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Semi-conducting mixed-valent $X_4TCNQ^{-I/-II}$ (X = H, F) charge-transfer complexes with $C_6H_2(NH_2)_4$

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We report further characterisation on the previously described $[C_6H_2(NH_2)_4][TCNQ]$ charge-transfer (CT) complex. An in-depth analysis of the crystallographic data aided by spectroscopic methods indicates the compound is mixed-valent with $TCNQ^{-I/-II}$ species. The analogous F_4TCNQ CT complex has been synthesised and spectroscopic methods suggest that $[C_6H_2(NH_2)_4][F_4TCNQ]$ is also mixed-valent. Electrical conductivity measurements on both complexes indicate semi-conductor behaviour, with $[C_6H_2(NH_2)_4][TCNQ]$ exhibiting a $\sigma_{300K} = 9.8 \times 10^{-4}$ S/cm and an of $E_a = 0.10(1)$ eV. Density Functional Theory studies on both CT complexes reveal band structures suggestive of ambipolar transport, with a super-exchange mechanism.

Introduction

Charge-transfer (CT) complexes of 7,7,8,8-tetracyanoquinodimethane, TCNQ, have been of appreciable interest since the 1970's, owing to their unusual and interesting electronic properties.[1] Perhaps the most well-known CT complex is tetrathiafulvalene-TCNQ (TTF-TCNQ), which was the first purely organic CT complex shown to exhibit metallic behaviour.[2] The organic molecule, X_4TCNQ (X = H or F), is redox-active with three accessible oxidation states (Fig. 1). The neutral quinonoid form is a good π-acceptor, which is able to undergo a one electron reduction to yield a stable radical monoanion. A further one electron reduction gives an aromatic dianion, which in contrast to the quinonoid is a strong π-donor. In a similar fashion, TTF also has three possible oxidation states; a neutral form, a radical cation and dication.

In the case of TTF-TCNQ, the ionisation potential of TTF and the electron affinity of TCNQ, are conducive to the formation of a mixed-valent CT complex. The molecular formula of TTF-TCNQ can be represented as $TTF^{0.59+}TCNQ^{0.59-}$.[3] The structure of the complex is quasi one-dimensional, comprising discrete stacks of TTF and TCNQ. At room temperature, the mean plane separation between TTF units and TCNQ units are ~3.45 Å and ~3.19 Å respectively,[4] ideal for π-π stacking. The electrical conductivity is $>10^5$ S/cm at 58 K, with a Peierls transition occurring below this temperature.[5]

The majority of CT complexes reported with TCNQ involve a 1:1 stoichiometry of the acceptor and donor, akin to TTF-TCNQ. However, two distinct packing arrangements are common; discrete stacks of acceptors and donors (-AAAA- and –DDDD-, Fig. 2 left) and mixed-stacks of acceptors and donors (-ADADA-, Fig. 2 right). The physical properties of the CT complex are affected by the packing arrangement. For example, the CT complex tetramethyl-tetraselenafulvalene-TCNQ (TMTSF-TCNQ),[6-8] forms as two polymorphs and highlights the important relationship between structure and function. Red crystals of TMTSF-TCNQ are comprised of mixed-stacks of acceptors and donors and display semiconductor behaviour, whilst their black discrete-stack counterparts display metallic behaviour. The discrete stacking observed in TTF-TCNQ and the black polymorph of TMSTF-TCNQ is considered a prerequisite for metallic conductivity, however such an arrangement does not guarantee the behaviour.

The electronic properties of CT complexes are also defined by the degree of charge transfer (ρ) from the donor to acceptor. The ionisation energy of the donor (I_{Donor}), electron affinity of the acceptor ($E_{Acceptor}$), and Madelung energy of the crystal are together responsible for the magnitude of the charge transfer (ρ).‡ [9, 10] In broad terms, when $I_{Donor} >> E_{Acceptor}$ a neutral CT complex forms, whilst when $E_{Acceptor} >> I_{Donor}$ an ionic CT complex is obtained. A mixed-valent CT complex forms when $E_{Acceptor} \simeq I_{Donor}$.[1, 3, 11, 12] Mixed-valent complexes may be considered analogous to Robin-Day class II/III systems.[13]

CT complexes involving TCNQ reported prior to 2008 typically have been limited to TCNQ species in an oxidation state between the neutral quinonoid form and the radical monoanion. This is presumably the result of the reported air sensitivity of the aromatic dianion of TCNQ.[14] Starting from the air stable precursor of $TCNQ^{2-}$, $TCNQH_2$ (Fig. 3), we reported

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$TCNQ^{2-}$ based charge-transfer complexes in 2009.[15] We have subsequently extended this work to include the fluorinated derivative of $TCNQH_2$, F_4TCNQH_2.[16] These complexes represent the majority of X_4TCNQ^{2-} based CT complexes.

