Electronic Supplementary Information

Monoclinic to Two-dimensional Hexagonal Transformation in Hexacatenar Molecules with a 1,2,3-Triazole-Based Conjugated Rod: Morphology-Dependent Thermochromic Behavior

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Synthesis of the intermediate compounds. The synthetic procedure is outlined in Scheme S1.

*Synthesis of 1,2,3,-tris(alkyloxy)benzene (**1a** and **2a**).* 1,2,3,-Tris(octyloxy)benzene (**1a**) and 1,2,3,-tris(dodecyloxy)benzene (**2a**) were synthesized using the same procedure.[S1] A representative synthesis is described for compound **1a**. Pyrogallol (5.00 g, 39.65 mmol) and K_2CO_3 (32.88 g, 237.89 mmol) were dissolved in 350 mL of DMF. To this mixture, 1-bromooctane (17.76 mL, 237.89 mmol) was added dropwise. The reaction mixture was heated to reflux for 1 day at 90 °C under N_2 atmosphere. After removing DMF using a rotary evaporator, the mixture was extracted with deionized water and DCM. The DCM layer was washed with deionized water several times, and then dried over anhydrous $MgSO_4$. After removing DCM using a rotary evaporator, the resulting mixture was purified by silica gel column chromatography using an *n*-hexane:DCM = 4:1 solvent mixture as the eluent, yielding 15.21 g (82.91%) of a yellowish liquid. ^{1}H-NMR ($CDCl_3$, δ, ppm): 6.91 (t, 1H, *J* = 8.2 Hz, Ar-*H*), 6.54 (d, 2H, *J* = 8.4 Hz, Ar-*H*), 3.95 (t, 6H, *J* = 6.2 Hz, $OCH_2CH_2(CH_2)_5CH_3$), 1.78-1.76 (m, 6H, $OCH_2CH_2(CH_2)_5CH_3$), 1.46-1.26 (m, 30H, $OCH_2CH_2(CH_2)_5CH_3$), 0.88 (t, 9H, *J* = 6.8 Hz, $OCH_2CH_2(CH_2)_5CH_3$).

*1,2,3,-Tris(dodecyloxy)benzene (**2a**).* Yield: 89.91%. ^{1}H-NMR ($CDCl_3$, δ, ppm): 6.91 (t, 1H, *J* = 8.2 Hz, Ar-*H*), 6.54 (d, 2H, *J* = 8.2 Hz, Ar-*H*), 3.95 (t, 6H, *J* = 6.2 Hz, $OCH_2CH_2(CH_2)_9CH_3$), 1.83-1.76 (m, 6H, $OCH_2CH_2(CH_2)_9CH_3$), 1.46-1.26 (m, 54H, $OCH_2CH_2(CH_2)_9CH_3$), 0.88 (t, 9H, *J* = 6.8 Hz, $OCH_2CH_2(CH_2)_9CH_3$).

Preparation of silica gel-supported nitric acid ($HNO_3{\cdot}SiO_2$). Silica gel (60.00 g, mesh size 70-230) was added to 8 *N* nitric acid (140 mL), and the mixture was stirred for 2 h at 23 °C. After filtration, the silica gel was left to dry for 3 days before it was stored in an airtight flask. The nitric acid content (20%) was determined by titration of a suspension of reagent (1.00 g) in water (50 mL), with 0.1 *N* NaOH using phenolphthalein as the indicator.

*Synthesis of 1,2,3-tris(alkyloxy)-5-nitrobenzene (**1b** and **2b**).* 5-Nitro-1,2,3-tris(octyloxy)benzene (**1b**) and 1,2,3-tris(dodecyloxy)-5-nitrobenzene (**2b**) were synthesized using the same procedure.[S1] A representative synthesis is described for compound **1b**. Compound **1a** (14.00 g, 30.25 mmol) and $HNO_3{\cdot}SiO_2$ (14.50 g, 49.48 mmol) were dissolved in 250 mL of DCM. The reaction mixture was stirred at room temperature for 30 min under N_2 atmosphere. The mixture was then filtered. After removing DCM using a rotary evaporator, the resulting mixture was washed with methyl alcohol, and purified by silica gel column chromatography using *n*-hexane:DCM = 4:1 as the eluent, yielding 8.21 g (53.45%)

