Triplet Excitons in Isolated TCNQ$^{\cdot-}$ Dimers (TCNQ = tetracyanoquinodimethane)

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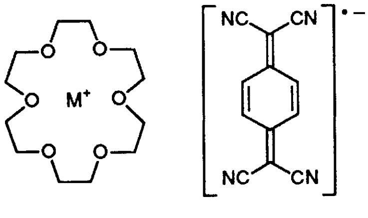
In the solid-state a monomethine cyanine TCNQ$^{\cdot-}$ salt and an 18-crown-6 K$^+$ TCNQ$^{\cdot-}$ complex both contain isolated, vertically stacked, TCNQ dimers which, despite the fundamentally different nature and location of the two cations, both show evidence for thermally excited triplet excitons.

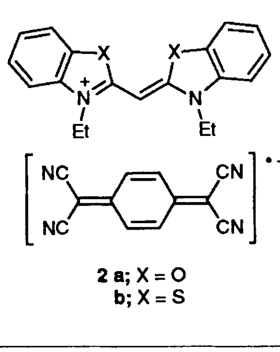
There are very few examples[1] of triplet excitons in 1 : 1 M$^+$ TCNQ$^{\cdot-}$ salts, such behaviour being generally associated with solid-state structures containing TCNQ oligomers ($\geqslant$3) or larger aggregates (*e.g.* dimerised columns). We have recently observed thermally excited triplets in powders and single crystals of the 18-crown-6- complex of Rb$^+$ TCNQ$^{\cdot-}$ **1c**,[2] which forms stacks of isolated TCNQ$^{\cdot-}$ dimers coordinated to crown-encapsulated Rb$^+$ packed into a brickwork array. We now present the preliminary results of spectroscopic and structural studies on two more TCNQ salts, both of which show such behaviour despite having markedly different chemical structures.

3,3′-Diethyloxacyanine–TCNQ$^{\cdot-}$ **2a** adopts a solid-state structure† consisting of vertically stacked TCNQ dimers alternating with pairs of cyanine cations to form$\cdots$D$^+$D$^+$A$^-$A$^-$D$^+$D$^+\cdots$columns (Fig. 1). These columns are packed into sheets, with neighbouring sheets forming a herringbone array. The cyanine cation is planar, with the ethyl substituents *cis*; neighbouring cations within the stack are short-axis inverted. Within a TCNQ dimer neighbouring anions are short-axis slipped (by 16°) and separated by 3.35 Å. Bond lengths are typical of those expected[4] for TCNQ^{1-}. Variable temperature ESR studies of **2a** show triplet-state behaviour similar to that reported for **1c**.[2] Whilst structural studies of several monomethine cyanine TCNQ salts are available, there are no data for the oxacyanine cation, and the solid-state stacking observed for **2a** is novel.[4] Indeed, in the solid state the sulphur analogue **2b** forms columns of dye cations separated by long-axis slipped (by 53.6°) TCNQ dimers (with an intradimer spacing of 3.23 Å).[5]

We have also found that 18-crown-6 K$^+$ TCNQ$^{\cdot-}$ **1b**‡[6] has a strong room-temperature ESR spectrum both when as a powder and a single crystal in marked contrast with previous reports.[7] In our hands **1b** shows variable temperature behaviour similar to that already reported for the Rb$^+$ salt **1c** and consistent with the presence of both static and mobile triplet species,[2] $E_{\mathrm{a,static}} = 0.37$ eV, $E_{\mathrm{a,mobile}} = 0.88$ eV; interestingly the former value is similar to that observed for **1c**, whereas the latter is significantly higher in energy (by a factor of *ca.* 5). In the solid state† K$^+$ (18-crown-6) TCNQ$^{\cdot-}$ forms dimers which pack into a brickwork array almost identical with that previously reported for the Rb$^+$ salt **1c**. As before,[2] within each dimer the TCNQ units are short-axis slipped by *ca.* 6°, separated by 3.24 Å and bridged by crown-encapsulated K$^+$ ions. The metal ions are pulled out of the crown ether-oxygen plane (by 0.76 Å) in contrast with the behaviour observed in other K$^+$ (18-crown-6) complexes, *e.g.* the thiocyanate 18-crown-6 complex,[8] though similar to that reported for the



1 a; M = Na
b; M = K
c; M = Rb



2 a; X = O
b; X = S

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† (**2a**) has m.p. 245 °C (lit.[3] 244–247 °C) and $\lambda_{\max}$/eV 1.275, 1.331, 1.861 and 1.903. *Crystal data*: A crystal of **2a** measuring 0.3 × 0.3 × 1.2 mm was mounted on an Enraf Nonius CAD-4F diffractometer equipped with a Cu-Kα radiation source (λ = 1.541 80 Å), $C_{31}H_{23}N_6O_2$. Space group $P2_1/c$, monoclinic, a = 14.401(5), b = 14.759(1), c = 13.707(2) Å, β = 116.34(2)°, Z = 4, D_c = 1.302 g cm^{-3}, U = 2610.57 Å^3. Data were collected in an ω–2θ scan mode from 1 to 70° to yield 4943 unique reflections of which 3892 were considered observed having $I > 3\sigma(I)$. The structure was solved by direct methods and refined using full matrix least squares to give a final R = 6.97% (R_w = 7.97%). SHELXS-86 (G. Sheldrick, SHELXS-86 User Guide, Göttingen, F.R.G., 1986) was used for direct methods and CRYSTALS (D. J. Watkin, J. R. Carruthers and P. W. Betteridge, CRYSTALS User Guide, Chemical Crystallography Laboratory, Oxford University, Oxford, U.K., 1985) for all other least-squares calculations.

