

Electronic Supporting Information

"Bent-core liquid crystalline cyanostilbenes: fluorescence switching and thermochromism"

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1. Synthesis of compounds β -BC₄ and β,β -BC₄

Compounds **2** and **3** were prepared according to procedures already reported in the literature¹ and the characterization data are in agreement with those previously reported, so the experimental details are not included.

Compound 1:² Sodium hydroxide (0.25 g, 6.3 mmol) was dissolved in ethanol (5 mL), and then (4-hydroxyphenyl)acetonitrile (0.80 g, 5.9 mmol) was added. After 15 minutes under stirring, the solvent was evaporated. The obtained residue was dissolved in dimethylformamide (DMF) (30 mL) at 0 °C and 1-bromobutane (0.81 g, 0.63 mL, 5.9 mmol) was added. After stirring for 16 hours, the mixture was poured into distilled water (50 mL) and the product was extracted with hexane/ethyl acetate 1:1. The organic phase was washed with water and dried with anhydrous magnesium sulfate. The solvent was evaporated and the product purified by column chromatography using dichloromethane/hexane (7:3) as eluent (73% yield); ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.25-7.18 (m, 2H), 6.92-6.86 (m, 2H), 3.96 (t, J = 6.5 Hz, 2H), 3.68 (s, 2H), 1.81-1.71 (m, 2H), 1.54-1.44 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 158.9, 129.0, 121.5, 118.2, 115.1, 67.8, 31.2, 22.8, 19.2, 13.8; IR, ν (KBr, cm⁻¹): 2959, 2873, 2250, 1616, 1513, 1473, 1250, 1178.

Compound β -AC₄: Methyl 4-formylbenzoate (0.43 g, 2.64 mmol) and compound **1** (0.50 g, 2.64 mmol) were added to a solution of potassium hydroxide (0.30 g, 5.28 mmol) in absolute ethanol (9 mL). To increase the solubility of the products, a mixture of tetrahydrofuran/ethanol (8/16 mL) was added and the stirred mixture was heated at 50 °C for 24 hours. Afterwards, the mixture was cooled at 0 °C, hydrochloric acid (6 M) was added dropwise until the mixture was acidic. The obtained solid was filtered and recrystallized from acetic acid to give a yellow solid (72 % yield). ¹H NMR (300 MHz, DMSO-*d*₆), δ (ppm): 8.08-8.02 (m, 2H), 8.01-7.95 (m, 3H), 7.77-7.67 (m, 2H), 7.12-7.02 (m, 2H), 4.03 (t, J = 6.5 Hz, 2H), 1.82-1.63 (m, 2H), 1.54-1.33 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆), δ (ppm): 166.6, 159.8, 138.0, 131.6, 129.6, 128.9, 127.4, 125.6, 117.6, 115.0, 112.0, 67.4, 30.6, 18.6, 13.6; IR, ν (KBr, cm⁻¹): 3260-2500, 2937, 2850, 2220, 1689, 1605, 1509, 1455, 1428, 1290, 1263, 1184; MS (MALDI⁺) m/z : 344.1 [M + Na]⁺.

1. (a) Shen, D.; Pegenau, A.; Diele, S.; Wirth, I.; Tschierske, C., Molecular design of nonchiral bent-core liquid crystals with antiferroelectric properties. *Journal of the American Chemical Society* **2000**, *122*, 1593-1601, (b) Gimeno, N.; Ros, M. B.; Serrano, J. L.; de la Fuente, M. R., Hydrogen-bonded banana liquid crystals. *Angewandte Chemie-International Edition* **2004**, *43*, 5235-5238.

2. Ding, A.-X.; Jia, W.-B.; Zhang, G.-B.; Pan, J.-T.; Zhang, Y.-Y.; Yang, J.-X., Synthesis, Crystal Structure, and Photoluminescence Properties of One Novel D- π -D Type α -Cyanostilbene Derivative. *Chinese J. Struct. Chem.* **2014**, *33*, 1239-1244.

