

Bi-continuous orthorhombic soft matter phase made of polycatenar molecules

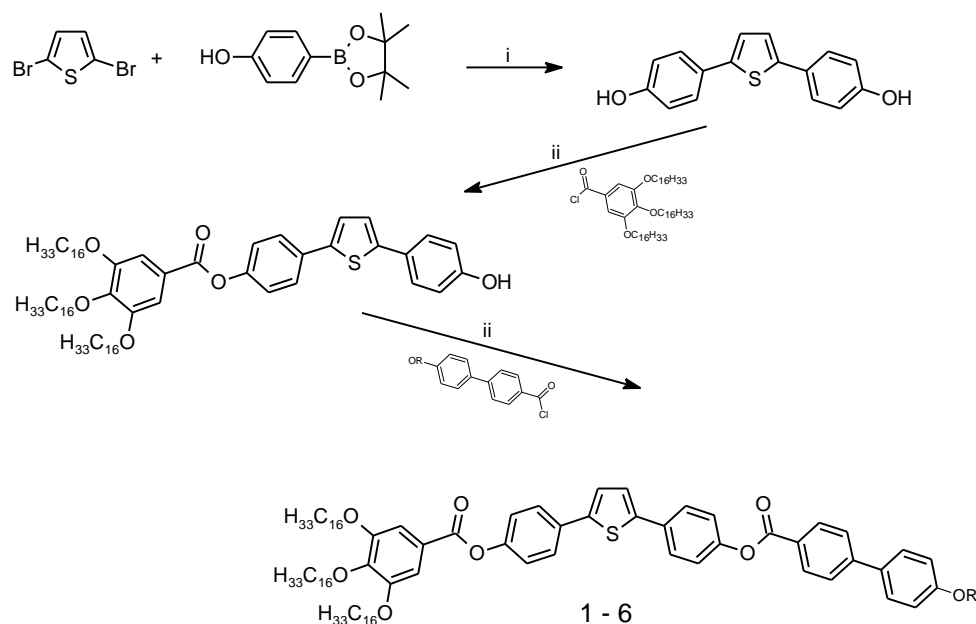
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Methods

The products were separated on the column chromatography using silica gel 60 Å (230-400 mesh Fluka). The molecular structure and purity of the synthesized compounds were confirmed by the following analytical methods: analytical thin-layer chromatography (TLC), ¹HNMR, ¹³CNMR spectroscopy and elemental analysis. Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 Å F254 (Merck) and visualized using iodine vapor and/or UV lamp (254 nm and 365 nm). NMR spectra were measured with NMR Bruker AVANCE 300 MHz or Bruker BioSpin GmbH 500 MHz spectrometer using tetramethylsilane as an internal standard. Chemical shifts are reported in ppm. High-resolution mass spectra were performed on Spectrometer Quattro LC (*Triple Quadrupole Mass Spectrometer*) apparatus using the TOF MS ES+ method.

The initial X-ray studies for all materials were performed with the Bruker Nanostar system (CuKα line, three-pinhole beam collimator, Vantec 2000 area detector). Samples were prepared as droplets on a heated surface. For chosen materials, additional X-ray measurements were carried out on the SAXS beam line (7.3.3) at the Advanced Light Source, Lawrence Berkeley National Laboratory at the wavelength 0.12398 nm. Samples were placed on heating plate as droplets. The scattering intensity was recorded using the Pilatus 2M detector. Optical studies were performed by using the Zeiss Axio Imager A2m polarizing microscope equipped with a Linkam heating stage. Samples were observed in glass cells of various thicknesses: from 1.8 to 10 μm. The birefringence was calculated from the optical retardation at green light (λ = 545 nm), measured with a CRI Abrio Imaging System. Knowing the sample thickness, the retardation was recalculated into optical birefringence. Calorimetric studies were performed with a TA DSC Q200 calorimeter, samples of mass from 1 to 3 mg were sealed in aluminum pans and kept in nitrogen atmosphere during measurement, both heating and cooling scans were performed with a rate of 5 – 10 K/min.

