Charge polarity of charge-transfer complexes based on fused and conjugated thiophenes

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Charge transfer (CT) complex refers to a series of cocrystals that are composed of electron donor (D) and acceptor (A). Although ambipolar transistor properties are expected [1], unipolar transport has been observed universally due to orthogonality between the D HOMO and A LUMO [2]. In this work, we have investigated mixed-stack tetracyanoquinodimethane (TCNQ, Fig. 1(a)) complexes of dithienothiophene (DTT, Fig. 1(b)) [3] and dihexylquarterthiophene (DH4T, Fig. 1(c)) [4]. Single-crystal transistors of the DTT complex show electron-only transport (Fig. 2(a)). Since the HOMO of DTT has horizontal nodes (Fig. 1(b)), the D HOMO and A LUMO are approximately orthogonal, and the partition method gives a significantly larger effective electron transfer (30 meV) than the hole transfer (8 meV). In this respect, fused thiophenes have some similarity to acenes. By contrast, (DH4T)(F_4TCNQ) shows electron-dominant ambipolar transistor properties (Fig. 2(b) and (c)). Similar to 4T [2], DH4T HOMO has vertical stripes (Fig. 1(c)), and the ambipolar properties are consistent with the non-orthogonality. Accordingly, fused thiophenes exhibit different charge transport properties from oligothiophenes.

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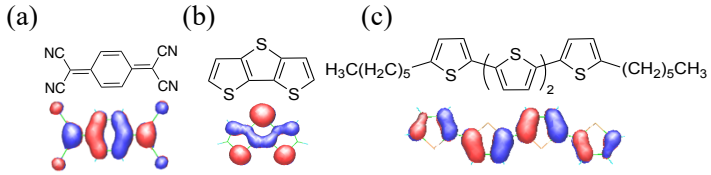

Fig. 1. (a) Chemical structure and LUMO of TCNQ. Chemical structure and HOMO of (b) DTT and (c) DH4T.

Table 1. Observed mobilities

mobility (cm^2/vs)	(DTT)(TCNQ)	(DH4T)(F_4TCNQ)
Maximum [Average]	N 3.1×10^{-4} [2.1×10^{-4}]	P 3.1×10^{-4}[1.4×10^{-4}] N 7.2×10^{-6} [2.7×10^{-6}]

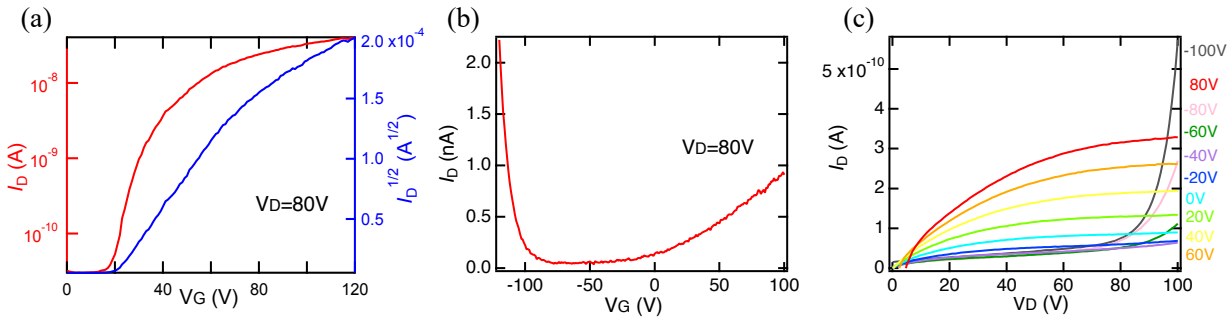

Fig. 2. (a) Transfer characteristics of a (DTT)(TCNQ) transistor. (b) Transfer, and (c) output characteristics of a (DH4T)(F_4TCNQ) transistor.