Supporting Information

Crystals of 4,7-di-2-thienyl-2,1,3-benzothiadiazole and Its Derivative with Terminal Trimethylsilyl Substituents: Synthesis, Growth, Structure and Optical-Fluorescent Properties

Valery A. Postnikov[1,2*], Georgy A. Yurasik[1,2], Artem A. Kulishov[1,2], Timofei A. Sorokin[1,2], Maria S. Lyasnikova[1], Nataliya I. Sorokina[1], Maxim S. Skorotetcky[2], Vlada V. Popova[2], Lev L. Levkov[2], Oleg V. Borshchev[2], Evgeniya A. Svidchenko[2], Nikolay M. Surin[2] and Sergey A. Ponomarenko[2*]

[1] FSRC "Crystallography and Photonics" of Russian Academy of Sciences, Shubnikov Institute of Crystallography, Moscow 119333, Russia;

[2] Enikolopov Institute of Synthetic Polymer Materials of Russian Academy of Sciences, Moscow 117393, Russia

1. DSC

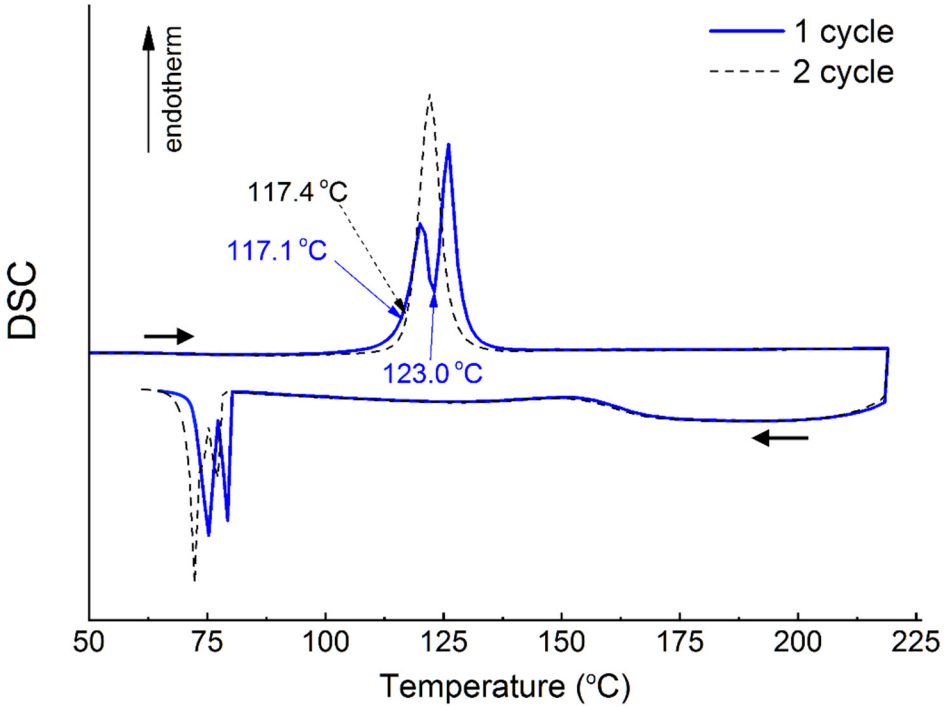

Figure S1. DSC curves characterizing the melting and crystallization of T-BDT sample in two consecutive heating and cooling cycles.

