Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Synergic approach of X-ray powder diffraction and Raman spectroscopy for crystal structure determination of 2,3-thienoimide capped oligothiophenes.

C. Cappuccino[a], P. P. Mazzeo[b-c], T. Salzillo*[d†], E. Venuti[d], A. Giunchi[d], R. G. Della Valle[d], A. Brillante[d], C. Bettini[e], M. Melucci[e] and L. Maini*[a]

Supporting Information

1. **Data mining**
2. **Simulated spectra of quaterthiophene (T4)**
3. **Eigenvectors for syn-anti-syn and anti-anti-anti configurations**
4. **Rietveld refinement details for the C6-NT4N-B and C8-NT4N-B**

[†]Present address:*Institut de Ciéncia de Materials de Barcelona (CSIC),Campus de la UAB, 08193 Bellaterra (Spain)*

*Corresponding authors

E-mail address: tommaso.salzillo@unibo.it

E-mail address: l.maini@unibo.it

1. Data mining

The CSD v 5.38 (updated May 2017) (C. R. Groom, I. J. Bruno, M. P. Lightfoot, S. C. Ward, IUCr, T. R., T. M., van de S. J., van de S. J., W. P. A. and O. A. G., *Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater.*, 2016, **72**, 171–179) was searched for all oligothiophene compounds with free rotation between two oligothiophene rings. The search was restricted to organic compounds without disorder. 353 structure fulfilled the request with a total of 588 torsion angles. Only 48 torsion angles have values between -40° and 40° (see Figure S1)

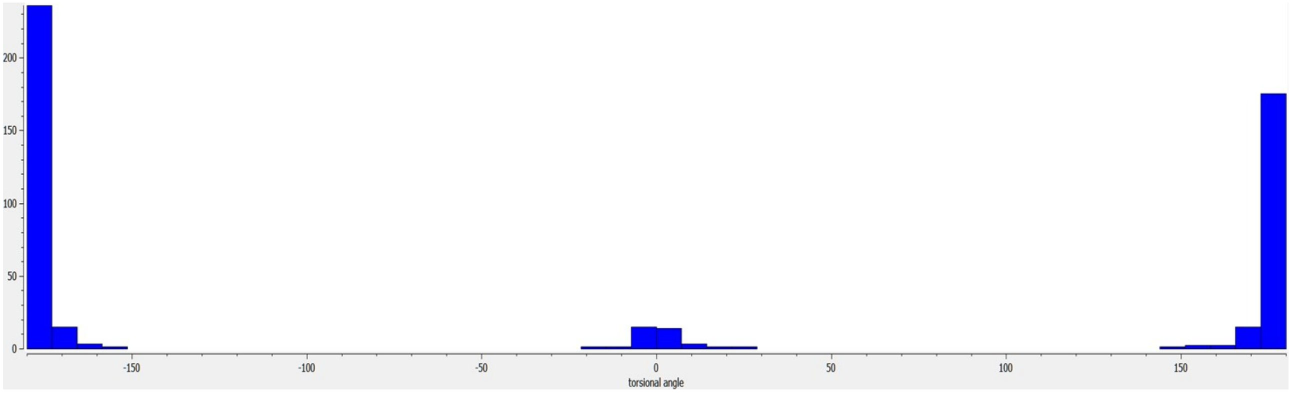

Figure S1 Results of the search on CSD.

