

Polymorphism of merocyanine dyes homologs with 1,3-diethyl-2-thiobarbituric acid and *p*-dimethylaminobenzene donor and acceptor and different polymethine chains connecting them

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SUPPORTING INFORMATION

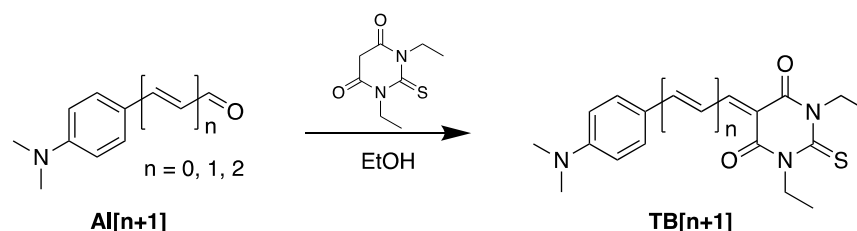
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1. Synthesis of Materials

All materials and reagents were commercially available and used as received except where noted. Starting aldehydes Al[n] for the syntheses of TB[1] – TB[5] were prepared as reported in our previous publication.¹

General procedure for the synthesis of 1,3-diethyl-2-thiobarbituric acid derivatives (TB[n])

Equimolar amounts of aromatic aldehyde Al[n] and 1,3-diethyl-2-thiobarbituric acid were separately dissolved in absolute ethanol with heating. Once dissolution was complete, the thiobarbituric acid solution was carefully transferred to the aldehyde solution in small portions by syringe, taking care not to allow the thiobarbituric acid to crystallize. The addition of the thiobarbituric acid solution causes an immediate color change and shortly thereafter (usually before addition is complete) crystalline precipitate began forming on the walls of the flask. Once the addition was complete, the reaction mixture was diluted with ethanol for ease of stirring (if necessary). The reaction mixture was stirred with gentle heat for 1 hour or until completion (as monitored by TLC typically using 3:1 ethyl acetate / hexane) before cooling to room temperature. The resulting



crystalline precipitate was collected by filtration, washed with cold ethanol and recrystallized. The resulting purified products were dried under vacuum. General reaction is shown in Figure S1.

Figure S1. Synthesis of TB[n+1] derivatives from corresponding aldehydes for n = 0, 1, and 2.

Chromophores are named to reflect the total length of the conjugated chain.

1,3-diethyl-5-[4-(dimethylamino)benzylidene]-2-thiobarbituric acid (TB[1])

TB[1] was prepared according to the TB[n] general procedure using **Al[1]** (1.02 g, 6.84 mmol) and 1,3-diethylthiobarbituric acid (1.37 g, 6.84 mmol) dissolved separately in ethanol (20 mL each) before being combined, causing a color change to bright red. Crude **TB[1]** was allowed to cool and collected by vacuum filtration, washed with cold ethanol and recrystallized from ethanol to give shiny red crystalline powder (2.11 g, 93%). Melting point is 217 – 218 °C. ¹H NMR (500 MHz, CD₂Cl₂) δ 8.44 (d, *J* = 9.2 Hz, 2H), 8.38 (s, 1H), 6.74 (d, *J* = 9.2 Hz, 2H), 4.57 (q, *J* = 7.0 Hz, 2H) 4.54 (q, *J* = 7.0 Hz, 2H), 3.17 (s, 6H), 1.29 (t, *J* = 7.0 Hz, 3H), 1.27 (t, *J* = 7.0 Hz, 3H) ppm. ¹³C NMR (100 MHz, CD₂Cl₂) δ 179.4, 162.4, 159.8, 159.6, 155.3, 140.2, 121.8, 111.5, 110.7, 44.2, 43.6, 40.4, 12.7, 12.6 ppm. Single crystals of **TB[1]** were grown by vapor diffusion of hexane or cyclohexane into a saturated solution of **TB[1]** in either chloroform or acetone. Additionally, single crystal growth was accomplished by layering ethanol on top of a saturated solution of **TB[1]** in dichloromethane. The crystal growth took approximately 3 weeks and yielded crystals which were brilliant red in appearance.

(E)-1,3-diethyl-5-(3-[4-(dimethylamino)phenyl]allylidene)-2-thiobarbituric acid (TB[2])

TB[2] was prepared according to the TB[n] general procedure using **Al[2]** (1.00 g, 5.71 mmol) and 1,3-diethylthiobarbituric acid (1.15 g, 5.71 mmol) separately dissolved with gentle heating in ethanol (about 15 mL each) before being combined, resulting in a dramatic color change to pink/purple. Crude **TB[2]** was allowed to cool and collected by filtration, washed with cold ethanol, and recrystallized from dichloromethane / ethanol to give silver and purple crystalline powder (1.80 g, 88%). Melting point is 227.4 °C (decomposition). ¹H NMR (500 MHz, CD₂Cl₂) δ 8.45 (dd, *J* = 14.8, 12.5 Hz, 1H), 8.18 (d, *J* = 12.5 Hz, 1H) 7.63 (d, *J* = 9.1 Hz, 2H), 7.49 (d, *J* = 14.8 Hz, 1H), 6.72 (d, *J* = 9.1 Hz, 2H), 4.54 (q, *J* = 7.0 Hz, 2H), 4.52 (q, *J* = 7.0 Hz, 2H), 3.11 (s, 6H), 1.28 (t, *J* = 7.0 Hz, 3H), 1.26 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CD₂Cl₂) δ 179.5, 161.4, 160.5, 159.6, 158.5, 154.0, 132.9, 123.8, 121.2, 112.4, 111.2, 43.8, 43.2, 40.4, 12.7, 12.6 ppm. Single crystals of **TB[2]** were grown by layering ethanol on top of a saturated solution of **TB[2]** in dichloromethane. Crystal growth took place over 4 – 6 weeks and gave lustrous prism shaped crystals which were purple and silver in appearance.

