Supporting Information

Controlling spontaneous mirror symmetry breaking in cubic liquid crystalline phases by the cycloaliphatic ring size

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1. Methods

Optical and calorimetric investigations. Phase transitions were determined by polarizing microscopy (Leica DMR XP) in conjunction with a heating stage (FP 82 HT, Mettler) and controller (FP 90, Mettler) and by differential scanning calorimetry (DSC-7, Perkin Elmer) at heating/cooling rates of 10 K min^{-1} (peak temperatures). If not otherwise noted transition temperatures and –enthalpies were taken from the second heating and cooling curve. Optical investigation was carried out under equilibrium conditions between glass slides which were used without further treatment, sample thickness was ~15 μm. A full wavelength retardation plate was used to determine the sign of birefringence. Optical micrographs were taken using a Leica MC120HD camera.

X-ray diffraction.
X-ray investigations (Kristalloflex 760H, Siemens) on powder-like samples were carried out using Ni filtered CuKα radiation (15 to 30 min exposure time). The samples were prepared in the isotropic state on a glass plate and cooled (rate: 5 K·min^{-1}) to the measuring temperature. The samples were held on a temperature controlled heating stage and the diffraction patterns were recorded with a 2D detector (Vantec 500, Bruker); exposure time was 15-20 min. The sample-detector distance for the samples was 9.00 cm for WAXD and 26.90 cm for SAXD measurements. The diffraction patterns obtained were transform to 1D plots using GADDS over the full Chi range.

2. Additional data

2.1 DSC traces and transition temperatures

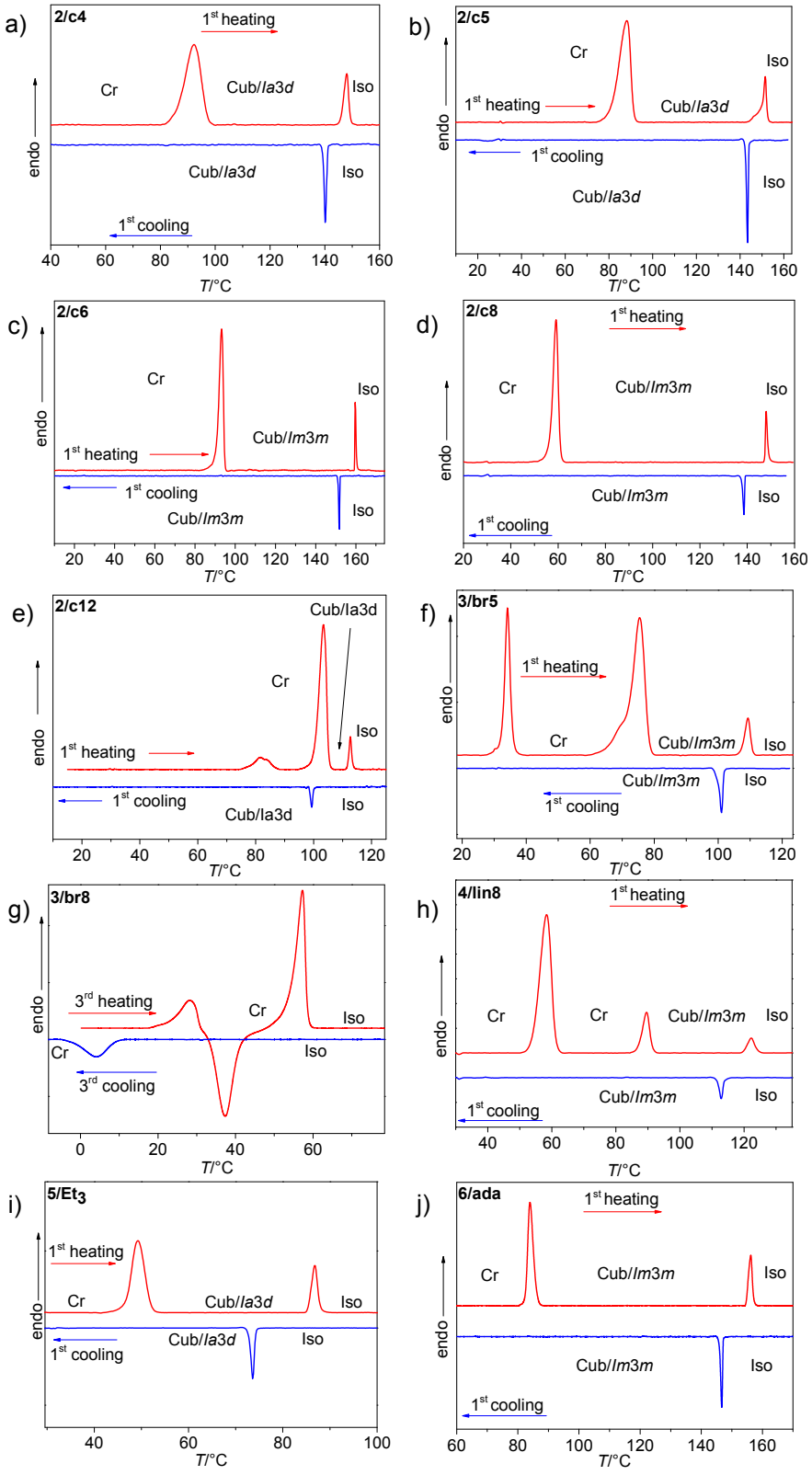
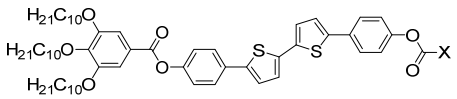


Figure S1. DSC traces (10 K·min^{-1}) of compounds **2-6**.

Table S1. Transition temperatures and –enthalpies of compounds **1-6** on heating (H) and cooling (C).



Compd.	X	T/°C [ΔH /kJ·mol^{-1}]
1/ph[S1]	phenyl	H: Cr 114 [39.7] Cub$_{bi}$/*Ia*$\bar{3}$*d* 162 [2.3] Iso C: Iso 156 [-1.7] Cub$_{bi}$/*Ia*$\bar{3}$*d* 69 [-3.8] Cr
2/c4	cyclobutyl	H: Cr 92 [17.7] Cub$_{bi}$/*Ia*$\bar{3}$*d* 148 [3.3] Iso C: Iso 141 [-2.6] Cub$_{bi}$/*Ia*$\bar{3}$*d* < 0 Cr
2/c5	cyclopentyl	H: Cr 88 [16.3] Cub$_{bi}$/*Ia*$\bar{3}$*d* 150 [3.0] Iso C: Iso 143 [-2.5] Cub$_{bi}$/*Ia*$\bar{3}$*d* < 0 Cr
2/c6	cyclohexyl	H1: Cr 93 [33.9] Cub$_{bi}$/*Im*$\bar{3}$*m*[*] 160 [4.3] Iso C1: Iso 152 [-3.0] Cub$_{bi}$/*Im*$\bar{3}$*m*[*] < 0 Cr
2/c8	cyclooctyl	H: Cr 59 [33.1] Cub$_{bi}$/*Im*$\bar{3}$*m*[*] 148 [4.5] Iso C: Iso 139 [-2.9] Cub$_{bi}$/*Im*$\bar{3}$*m*[*] < 0 Cr
2/c12	cyclododecyl	H: Cr 103 [36.6] Cub$_{bi}$/*Ia*$\bar{3}$*d* 113 [2.9] Iso C: Iso 99 [-1.5] Cub$_{bi}$/*Ia*$\bar{3}$*d* < 0 Cr
3/br5	3-pentyl	H: Cr 75 [29.8] Cub$_{bi}$/*Im*3*m*[*] 109 [3.4] Iso C: Iso 101 [-2.6] Cub$_{bi}$/*Im*3*m*[*] < 0 Cr
3/br8	4-octyl	H: Cr 57 [43.7] Iso C: Iso 4 [-13.9] Cr
4/lin8	-octyl	H: Cr 90 [5.7] Cub$_{bi}$/*Im*3*m*[*] 122 [1.9] Iso C: Iso 113 [-1.6] Cub$_{bi}$/*Im*3*m*[*] < 0 Cr
5/Et$_3$	2,2-(diethyl)propyl	H: Cr 49 [8.9] Cub$_{bi}$/*Ia*$\bar{3}$*d* 87 [2.7] Iso C: Iso 74 [-1.7] Cub$_{bi}$/*Ia*$\bar{3}$*d* < 0 Cr
6/ada	1-adamantyl	H1: Cr 84 [11.2] Cub$_{bi}$/*Im*3*m*[*] 156 [3.6] Iso C1: Iso 147 [-2.7] Cub$_{bi}$/*Im*3*m*[*] < 0 Cr

2.2 XRD data

Table S2. SAXS data of Cub$_{bi}$/*Ia*$\bar{3}$*d* phases of compounds **2/c4**, **2/c5**, **2/c12**, **5/Et$_3$**.