Synthesis



Scheme S1. The reaction chain leading to the studied molecules, R stands for the alkyl chain – see the main text. Reagents and conditions: (i) Pd(PPh₃)₄, saturated solution of NaHCO₃, inert gas atmosphere, reflux; (ii) THF, DMAP, TEA, reflux, 5h;

Below, we present the synthesis of a bent mesogenic molecule with $R = C_4H_9$ (compound 1) as a general method to obtain final compounds 1-6. Other molecules were obtained under similar reaction conditions and the same molar ratio of substrates. 1H NMR, ^{13}C NMR spectroscopy and elemental analysis of the obtained compounds confirmed the expected structures.

General procedure for the synthesis of target materials 1- 6

Synthesis of 4,4'-(thiophene-2,5-diyl)diphenol

To a solution of 2,5-dibromothiophene (12.0 g, 50.0 mmol) and 4-hydroxyphenylboronic acid pinacol ester (26.2 g, 119.0 mmol) in THF (150 mL) saturated solution of $NaHCO_3$ (70 mL) was added all at once. Then the reaction mixture was degassed with argon and palladium catalyst (1.4 g $Pd(PPh_3)_4$) was added. The reaction mixture was stirred and left for 8 h at the boiling point of solvents. After that it was extracted three times with chloroform, the collected organic layers were dried over anhydrous magnesium sulphate and the solvents were removed. The product was separated on column chromatography on silica gel and eluted with mixture of solvents gradually changing concentration of methanol in chloroform from 1% to 5%. Yield 60%.

1H -NMR (MeOD, 300 MHz): δ (ppm) 7.45 (4H, d, $J=8.7$ Hz), 7.12 (2H, s), 6.80 (4H, d, $J=8.6$ Hz);

^{13}C -NMR (MeOD, 75 MHz): δ (ppm) 158.38, 143.87, 127.84, 127.70, 123.63;

Elemental analysis ($C_{16}H_{12}O_2S$, $M=268.33$) - Calculated: C(71.62%), H(4.51%); Found: C(71.85%), H(4.48%);

Synthesis of 4-(5-(4-hydroxyphenyl)thiophen-2-yl)phenyl 3,4,5-tris(hexadecyloxy)benzoate

4,4'-(thiophene-2,5-diyl)diphenol (6.0 g, 20.1 mmol) was dissolved in dry THF (70 mL), DMAP (catalytic amount) and triethylamine (1 mL) was added all at once. Then a solution of 3,4,5-trihexadecyloxybenzoyl chloride (15.6 g, 18.0 mmol) in THF (15 mL) was added dropwise. The reaction mixture was stirred at room temperature over night. The solvent was evaporated and the crude compound was isolated on column chromatography on silica gel using $CHCl_3$ as eluent. Yield 68%.

1H -NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.66 (2H, d, $J=8.7$ Hz), 7.48 (2H, d, $J=8.5$ Hz), 7.45 (2H, s), 7.24 – 7.15 (4H, m), 6.81 (2H, d, $J=8.6$ Hz);

^{13}C -NMR ($CDCl_3$, 75 MHz): δ (ppm) 165.34, 155.48, 152.97, 150.14, 145.44, 143.86, 143.14, 143.07, 141.45, 132.38, 127.04, 126.54, 124.12, 123.67, 122.89, 122.23, 115.79, 108.59, 73.63, 69.28, 34.53, 31.92, 30.33, 29.71, 29.67, 29.64, 29.57, 29.40, 29.29, 27.99, 26.08, 22.68, 18.38, 14.11;

Elemental analysis ($C_{71}H_{112}O_6S$, $M=1093.71$) - Calculated: C(77.97%), H(10.32%); Found: C(78.08%), H(10.45%);

Synthesis of the final compound with $R = C_4H_9$ (1)

This synthesis was performed according to the previously described procedure 2 starting from the monosubstituted derivatives of thiophenediphenol (250 mg, 0.23 mmol) and 4'-butoxy-[1,1'-biphenyl]-4-carbonyl chloride (79 mg, 0.27 mmol). For purification by the column chromatography a mixture of solvents toluene/hexan (4/1, v/v) was used. Yield 93%.

