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Mesomorphic phase transitions of tetraphenylporphyrins with four long aliphatic chains

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Studies of 5,10,15,20-tetrakis(4-*n*-alkylphenyl)porphyrins revealed that the homologues with longer alkyl chains than hexyl were mesomorphic, in contrast to the non-mesomorphic alkoxy derivatives. Metal complexes (Co, Ni, Cu, Zn, and Pd) of the dodecyl derivative were also shown to exhibit mesophases. These mesophases were assigned as discotic lamellar (D_L) phases by X-ray diffraction studies.

1. Introduction

Metallomesogens are very attractive as candidates for novel advanced materials. In particular, the metalloporphyrins, which have been extensively studied for their chemical and physiochemical properties [1], are very interesting compounds for investigation on account of their mesomorphic properties.

Goodby *et al.* reported in 1980 that uro-porphyin I octa-*n*-dodecyl ester shows a monotropic mesophase within a very narrow temperature range (0·1°C) [2], and Gaspard *et al.* found that mixtures of some mono-substituted porphyrins exhibit mesophases [3]. Then Gregg *et al.* synthesized some 2,3,7,8,12,13,17,18-octa-substituted porphyrins and their metal complexes, some of which were mesomorphic [4], and recently, 5,10,15,20-tetrakis(4-*n*-dodecylphenyl)porphyrin was found to be mesomorphic by Shimizu *et al.* [5]. As far as we know, this is the first report of mesomorphic properties for pure tetraphenylporphyrins, in spite of the easier synthetic procedures that now enable materials to be made and the properties of their mesophases to be better understood.

In the present work, the homologues of 5,10,15,20-tetrakis(4-*n*-alkylphenyl)porphyrins, abbreviated as C*n*TPP (*n* is the number of carbon atoms in one alkyl chain), and of 5,10,15,20-tetrakis(4-*n*-alkoxyphenyl)porphyrins, denoted C*n*OTPP (see the scheme), were investigated for mesomorphic phase transitions. In addition, several metal complexes of the dodecyl derivative were preliminarily studied.

2. Experimental

The syntheses of C*n*TPP and C*n*OTPP were carried out by modification of the method by Adler *et al.* [6], whereby the one step reaction of pyrrole and an alkyl-/alkoxy-benzaldehyde in propionic acid can give quantitatively the required tetraphenylporphyrin derivatives. The purification procedures followed the methods of

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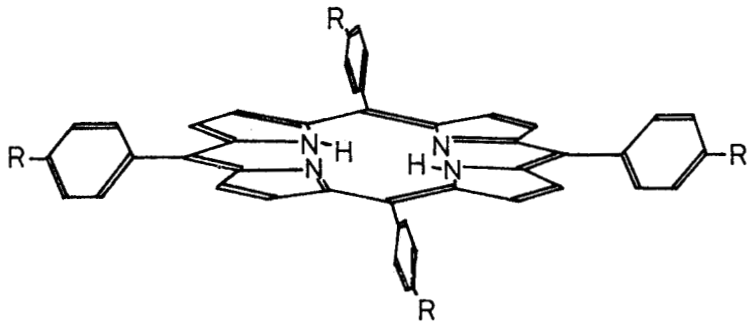


C_nTPP: $R = -CH_2(CH_2)_{n-2}CH_3$, $n = 5, 6, \ldots, 16$

C_nOTPP: $R = -OCH_2(CH_2)_{n-2}CH_3$, $n = 5, 6, \ldots, 14, 18$

Barnet *et al.* [7] and of Rousseau *et al.* [8] in part. The recrystallization from benzene acetone and Soxhlet extraction using acetone or methanol to remove impurities soluble in these solvents were performed after column chromatography (neutral activated alumina, chloroform as eluent). The products obtained were characterized by ^1H NMR and absorption spectroscopy.

