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Supporting Information

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Helical Networks of #-Conjugated Rods – A Robust Design Concept for Bicontinuous Cubic Liquid Crystalline Phases with Achiral $Ia\bar{3}d$ and Chiral $I23$ Lattice

Christian Dressel, Tino Reppe, Silvio Poppe, Marko Prehm, Huanjun Lu, Xiangbing Zeng, Goran Ungar, and Carsten Tschierske**

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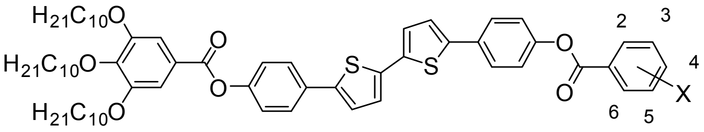
S1. Additional Data

S1.1 Transition temperatures and enthalpy values

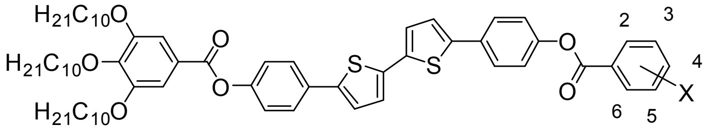
Table S1. Phase transitions, transition temperatures (T/°C) and transition enthalpy values of the investigated compounds **3/X**.[a]



Verb.	X	Pos.	T/°C [ΔH/kJ·mol^{-1}]	a_{cub}/nm
$\mathbf{3/^{4}F}$	F	4	H2: Cr 122 [22.4] Cub/$Ia\bar{3}d$ 199 [2.2] Iso K1: Iso 190 [-1.9] Cub/$Ia\bar{3}d$ 83 [-27.1] Cr	11.1
$\mathbf{3/^{4}I}$	I	4	H1: Cr 132 [39.3] Cub/$Ia\bar{3}d$ 221 [2.6] Iso K1: Iso 210 [-2.0] Cub/$Ia\bar{3}d$	11.3
$\mathbf{3/^{4}CN}$	CN	4	H1:Cr 104 [46.1] Cub/$Ia\bar{3}d$ 237 [2.5] Iso K1: Iso 224 [-2.1] Cub/$Ia\bar{3}d$ 87 [-0.3] M_x	11.2
$\mathbf{3/^{4}Me}$	CH_3	4	H1: Cr 118 [40.1] Cub/$Ia\bar{3}d$ 180 [1.6] Iso K2: Iso 175 [-0.1] Iso$_1^{[*]}$ 155 [-0.5] Cub/$Ia\bar{3}d$	11.4
$\mathbf{3/^{4}CF3}$	OCF_3	4	H2: Cr 127 [30.1] Cub$^{[*]}$/$I23$ 206 [2.0] Iso K2: Iso 194 [-2.1] Cub$^{[*]}$/$I23$	16.2
$\mathbf{3/^{4}NO2}$	NO_2	4	H2: Cr 128 [39.3] Cub/$Ia\bar{3}d$ 244 [2.1] Iso K1: Iso 233 [-1.8] Cub/$Ia\bar{3}d$	11.1
$\mathbf{3/^{4}OAc}$	$OOCCH_3$	4	H1: Cr 105 [20.2] Cub/$Ia\bar{3}d$ [1.7] Iso K1: Iso 189 [-0.9] Cub/$Ia\bar{3}d$	11.5
$\mathbf{3/^{3}F}$	F	3	H2: Cr 114 [26.1] Cub/$Ia\bar{3}d$ 176 [2.6] Iso K1: Iso 167 [-2.0] Cub/$Ia\bar{3}d$ 87 [-0.3] Cr′	10.9
$\mathbf{3/^{3}Br}$	Br	3	H2: Cr 109 [19.7] Cub$^{[*]}$/$I23$ 169 [0.3] Cub/$Ia\bar{3}d$ 173 [2.6] Iso K1: Iso 165 [-2.1] Cub/$Ia\bar{3}d$	$10.4_{Ia\bar{3}d}$ 16.4_{I23}
$\mathbf{3/^{3}I}$	I	3	H1: Cr 99 [22.5] Cub$^{[*]}$/$I23$ 154 [–] Cub/$Ia\bar{3}d$ 163 [2.3] Iso K1: Iso 155 [-1.6] Cub/$Ia\bar{3}d$	16.2_{I23}
$\mathbf{3/^{3}OMe}$	OMe	3	H1:Cr 107 [57.2] Cub$^{[*]}$/$I23$ 144 [2.8] Iso K1: Iso 140 [-2.0] Cub$^{[*]}$/$I23$ + Cub/$Ia\bar{3}d$< 0 Cr	$10.8_{Ia\bar{3}d}$ 16.0_{I23}
$\mathbf{3/^{3}ODec}$	$OC_{10}H_{21}$	3	H2: Cr 97 [37.2] Cub/$Ia\bar{3}d$ [3.4] 112 Iso K1: Iso 105 [-2.5] Col$_{hex}$→Cub/$Ia\bar{3}d^{c}$ 87 [-0.3] Cr′	9.8
$\mathbf{3/^{3}CN}$	CN	3	H1: Cr 99 [49.6] Cub/$Ia\bar{3}d$ 196 [2.8] Iso K1: Iso 186 [-1.9] Cub/$Ia\bar{3}d$	10.8
$\mathbf{3/^{2}F}$	F	2	H1: Cr 92 [34.9] Cub/$Ia\bar{3}d$ 143 [2.1] Iso K2: Iso 137 [-0.1] Iso$_1^{[*]}$ 133 [-1.4] Cub/$Ia\bar{3}d$	10.9
$\mathbf{3/^{2}NO2}$	NO_2	2	H2: Cr 106 [21.8] Cub/$Ia\bar{3}d$ 117 [1.0] Iso K2: Iso 100 [-0.8] M1 87 [-21.3] Cr	11.1
$\mathbf{3/^{2}I}$	I	2	H2: Cr 89 [35.5] Cub/$Ia\bar{3}d$ 135 [2.2] Iso K2: Iso 125 [-1.7] Cub/$Ia\bar{3}d$	10.3
$\mathbf{3/^{2}OMe}$	OMe	2	H1: Cr 131 [64.2] Iso K1: Iso 82 [-37.3] Cr	-

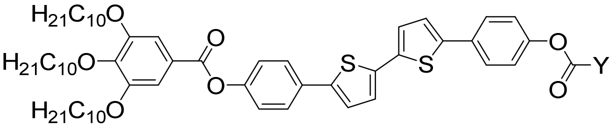
[a] Peak temperatures of the first (H1) or second DSC-heating (H2) or cooling scans (K1, K2) at 10 K/min; Abbreviations: Iso$_1^{[*]}$ = spontaneously mirror symmetry broken isotropic liquid phase; M1 = non cubic 3D phase (distorted $Ia\bar{3}d$ phase) M_x = unknown mesophases or crystalline phase; for the other abbreviations, see main text; [b]determined by polarizing microscopy; [c] the Col$_{hex}$ phase is formed on cooling from Iso which is immediately replaced by the $Ia\bar{3}d$ phase.

Table S1 (continued). Phase transitions, transition temperatures (T/°C) and transition enthalpy values of the investigated compounds **3/X**.^{a}



Verb.	X	Pos.	T/°C [ΔH/kJ·mol^{-1}]	a_{cub}/nm
3/^{34}F$_2$	F	3,4	H2: Cr 126 [27.6] Cub$^{[*]}$/$I$23 198 [0.3] Cub/$Ia\bar{3}d$ 203 [2.4] Iso K2:Iso 192 [-1.9] Cub/$Ia\bar{3}d$	16.0
3/^{35}F$_2$	F	3,5	H2: Cr 118 [27.9] Cub$^{[*]}$/$I$23 173 [2.9] Iso K1: Iso 162 [-2.1] Cub$^{[*]}$/$I$23	15.8
3/^{35}Br$_2$	Br	3,5	H1: Cr 118 [35.4] Cub$^{[*]}$/$I$23 157 [3.3] Iso K1: Iso 145 [-2.2] Cub$^{[*]}$/$I$23 < 0 Cr	16.1
3/^{35}NO2$_2$	NO$_2$	3,5	H1: Cr 131 [28.0] Cub$^{[*]}$/$I$23 209 [2.9] Iso K1: Iso 195 [-2.3] Cub$^{[*]}$/$I$23	15.8
3/^{35}I$_2$	I	3,5	H2:Cr 130 [41.1] Cub$^{[*]}$/$I$23 140 [2.0] Iso K2: Iso 127 [-1.7] Cub$^{[*]}$/$I$23	15.6
3/^{35}OMe$_2$	OMe	3,5	H2: Cr 124 [52.8] Iso K1: Iso 101 [-1.8] Cub$^{[*]}$/$I$23 69 [2.6] Cr	-
3/^{35}OEt$_2$	OEt	3,5	H2: Cr 119 [63.3] Iso K2: Iso 61 [-15.5] Cr	-
3/^{345}F$_3$	F	3,4,5	H2: Cr 129 [28.8] Cub$^{[*]}$/$I$23 200 [3.2] Iso K1: Iso 188 [-2.5] Cub$^{[*]}$/$I$23	15.6
3/^{23456}F$_5$	F	2,3,4,5,6	H1: Cr 115^{b} Cub$^{[*]}$/$I$23 184 [3.0] Iso K1: Iso 171 [-2.1] Cub$^{[*]}$/$I$23	15.6
3/^{26}F$_2$	F	2,6	H2: Cr 118 Iso K2: Iso 112 SmC$_s$ 53 Cr	-

Table S2. Phase transitions, transition temperatures (T/°C) and transition enthalpy values of compounds **3a/Y**.^{a}



Verb.	Y	T/°C [ΔH /kJ·mol^{-1}]	a_{cub}/nm
3a/Th	2-thienyl	H1: Cr 106 [34.0] Cub/$Ia\bar{3}d$ 158 [2.2] Iso K2: Iso 153 [-2.0] Cub/$Ia\bar{3}d$	10.8
3a/1-Npht	1-napthyl	H2: Cr 88 [19.5] Cub/$Ia\bar{3}d$ 136 [1.7] Iso K2: Iso 123 [-1.3] Cub/$Ia\bar{3}d$ <20 Cr	10.6
3a/2-Npht	2-napthyl	H2: Cr 120 [38.6] Cub/$Ia\bar{3}d$ 196 [2.0] Iso K2: Iso 187 [-0.1] Iso$_1^{[*]}$ 182 [-1.1] Cub/$Ia\bar{3}d$ 40 [-2.8] Cr′	11.6
3a/Biph	4-biphenyl	H1: Cr 125 [43.9] Cub/$Ia\bar{3}d$ 244 [2.2] Iso K1: Iso 233[-1.6] Cub/$Ia\bar{3}d$ 83 [-18.8] Cr	12.0
3a/Anth	9-anthranyl	H1: Cr156 [47.7] Iso K1: Iso 123 [-43.1] Cr	-

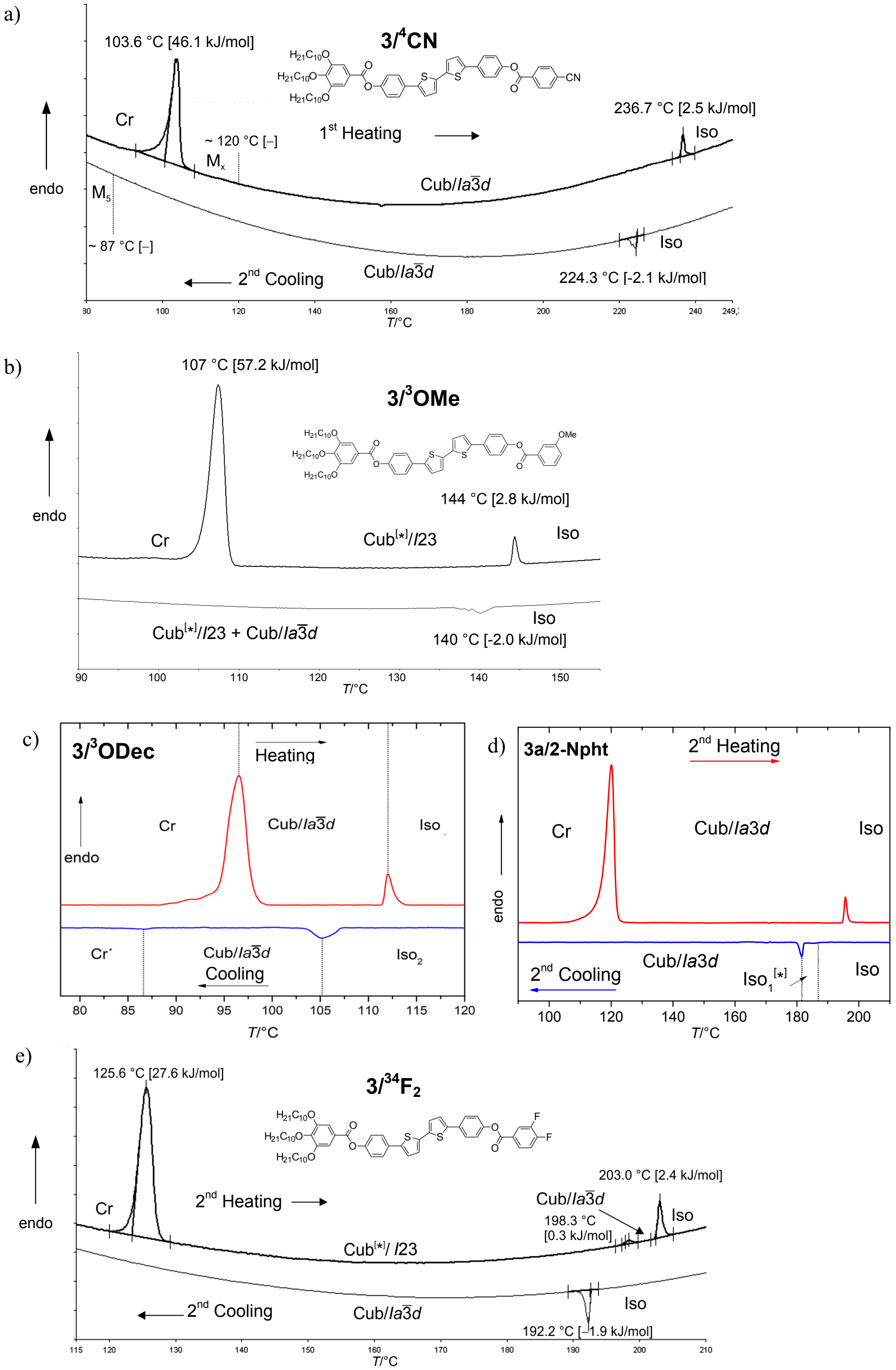


Figure S1. Representative DSC traces (10 K min^{-1}) of compounds a) **3/^{4}CN** b) **3/^{3}OMe**, c) **3/^{3}ODec**, d) **3a/2-Npht** and e) **3/^{34}F$_2$**.

S1.2 Additional textures

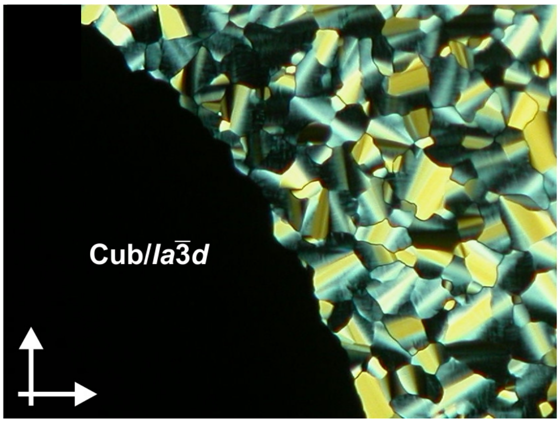


Figure S2. Textures of the mesophases of compound **3/^{3}ODec**. Growth of the Cub$_{bi}$/$Ia\bar{3}d_{(S)}$ phase (black, left) from the birefringent Col$_{hex}$ phase (right) first formed immediately upon cooling from Iso at T = 105 °C; the width of the image is 1 mm.

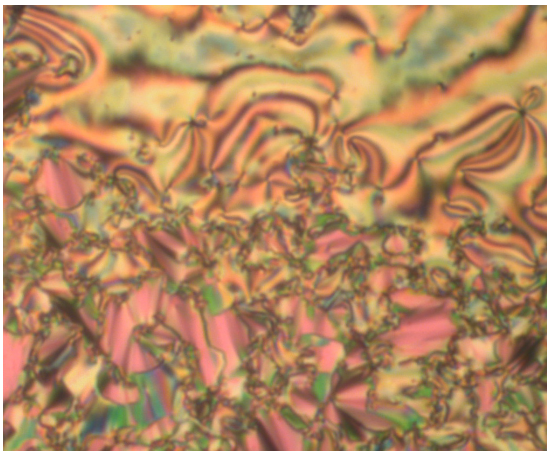


Figure S3. Texture of the SmC$_s$ phase as observed on cooling of compound **3/^{26}F$_2$** at T = 110 °C, showing the fan texture with extinctions inclined with the directions of the polarizers (bottom) and the Schlieren texture (top); the width of the image is 1 mm.

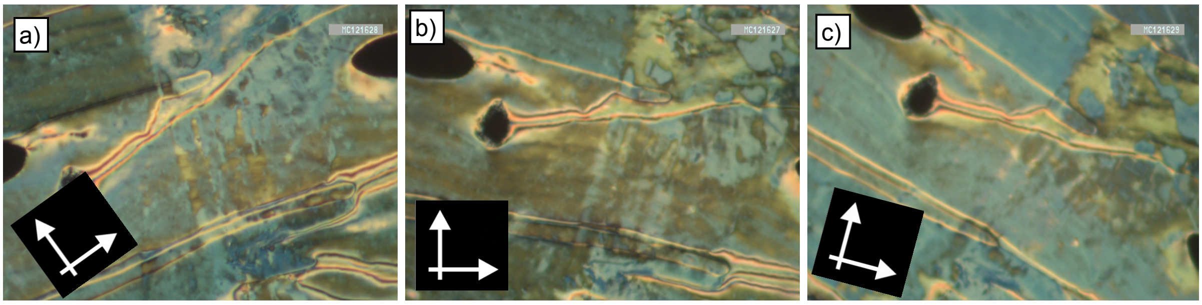


Figure S4. SmC$_s$ phase as observed on cooling compound **3/^{26}F$_2$** in a homeotropic cell at T = 110 °C, observed between crossed polarizers; the brightness of the domains does not change by rotating the sample between the polarizers, excluding a tilt alignment as origin of the change of domain brightness by rotating the polarizer (see Fig. 1g-h); the width of the images is 0.8 mm.

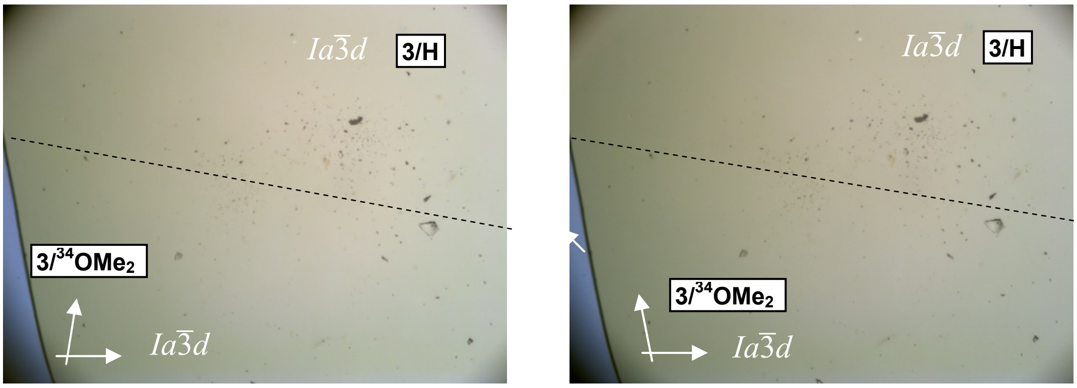


Figure S5. Contact region between the $Ia\bar{3}d$ phases of compounds **3/H** and **$3/^{34}OMe_2$** at T = 125 °C as observed between slightly uncrossed polarizers; the absence of an induced conglomerate texture of the *I*23 phase indicates that both $Ia\bar{3}d$ phases represent long pitch $Ia\bar{3}d_{(\mathrm{L})}$ type phases; the dashed line indicates approximate position of the phase boundary.