Extensive studies have also shown that TCNQ is able to exist in a mixed-valent state between the neutral quinonoid and radical monoanion forms. However in these oxidation states TCNQ is a poor ligand.[17] Reports of coordination polymers in which metal centres are bridged by $TCNQ^{2-}$ ligands indicate a rich diversity of structures which offer scope for the generation of mixed-valent species with interesting electronic and magnetic properties.[17, 18] In addition to these metal-based systems, we are also interested in the generation of mixed-valent systems in which organic species serve as counter-cations for TCNQ anions that possess an oxidation state between –1 and –2.

Recent work[16] has allowed us to review the oxidation state of TCNQ within $[C_6H_2(NH_2)_4][TCNQ]$. The $[C_6H_2(NH_2)_4]$ unit has three potential oxidation states as depicted in Fig. 4. The work described here represents an effort to determine the oxidation state of the components within the complex, $[C_6H_2(NH_2)_4][TCNQ]$, enabling studies of the spectroscopic and electrical conductivities of this, and the structurally related CT complex $[C_6H_2(NH_2)_4][F_4TCNQ]$. Density Functional Theory (DFT) calculations have provided a rationale for the observed behaviour.

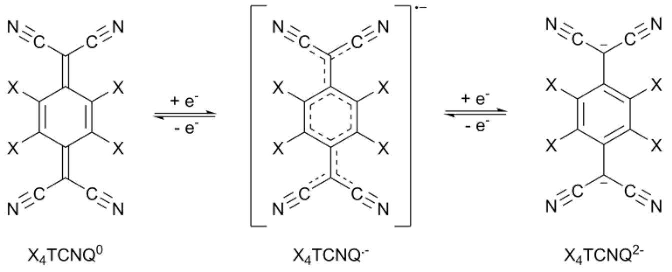

Fig. 1 Oxidation states of X_4TCNQ (X = H or F).

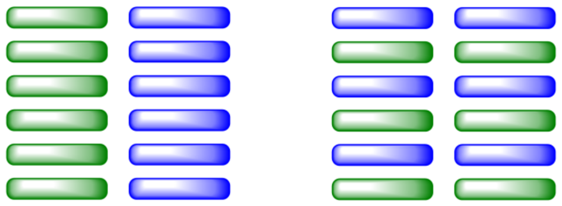

Fig. 2 Diagrams depicting the packing arrangements of CT complexes, segregated stacks (left), mixed stacks (right).

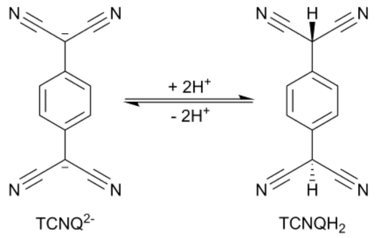

Fig. 3 The $TCNQ^{2-}$ dianion and its air-stable precursor, $TCNQH_2$.

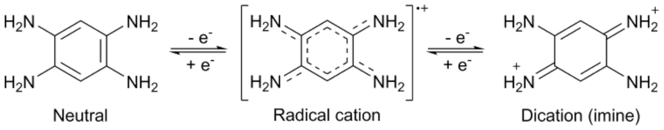

Fig. 4 Oxidation states of $C_6H_2(NH_2)_4$.

Results and discussion

We have previously described the synthesis and structure of $[C_6H_2(NH_2)_4][TCNQ]$.[15] The CT complex is comprised of 1D mixed-stacks of $[C_6H_2(NH_2)_4]$ and TCNQ units as shown in Fig. 5. The TCNQ species are co-planar, suggestive of partial double character along the $(NC)_2C\text{-}C_6H_4\text{-}C(CN)_2$ bonds. Within stacks, the mean plane separation between $[C_6H_2(NH_2)_4]$ and TCNQ units is *ca.* 3.3 Å. Hydrogen bonding occurs between the nitrile arms of TCNQ units and the NH_2 groups of $[C_6H_2(NH_2)_4]$ units of adjacent parallel columns.

