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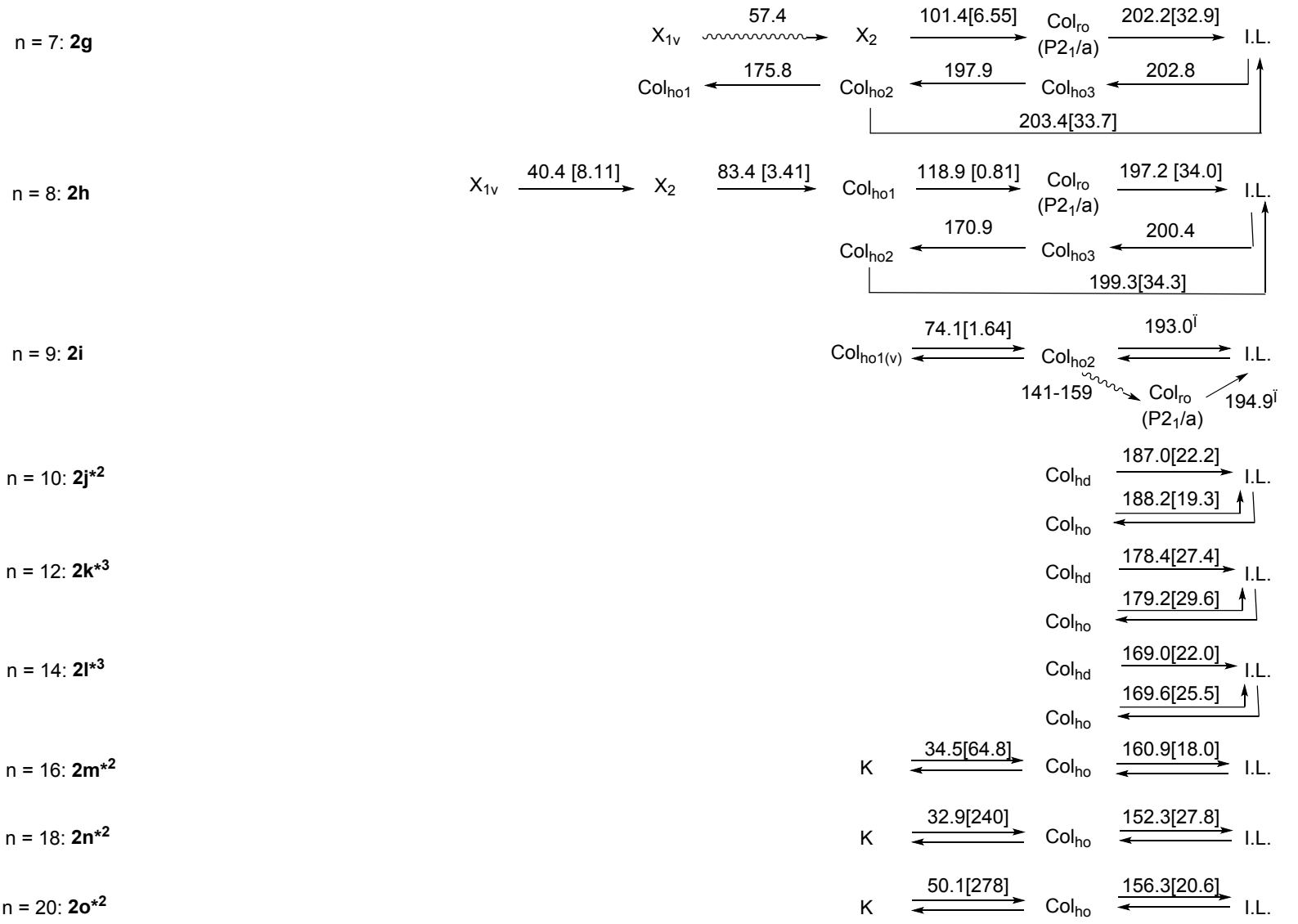
Table S1. Phase transition temperatures and enthalpy changes of (m-C_nOPhO)$_8$PcCu (n = 1-20: **2a-o**).

