Supporting Information

Photophysical properties and excited state dynamics of 4,7-dithien-2-yl-2,1,3-benzothiadiazole

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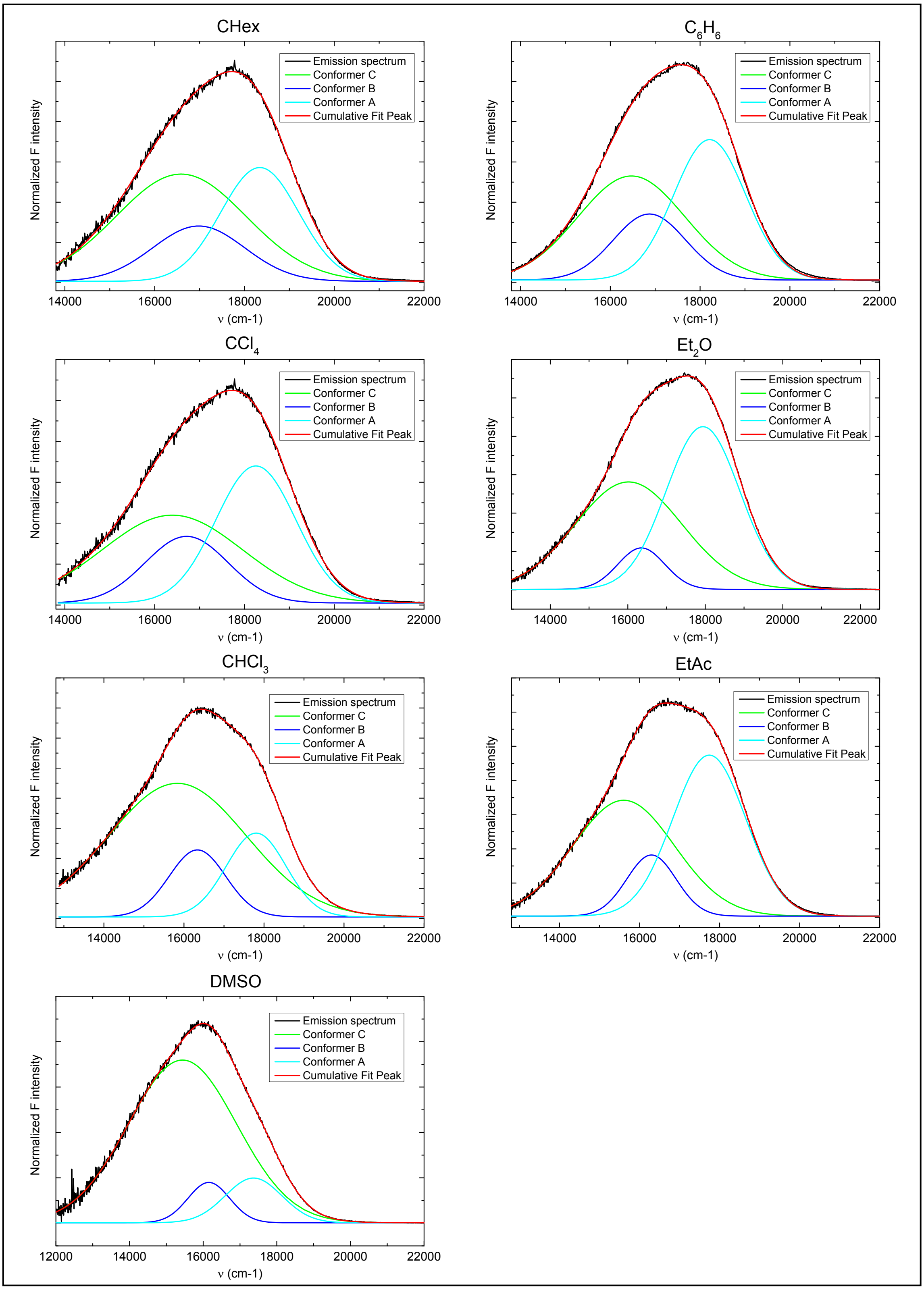
A