The metal complexes were synthesized according to the literature [9]. The corresponding metal-free porphyrin and a large molar excess of metal chloride were heated under reflux in *N*,*N*-dimethylformamide for 6 h and the crude product was

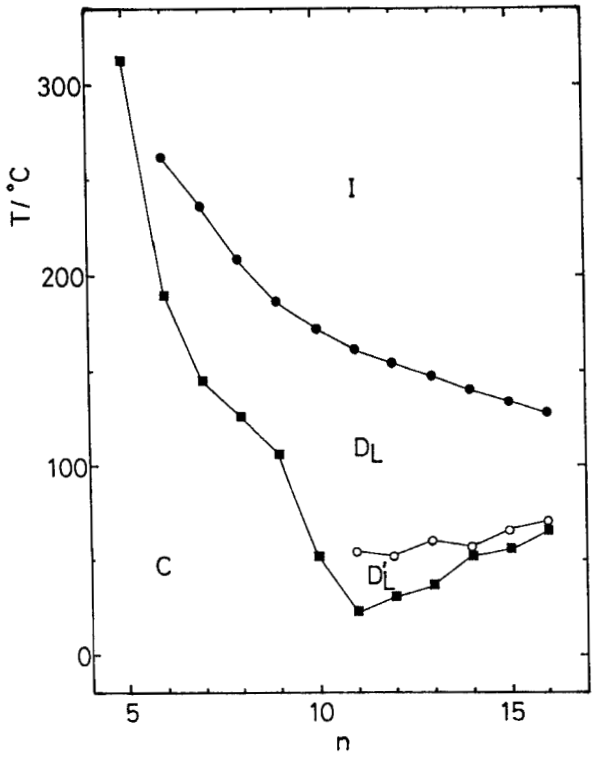


Figure 1. Phase transition temperatures of C*n*TPP homologues. ●, D_L–I; ○, $D_{L'}$–D_L; ■, C–$D_{L'}$; D_L or I.

Table 1. Transition temperatures, enthalpies and entropies of the 5, 10, 15, 20-tetrakis (4-*n*-alkylphenyl)porphyrins (*Cn*TPP).

	C→D′$_L$, D$_L$ or I			D′$_L$→D$_L$			D$_L$→I		
n	*T*/°C	Δ*H*/kJ mol^{-1}	Δ*S*/JK^{-1} mol^{-1}	*T*/°C	Δ*H*/kJ mol^{-1}	Δ*S*/JK^{-1} mol^{-1}	*T*/°C	Δ*H*/kJ mol^{-1}	Δ*S*/JK^{-1} mol^{-1}
5	313†								
6	190	24	51				263	33	61
7	145	23	55				237	29	56
8	126	24	61				209	25	52
9	107	25	67				187	25	55
10	52	20	61				173	25	57
11	23	50	169	55	19	57	162	23	53
12	31	46	152	52	14	43	155	23	54
13	37	42	136	60	27	80	148	27	64
14	52	63	193	57	37	112	141	27	65
15	56	92	280	66	31	93	135	27	65
16	65	99	289	71	35	100	129	27	67

† This phase transition occurred with decomposition.

purified by column chromatography (neutral activated alumina, chloroform) and recrystallized from benzene-acetone (1 : 9), followed by Soxhlet extraction.

The phase transition temperatures and enthalpies were determined by differential scanning calorimetry (Daini Seikosha, SSC-560S and Mac Science, DSC3200). Optical microscopic textures were observed using an Olympus polarizing microscope equipped with a Mettler FP 82HT heating stage and FP 80HT control unit. The X-ray diffraction studies were carried out using a Rigaku Geigerflex equipped with a handmade heating apparatus.

3. Results and discussion

3.1. *5,10,15,20-Tetrakis(4-n-alkylphenyl)porphyrins (CnTPP)*

The phase transition temperatures of C*n*TPP (pentyl to hexadecyl) are shown in figure 1. The pentyl homologue is not mesomorphic, having a direct phase transition from the crystal to the isotropic phase. The transition enthalpy and entropy could not be estimated because of decomposition. The homologues having undecyl or longer chains exhibit two phases between the crystal and isotropic phases, while the homologues with shorter chains give only one phase.

