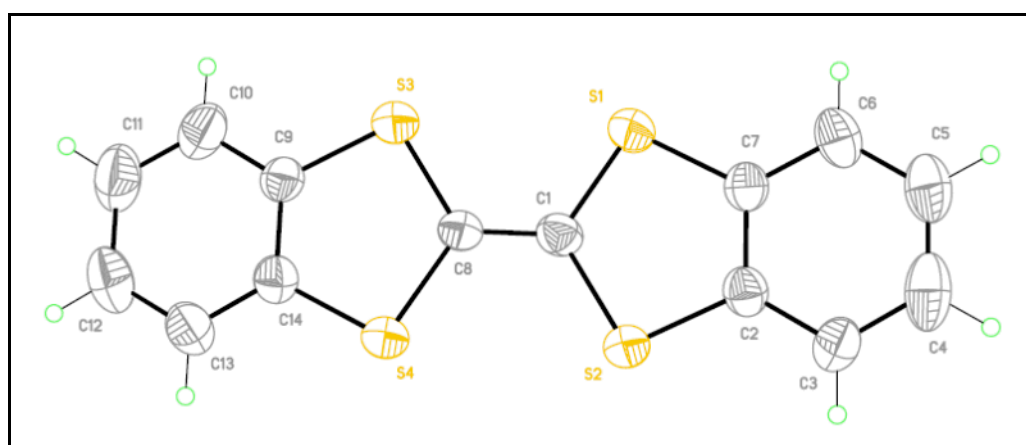


## THE FOUR POLYMORPHIC MODIFICATIONS OF THE SEMICONDUCTOR DIBENZO-TETRATHIAFULVALENE

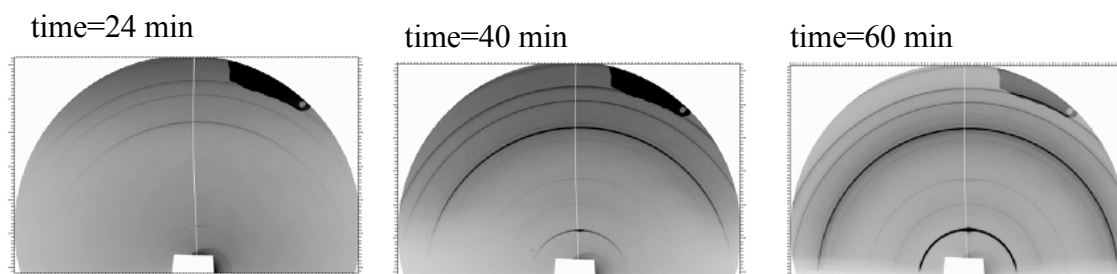
### Supplementary Material



**Figure S1.** Molecule of **C14 H8 S4** in the  $\beta$  phase (Ortep plot at 50% probability)



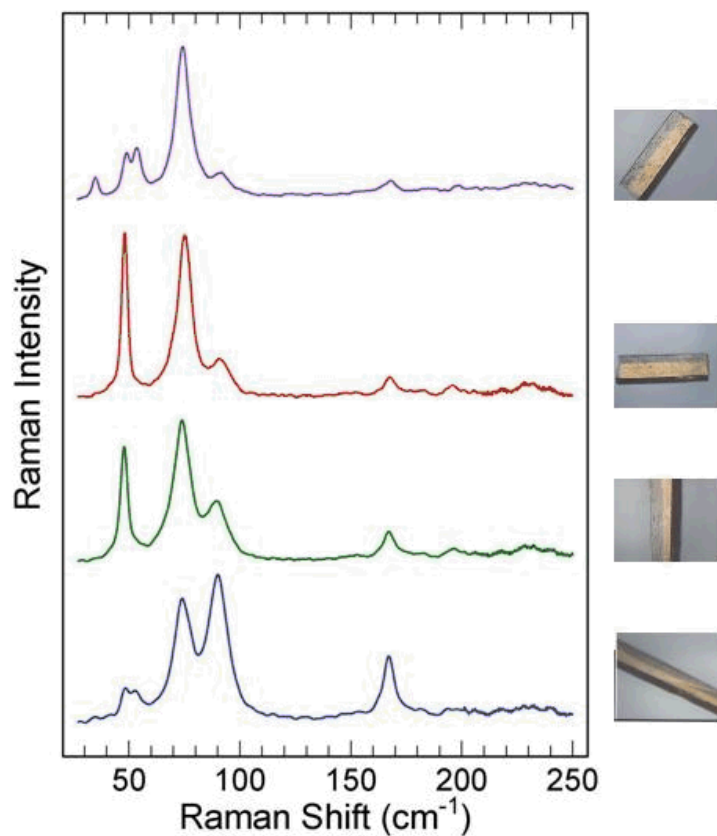
**Figure S2.** Sequence of 2D diffraction images of the  $\gamma$  phase formation, recorded during evaporation, after drop casting DBTTF/PS ( $d=150$  nm) on Si/HMDS substrate.