B

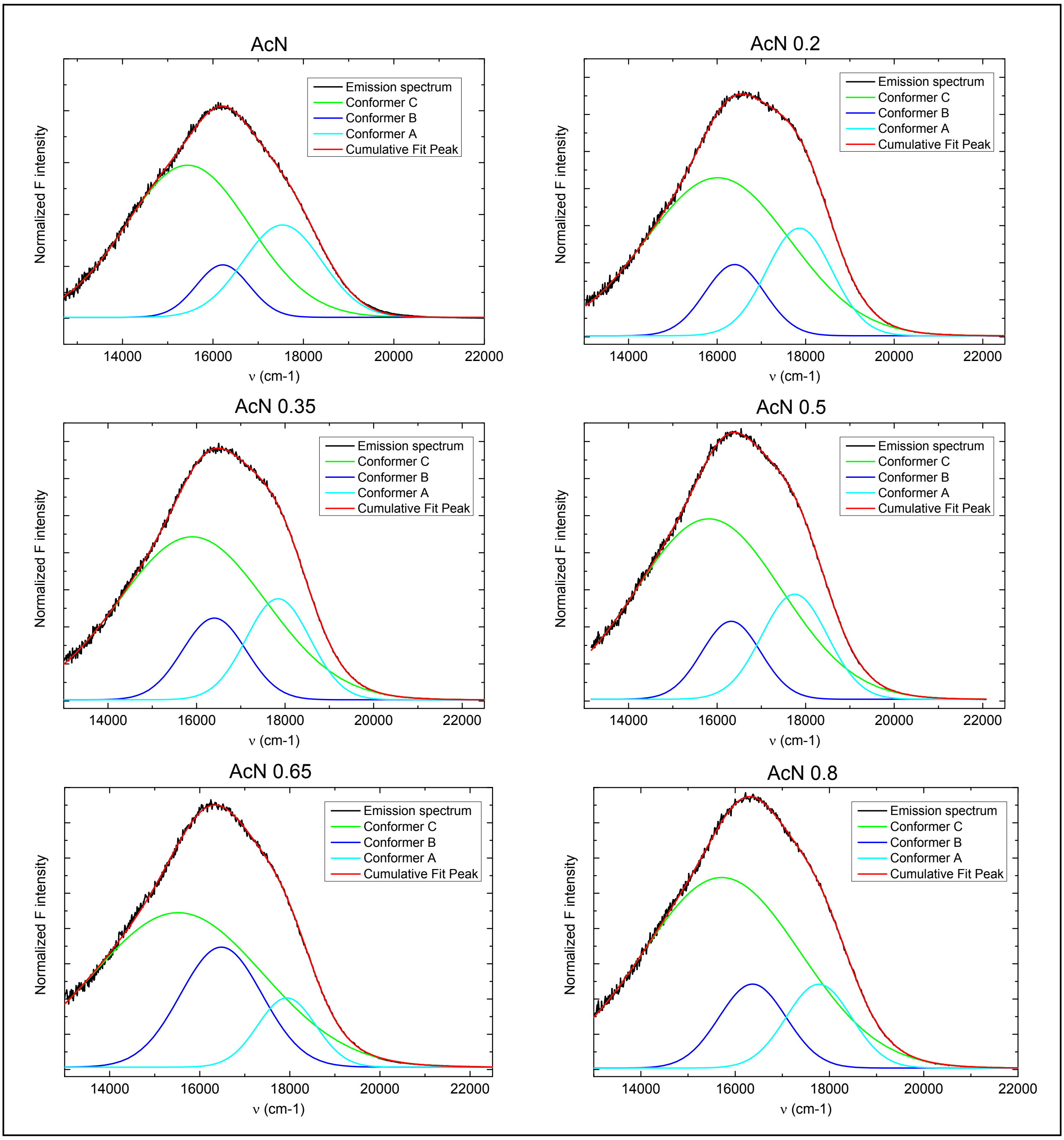
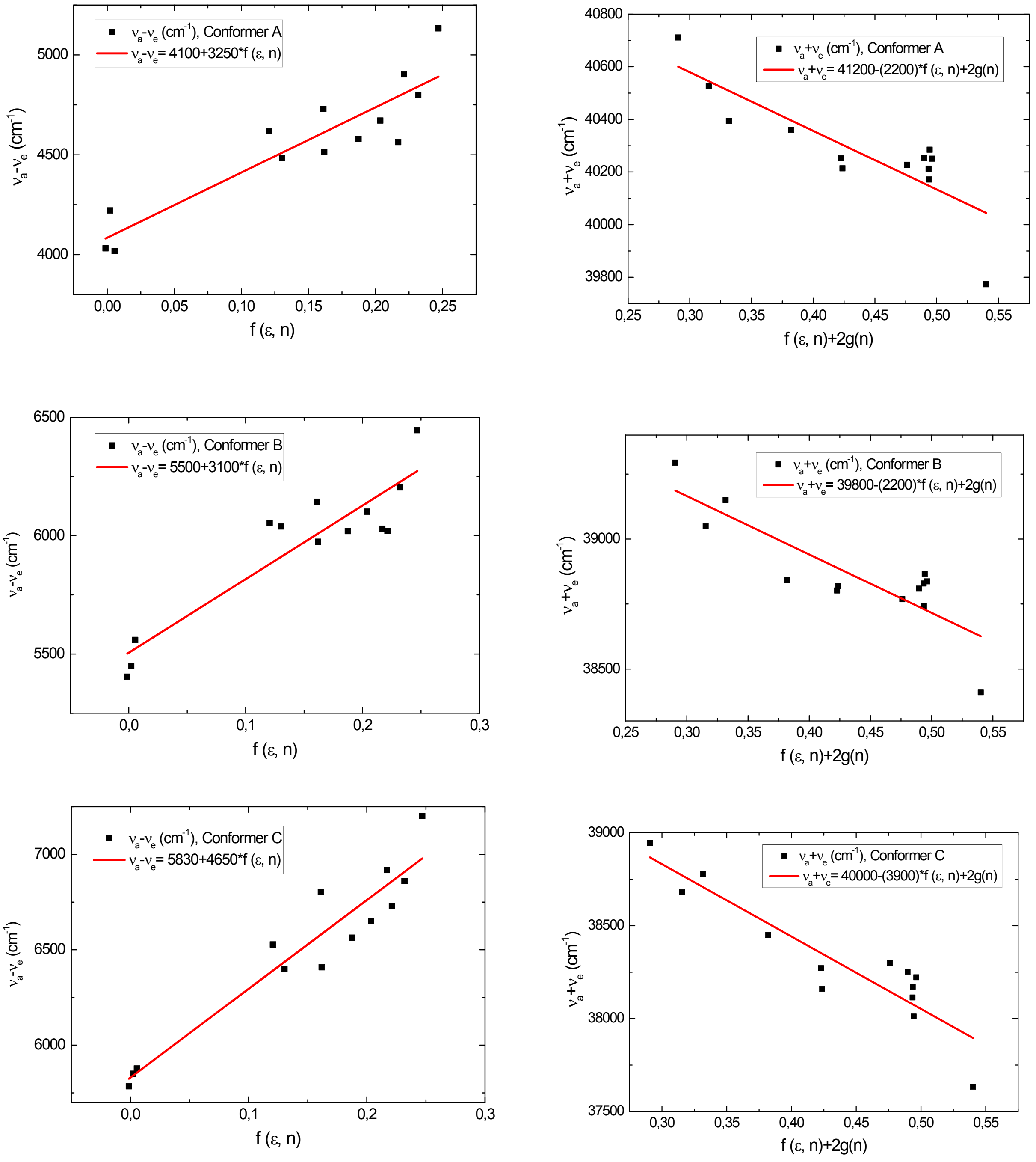


