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Supporting information for article:

Crystal structures and dielectric properties of 4,4'dimethyl6,6'-dichlorothioindigo (Pigment Red 181)

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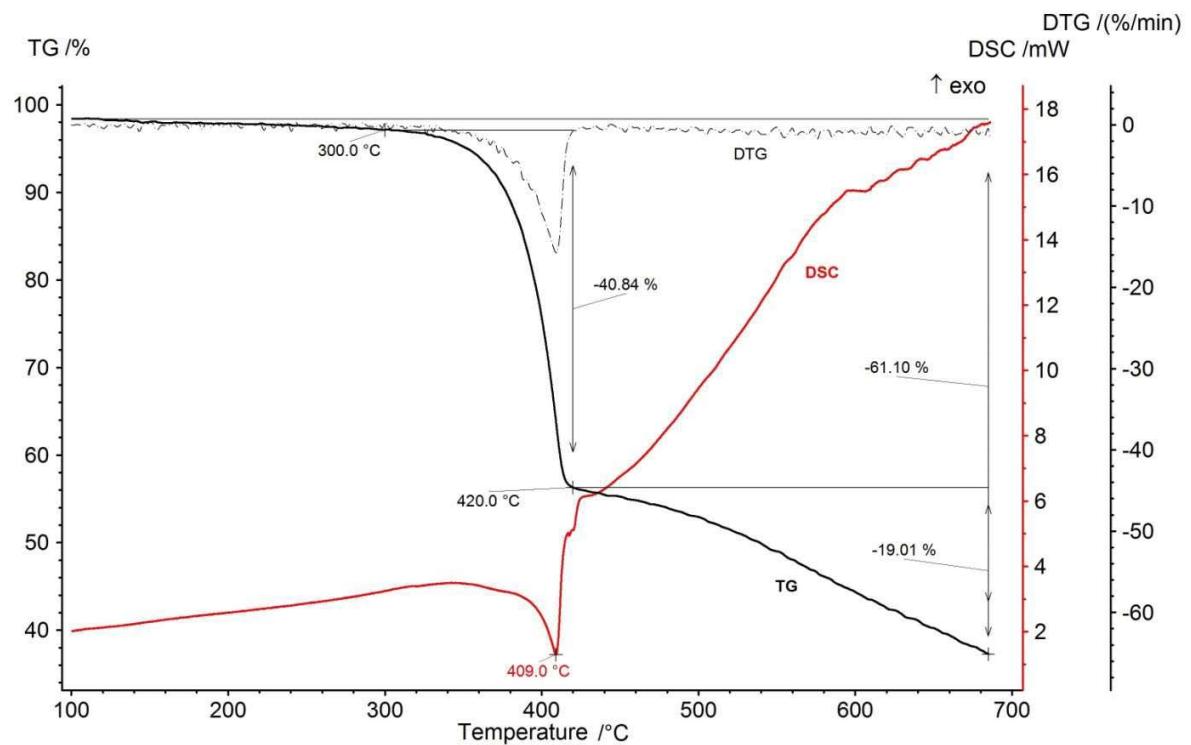


Figure S1. The results of simultaneous TG-DSC analysis of **2**

Table S1. Experimental and calculated lengths of non-covalent bonds in polymorphs **1** and **2** (Å)

Polymorph 1			Polymorph 2		
Bond	Exp.	Calc.	Bond	Exp.	Calc.
O1...S1	2.7853	2.771	O2...S1	2.7782	2.764
S1...C11	3.5384	3.573			
S1...C7	3.4414	3.465	S1...C3	3.6332 3.6782	3.665 3.707
O1...H5	2.8440	2.727	O2...H10C	2.768	2.628
			O2...H10B	2.715	2.576
C11...H3	3.045	2.986	C14...H1	3.0153	2.974
			C14...H9	2.9520	2.821

Table S2. Comparative assessment of the differences in the energy of weak hydrogen bonds (kcal/mol) in polymorphs based on Iogansen approach*; calculated intensities of the model IR spectra (kM/mol) in brackets.

