[60]Fullerene and TCNQ Donor–Acceptor Crystals of Octakis(dimethylamino)porphyrazine

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Reaction of octakis(dimethylamino)porphyrazine 1 with [60]fullerene gives a crystalline 2:1 charge-transfer (CT) complex as a three-dimensional network of chains; in contrast, reaction of 1 with tetracyanoquinodimethane (TCNQ) gives a crystalline 1:1 charge transfer salt as one-dimensional integrated stacks.

The wide interest in molecule-based metals[1,2] and magnets[3] has led us to consider peripherally substituted porphyrazines[4–6] as possible precursors to such materials. We recently reported the preparation of octakis(dimethylamino)porphyrazine 1 (OD-MAPz),[7] which, as expected, is readily oxidized [for the (+/0) couple, $E^0_{\frac{1}{2}} = -210$ mV (vs. Fc+/Fc)] and thus is ideally suited for incorporation in charge transfer molecular crystals. We report herein the synthesis and structure of two donor–acceptor crystals incorporating this molecule, (ODMAPz)₂C₆₀ 2 and (ODMAPz)(TCNQ) 3.

Evaporation, under nitrogen, of a toluene solution of 1 and C₆₀ in a 3:1 molar ratio yielded non-conducting black needles† of compound 2 that subsequently were handled in air. X-Ray analysis of the needles reveals that 2 is a 2:1 porphyrazine–C₆₀ complex. Each C₆₀ molecule is held between the slightly cupped 'hands' of a pair of dished porphyrazine units (Fig. 1), quite similar to the configuration observed for the 2:1 complex of BEDT–TTF [bis(ethylendithio)tetrathiafulvalene] and C₆₀.[8] The 'dishing' of the porphyrazine molecules is significant, the innermost quartet of nitrogen atoms lying ca. 0.5 Å out of the plane of the eight peripheral nitrogen atoms. The porphyrazine units are ordered, but the C₆₀ molecule exhibits rotational disorder; the orientation illustrated represents an optimization of one of several orientations present in the crystal. The disorder prevents definitive statements about the molecular charges, but as the solution oxidation of 1 by C₆₀ is unfavourable,[9] and by analogy with the [BEDT–TTF]₂C₆₀ material, we propose that 2 is a charge transfer complex, not a salt. The interaction between

porphyrazine and C₆₀ as visualized here is probably similar to the interaction of fullerenes and porphyrin-derivatized chromatographic materials.[10]

This 2:1 complex crystallizes as a toluene solvate that packs to form a three-dimensional network of intersecting, almost perpendicular, linear arrays of molecules (Fig. 2). These arrays are of three distinct types. If one denotes the porphyrazine and toluene solvent components as Pz and S, respectively, the three array types are: (a) C₆₀–Pz–Pz–C₆₀–Pz–Pz–, this sequence running both vertically and into the plane of the paper in Fig. 2; (b) C₆₀–C₆₀–C₆₀–C₆₀–, running horizontally in Fig. 2, and (c) C₆₀–S–C₆₀–S–C₆₀–, which runs both vertically and into the plane of the paper in Fig. 2. In both (a) and (b), the surfaces of the molecules are essentially in van der Waals contact. In (a) the distance from the centroid of the C₆₀ molecule to the planes defined by bracketing sets of innermost quartets of porphyrazine N atoms is ca. 6.3 Å and the interplane back-to-back separation between these planes (i.e. Pz–Pz distance) is ca. 3.2 Å. In (b) the C₆₀–C₆₀ centroid–centroid separations are ca. 10.5 Å and (c) the C₆₀–C₆₀ centroid–centroid separations are ca. 15.9 Å.