Figure S1 Peaks deconvolution of fluorescence spectra of DTB in organic solvents (**A**) and in AcN/Benzene mixtures (**B**). Gaussian functions have been utilized after converting the abscissa scale into wavenumbers and correcting fluorescence intensity according to the procedure reported in Ref.1.



m1			
Conformer	**A**	**B**	**C**
Intercept	4100 ± 75	5500 ± 70	5830 ± 75
Slope	3250 ± 450	3100 ± 400	4650 ± 450
m2			
Conformer	**A**	**B**	**C**
Intercept	41200 ± 200	39800 ± 200	40000 ± 200
Slope	2200 ± 400	2200 ± 400	3900 ± 500

Figure S2 Plots of Stokes' shift and of the sum of absorption and emission maxima (in cm^{-1}) as a function of the solvent polarity scale $g_{BK}(n)$ and $f_{BK}(\varepsilon, n)$ for all the DTB conformers dissolved in different solvents and in acetonitrile:benzene binary mixtures. Through the linear fit of the data the parameters m_1 and m_2 (representing the straight line slopes) which allow to estimate the dipole moments of ground and excited states (μ_g and μ_e) have been obtained.

Absolute Errors Evaluation

From Kawski equations:

$$\mu_g = \frac{m_2 - m_1}{2}\left(\frac{hca^3}{2m_1}\right)^{\frac{1}{2}} \qquad \mu_e = \frac{m_2 + m_1}{2}\left(\frac{hca^3}{2m_1}\right)^{\frac{1}{2}}$$

we derive the absolute error:

$$\Delta\mu = \left(\frac{hca^3}{2\sqrt{2}}\right)^{\frac{1}{2}} \sqrt{\left(\frac{1}{2}m_1^{-\frac{3}{2}}m_2 + \frac{1}{2}m_1^{-\frac{1}{2}}\right)^2 \Delta m_1^2 + \left(m_1^{-\frac{1}{2}}\right)^2 \Delta m_2^2}$$

Δm’s are derived from the fitting procedure (see Figure S2).