2. Simulated Raman spectra of quaterthiophene (T4)

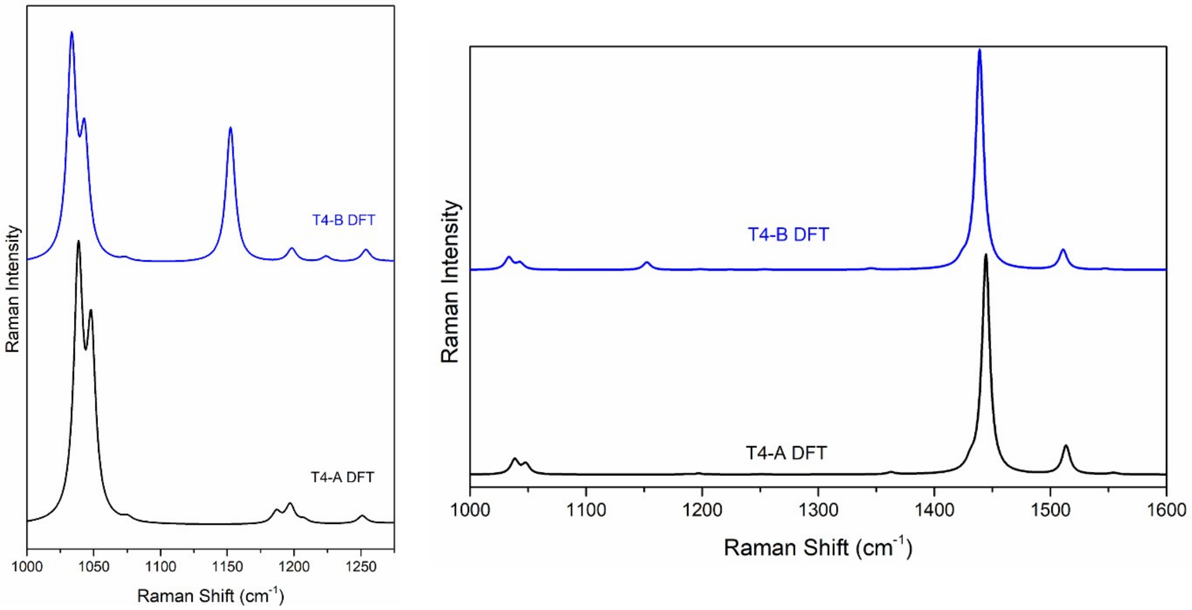

Figure S2 Simulated spectra of quaterthiophene (T4) in its anti-anti-anti and syn-anti-syn conformations.

3. Eigenvectors for *syn-anti-syn* and *anti-anti-anti* configurations

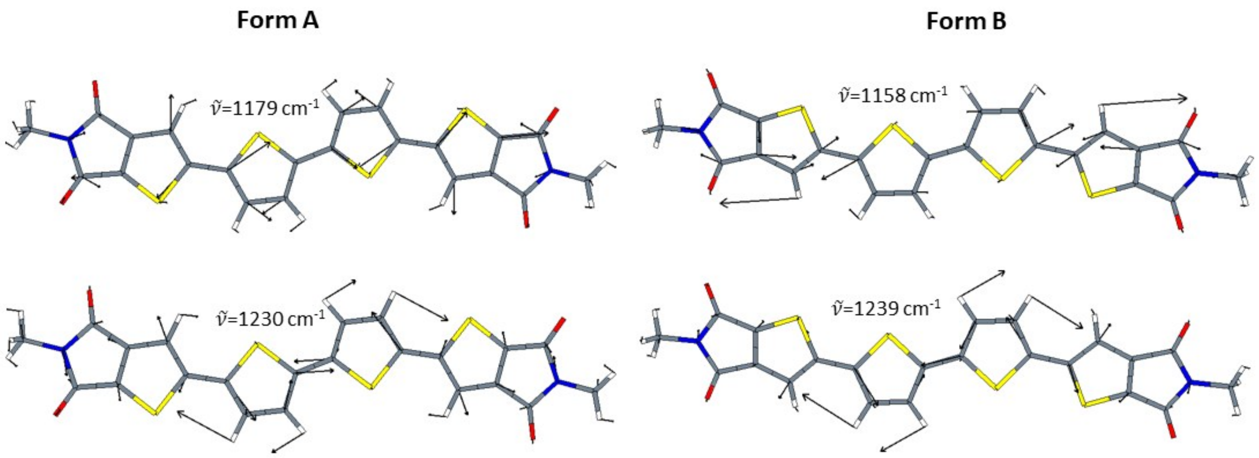

Figure S3 comparison of eigenvectors of the forms A and B.