Analytical data for target compounds

Compound 1 (with $R = C_4H_9$)

1H -NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.25 (2H, d, $J=8.4$ Hz), 7.72-7.67 (6H, m), 7.60 (2H, d, $J=8.5$ Hz), 7.42 (2H, s), 7.29 (2H, s), 7.25 – 7.22 (4H, m), 7.01 (2H, d, $J=8.7$ Hz), 4.08-4.01 (8H, m), 1.89-1.72 (8H, m), 1.57-1.45 (8H, m), 1.47-1.20 (72H, m), 1.00 (3H, t, $J=7.2$ Hz), 0.90 (9H, t, $J=6.6$ Hz);

^{13}C -NMR ($CDCl_3$, 125 MHz): δ (ppm) 165.11, 165.01, 159.65, 153.01, 150.50, 150.48, 146.11, 143.10, 142.93, 142.91, 132.10, 131.96, 130.78, 128.42, 127.36, 126.76, 126.73, 126.64, 124.29, 123.78, 122.33, 122.31, 115.02, 108.61, 115.02, 108.61, 73.62, 69.31, 67.87, 31.97, 31.33, 30.39, 29.80, 29.78, 29.75, 29.72, 29.71, 29.68, 29.62, 29.44, 29.42, 29.41, 29.34, 26.17, 26.10, 22.73, 19.29, 14.16, 13.89;

Elemental analysis ($C_{88}H_{128}O_8S$, $M=1346.02$) - Calculated: C(78.52%), H(9.59%); Found: C(78.65%), H(9.50%);

HRMS (TOF) m/z for $C_{88}H_{128}O_8S$ [$M+Na$] $^+$; Calculated: 1367.9228; Found 1367.9268;

Compound 2 (with $R = C_5H_{11}$)

1H -NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.25 (2H, d, $J=8.5$ Hz), 7.72-7.67 (6H, m), 7.61 (2H, d, $J=8.5$ Hz), 7.42 (2H, s), 7.29 (2H, s), 7.24 (4H, m), 7.02 (2H, d, $J=8.6$ Hz), 4.09-4.00 (8H, m), 1.86-1.74 (8H, m), 1.55-1.40 (8H, m), 1.35-1.24 (74H, m), 0.95 (3H, t, $J=7.2$ Hz), 0.88 (9H, t, $J=6.5$ Hz);

^{13}C -NMR ($CDCl_3$, 125 MHz): δ (ppm) 165.10, 165.00, 159.63, 153.00, 150.47, 146.11, 143.09, 142.92, 142.90, 132.09, 131.95, 130.77, 128.41, 127.35, 126.76, 126.73, 126.63, 124.29, 123.77, 122.32, 122.30, 115.01, 108.60, 73.61, 69.30, 68.17 31.95, 30.37, 29.78, 29.76, 29.74, 29.69, 29.67, 29.60, 29.43, 29.40, 29.39, 29.33, 28.98, 28.22, 26.11, 26.09, 22.71, 22.49, 14.14, 14.05;

Elemental analysis ($C_{89}H_{130}O_8S$, $M=1360.04$) - Calculated: C(78.60%), H(9.63%); Found: C(78.72%), H(9.78%);

HRMS (TOF) m/z for $C_{89}H_{130}O_8S$ [$M+Na$] $^+$; Calculated: 1381.9384; Found 1381.9399;

Compound 3 (with $R = C_6H_{13}$)

1H -NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.24 (2H, d, $J=8.4$ Hz), 7.71-7.66 (6H, m), 7.58 (2H, d, $J=8.7$ Hz), 7.42 (2H, s), 7.29-7.22 (6H, m), 6.99 (2H, d, $J=8.7$ Hz), 4.09-4.00 (8H, m), 1.88-1.72 (8H, m), 1.56-1.45 (8H, m), 1.43-1.22 (76H, m), 0.92 (3H, t, $J=7.0$ Hz) 0.89-0.86 (12H, m);