Compound β -BC₄: Compound β -AC₄ (0.20 g, 0.62 mmol), compound **2** (0.34 g, 0.54 mmol), DPTS (0.12 g, 0.41 mmol) and DCC (0.19 g, 0.91 mmol) were dissolved in dichloromethane (50 mL). After stirring at room temperature for 26 hours the reaction mixture was filtered through a pad of Celite®, the solvent was evaporated and the resulting solid was purified by column chromatography using dichloromethane/hexane 9:1 as eluent, followed by recrystallization from ethyl acetate and toluene (83% yield). **¹H NMR (300 MHz, CDCl₃), δ (ppm):** 8.36-8.26 (m, 4H), 8.21-8.13 (m, 2H), 8.03-7.95 (m, 2H), 7.73-7.60 (m, 4H), 7.52 (d, $J = 5.1$ Hz, 2H), 7.49 (s, 1H), 7.48-7.45 (m, 1H), 7.48-7.44 (m, 2H), 7.36-7.28 (m, 2H), 7.25-7.20 (m, 1H), 7.06-6.94 (m, 4H), 4.06 (t, $J = 6.6$ Hz, 2H), 4.03 (t, $J = 6.6$ Hz, 2H), 1.90-1.74 (m, 4H), 1.58-1.17 (m, 22), 1.00 (t, $J = 7.4$ Hz, 3H), 0.87 (t, $J = 6.6$ Hz, 3H); **¹³C NMR (75 MHz, CDCl₃), δ (ppm):** 164.6, 164.6, 164.5, 164.0, 160.7, 155.6, 151.5, 150.7, 142.2, 139.0, 138.3, 138.1, 132.6, 132.0, 130.8, 130.4, 130.0, 129.2, 128.5, 127.7, 127.0, 126.3, 124.9, 122.3, 122.2, 121.1, 120.8, 120.6, 117.8, 115.2, 114.6, 114.3, 68.6, 68.1, 32.1, 29.9, 29.8, 29.8, 29.8, 29.7, 29.5, 29.2, 26.1, 22.9, 19.4, 14.3, 14.0; **IR, ν (KBr, cm⁻¹):** 2920, 2850, 2220, 1743, 1726, 1603, 1510, 1475, 1254, 1158; **MS (MALDI⁺) m/z :** 935.5 [M + Na]⁺; **Elemental analysis:** Calcd. for C₆₀H₆₃NO₈: C 77.81, H 6.86, N 1.51; found C 77.61, H 7.03, N 1.59.

Compound β,β -BC₄: A mixture of β -AC₄ (0.40 g, 1.25 mmol), compound **3** (0.10 g, 0.55 mmol), DPTS (0.29 g, 1.00 mmol) and DCC (0.47 g, 2.25 mmol) were dissolved in dichloromethane (70 mL). After stirring at room temperature for 48 hours, the mixture was filtered through a pad of Celite® and the solvent was evaporated. The product was obtained by column chromatography using dichloromethane/hexane 9:1 as eluent followed by two recrystallizations from ethyl acetate (67 % yield). **¹H NMR (300 MHz, CDCl₃), δ (ppm):** 8.34-8.25 (m, 4H), 8.05-7.95 (m, 4H), 7.72-7.60 (m, 6H), 7.58-7.51 (m, 2H), 7.50 (s, 2H), 7.49-7.45 (m, 1H), 7.37-7.29 (m, 2H), 7.25-7.20 (m, 1H), 7.04-6.93 (m, 4H), 4.03 (t, $J = 6.5$ Hz, 4H), 1.87-1.73 (m, 4H), 1.60-1.41 (m, 4H), 1.00 (t, $J = 7.4$ Hz, 6H); **¹³C NMR (75 MHz, CDCl₃), δ (ppm):** 164.6, 160.7, 151.4, 150.8, 142.2, 139.1, 138.2, 138.1, 130.9, 130.8, 130.4, 130.1, 129.2, 128.5, 127.7, 126.3, 124.9, 122.2, 120.7, 120.6, 117.8, 115.2, 114.3, 68.1, 31.4, 19.4, 14.0; **IR, ν (KBr, cm⁻¹):** 2956, 2870, 2220, 1732, 1606, 1593, 1514, 1476, 1262, 1172; **MS (MALDI⁺) m/z :** 815.5 [M + Na]⁺; **Elemental analysis:** Calcd. for C₅₂H₄₄N₂O₆: C 78.77, H 5.59, N 3.53; found C 78.66, H 5.68, N 3.57.