2. Crystal growth

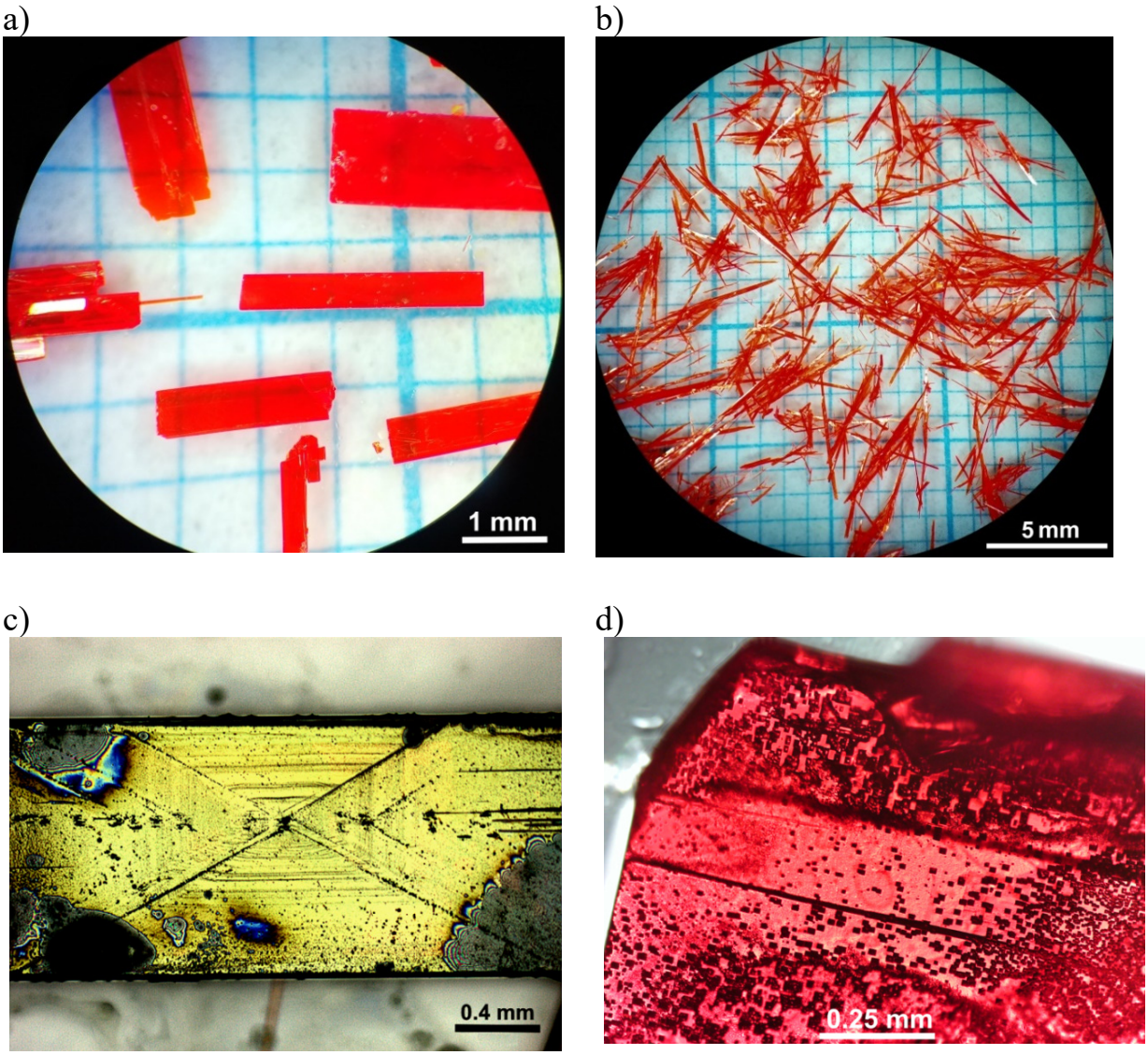

Figure S2. Crystals of T-BTD: (a) crystals grown from a solution in hexane with a small addition of THF (growth period 30 days); (b) crystals grown from a solution in acetone (growth period 7 days); (c), (d) images of the surface of the developed face of crystals grown from solution in hexane.

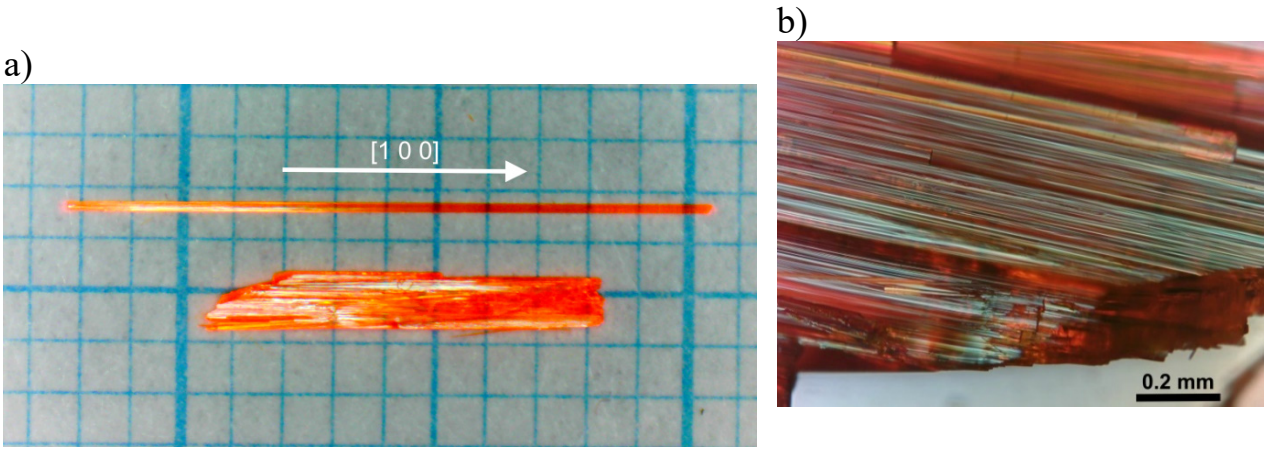

Figure S3. Crystals of TMS-T-BTD grown from a hexane solution (a) and enlarged image of the bottom crystal surface (b).