Recently we have been interested in F_4TCNQ^{2-} CT complexes and coordination polymers.[16, 17, 19-22] The synthesis of $[C_6H_2(NH_2)_4][F_4TCNQ]$ follows a similar procedure to $[C_6H_2(NH_2)_4][TCNQ]$, however despite our best efforts to grow single crystals suitable for X-ray diffraction we were unsuccessful. X-ray powder diffraction indicates that the structure is analogous to $[C_6H_2(NH_2)_4][TCNQ]$ (see ESI Fig. S2) and solid-state DFT studies provide further support for the structural similarity of $[C_6H_2(NH_2)_4][TCNQ]$ and $[C_6H_2(NH_2)_4][F_4TCNQ]$ (see ESI S8).

The degree of charge transfer (ρ) in X_4TCNQ based complexes may be estimated using both spectroscopic and structural approaches.[1, 6, 23-25] The Kistenmacher relationship, which is represented by the formula,

$$q = A[c/(b+d)] + B$$

relates the selected bond lengths, *b*, *c* and *d* of X_4TCNQ to the X_4TCNQ redox state (Fig. 6). The charge (q) of the X_4TCNQ species may be used to infer the degree of charge transfer (ρ).[6] Selected bond lengths obtained from the single crystal structure determination of $[C_6H_2(NH_2)_4][TCNQ]$ and the DFT dispersion-corrected optimised structure of $[C_6H_2(NH_2)_4][F_4TCNQ]$ at the PBE[26]-D3(BJ)[27] level of theory are listed in Table 1, along with the estimated charge (q) on the X_4TCNQ species. Fig. S5.1 (ESI) schematically represents the expected relationship between charge (q) of the X_4TCNQ species and the degree of charge transfer (ρ). For mixed-valent 0/-1 TCNQ-based CT complexes, a range of $0.5 < p < 0.74$ values has previously been reported.[1, 3] The degree of charge transfer (ρ) from X_4TCNQ to the $[C_6H_2(NH_2)_4]$ species is estimated as $0.6e^-$ and $0.4e^-$, for the $[C_6H_2(NH_2)_4]$[TCNQ] and $[C_6H_2(NH_2)_4][F_4TCNQ]$ complexes respectively. Thus, it is likely that these are $X_4TCNQ^{-1/-2}$ mixed-valent CT complexes.

Infrared spectroscopy is a useful tool for probing X_4TCNQ systems, with ν(CN) frequencies sensitive to the extent of charge transfer.[15] Whilst studies have been largely limited to systems in which X_4TCNQ is an acceptor, a similar approach may be employed when it acts as a donor. For both $[C_6H_2(NH_2)_4]$[TCNQ] and $[C_6H_2(NH_2)_4][F_4TCNQ]$, the infrared spectra are consistent with an intermediate -1/-2 oxidation state which falls within a mixed-valent regime (ESI, S4), in agreeance with the crystallographic and current DFT work.[28-31] In the case of $[C_6H_2(NH_2)_4]$[TCNQ] the charge on the TCNQ is estimated to be -1.23 whilst the charge on the F_4TCNQ in $[C_6H_2(NH_2)_4][F_4TCNQ]$ is estimated to be -1.54, values slightly lower than the charges calculated using the Kistenmacher relationship (Table 1).

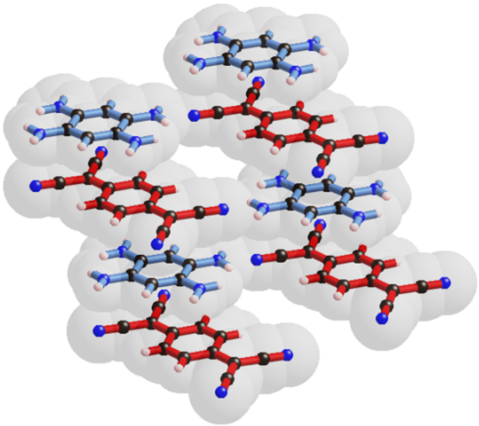

Fig. 5 The mixed-stack structure of $[C_6H_2(NH_2)_4]$[TCNQ].