(TB[3])

TB[3] was prepared according to the TB[n] general procedure using **AI[3]** (0.50 g, 2.5 mmol) and 1,3-diethylthiobarbituric acid (0.51 g, 2.55 mmol) separately dissolved in ethanol (20 mL each) before being combined. The reaction immediately changed to a dark green color that faded to dark blue as the aldehyde was consumed. The product mixture was allowed to cool and crude **TB[3]** was collected by filtration, washed with cold ethanol and recrystallized from dichloromethane and ethanol to give a dark green fibrous powder (0.84 g, 88%). Melting point is 229 °C (decomposition). ¹H NMR (500 MHz, CD₂Cl₂) δ 8.10 (d, *J* = 12.6 Hz, 1H), 8.03 (dd, *J* = 13.7, 12.6 Hz, 1H), 7.46 (d, *J* = 9.0 Hz, 2H), 7.38 (dd, *J* = 13.7, 11.0 Hz, 1H), 7.10 (d, *J* = 15.1 Hz, 1H), 7.02 (dd, *J* = 15.1, 11.0 Hz, 1H), 6.70 (d, *J* = 9.0 Hz, 2H), 4.52 (q, *J* = 6.8 Hz, 2H), 4.51 (q, *J* = 6.8 Hz, 2H), 3.06 (s, 6H), 1.27 (t, *J* = 7.01 Hz, 3H), 1.25 (t, *J* = 7.01 Hz, 3H) ppm. ¹³C NMR (100 MHz, CD₂Cl₂) δ 179.5, 161.3, 160.3, 158.8, 158.4, 152.6, 147.5, 130.7, 127.5, 124.2, 124.1, 130.7, 127.5, 124.2, 124.1, 112.4, 112.1, 43.8, 43.3, 40.3, 12.6, 12.5 ppm. Single crystals of **TB[3]** were grown by the slow evaporation of a saturated solution of **TB[3]** in ethyl acetate (**TB[3]α**) and layering ethanol on top of a saturated solution of **TB[3]** in dichloromethane (**TB[3]β**). Crystal growth took place over 3 – 4 weeks and gave prism-like blue and gold crystals (**TB[3]α**) as well as blue transparent needles (**TB[3]β**).

(TB[4])

TB[4] was prepared according to the TB[n] general procedure using **AI[4]** (0.50 g, 2.2 mmol) and 1,3-diethylthiobarbituric acid (0.44 g, 2.2 mmol) separately dissolved in ethanol (15 mL each) before being combined. The reaction immediately changed to a dark green color that faded to dark blue as the aldehyde was consumed. The product mixture was allowed to cool and crude **TB[4]** was collected by filtration, washed with cold ethanol and recrystallized from dichloromethane and ethanol to give shiny green fibrous powder (0.77 g, 91%). A slower crystallization gave incredibly thin lustrous green actinic crystals, which appeared almost metallic. Melting point 205 °C (decomposition). ¹H NMR (500 MHz, CD₂Cl₂) δ 8.07 (d, *J* = 12.6 Hz, 1H), 7.99 (dd, *J* = 14.1, 12.6 Hz, 1H), 7.39 (d, *J* = 8.9 Hz, 2H), 7.29 (dd, *J* = 14.1, 11.7 Hz, 1H), 6.99 (apparent dd, ABMX *J*_{MX} = 14.2 Hz, *J*_{AM} = 3.4 Hz, *J*_{BM} = 13.4 Hz, 1H), 6.91 (ABM, Δδ_{AB} = 0, *J*_{AB} = 15.0 Hz, *J*_{AM} = 3.4 Hz, 1H), 6.90 (ABM, Δδ_{AB} = 0.03, *J*_{AB} = 15.0 Hz, *J*_{BM} = 13.4 Hz, 1H), 6.74 (d, *J* = 8.9 Hz, 2H), 4.57 (q, *J* = 6.8 Hz, 2H), 4.53 (q, *J* = 6.8 Hz, 2H), 3.12 (s, 6H), 1.31 (t, *J* = 6.8 Hz, 3H), 1.30 (t, *J* = 6.8 Hz, 3H) ppm. All attempts at growing single crystals for X-ray structural analysis yielded only extremely thin and fragile actinic crystals which were shiny and bright green but not suitable for X-ray measurements.

(2*E*, 4*E*, 6*E*, 8*E*)-1,3-diethyl-5-(9-[4-(dimethylamino)phenyl]nonaa-2,4,6,8-tetraenylidene)-2-thiobarbituric acid (TB[5])