^{13}C -NMR ($CDCl_3$, 125 MHz): δ (ppm) 165.12, 165.01, 159.64, 153.01, 150.48, 146.12, 143.10, 142.91, 132.10, 131.10, 130.78, 128.42, 127.36, 126.77, 126.74, 126.65, 124.29, 123.78, 122.33, 122.31, 115.02, 108.61, 73.62, 69.31, 68.20, 31.96, 31.62, 30.38, 29.79, 29.77, 29.75, 29.71, 29.70, 29.67, 29.61, 29.43, 29.41, 29.40, 29.33, 29.25, 26.12, 26.09, 25.76, 22.72, 22.64, 14.15, 14.04;

Elemental analysis (C₉₀H₁₃₂O₈S, M=1374.07) - Calculated: C(78.67%), H(9.68%); Found: C(78.54%), H(9.60%);

HRMS (TOF) m/z for C₉₀H₁₃₂O₈S [M+Na]⁺; Calculated: 1395.9541; Found 1395.9518;

Compound 4 (with R = C₈H₁₇)

¹H-NMR (CDCl₃, 300 MHz): δ (ppm) 8.24 (2H, d, J=8.6Hz), 7.72-7.67 (6H, m), 7.60 (2H, d, J=8.6Hz), 7.42 (2H, s), 7.29 (2H, s), 7.25-7.22 (4H, m), **7.00 (2H, d, J=7.9Hz), 4.09-4.00 (8H, m), 1.88-1.72 (8H, m), 1.54-1.44 (8H, m), 1.41-1.24 (80H, m), 0.92-0.86 (12H, m)**;

¹³C-NMR (CDCl₃, 75 MHz): δ (ppm) 165.08, 164.98, 159.61, 152.97, 150.46, 146.09, 143.07, 142.90, 142.88, 132.06, 131.91, 130.75, 128.38, 127.32, 126.73, 126.70, 126.61, 124.26, 123.75, 122.30, 122.27, 114.99, 108.58, 73.58, 69.28, 68.17, 31.93, 30.35, 29.74, 29.71, 29.67, 29.64, 29.58, 29.40, 29.37, 29.34, 29.30, 29.25, 26.09, 22.69, 14.11;

Elemental analysis (C₉₂H₁₃₆O₈S, M=1402.12) - Calculated: C(78.81%), H(9.78%); Found: C(78.95%), H(9.84%);

Compound 5 (with R = C₁₁H₂₃)

¹H-NMR (CDCl₃, 300 MHz): δ (ppm) 8.25 (2H, d, J=8.4Hz), 7.72-7.67 (6H, m), 7.60 (2H, d, J=8.7Hz), 7.42 (2H, s), 7.29 (2H, s), 7.25-7.22 (4H, m), 7.01 (2H, d, J=8.7Hz), 4.09-4.00 (8H, m), 1.88-1.72 (8H, m), 1.55-1.44 (8H, m), 1.41-1.24 (86H, m), 0.92-0.86 (12H, m);

¹³C-NMR (CDCl₃, 75 MHz): δ (ppm) 165.08, 164.98, 159.61, 152.98, 150.46, 146.09, 143.07, 142.88, 132.06, 131.92, 130.75, 128.39, 127.32, 126.73, 126.71, 126.61, 124.26, 123.75, 122.27, 114.99, 108.58, 73.59, 69.28, 68.17, 31.93, 31.82, 30.35, 29.71, 29.67, 29.64, 29.58, 29.71, 29.68, 29.64, 29.58, 29.40, 29.37, 29.30, 29.25, 26.09, 22.69, 14.11;

Elemental analysis (C₉₅H₁₄₂O₈S, M=1444.20) - Calculated: C(79.01%), H(9.91%); Found: C(78.90%), H(9.96%);