2. NMR spectra of compounds β -BC₄ and β,β -BC₄.

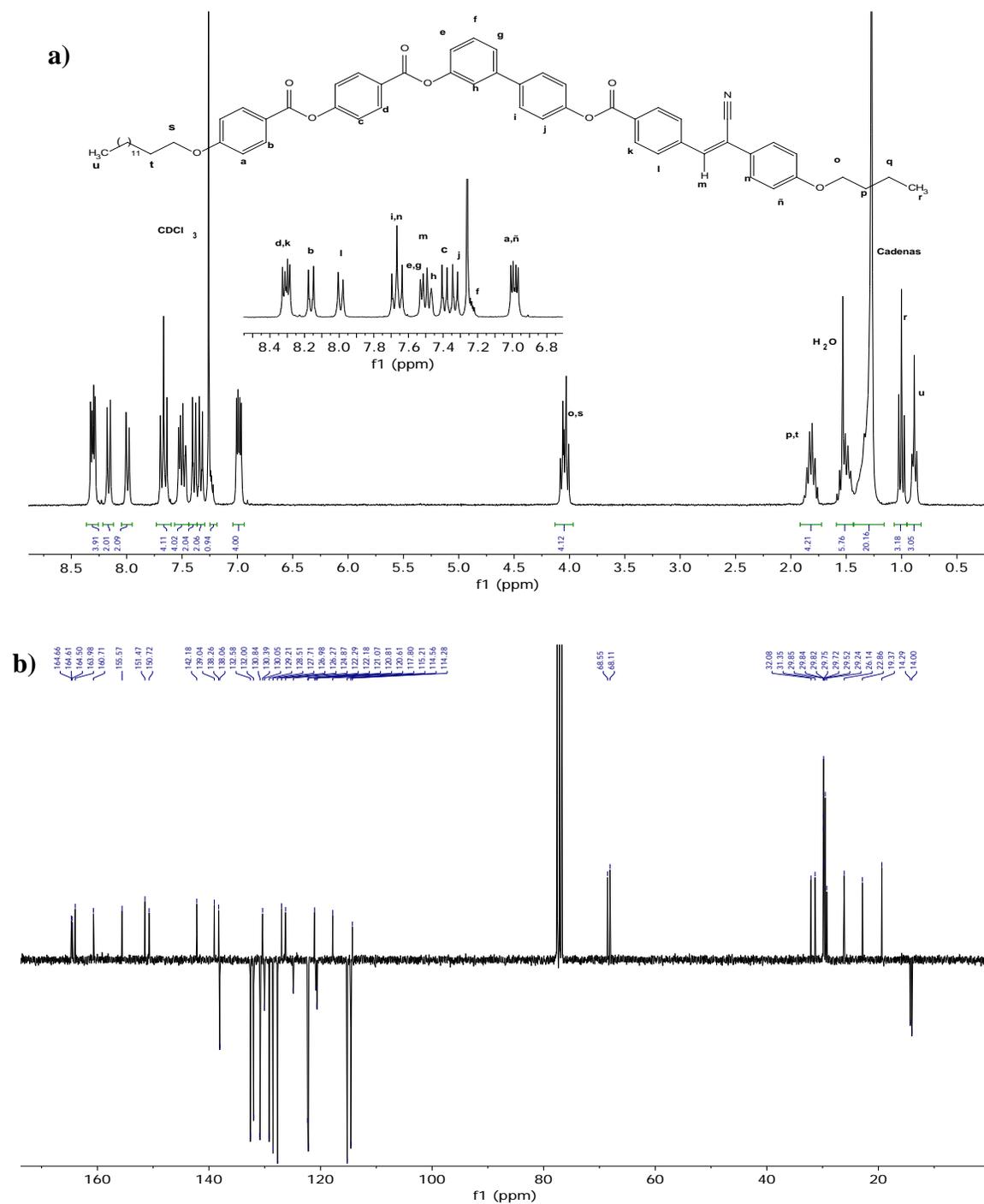
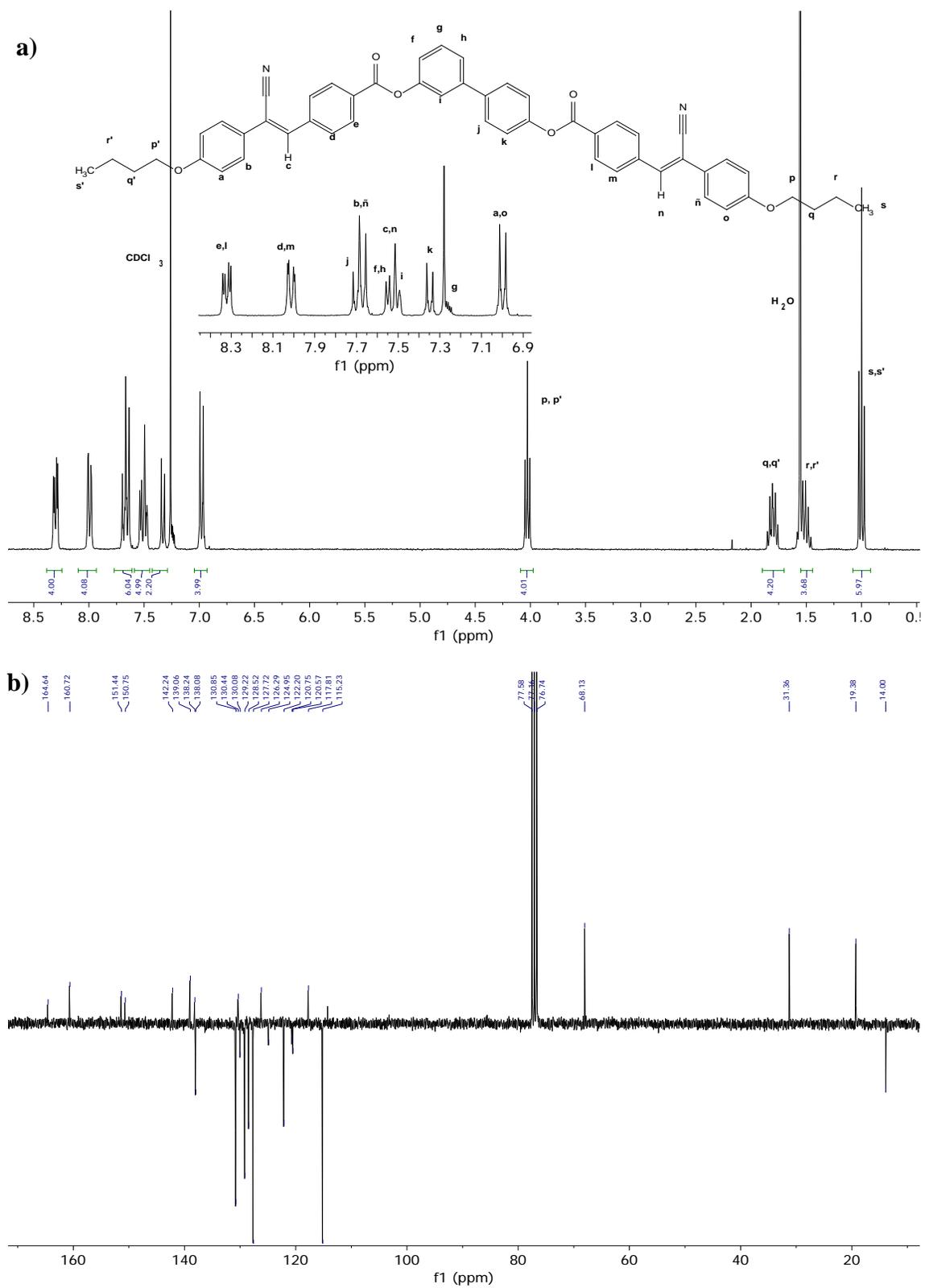


