Structure and Transport Properties of the Charge-Transfer Salt Coronene−TCNQ

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Coronene is a highly symmetric organic molecule whose molecular structure resembles a fragment of graphite. We have crystallized a charge-transfer complex based on coronene and TCNQ, and present crystal structure and transport properties. The complex adopts alternate stacking between coronene and TCNQ, and the charge-transfer was estimated to be of the order of 0.3 by the structure and IR analysis of TCNQ. This degree of charge-transfer is larger than those of other hydrocarbon based charge-transfer complexes reported. We find semiconductor behavior with an optical gap of 1.55 eV and a transport gap of 0.49 eV. The Child's law mobility is estimated to be 0.3 cm^2/Vs—this along with the small transport gap suggests this compound might be attractive for device applications.

Organic charge-transfer compounds offer fruitful routes to strongly correlated ground states such as superconductivity, spin density waves, and charge density waves. In addition to TTF-derivatives,[1] graphite and it's close relative C_{60} also become superconducting when crystallized with a charge-transfer counterion such as in graphite intercalation compounds (GICs),[2] or alkali-doped C_{60}.[3] It is therefore thought that coronene (Figure 1.), with its molecular structure resembling that of a graphite fragment, is a candidate for realizing superconductivity when incorporated in a charge-transfer environment.[4−6] Specifically, it has been shown that a shear-type mode at 1668 cm^{-1}, resulting from the finite-size of the coronene molecule, couples strongly to an (E_{1g}) electronic state. Using the MacMillan formalism, Kato et al. showed that for reasonable values of the density of states at the Fermi level, a superconducting transition temperature in the range 0.1−8.9 K would occur.[4] The occurrence of superconductivity is, of course, dependent on the absence of a Peirls distortion. Nevertheless, charged coronene and its molecular compounds might exhibit interesting physical properties.

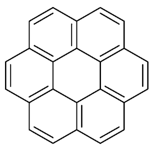

Figure 1. Schematic drawing of coronene molecule.

There are few known coronene-based charge-transfer salts. The coronene−tetracyanoquinodimethane (TCNQ) complex was reported two decades ago,[7] but that study focused on optical properties of powder samples, and the crystal structure was not reported. To explore the physical properties, large single crystals are needed. In the present paper we report a coronene compound, $(\text{coronene})_1-(\text{TCNQ})_1$ and present transport properties showing it to be a small-band-gap semiconductor with moderate charge-transfer between the counterions.

Experimental Section

We used two different methods for synthesizing coronene−TCNQ derived crystals. Method A consisted of mixing coronene (0.12 g, 0.4 mmol, TCI) in 15 mL of methylene chloride and TCNQ (0.08 g, 0.4 mmol, Aldrich) in 15 mL of the same solvent. These were added separately to the two arms of a H-cell with D frit. The two solutions were allowed to diffuse slowly, and black needle-shaped crystals were collected after one week. Elemental analysis. Calcd for $C_{24}H_{12} + C_{12}H_4N_4$: C, 85.69; H, 3.19; N, 11.10%. Found: C, 85.45; H, 2.98; N, 10.97%. In Method B, we added 30 mL of methylene chloride to a mixture of coronene (0.12 g, 0.4 mmol, TCI) and TCNQ (0.08 g, 0.4 mmol, Aldrich). The mixture was stirred overnight and filtered

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10.1021/cm049187+ CCC: $27.50

Table 1. X-ray Data Collection and Refinement Parameters

crystal formula	($C_{24}H_{12}$) + ($C_{12}H_4N_4$)
space group	$P2_1/c$
Z	4
a (Å)	10.9241(7)
b (Å)	7.1691(5)
c (Å)	15.8491(10)
β (deg)	106.598(2)
volume (Å^3)	1189.5 (2)
scan mode	Ω
measured reflections	8018
reflections used	1686
parameters	181
refinement	full matrix on F^2
Rf	0.041
Rw	0.093
GOF	0.87

by vacuum to obtain 0.15 g of black needles (75%). The black crystals dissolved in THF to give a dark green solution. By slow evaporation of the solvent, large crystals formed in 2 days. Method B gave larger crystals, with typical size of 3 × 1 × 0.2 mm, which were suitable for single-crystal IR measurement. In both cases, very thin slivers of the black crystals appeared green in transmitted light.