3. Crystal structure

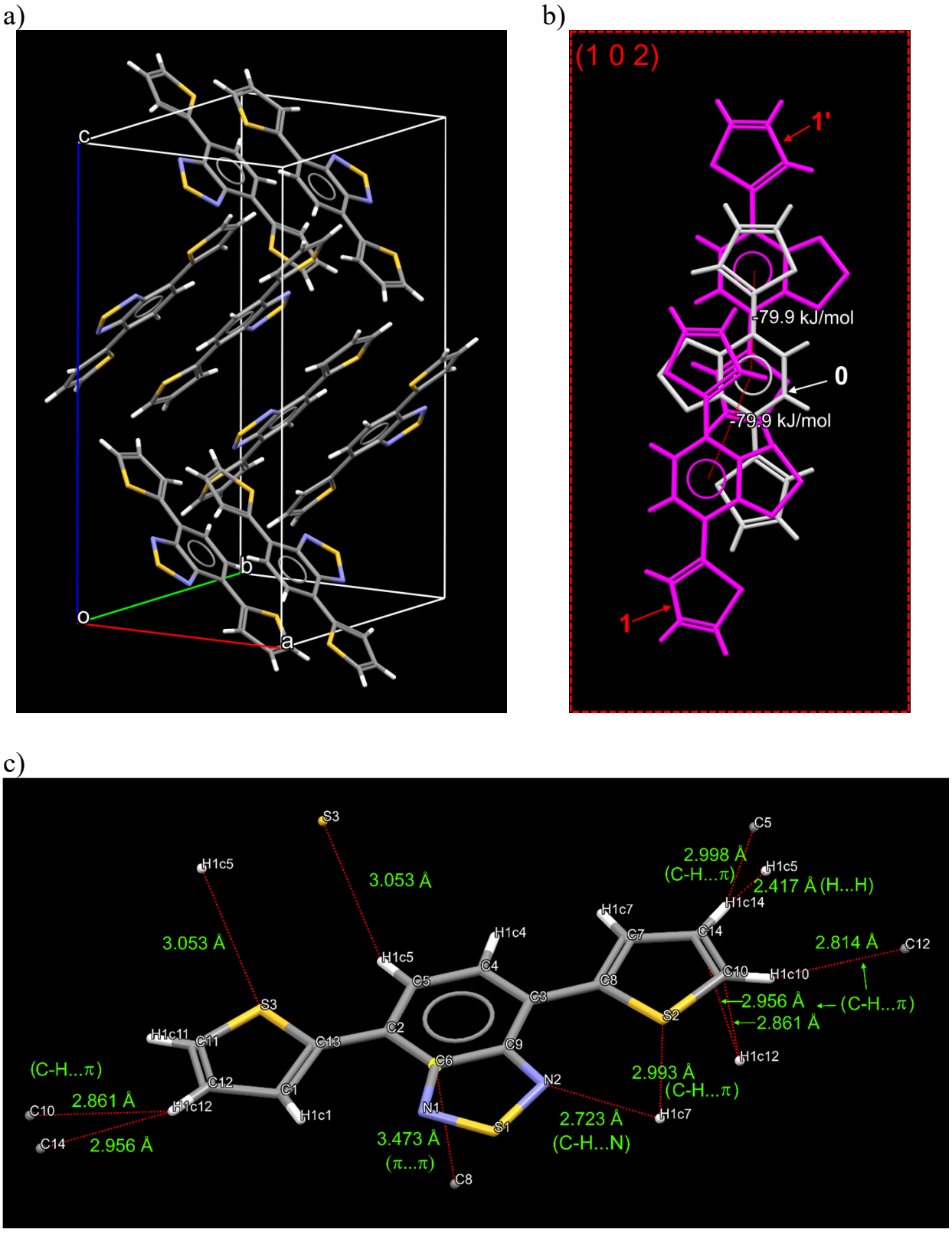

Figure S4. Crystal structure of T-BTD at 293 K: (a) View of unit cell; (b) projection of three neighboring molecules from a close-packed row [1 0 0] onto the (1 0 2) plane; (c) scheme of shortest contacts of a molecule with atoms of nearest neighbours.