Compound (m-C_nOPhO)$_8$PcCu	Phase $\xrightarrow{T\,(^oC)\,[\,\Delta H\,(kJmol^{-1})]}$ Phase ; relaxation
n = 1: **2a**[*1]	Glassy $Col_{ro}(P2_1/a)$ $\overset{Tg=69.9}{\rightsquigarrow}$ K $\xrightarrow{191.3\,[13.4]}$ Col_{ro1} ($P2_1/a$) $\xrightarrow{255.1\,[2.69]}$ Col_{ro2} ($P2_1/a$) $\xrightarrow{360.1\,[10.7]}$ M_x (1st dc.) $\xrightarrow{405}$ 2nd dc.
	K_1 $\underset{}{\overset{229.4}{\rightleftharpoons}}$ Col_r (P2m) $\underset{}{\overset{354.1\,[19.6]}{\rightleftharpoons}}$ I.L.
n = 2: **2b**	K_{2v} $\xrightarrow{84.2}$ K_3 $\xrightarrow{181.4}$ K_4 ; K_4 $\overset{274.7\,[100.5]}{\rightsquigarrow}$ Col_r (P2m) ; Col_r (P2m) $\overset{197.0}{\rightsquigarrow}$ K_4
n = 3: **2c**	K_1 $\underset{}{\overset{113.4\,[5.0]}{\rightleftharpoons}}$ K_{2v} $\xrightarrow{142.8[41.5]}$ K_3 $\underset{}{\overset{207.4[17.5]}{\rightleftharpoons}}$ K_4 $\underset{}{\overset{234.1[29.9]}{\rightleftharpoons}}$ Col_r (P2m) $\underset{}{\overset{300.1[17.3]}{\rightleftharpoons}}$ I.L.
n = 4: **2d**	Glassy $Col_r(P2m)_{(v)}$ $\overset{Tg=115.7}{\rightsquigarrow}$ K_2 $\xrightarrow{166.1[6.4]}$ Col_r (P2m) ; Glassy $Col_r(P2m)_{(v)}$ $\rightsquigarrow$ K_3 ; K_1 $\underset{}{\overset{147.5[10.6]}{\rightleftharpoons}}$ K_3 $\underset{}{\overset{174.2\,[21.0]}{\rightleftharpoons}}$ Col_r (P2m) $\underset{}{\overset{249.5\,[11.4]}{\rightleftharpoons}}$ I.L.
n = 5: **2e**	K_{1v} $\xrightarrow{68.4[6.02]}$ K_2 $\xrightarrow{131.0^{\ddot{I}}}$ $Col_r(P2m)$ $\underset{}{\overset{222.3[12.6]}{\rightleftharpoons}}$ I.L. ; Col_{ho} $\xleftarrow{169.3}$ $Col_r(P2m)$; $Col_r(P2m)$ $\rightsquigarrow$ K_3 $\overset{161.6^{\ddot{I}}}{\rightsquigarrow}$ K_4 $\overset{172.7^{\ddot{I}}}{\rightsquigarrow}$ K_5 $\overset{17\ 7.6^{\ddot{I}}}{\rightsquigarrow}$ K_6 $\overset{190.8^{\ddot{I}}}{\rightsquigarrow}$ $Col_r(P2m)$; Col_{ho} $\overset{ca.\ 130\sim150}{\rightsquigarrow}$ $Col_r(P2m)$
n = 6: **2f**	K_{1v} $\xrightarrow{50.4[3.83]}$ K_2 $\xrightarrow{129.5[8.85]}$ Col_{ro1} ($P2_1/a$) $\xrightarrow{201.\ 4^{\ddot{I}}}$ Col_{ro2} ($P2_1/a$) $\xrightarrow{204.8^{\ddot{I}}}$ I.L. ; Col_{ro1} $\overset{ca.\ 160}{\rightsquigarrow}$ Col_{ho3} ; Col_{ho1} $\underset{}{\overset{83.6}{\rightleftharpoons}}$ Col_{ho2} $\underset{}{\overset{141.0}{\rightleftharpoons}}$ Col_{ho3} $\xleftarrow{182.3}$ Col_{ho4} $\xleftarrow{203.6}$ I.L.

Table S1 (continued)



Phase nomenclature: K= crystal, Col_{ro} = rectangular ordered columnar, Col_{ho} = hexagonal ordered columnar mesophase, Col_{hd}=hexagonal disordered columnar mesophase, I.L. = isotropic liquid and v = virgin state. Ï: These peaks were so close to calcurate the enthalpy changes. *1: Ref[17], *2: Ref[21], *3: Ref[20].