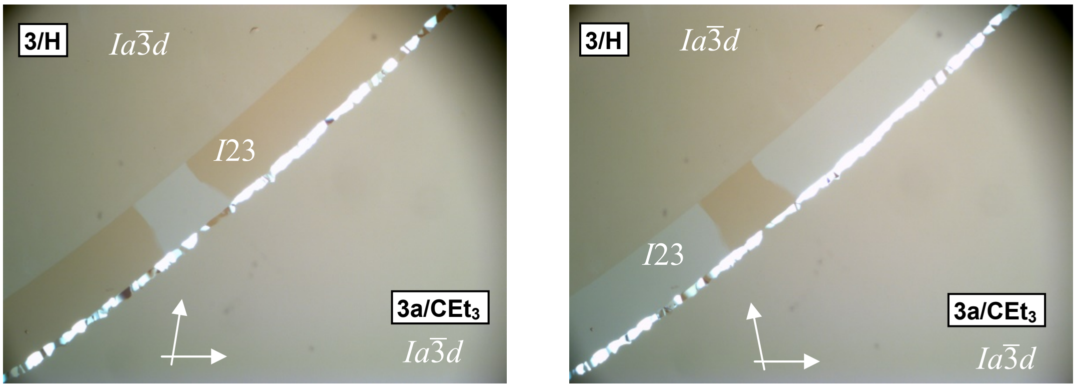


Figure S6. Contact region between the $Ia\bar{3}d$ phases of compounds **3/H** and **3a/CEt$_3$** at T = 73 °C as observed between slightly uncrossed polarizers; the induced conglomerate texture of the *I*23 phase indicates that the $Ia\bar{3}d$ phase of **3a/CEt$_3$** represent short pitch type phase $Ia\bar{3}d_{(\mathrm{S})}$; in this case an additional birefringent, most probably columnar phase is induced besides the *I*23 phase.

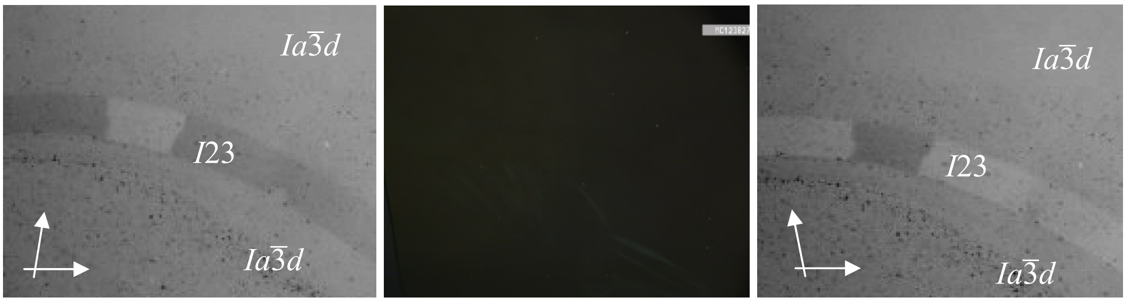


Figure S7. Contact region between the $Ia\bar{3}d$ phases of compounds **3a/CEt$_3$** (top) and **2-Npht** (bottom) at T = 125 °C as observed between slightly uncrossed polarizers (left, right) and crossed polarizers (middle); the induced conglomerate texture of the *I*23 phase (on cooling formed below 126 °C and on heating it disappears at 141 °C) indicates that the $Ia\bar{3}d$ phase of **2-Npht** represent long pitch type phase $Ia\bar{3}d_{(\mathrm{L})}$; contrast enhanced.

Figure S8. Contact region between the $Ia\bar{3}d$ phases of compounds **1-Npht** (top) and **2-Npht** (bottom) at T = 130 °C as observed between slightly uncrossed polarizers (left, right) and crossed polarizers (middle); the absence of an induced conglomerate texture of the $I23$ phase indicates that both $Ia\bar{3}d$ phases represent long pitch $Ia\bar{3}d_{(L)}$ type phases; the dashed line indicates approximate position of the phase boundary.

S1.3 Additional XRD data

Table S3. Crystallographic data of compounds **3/X**.

Comp.	T/°C	2θ/°	d/nm	hkl	d_{calc}/nm	Δ	a_{cub}/nm
3/^{4}F	130	1.952	4.526	211	4.526	0.00	$Ia\bar{3}d$: 11.09
		2.305	3.832	220	3.920	0.09	
		3.878	2.278	422	2.263	0.02	
3/^{4}I	140	1.921	4.599	211	4.599	0.00	$Ia\bar{3}d$: 11.26
		2.205	4.006	220	3.983	0.02	
		3.659	2.415	332	2.402	0.01	
3/^{4}Me	140	1.896	4.659	211	4.659	0.00	$Ia\bar{3}d$: 11.41
		2.179	4.054	220	4.035	0.02	
3/^{4}OCF3	150	2.040	4.330	321	4.330	0.00	$I23$: 16.20
		2.195	4.025	400	4.050	0.03	
		2.407	3.670	420	3.623	0.05	
3/^{4}NO2	150	1.950	4.530	211	4.530	0.00	$Ia\bar{3}d$: 11.10
		2.247	3.932	220	3.923	0.01	
3/^{4}OAc	140	1.884	4.690	211	4.690	0.00	$Ia\bar{3}d$: 11.49
		2.127	4.154	220	4.062	0.09	
3/^{3}Br	140	2.083	4.242	211	4.242	0.00	$Ia\bar{3}d$: 10.39
		2.402	3.679	220	3.674	0.01	
	171	2.014	4.386	321	4.386	0.00	$I23$: 16.41
		2.135	4.138	400	4.103	0.03	
		2.247	3.932	411	3.868	0.06	
		2.501	3.533	332	3.499	0.02	
3/^{3}I	130	2.038	4.335	321	4.335	0.00	$I23$: 16.22
		2.188	4.038	400	4.055	0.02	
		2.397	3.685	420	3.627	0.06	
3/^{3}CN	140	2,001	4,415	211	4.415	0.00	$Ia\bar{3}d$: 10.81
		2,303	3,836	220	3.823	0.01	

Table S3 (continued). Crystallographic data of compounds **3/X**.

Comp.	*T*/°C	2*θ*/°	*d*/nm	*hkl*	d_{calc}/nm	Δ	a_{cub}/nm
3/^{3}ODec	105	2.203	4.009	211	4.009	0.00	$Ia\bar{3}d$: 9.82
		2.525	3.499	220	3.472	0.02	
3/^{2}F	120	1,992	4,436	211	4.436	0.00	$Ia\bar{3}d$: 10.87
		2,291	3,856	220	3.842	0.02	
3/^{2}I	110	2.091	4.225	211	4.225	0.00	$Ia\bar{3}d$: 10.34
		2.380	3.712	220	3.659	0.05	
3/^{2}NO2	115	1.96	4.52	211	4.52	0.00	$Ia\bar{3}d$: 11.07
		2.25	3.92	220	3.91	0.01	
3/^{34}F$_2$	135	2068	4.271	321	4.271	0.00	$I23$: 15.98
		2.216	3.987	400	3.995	0.01	
		2.442	3.617	420	3.573	0.04	
		2.771	3.188	422	3.262	0.07	
3/^{35}I$_2$	135	2.121	4.165	321	4.165	0.00	$I23$: 15.58
		2.267	3.897	400	3.896	0.03	
3/^{35}NO2$_2$	180	2.10	4.21	321	4.21	0.00	$I23$: 15.76
		2.23	3.97	400	3.94	0.03	
3/^{345}F$_3$	150	2.121	4.165	321	4.165	0.00	$I23$: 15.58
		2282	3.872	400	3.896	0.02	
		2.483	3.558	420	3.485	0.07	
3/^{23456}F$_5$	140	2.116	4.175	321	4.175	0.00	$I23$: 15.62
		2.286	3.864	400	3.905	0.04	
		2.495	3.541	420	3.493	0.05	

Table S4. Crystallographic data of compounds **3a/Y**.

Comp.	*T*/°C	2*θ*/°	*d*/nm	*hkl*	d_{calc}/nm	Δ	a_{cub}/nm
3a/Th	125	1.99	4.43	211	4.43	0.00	$Ia\bar{3}d$: 10.85
		2.29	3.85	220	3.84	0.01	
		2.37	3.73	332	3.66	0.07	
3a/1-Nph	120	2.033	4.35	211	4.35	0.00	$Ia\bar{3}d$: 10.64
		2.34	3.78	220	3.76	0.02	
3a/2-Nph	180	1.86	4.75	211	4.75	0.00	$Ia\bar{3}d$: 11.63
		2.16	4.09	220	4.11	0.02	
3a/Biph	180	1.81	4.88	211	4.88	0.00	$Ia\bar{3}d$: 11.95
		2.08	4.25	220	4.22	0.03	

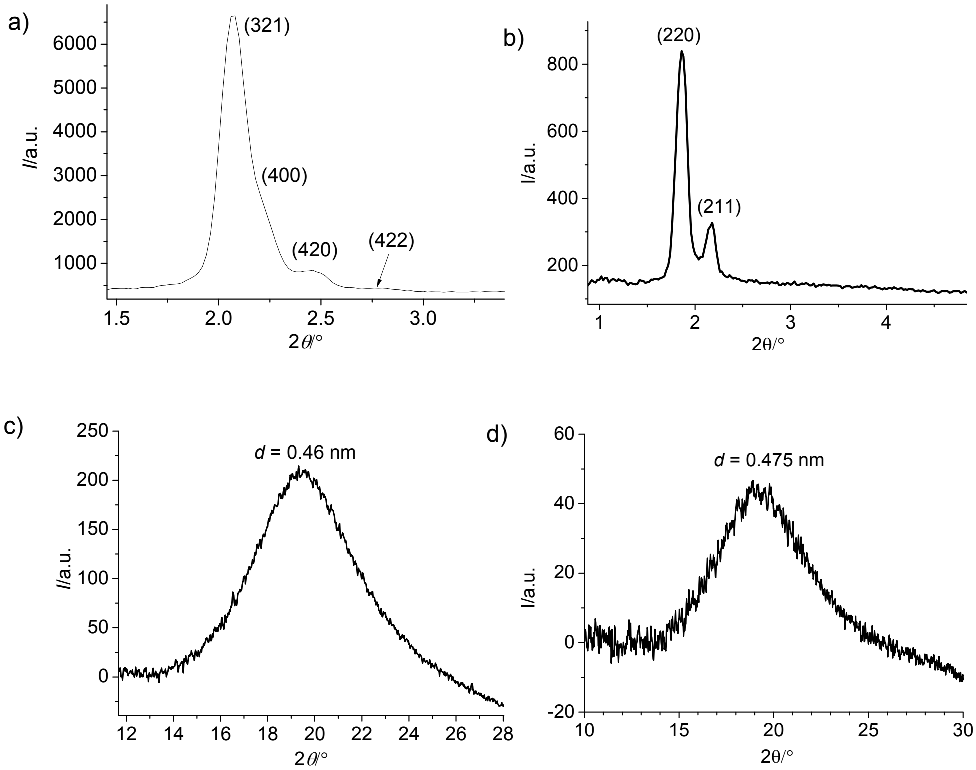


Figure S9. Representative 2θ scan of the diffraction patterns a) of the *I*23 phase of $\mathbf{3/^{34}F_2}$ at T = 135 °C and b) of the $Ia\bar{3}d$ phase of **3a/2-Napth** at T = 180 °C.

Table S5. Diffraction data of the $Ia\bar{3}d$ phase of compound $\mathbf{3/^{3}F}$, measured at 125 °C, including Miller indices, measured (d) and best-fit (d_{calc}) d-spacings of diffraction peaks, diffraction peak intensities (corrected by powder geometry and multiplicity), peak multiplicity and phases used in reconstruction of electron density maps. The best-fit lattice parameter a is 10.89 nm.

Indices (*hkl*)	*d* (nm)	d_{calc} (nm)	Intensity	Multiplicity	Phase
(211)	4.44	4.48	100	24	π
(220)	3.85	3.86	28.9	12	π
(321)	2.91	2.91	0.3	48	π
(400)	2.72	2.72	2.0	6	π
(420)	2.43	2.43	1.2	24	π
(332)	2.32	2.31	2.1	24	0
(422)	2.22	2.21	0.3	24	0
(440)	1.92	1.91	0.3	12	0
(611)	1.77	1.76	-	24	-
(444)	1.57	1.56	-	8	-
(543)	1.54	1.53	-	48	-

Table S6. Diffraction data of the *I*23 phase of compound **3/^{35}F$_2$**, measured at 125 °C, including Miller indices, measured (*d*-exp.) and best-fit (*d*-calc.) *d*-spacings of diffraction peaks, diffraction peak intensities (corrected by powder geometry and multiplicity), peak multiplicity and phases used in reconstruction of eletron density maps. The best-fit lattice parameter a_{cub} is 15.79 nm.

Indices (*hkl*)	*d*-exp. (nm)	*d*-calc. (nm)	Intensity	Multiplicity	Phase
(211)	6.44	6.45	-	24	–
(220)	5.58	5.58	-	12	–
(301) (310)*	5.00	4.99	1.4 -	12 12	0
(222)	4.56	4.56	8.0	8	–0.21π
(321) (312)*	4.22	4.22	58.3 70.0	24 24	–0.93π –0.59π
(400)	3.95	3.95	100	6	0
(411)	3.72	3.72	0.3	12	–0.80π
(330)	3.72	3.72	0.3	12 12	0
(420)	3.53	3.53	-	-	-
(422)	3.22	3.22	-	-	-
(431)/(510)	3.10	3.10	-	-	-
(521)	2.88	2.88	-	-	-
(440)	2.78	2.79	-	-	-
(433)/(530)	2.70	2.71	-	-	-
(442)	2.63	2.63	-	-	-
(532)/(611)	2.56	2.56	-	-	-
(620)	25.0	25.0	-	-	-
(541)	2.43	2.44	-	-	-
(631)	2.33	2.33	-	-	-
(444)	2.28	2.28	-	-	-
(550)	2.23	2.23	-	-	-
(640)	2.19	2.19	-	-	-
(721)	2.15	2.15	-	-	-
(642)	2.11	2.11	-	-	-

* *F*or *I*23 space groups a general reflection (*hkl*) where $h \neq k \neq l$ is inequivalent to (*hlk*), even though they overlap in the powder diffraction pattern, they could have different intensities and different structure factor *F*(*hkl*) phases. The intensity ratio between the two diffraction peaks is taken from the simulated diffraction pattern.

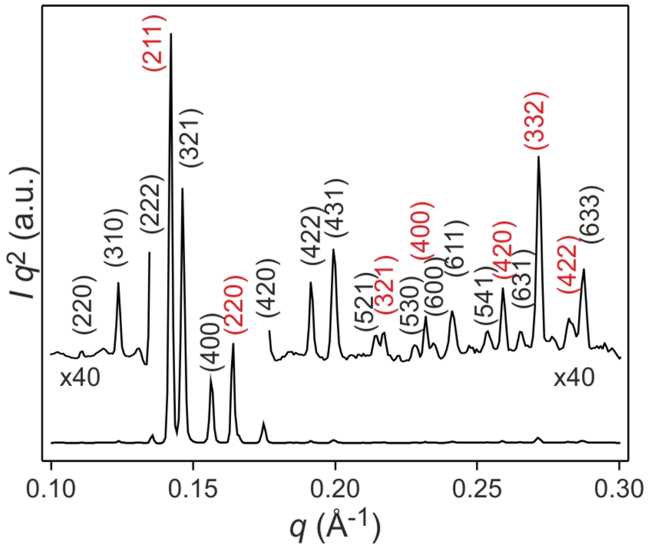


Figure S10. XRD pattern of compound **3/^{3}OMe** at 116 °C showing a mixture of *I*23 (peaks labelled in black) and *Ia*3*d* (peaks labelled in red) phases.

Table S7. Experimental and calculated *d*-spacings of XRD reflections of the $Ia\bar{3}d$ and *I*23 phases in **3/^{3}OMe** at 116 ºC.

$Ia\bar{3}d$:

(*hkl*)	*d* (nm)	$d_{calc.}$(nm)
(211)	4.42	4.43
(220)	3.83	3.84
(321)	2.89	2.90
(400)	2.71	2.71
(420)	2.43	2.42
(332)	2.32	2.31
(422)	2.23	2.21
a = 10.85 nm		

*I*23:

(*hkl*)	*d* (nm)	d_{calc} (nm)
(310)	5.06	5.08
(222)	4.65	4.64
(321)	4.30	4.30
(400)	4.03	4.02
(420)	3.59	3.60
(422)	3.27	3.29
(431)	3.16	3.15
(521)	2.93	2.93
(530)	2.75	2.75
(600)	2.68	2.68
(611)	2.61	2.61
(541)	2.47	2.48
(631)	2.37	2.37
(550)	2.28	2.27
(633)	2.19	2.19
a = 16.08 nm		

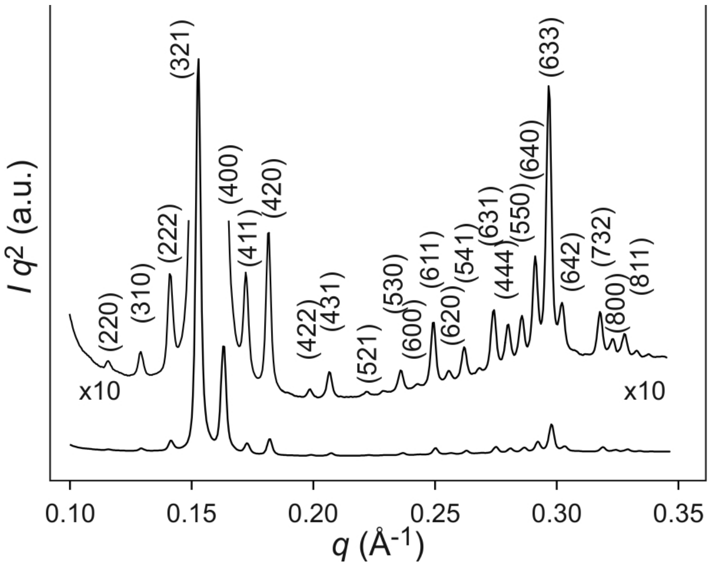


Figure S11. XRD pattern of the *I*23 phase of compound **3/^{35}Br$_2$** at 125°C.

Table S8. Experimental and calculated *d*-spacings of XRD reflections of the $Ia\bar{3}d$ and *I*23 phases in **3/^{35}Br$_2$** at 125 ºC.

