

## ドナーとアクセプターの軌道混成に基づく交互積層型錯体の高伝導化

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Orbital hybridization of donor and acceptor to enhance conductivity of mixed-stack complexes (<sup>1</sup>ISSP, The Univ. of Tokyo, <sup>2</sup>Department of Advanced Materials Science, The Univ. of Tokyo, <sup>3</sup>IMS, <sup>4</sup>CEMS, RIKEN, <sup>5</sup>Rigaku Corp., <sup>6</sup>Faculty of Science, Okayama Univ. of Science, <sup>7</sup>Department of Physical Science and Engineering, Nagoya Institute of Technology)

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Mixed-stack complexes, which comprise alternating layers of donors and acceptors, are organic conductors with typically poor electrical conductivity because they are either in a neutral or highly ionic state. In this study, mixed-stack complexes that uniquely exist at the neutral-ionic boundary were synthesized by combining donors and acceptors with similar energy levels and orbital symmetry between the donor's HOMO and the acceptor's LUMO. The orbitals were highly hybridized, endowing them with the highest room-temperature conductivity for single-crystal 1D complexes under ambient pressures. The unique electronic structures at the boundary exhibited structural perturbations between their electron-itinerant and localized states. **Keywords** : Charge transfer complex; Molecular crystal; Electrical conductivity; Oligothiophene

交互積層型の電荷移動錯体は電気伝導度が低いのが通例である。ほとんどの錯体が、キャリア数の乏しい中性かキャリアの局在化したイオン性状態にあるためである。本研究では、我々が最近開発している拡張共役系オリゴマー分子<sup>[1]</sup>をドナーに活用し、テトラシアノキノジメタン類をアクセプターとすることで、中性-イオン性境界に位置する錯体群を開発した(図1)。ドナーのHOMOとアクセプターのLUMOのエネルギー準位と軌道対称性に着目した分子設計に基づいたものである。1次元電荷移動錯体単結晶のなかで最高の室温伝導度を実現し、境界領域固有の相転移現象を見出した。

[1] Kameyama, R. *et al. Chem. Eur. J.* **2021**, 27, 6696–6700; Kameyama, R. *et al. Phys. Chem. Chem. Phys.*, **2022**, 24, 9130–9134; Kameyama, R. *et al. J. Mater. Chem. C*, **2022**, 10, 7543–7551; Onozuka, K. *et al. J. Am. Chem. Soc.*, **2023**, 145, 15152–15161; Fujino, T. *et al. Faraday Discuss.* in press.

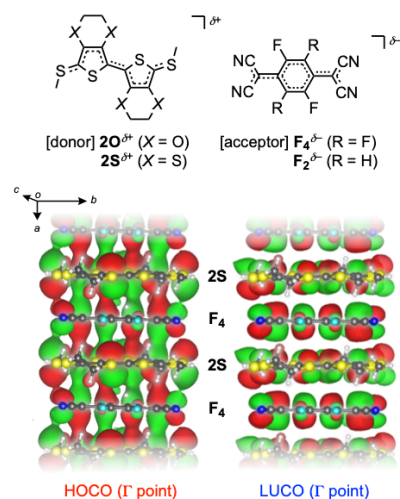


図1. 高伝導性交互積層型錯体の構造とΓ点での結晶軌道