TB[5] was prepared according to the TB[n] general procedure using **Al[5]** (0.25 g, 0.99 mmol) and 1,3-diethylthiobarbituric acid (0.20 g, 1.0 mmol) separately dissolved in ethanol (10 mL each) before being combined. The reaction immediately changed to a dark blue color that faded to nearly black as the aldehyde was consumed. The product mixture was allowed to cool and crude **TB[5]** was collected by filtration, washed with cold ethanol and recrystallized from dichloromethane and ethanol to give shiny olive-green fibrous powder (0.37 g, 87%). ¹H NMR (800 MHz, CD₂Cl₂) δ 8.06 (d, *J* = 12.6 Hz, 1H), 8.00 (dd, *J* = 13.9, 12.6 Hz, 1H), 7.35 (d, *J* = 8.9 Hz, 2H), 7.26 (dd, *J* = 13.9, 11.6 Hz, 1H), 6.91 (dd, *J* = 14.4, 11.5 Hz, 1H), 6.81 – 6.74 (m, 2H), 6.73 (d, *J* = 14.3 Hz, 1H), 6.67 (d, *J* = 8.9 Hz, 2H), 6.61 (dd, *J* = 14.4, 11.6 Hz, 1H), 6.51 – 6.46 (m, 1H), 4.51 (q, *J* = 6.9 Hz, 2H), 4.50 (q, *J* = 6.9 Hz, 2H), 3.00 (s, 6H), 1.26 (t, *J* = 6.9 Hz, 3H), 1.25 (t, *J* = 6.9 Hz, 3H) ppm. ¹³C NMR (201 MHz, CD₂Cl₂) δ 179.5, 161.1, 160.1, 157.7, 156.8, 151.4, 146.8, 143.0, 139.1, 131.5, 130.6, 129.2, 128.9, 125.1, 124.6, 113.3, 112.5, 43.9, 43.3, 40.4, 12.6, 12.5 ppm. Single crystals of TB[5] were grown by the slow evaporation of a saturated solution of TB[5] in ethyl acetate (TB[5]α) and layering ethanol on top of a saturated solution of TB[5] in dichloromethane (TB[5]β). Crystal growth took place over 5 – 6 weeks and gave yellowish green plate-like crystals (TB[5]α) as well as black opaque needles (TB[5]β).

2.Single Crystal X-ray Diffraction Studies

Table S1. Crystallographic data for all samples.

	TB[1] α	TB[1] β	TB[2]	TB[3] α	TB[3] β	TB[5] α	TB[5] β
Formula	C ₁₇ H ₂₁ N ₃ O ₂ S	C ₁₇ H ₂₁ N ₃ O ₂ S	C ₁₉ H ₂₃ N ₃ O ₂ S	C ₂₁ H ₂₅ N ₃ O ₂ S	C ₂₁ H ₂₅ N ₃ O ₂ S	C ₂₅ H ₂₉ N ₃ O ₂ S	C ₂₅ H ₂₉ N ₃ O ₂ S
Formula weight	331.43	331.43	357.46	383.50	383.50	435.57	435.57
Temperature, K	150.15	150.15	100(2)	100	100(2)	100(2)	293(2)
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P-1	P-1	P2 ₁ /c	P-1	P2 ₁ /c	P2 ₁ /c
a, Å	7.9084(16)	5.1729(12)	8.1770(4)	9.2174(11)	4.45013(15)	7.7503(13)	27.664(9)
b, Å	10.252(2)	11.586(3)	9.0390(5)	24.897(3)	9.6353(4)	63.988(11)	4.3348(13)
c, Å	10.378(2)	13.925(3)	12.1884(6)	9.1030(11)	22.3020(9)	9.3415(16)	20.022(7)
α , °	88.353(3)	82.075(3)	82.4078(8)	90	90.11(2)	90	90
β , °	79.484(3)	85.776(3)	82.9107(8)	110.648(2)	91.58(3)	90.377(3)	106.085(8)
γ , °	86.056(3)	84.756(3)	86.8849(8)	90	92.78(2)	90	90
Volume, Å ³	825.2(3)	821.6(3)	885.48(8)	1954.8(4)	954.78(7)	4632.6(14)	2307.0(13)
Z	2	2	2	4	2	8	4
ρ_{calc} , g/cm ³	1.334	1.340	1.341	1.303	1.334	1.249	1.254
μ , mm ⁻¹	0.210	0.210	0.201	0.187	1.676	0.166	0.167
F(000)	352.0	352.0	380.0	816.0	408.0	1856.0	928.0
Crystal size, mm ³	0.4 × 0.1 × 0.1	0.3 × 0.3 × 0.2	0.3 × 0.2 × 0.2	0.3 × 0.2 × 0.2	0.4 × 0.1 × 0.1	0.21 × 0.12 × 0.11	0.30 × 0.09 × 0.09
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	CuK α (λ = 1.54184)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection, °	3.982 to 63.728	2.958 to 63.73	4.55 to 60.224	8.478 to 61.112	7.932 to 141.6	4.406 to 60.016	4.234 to 50.358
Index ranges	-11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -14 ≤ l ≤ 14	-7 ≤ h ≤ 7, -17 ≤ k ≤ 16, -19 ≤ l ≤ 19	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -17 ≤ l ≤ 17	-13 ≤ h ≤ 13, -34 ≤ k ≤ 35, -13 ≤ l ≤ 12	-5 ≤ h ≤ 5, -11 ≤ k ≤ 11, -26 ≤ l ≤ 26	-10 ≤ h ≤ 10, -89 ≤ k ≤ 89, -13 ≤ l ≤ 13	-28 ≤ h ≤ 33, -4 ≤ k ≤ 5, -21 ≤ l ≤ 22
Reflections collected	9726	9637	11681	23101	12444	59665	15392
Independent reflections	5102 [R _{int} = 0.0175, R _{sigma} = 0.0255]	5041 [R _{int} = 0.0339, R _{sigma} = 0.0429]	5214 [R _{int} = 0.0159, R _{sigma} = 0.0175]	5956 [R _{int} = 0.0230, R _{sigma} = 0.0176]	3548 [R _{int} = 0.0470, R _{sigma} = 0.0307]	13075 [R _{int} = 0.0871, R _{sigma} = 0.0803]	3552 [R _{int} = 0.0897, R _{sigma} = 0.1673]
Data/restraints/parameters	5102/0/212	5041/0/212	5214/16/277	5956/0/248	3548/0/242	13075/0/567	3552/0/285
Goodness-of-fit on F ²	1.053	1.028	1.052	1.047	1.044	1.087	1.029
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0487, wR ₂ = 0.1440	R ₁ = 0.0417, wR ₂ = 0.1148	R ₁ = 0.0333, wR ₂ = 0.0960	R ₁ = 0.0358, wR ₂ = 0.0949	R ₁ = 0.0623, wR ₂ = 0.1629	R ₁ = 0.1040, wR ₂ = 0.1874	R ₁ = 0.0994, wR ₂ = 0.1892
Final R indexes [all data]	R ₁ = 0.0641, wR ₂ = 0.1595	R ₁ = 0.0524, wR ₂ = 0.1230	R ₁ = 0.0351, wR ₂ = 0.0979	R ₁ = 0.0385, wR ₂ = 0.0974	R ₁ = 0.0684, wR ₂ = 0.1682	R ₁ = 0.1425, wR ₂ = 0.2064	R ₁ = 0.2643, wR ₂ = 0.2489
Largest diff. peak/hole, e Å ⁻³	0.38/-0.24	0.38/-0.25	0.48/-0.22	0.51/-0.26	1.16/-0.47	0.57/-0.50	0.21/-0.19