(*hkl*)	*d* (nm)	d_{calc} (nm)
(220)	5.52	5.52
(310)	4.93	4.94
(222)	4.51	4.51
(321)	4.17	4.17
(400)	3.90	3.90
(411)/(330)	3.68	3.68
(420)	3.49	3.49
(422)	3.19	3.19
(431)/(510)	3.06	3.06
(521)	2.85	2.85
(440)	2.76	2.76
(530)	2.68	2.68
(611)	2.53	2.53
(620)	2.47	2.47
(541)	2.41	2.41
(622)	2.35	2.35
(631)	2.30	2.30
(444)	2.25	2.25
(550)	2.21	2.21
(640)	2.17	2.16
(633)	2.12	2.12
(642)	2.09	2.09
(732)	1.98	1.98
(800)	1.95	1.95
(811)	1.92	1.92
(820)	1.89	1.89
a = 16.08 nm		

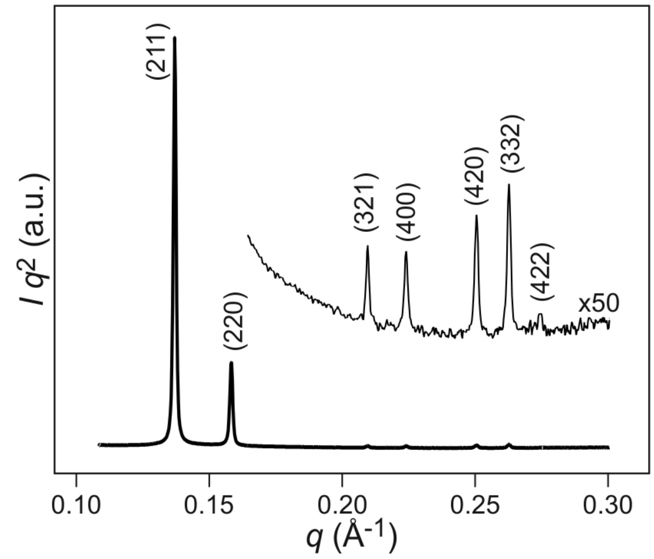


Figure S12. XRD pattern of the $Ia\overline{3}d$ phase of compound **3/^{4}CN** at 200°C.

Table S9. Experimental and calculated d-spacings of XRD reflections of the $Ia\overline{3}d$ phase of **3/^{4}CN** at 200 ºC. Best-fit lattice parameter a = 11.21 nm.

(*hkl*)	d (nm)	$d_{calc.}$(nm)
(211)	4.58	4.58
(220)	3.97	3.96
(321)	3.00	3.00
(400)	2.80	2.80
(420)	2.51	2.51
(332)	2.39	2.39
(422)	2.29	2.29

Table S10. Structural data of the investigated cubic phases (a_{cub}). [a]

Compd.	Ref.	Phase	a_{cub}/nm	V_{cell}/ nm^3	V_{mol}/ nm^3	n_{cell}	L_{net}/ nm	n_{raft}	Φ/°
3/H	S4	Cub/$Ia\bar{3}d_{(\mathrm{L})}$	10.8	1260	1.46	771	91.6	3.79	8.3
3/^{4}F	-	Cub/$Ia\bar{3}d_{(\mathrm{L})}$	11.1	1368	1.46	837	94.2	4.00	8.1
3/^{4}I	-	Cub/$Ia\bar{3}d_{(\mathrm{L})}$	11.3	1443	1.49	865	95.9	4.06	7.9
3/^{4}Me	-	Cub/$Ia\bar{3}d_{(\mathrm{L})}$	11.4	1482	1.48	894	96.7	4.16	7.9
3/^{4}OMe	S4	Cub/$Ia\bar{3}d_{(\mathrm{L})}$	11.4	1482	1.49	888	96.4	4.15	7.9
3/^{4}ODec	S4	Cub/$I23$	17.9	5753	1.71	3004	370.2	3.65	**7.8**
3/^{4}OCF3	-	Cub/$I23$	16.2	4252	1.51	2515	335.0	3.38	**8.6**
3/^{4}CN	-	Cub/$Ia\bar{3}d_{(\mathrm{L})}$	11.2	1405	1.48	848	95.0	4.02	8.0
3/^{4}NO2	-	Cub/$Ia\bar{3}d_{(\mathrm{L})}$	11.1	1368	1.47	831	94.2	3.97	8.1
3/^{4}OAc	-	Cub/$Ia\bar{3}d_{(\mathrm{L})}$	11.5	1517	1.52	891	97.6	4.11	7.8
3/^{3}F	-	Cub/$Ia\bar{3}d_{(\mathrm{L})}$	10.9	1295	1.46	792	92.5	3.85	8.2
3/^{3}Br	-	Cub/$Ia\bar{3}d_{(\mathrm{L})}$	10.4	1125	1.48	679	88.2	3.46	8.6
		Cub/$I23$	16.4	4411	1.48	2662	339.2	3.53	**8.5**
3/^{3}I	-	Cub/$I23$	16.2	4252	1.49	2548	335.0	3.42	**8.6**
3/^{3}CN	-	Cub/$Ia\bar{3}d_{(\mathrm{L})}$	10.8	1260	1.48	760	91.6	3.73	8.3
3/^{3}OMe	-	Cub/$Ia\bar{3}d_{(\mathrm{L})}$	10.85	1277	1.49	765	92.1	3.74	8.3
		Cub/$I23$	16.1	4173	1.49	2501	332.9	3.38	**8.7**
3/^{3}OEt	S4	Cub/$I23$	15.7	3840	1.51	2271	324.7	3.15	**8.9**
3/^{3}ODec	-	Cub/$Ia\bar{3}d_{(\mathrm{S})}$	9.8	941	1.71	491	83.2	2.66	**9.1**
3/^{34}F$_2$	-	Cub/$I23$	16.0	4096	1.47	2488	330.9	3.38	**8.7**
3/^{34}OMe$_2$	S4	Cub/$Ia\bar{3}d_{(\mathrm{L})}$	11.1	1368	1.52	804	94.2	3.84	8.1
3/^{35}F$_2$		Cub/$I23$	15.8	3944	1.47	2396	326.7	3.30	**8.8**
3/^{35}Br$_2$		Cub/$I23$	16.1	4173	1.51	2468	332.9	3.34	**8.7**
3/^{35}I$_2$	-	Cub/$I23$	15.6	3796	1.53	2216	322.6	3.09	**9.0**
3/^{35}NO2$_2$	-	Cub/$I23$	15.8	3944	1.49	2364	326.7	3.26	**8.8**
3/^{2}F	-	Cub/$Ia\bar{3}d_{(\mathrm{L})}$	10.9	1295	1.46	792	92.5	3.85	8.2
3/^{2}I	-	Cub/$Ia\bar{3}d_{(\mathrm{L})}$	10.3	1093	1.49	655	87.4	3.37	8.7
3/^{2}NO2	-	Cub/$Ia\bar{3}d_{(\mathrm{L})}$	11.1	1368	1.47	831	94.2	3.97	8.1
3/^{345}F$_3$	-	Cub/$I23$	15.6	3796	1.47	2306	322.6	3.22	**9.0**
3/^{345}OMe$_3$	S4	Cub/$I23$	15.4	3624	1.56	2075	318.5	2.93	**9.1**
3/^{23456}F$_5$	-	Cub/$I23$	15.6	3796	1.48	2290	322.6	3.19	**9.0**
3a/Th	-	Cub/$Ia\bar{3}d$	10.9	1277	1.44	792	92.5	3.85	8.3
3a/Cy	S5	Cub/$I23$	15.6	3796	1.49	2275	322.6	3.17	**9.0**
3a/Ad	S5	Cub/$I23$	15.1	3443	1.56	1971	312.3	2.84	**9.2**
3a/CEt$_3$	S5	Cub/$Ia\bar{3}d_{(\mathrm{S})}$	8.9	693	1.53	405	63.8	2.4	**10.1**
3a/1-Npht	-	Cub/$Ia\bar{3}d_{(\mathrm{L})}$	10.6	1191	1.53	695	89.9	3.48	8.5
3a/2-Npht	-	Cub/$Ia\bar{3}d_{(\mathrm{L})}$	11.6	1561	1.53	911	98.4	4.17	7.7
3a/Biph	-	Cub/$Ia\bar{3}d_{(\mathrm{L})}$	12.0	1728	1.56	989	101.8	4.37	7.5

[a] Abbreviations:. $V_{\mathrm{cell}} = a_{\mathrm{cub}}^3$ = volume of the unit cell; V_{mol} = molecular volume as calculated with the crystal volume increments of Immirzi;[S1] n_{cell} number of molecules in a unit cell, calculated according to 0.893 $V_{\mathrm{cell}}/V_{\mathrm{mol}}$, where the factor 0.893 is a correction for the different packing density in the crystalline and the LC state; L_{net} = total length of the networks per unit cell ($L_{\mathrm{net}} = 8.485a_{Ia3d}$ and $L_{\mathrm{net}} = 20.68a_{I23}$, respectively); n_{raft} = number of molecules organized in each 0.45 nm tick raft of the networks, calculated according to $n_{\mathrm{raft}} = n_{\mathrm{cell}}/(L_{\mathrm{net}}/0.45)$; Φ = twist angle between adjacent molecules in the networks of the $Ia\bar{3}d$- phases; $\Phi(Ia\bar{3}d) = 70.5°/[0.354a_{\mathrm{cub}}/0.45\mathrm{nm}]$, $\Phi(I23) = 90°/[0.290a_{\mathrm{cub}}/0.45\mathrm{nm}]$.[S3]

S1.4. Other Data

Table S11. Selected steric and electronic parameters of the substituents X.

X	V_{c}X/ x10^{-3} nm^3	σ_m	σ_p
H	6.9	-	-
F	12.8	0.34	0.06
Br	33.0	0.39	0.23
I	45.0	0.35	0.18
CN	31.3	0.56	0.66
NO_2	25.6	0.71	0.78
CH_3	31.7	-0.07	-0.17
OCH_3	46.3	0.12	-0.27
OC_2H_5	71.1	0.10	-0.24
$OC_{10}H_{21}$	269.5	0.10[a]	-0.32[a]
OCF_3	58.6	0.38	0.35
$OCOCH_3$	58.6	0.39	0.31

V_c is the crystal volume of the group estimated with the crystal volume increments reported by Immirzi;[S1] σ_m and σ_p are Hammett constants;[S2] σ_m is a measure of the strength of electron withdrawing (+) and electron donating (-) effects via the σ-bonds (inductive effect) and σ_p is an analogous measure for the delocalization mainly of the π-electrons (resonance effect); large positive values of σ_m and σ_p indicate electron acceptors whereas small positive and negative values are typically found for electron donating substituents. Data were taken from ref.S2; [a] values for OC_4H_9.

S1.4 Additional Discussion

S1.4.1 Dependence of cubic phase formation on the conditions.

Compound 3/^{3}OMe. - On heating the *I*23 phase of **3/^{3}OMe** is stable until the transition to the isotropic liquid. However, upon slow cooling (< 1 K min^{-1}) from the liquid state the achiral $Ia\bar{3}d$ phase is formed, only fast cooling (> 10 K min^{-1}) leads to the *I*23 phase. Cooling with an intermediate rate provides a mixture of both cubic phases, where chiral dark and bright domains (*I*23) coexist with achiral areas having an intermediate brightness ($Ia\bar{3}d$, see Fig. S13a). That indeed $Ia\bar{3}d$ and *I*23 coexist was confirmed by XRD where reflections of both phases coexist (Fig. S10 and Table S7). The ratio $Ia\bar{3}d$/*I*23 does not change on further cooling, as the transformation becomes slow at lower temperature. However, as shown in Fig. S13b,c, annealing the sample with coexisting $Ia\bar{3}d$ and *I*23 phases close to the Cub-Iso transition temperature slowly transforms $Ia\bar{3}d$ into *I*23. This means that the chiral *I*23 phase is the thermodynamically stable cubic phase, whereas the achiral $Ia\bar{3}d$ phase is formed upon slow cooling from the achiral Iso phase. However, upon fast cooling, leading to a stronger delay of the Iso-Cub transition (super-cooling) the formation of the chiral *I*23 phase takes place exclusively. It is postulated that at reduced temperature local symmetry breaking in the liquid phase (leading to a $Iso_1^{[*]}$-like local structure) becomes more important and favours the formation of the chiral *I*23 phase, though no separate $Iso_1^{[*]}$ range can be observed in this case.

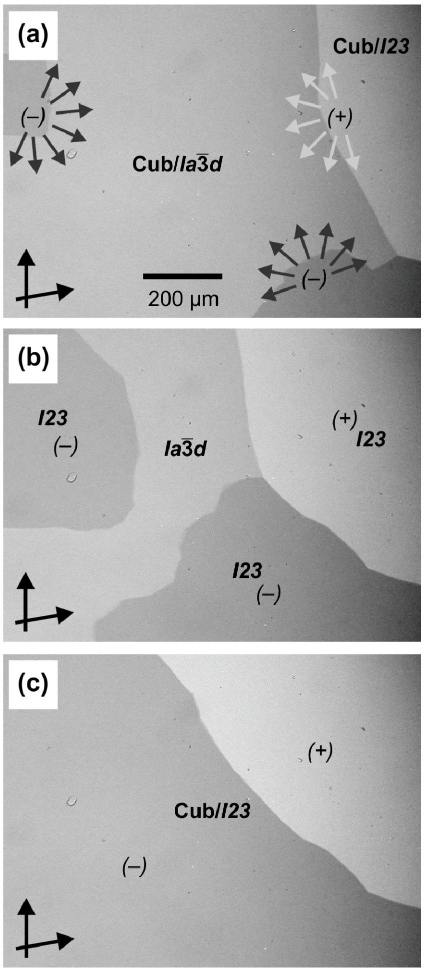


Figure S13. Cubic phases of **3/^{3}OMe** as observed by POM with polarizers being slightly uncrossed after cooling from the isotropic liquid at 130 °C; a) coexisting $I23$ and $Ia\bar{3}d$ phases as observed immediately after cooling; b) growing $I23$ which in c) after 10 min has replaced the $Ia\bar{3}d$ phase completely; contrast enhanced, the width of the images is 1 mm.

3/^{3}Br and **3/^{3}I. -** For **3/^{3}Br** and **3/^{3}I** there is an $I23 \rightarrow Ia\bar{3}d$ transition on heating (see Fig. S14), whereas on cooling from the isotropic liquid only the $Ia\bar{3}d$ phase is formed (see Table S1), independent on the cooling rate. Also in these cases the formation of the achiral $Ia\bar{3}d$ phase on cooling from the achiral Iso phase is favoured, but the transition to $I23$ cannot be observed. Hence, for these two compounds the formation of the mirror symmetry broken $I23$ phase appears to be a bit less favoured compared to **3/^{3}OMe** (see Fig. S14 and Table S1).

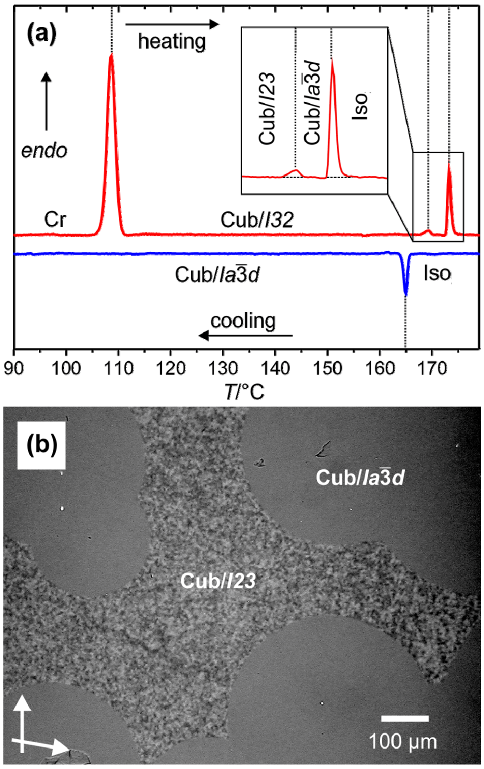


Figure S14. a) DSC traces of compound **3/^{3}Br** and b) $I23$-$Ia\bar{3}d$ transition on heating at T = 169 °C as observed between slightly uncrossed polarizers.

3/^{2}NO2. – The Cub$_{\mathrm{bi}}$/$Ia\bar{3}d$ phase of this compound is observed only on heating, whereas on cooling a non-cubic 3D phase with highly birefringent mosaic texture (M1) is formed, which is stable on further cooling (Table S1) and represents a distorted version of the $Ia\bar{3}d$ lattice.

S1.4.2 Birefringence in the cubic phase range.

In some cases birefringence can appear on cooling the Cub$_{\mathrm{bi}}$ phases. If the development of birefringence is associated with a change of the XRD pattern, these represent non-cubic LC phases with 3D lattice, denoted here as M (e.g. **3/^{4}CN**), which will be discussed in separate future contributions. In other cases development of a weak birefringence is not associated with any DSC peak or any change in the XRD pattern. This is shown in Fig. S15 for compound **3/H** as a representative example. We attribute this to a developing strain caused by thermal shrinkage, which slightly deforms the cubic domains.

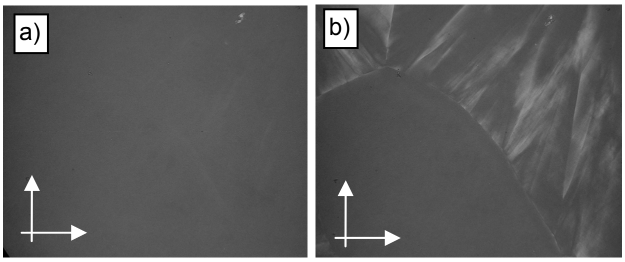


Figure S15. a, b) Developing strain-induced birefringence in the $Ia\bar{3}d$ phase of compound **3/H** as observed between crossed polarizers; a) completely isotropic appearance at T = 155 °C and b) weakly birefringent texture as observed on cooling to T = 80 °C.

S1.4.3 Effects of aromatic core length

The lattice parameter of **3a/1-Npht** is in the typical range for the long pitch $Ia\bar{3}d_{(L)}$ phase, whereas that of **3a/2-Npht** is even 1 nm larger and is the largest parameter of the $Ia\bar{3}d_{(L)}$ lattice of all synthesized compounds with the exception of **3a/Biph** having the longest core and the lowest twist. No $I23$ or any other phase is induced in the contact area between the $\mathrm{Cub_{bi}}$ phases of the two isomeric naphthyl compounds (Fig. S8), so that for both compounds the $\mathrm{Cub_{bi}}$ phase belongs to the same long pitch $Ia\bar{3}d_{(L)}$ type. This is further corroborated by the induction of a $I23$ phase in the contact region with the $Ia\bar{3}d_{(S)}$ phase of **3a/CEt$_3$** (Fig. S7). Polar substituents, especially CN, NO_2 and F at the aromatic apex also contribute to the expansion of the core unit, thus favouring the $Ia\bar{3}d_{(L)}$ phase (NO_2, CN), but also allowing $I23$ phase formation if attached to the sterically demanding lateral 3-positions or 3,5-positions.

S2. Investigation methods

Optical investigation. Phase transitions were observed by polarizing microscopy (Leica DMR XP) in conjunction with a heating stage (FP 82 HT, Mettler) and controller (FP 90, Mettler). 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.

Calometric investigation. Phase transitions were determined by differential scanning calorimetry (DSC-8000, 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.

XRD. - In-house XRD investigations were conducted at Cu K□ line (λ= 1.54 Å) using a standard Coolidge tube source with Ni-filter on powder-like samples. The samples were prepared on a glass plate and were heated to the isotropic state. The powder-like samples were obtained upon fast cooling in the LC phase and were measured in a temperature-controlled heating stage. The distance between sample and the detector was 9 cm (WAXS) or 26.8 cm (SAXS) and the exposure time was 15 min for WAXS and 30 min for SAXS. The diffraction patterns were recorded with a 2D detector (Vantec 500, Bruker), transformation to θ-scan was performed using GADDS. For high-resolution small-angle powder diffraction experiments (SAXS) with a synchrotron source the samples were held in evacuated 1 mm capillaries. A modified Linkam hot stage with a thermal stability within 0.2 ºC was used, with a hole for the capillary drilled through the silver heating block and mica windows attached to it on each side; a Pilatus 2M detector was used at DLS, and MarCCD detectors were used at ESRF and SSRF. 2D diffraction patterns were converted into 1D diffractograms by radially averaging with necessary corrections for diffraction geometries.

