Supplementary information:

Optical Properties of a Vibrationally Modulated Solid State Mott Insulator

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Resonant vibrational excitation of the ET molecule

The mode excited in the present work is the so-called ν_{30}[1,2]. In ET-F_2TCNQ this mode is located at ~1000 cm^{-1} in the equilibrium optical spectrum. This is shown in the supplementary Fig. S1(a), where the b-axis reflectivity measured by us with Fourier-transform Infrared Spectroscopy is displayed. This Ω=1000 cm^{-1} (10 μm) mode can be excited selectively by our light pulses, which have a ~10% bandwidth around 1000 cm^{-1}, thus covering the 900-1100 cm^{-1} range.

The normal mode displacement (ring deformation) and frequency of the 10 μm mode and the corresponding changes of the molecular orbital were calculated using Gaussian03 and are sketched in Figures S1(b) and (c). The molecular orbital distributions were calculated for the frozen displacements along the normal mode coordinate. The figure visualizes the "sloshing" of the electron-density from the left to the right as function of the normal mode displacement leading to an effectively enlarged molecular orbital distribution in time average. That results in a reduction of the effective screening and modulation of the on-site Coulomb repulsion U.

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[1] Kozlov, M. E., et al. The assignment of fundamental vibrations of BEDT-TTF and BEDT-TTF-d_8, *Spectrochimica Acta Part A: Molecular Spectroscopy* **43**, 323 (1987).
[2] Girlando, A., *J. Phys. Chem. C* **115**, 19371 (2011). uses another nomenclature and reports the 1010 cm^{-1} mode as ν_{26} in its supplemental material.

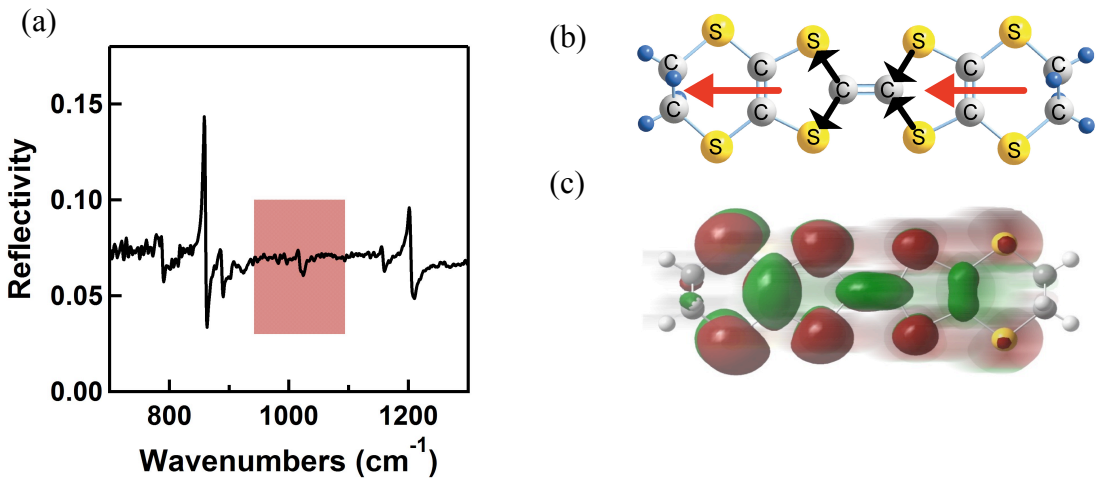

Figure S1: (a) b-axis (perpendicular to the ET chains) equilibrium reflectivity of ET-F_2TCNQ measured with Fourier-transform Spectroscopy. The ν_{30} mode is emphasized. (b) Sketch of the vibrational displacement of the ET molecule for the ν_{30} normal mode. (c) Calculated change of the molecular orbitals due to the normal mode displacement upon resonant excitation of the ν_{30} mode.