of a yellowish liquid. ^{1}H-NMR ($CDCl_3$, δ, ppm): 7.46 (s, 2H, Ar-*H*), 4.04 (t, 6H, *J* = 5.8 Hz, $OCH_2CH_2(CH_2)_5CH_3$), 1.87-1.70 (m, 6H, $OCH_2CH_2(CH_2)_5CH_3$), 1.47-1.26 (m, 30H, $OCH_2CH_2(CH_2)_5CH_3$), 0.88 (t, 9H, *J* = 6.8 Hz, $OCH_2CH_2(CH_2)_5CH_3$).

*1,2,3-tris(dodecyloxy)-5-nitrobenzene (**2b**).* Yield: 52.42%. ^{1}H-NMR ($CDCl_3$, δ, ppm): 7.43 (s, 2H, Ar-*H*), 4.04 (t, 6H, *J* = 6.0 Hz, $OCH_2CH_2(CH_2)_9CH_3$), 1.85-1.72 (m, 6H, $OCH_2CH_2(CH_2)_9CH_3$), 1.47-1.26 (m, 54H, $OCH_2CH_2(CH_2)_9CH_3$), 0.88 (t, 9H, *J* = 6.8 Hz, $OCH_2CH_2(CH_2)_9CH_3$).

*Synthesis of 3,4,5-tris(alkyloxy)aniline (**1c** and **2c**).* 3,4,5-Tris(octyloxy)aniline (**1c**) and 3,4,5-tris(dodecyloxy)aniline (**2c**) were synthesized using the same procedure.[S1] A representative synthesis is described for compound **1c**. Compound **1b** (8.00 g, 15.76 mmol), hydrazine (14.68 mL, 472.26 mmol), and graphite (7.10 g) were dissolved in 200 mL of ethyl alcohol. The reaction mixture was heated to reflux for 24 h at 90 °C under N_2 atmosphere. After removing ethyl alcohol using a rotary evaporator, the mixture was extracted with deionized water and DCM. The DCM layer was washed with deionized water several times, and then dried over anhydrous $MgSO_4$. After removing DCM using a rotary evaporator, the resulting mixture was washed with isopropyl alcohol, yielding 7.13 g (94.74%) of a yellowish liquid. ^{1}H-NMR ($CDCl_3$, δ, ppm): 5.91 (s, 2H, Ar-*H*), 3.87 (t, 6H, *J* = 6.4 Hz, $OCH_2CH_2(CH_2)_5CH_3$), 3.47 (s, 2H, Ar-NH_2) 1.80-1.68 (m, 6H, $OCH_2CH_2(CH_2)_5CH_3$), 1.44-1.28 (m, 30H, $OCH_2CH_2(CH_2)_5CH_3$), 0.88 (t, 9H, *J* = 6.8 Hz, $OCH_2CH_2(CH_2)_5CH_3$).

*3,4,5-Tris(dodecyloxy)aniline (**2c**).* Yield: 87.43%. ^{1}H-NMR ($CDCl_3$, δ, ppm): 5.91 (s, 2H, Ar-*H*), 3.87 (t, 6H, *J* = 6.4 Hz, $OCH_2CH_2(CH_2)_9CH_3$), 3.47 (s, 2H, Ar-NH_2), 1.81-1.71 (m, 6H, $OCH_2CH_2(CH_2)_9CH_3$), 1.44-1.26 (m, 54H, $OCH_2CH_2(CH_2)_9CH_3$), 0.88 (t, 9H, *J* = 6.8 Hz, $OCH_2CH_2(CH_2)_9CH_3$).