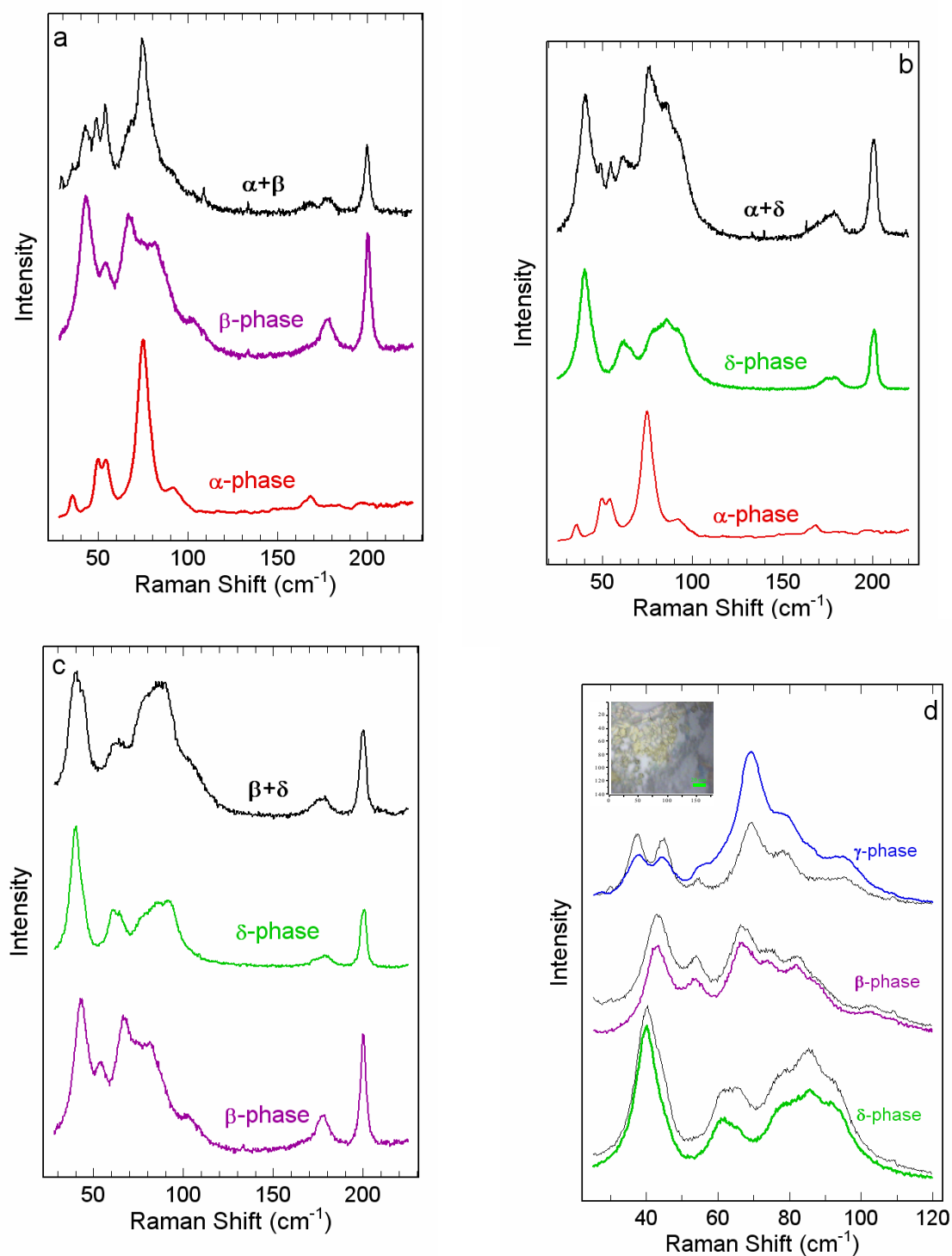
**Table S1** Data of the unit cell of the  $\beta$  phase as well as the refinement.

	$\beta$ phase	$\beta$ phase refined	Difference
a	15.1540	15.1801	0.1027
b	11.5710	11.6083	0.0163
c	8.0270	8.0638	0.0548
$\alpha$	90.00	90.00	0.000
$\beta$	111.64	111.55	0.886
$\gamma$	90.00	90.00	0.000
V	1308.308	1321.629	20.570

**Figure S3.** Anisotropy of the Raman spectra of a DB-TTF single crystal of the  $\alpha$ -phase in the low frequency region.