Figure S1. a) ¹H NMR (300 MHz) and b) ¹³C NMR (75 MHz), in CDCl₃ at 25 °C of β -BC₄.



3. DSC thermograms of compounds β -BC₄ and β,β -BC₄.

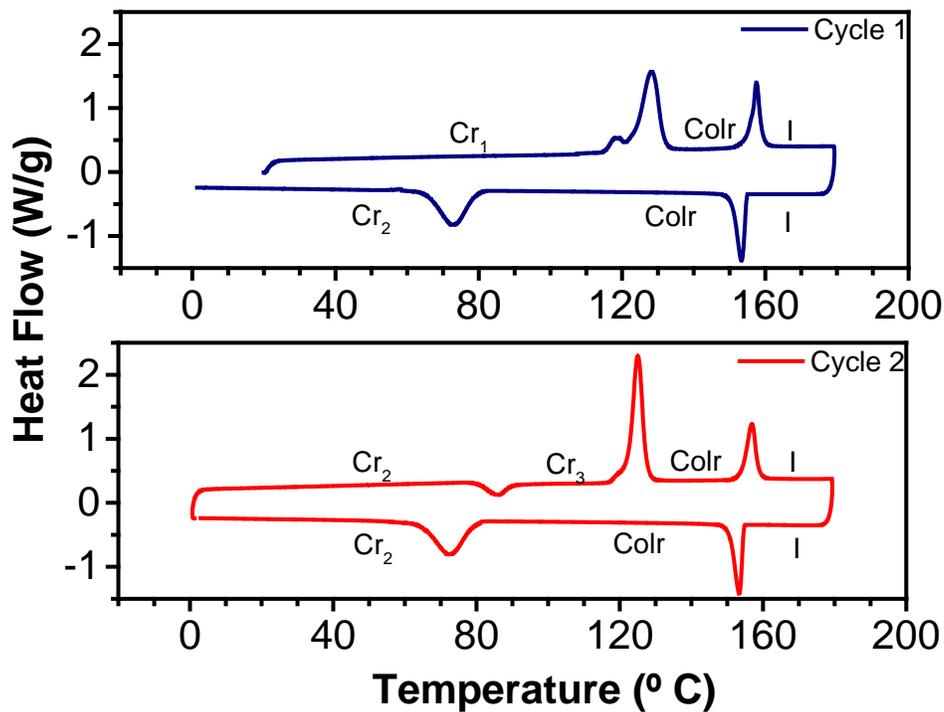


Figure S3. DSC thermograms (10 °C min⁻¹) of β -BC₄.

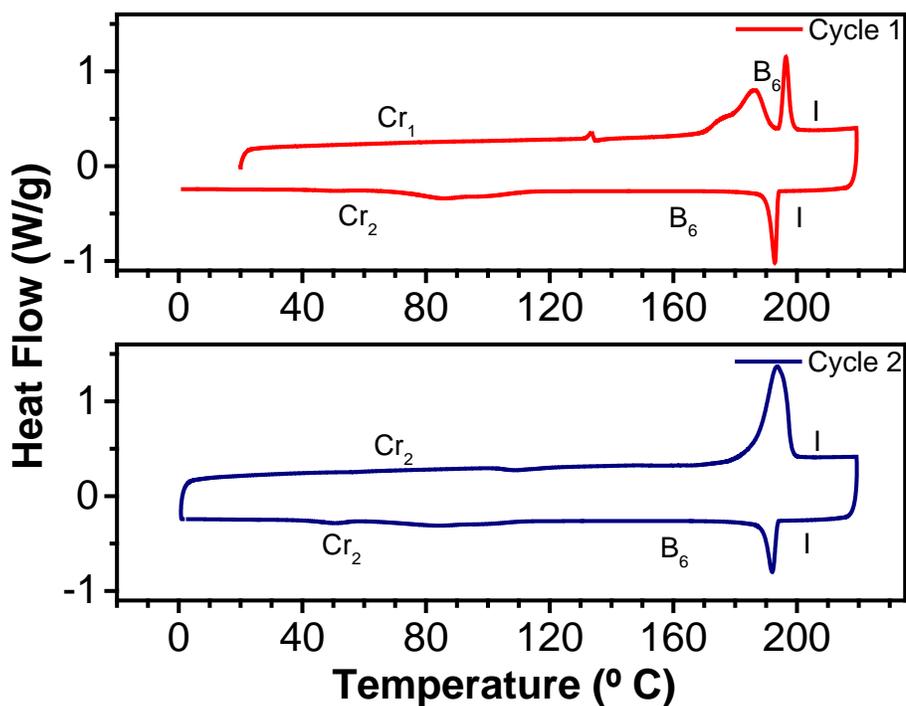


Figure S4. DSC thermograms (10 °C min⁻¹) of β,β -BC₄.