Compd.	(*hkl*)	d_{obs} – spacing/nm	d_{calc} – spacing/nm	$d_{obs} - d_{calc}$	a_{cub}/nm (T/°C)
2/c4	(211)	4.23	4.23	0.00	10.35 (130)
	(220)	3.73	3.66	0.07	
2/c5	(211)	4.28	4.28	0.00	10.49 (135)
	(220)	3.73	3.71	0.02	
2/c12	(211)	3.84	3.84	0.00	9.40 (108)
	(220)	3.34	3.33	0.01	
5/Et$_3$	(211)	3.61	3.61	0.00	8.85 (70)
	(220)	3.15	3.13	0.02	

Table S3. SAXS data of $Cub_{bi}/Im3m^{[*]}$ phases of compounds **2/c6**, **2/c8**, **3/br5**, **4/lin8** and **6/ada**.

Compd.	(hkl)	d_{obs} – spacing/nm	d_{calc} – spacing/nm	$d_{obs} - d_{calc}$	a_{cub}/nm (T/°C)
2/c6	(321)	4.18	4.18	0.00	15.64 (125)
	(400)	3.87	3.91	0.04	
	(420)	3.53	3.50	0.04	
	(422)	3.14	3.19	0.05	
2/c8	(321)	4.11	4.11	0.00	15.38 (100)
	(400)	3.83	3.85	0.02	
	(420)	3.44	3.44	0.00	
2/c8	(321)	4.07	4.07	0.00	15.24 (140)
	(400)	3.80	3.81	0.01	
	(420)	3.45	3.41	0.04	
3/br5	(321)	3.96	3.96	0.00	14.81 (90)
	(400)	3.67	3.70	0.03	
	(420)	3.36	3.31	0.05	
4/lin8	(321)	4.28	4.28	0.00	16.01 (110)
	(400)	4.03	4.00	0.03	
	(420)	3.57	3.58	0.01	
6/ada	(321)	4.04	4.04	0.00	15.13 (120)
	(400)	3.76	3.78	0.03	
	(420)	3.41	3.38	0.03	

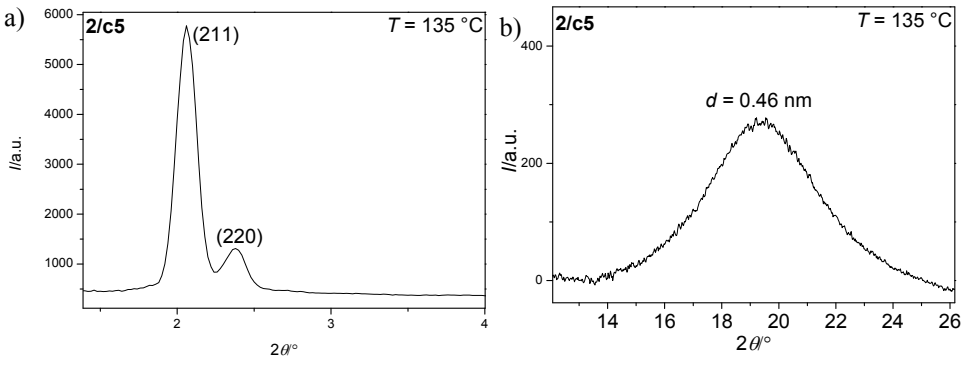


Figure S2. XRD data of the $Cub_{bi}/Ia3d$ phase of compound **2/c5**, a) 2θ scan of the small angle area, as inset powder-like diffraction pattern with indexed reflexes, b) 2θ scan of the wide angle area.

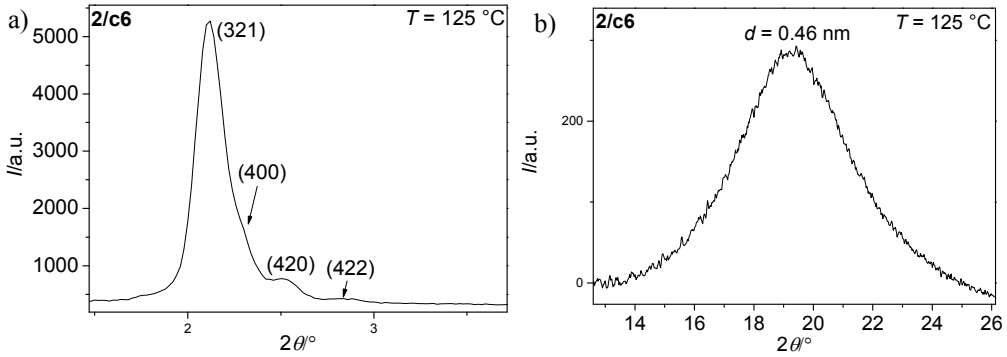


Figure S3. XRD data of the $Cub_{bi}/Im3m^{[*]}$ phase of compound **2/c6**, a) 2θ scan of the small angle area, as inset powder-like diffraction pattern with indexed reflexes, b) 2θ scan of the wide angle area.

Table S4. Structural data of the investigated cubic phases.[a]

Compd.	Phase	a_{cub}/nm	V_{cell}/nm^3	V_{mol}/nm^3	n_{cell}[b]	n_{rod}[c]	d_{node}/nm	n_{strat}[d]	Φ/°
1/ph	Cub/$Ia\bar{3}d$	11.0	1331	1.46	814	34	3.89	3.9	8.2
2/c4	Cub/$Ia\bar{3}d$	10.4	1125	1.44	698	29	3.68	3.5	8.6
2/c5	Cub/$Ia\bar{3}d$	10.5	1158	1.46	708	30	3.71	3.6	8.5
2/c6	$Cub_{bi}/Im3m^{[*]}$	15.6	3796	1.49	2275	-	-	-	-
2/c8	$Cub_{bi}/Im3m^{[*]}$	15.4	3652	1.54	1991	-	-	-	-
2/c12	Cub/$Ia\bar{3}d$	9.4	831	1.64	452	19	3.32	2.6	9.5
3/br5	$Cub_{bi}/Im3m^{[*]}$	14.8	3242	1.48	1956	-	-	-	-
4/lin8	$Cub_{bi}/Im3m^{[*]}$	16.0	4096	1.55	2360	-	-	-	-
5/Et$_3$	Cub/$Ia\bar{3}d$	8.9	693	1.53	405	17	3.13	2.4	10.1
6/ada	$Cub_{bi}/Im3m^{[*]}$	15.1	3443	1.56	1971	-	-	-	-