Vibration assignments	Calculated IR frequencies for 1 (black)	Calculated IR frequencies for 2 (red)	Differences of intensities, $I_{(1)}^{1/2} - I_{(2)}^{1/2}$	$ \Delta H_{HB} $
ν_{C-H} (benzene ring)	3094w (7.74)	3105w (4.83)	0.58	0.17
ν_{C-H} asym (methyl group)	3059w (4.09)	3047w (5.31)	-0.28	0.08
	3028m (60.72)	3018w (2.25)	6.29	1.82
ν_{C-H} sym (methyl group)	2950s (182.19)	2947vw (0.41)	12.86	3.73

* Iogansen, A.V. (1999). Spectrochim. Acta - Part A Mol. Biomol. Spectrosc. 55, 1585–1612.

* Katsyuba, S. A., Vener, M. V., Zvereva, E. E., Fei, Zhaofu, Scopelliti, R., Brandenburg, J. G., Siankevich, S. & Dyson, P. J. (2015). J. Phys. Chem. Lett. 6, 4431–4436.

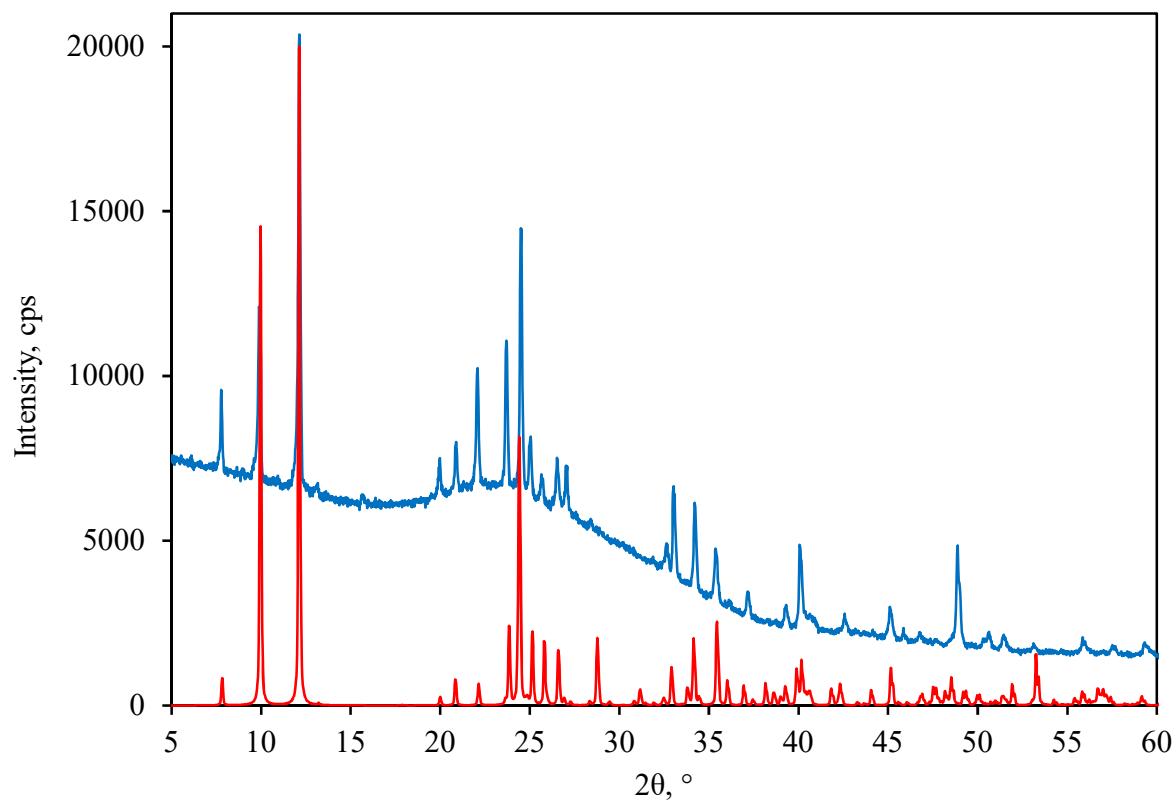


Figure S2. The PXRD pattern of **2** (top curve) compared with simulated pattern of **2** according single crystal structure solution (bottom curve)