Electron density calculation. The diffraction peaks are indexed on the basis of their peak positions, and the lattice parameters and the space groups are subsequently determined. Once the diffraction intensities are measured and the corresponding space group determined, 3-d electron density maps can be reconstructed, on the basis of the general formula

$$E(xyz) = \Sigma_{hkl}F(hkl)\ \exp[\mathrm{i}2\pi(hx+ky+lz)] \qquad \text{(Eqn. 1)}$$

Here $F(hkl)$ is the structure factor of a diffraction peak with index (hkl). It is normally a complex number and the experimentally observed diffraction intensity

$$I(hkl) = \mathrm{K}\cdot F(hkl)\cdot F^*(hkl) = \mathrm{K}\cdot|F(hkl)|^2 \qquad \text{(Eqn. 2)}$$

Here K is a constant related to the sample volume, incident beam intensity etc. In this paper we are only interested in the relative electron densities, hence this constant is simply taken to be 1. Thus the electron density

$$E(xyz) = \Sigma_{hkl}\, \mathrm{sqrt}[I(hkl)]\, \exp[\mathrm{i}2\pi(hx+ky+lz)+\phi_{hkl}] \qquad \text{(Eqn. 3)}$$

As the observed diffraction intensity $I(hkl)$ is only related to the amplitude of the structure factor $|F(hkl)|$, the information about the phase of $F(hkl)$, ϕ_{hkl}, can not be determined directly from experiment. However, the problem is much simplified when the structure of the ordered phase is centrosymmetric, and hence the structure factor $F(hkl)$ is always real and ϕ_{hkl} is either 0 or π. In the case of the centrosymmetric $Ia3d$ phase it is possible for a trial-and-error approach, where candidate electron density maps are reconstructed for all possible phase combinations, and the “correct” phase combination is then selected on the merit of the maps, helped by prior physical and chemical knowledge of the system.

$I23$ phase is non-centrosymmetric so the above approach does not work. In addition, a general (hkl) peak with $h\neq k\neq l$ is only cyclically permutable: it is equivalent to (klh) and (lhk) but not to (hlk), (lkh) and (khl) peaks. Consequently even though the (hkl) and (lkh) peaks coincide in a powder diffractogram, their intensities and corresponding structure factor phases are different. In order to circumvent these two problems for $I23$ phase we have calculated the diffraction intensities and phases for each observed peak from the Fourier transform of a mathematical model of the phase, where the electron density of a point in the unit cell is chosen to be a higher constant value if it is within a certain distance to the network segments, and a lower constant value if it is not. The distance is chosen so that the volume ratio of the high electron density regions in the unit cell matches that of the rigid aromatic core in the molecule. After that, we have simply taken from the simulation the intensity ratio of (hkl) and (lkh) peaks, and the phase angle of each peak, combining them with experimentally observed diffraction intensities to reconstruct the electron density map as shown in Figure 2. More details see ref. [S3].

S3. Synthesis and Analytical Data

S3.1 General

Dry solvents were purchased from commercial sources and used without further purification. 4-fluorobenzoic acid, 4-iodobenzoic acid, 4-(trifluoromethoxy)benzoic acid, 4-nitrobenzoic acid, 4-acetoxybenzoic acid, 3-cyanobenzoic acid, 3-iodobenzoic acid, 2-fluorobenzoic acid, 2-iodobenzoic acid, 2-nitrobenzoic acid, 3,5-dimethoxybenzoic acid, 3,5-difluorobenzoic acid, 3,5-dibromobenzoic acid, 3,5-dinitrobenzoic acid, 2,6-difluorobenzoic acid, 3,4,5-trifluorobenzoic acid, 2,3,4,5,6-pentafluorobenzoic acid, 2-thiophenecarbonyl chloride, cyclohexane carboxylic acid, adamantane-9-carboxylic acid, anthracene-9-carboxylic acid, biphenyl-4-carboxylic acid, 1-naphthoic acid, 2-naphthoic acid were obtained from Sigma Aldrich, 3,4-difluorobenzoic acid from abcr and 3-bromobenzoic acid from Alfa Aesar were used as obtained. 5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(4-hydroxybenzoyloxy)-phenyl]-2,2′-bithiophene (**3b/OH**) was prepared according to the procedures reported previously.[S4]

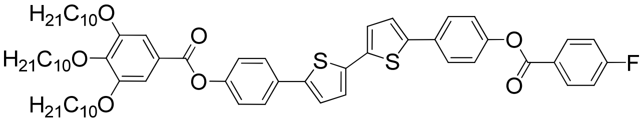
Column chromatography was performed with Macherey-Nagel silica gel 60 (230–400 mesh).NMR spectra were recorded on Varian Gemini 2000 or Unity 500 spectrometers at 27 °C with trimethylsilane as internal standard. Mass spectra were taken on Finnigan LCQ (electrospray, sprayvoltage 6.7 kV, sheath gas nitrogen). Microanalyses were performed using a Leco CHNS-932 elemental analyser.

Compound **3/H,** the alkoxy substituted compounds **3/^{4}OMe,**^{S4} **3/^{34}OMe$_2$,**^{S4} **3/^{345}OMe$_3$,**^{S4} **3/^{3}OEt**^{S4} and **3/^{4}ODec**^{S4} and compounds **3a/Cy,**^{S5} **3a/Ada,**^{S5} and **3a/CEt$_3$**^{S5} have been reported in the given previous communications. The detailed procedures for the preparation of all other compounds and their analytical data are reported below.

General procedure: 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 **3b/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^{S4}.

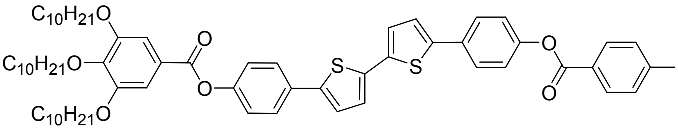
S3.2 Compounds 3/X

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(4-fluorobenzoyloxy)phenyl]-2,2′-bithiophene **3/^{4}F**



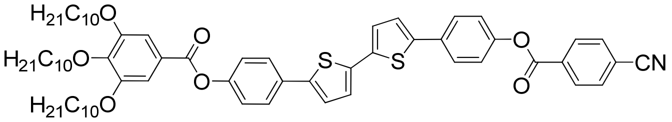
Prepared from **3b/OH** (55 mg, 0.060 mmol) and 4-fluorobenzoic acid (11 mg, 0.075 mmol); purified by column chromatography (eluent: $CHCl_3$/*n*-hexane 2/1, v/v) and repeated crystallization from THF/EtOH; yield 46 mg (0.044 mmol, 73%); yellow solid; $C_{64}H_{81}FO_7S_2$; M = 1045.45 g/mol; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (dd, $^3J_{H,H}$ = 8.8 Hz, $^4J_{H,F}$ = 5.4 Hz, 2H, Ar-H), 7.67 (d, $^3J_{H,H}$ = 9.0 Hz, 2H, Ar-H), 7.66 (d, $^3J_{H,H}$ = 9.0 Hz, 2H, Ar-H), 7.42 (s, 2H, Ar-H), 7.25–7.20 (m, 8H, Ar-H + Th-H), 7.19 (d, $^3J_{H,H}$ = 3.5 Hz, 2H, Th-H), 4.09–4.05 (m, 6H, OCH_2CH_2), 1.91–1.80 (m, 4H, OCH_2CH_2), 1.80–1.73 (m, 2H, OCH_2CH_2), 1.51–1.47 (m, 6H, CH_2), 1.38–1.25 (br, 36H, CH_2), 0.93–0.85 (m, 9H, CH_3); ^{19}F NMR (376 MHz, $CDCl_3$) δ –104.23 (tt, $^3J_{F,H}$ = 8.8 Hz, $^4J_{F,H}$ = 5.6 Hz, 1F); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2 (d, $^1J_{C,F}$ = 255.4 Hz, C-F), 165.0, 164.1 (C=O), 153.0, 150.5, 150.3, 143.2, 142.3, 142.2, 136.9, 136.8, 132.8 (d, $^3J_{C,F}$ = 9.4 Hz, Ar-C), 132.0, 131.8, 126.8, 126.7, 125.7 (d, $^4J_{C,F}$ = 3.7 Hz, Ar-C), 124.6, 124.6, 124.1, 124.0, 123.7, 122.3, 122.2, 115.8 (d, $^2J_{C,F}$ = 22.1 Hz, Ar-C), 108.7 (Ar-C + Th-C), 73.6, 69.3 (OCH_2), 31.9, 31.9, 30.4, 29.7, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 26.1, 26.1, 22.7, 22.7 (CH_2), 14.1 (CH_3); MS (ESI, CH_2Cl_2): *m/z* (%) = 1044.45 ([M•]$^+$, 100); elemental analysis: calc for $C_{64}H_{81}FO_7S_2$: C 73.53%, H 7.81%; found: C 73.44%, H 7.97%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(4-iodobenzoyloxy)phenyl]-2,2′-bithiophene **3/^{4}I**



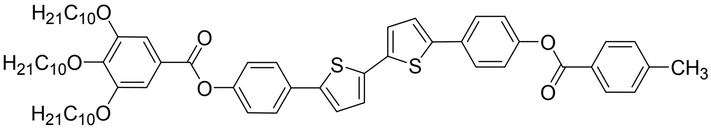
Prepared from **3b/OH** (101 mg, 0.109 mmol) and 4-iodobenzoic acid (34 mg, 0.137 mmol); purified by column chromatography (eluent: $CHCl_3$/*n*-hexane 4/1, v/v) and repeated crystallization from THF/MeOH; yield 90 mg (0.078 mmol, 72%); yellow solid; $C_{64}H_{81}IO_7S_2$; M = 1153.36 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.86 (m, 4H, Ar-H), 7.66 (d, ^3J = 8.5 Hz, 2H, Ar-H), 7.65 (d, ^3J = 8.5 Hz, 2H, Ar-H), 7.42 (s, 2H, Ar-H), 7.26–7.20 (m, 6H, Ar-H + Th-H), 7.19 (d, ^3J = 3.8 Hz, 2H, Th-H), 4.10–4.02 (m, 6H, OC*H*$_2$CH$_2$), 1.88–1.79 (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$_2$), 1.41–1.21 (m, 36H, CH$_2$), 0.92–0.82 (m, 9H, CH$_3$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 164.9, 164.6 (C=O), 153.0, 150.5, 150.2, 143.1, 142.3, 142.1, 138.0, 136.9, 136.7, 132.1, 131.8, 131.5, 128.9, 126.7, 126.7, 126.7, 126.7, 124.6, 124.6, 124.6, 124.6, 124.1, 124.0, 123.7, 122.3, 122.1, 108.6, 101.7 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 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 (CH$_2$), 14.1 (CH$_3$); elemental analysis: calc for $C_{64}H_{81}IO_7S_2$: C 66.65%, H 7.08%; found: C 66.65%, H 7.03%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(4-cyanobenzoyloxy)phenyl]-2,2′-bithiophene **3/^{4}CN**



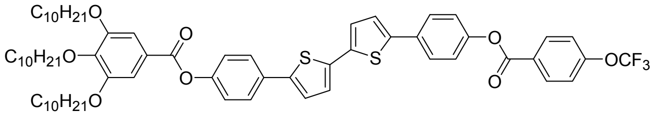
Prepared from **3b/OH** (138 mg, 0.149 mmol) and 4-cyanobenzoic acid (28 mg, 0.186 mmol); purified by column chromatography (eluent: CHCl$_3$) and repeated crystallization from EtOAc; yield 43mg (0.041 mmol, 27%); yellow solid; $C_{65}H_{81}NO_7S_2$; *M* = 1052.47 g/mol; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.31 (d, ^{3}J = 8.4 Hz, 2H, Ar-H), 7.82 (d, ^{3}J = 8.4 Hz, 2H, Ar-H), 7.66 (d, ^{3}J = 8.4 Hz, 2H, Ar-H), 7.64 (d, ^{3}J = 8.4 Hz, 2H, Ar-H), 7.40 (s, 2H, Ar-H), 7.26–7.20 (m, 6H, Ar-H + Th-H), 7.17 (d, ^{3}J = 3.8 Hz, 2H, Th-H), 4.07–4.02 (m, 6H, OC*H*$_2$CH$_2$), 1.87–1.79 (m, 4H, OCH$_2$C*H*$_2$), 1.79–1.70 (m, 2H, OCH$_2$C*H*$_2$), 1.50–1.44 (m, 6H, CH$_2$), 1.38–1.21 (m, 36H, CH$_2$), 0.90–0.82 (m, 9H, CH$_3$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 165.0, 163.5 (C=O), 153.0, 150.6, 149.9, 143.2, 142.4, 141.9, 137.1, 136.7, 133.3, 132.4, 131.8, 130.7, 126.8, 126.7, 124.7, 124.6, 124.3, 124.1, 123.7, 122.4, 122.0, 117.8, 117.2, 108.7 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 32.0, 31.9, 30.4, 29.9, 29.9, 29.8, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 29.5, 26.1, 26.1, 22.7, 22.7 (CH$_2$), 14.1 (CH$_3$); elemental analysis: calc for $C_{65}H_{81}NO_7S_2$: C 74.18%, H 7.76%, N 1.33%; found: C 73.91%, H 7.81%, N 1.13%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(4-methylbenzoyloxy)phenyl]-2,2′-bithiophene **3/^{4}Me**



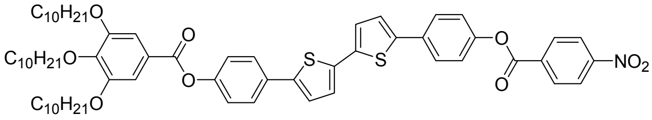
Prepared from **3b/OH** (98 mg, 0.106 mmol) and 4-methylbenzoic acid (18 mg, 0.133 mmol); purified by column chromatography (eluent: CHCl$_3$/*n*-Hexan 3:1, v/v) and repeated crystallization from THF/MeOH; yield 42 mg (0.040 mmol, 38%); yellow solid; $C_{65}H_{84}O_7S_2$; *M* = 1041.49 g/mol; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.11 (d, ^{3}J = 8.2 Hz, 2H, Ar-H), 7.66 (d, ^{3}J = 8.7 Hz, 4H, Ar-H), 7.42 (s, 2H, Ar-H), 7.33 (d, ^{3}J = 7.9 Hz, 2H, Ar-H), 7.27–7.22 (m, 6H, Ar-H + Th-H), 7.19 (d, ^{3}J = 3.8 Hz, 2H, Th-H), 4.09–4.04 (m, 6H, OC*H*$_2$CH$_2$), 2.47 (s, 3H, CH$_3$), 1.88–1.80 (m, 4H, OCH$_2$C*H*$_2$), 1.80–1.73 (m, 2H, OCH$_2$C*H*$_2$), 1.53–1.45 (m, 6H, CH$_2$), 1.41–1.21 (m, 36H, CH$_2$), 0.91–0.86 (m, 9H, CH$_3$); ^{13}C NMR (100 MHz, CDC3) δ 165.1, 164.9 (C=O), 153.0, 150.5, 144.5, 143.1, 142.3, 142.3, 136.8, 136.7, 131.8, 131.8, 130.2, 129.3, 126.7, 124.6, 124.0, 123.7, 122.3, 122.3, 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 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 (CH$_2$), 21.8 (Ar-CH$_3$), 14.1 (CH$_3$); elemental analysis: calc for $C_{65}H_{84}O_7S_2$: C 74.96%, H 8.13%; found: C 74.81%, H 8.19%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(4-trifluoromethoxybenzoyloxy)phenyl]-2,2′-bithiophene **3/^{4}OCF3**



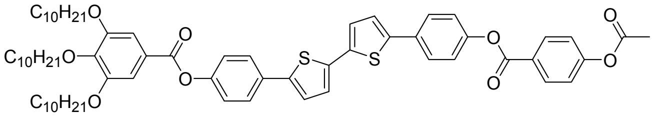
Prepared from **3b/OH** (96 mg, 0.104 mmol) and 4-(trifluoromethoxy)benzoic acid (27 mg, 0.130 mmol); purified by column chromatography (eluent: $CHCl_3$/*n*-Hexan 4:1, v/v) and repeated crystallization from THF/MeOH; yield 109 mg (0.098 mmol, 94%); yellow solid; $C_{65}H_{81}F_3O_8S_2$; *M* = 1111.46 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, ^3J = 8.9 Hz, 2H, Ar-H), 7.67 (d, ^3J = 8.6 Hz, 2H, Ar-H), 7.66 (d, ^3J = 8.6 Hz, 2H, Ar-H), 7.42 (s, 2H, Ar-H), 7.36 (d, ^3J = 8.1 Hz, 2H, Ar-H), 7.27–7.21 (m, 6H, Ar-H + Th-H), 7.19 (d, ^3J = 3.8 Hz, 2H, Th-H), 4.09–4.03 (m, 6H, OC*H*$_2$CH$_2$), 1.88–1.80 (m, 4H, OCH$_2$C*H*$_2$), 1.79–1.73 (m, 2H, OCH$_2$C*H*$_2$), 1.52–1.45 (m, 6H, CH$_2$), 1.41–1.22 (m, 36H, CH$_2$), 0.92–0.85 (m, 9H, CH$_3$); ^{19}F NMR (376 MHz, $CDCl_3$) δ –57.62 (s, 3F); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 163.9 (C=O), 153.0, 150.5, 150.1, 143.1, 142.3, 142.1, 136.9, 136.7, 132.2, 132.1, 131.8, 127.8, 126.8, 126.7, 124.6, 124.6, 124.1, 124.0, 123.7, 122.3, 122.1, 120.4, 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 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 (CH$_2$), 14.1 (CH$_3$); elemental analysis: calc for $C_{65}H_{81}F_3O_8S_2$: C 74.96%, H 8.13%; found: C 74.81%, H 8.19%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(4-nitrobenzoyloxy)phenyl]-2,2′-bithiophene **3/^{4}NO2**



Prepared from **3b/OH** (101 mg, 0.109 mmol) and 4-nitrobenzoic acid (23 mg, 0.137 mmol); purified by column chromatography (eluent: $CHCl_3$/*n*-Hexan 4:1, v/v) and repeated crystallization from THF/MeOH; yield 78 mg (0.073 mmol, 67%); yellow solid; $C_{64}H_{81}NO_9S_2$; *M* = 1072.46 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42–8.35 (m, 4H, Ar-H), 7.71–7.63 (m, 4H, Ar-H), 7.42 (s, 2H, Ar-H), 7.28 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.26–7.21 (m, 4H, Ar-H + Th-H), 7.19 (d, 3*J* = 3.8 Hz, 2H, Th-H), 4.09–4.02 (m, 6H, OC*H*$_2$CH$_2$), 1.88–1.80 (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$_2$), 1.42–1.20 (m, 36H, CH$_2$), 0.93–0.84 (m, 9H, CH$_3$); ^{13}C NMR (125 MHz, cdcl$_3$) δ 164.9, 163.2 (C=O), 153.0, 151.0, 150.6, 149.9, 143.2, 142.4, 141.9, 137.1, 136.6, 134.8, 132.5, 131.8, 131.3, 126.8, 126.7, 124.7, 124.6, 124.3, 124.0, 123.7, 123.7, 122.3, 122.0, 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 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 (CH$_2$), 14.1 (CH$_3$); elemental analysis: calc for $C_{64}H_{81}NO_9S_2$: C 71.67%, H 7.61%, N 1.31%; found: C 71.41%, H 7.49%, N 1.31%.