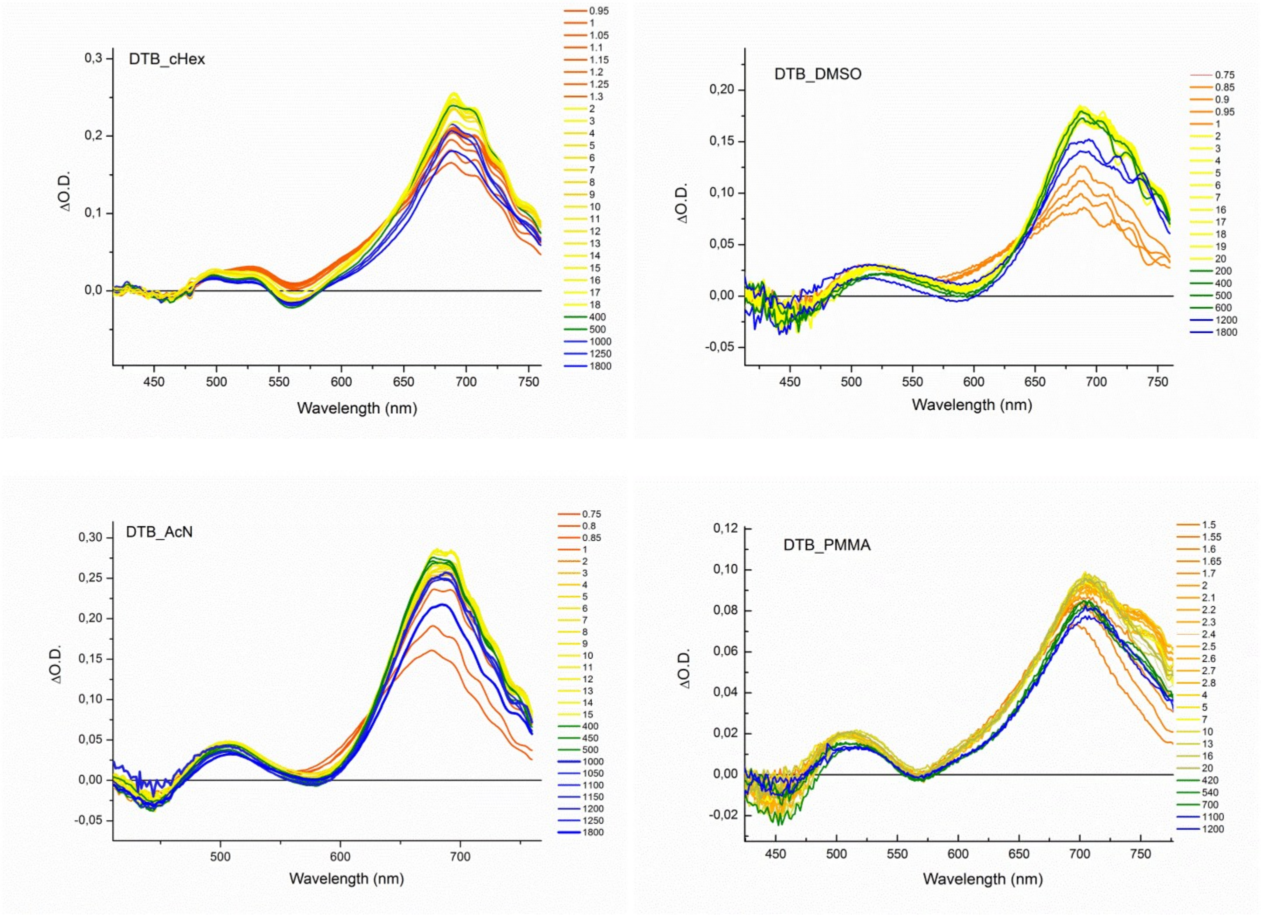


Figure S3 A set of transient absorption spectra of DTB in c-hex, AcN, DMSO and PMMA at selected significant delay times (picoseconds).

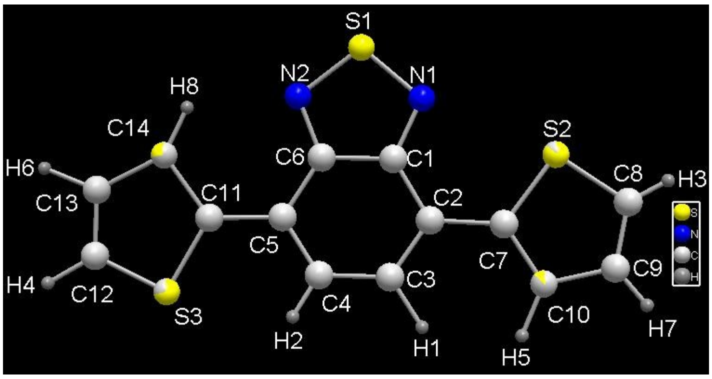


Figure S4 Definition of the atoms of DTB as utilized in the main text, in Tab. S1, S2, S5 and S6.