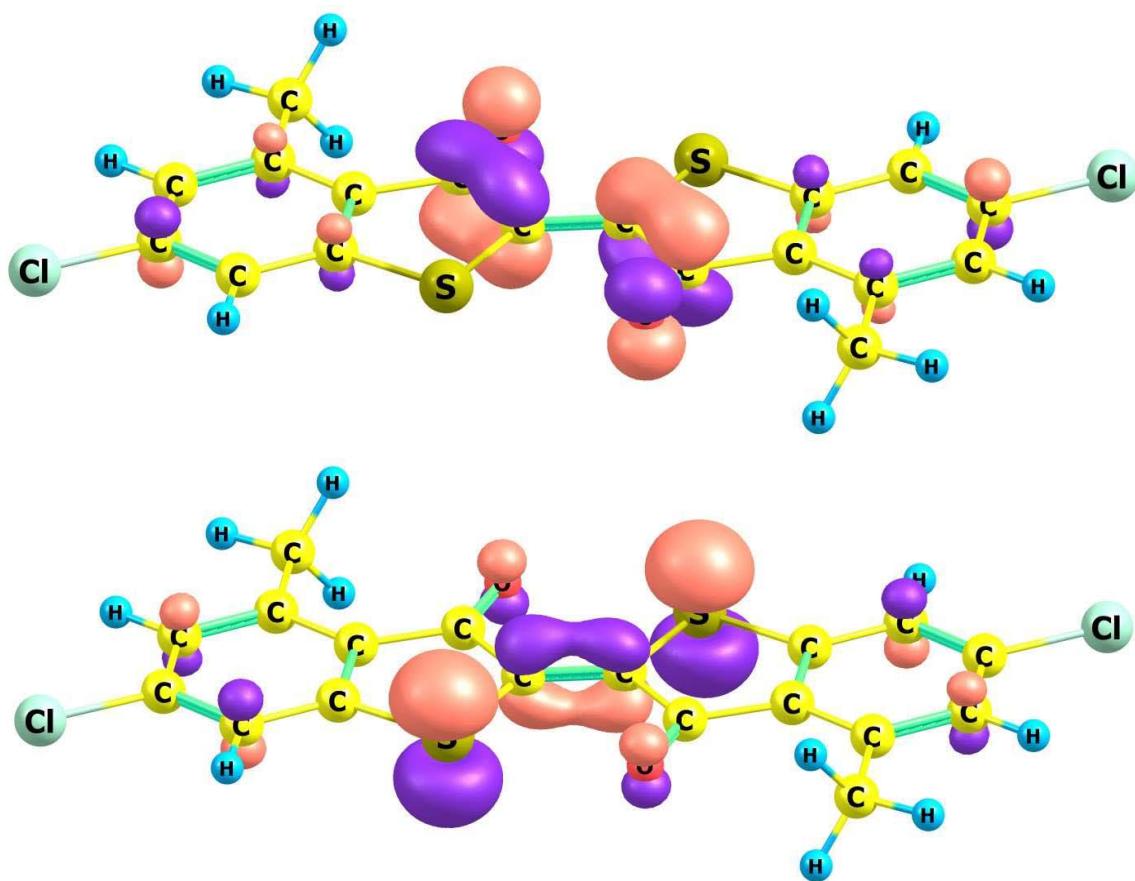


Figure S3. Calculated LUMO (top) and HOMO (bottom) orbitals of 4,4'-dimethyl-6,6'-dichlorothioindigo molecule in benzene media

Table S3. Assigned IR frequencies of observable bands for crystal **2** (cm^{-1})

