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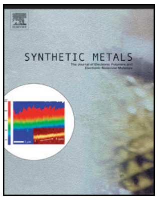

Short communication

TTF-DDQ: Two “green” synthetic routes, crystal structure and band gap from FT-IR spectroscopy

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ABSTRACT

TTF-DDQ (DDQ = 2,3-dichloro-5,6-dicyano-*p*-benzoquinone) is an ionic and diamagnetic charge transfer salt. Polycrystalline powders of TTF-DDQ were obtained by three synthetic methods: solvent evaporation from MeCN solution (**1**), MeCN vapor digestion (**2**), and mechanochemistry (liquid assisted grinding with DMSO) (**3**). The analysis of the synchrotron X-ray powder diffraction data of **1** afforded the crystal structure, which is isomorphous to that of the black polymorph of TTF-CA (CA = chloranil). TTF-DDQ is composed of $(TTF^{+\bullet})_2$ and $(DDQ^{-\bullet})_2$ dimeric radical ions arranged in segregated columnar stacks, linked by weak hydrogen bonds. The —Cl and —CN substituents in DDQ are disordered, and this was modeled by Rietveld analysis.

The FT-IR absorption spectra as a function of the temperature in the 300–10 K interval showed an absorption edge, indicating that TTF-DDQ is a semiconductor with a small band gap of (0.21 ± 0.01) eV. The monotonous evolution of the FT-IR spectra denotes the absence of crystallographic phase transitions in the temperature interval studied, likely due to the thermodynamic stability of this packing motif compared to the less stable donor-acceptor alternating stacks; or the segregated, potentially conducting stacks.

1. Introduction

Since the discovery of tetrathiafulvalene (TTF) by Wudl et al. in the early 1970s [1], charge transfer salts of TTF and its derivatives have been extensively studied in the search of molecular conductors and superconductors. Recent applications in modern organic electronic devices such as organic field effect (OFET) transistors [2–4], and 1-D organic nanostructures [4,5], have been reported. The use of charge transfer salts in organic electronics has recently increased mainly due to their excellent donor properties, their facile synthesis, and the low-dimensionality of their properties [4]. Low-dimensional charge transfer salt systems have been also used to test the validity of theoretical physics models in reduced dimensions [6].

An acetonitrile (MeCN) slow diffusion synthesis of the charge transfer salt tetrathiafulvalene 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (TTF-DDQ) has been reported in 1981 [7]. At that time, it was understood that TTF-DDQ is an ionic and diamagnetic material, composed of strongly distorted stacks of DDQ and relatively isolated TTF dimers [7]. However, single crystal structure analysis could not be completed and its atomic coordinates have remained unavailable.

We have recently reported the mechanochemical and vapor digestion synthesis, the crystal structure from powders, the FT-IR spectra and electronic structure of the black polymorph of TTF-CA (CA = chloranil) [8]. We have revisited TTF-DDQ, due to our interest in studying the solvent effect towards product polymorph control in “green” chemical synthesis methods largely reducing the use of harmful organic solvents, such as liquid assisted grinding (LAG) and vapor digestion (VD).

Liquid assisted grinding consists of grinding the reactants manually or in a ball mill, together with small quantities of solvents. In comparison to neat grinding, LAG can induce mechanochemical reactivity [9–11], increase reaction rates [9–13], afford sufficiently crystalline products amenable to crystal structure determination from powders [10,11], and it leads to the

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formation of particular product polymorphs depending on the solvent used [9–13]. Thus, LAG is a good method for product polymorph control and polymorph screening. This is significant in many research fields (*e.g.,* pharmaceutical, agrochemicals, pigments and dyes, food chemistry, etc.), as well as in the organic conductors field, since the physical properties (*e.g.,* electrical conductivity) of charge transfer salt polymorphs may be noticeably different.

Moreover, the interest in understanding LAG and VD mechanisms has recently increased due to modern “green chemistry” expectations for new industrial processes (*e.g.,* pharmaceutical [14]), the increasing number of solid state reactions reported, and the advent of modern solid state characterization methods such as direct-space methods for crystal structure solution from powders [15,16], affording the essential structural description of materials synthesized by mechanochemistry. In addition, the information gathered from the LAG synthesis of a series of chemically similar charge transfer salts (such as TTF and benzoquinone derivatives) can lead to an improved understanding of the “solvent effect” in LAG resulting in polymorphs with different charge transferred (ionicity), as well as new polymorphs of known compounds.