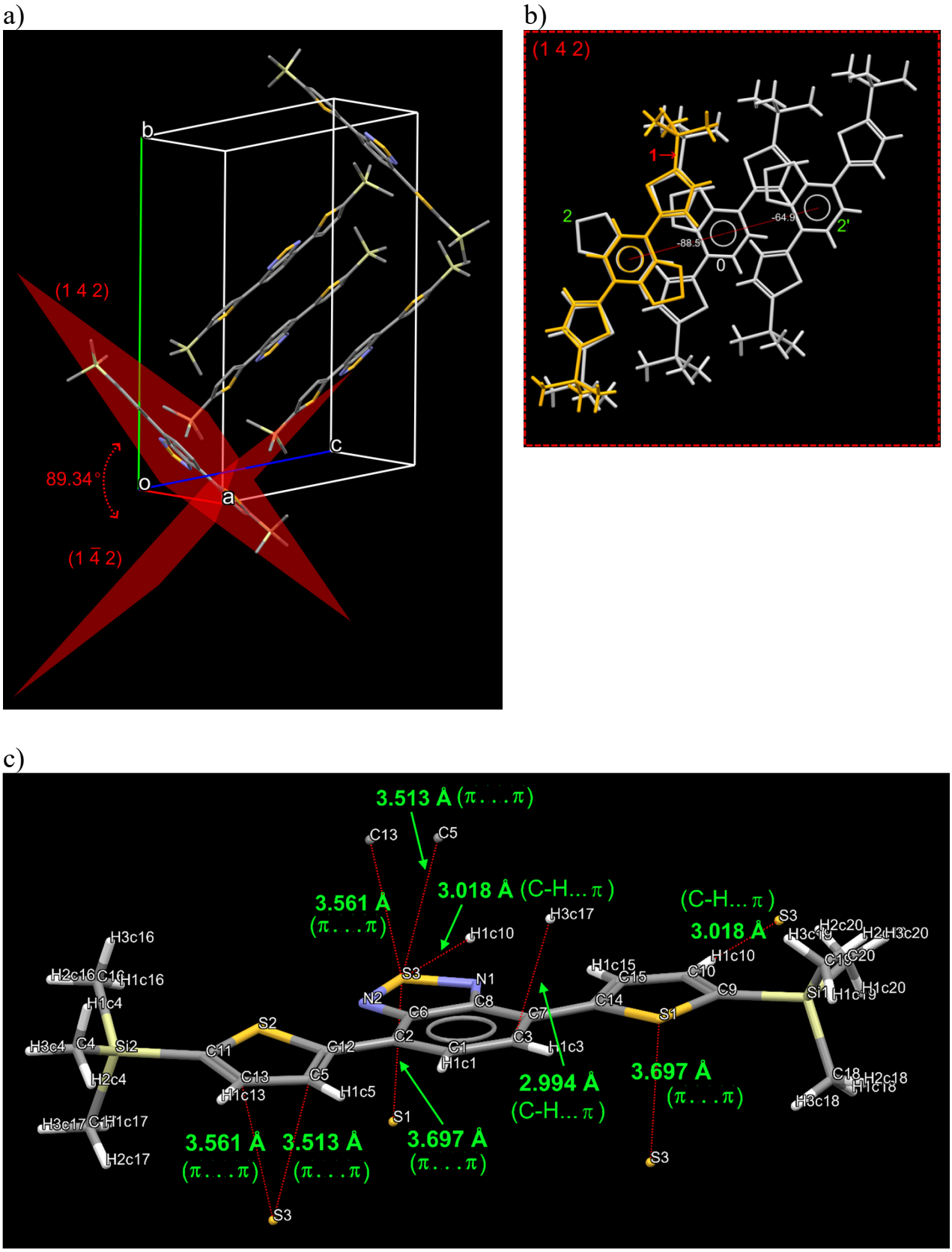

Figure S5. Crystal structure of TMS-T-BTD at 293 K: (a) View of unit cell; (b) projection of for neighboring molecules onto the (1 4 2) plane; (c) scheme of shortest contacts of a molecule with atoms of nearest neighbours.