	Experimental	Conformer A	Conformer B	Conformer C
S_1N_1	1.610	1.611	1.612	1.612
S_1N_2	1.607	1.611	1.612	1.613
N_1C_1	1.340	1.338	1.337	1.338
C_1C_6	1.436	1.453	1.450	1.448
C_1C_2	1.434	1.435	1.435	1.430
C_2C_3	1.374	1.382	1.383	1.383
C_3C_4	1.410	1.407	1.407	1.407
C_2C_7	1.460	1.457	1.457	1.458
S_2C_7	1.719	1.746	1.741	1.742
S_2C_8	1.695	1.715	1.712	1.712
C_7C_{10}	1.411	1.377	1.380	1.380
C_8C_9	1.333	1.364	1.367	1.367
C_9C_{10}	1.425	1.416	1.411	1.411
N_2C_6	1.348	1.338	1.434	1.430
C_5C_6	1.422	1.435	1.434	1.430
C_4C_5	1.376	1.382	1.383	1.383
C_5C_{11}	1.469	1.456	1.458	1.458
S_3C_{11}	1.699	1.746	1.746	1.742
S_3C_{12}	1.630	1.714	1.715	1.712
$C_{12}C_{13}$	1.327	1.365	1.365	1.367
$C_{13}C_{14}$	1.533	1.416	1. 416	1. 411
$C_{14}C_{11}$	1.559	1.378	1. 380	1. 380
$\vec{\mu}\,(D)$		0.280	1.050	1.810
$\Upsilon C_1C_2C_7C_{10}$		7.048	165.729 (2.331)	167.668

Table S1 Experimental and calculated interatomic distances (Å), dipole moments $|\vec{\mu}|$ and torsional angle ($\Upsilon C_1C_2C_7C_{10}$) of DTB conformers calculated for the ground state.

	Conformer A	Conformer B	Conformer C
S_1N_1	1.658 (0.047)	1.660 (0.048)	1.661 (0.049)
S_1N_2	1.658 (0.047)	1.659 (0.047)	1.661 (0.048)
N_1C_1	1.349 (0.011)	1.347 (0.010)	1.347 (0.009)
C_1C_6	1.425 (-0.028)	1.422 (-0.028)	1.419 (-0.029)
C_1C_2	1.434 (0.001)	1.428 (-0.007)	1.428 (-0.002)
C_2C_3	1.419 (0.037)	1.420 (0.037)	1.421 (0.038)
C_3C_4	1.370 (-0.037)	1.370 (-0.037)	1.373 (-0.034)
C_2C_7	1.429 (-0.028)	1.429 (-0.028)	1.421 (-0.037)
S_2C_7	1.760 (0.014)	1.754 (0.013)	1.754 (0.012)
S_2C_8	1.706 (-0.09)	1.705 (-0.07)	1.705 (-0.007)
C_7C_{10}	1.396 (0.019)	1.401 (0.021)	1.400 (0.020)
C_8C_9	1.376 (0.012)	1.380 (0.013)	1.380 (0.013)
C_9C_{10}	1.401 (-0.015)	1.395 (-0.016)	1.395 (-0.016)
N_2C_6	1.349 (0.011)	1.349 (0.010)	1.346 (0.008)
C_5C_6	1.434 (-0.001)	1.434 (0.001)	1.428 (-0.002)
C_4C_5	1.419 (0.037)	1.420 (0.037)	1.421 (0.038)
C_5C_{11}	1.429 (-0.027)	1.429 (-0.029)	1.429 (-0.029)
S_3C_{11}	1.760 (0.014)	1.760 (0.014)	1.754 (0.012)
S_3C_{12}	1.706 (-0.008)	1.707 (-0.008)	1.705 (-0.007)
$C_{12}C_{13}$	1.376 (0.011)	1.376 (0.011)	1.380 (0.013)
$C_{13}C_{14}$	1.401 (-0.015)	1.402 (-0.014)	1.395 (-0.016)
$C_{14}C_{11}$	1.395 (0.017)	1.395 (0.015)	1.400 (0.020)
$\Upsilon C_1C_2C_7C_{10}$	0.137	179.91 (0.022)	179.97

Table S2 Interatomic distances (Å), variation respect to ground state values (reported in the brackets) and torsional angle ($\Upsilon C_1C_2C_7C_{10}$) of DTB conformers calculated for the S_1 state.

Crystal Structure Determination of 4,7-dithien-2-yl-2,1,3-benzothiadiazole

The molecular and crystal structure of the compound 4,7-dithien-2-yl-2,1,3-benzothiadiazole has been determined by single crystal X-ray diffraction analysis. The structure has been deposited at the Cambridge Crystallographic Data Centre with deposition number CCDC 1503592.

