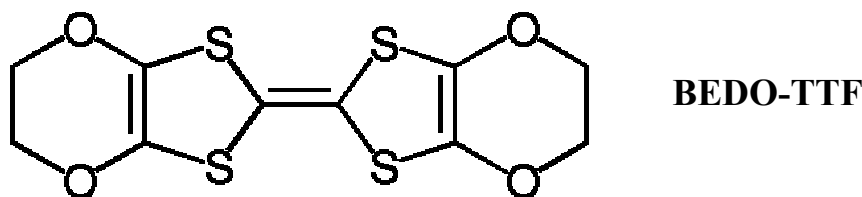


Phase transformation and optical properties of κ and β'' - BEDO-TTF charge transfer salts with CF_3SO_3^-

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BEDO-TTF is an electron donor molecule, which in complexes with various acceptors produced a large number of stable organic metals. The major packing motif was that of β'' type promoting a large two-dimensional π -orbital overlap. However, from the point of view of synthesizing novel organic superconductors the κ type has shown to be effective in the complexes of a related donor BEDT-TTF. So far only one κ type salt was obtained among BEDO-TTF complexes, κ -(BEDO-TTF) $_2\text{CF}_3\text{SO}_3$ [1]. Despite the favorable structure, the compound was reported to be metallic around RT ($\sigma_{\text{RT}} = 100 \text{ S cm}^{-1}$) with a slow change towards semiconducting behavior. Besides the κ type, the same synthetic procedure gave a different salt, β'' -(BEDO-TTF) $_2\text{CF}_3\text{SO}_3(\text{C}_4\text{H}_8\text{O})_{0.5}$ with a comparable dc conductivity [1].



In this work, optical and electrical properties of κ -(BEDO-TTF) $_2\text{CF}_3\text{SO}_3$ and β'' -(BEDO-TTF) $_2\text{CF}_3\text{SO}_3(\text{C}_4\text{H}_8\text{O})_{0.5}$ were studied. At high pressures up to 1 GPa and temperatures down to 2 K the β'' phase was metallic while no superconductivity was found in the κ phase. In the Raman spectra the C=C stretching (A_g) modes of BEDO-TTF were found as sharp peaks at 1468-1472 and 1620 -1626 cm^{-1} corresponding to +0.5 charged BEDO-TTF. No charge separation was found down to 4.2 K.

An irreversible phase transformation related to a loss of the solvent and rearrangement of BEDO-TTF molecules was found in crystals of β'' phase while they were kept under vacuum of $\sim 10^{-3}$ Pa at 293 K for 12 hours and then at 343 K for 2 hours. Further treatment did not induce any more change in the optical spectra and the tempered phase was stable. Though the newly obtained structure was inevitably disordered, it possessed its own well-defined optical axes with anisotropy in both electronic and vibrational spectra resembling that found in κ -(BEDO-TTF) $_2\text{CF}_3\text{SO}_3$. This suggests existence of a long order in the molecular (BEDO-TTF) orientation similar to that in κ -phase.

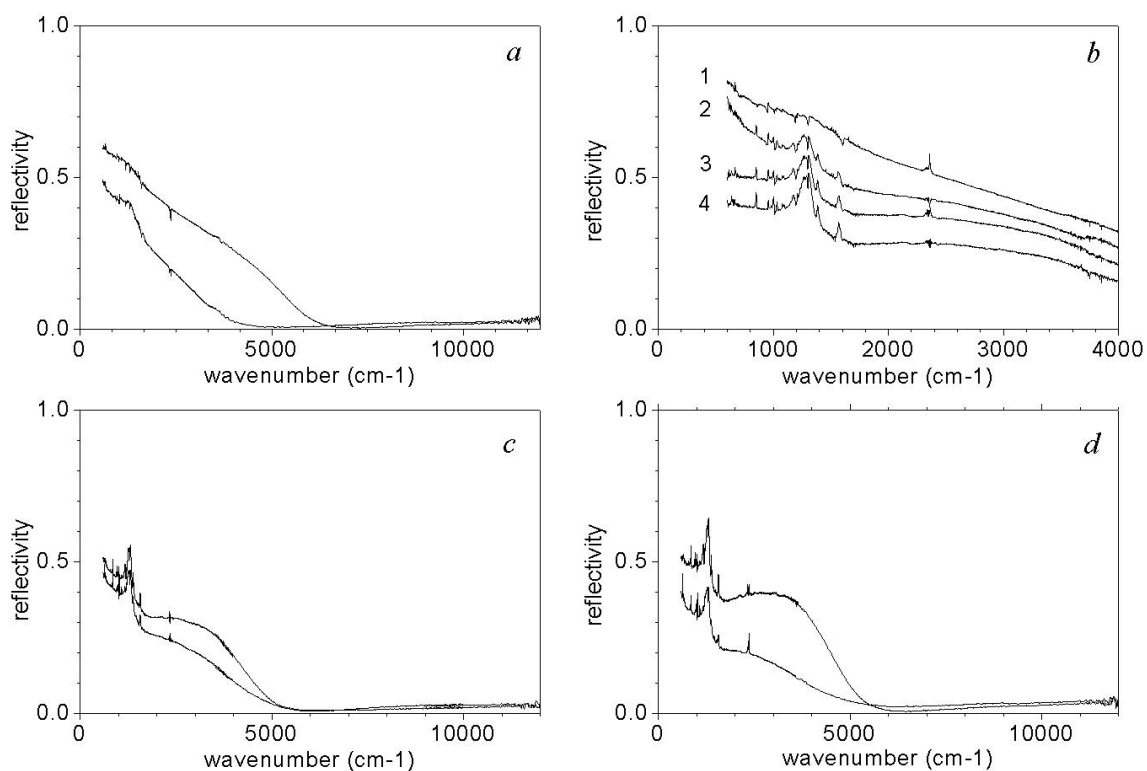


Figure 1:

(a) typical reflectivity spectra of β'' -(BEDO-TTF) $_2$ CF $_3$ SO $_3$ (C $_4$ H $_8$ O) $_{0.5}$.

(b) spectral change of the same spot on the sample surface during the phase transformation:
1 - fresh sample of β'' phase; **2** - after 12 hrs of vacuum; **3** - after one hour at 350 K; **4** - three more hours at 350 K.

(c) anisotropy of the reflectivity spectra of the tempered phase.

(d) reflectivity spectra along two main in-plane directions of κ -(BEDO-TTF) $_2$ CF $_3$ SO $_3$.

[1] M. Fettouhi, L. Ouahab, D. Serhani, J.-M. Fabre, L. Ducasse, J. Amiell, R. Canet, P. Delhaes. J. Mater. Chem. **3** (1993) 1101-1107.