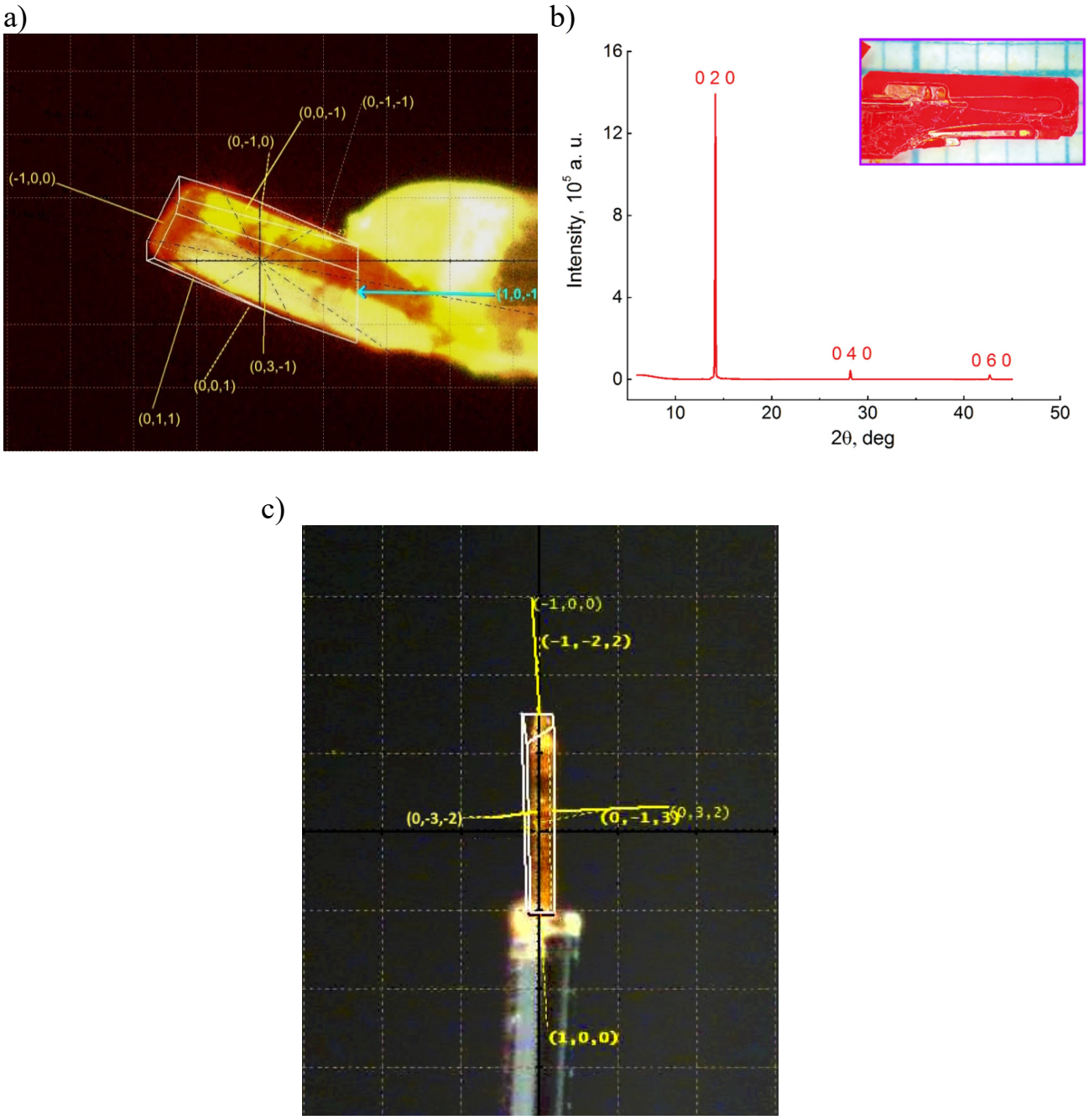

Figure S6. (a) Photographic image of T-BTD single crystal with face indices determined in the X-ray diffraction experiment; (b) XRD pattern obtained by reflection from a developed face of a flat T-BTD crystal (photo in the insert); (c) Photographic image of TMS-T-BTD single crystal with face indices determined in the X-ray diffraction experiment.