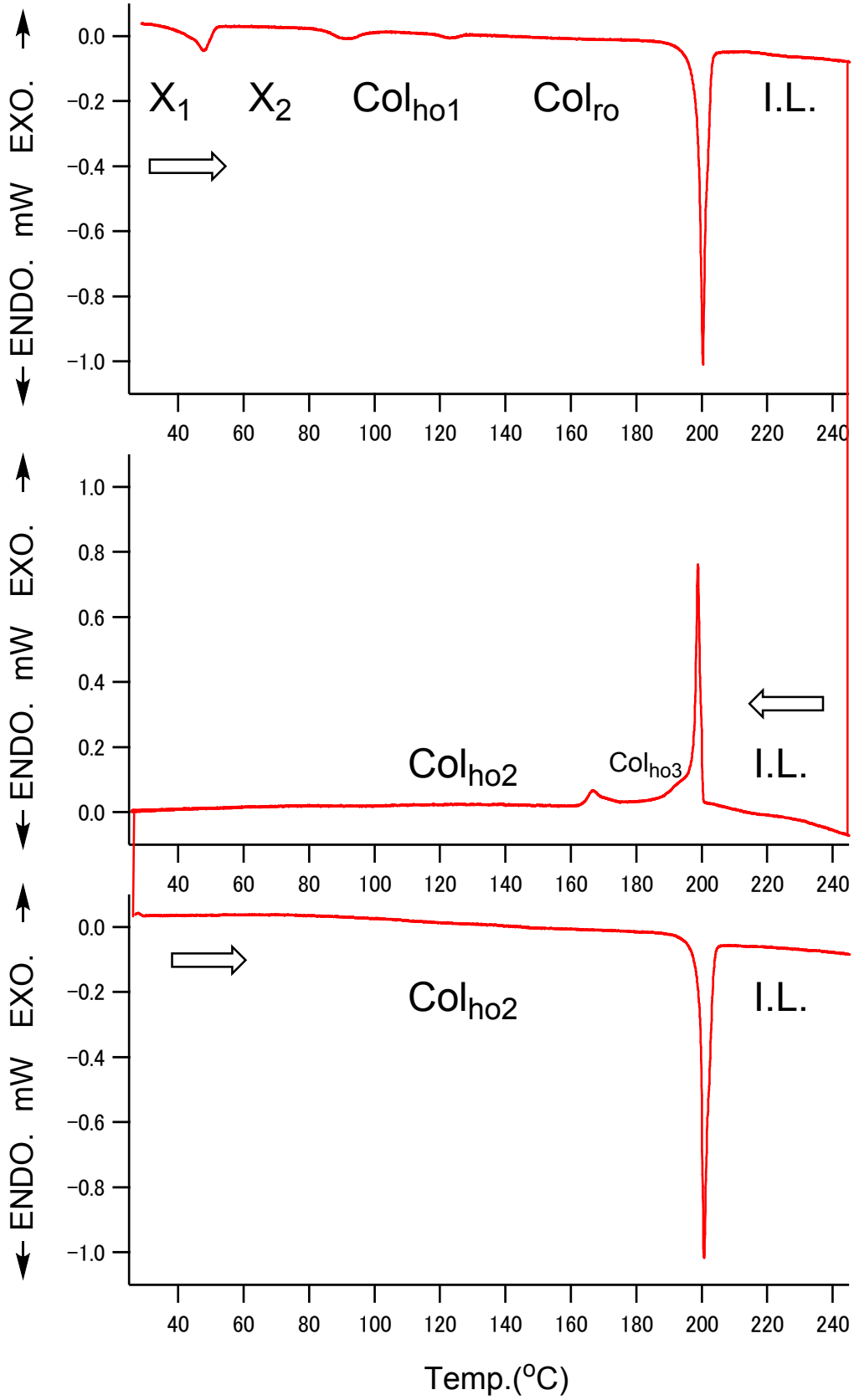


Fig. S1. DSC thermograms of (m-C_8OPhO)$_8$PcCu (**2h**). The heating and cooling rates were 2.5°C/min.