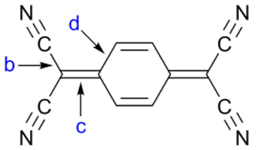

Fig. 6 Diagram of the TCNQ molecule with selected bond lengths labelled

Table 1 Selected bond lengths of the TCNQ species within the charge-transfer complexes.

Compound	*b* (Å)	*c* (Å)	*d* (Å)	*c*/(*b*+*d*)	Charge (*q*)
$[C_6H_2(NH_2)_4][TCNQ]^{(exp)}$	1.409	1.435	1.411	0.509	-1.39
$[C_6H_2(NH_2)_4][F_4TCNQ]^{(cal)}$	1.401	1.443	1.412	0.513	-1.63

The charge, q, has been estimated using the Kistenmacher relationship, $q = A[c/(b+d)] + B$. For F_4TCNQ, A = -45.756 and B = 21.846; for TCNQ A = -41.667 and B = 19.818; b, c, and d refer to the bonds indicated in Fig. 6.

Similar to X_4TCNQ, the bond lengths of $[C_6H_2(NH_2)_4]$ vary with oxidation state. The C-C bonds of the aromatic ring within $[C_6H_2(NH_2)_4]$ would all be expected to be ca. 1.39 Å. In contrast, the imine of $[C_6H_2(NH_2)_4]$ would consist of both short and long C-C bonds. The bond indicated by '*y*' in Fig. 7, in the imine form of $[C_6H_2(NH_2)_4]$ should be considered a formal single bond with a length of ca. 1.54 Å. The equivalent '*y*' C-C bonds in the complexes $[C_6H_2(NH_2)_4]$[TCNQ] and $[C_6H_2(NH_2)_4][F_4TCNQ]$ are 1.459 Å determined by single-crystal X-ray diffraction and 1.479 Å predicted by dispersion-corrected DFT optimisation, respectively. For both complexes the bond lengths are consistent with the $[C_6H_2(NH_2)_4]$ species being present in a redox state intermediate between that of the imine and the aromatic forms.

Mixed-valent CT complexes often exhibit a characteristic low energy CT band which extends into the near-infrared region.[3] Visible near-infrared spectroscopy on the deep black $[C_6H_2(NH_2)_4]$[TCNQ] complex reveals a broad absorption between 5000 and 25000 cm^{-1} (see ESI Fig. S6.1) and a tail that extends beyond 5000 cm^{-1}. This spectral result suggests the complex exhibits mixed valency. Tauc analysis[32] provides an optical band gap of 0.56 eV (see ESI Fig. S6.2).

CT complexes which are neutral ($\rho = 0$) or ionic ($\rho = 1$) typically form mixed-stack insulators or semi-conductors ($\sigma = 10^{-12}$ - 10^{-6} S/cm).[1] Mixed-valent CT complexes, in contrast, are often discrete-stacked and may display metallic conductivity ($\sigma = 10^1$ – 10^3 S/cm).[1] The electrical conductivities of the CT complexes were of particular interest as they represent an unusual class, being both mixed-stack and mixed-valent. Two-point, pressed-pellet measurements were performed on both compounds. At 300 K, $[C_6H_2(NH_2)_4]$[TCNQ] exhibits an electrical conductivity of 9.8×10^{-4} S/cm whilst $[C_6H_2(NH_2)_4][F_4TCNQ]$ exhibits a lower electrically conductivity of 2.8×10^{-5} S/cm at 300 K. Variable conductivity measurements between 220 and 300 K revealed that both compounds are thermally activated semiconductors with activation energies of 0.10(1) eV and 0.40(1) eV for the $[C_6H_2(NH_2)_4]$[TCNQ] and $[C_6H_2(NH_2)_4][F_4TCNQ]$ compounds respectively (Fig. 8). The complexes exhibit moderate electrical conductivity, with $[C_6H_2(NH_2)_4]$[TCNQ] being on par with some of the most conductive mixed-stacked X_4TCNQ CT complexes reported to-date.[31]

Solid-sate DFT calculations were undertaken to aid in understanding the unusual electrical conductivity in these mixed-stack CT complexes. Band structure and density of

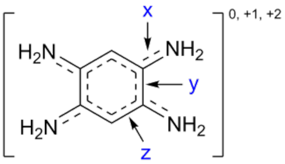

Fig. 7 Diagram of $[C_6H_2(NH_2)_4]$ with selected bonds labelled.

states plots are present in Fig. 9 and ESI Fig. S8.1. Calculations at the HSE06[33]//PBE-D3(BJ) level of theory provide an estimated bandgap of 0.49 eV for $[C_6H_2(NH_2)_4][TCNQ]$ which agrees well with experimental measurements.