4. Photophysical Data

Table S1: Fluorescence data of the compounds; emission wavelength λ_{em} , results if the (multi)exponential fits (amplitudes A_i , lifetimes τ_i), amplitude averaged lifetimes τ , intensity averaged lifetimes $\langle\tau\rangle$, quantum yield, radiative and non-radiative rates k_r , k_{nr} .

	sample	λ_{em} (nm)	Φ_F^a	A_1	A_2	A_3	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	τ (ns)	$\langle\tau\rangle$ (ns)	k_r (s ⁻¹)	k_{nr} (s ⁻¹)
α -B	pristine ^b	497	0.03	38624	11935	4094	0.29	2.14	5.01	1.05	2.80	$1.1 \cdot 10^7$	$3.5 \cdot 10^8$
	scf	476	0.01	1570.7	11246	66450	4.21	1.05	0.28	1.23	0.47	$2.1 \cdot 10^7$	$2.1 \cdot 10^9$
	fcf (SmCP _g)	471	0.01	2867.4	12920	355.4	2.16	0.64	7.66	2.30	1.06	$9.4 \cdot 10^6$	$9.3 \cdot 10^8$
	PMMA	422	0.01	2779.3	13454	-	1.54	0.53	-	0.90	0.70	$1.4 \cdot 10^7$	$1.4 \cdot 10^9$
β -B	pristine	468	0.03	21679	3900.9	442.4	0.97	2.91	11.45	2.75	1.43	$2.1 \cdot 10^7$	$6.8 \cdot 10^8$
	scf	455	0.24	13025.4	8705	321.7	1.49	0.80	3.58	1.40	1.25	$1.9 \cdot 10^8$	$6.1 \cdot 10^8$
	fcf (SmCP _g)	457	0.04	336.62	1643.2	2651	15.33	4.37	1.33	7.26	3.43	$1.2 \cdot 10^7$	$2.8 \cdot 10^8$
	PMMA	422	0.55	25669	8343	-	1.83	0.91	-	1.70	1.60	$3.4 \cdot 10^8$	$2.8 \cdot 10^8$
β -BC ₄	pristine	495	0.72	22480.9	4461	1499.8	13.37	5.27	28.84	14.67	12.9	$5.6 \cdot 10^7$	$2.2 \cdot 10^7$
	scf	478	0.27	4732.2	5920.4	15203	18.70	7.31	1.44	13.03	5.94	$4.5 \cdot 10^7$	$1.2 \cdot 10^8$
	PMMA	423	0.55	21603.1	7145	-	1.88	0.91	-	1.74	1.66	$3.3 \cdot 10^8$	$2.7 \cdot 10^8$
α, α -B	pristine	495	0.01	7537	1145200	462.9	2.24	0.66	14.83	0.82	0.68	$1.5 \cdot 10^7$	$1.5 \cdot 10^9$
	scf	494	0.01	1208.3	5544.0	7379	7.55	2.25	0.61	3.82	1.84	$1.1 \cdot 10^7$	$5.3 \cdot 10^8$
	fcf (Col _r _g)	494	0.01	6080.2	22987	56840	6.55	1.82	0.53	3.16	1.30	$7.7 \cdot 10^6$	$7.6 \cdot 10^8$
	PMMA	431	0.01	9976.2	59746	-	1.08	0.36	-	0.60	0.46	$2.2 \cdot 10^7$	$2.2 \cdot 10^9$
β, β -B	pristine	493	0.04	304.8	1659.7	1906.5	14.17	4.37	1.47	6.75	3.71	$1.1 \cdot 10^7$	$2.6 \cdot 10^8$
	scf	470	0.15	5686.3	7971	361.2	2.63	1.02	9.82	3.10	1.90	$7.9 \cdot 10^7$	$4.5 \cdot 10^8$
	fcf (DC- SmCP _g)	478	0.12	27498	311700	6364	9.51	2.36	24.02	6.87	3.33	$3.6 \cdot 10^7$	$2.6 \cdot 10^8$
	PMMA	427	0.62	24895.3	9836	-	1.81	0.95	-	1.66	1.56	$4.0 \cdot 10^8$	$2.4 \cdot 10^8$
β, β -BC ₄	pristine	476	0.35	8470.4	12737	1486.2	8.49	2.94	25.13	11.31	6.47	$5.4 \cdot 10^7$	$1.0 \cdot 10^8$
	scf	475	0.63	7609.6	8228	1019	4.82	1.82	15.00	6.47	3.97	$1.6 \cdot 10^8$	$9.3 \cdot 10^7$
	PMMA	426	0.61	22550.9	7322	-	1.87	0.98	-	1.74	1.65	$3.7 \cdot 10^8$	$2.4 \cdot 10^8$