Experimental

Since the sample was defined very sensible to the visible light, preliminary powder X-ray diffraction (XRD) data collections were carried out in order to evaluate the possible photodegradation of the title compound under the experimental conditions. XRD data were collected by using a PANalytical X'PERT PRO diffractometer, using CuKα radiation (λ = 1.54178 Å), equipped with a RTMS (real-time multiple strip) detector. A number of 10 subsequent scans were carried out over the 7° ≤ 2θ ≤ 60° angular region, with a step size of 0.008° 2θ and an accumulation time of 100 s/step. Since all the collected scans were perfectly equivalent it was possible to conclude that the title compound is stable under the X-ray beam and the laboratory light. Single crystal X-ray diffraction analysis was performed using a Nonius KappaCCD diffractometer equipped with a CCD detector and MoKα radiation (λ = 0.71069Å). The DENZO-SMN

[2] package was used for the refinement of the unit cell parameters and data reduction [3]. During the single crystal X-ray diffraction analysis six sets of frames were collected: the first set (10 frames) was used for initial cell determination. An orthorhombic unit cell was readily found and used for the data reduction. The same unit cell was confirmed on other crystals and for the final data collection the specimen with the best scattering behavior was selected. All the reflections collected in the five sets of frames were finally used for the refinement of the unit cell parameters. More details concerning the data collection were reported in table S3, whereas refined unit cell parameters and data reduction information are given in table S4. From the same table is possible to see that the data collection was confined in the theta range 1-30°, with a resolution, in *d* spacing, between 20 and 0.71 Å.

Crystal Structure Determination

For the crystal structure determination of the title compound, the extracted diffraction intensities were introduced in the direct methods program SIR-2004 [4]. According to the orthorhombic set reported in table S3, the analysis of the systematic absence suggested the *Pcab* as the possible space group. Although re-labeling of some atoms was necessary, a structural model was readily found using the ideal chemical formula reported in table S4. It must be pointed out that the structural model obtained by direct methods seemed to indicate different orientations for the thiophene groups (Figure S5). This feature was taken into account during the refinement of the crystal structure (see following section).

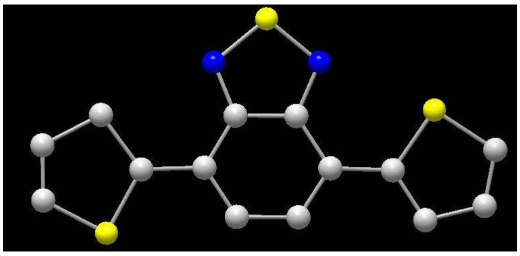


Figure S5 Molecular structure of the title compound as obtained by direct methods. Atoms: C (gray), S (yellow), N (blue).

Cristal Structure Refinement and Description of the Structure

In the early stage of the refinement, the inspection of the model of the title compound revealed that the geometry of the thiophene rings deviates from the ideal one. In particular, the S-C bond distances were found to be slightly but significantly shorter than that expected (1.73 Å), indicating a possible 180° rotational disorder of the thiophene rings. Such a behavior has already been observed in other similar molecules [5] and was taken into account in the course of the refinement. In particular, the disorder was accounted for by the introduction two carbon atoms (i.e. S2C and S3C, constrained to have the same position and displacement parameters of S2 and S3, respectively) and two sulfur atoms (i.e. C10S and C14S, constrained to have the same position and displacement parameters of C10 and C14, respectively). Free variables were used for the occupancies of the sulfur atoms S2 and S3 and the carbon atoms C10 and C14. The values of the free variables were refined constraining to 1 the sum of the occupancy of the atoms occupying the same position (e.g. S3 and SC3) and constraining sulphur and carbon atoms related by the 180° rotation of the thiophene rings to have the same occupancy (e.g. C14 and S3). This refinement strategy produces a dramatic decrease of the discrepancy factors. The refined occupancy values are reported in table S5. A careful inspection of the Fourier map allowed us to localize the missing hydrogen atoms and complete the structural model. The positions of hydrogen atoms were kept fixed during structure refinement with U_{iso} = 0.1 also kept fixed. Moreover in case of H5 and H8 the occupancies were fixed to the same value obtained for C10 and C14, respectively. Final refined atomic coordinates and displacement parameters are listed in table S5, selected bond lengths in table S6. The crystal structure refinement was satisfactorily completed in the *Pcab* space group whit a residual R factor of 5.1% for 2263 unique whit Fo > 4σ (Fo) and 174 parameters; more details concerning the crystal structure refinement are in table S4. The refined molecular structure of the title compound is shown in Figure S4. The packing of the molecules is shown in Figure S6.

