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SUPRAMOLECULAR CONTROL OF MOLECULAR ELECTRONIC BEHAVIOUR OF $TCNQ^{-\cdot}$ SALTS

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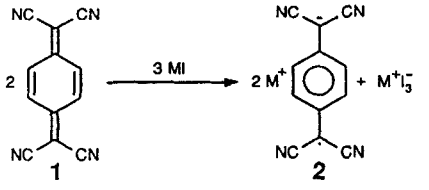
Crown ether complexation of 1 : 1 alkali metal TCNQ salts, MTCNQ (M = K, Rb, Tl) leads to structures containing isolated TCNQ dimers. These materials provide valuable models for investigating the spectroscopic and electronic behaviour of $TCNQ^{-\cdot}$ dimer components which are key structural fragments of, for example, organic metals and semiconductors.

INTRODUCTION

Since its discovery in 1960[1], the solid-state properties of radical anion salts of 7,7′, 8,8′-tetracyano-*p*-quinodimethane (TCNQ)(**1**) have been of considerable interest. The physical behaviour observed is dependent on a number of factors,[2] which include the nature of the counter ion, the solid-state architecture of the crystal phase and the stoichiometry of the salt. For example, the salts of tetrathiafulvalene ($TTF^{+\cdot}$) and tetramethyltetraselenofulvalene ($TMTSF^{+\cdot}$) show metallic behaviour[3,4] whereas that of decamethylferrocenium cation ($Me_{10}Fc^{+\cdot}$) has meta- and paramagnetic phases.[5,6] Addition of neutral TCNQ can also dramatically alter the behaviour of these materials.[2]



where M = Li, Na, K, Rb

Many of these variations in behaviour can be related to the solid-state structures of the salts. For example, a common feature of these materials is the packing of the $TCNQ^{-\cdot}$ moieties into face-to-face π-stacked columns. In TTF–TCNQ and one modification of RbTCNQ (type II)[7] neighbouring anion columns are parallel stacked, whereas for NaTCNQ,[8] KTCNQ[9] and RbTCNQ (type I)[10] neighbouring columns are arranged perpendicularly. Whilst high electronic conductivity is associated with infinite parallel stacked $TCNQ^{-\cdot}$ columns, other interesting phenomena occur in semi-insulating systems. For example, metamagnetic $Me_{10}Fc^{+\cdot}$ $TCNQ^{-\cdot}$ has linear chains of $\ldots D^+A^-D^+A^-\ldots$ (D^+ = donor, A^- = acceptor)[5] whereas the paramagnetic phase has herringbone-packed subunits $D^+A^-A^-D^+$.[6] Similar subunits are present in the infinite face-to-face π-stacked columns of 3,3′-diethyloxacyanine $TCNQ^{-\cdot}$.[11]

IONOPHORE-COMPLEXED METAL TCNQ SALTS

A potentially more subtle method of controlling the behaviour and solid-state architecture of metal TCNQ salts involves ionophore complexation of the metal cation. A large number of such salts have been prepared[12–15] but until recently little has been known about their solid-state structures.[11,16–18] Although the introduction of a bulky ionophore into the material impedes the formation of close-packed $TCNQ^{-\cdot}$ columns, it does permit a study of the solid-state behaviour of the structural components in isolation.

18-Crown-6 complexes

Dunitz, Phizackerley and co-workers[19] have determined the solid-state structures of the series of 18-crown-6 MSCN complexes, M = Na, K, Rb, Cs. For the 'best-fit' cation, K^+, a linear chain structure is observed, the anions being coordinated to both faces of the cation–crown plate. Larger cations are forced to lie above the crown ether oxygen plane and this results in

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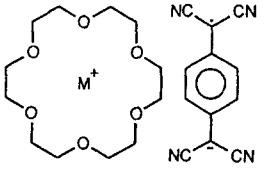
dimer formation in which two 18-crown-6 M^+ units are linked through two synfacially coordinated anion bridges. In contrast, in the sodium salt the crown ether is puckered and partially encapsulates the relatively smaller cation.

Slow crystallization of solutions of KTCNQ or RbTCNQ in acetonitrile in the presence of one molar equivalent of 18-crown-6 affords crystals of the 1 : 1 crown : MTCNQ complex **3**. Attempts to prepare the sodium complex **3a** by this method afford a brown powder, analytical data for which support the formation of a 1 : 1 complex but no crystals of this material have as yet been isolated. We have determined the solid state structures of both the potassium and rubidium salts **3b** and **3c**.