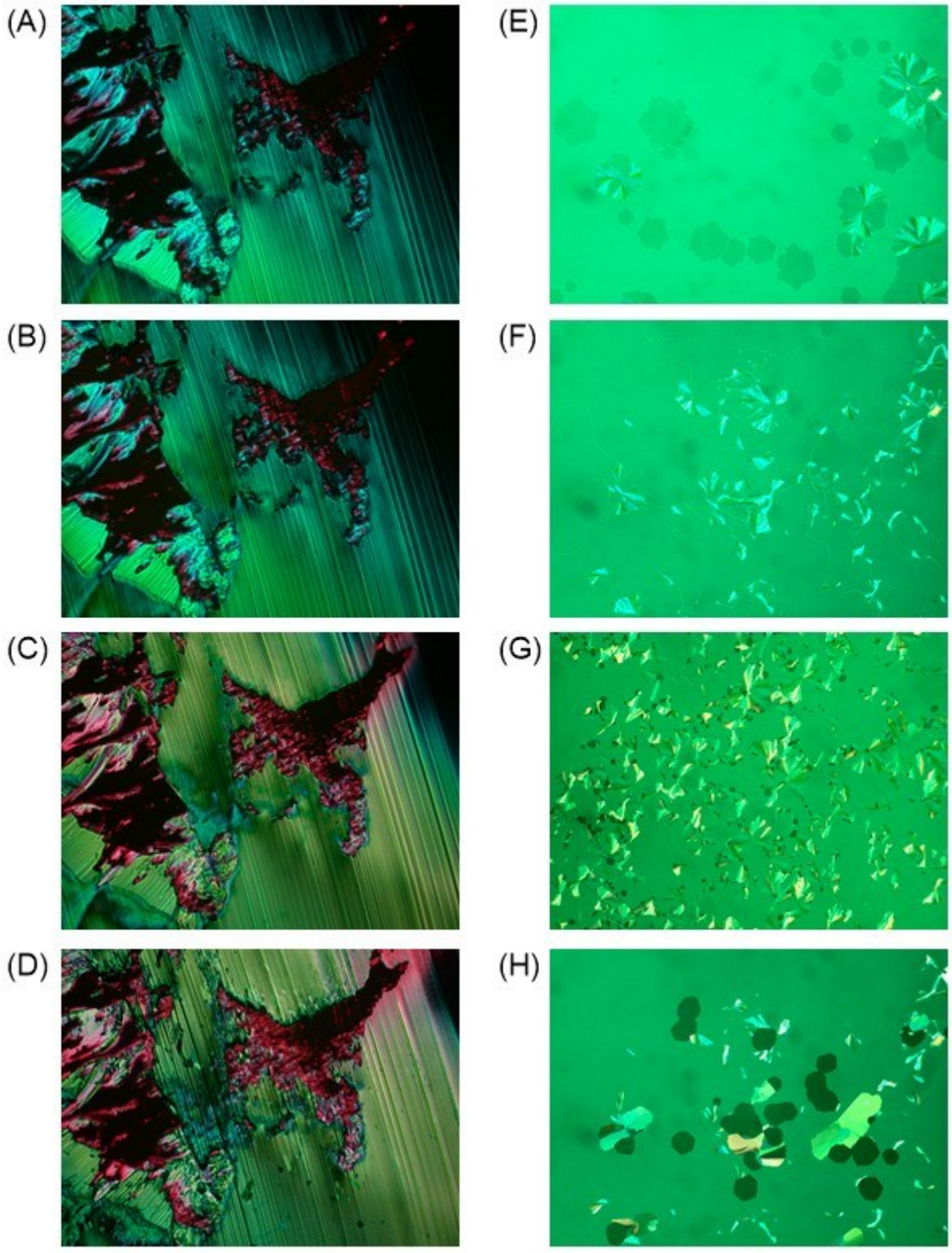


Fig. S2. Photomicrographs of (*m*-C_8OPhO)$_8$PcCu (**2h**) at various temperatures. (A) The virgin state of X_1 at 27.7^{o}C; (B) X_2 at 60.0^{o}C without discernible change; (C) Col_{ho1} at 100.0^{o}C with change of the birefringence; (D) Col_{ro} at 160.0^{o}C; (E) when IL heated over 205.0^{o}C was cooled down to 200.0^{o}C, it was transforming into Col_{ho3}; (F) the IL was completely transformed into Col_{ho3} at 200.0^{o}C; (G) when the Col_{ho3} in (F) was rapidly cooled down to RT, a mixture of supercooled Col_{ho3} and partially resulted Col_{ho2} (small dark dots); (H) only when the supercooled Col_{ho3} was held at 165.0^{o}C, the Col_{ro} (bright platelets) phase appeared with Col_{ho2} (dark hexagons).

Table S1. X-ray data of **2a-o**.