Optical spectra were obtained using a Bruker IFS 66v/S spectrometer in the range from 400 to 17 000 cm^{-1} at room temperature. The measurements were obtained in transmission mode with the single-crystal mounted on a sample holder with a 2-mm-diameter aperture. For measurements of the nonlinear conductivity, typical crystal dimensions were 1−2 mm length, 0.2−1 mm width, and 0.05−0.5 mm thickness. Two types of contacts were used: colloidal graphite and silver paste contact.[8] A typical separation between contacts was ~150 μm, and the width of the contact pads was ~150 μm. The electrical measurements were made in darkness in a Quantum Design cryostat at fixed temperature in a vacuum of 10^{-5} Torr. Current (I) and voltage (V) were measured with a Keithley 6517A electrometer. Currents down to 10^{-13} A, and voltages up to 350 V applied between two contacts were routinely obtained. For these measurements, 2.5-V steps and a 5−10-s delay between each measurement was sufficient to avoid charging effects.

For the structural evaluation, several single crystals from the different synthesis routes were used, and all showed the same monoclinic unit cell. Initial diffraction data obtained at room temperature using a laboratory source showed the coronene molecule to have strong rotational disorder, severely reducing the number of observable reflections. Further data were collected at the MAX-II synchrotron beamline I-711 MAXLAB (Lund, Sweden), using a Bruker Smart CCD system mounted on a Bruker platform goniometer. To reduce the effect of the thermal disorder, the sample temperature was held at 100 K. The crystal structure was solved using SIR92[9] within WINGX,[10] and further refinement was carried out using the NRCVAX[11] and CRYSTALS[12] program suites. Details of the data collections and of the refinement are given in Table 1.

Results

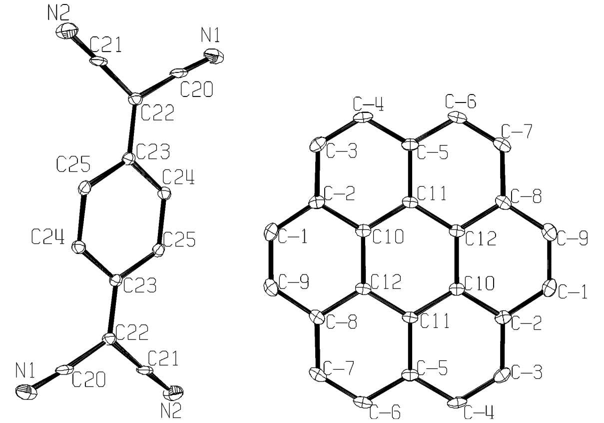

Figure 2. Molecular structure and atom numbering of coronene and TCNQ.

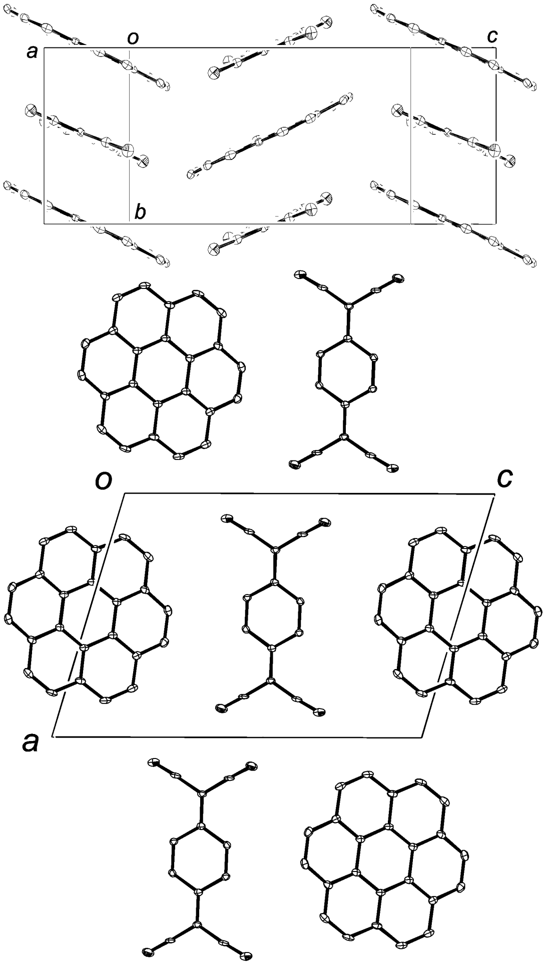

Figure 3. Mixed stacks of coronene and TCNQ along b axis.