3 a, M = Na
b, M = K
c, M = Rb
d, M = Tl

In marked contrast to the different behaviours of the corresponding thiocyanates,[19] the K^+ and Rb^+ salts adopt almost identical solid-state structures built up from a dimer subunit consisting of two crown ether complexed metal ions linked through a TCNQ dimer bridge (Figure 1) in a manner similar to that observed for Rb(18-crown-6)SCN.[19] Anion coordination occurs through two cyanide nitrogens at each end of the TCNQ dimer in a transoid fashion (Figure 2). This leads to an offset geometry for the cations such that the crown ether planes are parallel to each other but at an angle of *ca* 25 °C relative to the TCNQ dimer long axis (Figure 3). These offset dimer subunits pack into a herringbone array (Figure 4) rather than the dimer columns observed for Rb(18-crown-6)SCN.[19]

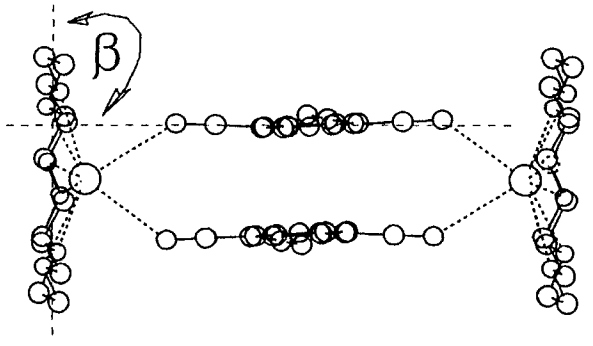


Figure 1. Side view of a dimer subunit in **3c**, β being the angle of tilt between the TCNQ molecular plane and the crown ether oxygen best plane (the value $|90-\beta|$ used in Table 2 thus measures the deviation from a perpendicular geometry)

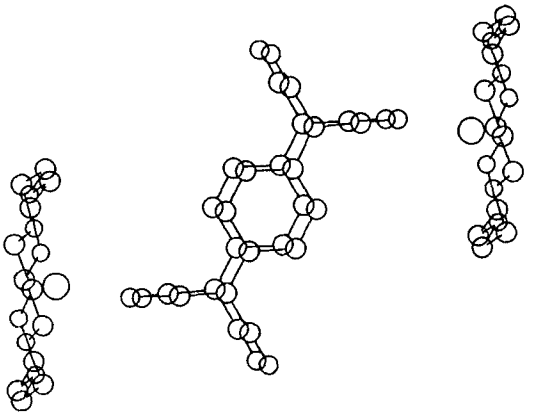


Figure 2. Top view of a dimer subunit in **3b**

There are very few structures known in which K^+ is located out of the plane of an 18-crown-6 host ring. Other examples include two hydrido complexes: (18-crown-6)$K^+[(Me_3P)_3WH_5]^-$, in which the K^+ is located 0·75 Å above the crown ether oxygen plane,[20] and (18-crown-6)$K^+[(\mu\text{-H})Mo(C_5H_5)_2]^-$, where it is displaced by 0·87 Å.[21] In **3b** the corresponding distance is 0·76 Å, which compares with a displacement of 0·94 Å for Rb^+ out of this plane in the complex **3c**.

In order to explore further the role of cation size on the solid-state behaviour of these complexes, we have also prepared the novel thallium(I) complex **3d**.[22] This

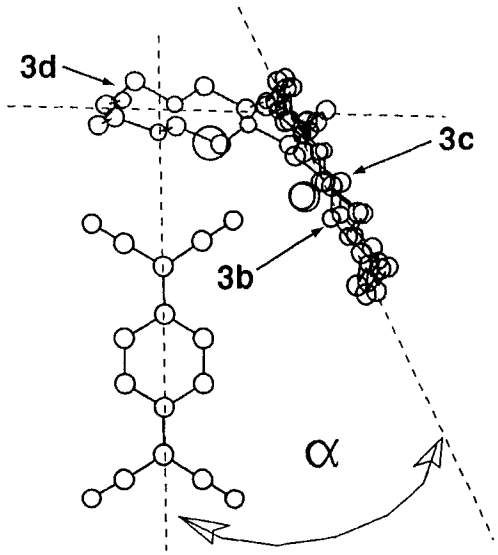


Figure 3. Overlap of the crown ethers in **3b–d** showing their arrangement around TCNQ, α being the angle between the TCNQ long axis and the crown ether oxygen best plane