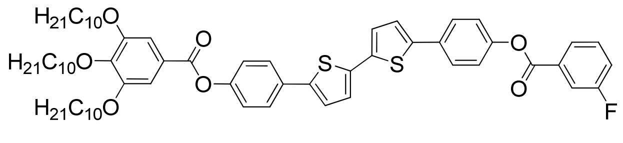
5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(4-acetyloxybenzoyloxy)phenyl]-2,2′-bithiophene **3/^{4}OAc**



Prepared from **3b/OH** (99 mg, 0.107 mmol) and 4-(acetyloxy)benzoic acid (24 mg, 0.134 mmol); purified by column chromatography (eluent: $CHCl_3$/*n*-Hexan 3:1, v/v) and repeated crystallization from THF/MeOH; yield 66 mg (0.061 mmol, 57%); yellow solid; $C_{66}H_{84}O_9S_2$; *M* = 1085.50 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.66 (d, ^3J = 8.6 Hz, 2H, Ar-H), 7.65 (d, ^3J

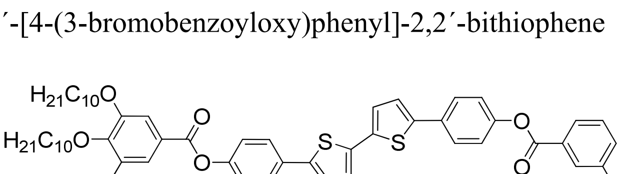
= 8.6 Hz, 2H, Ar-H), 7.42 (s, 2H, Ar-H), 7.28–7.21 (m, 8H, Ar-H + Th-H), 7.19 (d, ^3J = 3.8 Hz, 2H, Th-H), 4.09–4.03 (m, 6H, OC*H*$_2$CH$_2$), 2.35 (s, 3H, O(O)CCH$_3$), 1.88–1.80 (m, 4H, OCH$_2$C*H*$_2$), 1.79–1.72 (m, 2H, OCH$_2$C*H*$_2$), 1.52–1.44 (m, 6H, CH$_2$), 1.41–1.22 (m, 36H, CH$_2$), 0.92–0.85 (m, 9H, CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.7, 164.9, 164.3 (C=O), 154.9, 153.0, 150.5, 150.3, 143.1, 142.3, 142.2, 136.8, 136.8, 132.0, 131.8, 126.9, 126.7, 126.7, 124.6, 124.1, 124.0, 123.7, 122.3, 122.2, 121.9, 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 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 (CH$_2$), 21.1 (O(O)C*C*H$_3$), 14.1 (CH$_3$); elemental analysis: calc for $C_{66}H_{84}O_9S_2$: C 73.03%, H 7.80%; found: C 72.93%, H 7.70%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(3-fluorobenzoyloxy)phenyl]-2,2′-bithiophene **3/^{3}F**



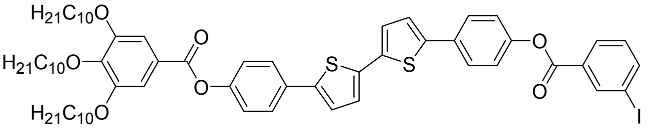
Prepared from **3b/OH** (94 mg, 0.102 mmol) and 3-fluorobenzoic acid (18 mg, 0.128 mmol); purified by column chromatography (eluent: CHCl$_3$/*n*-hexane 5/1, v/v) and repeated crystallization from THF/EtOH; yield 49 mg (0.047 mmol, 46%); yellow solid; $C_{64}H_{81}FO_7S_2$; *M* = 1045.45 g/mol; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.02 (ddd, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.6 Hz, $^4J_{H,H}$ = 1.0 Hz, 1H, Ar-H), 7.90 (ddd, $^3J_{H,F}$ = 9.2 Hz, $^4J_{H,H}$ = 2.5 Hz, $^4J_{H,H}$ = 1.6 Hz, 1H, Ar-H), 7.67 (d, $^3J_{H,H}$ = 8.7 Hz, 2H, Ar-H), 7.66 (d, $^3J_{H,H}$ = 8.7 Hz, 2H, Ar-H), 7.51 (ddd, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,F}$ = 5.6 Hz, 1H, Ar-H), 7.42 (s, 2H, Ar-H), 7.36 (dddd, $^3J_{H,F}$= 9.2 Hz, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 2.6 Hz, $^4J_{H,H}$ = 1.0 Hz, 1H, Ar-H), 7.28–7.21 (m, 6H, Ar-H + Th-H), 7.19 (d, $^3J_{H,H}$ = 3.8 Hz, 2H, Th-H), 4.07 (t, $^3J_{H,H}$ = 6.4 Hz, 2H, OC*H*$_2$CH$_2$), 4.06 (t, $^3J_{H,H}$ = 6.4 Hz, 4H, OC*H*$_2$CH$_2$), 1.89–1.80 (m, 4H, OCH$_2$C*H*$_2$), 1.80–1.72 (m, 2H, OCH$_2$C*H*$_2$), 1.51–1.46 (m, 6H, CH$_2$), 1.43–1.19 (br, 36H, CH$_2$), 0.89 (t, $^3J_{H,H}$ = 6.4 Hz, 3H, CH$_3$), 0.88 (t, $^3J_{H,H}$ = 6.4 Hz, 6H, CH$_3$); ^{19}F NMR (376 MHz, CDCl$_3$) δ –111.83 (ddd, $^3J_{F,H}$ = 8.6 Hz, $^4J_{F,H}$ = 5.3 Hz); ^{13}C NMR (125 MHz, CDCl$_3$) δ 165.0 (C=O), 164.0 (d, $^4J_{C,F}$ = 2.9 Hz, C=O), 162.6 (d, $^1J_{C,F}$= 246 Hz, C-F), 153.0, 150.5, 150.2, 143.1, 142.3, 142.1, 136.9, 136.7, 132.1, 131.8, 131.6 (d, $^3J_{C,F}$ = 7.1 Hz, Ar-C), 130.3 (d, $^3J_{C,F}$ = 8.1 Hz, Ar-C), 126.8, 126.7, 126.0 (d, $^4J_{C,F}$ = 3.2 Hz, Ar-C), 124.6, 124.6, 124.1, 124.0, 123.7, 122.3, 122.1, 120.8 (d, $^2J_{C,F}$ = 21.0 Hz, Ar-C), 117.1 (d, $^2J_{C,F}$ = 22.9 Hz, Ar-C), 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 31.9, 31.9, 30.3, 29.7, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 26.1, 26.1, 22.7, 22.7 (CH$_2$), 14.1 (CH$_3$); MS (ESI, CH$_2$Cl$_2$): *m/z* (%) = 1044.45 ([M•]$^+$, 100); elemental analysis: calc for $C_{64}H_{81}FO_7S_2$: C 73.53%, H 7.81%; found: C 73.34%, H 7.75%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(3-bromobenzoyloxy)phenyl]-2,2′-bithiophene **3/^{3}Br**



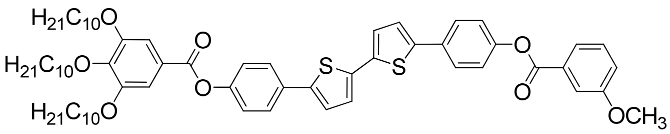
Prepared from **3b/OH** (89 mg, 0.096 mmol) and 3-bromobenzoic acid (24 mg, 0.120 mmol); purified by column chromatography (eluent: CHCl$_3$/*n*-hexane 4/1, v/v) and repeated crystallization from THF/EtOH; yield 94 mg (0.085 mmol, 89%; yellow solid; $C_{64}H_{81}BrO_7S_2$; *M* = 1106.36 g/mol; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.36 (dd, ^4J = 1.8 Hz, 1H, Ar-H), 8.15 (ddd, ^3J = 8.0 Hz, ^4J = 1.8 Hz, ^4J = 1.1 Hz, 1H, Ar-H), 7.78 (ddd, ^3J= 8.0 Hz, ^4J = 1.8 Hz, ^4J = 1.1 Hz, 1H, Ar-H), 7.68 (d, ^3J = 8.4 Hz, 2H, Ar-H), 7.67 (d, ^3J = 8.4 Hz, 2H, Ar-H), 7.41 (s, 2H, Ar-H), 7.41 (dd, ^3J = 8.0 Hz, 1H, Ar-H), 7.29–7.20 (m, 6H, Ar-H + Th-H), 7.19 (d, ^3J = 3.7 Hz, 2H, Th-H), 4.08–4.04 (m, 6H, OC*H*$_2$CH$_2$), 1.88–1.80 (m, 4H, OCH$_2$C*H*$_2$), 1.79–1.73 (m, 2H, OCH$_2$C*H*$_2$), 1.53–1.46 (m, 6H, CH$_2$), 1.42–1.19 (br, 36H, CH$_2$), 0.94–0.84 (m, 9H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 163.8 (C=O), 153.0, 150.5, 150.1, 143.1, 142.3, 142.1, 136.9, 136.7, 136.6, 133.1, 132.1, 131.8, 131.4, 130.2, 128.8, 126.8, 126.7, 124.6, 124.6, 124.2, 124.0, 123.7, 122.7, 122.3, 122.1, 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH_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, 26.1, 22.7, 22.7 (CH_2), 14.1 (CH_3); elemental analysis: calc for $C_{64}H_{81}BrO_7S_2$: C 69.48%, H 7.38%, S 5.80%; found: C 69.59%, H 7.36%, S 5.84%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(3-iodobenzoyloxy)phenyl]-2,2′-bithiophene **3/^{3}I**



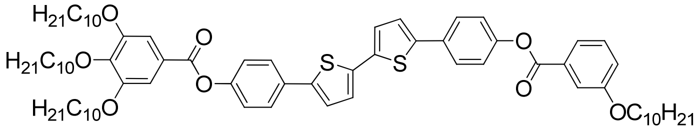
Prepared from **3b/OH** (89 mg, 0.096 mmol) and 3-iodobenzoic acid (30 mg, 0.120 mmol); purified by column chromatography (eluent: $CHCl_3$/*n*-hexane 4/1, v/v) and repeated crystallization from THF/EtOH; yield 75 mg (0.065 mmol, 68%); yellow solid; $C_{64}H_{81}IO_7S_2$; M = 1153.36 g/mol; ^1H NMR (500 MHz, $CDCl_3$) δ 8.58–8.56 (m, 1H, Ar-H), 8.21–8.18 (m, 1H, Ar-H), 8.01–7.98 (m, 1H, Ar-H), 7.70–7.65 (m, 4H, Ar-H), 7.43 (s, 2H, Ar-H), 7.31–7.23 (m, 7H, Ar-H +Th-H), 7.20 (d, ^3J = 3.7 Hz, 2H, Ar-H), 4.10–4.05 (m, 6H, OCH_2CH_2), 1.89–1.82 (m, 4H, OCH_2CH_2), 1.81–1.74 (m, 2H, OCH_2CH_2), 1.53–1.46 (m, 6H, CH_2), 1.42–1.23 (m, 36H, CH_2), 0.93–0.86 (m, 9H, CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 164.9, 163.6 (C=O), 153.0, 150.5, 150.1, 143.1, 142.5, 142.3, 142.1, 139.0, 136.9, 136.7, 132.1, 131.8, 131.3, 130.2, 129.3, 126.7, 126.7, 124.6, 124.6, 124.1, 124.0, 123.7, 122.3, 122.1, 108.6, 93.9 (Ar-C + Th-C), 73.6, 69.3 (OCH_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 (CH_2), 14.1 (CH_3); elemental analysis: calc for $C_{65}H_{81}IO_7S_2$: C 66.65%, H 7.08%; found: C 66.43%, H 6.99%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(3-methoxybenzoyloxy)phenyl]-2,2′-bithiophene **3/^{3}OMe**



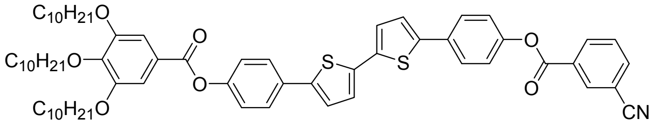
Prepared from **3b/OH** (62 mg, 0.067 mmol) and 3-methoxybenzoic acid (13 mg, 0.084 mmol); purified by column chromatography (eluent: $CHCl_3$) and repeated crystallization from THF/EtOH; yield 54 mg (0.051 mmol, 76%); yellow solid; $C_{65}H_{84}O_8S_2$; M = 1057.49 g/mol; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, ^3J = 7.7 Hz, 1H, Ar-H), 7.72 (s, 1H, Ar-H), 7.66 (d, ^3J = 8.4 Hz, 2H, Ar-H), 7.65 (d, ^3J = 8.4 Hz, 2H, Ar-H), 7.43 (t, ^3J = 7.7 Hz, 1H, Ar-H), 7.42 (s, 2H, Ar-H), 7.27–7.20 (m, 7H, Ar-H+ Th-H), 7.19 (d, ^3J = 3.7 Hz, 2H, Th-H), 4.08–4.04 (m, 6H, OCH_2CH_2), 3.90 (s, 3H, OCH_3), 1.94–1.79 (m, 4H, OCH_2CH_2), 1.79–1.76 (m, 2H, OCH_2CH_2), 1.51–1.43 (m, 6H, CH_2), 1.40–1.22 (s, 36H, CH_2), 0.95–0.83 (m, 9H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9 (C=O), 159.7, 153.0, 150.5, 150.4, 143.1, 142.3, 142.3, 136.8, 136.8, 131.9, 131.8, 130.7, 129.6, 126.7, 126.7, 124.6, 124.1, 124.0, 123.7, 122.6, 122.3, 122.2, 120.3, 114.5, 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH_2), 55.5 (OCH_3), 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 (CH_2), 14.1 (CH_3); elemental analysis: calc for $C_{65}H_{84}O_8S_2$: C 73.83%, H 8.01%; found.: 73.46%, H 7.93%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(3-*n*-decyloxybenzoyloxy)phenyl]-2,2′-bithiophene **3/^{3}ODec**



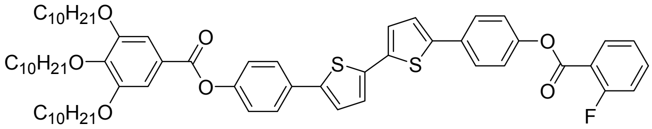
Prepared from **3b/OH** (96 mg, 0.104 mmol) and 3-decyloxybenzoic acid (36 mg, 0.130 mmol); purified by column chromatography (eluent: $CHCl_3$/*n*-hexane 2/1, v/v) and repeated crystallization from THF/EtOH; yield 94 mg (0.079 mmol, 76%); yellow solid; $C_{74}H_{102}O_8S_2$; M = 1183.73 g/mol; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (ddd, ^3J = 7.6 Hz, ^4J = 1.6 Hz, ^4J = 1.0 Hz, 1H, Ar-H), 7.69 (dd, ^4J = 2.5 Hz, ^4J = 1.6 Hz, 1H, Ar-H), 7.64 (d, ^3J =8.8 Hz, 2H, Ar-H), 7.63 (d, ^3J =8.8 Hz, 2H, Ar-H), 7.40 (s, 2H, Ar-H), 7.40 (dd, ^3J = 7.6 Hz, 1H, Ar-H), 7.25–7.20 (m, 6H, Ar-H + Th-H), 7.17 (d, ^3J = 3.7 Hz, 2H, Th-H), 7.16 (ddd, ^3J = 7.6 Hz, ^4J = 2.5 Hz, ^4J = 1.0 Hz, 1H, Ar-H), 4.07–4.00 (m, 8H, OCH_2CH_2), 1.85–1.79 (m, 6H, OCH_2CH_2), 1.78–1.71 (m, 2H, OCH_2CH_2), 1.51–1.42 (m, 8H, CH_2), 1.38–1.22 (br, 48H, CH_2), 0.90–0.82 (m, 12H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 165.0 (C=O), 159.3, 153.0, 150.5, 150.4, 143.1, 142.3, 142.3, 136.8, 136.8, 131.9, 131.8, 130.6, 129.6, 126.7, 126.7, 124.6, 124.1, 124.0, 123.7, 122.4, 122.3, 122.3, 120.7, 115.3, 108.6 (Ar-C + Th-C), 73.6, 69.3, 68.3 (OCH_2), 31.9, 31.9, 31.9, 30.3, 29.7, 29.7, 29.6, 29.6, 29.6, 29.5, 29.4, 29.4, 29.3, 29.3, 29.2, 26.1, 26.1, 26.0, 22.7, 22.7 (CH_2), 14.1 (CH_3); elemental analysis: calc for $C_{74}H_{102}O_8S_2$: C 75.08%, H 8.69%; found: C 75.08%, H 8.95%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(3-cyanobenzoyloxy)phenyl]-2,2′-bithiophene **3/^{3}CN**



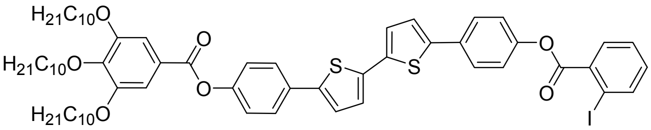
Prepared from **3b/OH** (93 mg, 0.101 mmol) and 3-cyanobenzoic acid (19 mg, 0.126 mmol); purified by column chromatography (eluent: $CHCl_3$/*n*-Hexan 4:1, v/v) and repeated crystallization from THF/MeOH; yield 81 mg (0.077 mmol, 76%); yellow solid; $C_{65}H_{81}NO_7S_2$; M = 1052.47 g/mol; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (t, ^4J = 1.4 Hz, 1H, Ar-H), 8.45 (dt, ^3J = 8.4 Hz, ^4J = 1.4 Hz, 1H, Ar-H), 7.94 (dt, ^3J = 7.7 Hz, ^4J = 1.2 Hz, 1H, Ar-H), 7.70–7.64 (m, 5H, Ar-H), 7.42 (s, 2H, Ar-H), 7.28–7.22 (m, 6H, Ar-H + Th-H), 7.19 (d, ^3J = 3.7 Hz, 2H, Th-H), 4.10–4.03 (m, 6H, OCH_2CH_2), 1.88–1.81 (m, 4H, OCH_2CH_2), 1.80–1.74 (m, 2H, OCH_2CH_2), 1.53–1.45 (m, 6H, CH_2), 1.41–1.22 (m, 36H, CH_2), 0.92–0.86 (m, 9H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 163.1 (C=O), 153.0, 150.5, 149.8, 143.1, 142.4, 141.9, 137.0, 136.7, 136.6, 134.1, 133.8, 132.4, 131.8, 130.8, 129.7, 126.8, 126.7, 124.7, 124.6, 124.2, 124.0, 123.7, 122.3, 122.0, 117.7, 113.3, 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH_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, 26.1, 22.7, 22.7 (CH_2), 14.1 (CH_3); elemental analysis: calc for $C_{65}H_{81}NO_7S_2$: C 74.18%, H 7.76%, N 1.33%; found: C 73.84%, H 7.76%, N 1.35%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(2-fluorobenzoyloxy)phenyl]-2,2′-bithiophene **3/^{2}F**



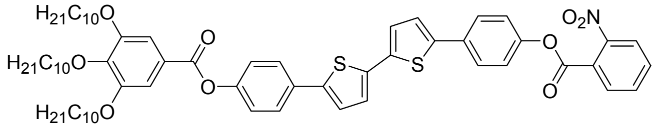
Prepared from **3b/OH** (95 mg, 0.103 mmol) and 2-fluorobenzoic acid (18 mg, 0.129 mmol); purified by column chromatography (eluent: $CHCl_3$/*n*-Hexan 4:1, v/v) and repeated crystallization from THF/MeOH; yield 56 mg (0.054 mmol, 52%); yellow solid; $C_{64}H_{81}FO_7S_2$; M = 1045.45 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (td, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.8 Hz, 1H, Ar-H), 7.66 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, Ar-H), 7.66 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, Ar-H), 7.64–7.58 (m, 1H, Ar-H), 7.42 (s, 2H, Ar-H), 7.32–7.26 (m, 3H, Ar-H), 7.25–7.20 (m, 5H, Ar-H + Th-H), 7.19 (d, $^3J_{H,H}$ = 3.8 Hz, 2H, Th-H), 4.09–4.03 (m, 6H, OCH_2CH_2), 1.88–1.79 (m, 4H, OCH_2CH_2), 1.79–1.72 (m, 2H, OCH_2CH_2), 1.52–1.44 (m, 6H, CH_2), 1.41–1.21 (m, 36H, CH_2), 0.92–0.85 (m, 9H, CH_3); ^{19}F NMR (470 MHz, $CDCl_3$) δ –108.01 (m, 1F); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9 (C=O), 162.7 (d, $^3J_{C,F}$ = 4.0 Hz, C=O), 162.3 (d, $^1J_{C,F}$ = 261.5 Hz, C-F), 153.0, 150.5, 150.1, 143.1, 142.3, 142.2, 136.8, 136.8, 135.3, 135.2, 132.5, 132.0, 131.8, 126.7, 126.7, 124.6, 124.6, 124.2, 124.1, 124.1, 124.0, 123.7, 122.3, 122.2, 118.0, 117.9, 117.23 (d, ^2J = 22.3 Hz, Ar-C), 108.6 (Ar-C + Th-C), 73.6, 69.3(OCH_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(CH_2), 14.1 (CH_3); elemental analysis: calc for $C_{64}H_{81}FO_7S_2$: C 73.53%, H 7.81%, found: C 73.32%, H 7.73%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(2-iodobenzoyloxy)phenyl]-2,2′-bithiophene **3/^{2}I**