*Synthesis of 5-azido-1,2,3-tris(alkyloxy)benzene (**1d** and **2d**).* 5-Azido-1,2,3-tris(octyloxy)benzene (**1d**) and 5-azido-1,2,3-tris(dodecyloxy)benzene (**2d**) were synthesized using the same procedure.[S2] A representative synthesis is described for compound **1d**. Compound **3a** (7.00 g, 14.65 mmol) was dissolved in 90 mL of THF and 60 mL of ACN. After cooling to 0 °C in an ice bath, *t*-butyl nitrite (6.97 mL, 58.60 mmol) and trimethylsilyl azide (7.70 mL, 58.60 mmol) were carefully added to the reaction mixture, which was then stirred at room temperature for 12 h under N_2 atmosphere. After removing solvent using a rotary evaporator, the resulting mixture was purified by silica gel column chromatography using *n*-hexane:DCM = 4:1 as the eluent, yielding 6.10 g (82.72%) of a yellowish liquid. ^{1}H-NMR ($CDCl_3$, δ, ppm): 6.20 (s, 2H, Ar-*H*), 3.92 (t, 6H, *J* = 6.4 Hz, $OCH_2CH_2(CH_2)_5CH_3$),

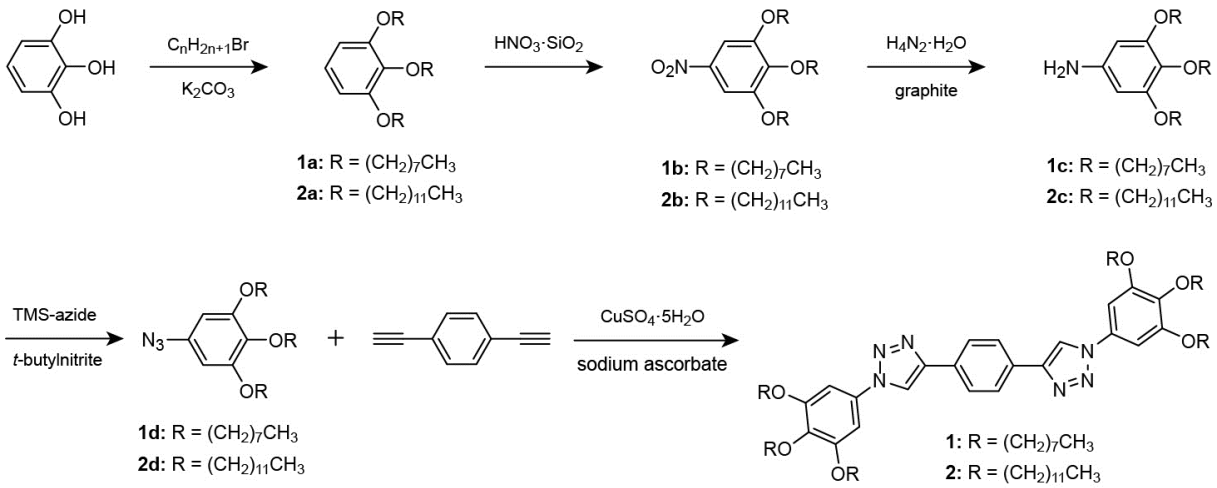
1.83-1.68 (m, 6H, $OCH_2CH_2(CH_2)_5CH_3$), 1.45-1.28 (m, 30H, $OCH_2CH_2(CH_2)_5CH_3$), 0.88 (t, 9H, J = 6.8 Hz, $OCH_2CH_2(CH_2)_5CH_3$).

*5-Azido-1,2,3-tris(dodecyloxy)benzene (**2d**).* Yield: 78.45%. ^{1}H-NMR ($CDCl_3$, δ, ppm): 6.21 (s, 2H, Ar-*H*), 3.92 (t, 6H, J = 6.6 Hz, $OCH_2CH_2(CH_2)_9CH_3$), 1.83-1.72 (m, 6H, $OCH_2CH_2(CH_2)_9CH_3$), 1.45-1.26 (m, 54H, $OCH_2CH_2(CH_2)_9CH_3$), 0.88 (t, 9H, J = 6.8 Hz, $OCH_2CH_2(CH_2)_9CH_3$).