4. Rietveld refinement details for the C6-NT4N-B and C8-NT4N-B

Considering the similarities between the two structures, the procedure described is valid for both molecules. The software TOPAS5 was used for structure determination in direct space. The best solution was chosen for a Rietveld refinement that was performed using the software TOPAS 5. A Chebyshev function and a pseudo Voigt (TCHZ type) were used to fit the background and the peak shape respectively. The pattern was indexed with a P-1 cell (C6-NT4N: a=4.914(6) Å; b=5.655(7) Å, c=28.95(3) Å, α=87.035(5)°, β=84.310(4)°, γ=85.513(4)°, Vol=797(2) Å^3; C8-NT4N: a=5.406(6) Å; b=5.135(5) Å, c=32.36(3) Å, α=101.877(3)°, β=91.550(3)°, γ=94.423(2)°, Vol=875.5(16) Å^3) whose volume corresponds to one molecule volume hence the asymmetric unit contains half molecule. Crystalline structure was solved with simulated annealing method; the z-matrix consist of half molecule modeled from single crystal structure of C6-NT4N form A (refcode LOTCOO), the bond distances and angles were optimized according to CSD statistics. To reduce the degrees of freedom, a dummy atom bonded to C1 carbon atom at the distance of 0.726 Å (corresponding to half-distance of a carbon-carbon single bond) was added. The dummy atom was forced on the inversion centre, keeping fixed the translational parameters and while the rotational degrees of freedom were refined. In the Rietveld refinement step only the torsion angle of S2-C5-C4-S1 and the torsion angles of the alkyl chain were allowed to rotate without restrictions and the structures autonomously assumed an almost perfect planar configuration. In the pictures below are shown the Rietveld analysis plots for the two samples (first: C6-NT4N, second: C8-NT4N).

During the refinement, couple of peaks are not described by the cell, which suggest the presence of a polymorphic impurity.