Table S2. Dihedral angles (°) between planar fragments and selected bond lengths (Å) for all samples.

	TB[1] α	TB[1] β	TB[2]	TB[3] α	TB[3] β	TB[5] α		TB[5] β
						Molecule A	Molecule B	
Dihedral angle Acceptor – Bridge	4.65(8)	4.06(9)	6.131(19)	3.64(7)	6.76(4)	15.36(16)	13.15(18)	25.5(5)
Dihedral angle Donor – Bridge	1.73(6)	6.02(15)	9.01(6)	2.66(7)	6.4(2)	27.16(17)	27.03(17)	12.6(9)
Dihedral angle Donor – Acceptor	2.97(3)	8.57(3)	6.58(3)	1.14(2)	8.93(7)	36.36(8)	36.64(8)	17.09(16)
C1–N1	1.3713(17)	1.3752(16)	1.3827(14)	1.3811(13)	1.387(3)	1.380(4)	1.383(4)	1.359(10)
N1–C2	1.4097(17)	1.4176(16)	1.4098(12)	1.4094(13)	1.406(3)	1.397(4)	1.386(4)	1.413(10)
C2–C3	1.444(2)	1.4531(15)	1.4501(12)	1.4525(11)	1.461(4)	1.458(5)	1.467(5)	1.440(10)
C3–C4	1.4606(18)	1.4635(17)	1.4590(11)	1.4614(14)	1.457(4)	1.474(5)	1.471(5)	1.435(13)
C4–N2	1.4089(17)	1.4099(16)	1.4074(15)	1.4027(13)	1.396(3)	1.407(4)	1.394(4)	1.412(9)
N2–C1	1.3765(19)	1.3790(14)	1.3801(18)	1.3796(10)	1.389(3)	1.375(5)	1.385(5)	1.377(9)
C5–C6	1.416(2)	1.4194(17)	1.4168(11)	1.4099(12)	1.415(4)	1.400(4)	1.402(4)	1.371(14)
C6–C7	1.369(2)	1.373(2)	1.3723(12)	1.3768(15)	1.370(4)	1.382(5)	1.386(5)	1.353(13)
C7–C8	1.415(2)	1.4210(17)	1.4260(13)	1.4236(13)	1.420(4)	1.415(4)	1.423(4)	1.406(11)
C8–C9	1.412(2)	1.4221(18)	1.4227(11)	1.4167(12)	1.422(4)	1.407(4)	1.410(4)	1.389(14)
C9–C10	1.3623(19)	1.3719(17)	1.3764(12)	1.3794(15)	1.370(4)	1.385(5)	1.378(5)	1.360(13)
C10–C5	1.4154(19)	1.4201(15)	1.4135(13)	1.4100(12)	1.408(4)	1.402(4)	1.403(4)	1.384(11)
C8–N3	1.3522(18)	1.3573(18)	1.3528(11)	1.3595(14)	1.351(3)	1.378(4)	1.380(4)	1.357(13)
C3–C17	1.3789(18)	1.3868(16)	1.3881(12)	1.3783(14)	1.373(4)	1.367(5)	1.367(5)	1.373(11)
C17–C18	-	-	1.4057(12)	1.4174(15)	1.411(4)	1.432(5)	1.429(5)	1.408(13)
C18–C19	-	-	1.3780(13)	1.3721(15)	1.365(4)	1.364(5)	1.363(5)	1.343(11)
C19–C20	-	-	-	1.4212(16)	1.421(4)	1.433(5)	1.433(5)	1.414(13)
C20–C21	-	-	-	1.3668(14)	1.361(4)	1.361(5)	1.363(4)	1.347(11)
C21–C22	-	-	-	-	-	1.430(5)	1.434(5)	1.409(13)
C22–C23	-	-	-	-	-	1.359(4)	1.357(4)	1.350(11)
C23–C24	-	-	-	-	-	1.434(5)	1.436(5)	1.443(13)
C24–C25	-	-	-	-	-	1.351(4)	1.356(4)	1.353(11)
C17–C5	1.4248(18)	1.4301(17)	-	-	-	-	-	-
C19–C5	-	-	1.4255(12)	-	-	-	-	-
C21–C5	-	-	-	1.4358(15)	1.431(4)	-	-	-
C25–C5	-	-	-	-	-	1.455(5)	1.458(5)	1.440(14)

Table S3. Hydrogens bonds for all samples.