^a from absolute measurements in an integrating sphere. ^b pristine: powder as-obtained solid sample, scf : film from processed solid by slow cooling at $10 \text{ }^\circ\text{C min}^{-1}$, fcf : film from processed solid by fast cooling from mesophase ($0 \text{ }^\circ\text{C}$ quenching), PMMA: in PMMA matrix; SmCP_g: vitrified SmCP mesophase; Col_r_g: vitrified Col_r mesophase.

5. Quantum Chemical Calculations

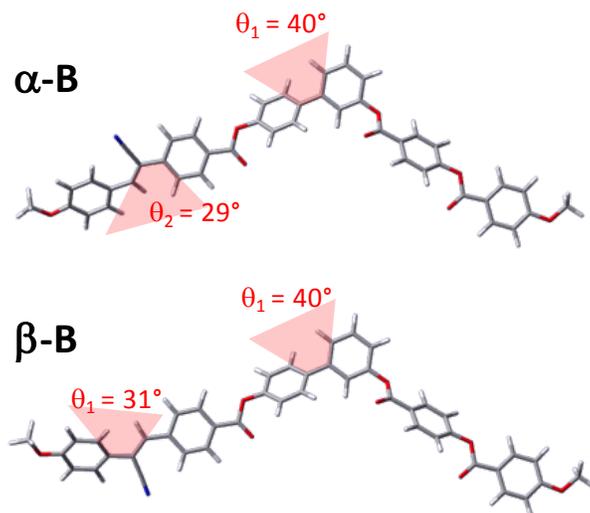


Fig. S5: Optimized geometries α -B and β -B bent-core compounds with methoxy-terminal tails.