2. Experimental

2.1. Materials

Tetrathiafulvalene (99% purity) and DDQ (98% purity) were obtained from Sigma-Aldrich. MeCN 99.5% was purchased from Alfa-Aesar and DMSO +99.9% from Sigma. All reactants were used as received.

2.2. Mechanochemical and solution syntheses

The powder sample of TTF-DDQ used for crystal structure determination from synchrotron X-ray powder diffraction (XRPD) was prepared by dissolving 0.0118 g (5.77×10^{-5} moles) of TTF and 0.0131 g (5.77×10^{-5} moles) of DDQ in 15 mL of MeCN. The solvent was evaporated in the fumehood.

The sample for FT-IR spectroscopy was prepared by dissolving 0.0456 g (2.23×10^{-4} moles) of TTF and 0.0506 g (2.23×10^{-4} moles) of DDQ in approximately 20 mL of MeCN and the solvent was evaporated in the fumehood.

A reddish-brown TTF-DDQ sample was prepared by LAG, manually grinding under air for 30 minutes in an agate mortar with pestle 0.0118 g (5.77×10^{-5} moles) of TTF (brown, triclinic form) and 0.0131 g (5.77×10^{-5} moles) of DDQ, together with 5 μL of DMSO ($\eta = 0.2$ μL/mg) added immediately before start grinding.

2.3. Vapor digestion synthesis

The vapor digestion (VD) synthesis of TTF-DDQ was carried out from 0.0102 g (5.0×10^{-5} moles) of brown TTF (that has been previously slightly ground) and 0.0114 g (5.0×10^{-5} moles) of DDQ, gently mixed with a spatula and loaded in a glass vial. The vial was placed in a glass jar with lid, together with other vial containing a few milliliters of MeCN. The glass jar was purged with N_2 for five minutes, closed tightly, and covered with Al foil. The vapor digestion product was recovered from the sealed glass jar after 15 days.

2.4. X-ray powder diffraction

The synchrotron XRPD patterns of TTF-DDQ were collected at the beamline X16C, N.S.L.S., Brookhaven National Laboratory, USA. The data was collected at room temperature (RT) from glass capillaries in transmission geometry at $\lambda = 0.700080$ Å; except for the sample digested in MeCN vapor, which pattern was measured at 0.700095 Å. The wavelength was selected with a Si(111) double monochromator and the incident parallel beam was monitored with an ion chamber. A Ge(111) analyzer crystal was placed after the sample and before the detector to obtain good angular resolution, whereas the out-of-plane resolution was given by slits. A NaI(Tl) scintillation detector was used to measure the diffracted radiation.

Whole pattern decomposition of the diffraction data of TTF-DDQ synthesized from MeCN solution (**1**) using the Le Bail method [17], was carried out with the lattice parameters previously published [7]. The crystal structure was solved with the direct-space methods program PSSP [16], modeling the disorder through a DDQ molecule with 0.5 occupancy factor for both —Cl and —CN substituents at all four sites (2, 3, 5 and 6) in DDQ (see Scheme S1). Thus, DDQ molecules were permitted to adopt two opposite configurations, which can be labelled 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (configuration I) and 2,3-dicyano-5,6-dichloro-*p*-benzoquinone (configuration II).

The Rietveld [18] refinement reported was carried out with the program GSAS [19]. A disorder parameter for DDQ was refined permitting the variation of the initial 0.5 occupancy factors of —CN and —Cl substituents (at each site) subjected to a group constraint, so that the total occupancy (at all four sites) of the —Cl and —CN

Table 1
Crystal data for TTF-DDQ ($C_{14}H_4Cl_2N_2O_2S_4$, $M_r = 431.33$).

	1	2	3
Synthesis conditions	Solvent evaporation (MeCN solution)	MeCN vapor digestion	LAG synthesis using DMSO
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	2	2	2
$d_{calculated}$ (g/cm^3)	1.794	1.796	1.810
R_{wp} (%)	6.06	9.51	8.86
R_I (%)	5.05	6.31	3.55
χ^2	2.24	1.91	1.56
a (Å)	10.2567(3)	10.2317(8)	10.208(4)
b (Å)	12.1733(3)	12.1960(8)	12.152(4)
c (Å)	6.61547(13)	6.6101(3)	6.5939(13)
α (°)	77.5468(13)	77.529(4)	77.482(19)
β (°)	81.9718(18)	81.990(5)	82.54(2)
γ (°)	87.3646(9)	87.301(3)	87.273(11)
V (Å^3)	798.55(3)	797.40(9)	791.6(4)
—Cl and —CN disorder parameter in DDQ	0.734(9)	0.75(2)	0.66(3)