[a] Abbreviations:. n_{cell} number of molecules in a unit cell; $V_{cell} = a_{cub}^3$ = volume of the unit cell; V_{mol} = molecular volume as calculated with the crystal volume inctrements of Immirzi[S2], Φ = twist angle between adjacent molecules in the networks of the $Ia\bar{3}d$- phases; [b]calculated according to 0.893 V_{cell}/V_{mol}, where the factor 0.893 is a correction for the different packing density in the crystalline and the LC state; $\Phi(Ia\bar{3}d)$ = 70.5°/[0.354a_{cub}/0.45nm]; [c] $n_{rod} = n_{cell}/24$ = number of molecules in each column segment between two junctions; [d] n_{strat} = number of molecules organized side by side in each 0.45 nm high stratum of the column segments, calculated from the distance between the junctions $d_{node} = a_{cub}/(2\sqrt{2})$ and an assumed height of each stratum of h = 0.45 nm, according to: $n_{strat} = n_{rod}/(d_{node}/h)$

Table S5. Structural data of the investigated $Cub_{bi}/Ia3d$ phases.[a]

Compd.	Phase	a_{cub}/nm	d/nm	L_{mol}/nm	d/L_{mol}
1/ph	Cub/$Ia\bar{3}d$	11.0	4.8	4.4	1.09
2/c4	Cub/$Ia\bar{3}d$	10.4	4.5	4.3	1.05
2/c5	Cub/$Ia\bar{3}d$	10.5	4.5	4.4	1.02
2/c12	Cub/$Ia\bar{3}d$	9.4	4.1	4.7	0.87
5/Et$_3$	Cub/$Ia\bar{3}d$	8.9	3.8	4.4	0.86

[a] d = "layer spacing" along the body diagonal of the unit cell: $d = \sqrt{3}a_{cub}/4$, see ref.[S3]; L_{mol} was determined with space filling CPK models assuming the most stretched molecular conformation.

2.3 Additional textures

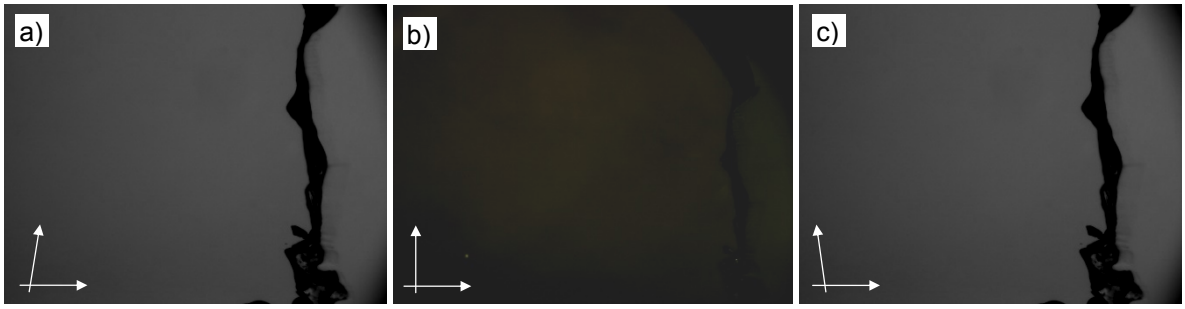


Figure S4. *Ia*$\bar{3}$*d* phase of **5/Et$_3$** at 52 °C as observed between b) crossed polarizers polarizers and being slightly uncrossed either in a) anticlockwise or c) clockwise direction; at the right there is a phase boundary to air.

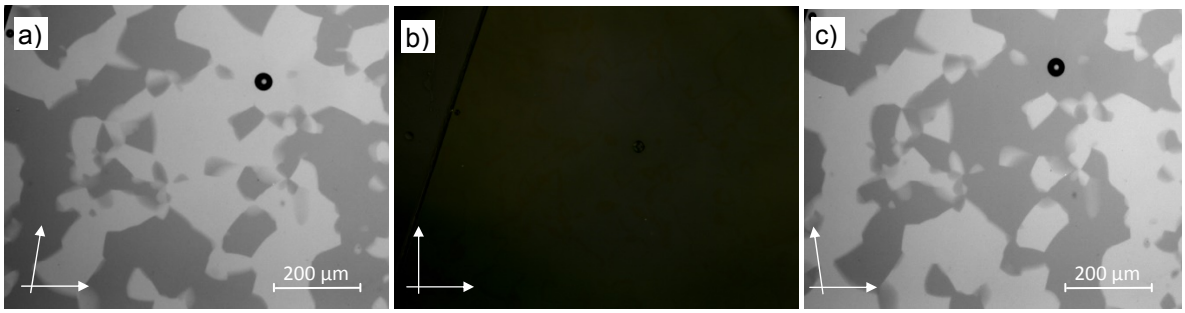


Figure S5. *Im*3*m*$^{[*]}$ phase of **3/br5** at 100 °C as observed between b) crossed polarizers polarizers and being slightly uncrossed either in a) anticlockwise or c) clockwise direction.

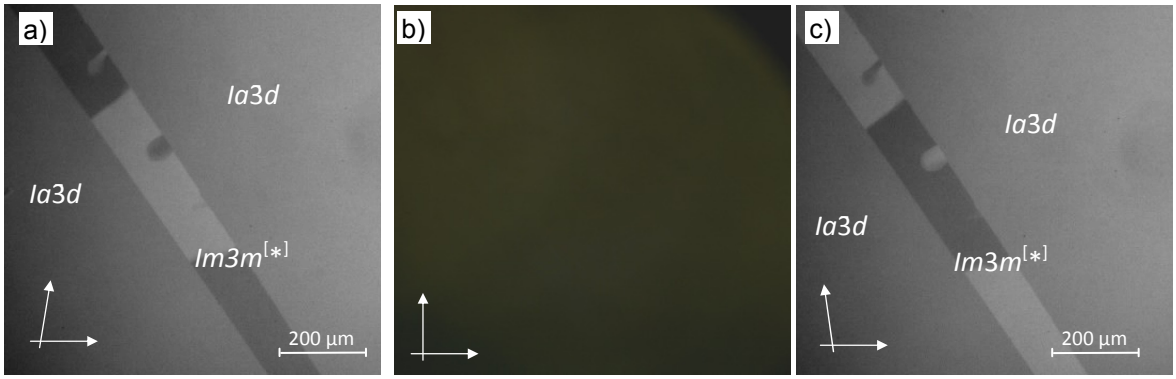


Figure S6. Chiral domains of the *Im*3*m*$^{[*]}$ phase, induced between the achiral *Ia*$\bar{3}$*d* phases of compounds **2/c4** (top/right) and **5/Et$_3$** (bottom/left) at T = 124 °C; the *Im*3*m*$^{[*]}$ phase appears at 125 °C on cooling and disappears at T = 141 °C on heating.

2.4 Structural models

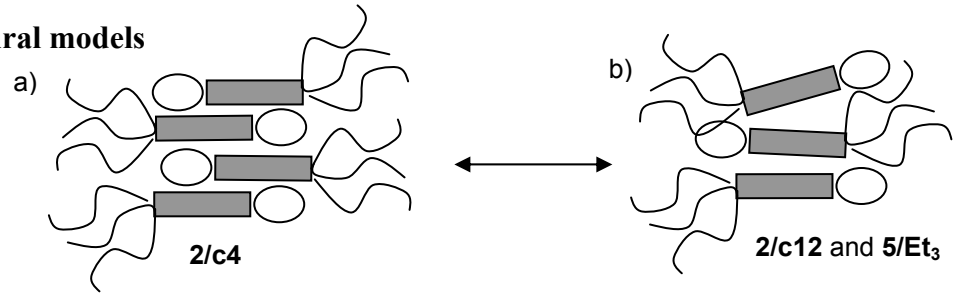


Figure S7. Transition between a) the intercatated structure where the apexes are mixed with the polayromatic cores and b) the fully segregated structure of aromatic cores with apexes

mixed with the alkyl chains (see Table S5 for the calculated d/L_{mol} ratios). The decreasing intercalation of apex and polyaromatic rods with growing apex size indicates a distinct reversed behaviour of these compounds with cycloaliphatic apex if compared with the DABHs having only linear alkyl chains.[S3]