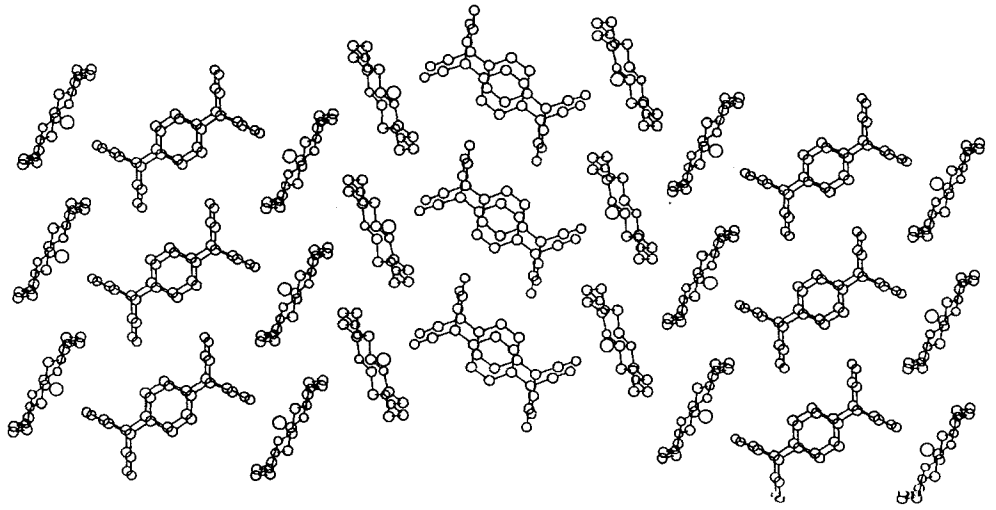


Figure 4. Solid-state structure of **3b** showing the herringbone structure

again favours a dimerized structure similar to those observed for the K^+ and Rb^+ salts **3b** and **3c** with the Tl^+ ion located 0·89 Å above the crown ether oxygen plane. For all three salts the M^+—NC distance is similar (Table 1), but in the case of the Tl^+ salt the cation no longer lies close to the CN bond axis (as viewed from above the TCNQ molecular plane) and the crown ether best plane lies more nearly perpendicular to the TCNQ dimer long axis (as viewed from above), but is significantly tilted relative to the TCNQ dimer plane (see angles α and β, respectively, in Figures 3 and 1 and Table 1).

No solid-state structures of 18-crown-6 Tl^+ complexes have been previously reported although binding constants in solution have been determined.[24] However, the structure of **3d** may be atypical in view of the unusual behaviour of its K^+ analogue **3b**. It is also interesting that (18-crown-6)$NH_4{}^+TCNQ^{-\cdot}$ appears to be isostructural with the potassium salt **3b**.[18]

15-Crown-5 and 12-crown-4 complexes

In view of the fact that in the K^+ salt **3b** the metal ion is pulled out of the crown ether plane by interaction with the $(TCNQ^{-\cdot})_2$ dimer, we decided to investigate whether similar behaviour would arise in a 'poor-fit'

Table 1. Metal—oxygen and metal—nitrile distances in **3b–d** and the hydrido complexes

Parameter	**3b**	**3c**	**3d**	(18C6)K^+ $[(Me_3P)_3WH_5]^-$ (see Ref. 20)	(18C6)K^+ $[(\mu\text{-H})Mo(C_5H_5)_2]^-$ (see Ref. 21)
Cation diameter (Å)[23]	2·66	2·94	2·80	2·66	2·66
M^+—O distance, min., max. (Å)[a]	2·812, 2·962	2·874, 3·031	2·839, 3·043	2·812, 2·949	2·844, 2·935
M^+—NC distances (Å)[a]	2·843, 3·013	2·978, 3·095	2·986, 3·209	–	–
Displacement of M^+ from crown ether plane (Å)	0·76	0·94	0·89	0·75	0·87
Angle of crown best plane relative to TCNQ:	26·60	27·10	78·72	–	–
$\alpha(^\circ)$ | 90-β | $(^\circ)$[b]	1·57	4·14	10·25	–	–

[a] The deviation from a perpendicular crown ether TCNQ geometry.
[b] Atom positions in the structures **3b–d** are known to a precision of 0·001.