Compound 6 (with R = (R) CH(C₂H₅)C₅H₁₁)

¹H-NMR (CDCl₃, 500 MHz): δ (ppm) 8.24 (2H, d, J=8.4Hz), 7.72-7.67 (6H, m), 7.59 (2H, d, J=8.7Hz), 7.42 (2H, s), 7.29 (2H, s), 7.25-7.22 (4H, m), 6.99 (2H, d, J=8.5Hz), 4.28-4.20 (1H, m), 4.09-4.04 (6H, m), 1.88-1.59 (10H, m), 1.53-1.43 (8H, m), 1.41-1.22 (76H, m), 0.98 (3H, t, J=7.5Hz), 0.94-0.86 (12H, m);

¹³C-NMR (CDCl₃, 125 MHz): δ (ppm) 165.11, 165.00, 159.29, 153.00, 150.49, 146.13, 143.10, 142.93, 142.90, 132.08, 131.75, 130.77, 128.46, 127.30, 126.76, 126.73, 126.60, 124.29, 123.77, 122.32, 122.30, 116.25, 108.60, 79.23, 73.61, 69.30, 33.43, 32.00, 31.94, 30.38, 29.78, 29.77, 29.74, 29.71, 29.70, 29.67, 29.61, 29.43, 29.41, 29.40, 29.33, 26.61, 26.12, 26.09, 25.14, 22.72, 22.64, 14.15, 14.06, 9.61 ;

Elemental analysis (C₉₂H₁₃₆O₈S, M=1402.12) - Calculated: C(78.81%), H(9.78%); Found: C(78.75%), H(9.76%);

HRMS (TOF) m/z for C₉₂H₁₃₆O₈S [M+Na]⁺; Calculated: 1423.98541; Found 1423.9829;