3. Synthesis and analytical data

3.1 General

Unless otherwise noted, all starting materials were purchased from commercial sources and were used without further purification. Column chromatography was performed with silica gel 60 (63-200 μm, Fluka). Determination of structures and purity of intermediates and products was obtained by NMR spectroscopy (VARIAN Gemini 2000 and Unity Inova 500, all spectra were recorded at 27 °C). Microanalyses were performed using a CARLO Erba-CHNO 1102 elemental analyzer. The purity of all products was checked with thin layer chromatography (silicagel 60 F_{254}, Merck). $CHCl_3$ and $CHCl_3$/*n*-hexane mixtures were used as eluents and the spots were detected by UV radiation. Nonanoic acid, 2-ethylbutyric acid, 1-adamantanecarboxylic acid, the cycloalkanecarboxylic acids, exept the cyclooctanecarboxylic acid, were purchased from Sigma Aldrich. 2,2-diethylbutyric acid and cyclooctanecarboxlic acid was purchased from Enamine. The phenol **1/OH** was prepared according to reported standard procedures.[S1,S4]

3.2 Procedures

Procedure 1: The appropriate carboxylic acid (1.25 equ) and $SOCl_2$ (2 ml/mmol) were refluxed for 30 minutes. $SOCl_2$ was removed under vacuum and dry pyridine (30 ml/mmol) and **1/OH** (1.0 equ) were added and the resulting mixture was stirred at room temperature overnight. The solution was poured into ice/water and the resulting crude solid product was filtered off, dried and was purified by column chromatography and crystallization.

Procedure 2: Phenol **1/OH** (1 equ), the appropriate carboxylic acid (1.25 equ), DMAP (catalytic amount) and DCC (1.25 equ) were stirred in dry CH_2Cl_2 (25 ml) at room temperature overnight. The reaction mixture was filtered through a short column of silica gel (eluent: CH_2Cl_2) and the solvent was removed under reduced pressure. The obtained crude product was purified by column chromatography and repeated crystallization.

2-Propylhexanoic acid[S5,S6,S7] was synthesized from diethyl *n*-butylmalonate (5.0 g, 0.023 mol), 1-bromopropane (4.3 g, 0.035 mol) and NaH (1.4 g, 0.058 mol) to give diethyl butylpropyl malonate (5.2 g, 0.020 mol). In a next deethoxycarbonylation step with LiCl (3 equ) and H_2O (1 equ) in DMSO the intermediate ethyl 2-propylhexanate was obtained after a purification of the crude product by column chromatography (eluent: $CHCl_3$/*n*-hexane 1/1, v/v). After the saponification with solved NaOH in water (0.1 g/ml) and ethanol the solution was acidified with concentrated hydrochloric acid and extracted with diethyl ether. The organic solvent was removed under reduced pressure and the product was obtained as a colourless liquid. Yield 1.0 g (6.43 mmol, 28%); $C_9H_{18}O_2$; M = 158.24 g/mol; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.37 (m, 1H, COCH), 1.68–1.58 (m, 2H, CH_2), 1.52–1.41 (m, 2H, CH_2), 1.39–1.24 (m, 6H, CH_2), 0.94–0.86 (m, 6H, CH_3).

3.3 Compounds 2-6

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5´-(4-cyclobutanoyloxyphenyl)-2,2´-bithiophene (2/c4)

Prepared according to **procedure 2** from **1/OH** (74 mg, 0.08 mmol), cyclobutanecarboxylic acid (10 mg, 0.10 mmol), DMAP (1 mg, 0.01 mmol) and DCC (21 mg, 0.10 mmol). The obtained crude product was purified by column chromatography (eluent: $CHCl_3$/*n*-hexane 3/1, v/v) and repeated crystallization from THF/MeOH; yield 73 mg (0.073 mmol, 91%); %); pale yellow solid; $C_{62}H_{84}O_7S_2$; *M* = 1005.46 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.60 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.41 (s, 2H, Ar-H), 7.25–7.21 (m, 3H, Ar-H + Th-H), 7.20 (d, ^3J = 3.8 Hz, 1H, Th-H), 7.18–7.16 (m, 2H, Th-H), 7.12 (d, ^3J = 8.7 Hz, 2H, Ar-H), 4.09–4.02 (m, 6H, OC*H*$_2$CH$_2$), 3.46–3.35 (m, 1H, (O)CCH), 2.51–2.40 (m, 2H, Cb-CH$_2$), 2.39–2.29 (m, 2H, Cb-CH$_2$), 2.14–1.95 (m, 2H, Cb-CH$_2$), 1.89–1.79 (m, 4H, OCH$_2$C*H*$_2$), 1.79–1.72 (m, 2H, OCH$_2$C*H*$_2$), 1.52–1.44 (m, 6H, CH$_2$), 1.41–1.20 (m, 36H, CH$_2$), 0.93–0.84 (m, 9H, CH$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.8, 164.9 (C=O), 153.0, 150.5, 150.3, 143.1, 142.3, 142.2, 136.8, 136.7, 131.8, 131.7, 126.7, 126.6, 124.6, 124.0, 124.0, 123.7, 122.3, 122.1, 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 38.14 ((O)C*C*H), 31.9, 31.9, 30.3, 29.7, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 26.1, 26.0, 25.3, 22.7, 22.7, 18.4 (CH$_2$), 14.1 (CH$_3$); elemental analysis: calc for $C_{62}H_{84}O_7S_2$: C 74.06%, H 8.42%; found C 73.88%, H 8.39%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5´-(4-cyclopentanoyloxyphenyl)-2,2´-bithiophene (2/c5)

Prepared according to **procedure 2** from **1/OH** (66 mg, 0.071 mmol), cyclopentanecarboxylic acid (10 mg, 0.089 mmol), DMAP (1 mg, 0.01 mmol) and DCC (18 mg, 0.089 mmol). The obtained crude product was purified by column chromatography (eluent: $CHCl_3$/*n*-hexane 3/1, v/v) and repeated crystallization from THF/MeOH; yield 54 mg (0.053 mmol, 75%); pale yellow solid; $C_{63}H_{86}O_7S_2$; *M* = 1019.48 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, ^3J = 8.6 Hz, 2H, Ar-H), 7.60 (d, ^3J = 8.6 Hz, 2H, Ar-H), 7.41 (s, 2H, Ar-H), 7.25–7.21 (m, 3H, Ar-H + Th-H), 7.20 (d, ^3J = 3.8 Hz, 1H, Th-H), 7.18–7.16 (m, 2H, Th-H), 7.11 (d, ^3J = 8.6 Hz, 2H, Ar-H), 4.09–4.03 (m, 6H, OC*H*$_2$CH$_2$), 3.05–2.96 (m, 1H, (O)CCH), 2.09–1.92 (m, 4H, Cp-CH$_2$), 1.88–1.60 (m, 10H, OCH$_2$C*H*$_2$ + Cp-CH$_2$), 1.53–1.44 (m, 6H, CH$_2$), 1.41–1.21 (m, 36H, CH$_2$), 0.92–0.85 (m, 9H, CH$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 164.9 (C=O), 153.0, 150.5, 150.4, 143.1, 142.3, 142.2, 136.8, 136.7, 131.8, 131.6, 126.7, 126.6, 124.5, 124.0, 123.9, 123.7, 122.3, 122.1, 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 43.9 ((O)C*C*H), 31.9, 31.9, 30.3, 30.1, 29.7, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 26.1, 26.0, 25.9, 22.7, 22.7 (CH$_2$), 14.1 (CH$_3$); elemental analysis: calc for $C_{63}H_{86}O_7S_2$: C 74.22%, H 8.50%; found C 74.24%, H 8.45%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5´-(4-cyclohexanoyloxyphenyl)-2,2´-bithiophene (2/c6)