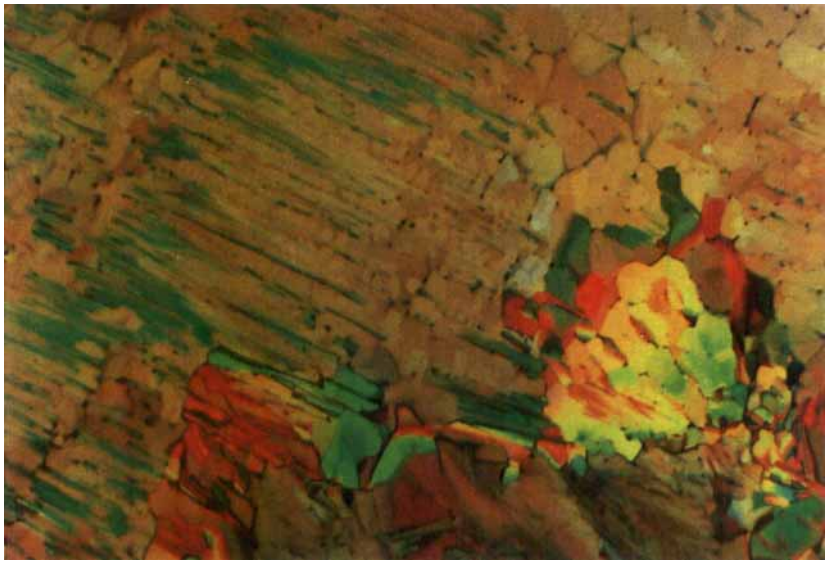
The upper phases are highly viscous, whilst the lower ones are very similar in rigidity to the crystal phase, but not brittle. The parameters for the phase transitions are summarized in table 1. The entropies for the upper phase to isotropic transitions are approximately the same for all the homologues. On the other hand, the entropies for the crystal to the upper and lower phase transitions depend on the alkyl chain length; large transition entropies are found for the homologues with undecyl or longer alkyl chains.

The upper phase gives a mesomorphic texture like that in figure 2 (*a*), with a fanlike texture. A lot of cracking due to shrinking of the domains occurs at the phase transition to the lower phase as shown in figure 2 (*b*). No drastic change in the texture was observed at the phase transition between the upper and lower phases.

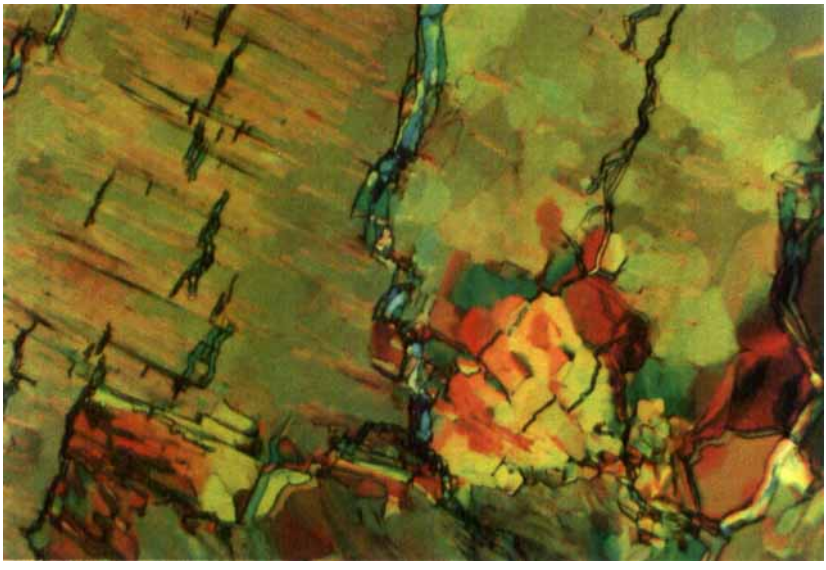
X-ray diffraction studies of these two phases indicate that both have discotic lamellar (D_L) structures and that the lower one is highly ordered because of the many reflection peaks in the wider angle region (see figure 3). The widely broadened peak around $2\theta = 20°$ for the upper phase indicates this phase to be mesomorphic. These results strongly indicate that the upper phase is a mesophase assigned to be D_L, and that the lower one is a crystal.