Additional figures and tables

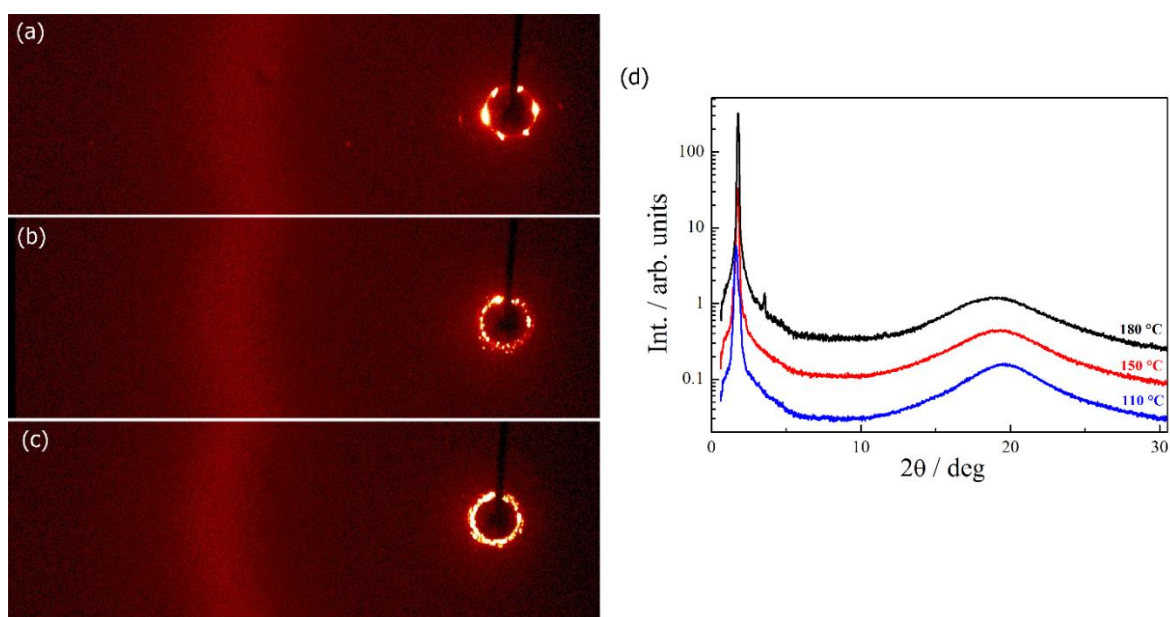


Figure S1. Wide angle 2D X-ray diffraction patterns taken for compound with $n = 6$ in (a) Col_h phase at $T = 180$ °C, (b) $\text{Ia}\bar{3}d$ at $T = 150$ °C and (c) Pcab phase at $T = 110$ °C. In all cases diffused signal at high diffraction angle range confirms liquid crystalline character of the phase. (d) 1D XRD patterns obtained by integration of 2D patterns over azimuthal angle. The curves were vertically shifted for clarity of presentation.

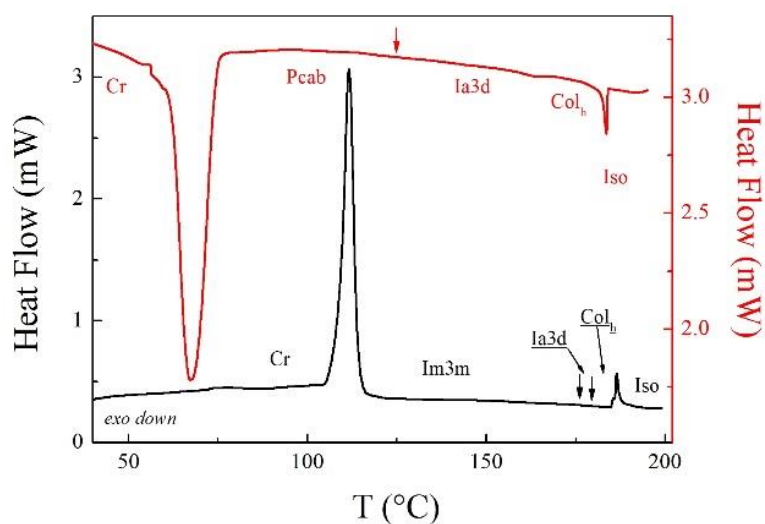


Figure S2. DSC thermograms for heating (black) and cooling (red) scans for compound with $n = 6$. Arrows mark temperatures of a phase transition detected by the X-ray diffraction studies.

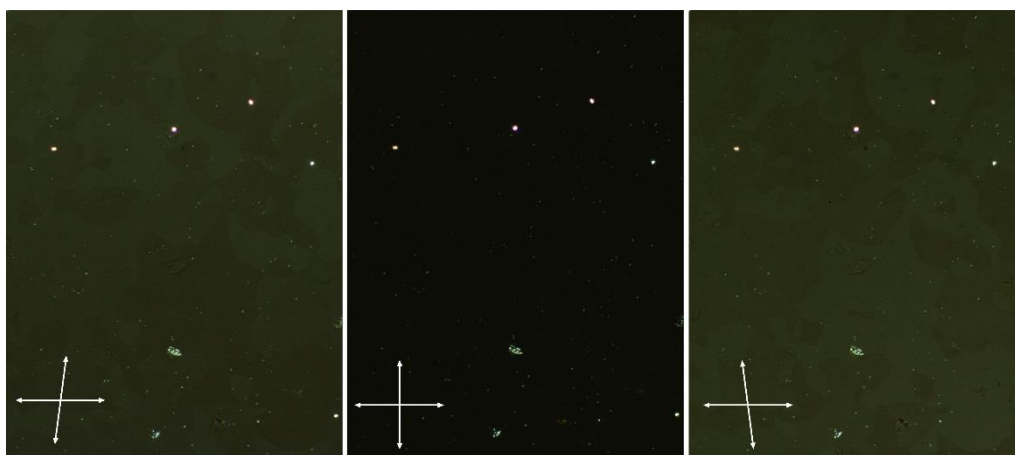


Figure S3. Optically isotropic texture of the cubic $Im\bar{3}m$ phase of compound with $R = C_6H_{13}$; domains showing optical activity are visible under slightly de-crossed polarizers.