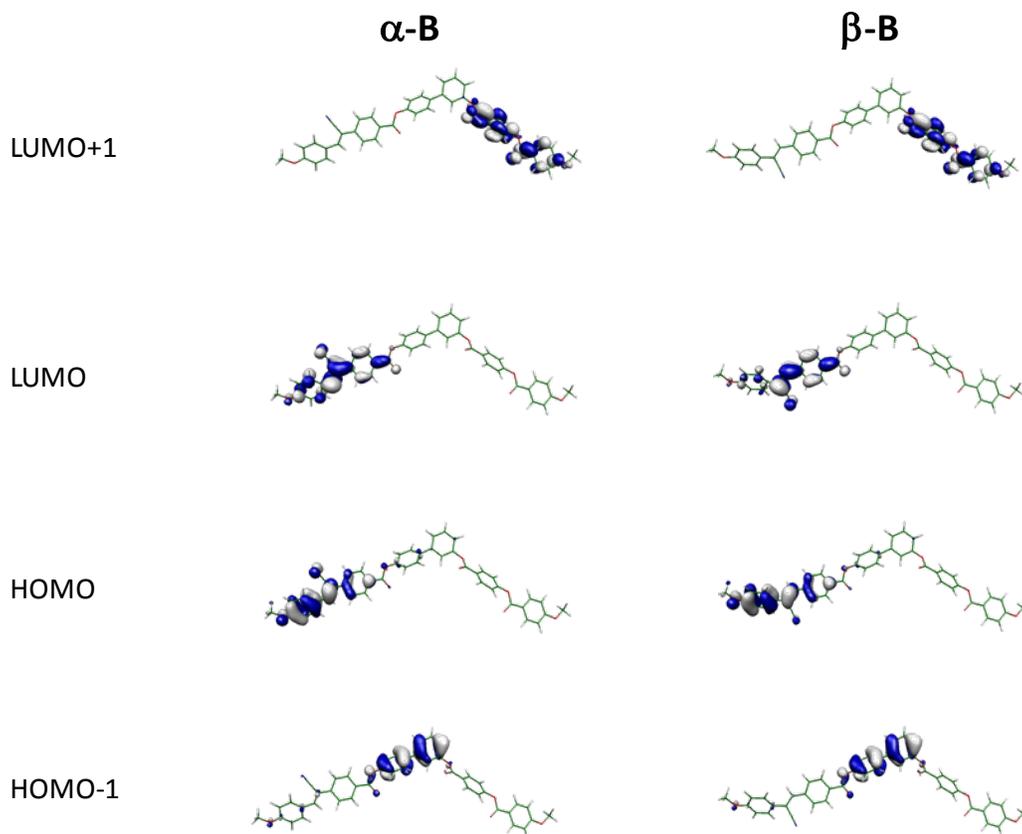


Fig. S6: Frontier MOs of α -B and β -B bent-core compounds with methoxy-terminal tails.

Table S2: Relevant electronic transition energies E with oscillator strength f and configuration interaction (CI) description (with contributions ≥ 5).

System	band	state	E / eV (λ / nm)	f	main CI configuration
α -B	A ₁	S ₁	3.37 (368)	1.09	H→L (85%) H-1→L (13%)
		S ₂	3.51 (353)	0.30	H-1→L (85%) H→L (13%)
	A ₂	S ₁₀	4.36 (284)	0.08	H-11→L (44%) H→L+2 (17%) H→L+5 (12%) H-8→L (11%)
		S ₁₁	4.41 (281)	0.90	H-2→L+1 (63%) H-3→L+1 (12%) H-1→L+2 (11%)
		S ₁₃	4.46 (278)	0.10	H-1→L+2 (63%) H-2→L+1 (15%) H-7→L (10%)
β -B	A ₁	S ₁	3.19 (389)	0.98	H→L (92%) H-1→L (6%)
		S ₂	3.32 (373)	0.07	H-1→L (92%) H→L (6%)
	A ₂	S ₁₁	4.31 (288)	0.48	H-6→L (50%) H-8→L (34%)
		S ₁₂	4.42 (281)	0.75	H-2→L+1 (79%) H-3→L+1 (12%)
α,α -B	A ₁	S ₁	3.36 (369)	1.47	H→L (58%) H-1→L (14%) H-2→L (9%) H-1→L+1 (9%) H→L+1 (8%)
		S ₂	3.42 (363)	0.68	H→L+1 (48%) H-1→L+1 (26%) H→L (14%) H-2→L+1 (7%)
		S ₃	3.47 (357)	0.20	H-1→L+1 (58%) H-2→L+1 (23%) H→L+1 (18%)
		S ₄	3.49 (355)	0.09	H-1→L (82%)

					H→L (9%) H-2→L (8%)
		S ₅	3.53 (352)	0.16	H-2→L (79%) H→L (18%)
	A ₂	S ₁₈	4.46 (278)	0.18	H-2→L+2 (65%) H-5→L (9%) H→L+2 (6%)
β,β-B	A ₁	S ₁	3.17 (391)	1.63	H→L+1 (50%) H-1→L (14%) H-1→L+1 (14%) H→L (10%)
		S ₂	3.21 (386)	0.30	H-1→L (37%) H→L (29%) H→L+1 (29%) H-1→L+1 (9%)
	A ₂	S ₁₀	4.17 (297)	0.15	H-8→L+1 (26%) H-7→L (26%) H-5→L+1 (19%) H-6→L (18%)
		S ₁₅	4.31 (288)	0.49	H-5→L+1 (41%) H-8→L+1 (32%) H-6→L (9%) H-7→L (7%)
		S ₁₆	4.33 (286)	0.19	H-6→L (44%) H-7→L (26%) H-5→L+1 (12%) H-8→L+1 (6%)