Figure 2 shows the molecular structure and atom numbering of coronene and TCNQ, and Figure 3 illustrates the packing mode of the molecules in the crystal structure. The complex forms mixed stacks along the b-axis, where the coronene and the TCNQ molecule alternate. Adjacent stacks form a pseudohexagonal arrangement where around a TCNQ molecule two more TCNQ and four coronene molecules are found (Figure 3). Of the six adjacent stacks, two have the same tilt angle (with the same molecules, respectively), while the other four stacks are tilted away. In this respect, conductivity is expected to be anisotropic, with charge transfer in the direction of the stacks (b-axis).

The charge of TCNQ can be determined by the infrared spectra, particularly the CN stretching frequency.[13] The single-crystal FTIR spectrum is shown in Figure 5, showing a CN stretching frequency at 2217

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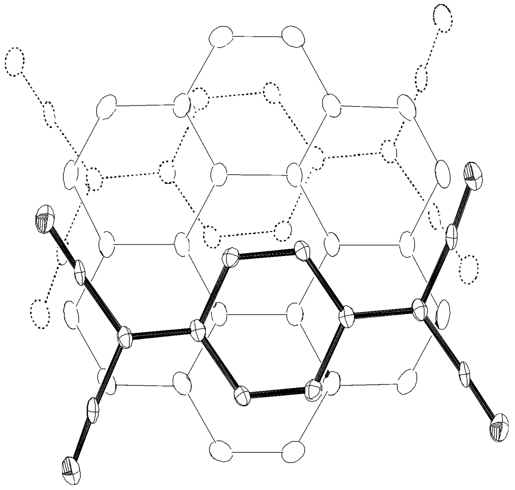

Figure 4. Overlap between coronene and TCNQ (view perpendicular to the coronene plane). The TCNQ in black thick line is above the coronene plane; the one in dotted line is below.

cm^{-1}. Based on the frequency shift from the neutral TCNQ, the degree of charge transfer is estimated to be 0.24. This value is close to that obtained by the structure analysis, as shown below. Figure 5 also shows a strong absorption, which starts from 860 nm and saturates at 710 nm. This is probably also due to the charge-transfer transition. The charge-transfer transition of coronene with TCNQ was first observed by Beukers et al. in solution at 740 nm.[14] Apparently this transition is significantly broadened in the solid state.

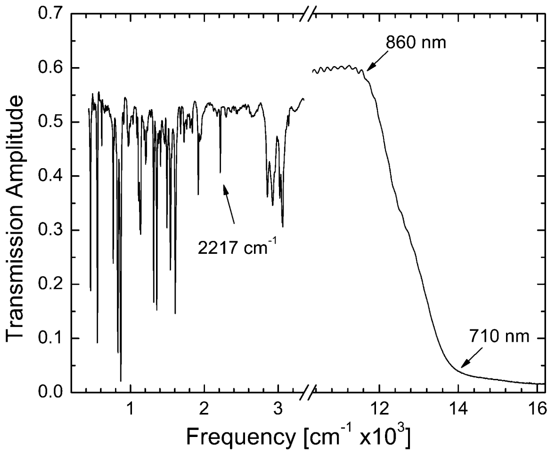

Figure 5. FTIR transmission spectrum of a single crystal of coronene−TCNQ.

A previous measurement[7] of the CN stretching frequency gave 2222 cm^{-1}, which is close to that of neutral TCNQ (2224 cm^{-1}). Thus the authors claimed that the complex is neutral in the ground state with weak interaction between coronene and TCNQ. The different synthetic procedure that we used may have lead to a different crystal packing, which could explain the different IR mode that we observe.

