Probing charge-transfer complexes by field-effect transistors

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Transistor properties have been investigated in various charge-transfer complexes [1]. Since these compounds consist of donor (D) and acceptor (A) molecules, ambipolar transport is expected [2], but only n-channel transport has been observed in many complexes containing TCNQ [3]. In addition to the strong acceptor ability of TCNQ, this has been attributed to the orthogonality of D HOMO and A LUMO, where hybridization of the D next HOMO mediates the electron transport [4,5]. In such complexes, the solid-state charge-transfer absorption comes from the D next HOMO to the A LUMO transition instead of the HOMO-LUMO transition [6]. Here, we have investigated transistors of TCNQ complexes of three-ring donors (Fig. 1a). The fluorene, dibenzothiophene, dithienothiophene, carbazole and terphenyl complexes show n-channel transport, whereas the dihexylquarterthiophene and phenothiazine complexes ($\mu_e = 0.078 \text{ cm}^2/\text{Vs}$) exhibit ambipolar transport (Fig. 1b). In addition to the orbital nonorthogonality, it is necessary to show ambipolar transport that the dimer HOMO is above the ordinary criterion of the hole transport.

When tetramethylbenzidine (TMB) is combined with various acceptors, a neutral-ionic transition takes place [7]. The transistor changes from p-channel (chloranil) to n-dominant ambipolar (TCNQ), but the bulk conduction increases gradually. The temperature dependence loses the $V_{\rm G}$ dependence by 0.2 eV above the equal D HOMO and A LUMO levels corresponding to the neutral-ionic transition.

Although these complexes have mixed stacks, it is more difficult to observe the transistor properties in segregated stack complexes [1]. Diaminoperylene forms a segregated TCNQ complex with high conductivity (0.2 S/cm) [8]. Nonetheless, balanced ambipolar transistor characteristics are obtained after subtracting the bulk conductivity (Fig. 1c).

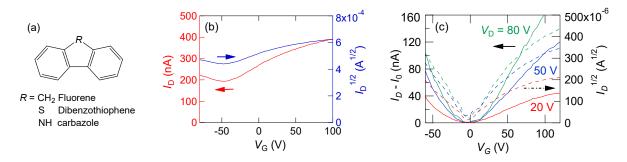


Fig. 1. (a) Carbazole-like molecules. (b) Transfer characteristics of a single-crystal (phenothiazine)(TCNQ) transistor. (c) Transfer characteristics of a thin-film (diaminoperylene)(TCNQ) transistor.

References

[1] Hasegawa, Appl. Phys. Lett. 107, 043711 (2007); Sakai, Phys. Rev. B 69, 045111 (2007); Yamamoto, Nat. Commun. 4, 2379 (2013); Higashino and Mori, Phys. Chem. Chem. Phys. DOI: 10.1039/d1cp05799e. [2] Zhu, J. Am. Chem. Soc. 134, 2340 (2012). [3] Sato, J. Phys. Chem. C 121, 6561 (2017); Tsutsumi, J. Mater. Chem. C 3, 1976 (2015). [4] Sato, J. Mater. Chem. C 7, 567 (2019). [5] Sanada, J. Phys. Chem. C 123, 12088 (2019). [6] Kato, J. Phys. Chem. A 124, 146 (2021). [7] Uekusa, ACS Appl. Mater. Interf. 12, 24174 (2020). [8] Inabe, Acta Chim. Hung. 130, 537 (1993).