Table S1. Positions (q_{exp} and d_{exp}) and relative intensities (I) of XRD signals recorded in the $Pcab$ phase, their Miller indices (hkl) and calculated positions (q_{calc} and d_{calc}).

$q_{exp} / \text{\AA}^{-1}$	$d_{exp} / \text{\AA}$	I	(hkl)	$q_{calc} / \text{\AA}^{-1}$	$d_{calc} / \text{\AA}$
0.09159	68.60	0.03	(002)	0.09121	68.89
0.09313	67.47	0.19	(200)	0.09326	67.37
0.1043	60.23	1.22	(012)	0.1041	60.38
0.1106	56.82	13.27	(120)	0.1105	56.84
0.1141	55.08	87.73	(112)	0.1140	55.10
0.1153	54.48	100	(211)	0.1153	54.51
0.1197	52.51	69.71	(121)	0.1196	52.55
0.1304	48.18	18.52	(202)	0.1305	48.16
0.1356	46.34	7.03	(022)	0.1355	46.37
0.1368	45.92	8.89	(220)	0.1369	45.90
0.1398	44.95	1.06	(212)	0.1398	44.96
0.1437	43.72	1.90	(122)	0.1433	43.84
			(221)	0.1443	43.54
0.1534	40.97	1.32	(113)	0.1530	41.07
0.1553	40.45	0.17	(311)	0.1554	40.42
0.1644	38.23	0.16	(131)	0.1639	38.34
			(222)	0.1645	38.20
0.1659	37.88	0.17	(203)	0.1656	37.95
0.1725	36.42	0.02	(320)	0.1721	36.51
			(213)	0.1730	36.32
0.1762	35.68	0.16	(032)	0.1758	35.73
			(123)	0.1759	35.72
0.1827	34.41	0.34	(004)	0.1824	34.44
			(231)	0.1827	34.39
0.1935	32.47	0.30	(223)	0.1936	32.46
0.1952	32.19	0.06	(322)	0.1948	32.26
			(114)	0.1948	32.25
0.2010	31.26	0.37	(040)	0.2005	31.34
			(313)	0.2020	31.11
			(331)	0.2104	29.87
0.2109	29.82	0.16	(141)	0.2108	29.81
			(214)	0.2109	29.79
			(420)	0.2118	29.67
0.2197	28.57	0.10	(323)	0.2198	28.58
0.2211	28.42	0.15	(240)	0.2211	28.42
0.2294	27.38	0.13	(224)	0.2281	27.55
			(422)	0.2306	27.25
0.2447	25.67	0.03	(340)	0.2444	25.71
0.2486	25.27	0.11	(341)	0.2486	25.27

Table S2. Positions (q_{exp} and d_{exp}) and relative intensities (I) of XRD signals recorded in the $Ia\bar{3}d$ phase, their Miller indices (hkl) and calculated positions (q_{calc} and d_{calc}).

$q_{exp} / \text{\AA}^{-1}$	$d_{exp} / \text{\AA}$	I	(hkl)	$q_{calc} / \text{\AA}^{-1}$	$d_{calc} / \text{\AA}$
0.1206	52.10	100	(211)	0.1206	52.11
0.1391	45.18	13.70	(022)	0.1392	45.13
0.1841	34.13	0.10	(321)	0.1842	34.11
0.1968	31.93	0.32	(004)	0.1969	31.91
0.2204	28.50	0.31	(042)	0.2201	28.54
0.2411	26.06	0.12	(422)	0.2412	26.05
0.2507	25.06	0.20	(431)	0.2510	25.03
0.2784	22.57	0.02	(044)	0.2785	22.56
0.3037	20.69	0.08	(532), (611)	0.3034	20.70
0.3476	18.08	0.08	(543)	0.3481	18.05

Table S3. Positions (q_{exp} and d_{exp}) and relative intensities (I) of XRD signals recorded in $Im\bar{3}m$ phase, their Miller indices (hkl) and calculated positions (q_{calc} and d_{calc}).