4. Absorption and fluorescent properties

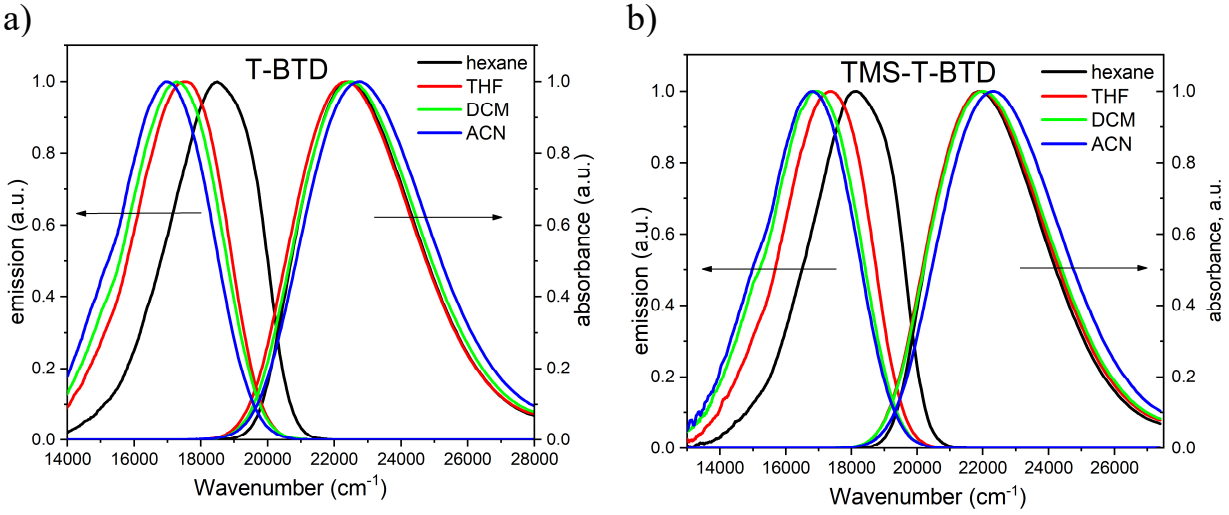

Figure S7. Normalized absorption (right axis) and fluorescence (left axis) spectra of solutions of T-BTD (a) and TMS-T-BTD (b) in hexane, THF, dichloromethane (DCM), and acetonitrile (ACN). Excitation was carried out at the maximum of the long-wave absorption band.