References

(S1) V. Percec, E. Aqad, M. Peterca, J. G. Rudick, L. Lemon, J. C. Ronda, B. B. De, P. A. Heiney and E. W. Meijer. *J. Am. Chem. Soc.*, 2006, **128**, 16365-16372.

(S2) K. Barral, A. D. Moorhouse and J. E. Moses, *Org. Lett.*, 2007, **9**, 1809-1811.



Scheme S1. Synthesis of hexacatenar molecules **1** and **2** via a click reaction.

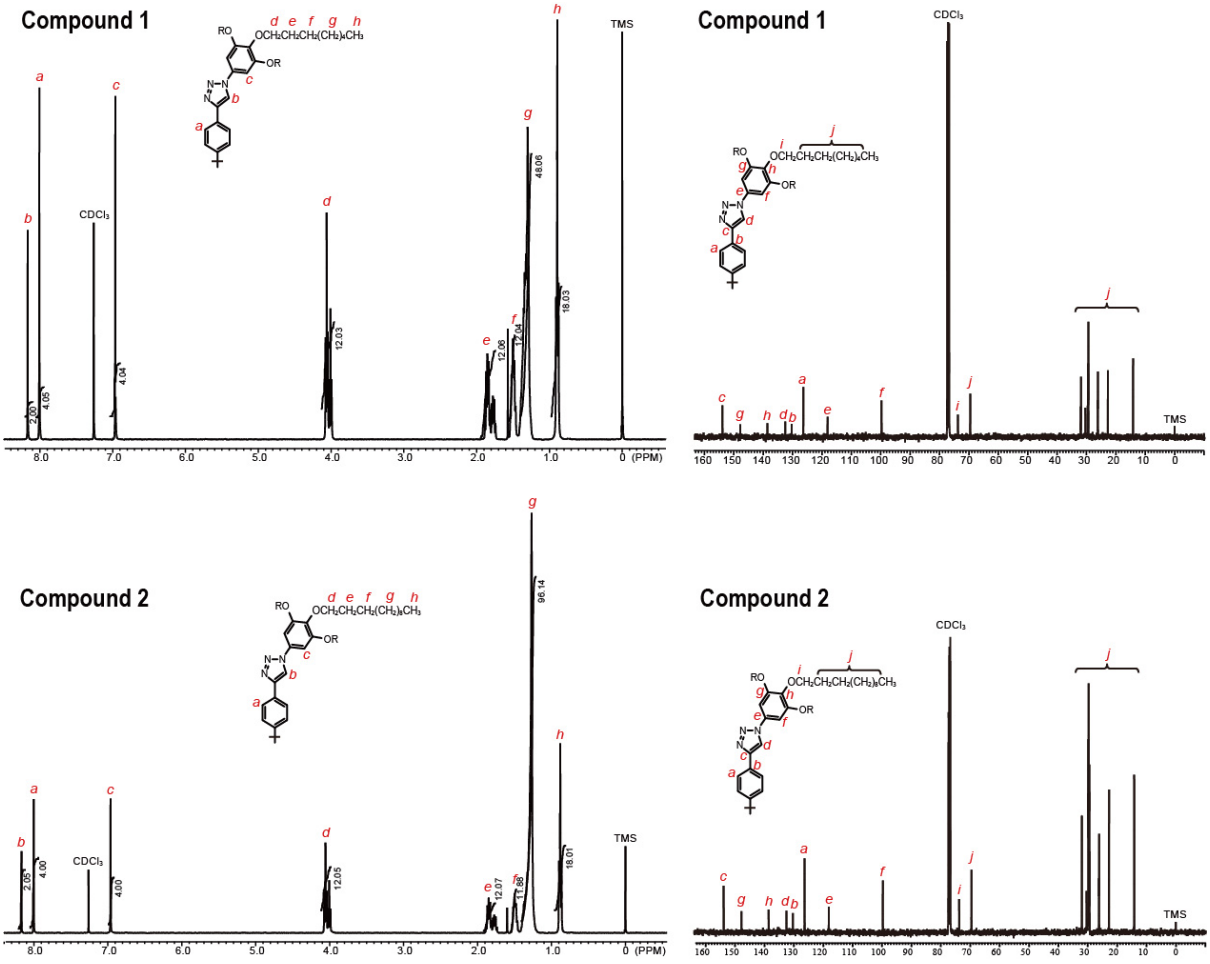


Fig. S1 ^{1}H- and ^{13}C-NMR spectra of hexacatenar molecules **1** and **2**.

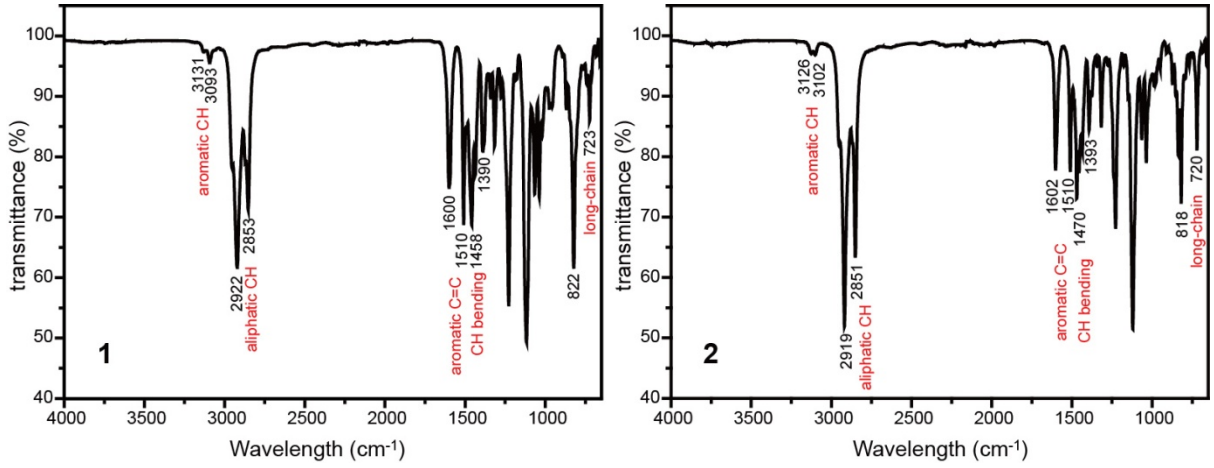


Fig. S2 IR spectra of hexacatenar molecules **1** and **2**.

