Electrochemical Preparation and Crystal Structure of (BEDT-TTF)PF_6: Towards a Rational Control of the Stoichiometry of Cation Radical Salts

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As indicated by thin layer cyclic voltammetry, electrocrystallization of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) at the second oxidation potential affords a charge-transfer salt of 1 : 1 stoichiometry, *i.e.* (BEDT-TTF)$PF_6 \cdot 0.5CH_2Cl_2$, the crystal structure of which is presented.

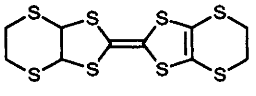
The experimental conditions for the electrochemical growth of high-quality single crystals of conducting cation-radical salts are still essentially adjusted through empirical approaches and the stoichiometry of the resulting materials, a critical manifestation of mixed valence, eventually associated with metallic conductivity, appears in most instances as a serendipity.[1,2]

A first step in the rationalization of the electrocrystallization of charge-transfer salts is the recent obtention of BEDT-TTF$(ClO_4)_2$ by electrochemical oxidation of a chemically prepared cation radical solution.[3] In that respect, we have recently shown that thin layer cyclic voltammetry (TLCV) constitutes a powerful method for the rapid detection and quantification of mixed-valence states and thus for the prediction of the stoichiometry of the corresponding charge-transfer salts.[4] In order to confirm the validity of this technique, we report here a first example of application to the case of hexafluorophosphate (BEDT-TTF) charge-transfer salts. The 1 : 1 stoichiometry predicted by TLCV for the new 1 : 1 (BEDT-TTF)/PF_6 charge-transfer salt has been experimentally confirmed by potentiostatic electrocrystallization of this material whose crystal structure is presented.

The cyclic voltammogram of BEDT-TTF in CH_2Cl_2 exhibits two successive reversible oxidation steps at 0.50 and 0.90 V *vs.* SCE. Although these two redox systems are usually attributed to two successive one-electron processes,[5] the analysis of the electrochemical behaviour of BEDT-TTF by TLCV leads to quite different conclusions.

Contrary to conventional CV, in TLCV the current is not limited by diffusion, all the species confined within the thin layer are involved in the electrochemical reaction,[6] and the number of electrons involved in each oxidation step (n) is directly obtained by integration of the voltammetric peaks and comparison with a standard compound of known n value.[4]

The TLCV response of BEDT-TTF in CH_2Cl_2 (Fig. 1) shows two reversible oxidation steps at 0.51 and 0.87 V. The integration of the oxidation and reduction peaks shows that, unlike what could be expected from the CV, each of these peaks corresponds in fact to a n value of 0.5 F mol^{-1} after comparison with the monoelectronic reduction peak of dichloronaphthoquinone as the standard. These results suggest that the stoichiometry of BEDT-TTF charge transfer salts could be *a priori* controlled by performing electrocrystallization at a fixed constant potential. Thus, a potentiostatic electrooxidation carried out at the first oxidation potential should afford a 2 : 1 mixed-valence salt. Although such materials are generally obtained in galvanostatic electrocrystallization,[1,2] it is likely that the low applied intensities (1–10 μA) and controlled amount of electricity allow one to reach only the first oxidation potential.



BEDT-TTF

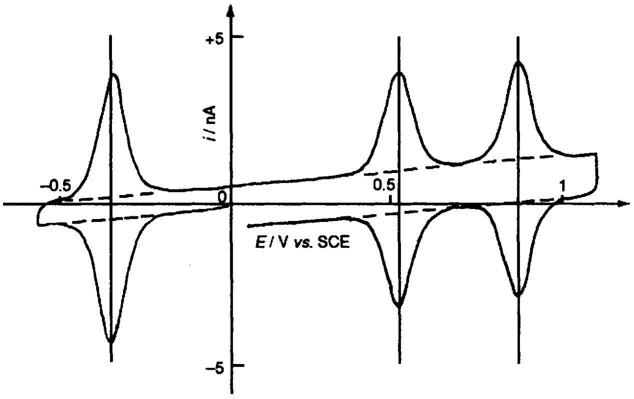


Fig. 1 Thin layer cyclic voltammogram of 4.36×10^{-4} mol dm^{-3} BEDT-TTF in 0.5 mol dm^{-3} NBu_4PF_6–CH_2Cl_2; dichloronaphthoquinone 2.64×10^{-4} mol dm^{-3} as the standard (reduction peak: −0.37 V *vs.* SCE); scan rate 5 mV s^{-1}