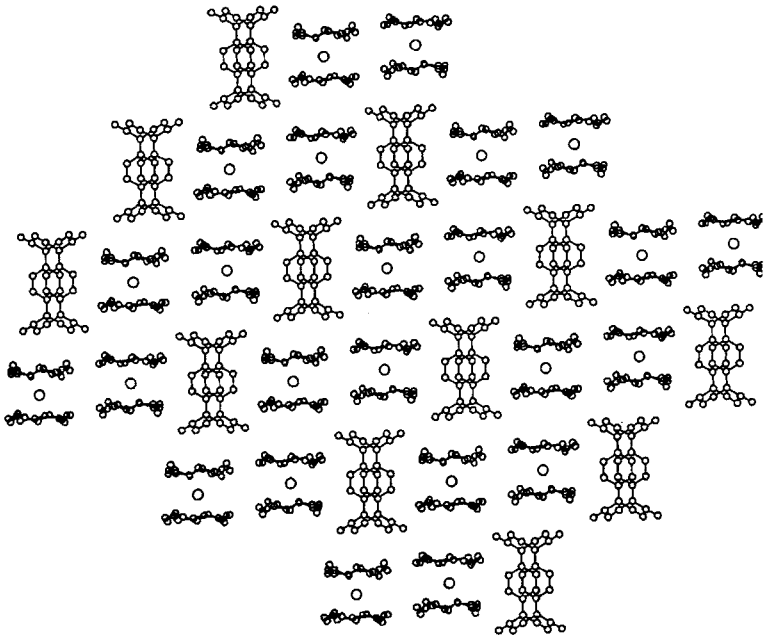


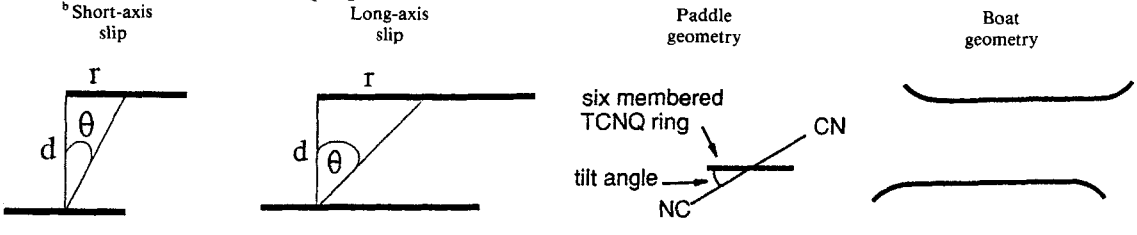
Figure 5. A view of the solid-state structure of **4** showing the sheets of TCNQ dimers isolated by crown ether–cation 'barrels'

Table 2. $TCNQ^{-\cdot}$ dimer geometries

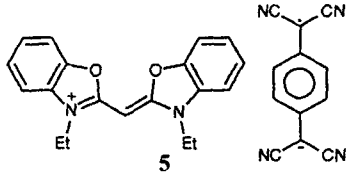
M^+	$(18C6)K^+$ **3b**	$(18C6)Rb^+$ **3c**	$(18C6)Tl^+$ **3d**	$(15C5)_2K^+$ **4**	Oxacyanine **5**
Short-axis slip[a]:					
r(Å)	0·33	0·51	0·69	1·28	0·94
θ(°)	5·82	9·13	12·38	22·05	16·29
Long-axis slip[a]:					
r(Å)	0·08	0·09	0·10	0·01	0·04
θ(°)	1·42	1·58	1·73	0·15	0·66
Intradimer perpendicular spacing, d(Å)	3·23	3·19	3·15	3·16	3·21
$TCNQ^{-\cdot}$ geometry[b]	Paddle	Paddle	Distorted boat	Paddle	Paddle

[a] From TCNQ ring centre of mass to TCNQ ring centre of mass.