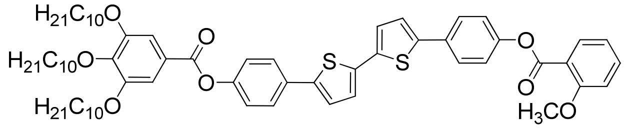
Prepared from **3b/OH** (100 mg, 0.108 mmol) and 2-iodobenzoic acid (34 mg, 0.137 mmol); purified by column chromatography (eluent: $CHCl_3$/*n*-Hexan 4:1, v/v) and repeated crystallization from THF/MeOH; yield 92 mg (0.080 mmol, 74%); yellow solid; $C_{64}H_{81}IO_7S_2$; M = 1153.36 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, ^3J = 7.9 Hz, 1H, Ar-H), 8.05 (dd, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 1H, Ar-H), 7.67 (d, ^3J = 8.5 Hz, 2H, Ar-H), 7.66 (d, ^3J = 8.5 Hz, 2H, Ar-H), 7.50 (t, ^3J = 7.3 Hz, 1H, Ar-H), 7.42 (s, 2H, Ar-H), 7.31 (d, ^3J = 8.6 Hz, 2H, Ar-H), 7.25–7.21 (m, 5H, Ar-H + Th-H), 7.19 (d, ^3J = 3.7 Hz, 2H, Th-H), 4.12–4.00 (m, 6H, OCH_2CH_2), 1.88–1.80 (m, 4H, OCH_2CH_2), 1.79–1.72 (m, 2H, OCH_2CH_2), 1.52–1.44 (m, 6H, CH_2), 1.42–1.21 (m, 36H, CH_2), 0.95–0.82 (m, 9H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 164.8 (C=O), 153.0, 150.5, 150.1, 143.1, 142.3, 142.1, 141.7, 136.9, 136.7, 134.1, 133.3, 132.2, 131.8, 131.5, 128.1, 126.7, 126.7, 124.6, 124.6, 124.1, 124.0, 123.7, 122.3, 122.1, 108.6, 94.6 (Ar-C + Th-C), 73.6, 69.3 (OCH_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 (CH_2), 14.1 (CH_3); elemental analysis: calc for $C_{64}H_{81}IO_7S_2$: C 66.65%, H 7.08%; found: C 66.64%, H 7.05%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(2-nitrobenzoyloxy)phenyl]-2,2′-bithiophene **3/^{2}NO2**



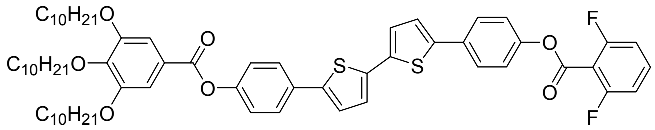
Prepared from **3b/OH** (100 mg, 0.108 mmol) and 2-nitrobenzoic acid (23 mg, 0.135 mmol); purified by column chromatography (eluent: $CHCl_3$/*n*-hexane 5/1, v/v) and repeated crystallization from THF/MeOH; yield 76 mg (0.071 mmol, 66%), yellow solid; $C_{66}H_{81}NO_9S_2$; M = 1072.46 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, ^{3}J = 8.0 Hz, ^{4}J = 1.2 Hz, 1H, Ar-H), 7.91 (dd, ^{3}J = 7.5 Hz, ^{4}J = 1.5 Hz, 1H, Ar-H), 7.78 (td, ^{3}J = 7.5 Hz, ^{4}J = 1.4 Hz, 1H, Ar-H), 7.76–7.70 (m, 1H, Ar-H), 7.67 (d, ^{3}J = 8.7 Hz, 2H, Ar-H), 7.66 (d, ^{3}J = 8.7 Hz, 2H, Ar-H), 7.42 (s, 2H, Ar-H), 7.30 (d, ^{3}J = 8.8 Hz, 2H, Ar-H), 7.25–7.21 (m, 4H, Ar-H + Th-H), 7.19 (dd, ^{3}J = 3.7 Hz, ^{3}J = 1.4 Hz, 2H, Th-H), 4.10–4.03 (m, 6H, OCH_2CH_2), 1.89–1.80 (m, 4H, OCH_2CH_2), 1.80–1.72 (m, 2H, OCH_2CH_2), 1.52–1.43 (m, 6H, CH_2), 1.43–1.20 (m, 36H, CH_2), 0.93–0.82 (m, 9H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 164.1 (C=O), 153.0, 150.5, 149.8, 143.1, 142.3, 142.0, 137.0, 136.7, 132.5, 131.8, 127.4, 123.7 (Ar-C + Th-C), 73.6, 69.3 (OCH_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 (CH_2), 14.1 (CH_3); elemental analysis: calc for $C_{66}H_{81}NO_9S_2$: C 71.67%, H 7.61%, N 1.31%; found: C 71.62%, H 7.58%, N 1.40%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(2-methoxybenzoyloxy)phenyl]-2,2′-bithiophene **3/^{2}OMe**



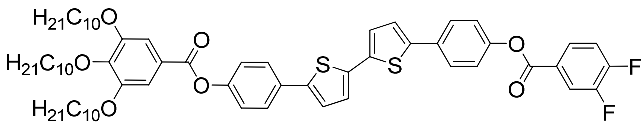
Prepared from **3b/OH** (54 mg, 0.058 mmol) and 2-methoxybenzoic acid (11 mg, 0.073 mmol); purified by column chromatography (eluent: $CHCl_3$/*n*-hexane 4/1, v/v) and repeated crystallization from THF/EtOH; yield 30 mg (0.028 mmol, 49%), yellow solid; $C_{65}H_{84}O_8S_2$; M = 1057.49 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, ^{3}J = 7.5 Hz, ^{4}J = 1.5 Hz, 1H, Ar-H), 7.65 (d, ^{3}J = 8.8 Hz, 2H, Ar-H), 7.64 (d, ^{3}J = 8.8 Hz, 2H, Ar-H), 7.59–7.53 (m, 1H, Ar-H), 7.29–7.21 (m, 8H, Ar-H + Th-H), 7.18 (d, ^{3}J = 3.7 Hz, 2H, Th-H), 7.05 (d, ^{3}J = 8.0 Hz, 2H, Ar-H), 4.08–4.04 (m, 6H, OCH_2CH_2), 3.96 (s, 3H, OCH_3), 1.87–1.80 (m, 4H, OCH_2CH_2), 1.79–1.70 (m, 2H, OCH_2CH_2), 1.51–1.46 (m, 6H, CH_2), 1.39–1.24 (br, 36H, CH_2), 0.91–0.86 (m, 9H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 164.3 (C=O), 160.0, 153.0, 150.5, 143.2, 142.4, 142.3, 136.8, 136.7, 134.4, 132.2, 131.9, 131.7, 126.7, 126.6, 124.6, 124.6, 124.0, 124.0, 123.7, 122.4, 122.3, 120.3, 119.0, 112.7, 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH_2), 56.1 (OCH_3), 31.9, 31.9, 30,4, 29.7, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 26.1, 26.1, 22.7, 22.7 (CH_2), 14.1 (CH_3); elemental analysis: calc for $C_{65}H_{84}O_8S_2$: C 73.83%, H 8.01%; found: C 73.72%, H 7.99%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(2,6-difluorobenzoyloxy)phenyl]-2,2′-bithiophene **3/^{26}F$_2$**



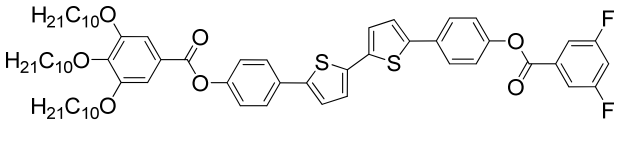
Prepared from **3b/OH** (67 mg, 0.073 mmol) and 2,6-difluorobenzoic acid (14 mg, 0.091 mmol); purified by column chromatography (eluent: $CHCl_3$/*n*-hexane 4/1, v/v) and repeated crystallization from THF/MeOH; yield 33mg (0.031 mmol, 43%); yellow solid; $C_{64}H_{80}F_2O_7S_2$; M = 1063.44 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, Ar-H), 7.66 (d, $^3J_{H,H}$ = 8.7 Hz, 2H, Ar-H), 7.51 (tt, $^3J_{H,H}$ = 8.5, $^4J_{H,F}$ = 6.1 Hz, 1H, Ar-H), 7.42 (s, 2H, Ar-H), 7.30 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, Ar-H), 7.25–7.21 (m, 4H Ar-H + Th-H), 7.19 (d, $^3J_{H,H}$ = 3.7 Hz, 2H, Th-H), 7.04 (dd, $^3J_{H,H}$ = 8.5 Hz, $^3J_{H,F}$ = 7.9 Hz, 2H, Ar-H), 4.10–4.02 (m, 6H, OC*H*$_2$CH$_2$), 1.88–1.80 (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$_2$), 1.41–1.22 (m, 36H, CH$_2$), 0.92–0.85 (m, 9H, CH$_3$); ^{19}F NMR (376 MHz, $CDCl_3$) δ –109.35 (dd, $^3J_{H,F}$ = 8.0 Hz, $^4J_{H,F}$ 6.2 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9 (C=O), 161.0 (dd, $^1J_{C,F}$ = 258.0 Hz, $^3J_{C,F}$ = 5.7 Hz), 159.8 (t, $^3J_{C,F}$ = 1.4 Hz), 153.0, 150.5, 149.8, 143.1, 142.3, 142.0, 136.9, 136.7, 133.5 (t, $^3J_{C,F}$ = 10.5 Hz), 132.3, 131.8, 126.7, 126.7, 124.6, 124.6, 124.2, 124.0, 123.7, 122.3, 122.1, 112.4, 112.2 (dd, $^2J_{C,F}$ = 17.6 Hz, $^4J_{C,F}$ = 1.8 Hz) 112.1, 110.4 (t, $^2J_{C,F}$ = 17.5 Hz), 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 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 (CH$_2$), 14.1 (CH$_3$); HR-ESI: calc.: 1069.5469 (M^- + Li), found.: 1069.5446 (M^- + Li).

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(3,4-difluorobenzoyloxy)phenyl]-2,2′-bithiophene **3/^{34}F$_2$**



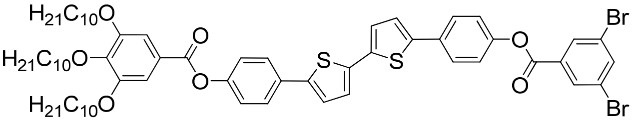
Prepared from **3b/OH** (91 mg, 0.099 mmol) and 3,4-difluorobenzoic acid (20 mg, 0.124 mmol); purified by column chromatography (eluent: CHCl$_3$/*n*-hexane 5/1, v/v) and repeated crystallization from THF/EtOH; yield 85 mg (0.080 mmol, 81%); yellow solid; $C_{64}H_{80}F_2O_7S_2$; M = 1063.44 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08–7.98 (m, 2H, Ar-H), 7.67 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, Ar-H), 7.66 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, Ar-H), 7.42 (s, 2H, Ar-H), 7.35–7.28 (m, 1H, Ar-H), 7.25–7.21 (m, 6H, Ar-H+ Th-H), 7.19 (d, $^3J_{H,H}$ = 3.8 Hz, 2H, Th-H), 4.08 (t, $^3J_{H,H}$ = 6.4 Hz, 2H, OC*H*$_2$CH$_2$), 4.06 (t, $^3J_{H,H}$ = 6.4 Hz, 4H, OC*H*$_2$CH$_2$), 1.88–1.80 (m, 4H, OCH$_2$C*H*$_2$), 1.79–1.73 (m, 2H, OCH$_2$C*H*$_2$), 1.51–1.46 (m, 6H, CH$_2$), 1.42–1.21 (br, 36H, CH$_2$), 0.89 (t, $^3J_{H,H}$ = 6.8 Hz, 3H, CH$_3$), 0.88 (t, $^3J_{H,H}$ = 6.8 Hz, 6H, CH$_3$); ^{19}F NMR (376 MHz, $CDCl_3$) δ –128.66 (m, 1F), –133.84 (m, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 163.2 (C=O), 154.1 (dd, $^1J_{C,F}$ = 258 Hz, $^2J_{C,F}$ = 12.8 Hz, 1C, C-F), 153.0, 150.5, 150.2 (dd, $^1J_{C,F}$ = 251 Hz, $^2J_{C,F}$ = 13.0 Hz, 1C, C-F), 150.0, 143.2, 142.4, 142.0, 137.0, 136.7, 132.2, 131.8, 127.5 (dd, $^3J_{C,F}$ = 7.5 Hz, $^4J_{C,F}$ = 3.8 Hz), 126.8, 126.7, 126.4 (dd, $^3J_{C,F}$ = 5.6 Hz, $^4J_{C,F}$ = 3.6 Hz), 124.6, 124.6, 124.2, 124.0, 123.7, 122.3, 122.1, 119.6 (dd, $^2J_{C,F}$ = 18.8 Hz, $^3J_{C,F}$ = 1.8 Hz), 117.6 (d, $^2J_{C,F}$ = 18.0 Hz), 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 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 (CH$_2$), 14.1 (CH$_3$); MS (ESI, CH$_2$Cl$_2$): *m/z* (%) = 1062.40 ([M•]$^+$, 100); elemental analysis: calc for $C_{64}H_{80}F_2O_7S_2$: C 72.28%, H 7.58%, found: 72.21%, H 7.61.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(3,5-difluorobenzoyloxy)phenyl]-2,2′-bithiophene **3/^{35}F$_2$**



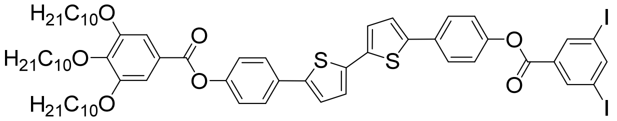
Prepared from **3b/OH** (91 mg, 0.099 mmol) and 3,5-difluorobenzoic acid (20 mg, 0.124 mmol); purified by column chromatography (eluent: CHCl$_3$/*n*-hexane 5/1, v/v) and repeated crystallization from THF/EtOH; yield 93 mg (0.087 mmol, 88%); yellow solid; $C_{64}H_{80}F_2O_7S_2$; M = 1063.44 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.70 (m, 2H, Ar-H), 7.67 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, Ar-H), 7.66 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, Ar-H), 7.41 (s, 2H, Ar-H), 7.24 (m, 4H, Ar-H), 7.23 (d, $^3J_{H,H}$ = 3.9 Hz, 2H, Th-H), 7.19 (d, $^{3}J_{\mathrm{H,H}}$ = 3.8 Hz, 2H, Th-H), 7.11 (tt, $^{3}J_{\mathrm{H,F}}$ = 8.5 Hz, $^{4}J_{\mathrm{H,H}}$ = 2.4 Hz, 1H, Ar-H), 4.08–4.04 (m, 6H, OC*H*$_2$CH$_2$), 1.88–1.80 (m, 4H, OCH$_2$C*H*$_2$), 1.79–1.73 (m, 2H, OCH$_2$C*H*$_2$), 1.55–1.44 (m, 6H, CH$_2$), 1.40–1.22 (br, 36H, CH$_2$), 0.93–0.83 (m, 9H, CH$_3$); ^{19}F NMR (376 MHz, CDCl$_3$) δ –107.94 (m, 2F); ^{13}C NMR (125 MHz, CDCl$_3$) δ 165.0, 162.9 (C=O), 162.9 (dd, $^{1}J_{\mathrm{C,F}}$ = 249 Hz, $^{3}J_{\mathrm{C,F}}$ = 12.1 Hz, C-F), 153.0, 150.5, 149.9, 143.2, 142.4, 142.0, 137.0, 136.7, 132.6 (t, $^{3}J_{\mathrm{C,F}}$ = 9.2 Hz), 132.3, 131.8, 126.8, 126.7, 124.7, 124.6, 124.2, 124.0, 123.7, 122.3, 122.0, 113.6, 113.2 (m), 113.1, 109.2 (t, $^{2}J_{\mathrm{C,F}}$ = 26.7 Hz), 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 31.9, 31.9, 30.3, 29.7, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 26.1, 26.1, 22.7, 22.7 (CH$_2$), 14.1 (CH$_3$); MS (ESI, CH$_2$Cl$_2$): *m/z* (%) = 1062.40 ([M•]$^+$, 100); elemental analysis: calc for $C_{64}H_{80}F_2O_7S_2$: C 72.28%, H 7.58%; found: C 72.67%, H 7.57%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(3,5-dibromobenzoyloxy)phenyl]-2,2′-bithiophene **3/^{35}Br$_2$**



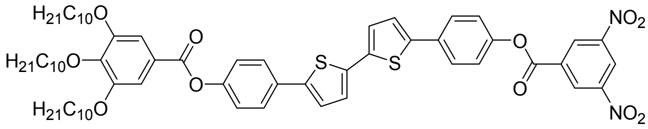
Prepared from **3b/OH** (95 mg, 0.103 mmol) and 3,5-dibromobenzoic acid (36 mg, 0.129 mmol); purified by column chromatography (eluent: CHCl$_3$/*n*-hexane 4/1, v/v) and repeated crystallization from THF/EtOH; yield 99 mg (0.084 mmol, 81%); yellow solid; $C_{64}H_{80}Br_2O_7S_2$; *M* = 1185.25 g/mol; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.28 (d, ^{4}J = 1.8 Hz, 2H, Ar-H), 7.94 (t, ^{3}J = 1.8 Hz, 1H, Ar-H), 7.67 (d, ^{3}J = 8.7 Hz, 2H, Ar-H), 7.66 (d, ^{3}J = 8.7 Hz, 2H, Ar-H), 7.41 (s, 2H, Ar-H), 7.26–7.21 (m, 6H, Ar-H + Th-H), 7.19 (d, ^{3}J = 3.8 Hz, 2H, Th-H), 4.08–4.04 (m, 6H, OC*H*$_2$CH$_2$), 1.89–1.79 (m, 4H, OCH$_2$C*H*$_2$), 1.78–1.72 (m, 2H, OCH$_2$C*H*$_2$), 1.54–1.44 (m, 6H, CH$_2$), 1.42–1.19 (br, 36H, CH$_2$), 0.96–0.80 (m, 9H, CH$_3$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 165.0, 162.6 (C=O), 153.0, 150.5, 149.9, 143.1, 142.4, 141.9, 139.0, 137.0, 136.7, 132.6, 132.4, 131.9, 131.8, 126.8, 126.7, 124.7, 124.6, 124.2, 124.0, 123.7, 123.3, 122.3, 122.0, 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 31.9, 31.9, 30.3, 29.7, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 26.1, 26.1, 22.7, 22.7 (CH$_2$), 14.1 (CH$_3$); elemental analysis: calc for $C_{64}H_{88}Br_2O_7S_2$: C 64.85%, H 6.80%; found.: C 64.95%, H 6.84%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(3,5-diiodobenzoyloxy)phenyl]-2,2′-bithiophene **3/^{35}I$_2$**