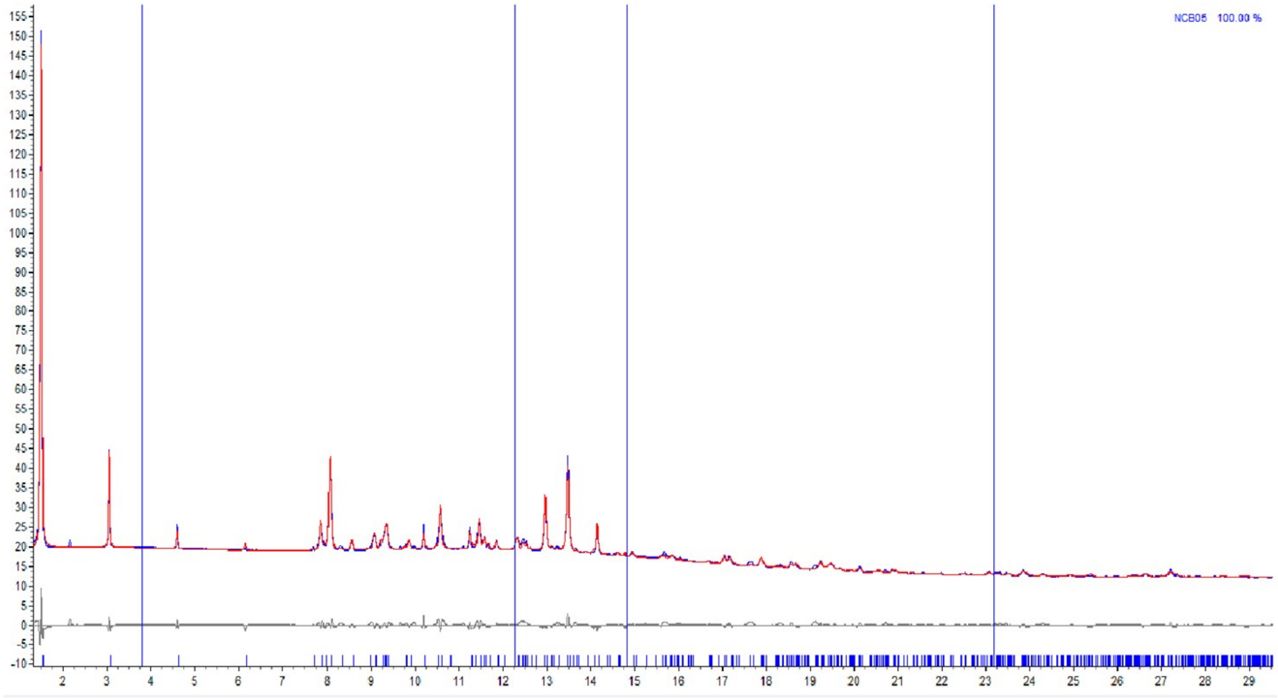

Figure S4 Rietveld refinement of C6-NT4N. Red line is the calculated diffractogram, blue line is the observed diffractogram and grey line is the difference plot.

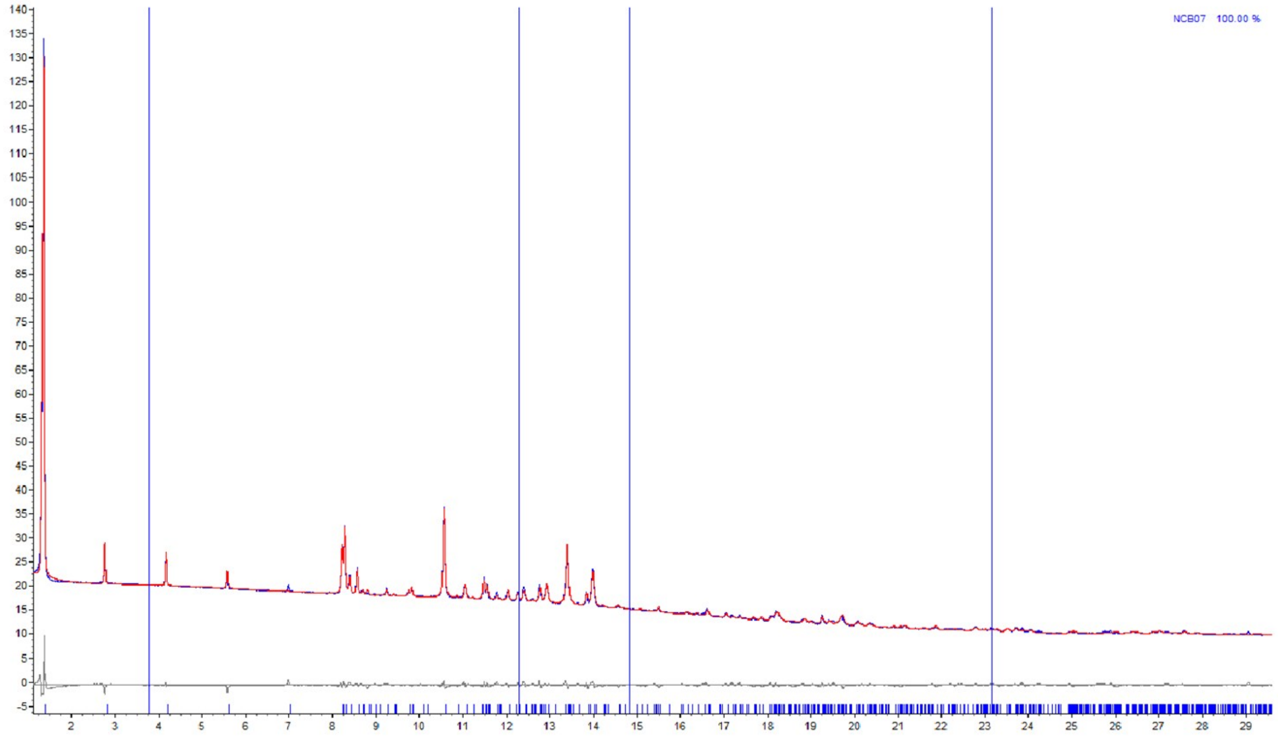

Figure S5 Rietveld refinement of C8-NT4N. Red line is the calculated diffractogram, blue line is the observed diffractogram and grey line is the difference plot.