**Figure S4.** Some examples of Raman spectra for crystals with phase mixing: a), b) and c): Phase mixing ( $\alpha+\beta$ ,  $\alpha+\delta$ ,  $\beta+\delta$ ) occurring on crystal microdomains on scales below our spatial resolution ( $\approx 0.9 \mu\text{m}$ ); d) Phase mixing occurring on larger domains ( $\geq 1 \mu\text{m}$ ), individually probed by Raman microscopy of a single specimen (see picture in the inset). The specimen was obtained by drop casting a pure acetone solution on a Si/HMDS substrate. Colour spectra refer to the reference spectra of the pure phases.



## Theoretical calculations

In the QHLD method [Valle96] the Gibbs free energy of the crystal is computed as the free energy of an ensemble of phonons of frequency  $\nu_i$ :

$$G(p, T) = \Phi_0 + pV + \sum_i \frac{h\nu_i}{2} + k_B T \sum_i \ln \left[ 1 - \exp \left( -\frac{h\nu_i}{k_B T} \right) \right]$$

Here  $\Phi_0$  is the total potential energy of the crystal in its average structure (the electronic ground state energy),  $pV$  is the pressure-volume term,  $\sum_i h\nu_i/2$  is the zero-point energy, and the last term is the entropic contribution.

Given an initial lattice structure, one computes  $\Phi_0$  and its second derivatives with respect to the displacements of the molecular coordinates. The second derivatives form the dynamical matrix, which is numerically diagonalized to obtain the phonon frequencies  $\nu_i$  and the corresponding eigenvectors. The structure as a function of  $p$  and  $T$  is then determined self-consistently by minimizing  $G(p, T)$  with respect to lattice parameters, molecular positions and orientations. The total potential  $\Phi_0$  is made of *inter*- and *intra*-molecular terms,  $\Phi_{\text{inter}}$  and  $\Phi_{\text{intra}}$  respectively.

In the present treatment, molecules do vibrate but maintain their average geometry. The interactions are represented by  $\Phi_{\text{inter}}$ , expressed as a pairwise additive atom-atom potential (in the LJ's form) to which an electrostatic term is added. This term is expressed as a Coulomb interaction by means of charges residing on atoms. The Ewald's method is applied to accelerate the convergence of the Coulombic interactions [Signorini91]. *Ab-initio* methods are usually used to compute atomic charge distributions fitted on the molecular electrostatic potential (ESP charges [Gaussian03]) which are better suited than the Mulliken values, derived from molecular orbital coefficients. *Ab-initio* methods are often employed also for the input molecular geometry, although the experimental X-ray data can be used.

To compute the phonon frequencies one needs all second derivatives  $\partial^2 \Phi_0 / \partial Q_{ri} \partial Q_{sj}$  of the total potential with respect to all pairs of molecular coordinates  $Q_{ri}$  and  $Q_{sj}$ . Here  $r$  and  $s$  label molecules in the crystal, while  $i$  and  $j$  distinguish between molecular coordinates. An efficient way to evaluate the effect of the internal modes is the exciton-like model [Califano81], in which  $\Phi_{\text{intra}}$  corresponds to the harmonic potential of an isolated molecule. Thus the diagonal derivatives of  $\Phi_{\text{intra}}$  coincide with those of an isolated molecule, and correspond to the frequencies of the normal modes of the molecule, while off diagonal derivatives are zero. The coupling between the molecular coordinates is given solely by the intermolecular potential  $\Phi_{\text{inter}}$ , which is a function of the interatomic distances. Since the distances depend on the Cartesian coordinates  $X_{ra}$  of the atom  $a$ ,  $\Phi_{\text{inter}}$  second derivatives can be computed in terms of  $X_{ra}$ , and then converted to molecular coordinates  $Q_{ri}$ :

$$\frac{\partial^2 \Phi_{\text{inter}}}{\partial Q_{ri} \partial Q_{sj}} = \sum_{ab} \frac{\partial^2 \Phi_{\text{inter}}}{\partial X_{ra} \partial X_{sb}} \frac{\partial X_{ra}}{\partial Q_{ri}} \frac{\partial X_{sb}}{\partial Q_{sj}}$$

Here  $a$  and  $b$  label the Cartesian coordinates of the atoms in molecules  $r$  and  $s$ , and the matrix  $\partial X_{ra} / \partial Q_{ri}$  describes the Cartesian displacements which correspond to each molecular coordinate  $Q_{ri}$ .

The displacements corresponding to rigid translations and rotations of the molecules can be derived by simple geometric considerations [Califano81]. The displacements associated to the intramolecular degrees of freedom are the cartesian eigenvectors of the normal modes of the isolated molecule, which are usually computed with *ab-initio* methods.

***[References to be numbered]***

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