Crystal data for (**1b**): A crystal measuring 0.3 × 0.3 × 0.5 mm was mounted on an Enraf Nonius CAD-4F diffractometer equipped with a Cu-Kα radiation source (λ = 1.541 80 Å). $C_{24}H_{28}N_4O_6K$. Space group $A2/n$ (a non-standard setting of $C2/c$), monoclinic, a = 26.670(4), b = 8.223(4), c = 24.341(4) Å, β = 81.22(1)°, Z = 8, D_c = 1.278 g cm^{-3}, U = 5275.56 Å.[3] Data were collected in an ω–2θ scan mode from 1 to 70° to yield 4985 unique reflections of which 3084 were considered observed having $I > 3\sigma(I)$. The structure was solved using SHELXS-86 and refined using CRYSTALS to give a final R = 4.34% (R_w = 5.03%). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ Many crown ether-complexed metal TCNQ salts are already known;[6] however, we find that pure samples are more readily obtained from a modified procedure in which stoichiometric quantities of crown ether and the metal TCNQ salt (1 : 1, 2 : 1, *etc.*) are dissolved in boiling acetonitrile, the required complex crystallising as the mixture is slowly cooled. Complex **1b** forms dark purple crystals, m.p. 185 °C (decomp.), which have $\nu_{\max}$/cm^{-1} (KBr disc) 2899 (CH), 2186 (CN) and 2177 (CN); $\lambda_{\max}$/eV 1.46, 1.86, 2.06 and 3.34; Satisfactory elemental analyses were obtained.

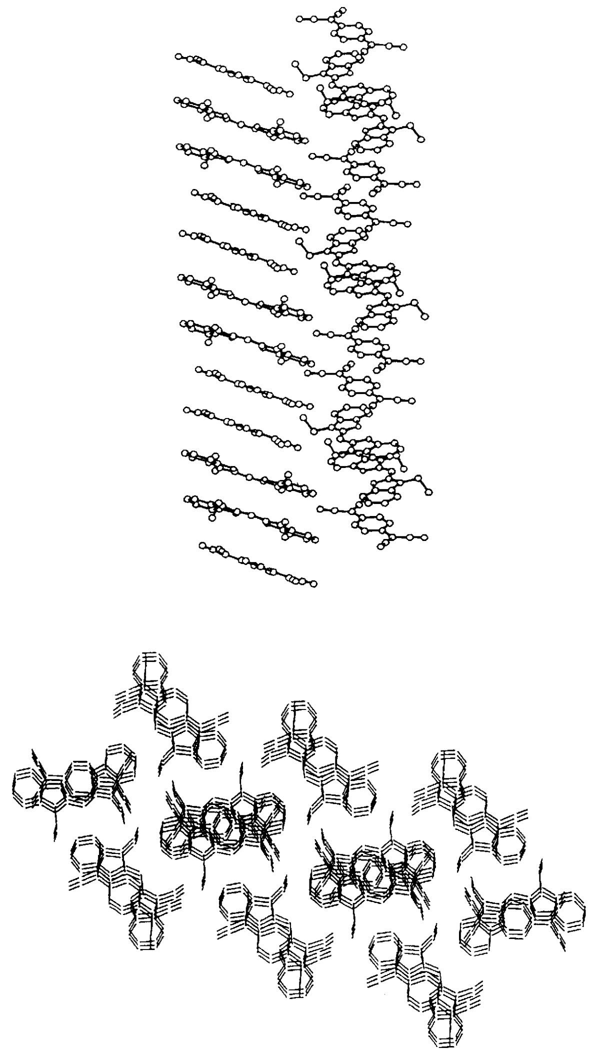

Fig. 1 Two views of the solid-state structure within 3,3′-diethyloxacyanine–TCNQ$^{\cdot -}$ **2a** showing packing within individual columns and the herringbone relationship of neighbouring sheets.

(μ-H)Mo(η-C_5H_5)$_2^-$ salt, (where K^+ is displaced by 0.866 Å from oxygen plane).[9]

AC dielectric spectroscopic studies (10^4 to 10^{-3} Hz; −150 to *ca.* 90 °C) of the complex TCNQ salts **1**[10] reveal low-frequency dispersive behaviour suggesting ionic rather than electronic conduction as the major charge-transport process in these materials. This is in accord with the solid-state structure of **1b** and optical spectra.‡ Indeed the absence of a facile electronic conduction pathway is presumably a prerequisite for observation of the triplet state in these materials. A much higher activation energy is observed in the K^+ salt **1b** [$\sigma_{293\,K} = 1.85 \times 10^{-8}$ S m^{-1}; $E_a = 0.96$ eV; calculated assuming $\sigma = \sigma_0 \exp(-E_a/kT)$] than for the Na^+ **1a** [$\sigma_{293\,K} = 1.69 \times 10^{-3}$ S m^{-1}; $E_a = 0.25$ eV) and Rb^+ **1c** ($\sigma_{293\,K} = 4.71 \times 10^{-8}$ S m^{-1}; $E_a = 0.61$ eV) salts consistent with tighter binding of the K^+ in the complex. Powder diffraction studies of the Na^+ salt reveal disorder and poor crystallinity and thus relatively high conductivity is not unexpected.

It is interesting to note that in other examples of vertically stacked isolated TCNQ dimers triplet exciton behaviour has not been observed.[11] A detailed study is now underway of the ESR behavioural differences between **1b** and **1c** together with an investigation of the optical and magnetic properties (at elevated temperatures) of **1**, **2** and their analogues, both as powders and oriented single crystals.

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