$q_{exp} / \text{\AA}^{-1}$	$d_{exp} / \text{\AA}$	I	(hkl)	$q_{calc} / \text{\AA}^{-1}$	$d_{calc} / \text{\AA}$
0.04421	142.11	0.01	(011)	0.04409	142.52
0.07636	82.28	0.17	(211)	0.07636	82.28
0.08833	71.13	0.10	(022)	0.08817	71.26
0.09863	63.70	0.85	(031)	0.09858	63.74
0.1080	58.15	2.56	(222)	0.1080	58.18
0.1166	53.86	100	(321)	0.1166	53.87
0.1247	50.39	25.71	(004)	0.1247	50.39
0.1323	47.51	2.98	(033)	0.1322	47.51
0.1394	45.08	6.76	(042)	0.1394	45.07
0.1527	41.15	0.52	(422)	0.1527	41.14
0.1589	39.54	1.26	(051), (431)	0.1590	39.53
0.1707	36.81	0.12	(521)	0.1707	36.80
0.1762	35.67	0.02	(044)	0.1764	35.63
0.1817	34.58	0.22	(433), (053)	0.1818	34.57
0.1870	33.61	0.07	(006), (442)	0.1871	33.59
0.1921	32.71	0.21	(532), (611)	0.1922	32.70
0.1970	31.89	0.01	(062)	0.1972	31.87
0.2019	31.12	0.08	(541)	0.2020	31.10
0.2112	29.75	0.05	(631)	0.2114	29.72
0.2159	29.10	0.02	(444)	0.2160	29.09
0.2250	27.93	0.03	(064)	0.2248	27.95
0.2289	27.45	0.06	(552), (633), (721)	0.2291	27.43
0.2330	26.97	0.01	(642)	0.2333	26.93
0.2453	25.61	0.02	(732), (651)	0.2454	25.60
0.2531	24.82	0.02	(811), (741), (554)	0.2532	24.81
0.2680	23.45	0.03	(075), (831), (743)	0.2682	23.43

Table S4. Experimentally obtained intensities (in arbitrary units) for the X-ray peaks with Miller indices (h, k, l) for the $Ia\bar{3}d$ (I_{Ia3d}) and $Pcab$ (I_{Pcab}) phases, multiplicity of the peaks (M_{Ia3d} and M_{Pcab}), their relative amplitudes (F_{Ia3d} and F_{Pcab}), 1 being assigned to the highest amplitude, and the phases (ϕ) of the peaks in the $Ia\bar{3}d$ phase. The data for the $Pcab$ phase is given at two temperatures, 113 °C and 93 °C, denoted by (1) and (2), respectively. The unit cell dimensions are $13.47 \times 12.54 \times 13.78 \text{ nm}^3$ in case (1) and $13.90 \times 12.59 \times 14.11 \text{ nm}^3$ in case (2). In the $Ia\bar{3}d$ phase, the unit cell length is 12.76 nm.

(h, k, l)	M_{Ia3d}	$I_{Ia3d}[\text{au}]$	ϕ	F_{Ia3d}	M_{Pcab}	$I_{Pcab}^{(1)}$	$F_{Pcab}^{(1)}$	$I_{Pcab}^{(2)}$	$F_{Pcab}^{(2)}$
(1,2,0)	/	/	/	/	4	3.0	0.50	2.9	0.48
(1,1,2)					8	18.2	0.87	19.7	0.89
(2,1,1)	24	10.2	π	1	8	24.3	1	25.1	1
(1,2,1)					8	16.6	0.83	17.8	0.84
(2,0,2)					4	4.0	0.57	5.6	0.67
(0,2,2)	12	1.15	π	0.48	4	1.5	0.35	2.5	0.45
(2,2,0)					4	1.8	0.39	1.7	0.37
(3,2,1)	48	0.01	0	0.02	/	/	/	/	/
(0,0,4)	6	0.04	π	0.12	/	/	/	/	/