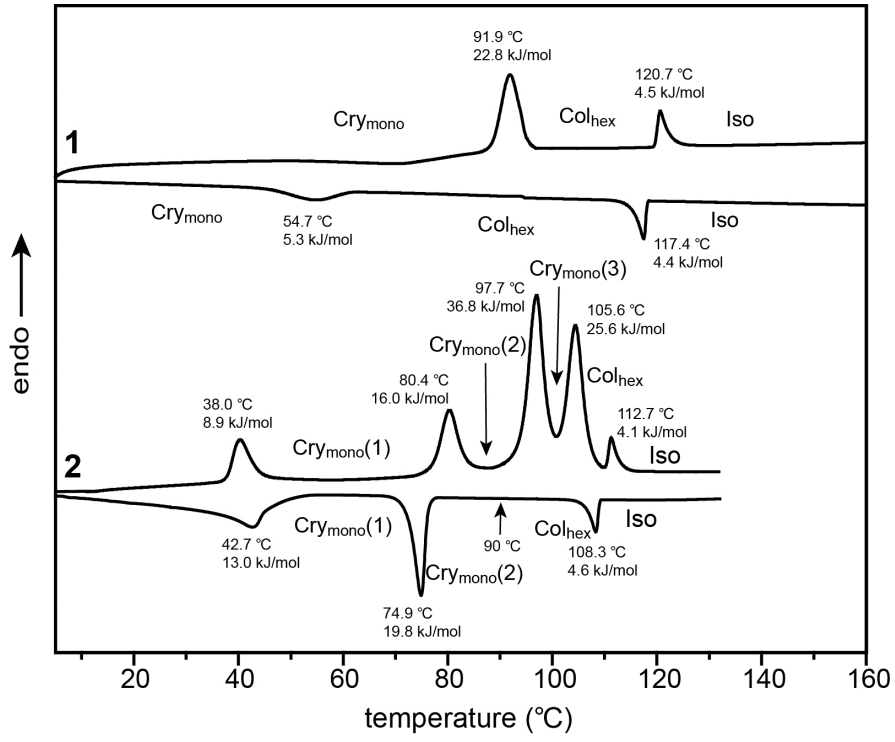


Fig. S3 DSC thermograms of hexacatenar molecules **1** and **2**.