Prepared according to **procedure 1** from **1/OH** (93 mg, 0.101 mmol) and cyclohexanecarboxylic acid (16 mg, 0.126 mmol). The obtained crude product was purified by column chromatography (eluent: $CHCl_3$/*n*-hexane 4/1, v/v) and repeated crystallization from THF/EtOH; yield 81 mg (0.078 mmol, 78%); pale yellow solid; *M* = 1033.51 g/mol; ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.65 (d, ^3J = 8.6 Hz, 2H, Ar-H), 7.60 (d, ^3J = 8.6 Hz, 2H, Ar-H), 7.42 (s, 2H, Ar-H), 7.25–7.15 (m, 6H, Ar-H + Th-H), 7.10 (d, ^3J = 8.5 Hz, 2H, Ar-H), 4.07 (t, ^3J = 6.5 Hz, 2H, OCH_2CH$_2$), 4.06 (t, ^3J = 6.5 Hz, 4H, OCH_2CH$_2$), 2.58 (tt, $^3J_{H(ax),H(ax)}$ = 11.0 Hz, $^3J_{H(ax),H(eq)}$ = 3.8 Hz, 1H, (O)CCH), 2.08 (m, 2H, Cy-CH$_2$), 1.89–1.54 (m, 12H, OCH$_2$CH_2 + Cy-CH$_2$), 1.51–1.46 (m, 6H, CH$_2$), 1.43–1.21 (br, 38H, CH$_2$ + Cy-CH$_2$), 0.90–0.86 (m, 9H, CH$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.4, 165.0 (C=O), 153.0, 150.5, 150.4, 143.1, 142.3, 142.3, 136.8, 136.7, 131.8, 131.6, 126.7, 126.6, 124.6, 124.0, 124.0, 123.7, 122.3, 122.1, 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 43.2 1, 31.9, 30.3, 29.7, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 29.0, 26.1, 26.1, 25.7, 25.4, 22.7, 22.7 (CH$_2$), 14.1 (CH$_3$); elemental analysis: calc for $C_{64}H_{88}O_7S_2$: C 74.38%, H 8.58%; found: C 74.59%, H 8.61%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5´-[4-(cyclooctanoyloxy)phenyl]-2,2´-bithiophene (2/c8)

Prepared according to **procedure 1** from **1/OH** (101 mg, 0.109 mmol) and cyclooctanecarboxylic acid (21 mg, 0.137 mmol). The obtained crude product was purified by column chromatography (eluent: $CHCl_3$/*n*-hexane 3/1, v/v) and repeated crystallization from THF/MeOH; yield 83 mg (0.078 mmol, 72%); pale yellow solid; $C_{66}H_{92}O_7S_2$ *M* = 1061.56 g/mol; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.60 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.42 (s, 2H, Ar-H), 7.25–7.21 (m, 3H, Ar-H + Th-H), 7.20 (d, ^3J = 3.8 Hz, 1H, Th-H), 7.18–7.16 (m, 2H, Th-H), 7.10 (d, ^3J = 8.7 Hz, 2H, Ar-H), 4.09–4.03 (m, 6H, OCH_2CH$_2$), 2.83–2.76 (m, 1H, (O)CCH), 2.11–2.03 (m, 2H, Co-CH$_2$), 1.91–1.73 (m, 10H, OCH$_2$CH_2 + Co-CH$_2$), 1.68–1.55 (m, 8H, Co-CH$_2$), 1.53–1.46 (m, 6H, CH$_2$), 1.40–1.23 (m, 36H, CH$_2$), 0.91–0.86 (m, 9H, CH$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 164.9 (C=O), 153.0, 150.5, 150.4, 143.1, 142.3, 142.2, 136.8, 136.7, 131.8, 131.6, 126.7, 126.6, 124.5, 124.0, 123.9, 123.7, 122.3, 122.1, 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 43.6 ((O)C*C*H), 31.9, 31.9, 30.3, 29.7, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 28.7, 26.8, 26.1, 26.1, 26.0, 25.2, 22.7, 22.7 (CH$_2$), 14.1 (CH$_3$); elemental analysis; calc for $C_{66}H_{92}O_7S_2$: C 74.67%, H 8.74%; found C 74.43%, H 8.73%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5´-[4-(cyclododecanoyloxy)phenyl]-2,2´-bithiophene (2/c12)

Prepared according to **procedure 1** from **1/OH** (94 mg, 0.102 mmol) and cyclododecanecarboxylic acid (27 mg, 0.127 mmol); The obtained crude product was purified by column chromatography (eluent: $CHCl_3$/*n*-hexane 4/1, v/v) and repeated crystallization from THF/MeOH; yield 85 mg (0.076 mmol, 75%); pale yellow solid; $C_{70}H_{100}O_7S_2$ *M* = 1117.67 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, ^3J = 8.5 Hz, 2H, Ar-H), 7.60 (d, ^3J = 8.4 Hz, 2H, Ar-H), 7.41 (s, 2H, Ar-H), 7.25–7.19 (m, 4H, Ar-H + Th-H), 7.19–7.15 (m, 2H, Th-H), 7.10 (d, ^3J = 8.4 Hz, 2H, Ar-H), 4.11–4.01 (m, 6H, OCH_2CH$_2$), 2.81–2.72 (m, 1H, (O)CCH), 1.88–1.72 (m, 10H, OCH$_2$CH_2 + Cd-CH$_2$), 1.52–1.21 (m, 60H, CH$_2$ + Cd-CH$_2$), 0.94–0.82 (m, 9H, CH$_3$); ^{13}C NMR (100 MHz, cdcl$_3$) δ 175.1, 164.9 (C=O), 153.0, 150.5, 150.4, 143.1, 142.3, 136.8, 136.7, 131.8, 131.6, 126.7, 126.6, 124.5, 124.0, 123.9, 123.7, 122.3, 122.1, 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 40.7 ((O)C*C*H), 31.9, 31.9, 30.3, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 29.3, 26.6, 26.1, 26.0, 23.8, 23.6, 23.5, 23.5, 22.7, 22.7, 22.4

(CH_2), 14.1(CH_3); elemental analysis; calc for $C_{70}H_{100}O_7S_2$: C 75.22%, H 9.02%, found C 74.94%, H 8.98%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5´-[4-(2-ethylbutanoyloxy)phenyl]-2,2´-bithiophene 3/br5

Prepared according to **procedure 2** from **1/OH** (77 mg, 0.083 mmol) and 2-ethylbutyric acid (12 mg, 0.104 mmol), DMAP (1 mg, 0.01 mmol) and DCC (22 mg, 0.104 mmol). The obtained crude product was purified by column chromatography (eluent: $CHCl_3$/*n*-hexane 4/1, v/v) and repeated crystallization from THF/MeOH; yield 56 mg (0.055 mmol, 66%); pale yellow solid; $C_{63}H_{88}O_7S_2$; M = 1021.50 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.61 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.42 (s, 2H, Ar-H), 7.25–7.22 (m, 3H, Ar-H + Th-H), 7.20 (d, ^3J = 3.8 Hz, 1H, Th-H), 7.19–7.16 (m, 2H, Th-H), 7.11 (d, ^3J = 8.7 Hz, 2H, Ar-H), 4.09–4.03 (m, 6H, OCH_2CH$_2$), 2.52–2.44 (m, 1H, (O)CCH), 1.88–1.62 (m, 10H, OCH$_2$CH_2 + CHCH_2CH$_3$), 1.53–1.44 (m, 6H, CH$_2$), 1.41–1.22 (m, 36H, CH$_2$), 1.04 (t, ^3J = 7.4 Hz, 6H, CHCH$_2$CH_3), 0.92–0.85 (m, 9H, CH$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.6, 164.9 (C=O), 153.0, 150.5, 150.3, 143.1, 142.3, 142.3, 136.8, 136.7, 131.8, 131.7, 126.7, 126.6, 124.6, 124.0, 124.0, 123.7, 122.3, 122.2, 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 49.0 (O)C*C*H), 31.9, 31.9, 30.3, 29.7, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 26.1, 26.0, 25.1, 22.7, 22.7 (CH$_2$), 14.1, 11.8 (CH$_3$); elemental analysis; calc for $C_{63}H_{88}O_7S_2$: C 74.07%, H 8.68%; found C 74.02%, H 8.59%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5´-[4-(2-propylhexanoyloxy)phenyl]-2,2´-bithiophene (3/br8)