The band structures of the two compounds are very similar, with the $[C_6H_2(NH_2)_4][TCNQ]$ complex exhibiting a slightly smaller band gap and increased valence and conduction band dispersions. The remainder of the discussion will focus on the band structure of $[C_6H_2(NH_2)_4][TCNQ]$, although the general concepts also apply to $[C_6H_2(NH_2)_4][F_4TCNQ]$.

The band structure of $[C_6H_2(NH_2)_4][TCNQ]$ (Fig. 9) reveals a remarkable quasi-symmetry between the valence and conduction bands. Band dispersions are detailed in ESI S8. This suggests that $[C_6H_2(NH_2)_4][TCNQ]$ can transport both electrons and holes - acting as an ambipolar semiconductor - an area with significant applications.[34] In addition, the quasi-symmetry suggests that the charge-transport occurs via a super-exchange mechanism – a process of interest in other mixed-stack TCNQ CT complexes.[35-37]

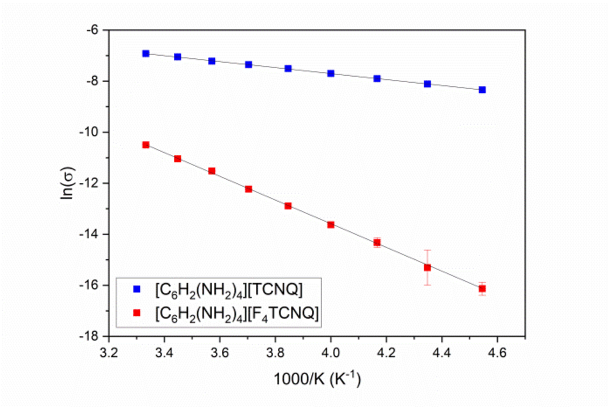

Fig. 8 Arrhenius plots for the $[C_6H_2(NH_2)_4][TCNQ]$ and $[C_6H_2(NH_2)_4][F_4TCNQ]$ complexes.

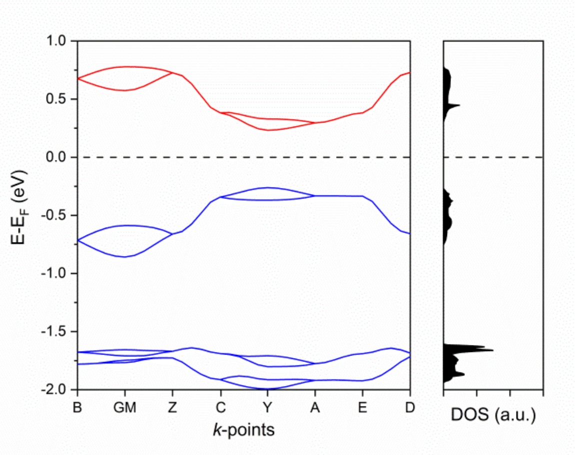

Fig. 9 Band structure and density of states (DOS) for $[C_6H_2(NH_2)_4][TCNQ]$.

Conclusions

In conclusion, the spectroscopic and electronic properties of the mixed-valent charge-transfer complexes $[C_6H_2(NH_2)_4][TCNQ]$ and $[C_6H_2(NH_2)_4][F_4TCNQ]$ have been described. Coordination frameworks involving mixed-valent ligands are emerging as materials that may offer both unusual and useful electronic and magnetic properties. Recent $TCNQ^{2-}$ and F_4TCNQ^{2-} based coordination polymers[17] demonstrate that these materials are attractive targets for mixed valency and the present work highlights the possibility of mixed-valent $X_4TCNQ^{-1/-2}$ species.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The support of the Australian Research Council (DP180101413 and DP170100283) is gratefully acknowledged. ALS thanks the Australian Government for an Australian Postgraduate Award. This research was undertaken with the assistance of resources and services from the National Computational Infrastructure (NCI), within the National Computational Merit Allocation Scheme (project fk5).

Notes and references

‡ For clarity, electron affinity is defined as $X + e^- \rightarrow X^-$ and is highly positive (when considered in eV) for strongly electron accepting species. Ionisation energy is defined as $X \rightarrow X^+ + e^-$.

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