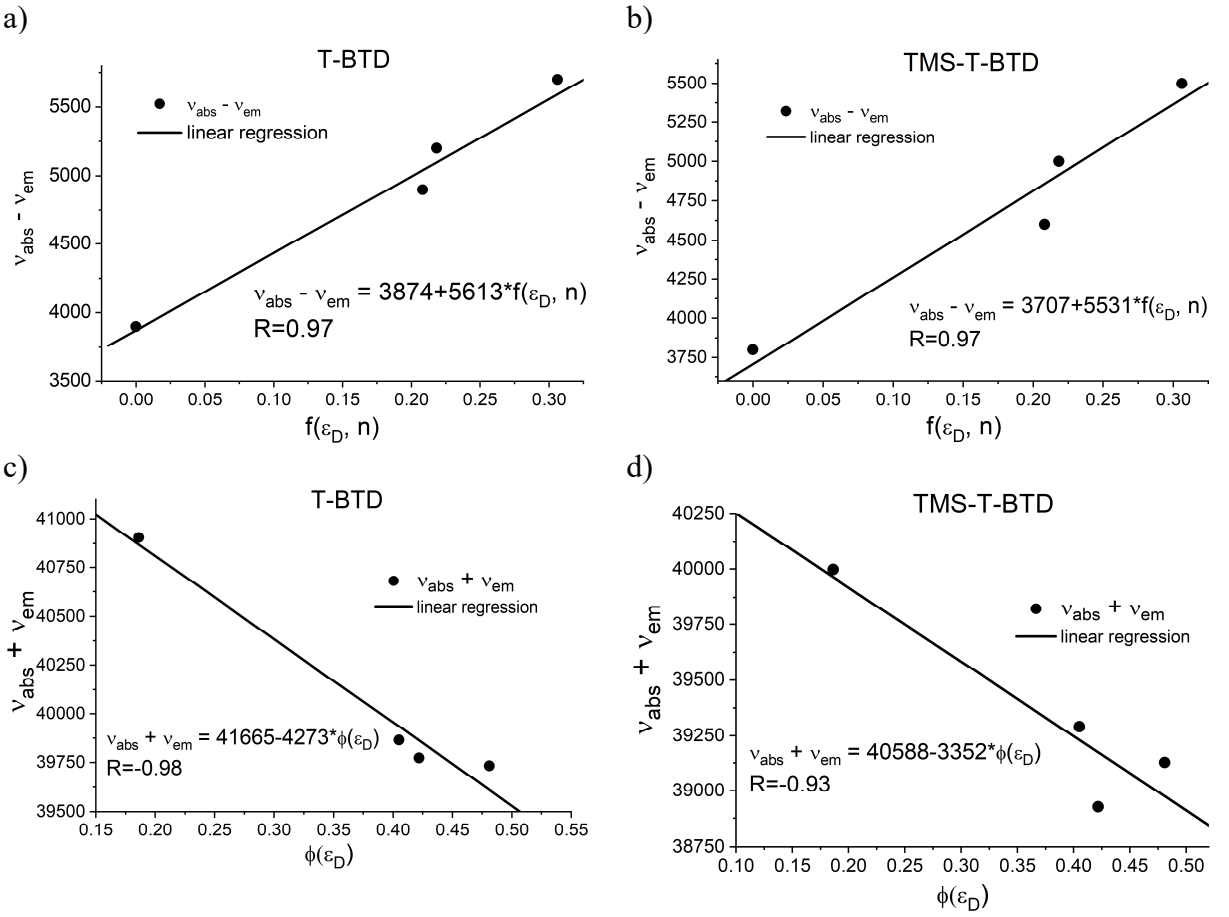

Figure S8. To the calculation of the dipole moments of T-BTD (a, c) and TMS-T-BTD (b, d) molecules: dependence of the difference (a, b) and sum (c, d) of the absorption and fluorescence band maxima on the solvent functions $f(\varepsilon_D, n)$ and $\varphi(\varepsilon_D)$. The points are experimental data, the lines are linear regression (the equations of dependencies and the linear regression coefficient are given).

