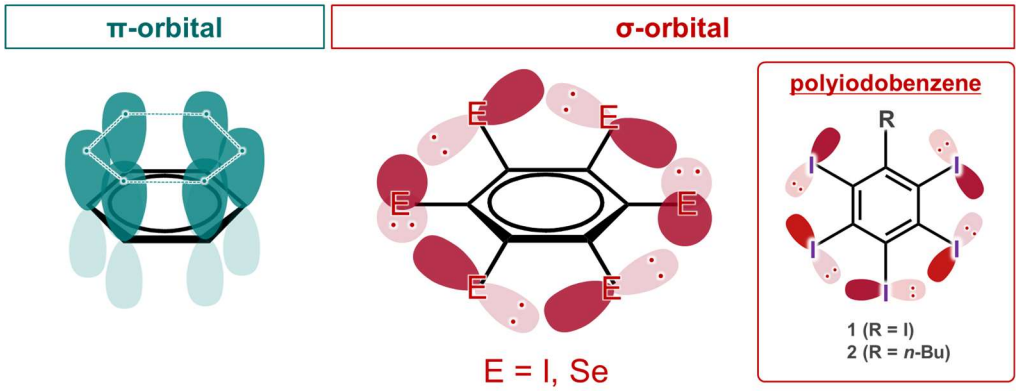

Figure 1. Schematic drawings of a π-orbital (left) and a σ-orbital (right), and chemical structures of the target molecules **1** and **2**.

1) Okamoto, T.; Nakahara, K.; Saeki, A.; Seki, S.; Oh, J. H.; Akkerman, H. B.; Bao, Z.; Matsuo, Y. *Chem. Mater.* **2011**, *23*, 1646–1649.