Compound	Mesophase lattice constants(Å)	Peak No.	Spacing(Å)		Miller indices (*h k l*)
			Observed	Calculated	
2a: (*m*-C_1OPhO)$_8$PcCu^{I}	$Col_{ro1}(P2_1/a)$ at 230 °C	1	20.1	19.7	(1 1 0)
	a = 29.4 b = 26.5	2	13.2	13.3	(0 2 0)
	h = 6.09	3	11.8	12.1	(1 2 0)
	Z = 2.0 for ρ = 1.1	4	9.24	9.19	(3 1 0)
		5	8.46	8.46	(1 3 0)
		6	7.39	7.35	(4 0 0)
		7	6.51	6.47	(1 4 0)
		8	6.09	-	*h*
		9	5.17	5.22	(1 5 0)
		10	4.84	4.82	(6 1 0)
		11	4.54	4.60	(6 2 0)
		12	4.41	4.41	(0 6 0)
		13	4.15	4.15	(7 1 0)
	$Col_{ro2}(P2_1/a)$ at 310 °C	1	21.1	21.1	(1 1 0)
	a = 33.6 b = 27.1	2	16.8	16.8	(2 0 0)
	h = 5.00	3	13.6	13.6	(0 2 0)
	Z = 2.0 for ρ = 1.1	4	8.61	8.64	(3 2 0)
		5	7.18	7.14	(4 2 0)
		6	6.48	6.52	(5 1 0)
		7	5.73	5.80	(3 4 0)
		8	5.33	5.36	(1 5 0)
		9	5.00	-	*h*
		10	4.57	4.56	(4 5 0)
		11	4.32	4.32	(6 4 0)
		12	3.97	3.98	(4 6 0)
		13	3.72	3.74	(5 6 0)
		14	3.55	3.55	(8 4 0)
		15	3.42	3.42	(0 8 0)
	M_x at 370 °C	1	19.5	-	-
		2	*ca.* 3.8	-	*h*
2b: (*m*-C_2OPhO)$_8$PcCu	Col_r(P2m) at 290°C	1	21.2	21.2	(1 0 0)
	a = 21.2 b = 17.3	2	17.4	17.3	(0 1 0)
		3	13.4	13.4	(1 1 0)
		4	8.64	8.64	(0 2 0)
		5	6.71	6.71	(2 2 0)
		6	*ca.* 5.10	-	#1
2c: (*m*-C_3OPhO)$_8$PcCu	Col_r(P2m) at 265°C	1	22.7	22.5	(1 0 0)
	a = 22.5 b = 18.5	2	18.5	18.5	(0 1 0)
		3	14.1	14.3	(1 1 0)
		4	9.10	9.22	(0 2 0)
		5	7.08	7.14	(2 2 0)
		6	*ca.* 5.06	-	#1
2d: (*m*-C_4OPhO)$_8$PcCu	Col_r(P2m) at 210°C	1	23.6	23.6	(1 0 0)
	a = 23.6 b = 20.3	2	20.3	20.3	(0 1 0)
		3	9.43	9.43	(1 2 0)
		4	7.67	7.70	(2 2 0)
		5	*ca.* 4.90	-	#1
2e: (*m*-C_5OPhO)$_8$PcCu	Col_{ho} at 150°C	1	27.2	27.2	(1 0 0)
	a = 31.4	2	16.2	15.7	(1 1 0)
	h = 3.41	3	10.2	10.3	(1 2 0)
	Z = 1.0 for ρ = 1.1	4	9.10	9.06	(3 0 0)
		5	*ca.* 4.82	-	#2
		6	3.41	-	*h*
	Col_r(P2m) at 210°C	1	24.8	24.8	(1 0 0)
	a = 24.8 b = 22.1	2	22.1	22.1	(0 1 0)
		3	9.95	10.1	(1 2 0)
		4	8.38	8.27	(2 2 0)
		5	*ca.* 4.87	-	#1
2f: (*m*-C_6OPhO)$_8$PcCu	$Col_{ro1}(P2_1/a)$ at 178°C	1	28.9	28.1	(1 1 0)
	a = 47.6 b = 36.3	2	23.8	23.8	(2 0 0)
	h = 3.50	3	17.3	17.4	(0 2 0)
	Z = 2.0 for ρ = 1.2	4	10.4	10.4	(2 3 0)
		5	9.47	9.53	(3 3 0)
		6	8.59	8.54	(1 4 0)
		7	7.38	7.36	(5 3 0)
		8	6.22	6.34	(7 2 0)
		9	*ca.* 5.08	-	#1
		10	3.50	-	*h*
	$Col_{ro2}(P2_1/a)$ at 203°C	1	28.8	28.4	(1 1 0)
	a = 47.8 b = 35.3	2	24.2	23.9	(2 0 0)
	h = 3.51	3	10.5	10.6	(2 3 0)
	Z = 2.0 for ρ = 1.2	4	9.49	9.46	(3 3 0)
		5	8.61	8.67	(1 4 0)
		6	7.45	7.42	(5 3 0)
		7	6.76	6.77	(2 5 0)
		8	6.30	6.45	(3 5 0)
		9	*ca.* 5.34	-	#1
		10	4.70	4.73	(6 6 0)
		11	3.82	3.81	-
		12	3.51	-	*h*
		13	3.23	3.23	-

Table S1. (*Continued*).