3.2. *5,10,15,20-Tetrakis(4-n-alkoxyphenyl)porphyrins (CnOTPP)*

Figure 4 shows the phase transition temperatures for C*n*OTPP. All C*n*OTPPs ($n = 5$–18) are non-mesomorphic, in contrast to the C*n*TPP series. The phase transitions to the isotropic phase for C*n*OTPP have extremely large transition entropies and the entropies can be seen to be comparable to the sum of those for all the phase transitions occurring for a C*n*TPP with the corresponding chain length (see Table 2). Kugimiya *et al.*, however, reported that some C*n*OTPPs are mesomorphic [10]. Our X-ray diffraction studies however indicate that C*n*OTPPs are not mesomorphic, because no broad peaks are seen and several peaks around $2\theta = 20°$ exist as shown in figure 5. Furthermore, a binary phase diagram of C_{11}OTPP–C_{14}OTPP reveals the existence of a eutectic point for the phase transition to the isotropic liquid (see figure 6). In addition, the C*n*OTPP series shows the better crystallinity, giving needles or plate-like crystals, as compared with the C*n*TPP series.



(*a*)



(*b*)

Figure 2. Polarized optical microscopic textures of (*a*) D_L and (*b*) D'_L phases of C_{12}TPP at 120°C and 60°C, respectively (× 200).