[b]



situation resulting from the use of a smaller crown ether. However, cooling of an acetonitrile solution of a 1 : 1 mixture of 15-crown-5 and KTCNQ afforded crystals the combustion analytical data for which corresponded with the complex $(15\text{-crown-5})_2KTCNQ$ (**4**).[25] Perversely, a 2 : 1 crown–salt solution fails to crystallize in this manner, presumably as a result of increased solubility of the salt in the presence of excess ionophore. An x-ray structural study of this salt[25] shows isolated and significantly short-axis slipped TCNQ dimers (Figure 5 and Table 2) separated by $(15\text{-crown-5})_2K^+$ barrels. In the absence of direct cation coordination and of any other unusual intermolecular interactions, it would seem reasonable to suggest that this $TCNQ^{-\cdot}$ dimer geometry should represent an energy minimum situation. Indeed, we have reported similar, although not exactly identical, behaviour (Table 2) for the oxacyanine $TCNQ^{-\cdot}$ salt **5**, the solid-state structure of which also consists of isolated $TCNQ^{-\cdot}$ dimers sandwiched between face-to-face π-associated cyanine cations (Figure 6).[11]



5

We have also prepared $(12\text{-crown-4})_2LiTCNQ$ and $(12\text{-crown-4})_2NaTCNQ$. Unfortunately, although the former is microcrystalline, no single crystals have yet been obtained suitable for an x-ray structural study. This is not the case for the corresponding sodium salt, the structure of which is currently being determined.

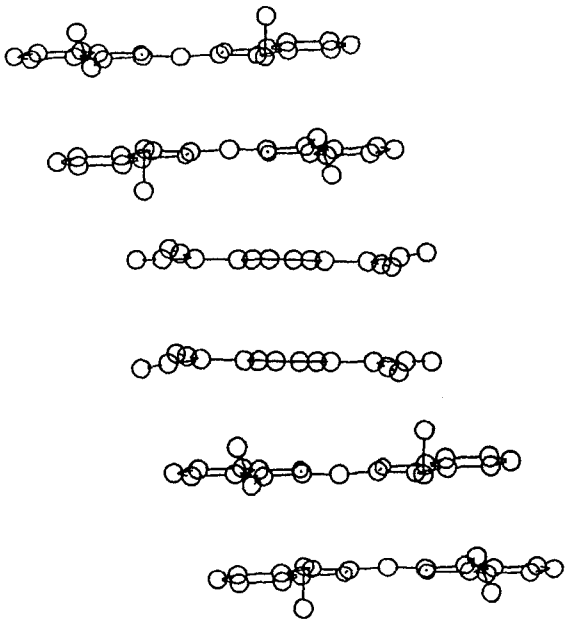


Figure 6. An extract from an infinite stack in **5**

PHYSICAL CONSEQUENCES

Optical spectra

UV–visible spectroscopic studies indicate that whereas the green solution ($\lambda_{max} = 737$ nm) of simple $TCNQ^{-\cdot}$ salts in most solvents (e.g. MeOH, MeCN) arises from the $TCNQ^{-\cdot}$ monomer,[26] the blue solution ($\lambda_{max} = 643$ nm) obtained from dissolution of LiTCNQ in water arises from $TCNQ^{-\cdot}$ dimers. The solid-state optical spectra of the $TCNQ^{-\cdot}$ salts **3b–d**, **4** and **5** (Table 3) bear a marked similarity to that for the aqueous solution but compare less well with the KTCNQ powder spectrum consistent with this interpretation of the solution data.[27]

The spectrum of the isolated dimer in **4** is somewhat different from those of the linearly metal coordinated dimers **3b** and **3c** but the trends are not clear cut, and probably reflect the interplay of several competing factors. The data relating to the cyanine TCNQ salt **5** are not directly comparable with those for the others since face-to-face $\pi-\pi$ interactions between the cyanine and $TCNQ^{-\cdot}$ are also a possible contributing factor in **5**.

Table 3. Optical spectra of (crown)MTCNQ salts and related systems

Material	CT_1[a] (eV)	LE_1[a] (eV)	LE_2[a] (eV)
$(TCNQ^{-\cdot})_{2\,(aq)}$[26a]	–	1·93	3·34
$(TCNQ^{-\cdot})_{2\,(aq)}$[26b]	1·36	1·95	4·48
3b	1·46	1·87	3·35
3c	1·38	1·84	3·22
3d	1·30	1·77	3·17
4	1·22	1·88	2·62
5	1·30	1·89	3·28

[a] CT_1 describes the charge transfer between two TCNQ radical anions. LE_1 describes the lowest energy local excitation within a TCNQ radical anion and correspondingly LE_2 describes the second lowest energy local excitation.