2f: (*m*-C_6OPhO)$_8$PcCu	Col_{ho1} at 31°C a = 32.4 *h* = 3.34 Z = 1.0 for ρ = 1.2	1 2 3 4 5 6 7	28.0 16.2 10.4 9.31 *ca.* 4.67 3.99 3.34	28.0 16.2 10.6 9.35 - 4.01 -	(1 0 0) (1 1 0) (1 2 0) (3 0 0) #2 (3 5 0) *h*
	Col_{ho2} at 100°C a = 32.9 *h* = 3.38 Z = 1.0 for ρ = 1.1	1 2 3 4 5 6	28.5 16.5 10.6 9.37 *ca.* 4.79 3.38	28.5 16.4 10.8 9.49 - -	(1 0 0) (1 1 0) (1 2 0) (3 0 0) #2 *h*
	Col_{ho3} at 155°C a = 32.9 *h* = 3.42 Z = 1.0 for ρ = 1.1	1 2 3 4 5	28.5 17.5 10.7 *ca.* 4.84 3.42	28.5 16.5 10.8 - -	(1 0 0) (1 1 0) (1 2 0) #2 *h*
	Col_{ho4} at 190°C a = 30.9 *h* = 3.61 Z = 1.0 for ρ = 1.2	1 2 3 4	26.7 9.92 *ca.* 4.85 3.61	26.7 10.1 - -	(1 0 0) (1 2 0) #2 *h*
2g: (*m*-C_7OPhO)$_8$PcCu	$Col_{ro}(P2_1/a)$ at 150°C a = 48.6 b = 36.1 *h* = 3.48 Z = 2.0 for ρ = 1.2	1 2 3 4 5 6 7 8 9 10 11	29.8 24.0 16.8 10.7 9.70 8.79 7.63 *ca.* 5.14 3.77 3.48 3.20	29.0 24.3 16.9 10.8 9.66 8.86 7.56 - - - -	(1 1 0) (2 0 0) (1 2 0) (2 3 0) (3 3 0) (1 4 0) (5 3 0) #1 *h*
	Col_{ho1} at r.t. a = 33.7 *h* = 3.34 Z = 1.0 for ρ = 1.1	1 2 3 4 5 6 7	29.2 16.7 11.0 9.69 7.55 *ca.* 4.69 3.34	29.2 16.8 11.0 9.72 7.29 - -	(1 0 0) (1 1 0) (1 2 0) (3 0 0) (4 0 0) #2 *h*
	Col_{ho2} at 179°C a = 34.7 *h* = 3.45 Z = 1.0 for ρ = 1.0	1 2 3 4 5	30.1 18.3 11.2 *ca.* 4.86 3.45	30.1 17.4 11.4 - -	(1 0 0) (1 1 0) (1 2 0) #2 *h*
	Col_{ho3} at 201.5°C a = 33.0 *h* = 3.53 Z = 1.0 for ρ = 1.1	1 2 3 4	28.6 10.7 *ca.* 4.89 3.53	28.6 10.8 - -	(1 0 0) (1 2 0) #2 *h*
2h: (*m*-C_8OPhO)$_8$PcCu	Col_{ho1} at 101°C a = 35.8 *h* = 3.38 Z = 1.0 for ρ = 1.0	1 2 3 4 5	31.0 17.4 11.5 *ca.* 4.74 3.38	31.0 17.9 11.7 - -	(1 0 0) (1 1 0) (1 2 0) #2 *h*
	$Col_{ro}(P2_1/a)$ at 158°C a = 49.3 b = 38.1 *h* = 3.48 Z = 2.0 for ρ = 1.2	1 2 3 4 5 6 7 8 9	31.0 25.0 17.4 11.2 10.0 7.83 6.55 *ca.* 5.13 3.48	30.1 24.7 17.8 11.3 10.0 7.80 6.61 - -	(1 1 0) (2 0 0) (1 2 0) (2 3 0) (3 3 0) (5 3 0) (7 2 0) #1 *h*
	Col_{ho2} at 135°C a = 35.9 *h* = 3.40 Z = 1.0 for ρ = 1.0	1 2 3 4 5	31.1 17.7 11.4 *ca.* 4.76 3.40	31.1 17.9 11.7 - -	(1 0 0) (1 1 0) (1 2 0) #2 *h*
	Col_{ho3} at 175°C a = 35.9 *h* = 3.44 Z = 1.0 for ρ = 1.0	1 2 3 4 5	31.1 18.1 11.5 *ca.* 4.78 3.44	31.1 17.9 11.7 - -	(1 0 0) (1 1 0) (1 2 0) #2 *h*

Table S1. (*Continued*).