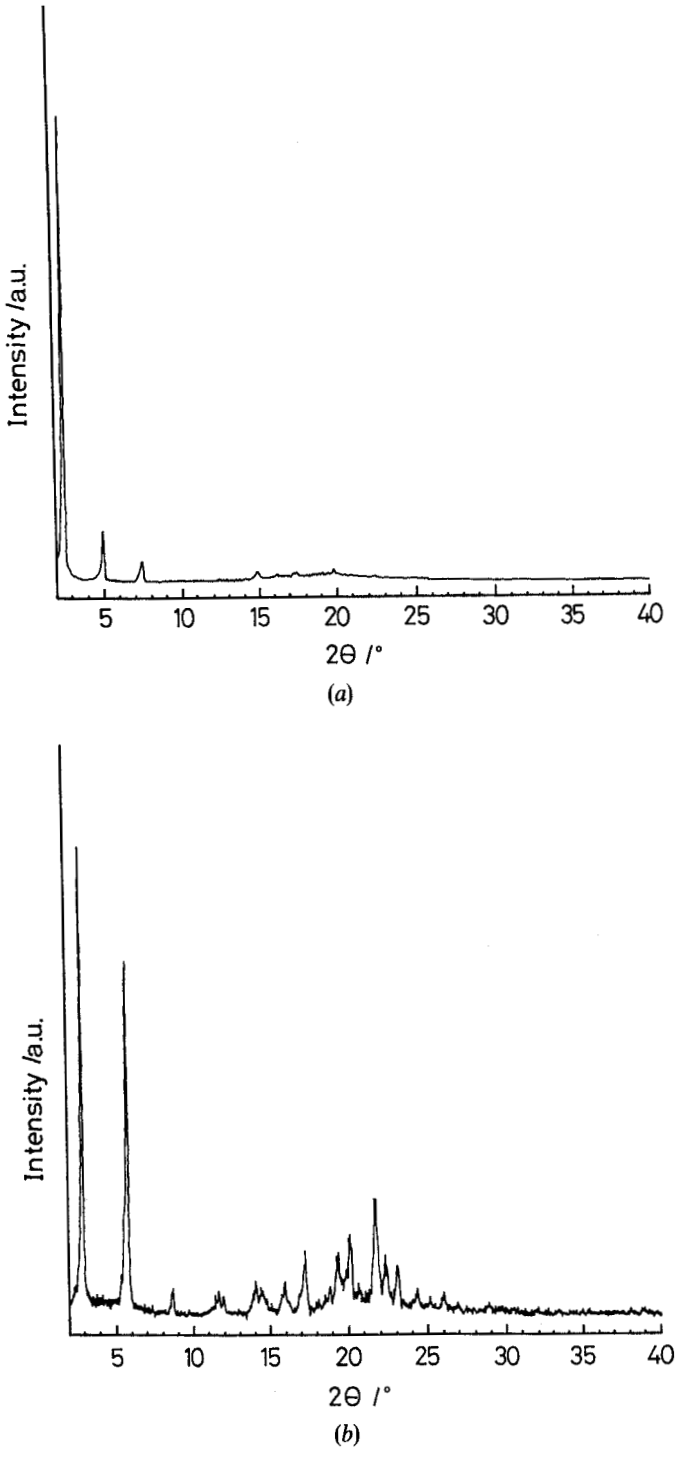


Figure 3. X-ray diffraction patterns of (*a*) D_L and (*b*) D'_L phases of C_{15}TPP at 120°C and 60°C, respectively.

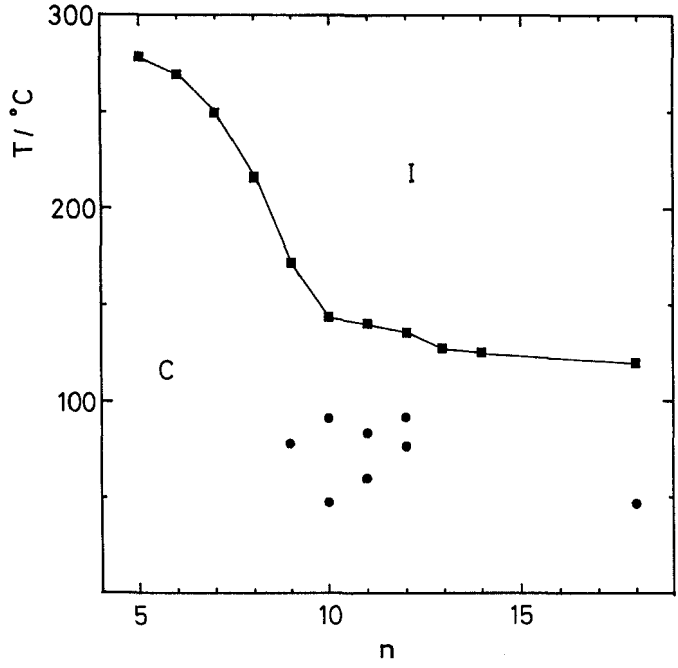


Figure 4. Phase transition temperatures of C*n*OTPP homologues. ■, C–I; ●, C–C.

The difference in mesogenicity between the alkyl and alkoxy derivatives discussed above is also found for some phthalocyanine derivatives [11].

3.3. [*5,10,15,20-Tetrakis(4-n-dodecylphenyl)porphinato*]*metals* ($C_{12}TPPM$)

Several metal complexes (metal: Co, Ni, Cu, Zn, and Pd) of C_{12}TPP were investigated, and the results are summarized in table 3. All metal complexes except the Ni complex exhibit similar types of phase transition to that of the C*n*TPP series. Two phases appear between the crystal and isotropic phases; the upper one is a D_L mesophase, and the lower one also has an essentially D_L structure. The Ni complex has only one mesophase assigned to be D_L.