Electrical behaviour

In Table 4 are presented electrical data for compressed powders of a number of (crown)MTCNQ salts and related systems, as determined by variable-temperature d.c. and a.c. dielectric response techniques (10^{-4}–10^5 Hz).[28,29] Comparison of the activation energies for charge migration in the 18-crown-6 complexes **3a–c** shows that highest activation energy corresponds

Table 4. Electrical properties of (18-crown-6)MTCNQ and related salts

Material	σ_{293} (S m^{-1})	E_a(eV)	Ref.
3a	$1{\cdot}8 \times 10^{-4}$	0·28(2)	17
3b	$3{\cdot}4 \times 10^{-9}$	0·87(5)	17
3c	$\sim 10^{-11}$	0·63(7)	17
5	$1{\cdot}2 \times 10^{-9}$	0·46(5)	30
DB18C6[a]–KTCNQ	$\sim 10^{-12}$	0·58(19)	17

[a] DB18C6 = dibenzo-18-crown-6.

to the 'best-fit' cation K^+. All materials show low-frequency dispersive dielectric behaviour consistent with short-range inefficient charge-hopping processes. The low activation energy for charge migration in the sodium salt **3a** is consistent with a disordered structure resulting from a non-planar crown complex conformation as reported by Dunitz and co-workers for the corresponding thiocyanate.[19] The behaviour of the TCNQ salt **3b** is very similar to that of the corresponding iodide and oxonol salts,[17] suggesting that the nature of the anion is not important in determining the charge-carrying process in these cases. The lowest energy optical transition for **3b** (Table 3) is sufficiently higher in energy that the accumulated evidence is consistent with K^+ ions acting as the predominant charge carriers in these materials. In the oxacyanine **5**, electronic charge transport seems to be the only viable charge migration pathway and the lower activation energy observed for this system probably reflects charge migration between relatively close $TCNQ^{-\cdot}$ dimers in neighbouring columns within the crystal.[11]

Thermally activated triplet exciton behaviour

A notable consequence of the isolated TCNQ dimer structures found for the (crown)MTCNQ salts is the formation of thermally activated triplet excitons in these systems.[31] Similar behaviour has been observed in simple MTCNQ salts but the close similarity of the structures of **3b** and **c** allows a rare opportunity for some interesting comparisons. Two triplet exciton signals are found and assigned to static and mobile exciton formation. Whilst the static exciton activation energy is similar for both salts, that for the mobile exciton is strongly cation dependent, the smaller cation markedly reducing exciton mobility. It is interesting to note the similarity of J_{static} (Table 5) and E_a for charge migration (Table 4) in (18-crown-6)KTCNQ.

Table 5. Single-crystal triplet exciton activation energies in **3b** and **c**

Material	J_{mobile} (eV)	J_{static} (eV)
3b	0·88(2)	0·37(2)
3c	0·18(2)	0·38(2)

Similar thermally activated triplet exciton behaviour is also observed for the other TCNQ salts discussed here. However, no mobile exciton is evident in the ESR spectra of single crystals of (15-crown-5)$_2$KTCNQ (**4**), reflecting the greater separation between neighbouring $TCNQ^{-\cdot}$ dimer pairs in this structure.

CONCLUSIONS

Ionophore complexation offers an interesting approach for manipulating and fine tuning of the molecular electronic properties of organic materials such as the alkali metal $TCNQ^{-\cdot}$ salts. Whilst 'bulking out' the structure by crown encapsulation of the cation prevents the formation of infinite $TCNQ^{-\cdot}$ columns typical of highly conducting electrical systems, it does lead to the isolation of the $TCNQ^{-\cdot}$ dimer component which is a key structural repeat unit in the semiconducting phases of, for example, TTF–TCNQ and the simple metal TCNQ salts. This has allowed us to begin to explore the spectroscopic properties and electronic behaviour of and interaction between such structural fragments as a function of their relative spatial relationships. Such complexes should provide an excellent opportunity for investigating the crystal engineering of molecular electronic behaviour.

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