2i: (*m*-C_9OPhO)$_8$PcCu	Col_{ho1} at 35 °C a = 36.3 *h* = 3.33 Z = 1.0 for ρ = 1.1	1 2 3 4 5 6 7	31.4 17.1 11.7 10.2 7.87 *ca.* 4.60 3.33	31.4 18.1 11.9 10.5 7.86 - -	(1 0 0) (1 1 0) (1 2 0) (3 0 0) (4 0 0) #2 *h*
	Col_{ho2} at 180 °C a = 36.7 *h* = 3.45 Z = 1.0 for ρ = 1.0	1 2 3 4 5	31.8 18.9 11.9 *ca.* 4.83 3.45	31.8 18.3 12.0 - -	(1 0 0) (1 1 0) (1 2 0) #2 *h*
	Col_{ro}($P2_1$/a) at 180°C a = 49.8 b = 39.6 *h* = 3.48 Z = 2.0 for ρ = 1.2	1 2 3 4 5 6 7 8 9 10	31.7 25.2 18.7 11.7 10.2 8.03 *ca.* 5.16 3.79 3.48 3.19	31.0 24.9 18.4 11.7 10.3 7.95 - - - -	(1 1 0) (2 0 0) (1 2 0) (2 3 0) (3 3 0) (5 3 0) #1 *h*
2j: (*m*-C_{10}OPhO)$_8$PcCu[ïî]	Col_{hd} at virgin r.t. a = 34.4 *h* = 3.5[¶] Z = *ca.* 1 for ρ = 1.0	1 2 3 4 5 6	29.8 17.1 11.2 8.4 6.7 *ca.* 4.4	29.8 17.1 11.3 8.3 6.8 -	(1 0 0) (1 1 0) (1 2 0) (1 3 0) (2 3 0) #2
	Col_{ho} at nonvirgin r.t. a = 34.4 *h* = 3.32 Z = *ca.* 1 for ρ = 1.0	1 2 3 4 5 6 7	29.8 17.1 11.2 8.4 6.7 *ca.* 4.4 3.32	29.6 17.1 11.3 8.3 6.8 - -	(1 0 0) (1 1 0) (1 2 0) (1 3 0) (2 3 0) #2 (0 0 1)
2k: (*m*-C_{12}OPhO)$_8$PcCu[ïîî]	Col_{hd} at virgin r.t. a = 38.6 *h* = 3.5[¶] Z = *ca.* 1 for ρ = 1.0	1 2 3 4 5 6 7	33.4 19.4 17.0 12.8 11.0 9.02 *ca.* 4.5	33.4 19.3 16.7 12.7 10.8 9.00 -	(1 0 0) (1 1 0) (2 0 0) (2 1 0) (3 0 0) (3 1 0) #2
	Col_{ho} at nonvirgin r.t. a = 37.5 *h* = 3.33 Z = *ca.* 1 for ρ = 1.0	1 2 3 4 5 6 7 8	32.4 19.0 16.4 12.4 11.3 9.48 *ca.* 4.5 3.33	32.4 18.8 16.3 12.3 11.1 9.65 - -	(1 0 0) (1 1 0) (2 0 0) (2 1 0) (3 0 0) (3 1 0) #2 (0 0 1)
2l: (*m*-C_{14}OPhO)$_8$PcCu[ïîî]	Col_{hd} at virgin r.t. a = 41.1 *h* = 3.5[¶] Z = *ca.* 1 for ρ = 1.0	1 2 3 4 5	35.6 20.6 18.0 13.5 *ca.* 4.5	35.6 20.6 17.8 13.5 -	(1 0 0) (1 1 0) (2 0 0) (2 1 0) #2
	Col_{ho} at nonvirgin r.t. a = 40.0 *h* = 3.33 Z = *ca.* 1 for ρ = 1.0	1 2 3 4 5	34.6 20.2 17.4 *ca.* 4.4 3.33	34.6 20.0 17.3 - -	(1 0 0) (1 1 0) (2 0 0) #2 (0 0 1)
2m: (*m*-C_{16}OPhO)$_8$PcCu[ïî]	Col_{ho} at 50°C a = 39.8 *h* = 3.36 Z = *ca.* 1 for ρ = 1.0	1 2 3 4 5	34.5 20.4 18.0 *ca.* 4.5 3.36	34.5 19.9 17.2 - -	(1 0 0) (1 1 0) (2 1 0) #2 (0 0 1)
2n: (*m*-C_{18}OPhO)$_8$PcCu[ïî]	Col_{ho} at 90°C a = 42.5 *h* = 3.36 Z = *ca.* 1 for ρ = 1.0	1 2 3 4 5	36.8 22.1 18.9 *ca.* 4.5 3.36	36.8 21.2 18.4 - -	(1 0 0) (1 1 0) (2 0 0) #2 (0 0 1)
2o: (*m*-C_{20}OPhO)$_8$PcCu[ïî]	Col_{ho} at 100°C a = 41.4 *h* = 3.35 Z = *ca.* 1 for ρ = 1.0	1 2 3 4 5	35.9 22.4 18.9 *ca.* 4.6 3.35	35.9 22.4 18.9 - -	(1 0 0) (1 1 0) (2 0 0) #2 (0 0 1)

h: Stacking distance = (0 0 1), #2: halos due to the molten alkyl groups, ρ: Assumed density (g/cm^3) and [¶]: Assumed value. [ïî]: Ref [21], [ïîî]: Ref [20].