Sample	D–H...A	D–H	H...A	D...A	Angle, °	Symmetry operation
TB[1] α	C6–H6...O1	0.95	2.07	2.8595(17)	139.8	-x, 1-y, 1-z
	C9–H9...O2	0.95	2.57	3.2319(17)	127.1	
TB[1] β	C6–H6...O1	0.95	2.08	2.8803(16)	140.9	2-x, 1-y, 1-z
	C10–H10...O2	0.95	2.64	3.4045(16)	137.7	
TB[2]	C18–H18...O1	0.95	2.29	2.8871(11)	120.1	1-x, 2-y, -z
	C10–H10...O2	0.95	2.52	3.414(3)	156.3	
TB[3] α	C6–H6...O2	0.95	2.40	3.3231(11)	162.4	1+x, +y, +z
	C16–H16C...O2	0.98	2.52	3.3733(14)	146.1	
TB[3] β	C9–H9...O2	0.95	2.41	3.337(3)	163.7	1-x, -y, 1-z
	C15–H15B...O1	0.98	2.62	3.445(4)	141.7	
	C16–H16A...O2	0.98	2.52	3.464(4)	161.4	
TB[5] α	C18B–H18B...O1B	0.95	2.26	2.859(4)	120.6	+x, 1.5-y, 0.5+z
	C18A–H18A...O1A	0.95	2.27	2.868(5)	120.6	
	C15B–H15C...O1A	0.98	2.43	3.325(4)	151.7	
	C15A–H15F...O1B	0.98	2.41	3.317(4)	154.3	
TB[5] β	C18–H18...O1	0.93	2.25	2.843(9)	120.9	-1+x, 1.5-y, -0.5+z
	C15–H15B...O1	0.96	2.62	3.361(10)	133.9	

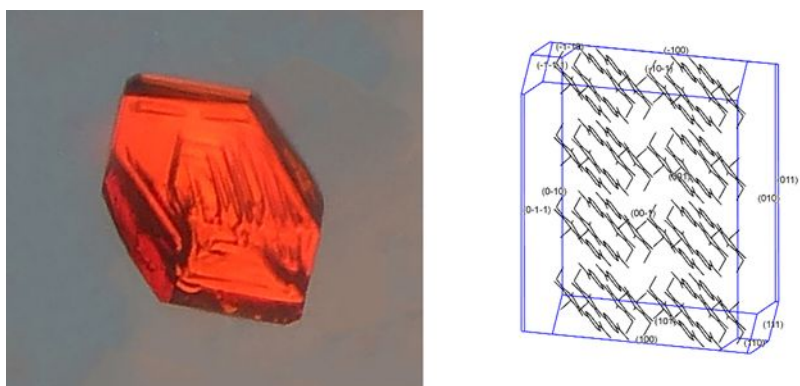


Figure S1. Crystal of TB[1] α and its calculated morphology.

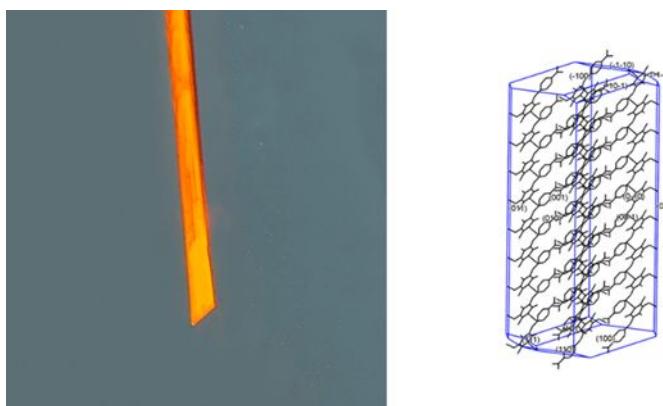


Figure S2. Crystal of TB[1] β and its calculated morphology.

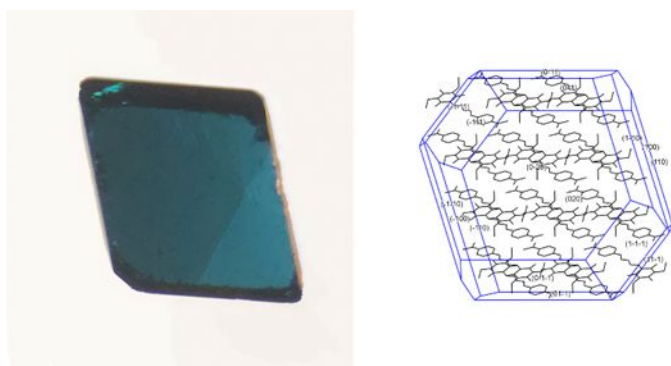


Figure S3. Crystal of TB[3] α and its calculated morphology.