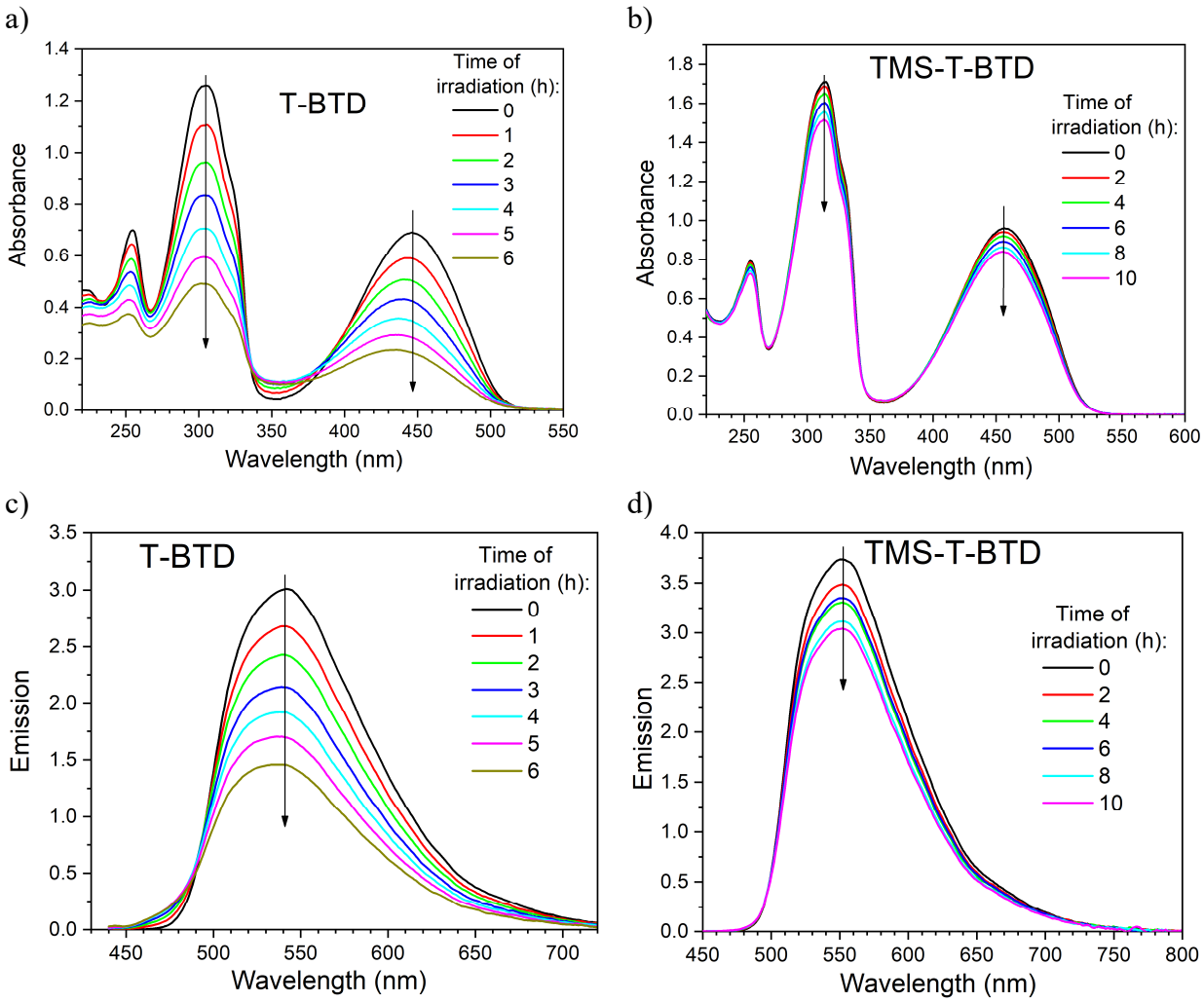

Figure S9. Changes in the absorption (a, b) and fluorescence (c, d) spectra of solutions of T-BTD (a, c) and TMS-T-BTD (b, d) in hexane upon irradiation. The initial concentration was $5 \cdot 10^{-5}$ mol/L, the cuvette thickness was 1 cm. Excitation was carried out with light with a wavelength of 446 nm (T-BTD) and 457 nm (TMS-T-BTD).

Table S1. Photoirradiation of T-BTD and TMS-T-BTD solutions in hexane.

Compound	Initial concentration (mol/L)	Lamp intensity (mol/(L*s))	Irradiation time (h)	Average absorbed light intensity (mol/(L*s))	Quantum yield of photodestruction
	C_0		t	I_{abs}^{mean}	QY_{PhD}
T-BTD	$5 \cdot 10^{-5}$	$5.88 \cdot 10^{-5}$	6	$4.21 \cdot 10^{-5}$	$4.07 \cdot 10^{-5}$
TMS-T-BTD	$5 \cdot 10^{-5}$	$5.88 \cdot 10^{-5}$	10	$5.88 \cdot 10^{-5}$	$2.99 \cdot 10^{-6}$

Notes. The average intensity of absorbed light (I_{abs}^{mean}) corresponds to the absorption of the system at an average irradiation time. The quantum yield of photodestruction QY_{PhD} was calculated as the ratio of the amount of decayed substance during the irradiation to the intensity of the absorbed light during this time, i.e.

$$QY_{PhD} = \frac{C_0 - C_t}{t \times I_{abs}^{mean}}.$$

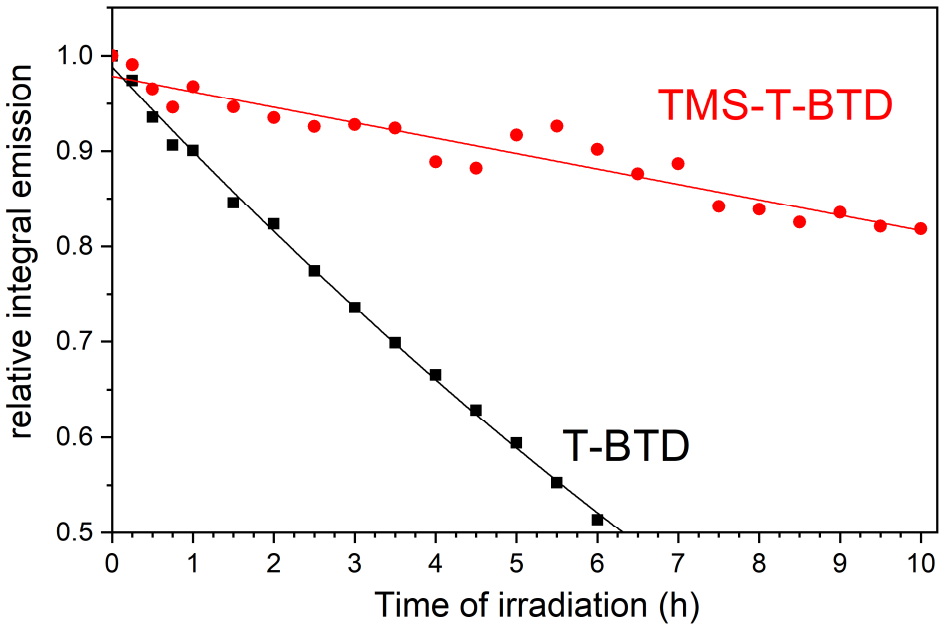

Figure S10. Change in the relative integral fluorescence of solutions of T-BTD and TMS-T-BTD in hexane upon irradiation. Points – experimental data, lines – approximation. Excitation was carried out with the light at wavelengths of 446 nm (T-BTD) and 457 nm (TMS-T-BTD).