Prepared according to **procedure 2** from **1/OH** (70 mg, 0.076 mmol), 2-propylhexanoic acid (15 mg, 0.095 mmol), DMAP (1 mg, 0.01 mmol) and DCC (20 mg, 0.095 mmol). The obtained crude product was purified by column chromatography (eluent: $CHCl_3$/*n*-hexane 4/1, v/v) and repeated crystallization from THF/MeOH; yield 65 mg (0.061 mmol, 81%); pale yellow solid; $C_{66}H_{94}O_7S_2$; M = 1063.58 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.60 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.41 (s, 2H, Ar-H), 7.25–7.21 (m, 3H, Ar-H + Th-H), 7.20 (d, ^3J = 3.8 Hz, 1H, Th-H), 7.19–7.16 (m, 2H, Th-H), 7.10 (d, ^3J = 8.7 Hz, 2H, Ar-H), 4.09–4.03 (m, 6H, OCH_2CH$_2$), 2.65–2.56 (m, 1H, (O)CC*H*), 1.88–1.72 (m, 4H, OCH$_2$CH_2), 1.65–1.55 (m, 2H, CH$_2$), 1.52–1.45 (m, 4H, CH$_2$), 1.45–1.20 (m, 46H, CH$_2$), 0.98 (t, ^3J = 7.3 Hz, 3H, CH$_3$), 0.94 (t, ^3J = 7.1 Hz, 3H, CH$_3$), 0.91–0.85 (m, 9H, CH$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.9, 164.9 (C=O), 153.0, 150.5, 150.3, 143.1, 142.3, 142.3, 136.8, 136.7, 131.8, 131.7, 126.7, 126.6, 124.6, 124.0, 124.0, 123.7, 122.3, 122.1, 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 45.6 ((O)C*C*H), 34.6, 32.2, 31.9, 31.9, 30.3, 29.7, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 26.1, 26.0, 22.7, 22.7, 22.6, 20.7 (CH$_2$), 14.1, 14.0, 14.0 (CH$_3$); elemental analysis; calc for $C_{66}H_{94}O_7S_2$: C 74.53%, H 8.91%; found C 74.39%, H 8.68%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5´-[4-(nonanoyloxy)phenyl]-2,2´-bithiophene (4/lin8)

Prepared according to **procedure 2** from **1/OH** (74 mg, 0.080 mmol) and nonanoic acid (16 mg, 0.100 mmol). The obtained crude product was purified by column chromatography (eluent: $CHCl_3$/*n*-hexane 4/1, v/v) and repeated crystallization from THF/MeOH; yield 47mg

(0.044 mmol, 55%); pale yellow solid; $C_{66}H_{94}O_7S_2$ *M* = 1063.58 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.60 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.41 (s, 2H, Ar-H), 7.25–7.21 (m, 3H, Ar-H + Th-H), 7.20 (d, ^3J = 3.8 Hz, 1H, Th-H), 7.18–7.16 (m, 2H, Th-H), 7.11 (d, ^3J = 8.7 Hz, 2H, Ar-H), 4.10–4.02 (m, 6H, OCH_2CH$_2$), 2.57 (t, ^3J = 7.5 Hz, 2H, (O)CCH_2), 1.88–1.72 (m, 8H, OCH$_2$CH_2 + O(O)CCH$_2$CH_2), 1.52–1.45 (m, 6H, CH$_2$), 1.44–1.22 (m, 46H, CH$_2$), 0.92–0.85 (m, 12H, CH$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.2, 164.9 (C=O), 153.0, 150.5, 150.2, 143.1, 142.3, 142.3, 136.8, 136.7, 131.8, 131.7, 126.7, 126.6, 124.6, 124.0, 124.0, 123.7, 122.3, 122.1, 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 34.4, 31.9, 31.9, 31.8, 30.3, 29.7, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 29.2, 29.1, 26.1, 26.0, 24.9, 22.7, 22.7, 22.6 (CH$_2$), 14.1, 14.1 (CH$_3$); elemental analysis; calc for $C_{66}H_{94}O_7S_2$: C 74.53%, H 8.91%; found C 74.29%, H 8.90%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5´-[4-(2,2-diethylbutanoyloxy)phenyl]-2,2´-bithiophene (5/Et$_3$)

Prepared according to **procedure 2** from **1/OH** (74 mg, 0.080 mmol) and 2,2-diethylbutyric acid (14 mg, 0.100 mmol), DMAP (1 mg, 0.01 mmol) and DCC (21 mg, 0.100 mmol). The obtained crude product was purified by column chromatography (eluent: $CHCl_3$/*n*-hexane 3/1, v/v) and repeated crystallization from THF/MeOH; yield 58 mg (0.055 mmol, 69%); pale yellow solid; $C_{65}H_{92}O_7S_2$; *M* = 1049.55 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.60 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.41 (s, 2H, Ar-H), 7.25–7.21 (m, 3H, Ar-H + Th-H), 7.20 (d, ^3J = 3.8 Hz, 1H, Th-H), 7.18–7.16 (m, 2H, Th-H), 7.07 (d, ^3J = 8.7 Hz, 2H, Ar-H), 4.09–4.03 (m, 6H, OCH_2CH$_2$), 1.88–1.71 (m, 12H, OCH$_2$CH_2 + CCH$_2$), 1.53–1.45 (m, 6H, CH$_2$), 1.41–1.23 (m, 36H, CH$_2$), 0.94–0.85 (m, 18H, CH$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 164.9 (C=O), 153.0, 150.6, 150.5, 143.1, 142.4, 142.2, 136.8, 136.7, 131.8, 131.6, 126.7, 126.6, 124.5, 124.0, 123.9, 123.7, 122.3, 122.2, 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 50.3 ((O)C*C*), 31.9, 31.9, 30.3, 29.7, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 26.1, 26.1, 26.0, 22.7, 22.7 (CH$_2$), 14.1, 8.4 (CH$_3$); elemental analysis; calc $C_{65}H_{92}O_7S_2$: C 74.38%, H 8.84%; found C 74.43%, H 8.73%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5´-[4-adamantanoyloxyphenyl]-2,2´-bithiophene (6/ada)

Prepared according to **procedure 1** from **1/OH** (101 mg, 0.109 mmol) and adamantane-1-carboxylic acid (25 mg, 0.136 mmol). The obtained crude product was purified by column chromatography (eluent: $CHCl_3$/*n*-hexane 4/1, v/v) and repeated crystallization from THF/MeOH; yield 64 mg (0.059 mmol, 54%); pale yellow solid; $C_{68}H_{92}O_7S_2$; *M* = 1085.58 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, ^3J = 8.6 Hz, 2H, Ar-H), 7.59 (d, ^3J = 8.6 Hz, 2H, Ar-H), 7.42 (s, 2H, Ar-H), 7.25–7.21 (m, 3H, Ar-H + Th-H), 7.20 (d, ^3J = 3.8 Hz, 1H, Th-H), 7.17 (d, ^3J = 3.7 Hz, 1H, Th-H), 7.17 (d, ^3J = 3.7 Hz, 1H, Th-H), 7.08 (d, ^3J = 8.6 Hz, 2H, Ar-H), 4.11–4.02 (m, 6H, OCH_2CH$_2$), 2.14–2.04 (m, 9H, Ad-CH$_2$), 1.89–1.72 (m, 12H, OCH$_2$CH_2 + Ad-CH$_2$), 1.52–1.43 (m, 6H, CH$_2$), 1.41–1.20 (m, 36H, CH$_2$), 0.93–0.84 (m, 9H, CH$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.1, 164.9 (C=O), 153.0, 150.6 150.5, 143.1, 142.4, 142.2, 136.8, 136.6, 131.8, 131.5, 126.7, 126.6, 124.5, 124.5, 124.0, 123.9, 123.7, 122.3, 122.1, 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 41.1 (O(O)C*C*), 38.8, 36.4, 31.9, 31.9, 30.3, 29.7, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 27.9, 26.1, 26.0, 22.7, 22.7 (CH$_2$), 14.1 (CH$_3$); elemental analysis; calc for $C_{68}H_{92}O_7S_2$: C 75.23%, H 8.54%; found C 75.22%, H 8.42%.