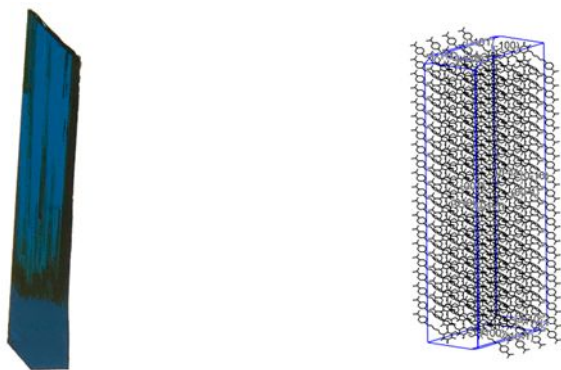


Figure S4. Crystal of TB[3] β and its calculated morphology.

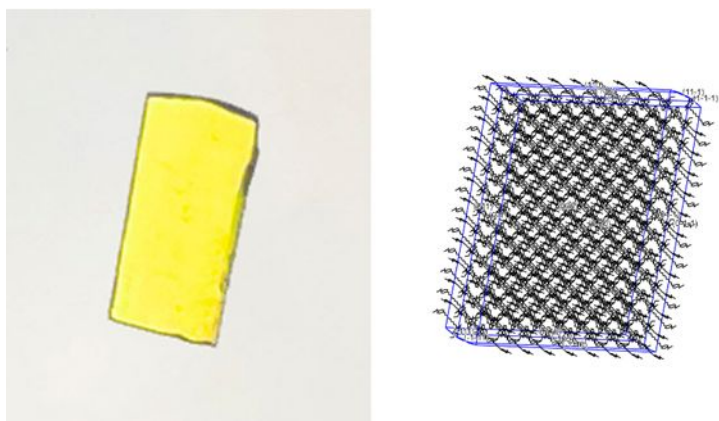


Figure S5. Crystal of TB[5] α and its calculated morphology.

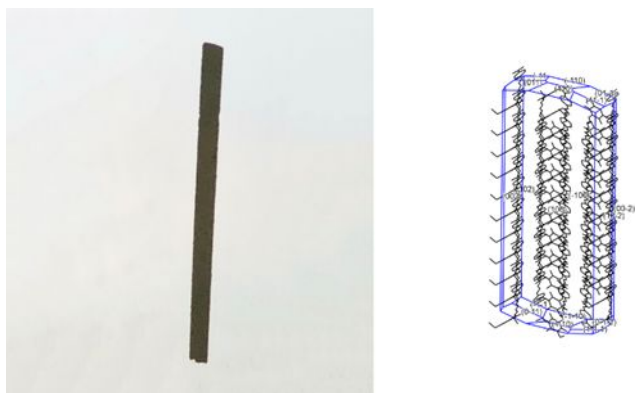


Figure S6. Crystal of TB[5] β and its calculated morphology.