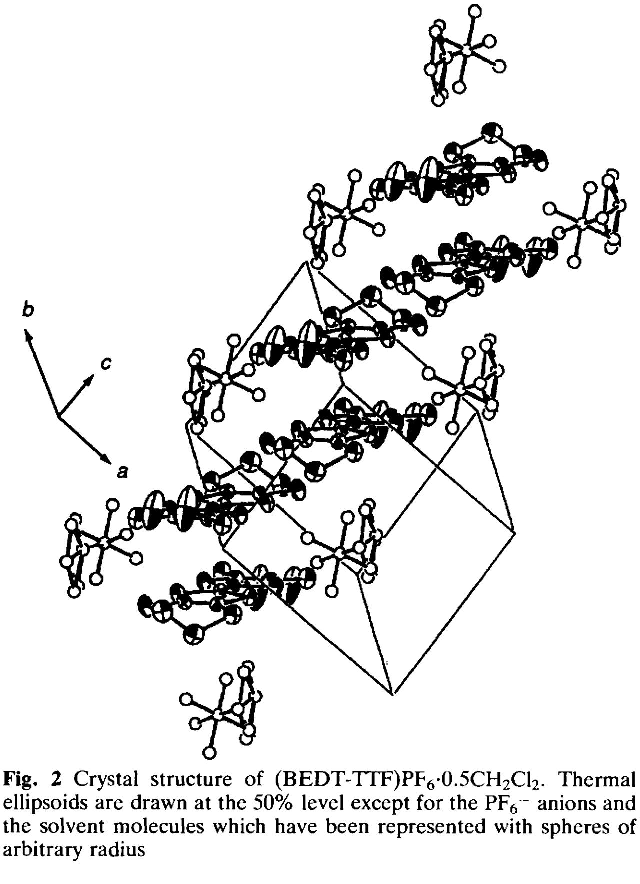


Fig. 2 Crystal structure of (BEDT-TTF)$PF_6 \cdot 0.5CH_2Cl_2$. Thermal ellipsoids are drawn at the 50% level except for the PF_6^- anions and the solvent molecules which have been represented with spheres of arbitrary radius

On the other hand, the TLCV of Fig. 1 suggests that it should be possible to prepare a 1:1 charge-transfer salt by electrocrystallization at the second oxidation potential. Thus, controlled potential electrocrystallization was carried out in a three-compartment H-cell fitted with platinum wire electrodes and a saturated calomel electrode (SCE) located in the median compartment. The electrolytic medium involved 0.6 mmol dm^{-3} BEDT-TTF in 0.1 mol dm^{-3} NBu_4PF_6 in CH_2Cl_2. Application of a fixed potential at 1.30 V *vs.* SCE, *i.e.* beyond the second oxidation peak, yields black single crystals of a material formulated as (BEDT-TTF)PF_6·0.5CH_2Cl_2 as determined by an X-ray diffraction study.†

Quasidiscrete dimers of BEDT-TTF molecules in a slipped, bond-over-ring configuration are identified in the crystal structure, as shown in Fig. 2. The long central C–C double bond (1.378 Å) and the short C–S double bond (1.719 Å) in the fulvalene rings are characteristic of the monooxidized BEDT-TTF cation radical.[7] The PF_6^- anions are located on each dimer side along the transverse short molecular axis direction. Note that PF_6^- anions and CH_2Cl_2 molecules alternate along channels parallel to the long molecular axis direction. There are four structural modifications[8–11] reported for (BEDT-TTF)$_2PF_6$ and it is the third structural modification[12,13] reported for this salt with 1:1 stoichiometry, albeit the only one incorporating a solvent molecule in the structure. This material shows a two-probe conductivity of 1.7×10^{-3} S cm^{-1}.

To summarize, a new BEDT-TTF charge-transfer salt of 1:1 stoichiometry has been prepared and characterized by X-ray diffraction. This result definitively confirms the validity of TLCV as a powerful method of prediction of the stoichiometry of charge transfer salts.

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† *Crystal data* for (BEDT-TTF)PF_6·0.5CH_2Cl_2, M = 1144.24, triclinic, space group $P\bar{1}$, a = 9.737(1), b = 12.636(1), c = 8.079(1) Å, α = 90.55(1), β = 99.81(1), γ = 82.95(1)°, V = 972.1(9) Å^3, D_c = 1.95 g cm^{-3}, Z = 2. X-ray diffraction data were collected on an Enraf-Nonius CAD4-SDP diffractometer system using the ω–2θ scan technique with graphite-monochromated Mo-Kα radiation. A total of 4053 reflections were measured from which 3495 were unique (R_{int} = 0.011) of which 2530 were judged to be observed [$I > 3\sigma(I)$]. The data were corrected for absorption (μ = 11.53 cm^{-1}) by a semiempirical method based on Ψ-scans. The structure was solved by direct methods and least-squares refinements gave R = 0.046 (R_w = 0.066) with a goodness of fit value of 2.005. 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.