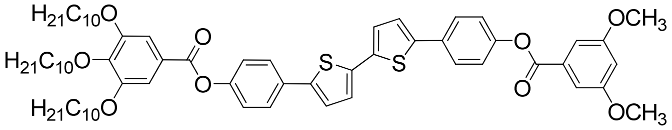
Prepared from **3b/OH** (104 mg, 0.113 mmol) and 3,5-diiodobenzoic acid (53 mg, 0.142 mmol); purified by column chromatography (eluent: CHCl$_3$/*n*-hexane 3/1, v/v) and repeated crystallization from THF/EtOH; yield 115 mg (0.090 mmol, 80%), yellow solid; $C_{64}H_{80}I_2O_7S_2$; *M* = 1279.25 g/mol; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.50–8.48 (m, 2H, Ar-H), 8.33–8.31 (m, 1H, Ar-H), 7.66 (d, ^{3}J = 8.6 Hz, 2H, Ar-H), 7.65 (d, ^{3}J = 8.6 Hz, 2H, Ar-H), 7.42 (s, 2H, Ar-H), 7.25–7.21 (m, 6H, Ar-H + Th-H), 7.19 (d, ^{3}J = 3.7 Hz, 2H, Th-H), 4.09–4.03 (m, 6H, OC*H*$_2$CH$_2$), 1.88–1.79 (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$_2$), 1.41–1.22 (m, 36H, CH$_2$), 0.93–0.84 (m, 9H, CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 164.9, 162.2 (C=O), 153.0, 150.5, 149.9, 143.1, 142.4, 142.0, 138.2, 137.0, 136.7, 132.6, 132.3, 131.8, 126.8, 126.7, 124.7, 124.6, 124.2, 124.0, 123.7, 122.3, 122.0, 108.6, 94.5 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 31.9, 31.9, 30.3, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 29.3, 26.1, 26.0, 22.7, 22.7 (CH$_2$), 14.1 (CH$_3$); elemental analysis: calc for $C_{64}H_{80}I_2O_7S_2$: C 60.09%, H 6.30%; found: C 60.11%, H 6.24%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(3,5-dinitrobenzoyloxy)phenyl]-2,2′-bithiophene **3/^{35}NO2$_2$**



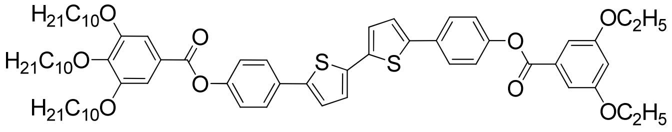
Prepared from **3b/OH** (91 mg, 0.099 mmol) and 3,5-dinitrobenzoic acid (26 mg, 0.123 mmol); purified by column chromatography (eluent: $CHCl_3$/*n*-hexane 3/1, v/v) and repeated crystallization from THF/MeOH; yield 77 mg (0.069 mmol, 70%), yellow solid; $C_{64}H_{80}N_2O_{11}S_2$; M = 1117.46 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35–9.32 (m, 2H, Ar-H), 9.31 (t, ^4J = 1.9 Hz, 1H, Ar-H), 7.73–7.68 (m, 2H, Ar-H), 7.66 (d, ^3J = 8.4 Hz, 2H, Ar-H), 7.41 (s, 2H, Ar-H), 7.31 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.28–7.21 (m, 4H, Ar-H + Th-H), 7.20 (d, ^3J = 3.5 Hz, 2H, Th-H), 4.10–4.02 (m, 6H, OCH_2CH_2), 1.89–1.79 (m, 4H, OCH_2CH_2), 1.79–1.72 (m, 2H, OCH_2CH_2), 1.52–1.44 (m, 6H, CH_2), 1.42–1.21 (m, 36H, CH_2), 0.93–0.84 (m, 9H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 161.1 (C=O), 153.0, 150.6, 149.4, 148.8, 143.1, 142.5, 141.6, 137.3, 136.6, 133.2, 132.9, 131.7, 129.9, 126.9, 126.7, 124.8, 124.6, 124.5, 124.0, 123.7, 123.0, 122.4, 121.7, 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH_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, 26.1, 22.7, 22.7 (CH_2), 14.1 (CH_3); elemental analysis: calc for $C_{64}H_{80}N_2O_{11}S_2$: C 68.79%, H 7.22%, N 2.51%; found: C 68.51%, H 7.13%, N 2.58%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(3,5-dimethoxybenzoyloxy)phenyl]-2,2′-bithiophene **3/^{35}OMe$_2$**



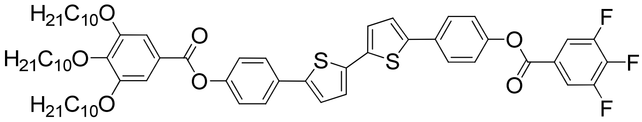
Prepared from **3b/OH** (52 mg, 0.056 mmol) and 3,5-dimethoxybenzoic acid (13 mg, 0.070 mmol); purified by column chromatography (eluent: $CHCl_3$/*n*-hexane/EtOAc 1/4/1, v/v/v) and repeated crystallization from THF/EtOH; yield 41 mg (0.038 mmol, 67%), yellow solid; $C_{66}H_{86}O_9S_2$; M = 1087.51 g/mol; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, ^3J = 9.0 Hz, 2H, Ar-H), 7.66 (d, ^3J = 8.5 Hz, 2H, Ar-H), 7.42 (s, 2H, Ar-H), 7.36 (d, ^4J = 2.4 Hz, 2H, Ar-H), 7.26–7.22 (m, 6H, Ar-H + Th-H), 7.19 (d, ^3J = 3.7 Hz, 2H, Th-H), 6.74 (t, ^4J = 2.4 Hz, 1H, Ar-H), 4.09–4.05 (m, 6H, OCH_2CH_2), 3.88 (s, 6H, OCH_3), 1.90–1.80 (m, 4H, OCH_2CH_2), 1.80–1.74 (m, 2H, OCH_2CH_2), 1.51–1.47 (m, 6H, CH_2), 1.39–1.24 (br, 36H, CH_2), 0.91–0.87 (m, 9H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 164.9 (C=O), 160.8, 153.0, 150.5, 150.4, 143.2, 142.3, 142.3, 136.8, 136.8, 131.9, 131.8, 131.2, 126.7, 126.7, 124.6, 124.1, 124.0, 123.7, 122.3, 122.2, 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH_2), 55.7 (OCH_3), 31.9, 31.9, 30.4, 29.7, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 26.1, 26.1, 22.7, 22.7 (CH_2), 14.1 (CH_3); elemental analysis: calc for $C_{66}H_{86}O_9S_2$: C 72.89%, H 7.97%; found.: C 73.11%, H 8.14%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(3,5-diethoxybenzoyloxy)phenyl]-2,2′-bithiophene **3/^{35}OEt$_2$**



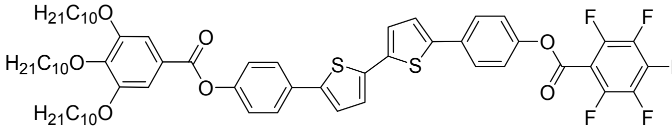
Phenol **3b/OH** (92 mg. 0.100 mmol), 3,5-diethoxybenzoic acid (21 mg, 0.100 mmol), DMAP (1 mg, 0.01 mmol) and DCC (27 mg, 0.130 mmol) were stirred in dry CH_2Cl_2 (25 ml) at room temperature overnight. The reaction mixture was filtered through a short column of silica gel (eluent: CH_2Cl_2) and the solvent was removed under reduced pressure. The obtained crude product was purified by column chromatography (eluent: CHCl$_3$) and repeated crystallization from THF/EtOH. Yield 87 mg (0.078 mmol, 78%); yellow solid; $C_{68}H_{90}O_9S_2$; M = 1115.57 g/mol; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.66 (d, ^3J = 8.6 Hz, 4H, Ar-H), 7.42 (s, 2H, Ar-H), 7.33 (d, ^4J = 2.3 Hz, 2H, Ar-H), 7.26–7.21 (m, 6H, Ar-H + Th-H), 7.18 (d, ^3J = 3.8 Hz, 2H, Th-H), 6.72 (t, ^4J = 2.3 Hz, 1H, Ar-H), 4.10 (q, ^3J = 7.0 Hz, 4H, OCH_2CH$_3$), 4.08–4.04 (m, 6H, OCH_2CH$_2$), 1.88–1.80 (m, 4H, OCH$_2$CH_2), 1.79–1.73 (m, 2H, OCH$_2$CH_2), 1.52–1.47 (m, 6H, CH$_2$), 1.44 (t, ^3J = 7.0 Hz, 6H, OCH$_2$CH_3), 1.41–1.22 (br, 36H, CH$_2$), 0.90–0.86 (m, 9H, CH$_3$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 164.9 (C=O), 160.1, 153.0, 150.5, 150.4, 143.1, 142.3, 142.3, 136.8, 136.8, 131.9, 131.8, 131.1, 126.7, 126.7, 124.6, 124.1, 124.0, 123.7, 122.3, 122.2, 108.6, 108.3, 107.3 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 63.9 (OCH$_2$CH$_3$), 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, 22.7, 22.7 (CH$_2$), 14.7 (OCH$_2$$\mathit{C}H_3$), 14.1 (CH$_3$); elemental analysis: calc for $C_{68}H_{90}O_9S_2$: C 73.21%, H 8.13%; found: C 73.28%, H 8.37%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(3,4,5-trifluorobenzoyloxy)phenyl]-2,2′-bithiophene **3/^{345}F$_3$**



Prepared from **3b/OH** (91 mg, 0.099 mmol) and 3,4,5-trifluorobenzoic acid (22 mg, 0.124 mmol); purified by column chromatography (eluent: CHCl$_3$/*n*-hexane) and repeated crystallization from THF/EtOH; yield 87 mg (0.080 mmol, 81%); yellow solid; $C_{64}H_{79}F_3O_7S_2$; M = 1081.43 g/mol; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87 (dd, $^3J_{H,F}$ = 7.5 Hz, $^4J_{H,F}$ = 6.5 Hz, 2H, Ar-H), 7.67 (d, $^3J_{H,H}$ = 8.6 Hz, 2H, Ar-H), 7.66 (d, $^3J_{H,H}$ = 8.6 Hz, 2H, Ar-H), 7.42 (s, 2H, Ar-H), 7.25–7.22 (m, 6H, Ar-H + Th-H), 7.19 (d, $^3J_{H,H}$ = 3.7 Hz, 2H, Th-H), 4.08–4.04 (m, 6H, OCH_2CH$_2$), 1.89–1.80 (m, 4H, OCH$_2$CH_2), 1.80–1.72 (m, 2H, OCH$_2$CH_2), 1.51–1.46 (m, 6H, CH$_2$), 1.42–1.13 (br, 36H, CH$_2$), 0.89 (t, $^3J_{H,H}$ = 6.9 Hz, 3H, CH$_3$), 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 6H, CH$_3$); ^{19}F NMR (376 MHz, CDCl$_3$) δ –132.02 (dd, $^3J_{F,F}$ = 20.1 Hz, $^3J_{F,H}$ = 7.5 Hz, 2F), –151.13 (tt, $^3J_{F,F}$ = 20.1 Hz, $^4J_{F,H}$ = 6.5 Hz, 1F); ^{13}C NMR (100 MHz, CDCl$_3$) δ 164.9 (C=O), 162.3 (m, C=O) 153.0, 151.1 (ddd, $^1J_{C,F}$ = 252.6 Hz, $^2J_{C,F}$ = 10.3 Hz, $^3J_{C,F}$ = 3.4 Hz), 150.6, 149.8, 143.6 (dt, $^1J_{C,F}$ = 260.9 Hz, $^2J_{C,F}$ = 15.3 Hz) 143.2, 142.4, 141.9, 137.1, 136.7, 132.4, 131.8, 126.8, 126.7, 125.4 (m) 124.7, 124.6, 124.3, 124.0, 123.7, 122.3, 121.9, 114.8 (dd, $^2J_{C,F}$ = 16.6 Hz, $^3J_{C,F}$ = 6.5 Hz), 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH$_2$), 31.9, 31.9, 30.3, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 29.3, 26.1, 26.0, 22.7, 22.7 (CH$_2$), 14.1 (CH$_3$); MS (ESI, CH$_2$Cl$_2$): *m/z* (%) = 1080.57 ([M•]$^+$, 100); elemental analysis: calc for $C_{64}H_{79}F_3O_7S_2$: C 71.08%, H 7.36%; found: C 70.74%, H 7.15%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(2,3,4,5,6-pentafluorobenzoyloxy)phenyl]-2,2′-bithiophene **3/^{23456}F$_5$**

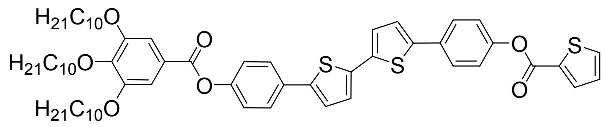


Prepared from **3b/OH** (97 mg, 0.105 mmol) and 2,3,4,5,6-pentafluorobenzoic acid (28 mg, 0.132 mmol); purified by column chromatography (eluent: CHCl$_3$/*n*-hexane 4/1, v/v) and repeated crystallization from THF/MeOH; yield 66 mg (0.059 mmol, 56%), yellow solid; $C_{64}H_{77}F_5O_7S_2$; M = 1117.41 g/mol; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.70–7.63 (m, 4H, Ar-H), 7.42 (s, 2H, Ar-H), 7.29 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.25–7.22 (m, 4H, Ar-H, Th-H), 7.19 (dd, ^3J = 3.7 Hz, ^4J = 1.2 Hz, 2H, Th-H), 4.09–4.03 (m, 6H, OCH_2CH$_2$), 1.88–1.80 (m, 4H, OCH$_2$CH_2), 1.80–1.73 (m, 2H, OCH$_2$CH_2), 1.53–1.45 (m, 6H, CH$_2$), 1.41–1.22 (m, 36H, CH$_2$), 0.92–0.85 (m, 9H, CH$_3$); ^{19}F NMR (470 MHz, CDCl$_3$) δ

–137.09 (m, 2F), –146.99 (tt, $^3J_{\mathrm{F,F}}$ = 20.8 Hz, $^4J_{\mathrm{F,F}}$ = 4.9 Hz, 1F), –159.79 (m, 2F); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9 (C=O), 157.4 (m, C=O), 153.0, 150.6, 149.3, 146.8 (m), 144.8 (m), 143.2, 142.5, 141.7, 138.9 (m), 137.2, 136.8 (m), 136.6, 132.8, 131.8, 126.8, 126.7, 124.7, 124.6, 124.4, 124.0, 123.7, 122.3, 121.8, 108.6 (Ar-C + TH-C), 107.5 (m, Ar-C) 73.6, 69.3 (OCH_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, 26.1, 22.7, 22.7 (CH_2), 14.1, 14.1 (CH_3); elemental analysis: calc for $C_{64}H_{77}F_5O_7S_2$: C 68.79%, H 6.95%; found: C 68.41%, H 6.76%.

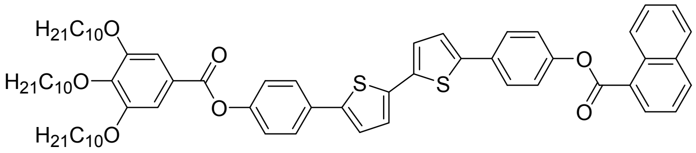
S3.3 Compounds 3a/Y

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5´-[4-(thiophene-2-carbonyloxy)phenyl]-2,2´-bithiophene **3a/Th**



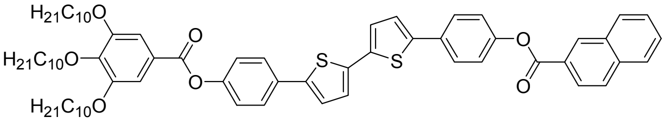
Prepared from **3b/OH** (129 mg, 0.140 mmol) and 2-thiophenecarbonyl chloride (26 mg, 0.175 mmol); purified by column chromatography (eluent: $CHCl_3$/*n*-pentane 2/1, v/v) and repeated crystallization from THF/EtOH; yield 44 mg (0.043 mmol, 31%); yellow solid; $C_{62}H_{80}O_7S_2$; M = 1033.49 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, ^3J = 3.8 Hz, ^4J = 1.2 Hz, 1H, Th-H), 7.69 (dd, ^3J = 5.0, Hz, ^4J = 1.3 Hz, 1H, Th-H), 7.66 (d, ^3J = 8.4 Hz, 2H, Ar-H), 7.65 (d, ^3J = 8.4 Hz, 2H, Ar-H), 7.42 (s, 2H, Ar-H), 7.29–7.17 (m, 9H, Ar-H + Th-H), 4.09–4.04 (m, 6H, $\mathrm{OC}H_2\mathrm{CH}_2$), 1.93–1.80 (m, 4H, $\mathrm{OCH_2C}H_2$), 1.79–1.73 (m, 2H, $\mathrm{OCH_2C}H_2$), 1.51–1.46 (m, 6H, CH_2), 1.43–1.18 (br, 36H, CH_2), 0.94–0.82 (m, 9H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 160.5 (C=O), 153.0, 150.5, 150.0, 143.1, 142.3, 142.2, 136.8, 136.8, 134.8, 133.6, 132.7, 132.0, 131.8, 128.1, 126.7, 124.6, 124.1, 124.0, 123.7, 122.3, 122.2, 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH_2), 31.9, 30.3, 29.7, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 26.1, 26.1, 22.7, 22.7 (CH_2), 14.1 (CH_3); elemental analysis: calc for $C_{62}H_{80}O_7S_3$: C 72.05%, H 7.80%; found: C 72.11%, H 8.01%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5´-[4-(naphthalene-1-ylcarbonyloxy)phenyl]-2,2´-bithiophene **3a/1-Npht**



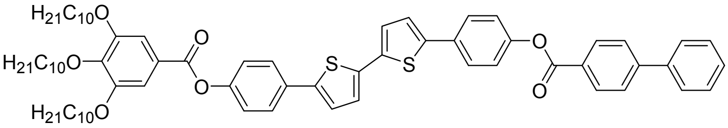
Prepared from **3b/OH** (81 mg, 0.087 mmol) and 1-naphthoic acid (19 mg, 0.110 mmol); purified by column chromatography (eluent: $CHCl_3$/*n*-hexane 4/1, v/v) and repeated crystallization from THF/MeOH; yield 65 mg (0.060 mmol, 69%); yellow solid; $C_{68}H_{84}O_7S_2$; M = 1077.52 g/mol: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (d, ^3J = 8.8 Hz, 1, Na-H), 8.50 (dd, ^3J = 7.3 Hz, ^4J = 1.2 Hz, 1H, Na-H), 8.13 (d, ^3J = 8.2 Hz, 1H, Na-H), 7.94 (d, ^3J = 8.8 Hz, 1H, Na-H), 7.71 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.69–7.64 (m, 3H, Ar-H + Na-H), 7.62–7.56 (m, 2H, Na-H), 7.42 (s, 2H, Ar-H), 7.34 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.26–7.22 (m, 4H, Ar-H + Th-H), 7.20 (d, ^3J = 3.8 Hz, 2H, Th-H), 4.10–4.03 (m, 6H, $\mathrm{OC}H_2\mathrm{CH}_2$), 1.88–1.80 (m, 4H, $\mathrm{OCH_2C}H_2$), 1.80–1.73 (m, 2H, $\mathrm{OCH_2C}H_2$), 1.53–1.45 (m, 6H, CH_2), 1.42–1.22 (m, 36H, CH_2), 0.93–0.85 (m, 9H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 164.9 (C=O), 153.0, 150.5, 150.4, 142.3, 136.8, 136.8, 134.4, 133.9, 131.9, 131.8, 131.7, 131.3, 128.7, 128.2, 126.8, 126.7, 126.4, 125.7, 124.6, 124.5, 124.1, 124.0, 123.7, 122.4, 122.3, 108.6 (Ar-C + Th-C + Na-C), 73.6, 69.3 (OCH_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 (CH_2), 14.1 (CH_3); elemental analysis: calc. for $C_{68}H_{84}O_7S_2$: C 75.80%, H 7.86%; found: C 75.75%, H 7.52%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(naphthalene-2-carbonyloxy)phenyl]-2,2′-bithiophene **3a/2-Npht**