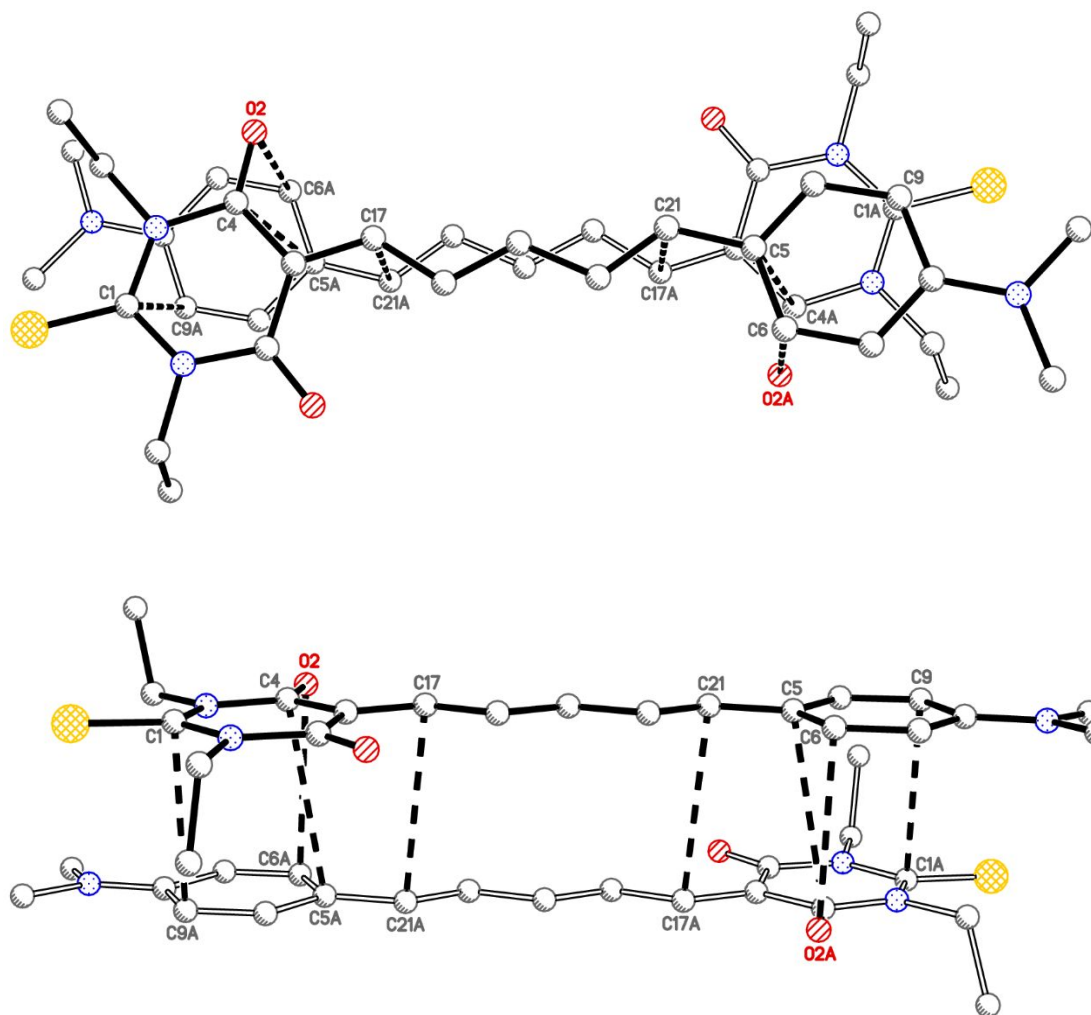


Figure S7. Relative molecular aggregation in crystal TB[3] α suggesting existence of π - π interactions in this crystal with interatomic C...C distances range 3.397(1)- 3.481(1) Å. Hydrogens atoms are omitted for clarity.

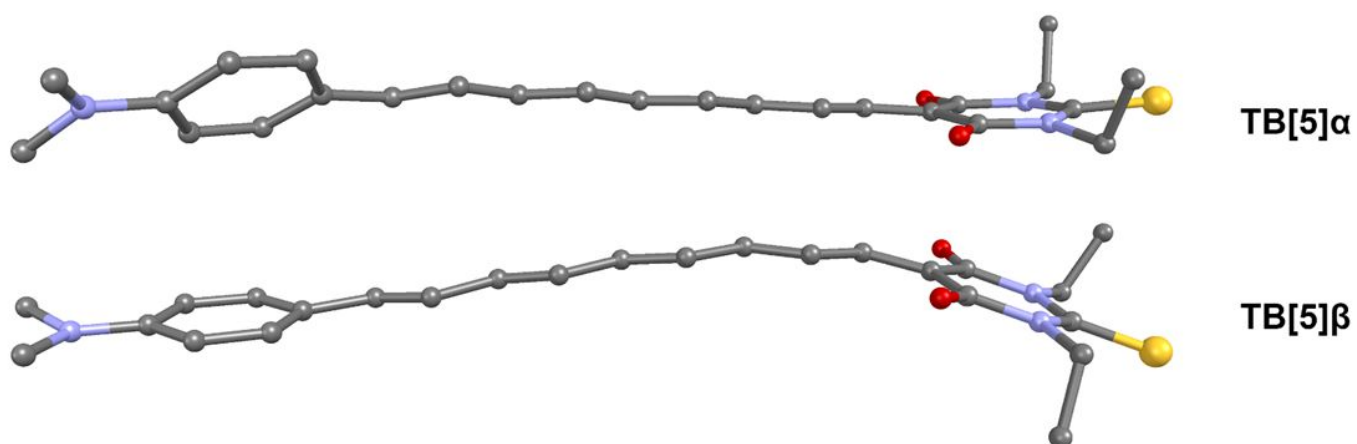


Figure S8. Molecular structures of TB[5] α A and TB[5] β showing different conformations of these molecules including different orientation of ethyl groups. Hydrogens atoms are omitted for clarity.

3.Molecular and Crystal Energy

Table S4. Lattice energy impacts and total lattice energy in crystals studied (kcal/mol).

	Coulombic	Polarization	Dispersion	Repulsion	Total
TB[1] α	-2.58	-10.17	-42.27	15.50	-39.90
TB[1] β	-3.21	-10.29	-43.13	16.72	-39.90
TB[2]	-4.93	-11.12	-49.64	23.32	-42.37
TB[3] α	-4.78	-11.03	-52.32	21.72	-46.41
TB[3] β	-1.98	-11.65	-54.14	22.73	-45.02
TB[5] α	-8.40	-11.72	-53.66	24.57	-54.00
TB[5] β	-2.92	-11.77	-55.17	19.67	-50.22

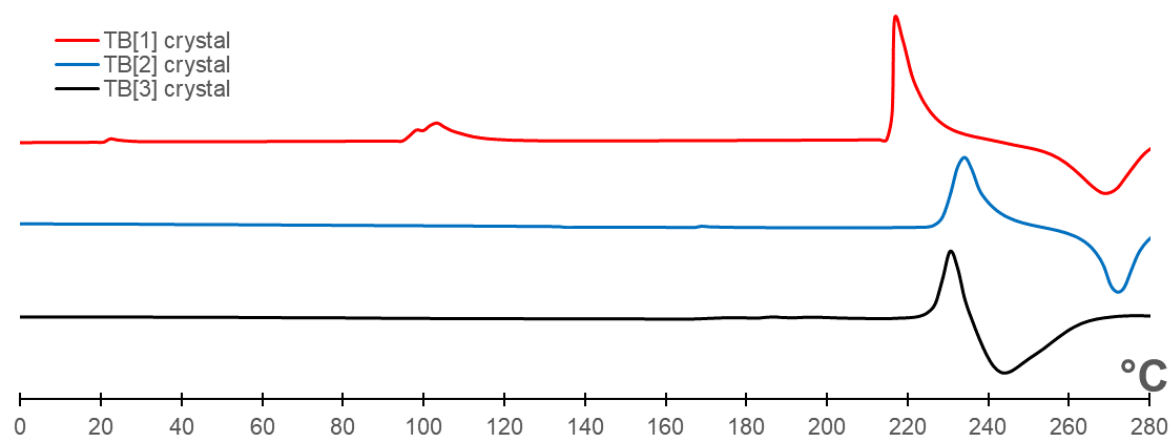
Table S5. Conformational energy (kcal/mol) and molecular dipole moments (Debye) calculated using DFT (B3LYP/6-311+g(d,p)). Molecular geometry in crystal was used for computations.