A typical room-temperature $I-V$ characteristic for coronene−TCNQ is shown in Figure 6. In general, two separate voltage regions can be distinguished. The samples at low voltage demonstrate a nearly ohmic $I-V$ dependence. At higher voltages, a distinct region with $I \propto V^2$ was routinely observed. Standard semiconductor theory predicts this type of $I-V$ behavior in case of space charge limited current (SCLC).[15] In the case that the present SCLC can be considered as the trap-free limit, we can apply Child's law,[16] $J = (^9/_8)\mu\epsilon\epsilon_0(V^2/L^3)$. Here J is the current density, μ is the free carrier mobility, ϵ is the dielectric constant (we assume $\epsilon \sim 3$), ϵ_0 is the permittivity in a vacuum, V is the applied voltage, and L is the distance between contacts. We also assume that the current flows only through a surface layer with thickness of 20% of the distance between the contacts, a conservative estimate given the strong dependence of the SCLC on the length of the current path. With these assumptions, we extract a value for the mobility of 0.3 cm^2/Vs at room temperature. Below room temperature the observed temperature-dependence of the current at the highest voltages is thermally activated, with an activation energy of E_a ~0.49 eV at 51 V (Figure 7). This value for the "transport gap" can be compared with the gap obtained from the IR data above, 1.55 eV. Thus we see that the transport gap is approximately 60% of half the optical gap, indicating the presence of states in the gap that pin the Fermi level. The small value of the transport gap and the relatively high SCLC mobility suggest that coronene−TCNQ might be a promising candidate for microelectronic applications.

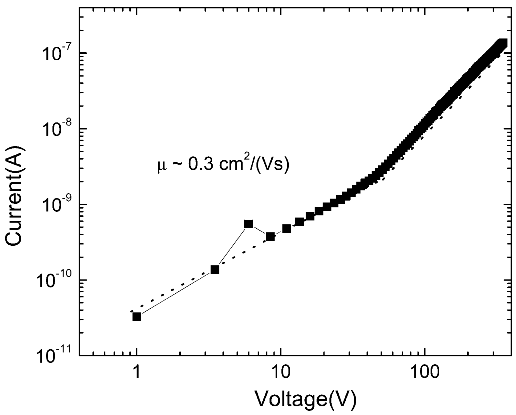

Figure 6. Current versus voltage at room temperature for coronene−TCNQ. The contacts were graphite with separation $L = 150\ \mu m$ and contact pad width of $D = 150\ \mu m$. The straight lines show the ohmic ($I \propto V$) and space charge limited current ($I \propto V^2$) regions. The mobility $\mu \approx 0.3\ cm^2/Vs$ is estimated from the V^2 behavior, as described in the text.

The intra-stack mean plane separation between coronene and TCNQ is about 3.30 Å, significantly shorter than the sum of the van der Waals radii of carbon atom (3.4 Å). However, no short intermolecular carbon−carbon (or nitrogen) contacts are present between stacks. Along an individual stack, the tilts for coronene and TCNQ are identical (see Figure 3). Furthermore, the central rings of both coronene and TCNQ align almost perfectly when viewed along the b-axis (e.g., C11 aligns with C23, C10 aligns with C25, C12 aligns with C24, etc.). However, the coronene is slightly twisted

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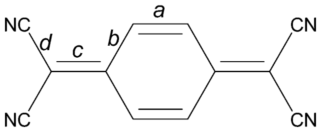
Table 2. Dimension of TCNQ in Charge-Transfer Complexes Based on Hydrocarbons and TCNQ and the Mean Plane Separations

	TCNQ[a]	perylene−TCNQ[b]	anthracene−TCNQ[c]	acenaphthene−TCNQ[d]	hexamethylbenzene−TCNQ[e]	coronene−TCNQ[f]
mean plane separation (Å)		3.44	3.5	3.37	3.55	3.30
a	1.346(3)	1.348(4)	1.35(2)	1.337(4)	1.358(7)	1.357(2)
b	1.448(4)	1.444(4)	1.46(1)	1.446(3)	1.462(7)	1.445(2)
c	1.374(3)	1.365(4)	1.37(2)	1.372(3)	1.391(7)	1.390(2)
d	1.441(3)	1.430(4)	1.42(1)	1.434(4)	1.445(7)	1.439(3)
c/(*b* + *d*)	0.476(3)	0.475(3)	0.48(1)	0.476(3)	0.478(5)	0.482(2)



[a] Reference 21. [b] Reference 22. [c] Reference 23. [d] Reference 17. [e] Reference 24. [f] This work.