3.5 Representative NMR spectra

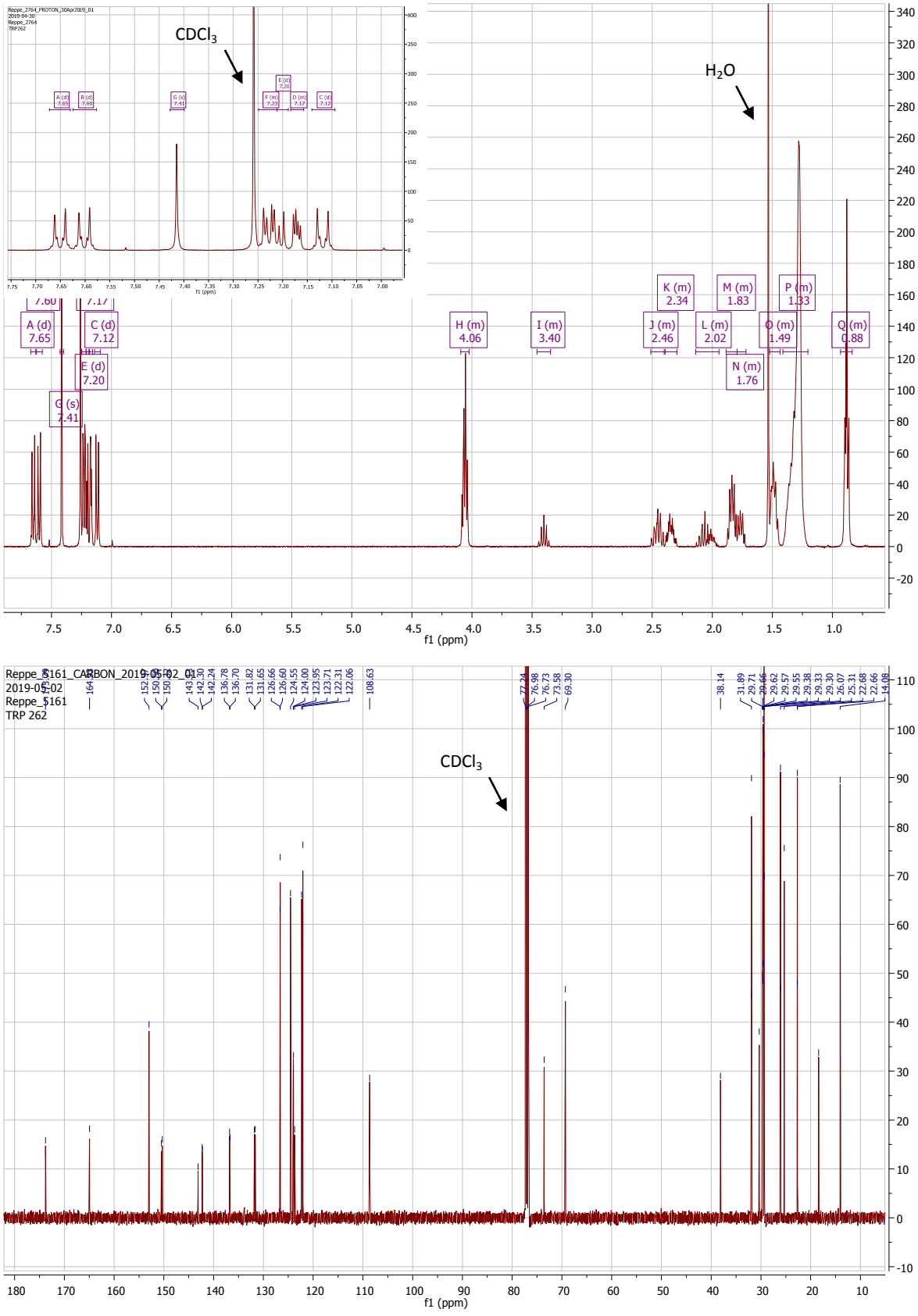
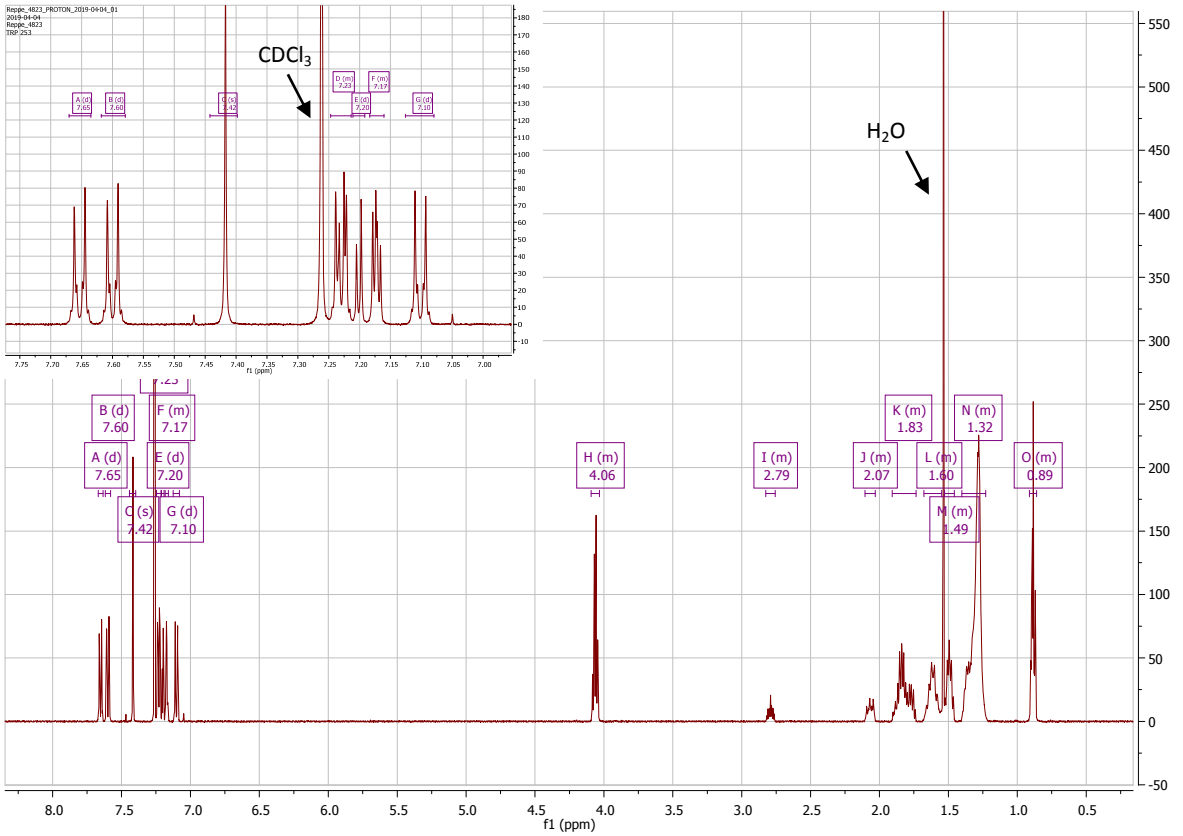


Figure S7 ^{1}H- and ^{13}C-NMR of compound **2/c4**. The spectra were measured at 27 °C, with the frequencies 400 MHz (^{1}H) and 125 MHz (^{13}C) in $CDCl_3$ as solvent; the small peaks at 7.0 and 7.5 ppm are ^{13}C satellites of the $CHCl_3$ peak).