Compound 3 was obtained as dark purple needles deposited at the interface formed by layering a solution of 1 in hexanes on top of a solution of TCNQ in toluene. The crystals‡ are comprised of integrated stacks with alternating donor 1 and acceptor (TCNQ) molecules (Fig. 3) and, as is typical of such
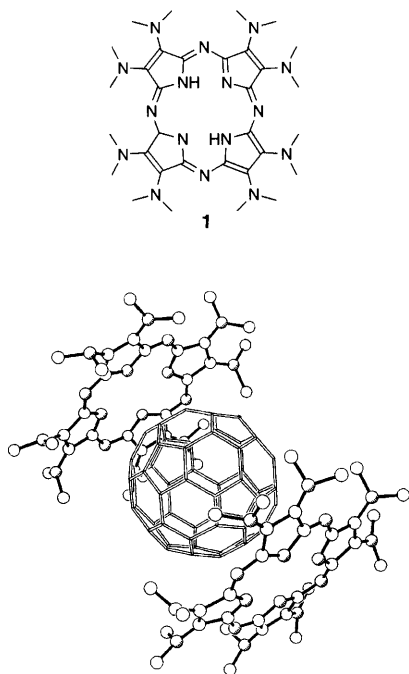

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Fig. 1 X-Ray structure of 2, showing a C₆₀ cupped between two molecules of 1

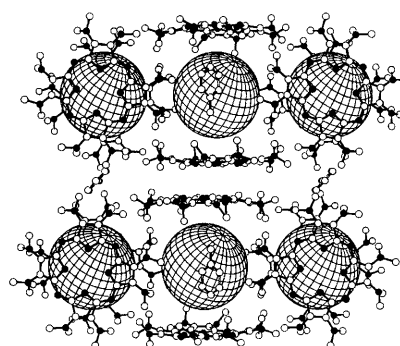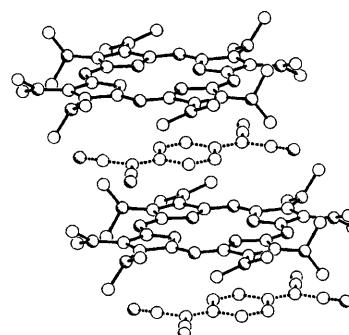Fig. 2 Packing diagram of 2, as described in text

Fig. 3 Perspective view of the alternating D–A stack in 3

materials, were found to be essentially insulating. The donor and acceptor are each situated about a crystallographic inversion centre. The dimethylamino groups are rotated by varying amounts out of the molecular plane, but the remainder of the porphyrazine is essentially planar with mean and maximum deviations from planarity of 0.013 and 0.037 Å, respectively, a geometry that contrasts with the dished conformation adopted in the 2:1 C_{60} complex. The TCNQ molecule is slightly non-planar, the cyano groups being rotated by *ca.* 3° out of the ring plane. The **1** and TCNQ molecules form a stepped stack that extends in the crystallographic *b* direction. The TCNQ–**1**–TCNQ centroid–centroid–centroid vector is inclined by 69° to the porphyrazine ring plane. The TCNQ and **1** molecules are only slightly inclined (3.5° between their mean planes) and have a mean interplanar separation of 3.3 Å.

Crystals of **3** would be expected to involve extensive charge transfer, given that the potential of the (**1**⁺/**1**) couple [E_0 = −210 mV (*vs.* Fc⁺/Fc)] is lower than those for tetrathiafulvalene [E_0 = −7 mV (*vs.* Fc⁺/Fc)][11] and tetramethyl-*p*-phenylenediamine [E_0 = −100 mV (*vs.* Fc⁺/Fc)],[11] each of which exhibits extensive charge transfer to TCNQ [$E_0^{0/-}$ = −180 mV (*vs.* Fc⁺/Fc)].[11] Both crystallographic analysis and vibrational spectroscopy can be used to analyse the extent of charge transfer in CT crystals involving TCNQ. IR[12] and resonance Raman[13,14] spectroscopies show linear relationships between the nitrile stretching frequencies and the negative charge on TCNQ, while X-ray diffraction reveals a similar correlation between the charge on TCNQ and the ratio of the sum of its C–C double bond lengths to the sum of its C–C single bond lengths.[15] Although these methods are often in agreement, some compounds show significant discrepancies,§ and **3** provides such a case. Analysis of the bond lengths in **3** yields a value of −0.17 for the charge on TCNQ, whereas the IR spectrum¶ of **3** shows a single nitrile stretching band at 2180 cm⁻¹, which is the same as that for the Cs⁺, K⁺ and Na⁺ salts of TCNQ and corresponds to a charge of −1.0 on TCNQ. Magnetic susceptibility masurements do not resolve this discrepancy. Compound **3** is essentially diamagnetic up to room temperature, consistent with **3** being either a neutral charge-transfer complex or a charge-transfer salt with very strong exchange couplings between donor and acceptor radical ions. Based on comparison of the redox potential of **1** with those of other donors, we provisionally accept the spectroscopic assignment indicating extensive charge transfer.