	Relative molecular energy	Dipole moment
TB[1] α	1.06	10.33
TB[1] β	0.0	10.45
TB[3] α	0.0	14.48
TB[3] β	1.63	14.08
TB[5] α	5.71	14.48
TB[5] β	0.0	16.70

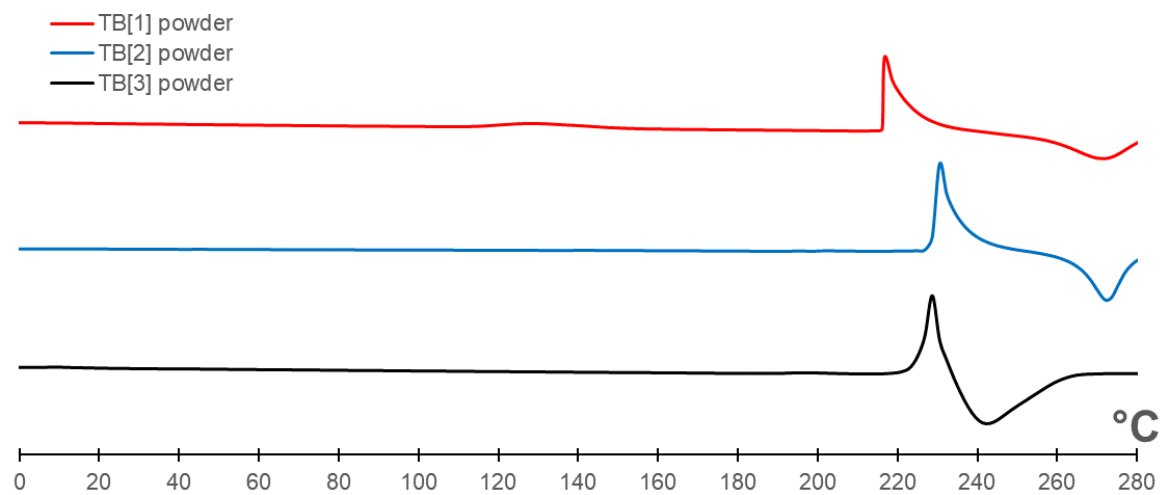
Table S6. Calculated HOMO/LUMO energies.

Crystal	Crystal geometry (X-ray)		Optimized geometry (DFT)	
	E_{HOMO}, eV	E_{LUMO}, eV	E_{HOMO}, eV	E_{LUMO}, eV
TB[1] α	-5.78242	-2.64359	-5.88338	-2.69774
TB[2]	-5.56255	-2.83407	-5.70351	-2.90944
TB[3] α	-5.45153	-2.92686	-5.55385	-3.03734
TB[5] α (Molecule A)	-5.22541	-3.09450	-5.32146	-3.19380

4.DSC Studies



(a)



(b)

Figure S9. DSC plots for crystal (a) and powder (b) samples of TB[1]–TB[3].

Table S7. Characteristic temperatures from DSC plot

	T _G , C°	T _M , C°	T _C , C°
TB[1] crystal	103.3	216.7	268.5
TB[2] crystal	-	234.1	271.9
TB[3] crystal	-	230.5	244.8
TB[1] powder	128.2	216.7	271.9
TB[2] powder	-	230.5	271.9
TB[3] powder	-	228.6	243.0

5.Spectroscopic Studies

Table S8. Absorbance maxima of thiobarbituric acid terminated merocyanines in various solvents.

Dye	CCl ₄	C ₆ H ₆	CHCl ₃	CH ₂ Cl ₂	Acetone	Acetonitrile	DMSO
TB[1]	476	485	495	491.5	490	493	506
TB[2]	542	552.5	573	568.5	565	566	587
TB[3]	557	571	602	597	587	588	633.5
TB[4]	579.1	589.7	621	610.8	594.5	591	632.6

Table S9. Measured first hyperpolarizabilities (β) of TB[1–4] in chloroform, acetonitrile (ACN) and N,N-dimethylformamide (DMF); β values referenced to solvent signals of CHCl₃, ACN and DMF respectively.² Error in HRS measurements estimated at $\pm 8\%$.

Dye	Solvent	$\beta \times 10^{-27}$ [esu]
TB[1]	CHCl ₃	n.d.
	ACN	1.06
	DMF	0.54
TB[2]	CHCl ₃	1.46
	ACN	1.58
	DMF	1.20
TB[3]	CHCl ₃	2.20
	ACN	2.60
	DMF	1.93
TB[4]	CHCl ₃	n.d.
	ACN	3.38
	DMF	n.d.

n.d. : not determined due to degradation

References

- (1) Tillotson, J. P.; Bogdanov, G.; Jucov, E. V.; Khrustalev, V. N.; Rigin, S.; Hales, J. M.; Perry, J. W.; Timofeeva, T. V. Synthesis, structure, linear and nonlinear properties of Tricyanofuran–Terminated merocyanine dyes. *J. Mol. Struct.* **2019**, *1189*, 146–154.
- (2) Campo, J.; Desmet, F.; Wenseleers, W.; Goovaerts, E. Highly sensitive setup for tunable wavelength hyper-Rayleigh scattering with parallel detection and calibration data for various solvents. *Opt. Express*, **2009**, *17*(6), 4587–4604.