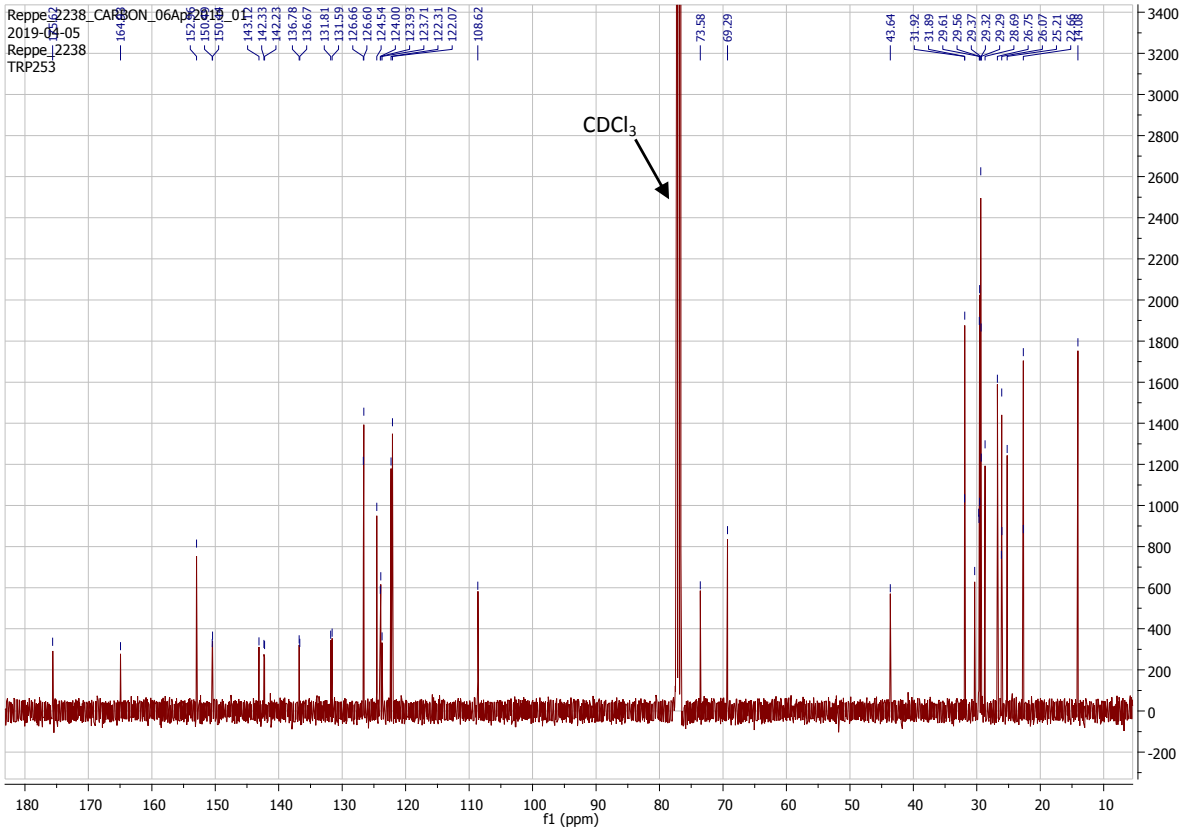


Figure S8 ^{1}H- and ^{13}C-NMR of compound **2/c8**. The spectra were measured at 27 °C, with the frequencies 500 MHz (^{1}H) and 100 MHz (^{13}C) in $CDCl_3$ as solvent.

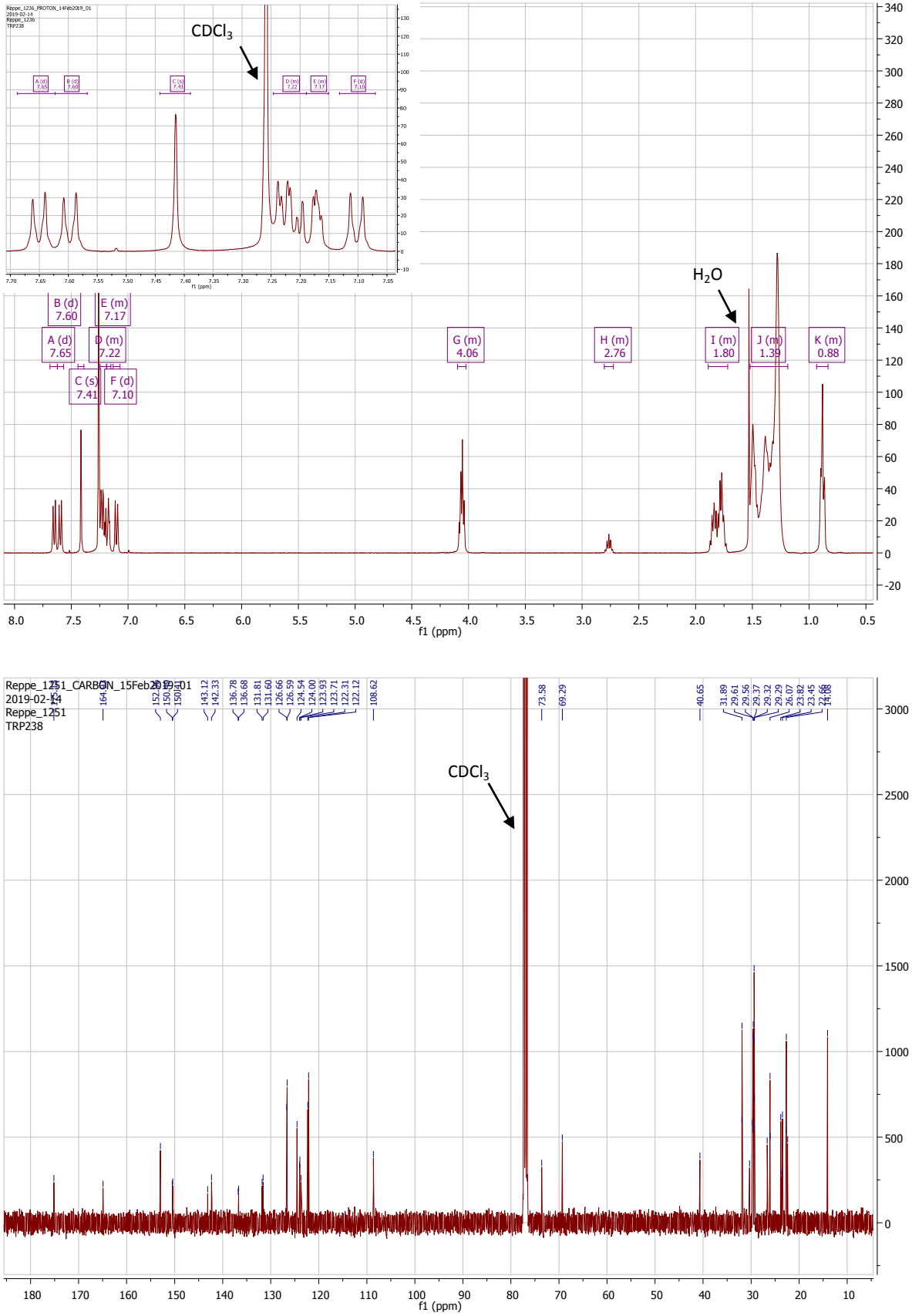


Figure S9 ^{1}H- and ^{13}C-NMR of compound **2/c12**. The spectra were measured at 27 °C, with the frequencies 400 MHz (^{1}H) and 100 MHz (^{13}C) in $CDCl_3$ as solvent.

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