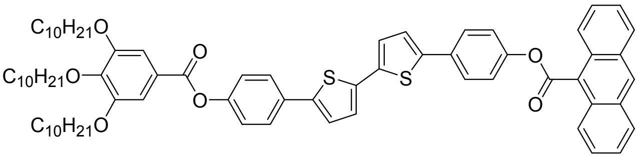
Prepared from **3b/OH** (72 mg, 0.078 mmol) and 2-naphthoic acid (17 mg, 0.097 mmol); purified by column chromatography (eluent: $CHCl_3$/*n*-hexane 4/1, v/v) and repeated crystallization from THF/MeOH; yield 72 mg (0.069 mmol, 85%); yellow solid; $C_{68}H_{84}O_7S_2$; M = 1077.52 g/mol: ^1H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H, Na-H), 8.21 (dd, ^3J = 8.6 Hz, ^4J = 1.7 Hz, 1H, Na-H), 8.03 (d, ^3J = 8.0 Hz, 1H, Na-H), 7.97 (d, ^3J = 8.8 Hz, 1H, Na-H), 7.94 (d, ^3J = 8.3 Hz, 1H, Na-H), 7.69 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.68–7.57 (m, 4H, Ar-H + Na-H), 7.42 (s, 2H, Ar-H), 7.32 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.26–7.21 (m, 4H, Ar-H + Th-H), 7.20 (d, ^3J = 3.7 Hz, 2H, Th-H), 4.10–4.03 (m, 6H, OCH_2CH_2), 1.88–1.80 (m, 4H, OCH_2CH_2), 1.80–1.73 (m, 2H, OCH_2CH_2), 1.53–1.44 (m, 6H, CH_2), 1.42–1.22 (m, 36H, CH_2), 0.92–0.86 (m, 9H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 164.9 (C=O), 153.0, 150.5, 143.1, 142.3, 136.8, 135.9, 132.5, 132.0, 131.9, 131.8, 129.5, 128.7, 128.4, 127.8, 126.9, 126.7, 126.7, 126.6, 125.4, 124.6, 124.1, 124.0, 123.7, 122.3, 108.6 (Ar-C + Th-C + Na-C), 73.6, 69.3 (OCH_2), 31.9, 31.9, 30.3, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 29.3, 26.1, 26.1, 22.7, 22.7 (CH_2), 14.1 (CH_3); elemental analysis: calc. for $C_{68}H_{84}O_7S_2$: C 75.80%, H 7.86%; found: C 75.81%, H 7.48%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(biphenyl-4-ylcarbonyloxy)phenyl]-2,2′-bithiophene **3a/Biph**



Prepared from **3b/OH** (100 mg, 0.108 mmol) and biphenyl-4-carboxylic acid (27 mg, 0.135 mmol); purified by column chromatography (eluent: $CHCl_3$/*n*-hexane 4/1, v/v) and repeated crystallization from THF/MeOH; yield 83 mg (0.075 mmol, 70%), yellow solid; $C_{70}H_{86}O_7S_2$; M = 1103.56 g/mol; ^1H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, ^3J = 8.5 Hz, 2H, Ar-H), 7.75 (d, ^3J = 8.5 Hz, 2H, Ar-H), 7.71–7.63 (m, 6H, Ar-H), 7.53–7.47 (m, 2H, Ar-H), 7.45–7.40 (m, 3H, Ar-H), 7.28 (d, ^3J = 8.6 Hz, 2H, Ar-H), 7.25–7.21 (m, 4H, Ar-H + Th-H), 7.19 (d, ^3J = 3.8 Hz, 2H, Th-H), 4.10–4.03 (m, 6H, OCH_2CH_2), 1.89–1.79 (m, 4H, OCH_2CH_2), 1.79–1.72 (m, 2H, OCH_2CH_2), 1.52–1.43 (m, 6H, CH_2), 1.41–1.21 (m, 36H, CH_2), 0.94–0.83 (m, 9H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 164.9 (C=O), 153.0, 150.5, 150.4, 146.4, 143.1, 142.3, 139.8, 136.8, 131.9, 131.8, 130.7, 129.0, 128.3, 128.1, 127.3, 127.3, 126.7, 126.7, 124.6, 124.1, 124.0, 123.7, 122.3, 122.3, 108.6 (Ar-C + Th-C), 73.6, 69.3 (OCH_2), 31.9, 31.9, 30.3, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 29.3, 26.1, 22.7, 22.7 (CH_2), 14.1 (CH_3); elemental analysis: calc for $C_{70}H_{86}O_7S_2$: C 76.19%, H 7.85%; found: C 76.23%, H 7.77%.

5-[4-(3,4,5-Tri-*n*-decyloxybenzoyloxy)phenyl]-5′-[4-(anthracene-9-ylcarbonyloxy)phenyl]-2,2′-bithiophene **3a/Anth**



Prepared from **3b/OH** (75 mg, 0.081 mmol) and 9-anthracenecarboxylic acid (23 mg, 0.102 mmol); purified by column chromatography (eluent: $CHCl_3$/*n*-hexane 4/1, v/v) and repeated crystallization from THF/MeOH; yield 56 mg (0.050 mmol, 61%); yellow solid; $C_{72}H_{86}O_7S_2$; M = 1127.58 g/mol: ^1H

NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H, An-H), 8.27 (dd, ^3J = 8.8 Hz, ^4J = 0.9 Hz, 2H, An-H), 8.09 (d, ^3J = 8.5 Hz, 2H, An-H), 7.75 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.67 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.65–7.60 (m, 2H, An-H), 7.58–7.53 (m, 2H, An-H), 7.51 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.42 (s, 2H, Ar-H), 7.28 (d, ^3J = 3.8 Hz, 1H, Th-H), 7.25–7.22 (m, 3H, Ar-H + Th-H), 7.22–7.20 (m, 2H, Th-H), 4.07 (t, ^3J = 6.5 Hz, 2H, $OC\mathit{H}_2CH_2$), 4.06 (t, ^3J = 6.5 Hz, 4H, $OC\mathit{H}_2CH_2$), 1.88–1.80 (m, 4H, $OCH_2C\mathit{H}_2$), 1.80–1.73 (m, 2H, $OCH_2C\mathit{H}_2$), 1.52–1.44 (m, 6H, CH_2), 1.41–1.21 (m, 36H, CH_2), 0.92–0.85 (m, 9H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 165.0 (C=O), 153.0, 150.5, 150.3, 143.2, 142.4, 142.1, 137.0, 136.7, 132.3, 131.8, 131.0, 130.2, 128.8, 128.8, 127.5, 126.9, 126.7, 126.4, 125.6, 124.8, 124.7, 124.6, 124.2, 124.0, 123.7, 122.3, 122.2, 108.7 (Ar-C + An-C + Th-C), 73.6, 69.3 (OCH_2), 31.9, 31.9, 30.4, 29.7, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 26.1, 26.1, 22.7, 22.7 (CH_2), 14.1 (CH_3); elemental analysis: calc. for $C_{72}H_{86}O_7S_2$: C 76.69%, H 7.69%; found: C 76.68%, H 7.61%.

S3.4. Representative NMR spectra

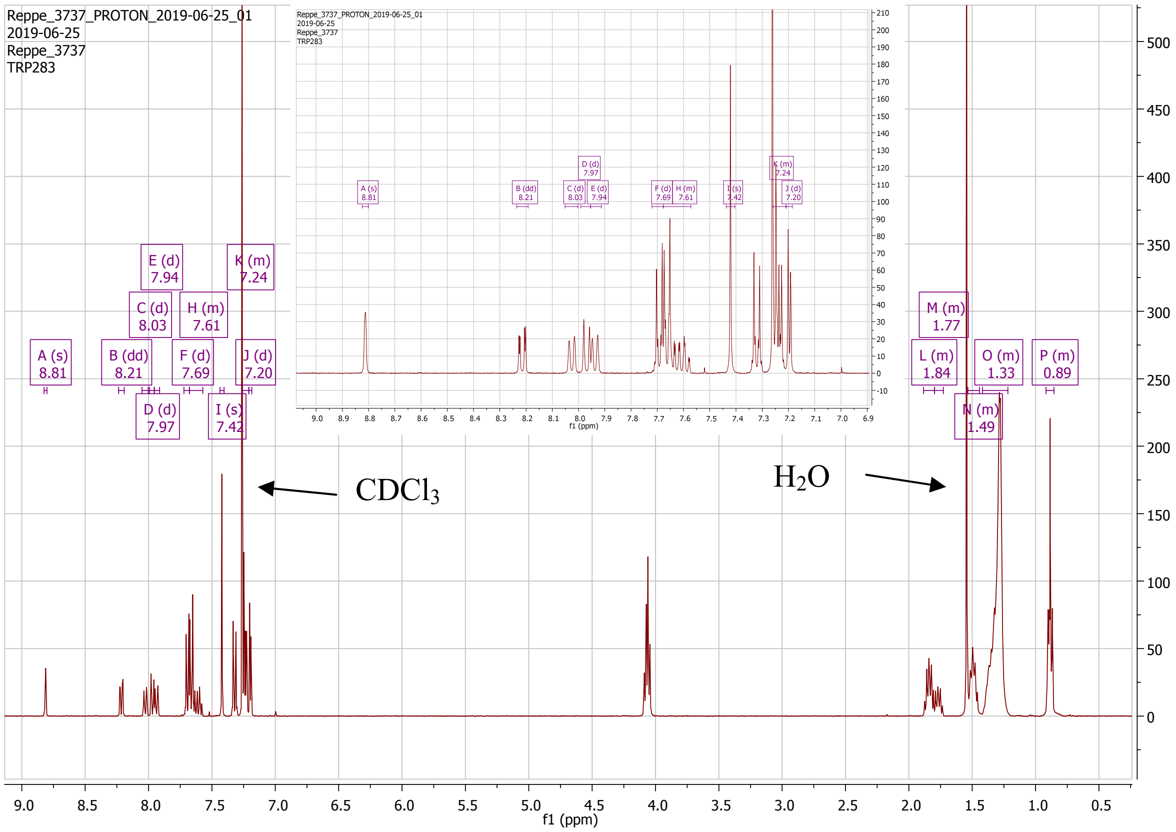


Figure S16. ^1H-NMR of compound **3a/2-Npht** (400 MHz, $CDCl_3$).

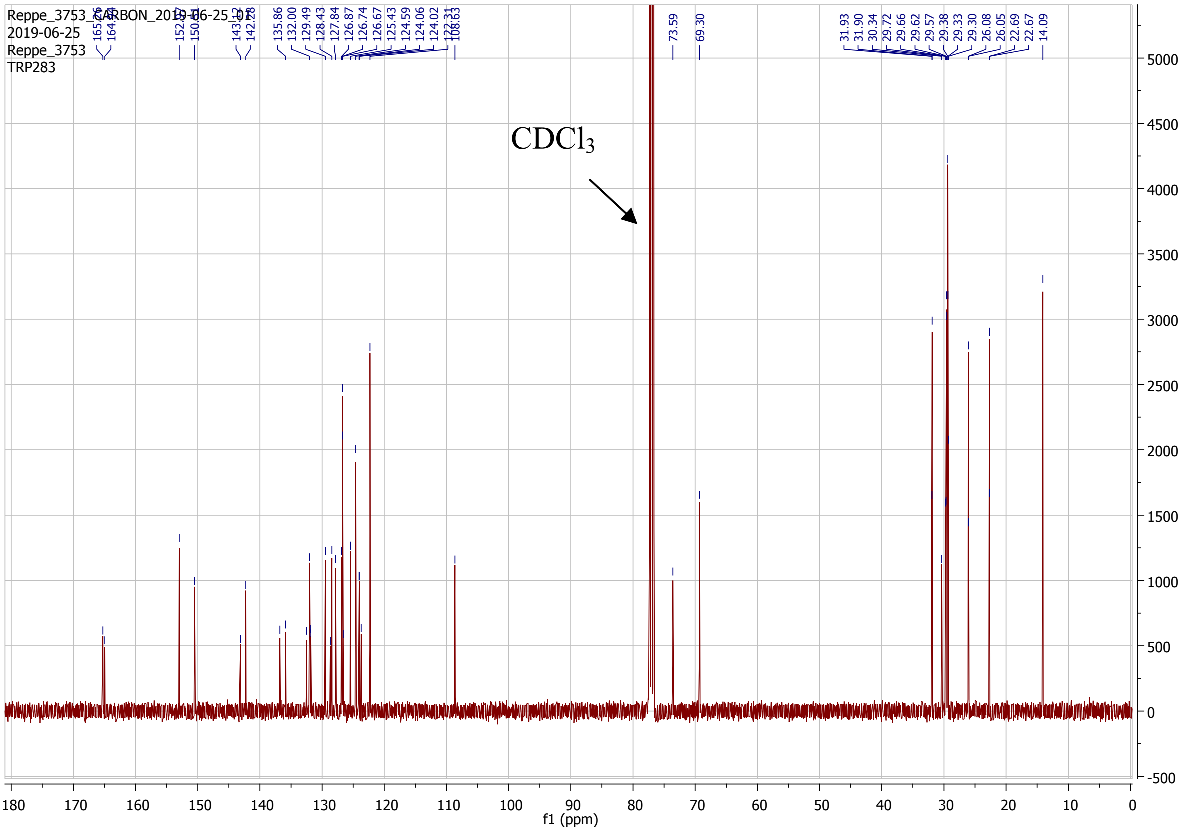


Figure S17. ^{13}C-NMR of compound **3a/2-Npht** (100 MHz, $CDCl_3$).

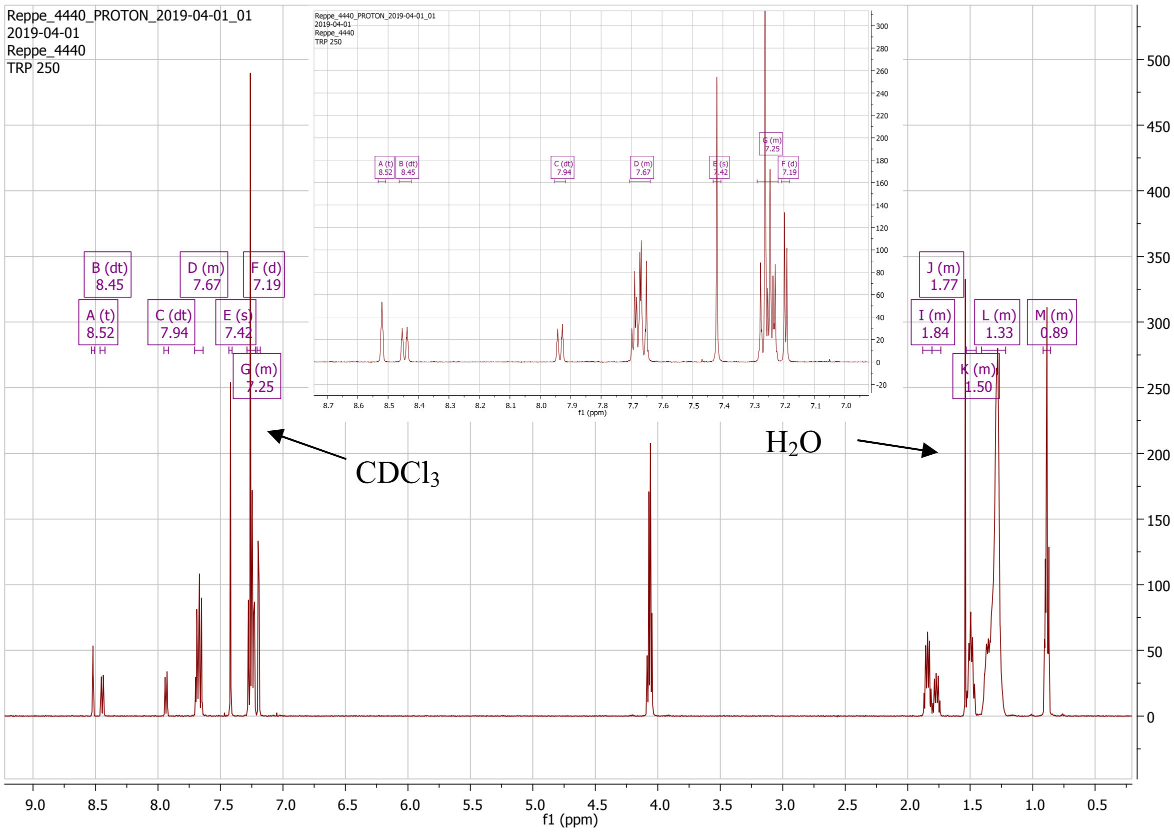


Figure S18. ^{1}H-NMR of compound **3/^{3}CN** (400 MHz, $CDCl_3$).

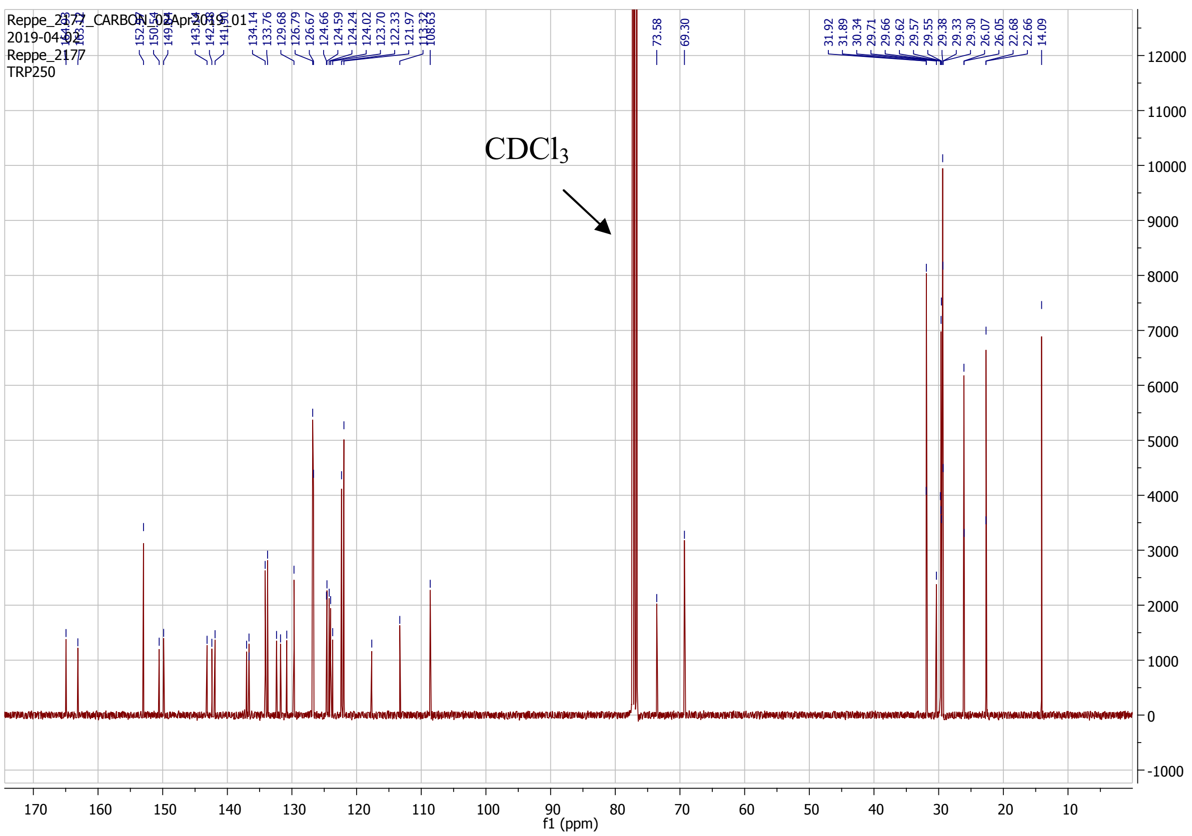


Figure S19. ^{13}C-NMR of compound **3/^{3}CN** (100 MHz, $CDCl_3$).

S4. References

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