Vibration assignments	Calculated IR frequencies	Experimental IR frequencies
$\nu_{\text{C}-\text{H}}$ asym and sym (benzene ring)	3105w	3075w
$\nu_{\text{C}-\text{H}}$ asym (methyl group)	3047w 3018w	2974w
	—	2928w
	—	1713w
$\nu_{\text{C}-\text{O}}$ (thiophene ring)	1675m	1653s
$\nu_{\text{C}-\text{C}-\text{C}}$ asym (benzene ring & thiophene ring)	1583m	1560s
$\nu_{\text{C}-\text{C}-\text{C}}$ sym (benzene & thiophene ring)	1560s	
$\delta_{\text{H}-\text{C}-\text{H}}$ sciss (methyl group)	1423m	1431m
$\delta_{\text{H}-\text{C}-\text{H}}$ sciss (methyl group)	1398w	
$\delta_{\text{C}-\text{C}-\text{H}}$ (benzene ring), $\delta_{\text{H}-\text{C}-\text{H}}$ sciss (methyl group), $\nu_{\text{C}-\text{C}-\text{C}}$ sym (benzene ring)	1369w	1381m
δ_{CH_3} sciss (methyl group)	1356w	
$\nu_{\text{C}-\text{C}-\text{C}}$ asym (benzene ring), $\delta_{\text{C}-\text{C}-\text{H}}$ (benzene ring), $\nu_{\text{C}-\text{C}-\text{C}}$ sym (thiophene ring), $\delta_{\text{H}-\text{C}-\text{H}}$ sciss (methyl group)	1330w	1300w
$\delta_{\text{C}-\text{C}-\text{H}}$ (benzene ring), $\nu_{\text{C}-\text{C}-\text{C}}$ asym (thiophene ring), $\nu_{\text{C}-\text{C}-\text{C}}$ sym (benzene ring), $\delta_{\text{H}-\text{C}-\text{H}}$ sciss (methyl group)	1230s	1242s
$\delta_{\text{C}-\text{C}-\text{H}}$ (benzene ring), $\nu_{\text{C}-\text{C}-\text{C}}$ & $\nu_{\text{C}-\text{C}-\text{S}}$ asym (thiophene ring), $\nu_{\text{C}-\text{C}-\text{C}}$ sym (benzene ring)	1171w	1182m
$\delta_{\text{H}-\text{C}-\text{C}-\text{C}-\text{H}}$ sciss (benzene ring), $\nu_{\text{C}-\text{Cl}}$, $\nu_{\text{C}-\text{C}-\text{C}}$ sym (benzene ring), $\delta_{\text{H}-\text{C}-\text{C}-\text{H}}$ rock (benzene ring & methyl group), $\nu_{\text{C}-\text{C}-\text{S}}$ asym (thiophene ring)	1085m	1096s
$\nu_{\text{C}-\text{C}}$ (thiophene ring), Δ (benzene ring)	1041m	1045m
δ_{CH_3} rock (benzene ring & methyl group), $\nu_{\text{C}-\text{S}}$ (thiophene ring), Δ (benzene ring)	972w	999m
	—	922w
Δ (benzene ring), $\nu_{\text{C}-\text{C}}$ (benzene – methyl group), $\nu_{\text{C}-\text{Cl}}$, $\nu_{\text{C}-\text{S}-\text{C}}$ sym (thiophene ring)	911w	
$\nu_{\text{C}-\text{S}}$ (thiophene ring), Δ (benzene ring), $\nu_{\text{C}-\text{C}}$ (benzene – methyl group)	895w	903m

	—	847s
$\gamma_{\text{H-C-C-C-H}}$ wagg (benzene ring) Δ (benzene ring), $\nu_{\text{C-S-C}}$ sym (thiophene ring), $\nu_{\text{C-Cl}}$	819w 804m	820m
	—	783m
Γ (benzene & thiophene ring)	652w	673s
	—	604w
Δ (benzene & thiophene ring), $\delta_{\text{H-C-C-C-H}}$ sciss (benzene ring & methyl group), $\delta_{\text{Cl-C-C-H}}$ sciss (benzene ring)	500w	509m
Δ (benzene ring), $\delta_{\text{H-C-C-C-H}}$ sciss (benzene ring & methyl group), $\delta_{\text{C-C-O}}$ (thiophene ring), $\nu_{\text{C-Cl}}$	459w	469s

Description of assignment: ν – stretching (symmetric & asymmetric), δ – in-plane bending (scissoring & rocking), γ – out-of-plane bending (twisting & wagging), Γ – out-of-plane ring deformation, Δ – in-plane ring deformation. The relative absorbance: w – weak, m – medium, s – strong.