Thus, **1** can readily be used to create donor–acceptor crystals. It is likely that compound **2** contains neutral components, but **3** exhibits complete charge transfer from the porphyrazine to TCNQ. The combination in **1** of ready oxidation and a π-network that can encompass both the porphyrazine ring and the peripheral nitrogen atoms will allow the synthesis of new charge transfer materials with extremely good intra- and inter-stack overlap, and thus with enhanced electronic and magnetic properties.

Footnotes

† *Crystal data* for **2**·MePh: $C_{131}H_{108}N_{32}$, M = 2130.5, tetragonal, $a = b$ = 22.349(3), c = 20.928(4) Å, V = 10556(3)′Å³, space group $P4_22_12$, Z = 4, D_c = 1.34 g cm⁻³, μ(Cu-Kα) = 6.60 cm⁻¹, $F(000)$ = 4472. A black tetragonal needle of dimensions 0.10 × 0.10 × 0.63 mm was used. Data

were measured on a Siemens P4/RA diffractometer with Cu-Kα radiation (graphite monochromator) using ω scans. The structure was solved by direct methods. The non-hydrogen atoms of the porphyrazine were refined anisotropically, while the solvent toluene and the resolved partial occupancy atoms of the disordered C_{60} component were refined isotropically using full matrix least squares to give R = 0.165, R_w = 0.171 for 5157 independent observed reflections [$|F_o|$ > 4σ($|F_o|$), 2θ ≤ 124°] and 636 parameters.

‡ *Crystal data* for **3**: $C_{44}H_{54}N_{20}$, M = 863, monoclinic, a = 13.466(2), b = 7.124(2), c = 23.405(5) Å, β = 104.48(2)°, V = 2174.0(6) Å³, space group $P2_1/n$ (no. 14), Z = 2, D_c = 1.318 g cm⁻³, μ(Cu-Kα) = 0.685 cm⁻¹, $F(000)$ = 916. A dark purple needle of dimensions 0.07 × 0.04 × 0.73 mm was used. Data were measured on a Siemens P4/RA Diffractometer with Cu-Kα radiation (graphite monochromator) using ω scans. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically using full-matrix least squares to give R = 0.042, R_w = 0.046 for 2748 unique reflections with $|F_o|$ > 4σ($|F_o|$), 2θ ≤ 124° and 294 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ For example, the *N*-methylphenazenium salt has been described by IR, Raman, and NMR spectroscopy and X-ray diffuse scattering studies to have a charge on TCNQ between −0.65 and −0.90[12,16–18] However, the analysis of the crystal structure by the method of Coppens and coworkers yields a charge of −0.4.[19] Additionally, the crystal structure of (Et₃N⁺) (TCNQ)₂⁻[20] shows two inequivalent TCNQ molecules, which would correspond to charges of −0.35 and −1.1 by the Coppens method, but the IR and Raman spectra show only one nitrile band corresponding to a charge of −0.5.[12,13]

¶ Attempts to record a resonance Raman spectrum of **3** were unsuccessful, possibly due to the very strong absorption by the porphyrazine.

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