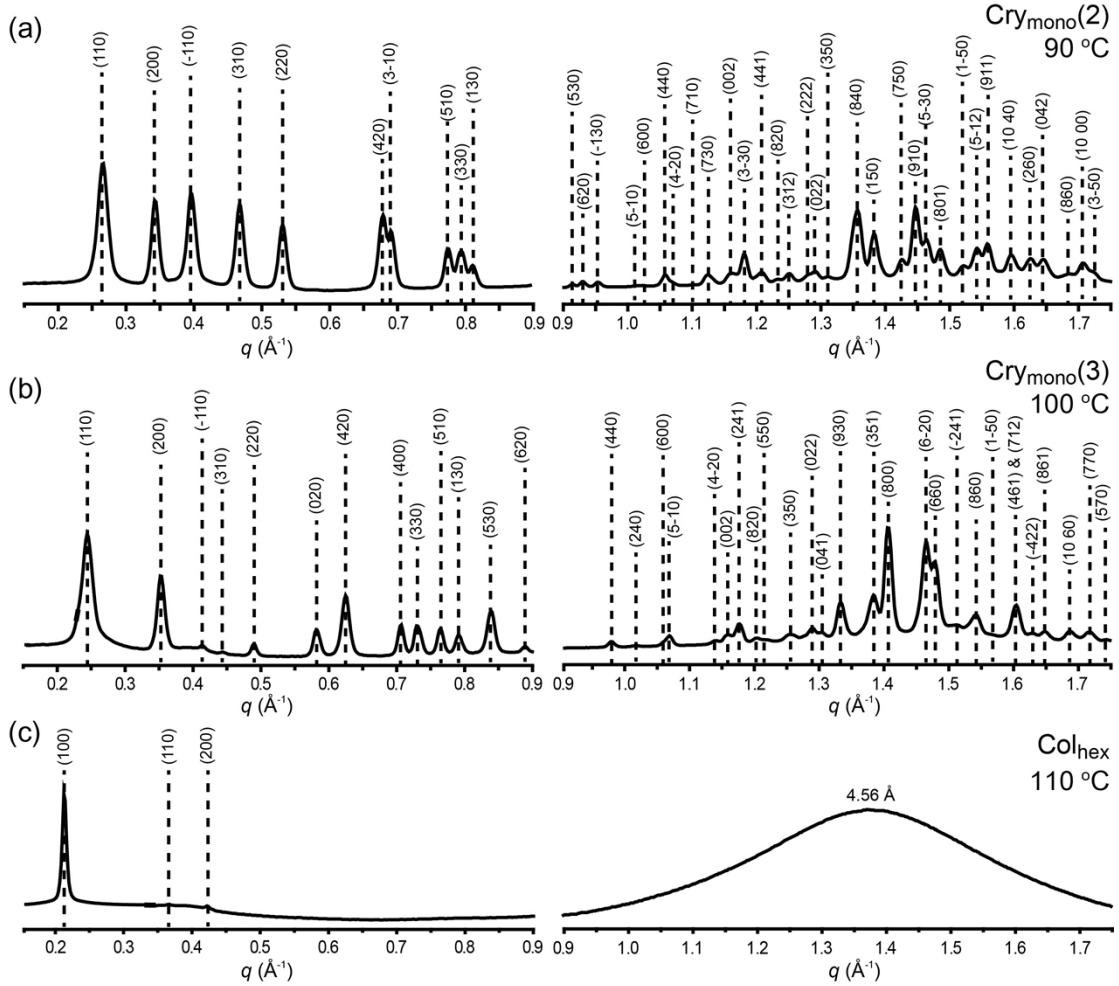


Fig. S4 SAXS and WAXS data of **2** in the Cry$_{mono}$(2), Cry$_{mono}$(3) and Col$_{hex}$ phases.

Table S1. Characterization of the X-ray data of **1**.

	d_{cal} /Å	d_{exp} /Å	*hkl*	d_{cal} /Å	d_{exp} /Å	*hkl*
30 ℃ (Cry_{mono})	38.61	38.60	(100)	5.66	5.67	(230)
	19.31	19.26	(200)	5.52	5.54	(130)
	17.09	17.13	(110)			&(700)
Lattice parmeters	15.83	15.87	(010)	5.41	5.41	(530)
	15.43	15.51	(210)	5.30	5.29	(-610)
	12.87	12.82	(300)	5.28	5.29	(030)
a = 41.7 Å	12.58	12.62	(310)	5.23	5.22	(-420)
b = 17.1 Å	10.46	10.42	(-210)	5.06	5.08	(820)
c = 10.4 Å	10.11	10.10	(410)	4.98	4.98	(-130)
γ = 67.8 °	9.65	9.62	(400)	4.83	4.83	(800)
	8.87	8.88	(111)	4.71	4.71	(-520)
	8.41	8.42	(120)	4.66	4.66	(-230)
	7.92	7.92	(020)	4.60	4.60	(910)
	7.72	7.77	(420)	4.44	4.44	(222)
			&(500)	4.34	4.34	(-330)
	7.13	7.10	(-410)	4.29	4.30	(900)
	7.01	7.03	(520)	4.23	4.23	(540)
	6.51	6.51	(-220)	4.20	4.19	(240)
	6.44	6.44	(600)			&(930)
	6.30	6.33	(021)	4.14	4.14	(640)
	6.29	6.28	(620)	4.13	4.12	(1010)
	6.09	6.08	(-510)	4.10	4.10	(140)
	5.96	5.97	(710)	4.03	4.03	(-430)
	5.83	5.82	(-320)	4.01	4.02	(740)
	5.70	5.71	(330)	3.96	3.96	(040)
110 ℃ (Col_{hex})	26.15	26.18	(100)			
	15.10	15.17	(110)			
	13.01	13.08	(200)			
Lattice parameters						
a = 30.2 Å						

d_{cal}, calculated lattice spacing; d_{exp}, experimental lattice spacing.

Table S2. Characterization of the X-ray data of **2**.