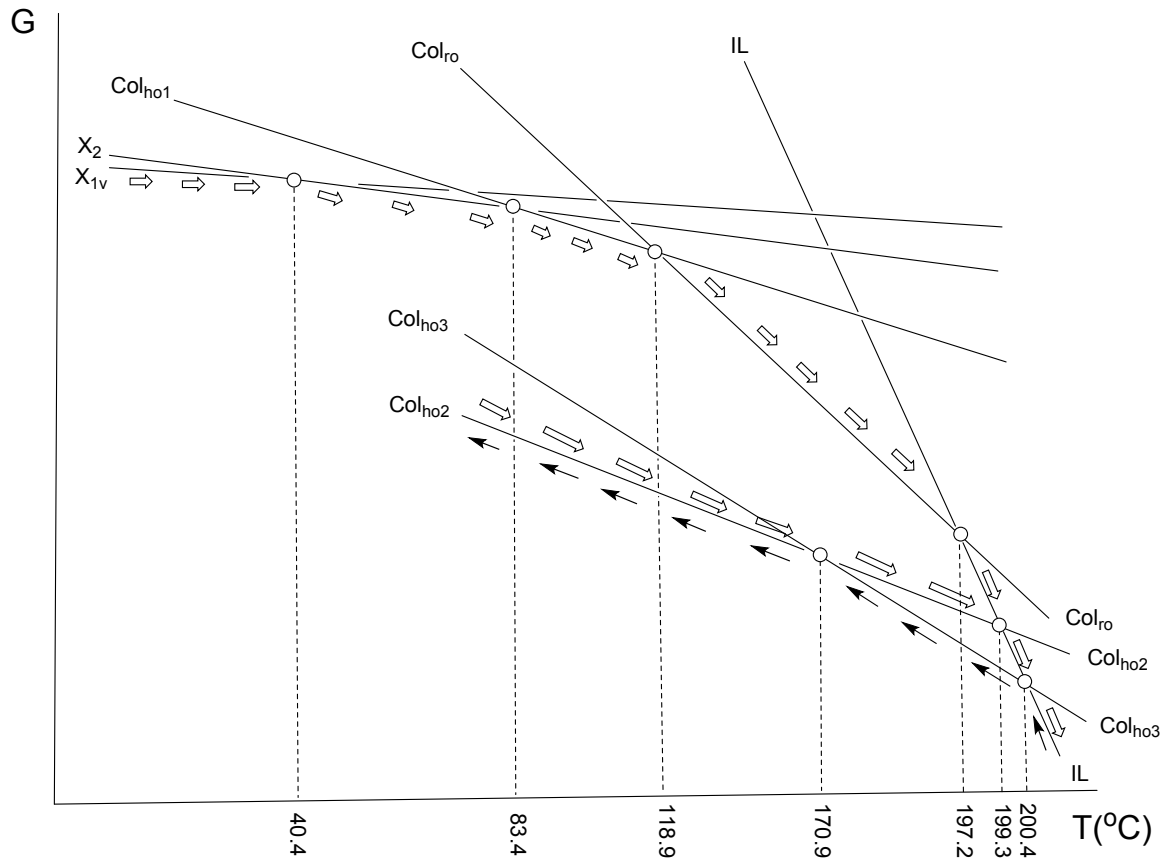


Fig. S3. Schematic free energy versus temperature (G-T) diagram of (*m*-C_8OPhO)$_8$PcCu (**2h**). On the 1st heating stage indicating small open arrows: when the virgin sample is heated from rt, an unidentifiable X_{1v} phase transforms into another unidentifiable X_2 phase at 40.4 °C of the intersection; the X_2 phase transforms into Col$_{ho1}$ phase at 83.4 °C and then into Col$_{ro}$($P2_1/a$) phase at 118.9 °C. On further heating, it clears into I.L. at 197.2 °C. On the 1st cooling stage indicating black arrows: when the IL over 210 °C is cooled, it transforms into Col$_{ho3}$ phase at 200.4 °C of the intersection and then into Col$_{ho2}$ at 170.9 °C. On the 2nd heating stage indicating long open arrows: when the Col$_{ho2}$ phase is heated, it is superheated till 199.3 °C of the clearing point without transforming into Col$_{ho3}$. These complicated phase transition behaviour can rationally explain the DSC thermograms illustrated in Fig. S1, by using the G-T diagram. The phase appearance greatly depends on the thermal history and heating and cooling rates. Only when the supercooled Col$_{ho3}$ was held at 165.0 °C for long hours, the Col$_{ro}$ phase partially appeared in Col$_{ho3}$ with Col$_{ho2}$, as shown in Fig. S2 Photo (H). At the present time, we cannot explain it by this G-T diagram. Further study is necessary.