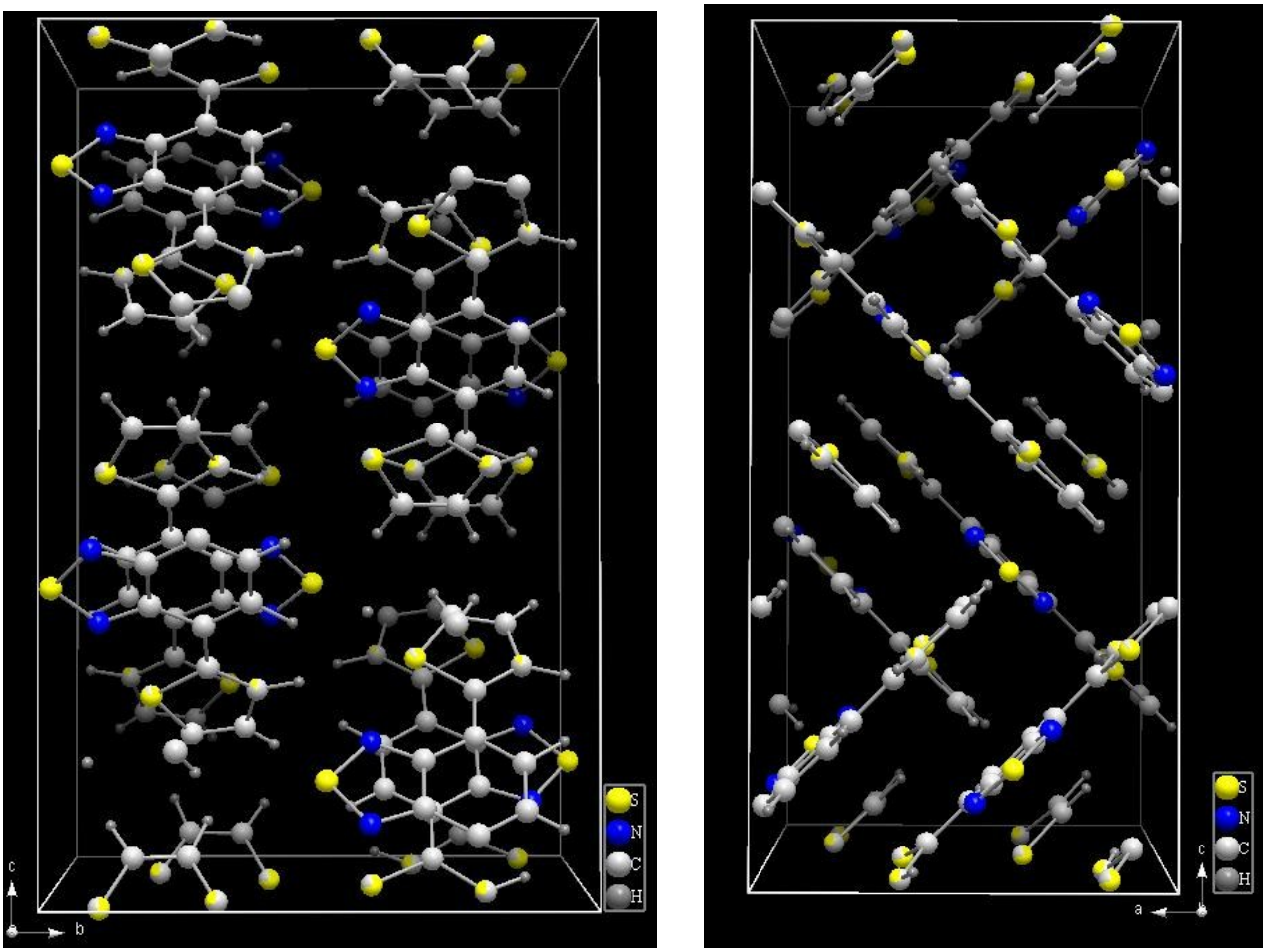


Figure S6 Packing of the molecules as viewed along a (left) and *b* (right) crystallographic directions. The diffraction pattern of DTB powder in XY format it is furnished in a separate file.

N° of images: Cell determination	10 (phi rotation 2°)
N° of images: Data collection	91 (phi rotation 2°) 81 (omega rotation 2°)
Exposure time: Cell determination	20 sec
Exposure time: Data collection	600 sec
Crystal to detector distance	25mm

Table S3 Data collection parameters.