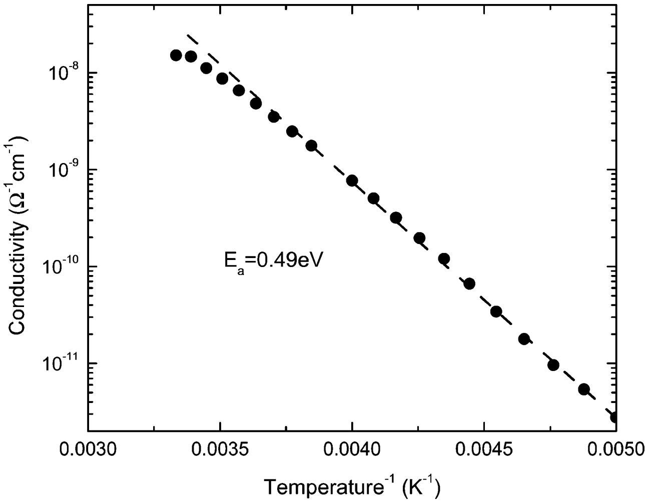


Figure 7. Dependence of the conductivity between two graphite contacts versus inverse temperature at $V = 51$ V. The straight line is a linear fit, yielding an activation energy of $E_a = 0.46$ eV.

relative to the TCNQ molecules above or below it, moving C5 away from C22 (see Figure 4). This small twist is always in the same direction, but it is expected that at higher temperatures the opposite twist direction will become accessible as well, resulting in partial disorder of the coronene at room temperature, consistent with its very large temperature factors observed at ambient temperature.

Figure 4 shows the overlap between coronene and TCNQ. The coronene molecule is sandwiched between two TCNQ molecules. The overlap pattern resembles that of the perylene−TCNQ complex,[17] where it was calculated that the overlap integral and hence the charge-transfer energy is maximized.[17,18] However, in the latter case, the mean plane separation is 3.44 Å, which is significantly larger than that (3.3 Å) of coronene−TCNQ. Thus, it is expected that interaction between coronene and TCNQ should be stronger than that between perylene and TCNQ, consistent with the degree of charge-transfer calculated in these complexes (see below).

It has been suggested[19,20] that the degree of charge transfer in a complex can be estimated by the geometry of TCNQ, reasoning from the nodal structure of the frontier b_{2g} molecular orbital. The population of an electron in the LUMO of TCNQ should cause the two double bonds (*a* and *c*) to be weakened, and thus their bond length to increase. Likewise the bond lengths of *b* and *d* should shorten. Kistenmacher et al. suggested a method[20] to estimate the degree of charge-transfer based on the ratio *c*/(*b* + *d*). Table 2 lists the bond lengths of TCNQ in several reported charge-transfer complexes based on TCNQ and hydrocarbons arranged in similar patterns. All these hydrocarbons adopt mixed stacking with TCNQ, and the intra-stack mean plane separations are close to or larger than 3.4 Å, except for coronene−TCNQ. The calculated ratios *c*/(*b* + *d*) in most of the complexes are very close to the value in neutral TCNQ (0.476), indicating that the ground states of these complexes are neutral. The calculated ratio in coronene−TCNQ is larger than 0.476, corresponding to a degree of charge-transfer of about 0.3(1). Thus, the estimate based on the structure analysis shows that although the ionicities in most of the reported charge-transfer complexes based on hydrocarbons and TCNQ are very small, the charge transfer in coronene−TCNQ is significantly different from zero, consistent with the IR stretch mode observation.

Conclusion

We have crystallized a charge-transfer complex based on coronene whose molecular structure resembles a fragment of graphite. The complex adopts alternate stacking between coronene and TCNQ, and the charge-transfer was estimated to be 0.3 from the structure and IR analysis of TCNQ. This degree of charge-transfer is larger than those reported in other hydrocarbon-based charge-transfer complexes. A moderate transport gap

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of 0.49 eV and a large SCLC mobility of 0.3 cm^2/Vs is observed, suggesting that this semiconductor might be amenable for studies of charge-injection via gate bias.

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Supporting Information Available: Crystallographic information files for coronene−TCNQ (CIF). Cambridge Crystallographic Data Centre number: CCDC 251572. This material is available free of charge via the Internet at http://pubs.acs.org.

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