	d_{cal} /Å	d_{exp} /Å	*hkl*	d_{cal} /Å	d_{exp} /Å	*hkl*		d_{cal} /Å	d_{exp} /Å	*hkl*	d_{cal} /Å	d_{exp} /Å	*hkl*		d_{cal} /Å	d_{exp} /Å	*hkl*	d_{cal} /Å	d_{exp} /Å	*hkl*
75 ℃	22.84	22.85	(110)	5.01	5.00	(241)	90 ℃	23.75	23.73	(110)	5.21	5.21	(441)	100 ℃	25.64	25.65	(110)	5.26	5.23	(820)
Cry_{mono}(1)	18.92	18.93	(200)	4.98	4.96	(731)	Cry_{mono}(2)	18.43	18.43	(200)	5.11	5.10	(820)	Cry_{mono}(3)	17.84	17.82	(200)	5.13	5.16	(550)
	15.51	15.51	(-110)	4.90	4.90	(222)		15.93	15.94	(-110)	5.04	5.03	(312)		15.14	15.12	(-110)	5.02	5.02	(350)
Lattice	13.84	13.84	(310)	4.81	4.81	(022)	Lattice	13.49	13.47	(310)	4.94	4.92	(222)	Lattice	14.20	14.18	(310)	4.85	4.87	(022)
parmeters	11.42	11.42	(220)	4.74	4.74	(-710)	parmeters	11.87	11.87	(220)	4.86	4.87	(022)	parmeters	12.82	12.82	(220)	4.82	4.83	(041)
	10.33	10.33	(020)			&(800)		9.29	9.27	(420)	4.80	4.80	(350)		10.76	10.77	(020)	4.73	4.72	(930)
a = 42.10 Å	9.32	9.32	(420)	4.65	4.66	(840)	**a** = 40.90 Å	9.13	9.11	(3-10)	4.64	4.64	(840)	**a** = 42.60 Å	10.09	10.07	(420)	4.55	4.55	(351)
b = 23.00 Å	9.14	9.14	(-310)	4.57	4.56	(-620)	**b** = 24.10 Å	8.14	8.12	(510)	4.55	4.55	(150)	**b** = 25.70 Å	8.92	8.91	(400)	4.46	4.48	(800)
c = 10.86 Å	8.40	8.42	(510)			&(550)	**c** = 10.86 Å	7.92	7.93	(330)	4.42	4.44	(750)	**c** = 10.86 Å	8.55	8.57	(330)	4.30	4.30	(6-20)
γ = 64.00 º	7.75	7.75	(-220)	4.47	4.45	(-222)	**γ** = 64.30 º	7.77	7.75	(130)	4.38	4.35	(910)	**γ** = 56.90 º	8.25	8.23	(510)	4.27	4.26	(660)
	7.61	7.62	(330)	4.42	4.41	(332)		6.86	6.85	(530)	4.31	4.30	(5-30)		7.92	7.93	(130)	4.17	4.17	(-241)
	7.37	7.36	(130)	4.32	4.32	(150)		6.75	6.74	(620)	4.24	4.24	(801)		7.51	7.49	(530)	4.09	4.09	(860)
	6.90	6.92	(620)	4.25	4.25	(-530)		6.58	6.57	(-130)	4.11	4.14	(1-50)		7.10	7.08	(620)	4.02	4.03	(1-50)
	6.79	6.79	(530)	4.16	4.15	(-241)		6.41	6.40	(5-10)	4.09	4.09	(5-12)		6.41	6.40	(440)	3.94	3.93	(461)
	6.31	6.30	(-130)	4.10	4.08	(5-12)		6.14	6.13	(600)	4.06	4.04	(911)		6.17	6.18	(240)			&(712)
	5.82	5.82	(-420)	4.02	4.04	(751)		5.94	5.93	(440)	3.95	3.95	(10 40)		5.95	5.93	(600)	3.88	3.88	(-422)
	5.71	5.71	(440)	3.96	3.96	(950)		5.88	5.86	(4-20)	3.88	3.88	(260)		5.88	5.88	(5-10)	3.83	3.83	(861)
	5.61	5.62	(730)	3.87	3.86	(-440)		5.72	5.71	(710)	3.84	3.83	(042)		5.54	5.52	(4-20)	3.76	3.74	(10 60)
	5.43	5.43	(002)	3.80	3.79	(-910)		5.56	5.59	(730)	3.74	3.74	(860)		5.43	5.43	(002)	3.66	3.68	(770)
	5.29	5.30	(640)	3.73	3.74	(-820)		5.43	5.43	(002)	3.69	3.69	(10 00)		5.36	5.34	(241)	3.64	3.62	(570)
	5.17	5.15	(040)	3.65	3.66	(860)		5.31	5.32	(3-30)	3.63	3.66	(3-50)							
110 ℃	29.88	29.91	(100)																	
Col_{hex}	17.25	17.21	(110)																	
	14.94	14.95	(200)																	
Lattice parameters																				
a = 34.5 Å																				

d_{cal}, calculated lattice spacing; d_{exp}, experimental lattice spacing.