Sample name	4,7-dithien-2-yl-2,1,3-benzothiadiazole
Composition	$C_{112}N_{16}S_{24}H_{64}$
Crystal size (mm)	0.3 × 0.3 × 0.45
Data collection temperature	20°C
***a* (Å)**	9.969(1)
***b* (Å)**	12.775(1)
***c* (Å)**	20.279(1)
V(Å^3)	2582.6(1)
Space group	Pcab
Maximum 2θ	60.2°
Index range	$-13 \leq h \leq 14$ $-18 \leq k \leq 16$ $-27 \leq l \leq 28$
Measured reflections	24242
Unique reflections	3766
Observed reflection > 4σ	2263
Rint(%)	5.0
R1(%)	5.1
No. of parameters	175
Largest diffraction peak and hole (e/Å^3)	0.34-0.33
$R1 = \Sigma \, \| \|Fo\| - \|Fc\| \| / \Sigma \|Fo\|$	

Table S4 Crystal dimensions, unit cell and crystal structure refinement parameters.

Atom	X	Y	Z	Occupancy	U. eq. or U_{iso}*
S1	0.88485(9)	0.01349(6)	0.35975(5)	1.0	0.0731(3)
S2	0.60145(8)	0.18260(6)	0.22774(4)	0.862(4)	0.0547(3)
S2C	0.60145(8)	0.18260(6)	0.22774(4)	0.138(4)	0.0547(3)
S3	1.1543(1)	0.4014(1)	0.49318(7)	0.717(4)	0.0891(6)
S3C	1.1543(1)	0.4014(1)	0.49318(7)	0.283(4)	0.0891(6)
N1	0.7936(2)	0.0947(1)	0.3189(1)	1.0	0.0579(5)
N2	0.9742(2)	0.0916(2)	0.4037(1)	1.0	0.0643(6)
C1	0.8310(2)	0.1907(2)	0.3389(1)	1.0	0.0455(6)
C2	0.7755(2)	0.2866(2)	0.3145(1)	1.0	0.0448(6)
C3	0.8270(3)	0.3756(2)	0.3429(2)	1.0	0.0578(7)
C4	0.9287(3)	0.3735(2)	0.3913(2)	1.0	0.0607(7)
C5	0.9861(3)	0.2835(2)	0.4156(1)	1.0	0.0517(6)
C6	0.9344(3)	0.1892(2)	0.3883(1)	1.0	0.0494(6)
C7	0.6726(3)	0.2914(2)	0.2633(1)	1.0	0.0441(6)
C8	0.4995(3)	0.2557(2)	0.1792(2)	1.0	0.0618(7)
C9	0.5172(3)	0.3579(3)	0.1880(2)	1.0	0.0648(8)
C10	0.6164(3)	0.3831(2)	0.2361(1)	0.862(4)	0.0787(7)
C10S	0.6164(3)	0.3831(2)	0.2361(1)	0.138(4)	0.0787(7)
C11	1.0912(3)	0.2855(3)	0.4663(1)	1.0	0.0608(8)
C12	1.2588(4)	0.3464(5)	0.5443(2)	1.0	0.0980(15)
C13	1.2553(4)	0.2425(5)	0.5459(2)	1.0	0.0910(12)
C14	1.1535(2)	0.1880(2)	0.50101(7)	0.717(4)	0.0827(7)
C14S	1.1535(2)	0.1880(2)	0.50101(7)	0.283(4)	0.0827(7)
H1	0.7850	0.4517	0.3190	1.0	0.1*
H2	0.9599	0.4385	0.4108	1.0	0.1*
H3	0.4438	0.2223	0.1526	1.0	0.1*
H4	1.3206	0.3902	0.5785	1.0	0.1*
H5	0.6554	0.4623	0.2460	0.862	0.1*
H6	1.3312	0.2090	0.5836	1.0	0.1*
H7	0.4758	0.4139	0.1654	1.0	0.1*
H8	1.1207	0.1122	0.4861	0.717	0.1*

Table S5 Atomic coordinates and displacement parameters obtained for DTB.

S1-N1 = 1.610 (2)
S1-N2 = 1.607 (3)
S2-C7 = 1.719 (3)
S2-C8 = 1.695 (3)
S3-C11 = 1.699 (4)
S3-C12 = 1.630 (5)
N2-C6 = 1.348 (3)
N1-C1 = 1.340 (3)

C1-C2 = 1.434 (3)
C2-C3 = 1.374 (4)
C2-C7 = 1.460 (4)
C3-C4 = 1.410 (4)
C4-C5 = 1.376 (4)
C5-C6 = 1.422 (4)
C5-C11 = 1.469 (4)
C6-C1 = 1.436 (4)

C7-C10 = 1.411 (4)
C8-C9 = 1.333 (5)
C9-C10 = 1.425 (4)
C11-C14 = 1.559 (4)
C12-C13 = 1.327 (7)
C13-C14 = 1.533 (5)

Table S6 Selected bond distances (Å) (e.s.d.'s in parentheses).

References

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