Only one mesophase, a D_L phase, appears in this series and hexagonal columnar mesophases are not seen. However, the mesophase thermal stability, the D_L to isotropic transition temperature, is extremely dependent on the central metal species as illustrated in figure 7. The Zn complex with the highest stability shows an enhancement of *c.* 60°C for the transition to isotropic as compared with that for the metal-free mesogen, while the stability of the Ni complex is lower than that of the metal-free material by *c.* 25°C. These results indicate that the non-coplanarity of tetraphenylporphyrins and the nature of the central metal are essentially concerned with the mesomorphic properties.

4. Summary

5,10,15,20-Tetrakis(4-*n*-alkylphenyl)porphyrins (C*n*TPP) are mesomorphic when the alkyl chains are hexyl or longer, in contrast to the non-mesomorphic alkoxy derivatives. The mesophases of all C*n*TPP ($n=6$–16) have a discotic lamellar (D_L)

Table 2. Transition temperatures, enthalpies and entropies of the 5, 10, 15, 20-tetrakis (4-*n*-alkoxyphenyl)porphyrins (*Cn*OTPP).

	C→C			C→C			C→I		
n	*T*/°C	ΔH/kJ mol^{-1}	ΔS/JK^{-1} mol^{-1}	*T*/°C	ΔH/kJ mol^{-1}	ΔS/JK^{-1} mol^{-1}	*T*/°C	ΔH/kJ mol^{-1}	ΔS/JK^{-1} mol^{-1}
5							279	52	95
6							271	69	128
7							250	68	130
8							217	61	124
9				78	12	33	173	59	133
10	48	7·0	22	91	1·5	4·2	145	58	138
11	58	2·0	6·0	84	2·0	5·6	141	63	153
12	77	2·9	8·4	92	3·5	9·7	136	75	184
13							128	81	205
14							126	93	232
18				47	21	66	121	111	282

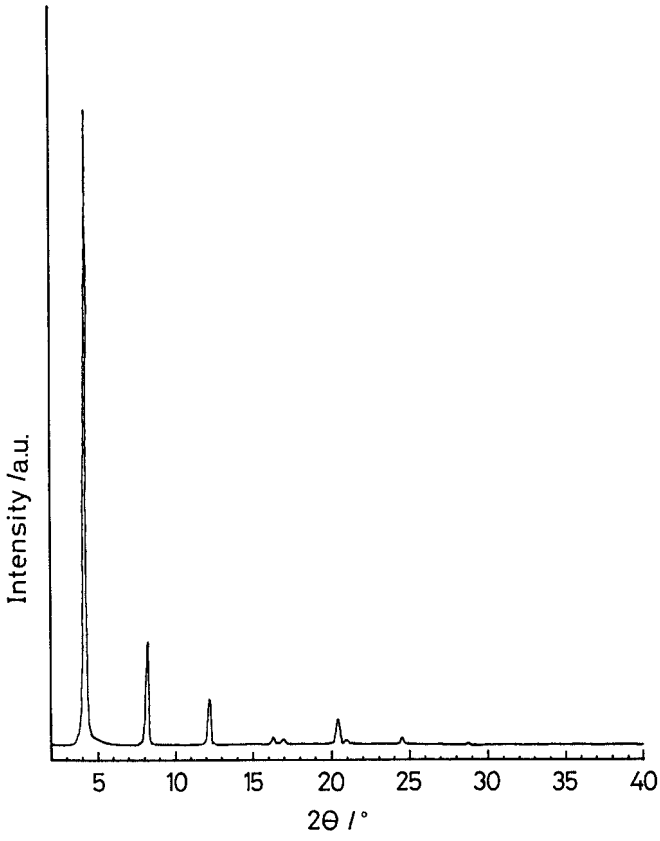


Figure 5. X-ray diffraction pattern of C_{12}OTPP at 120°C.

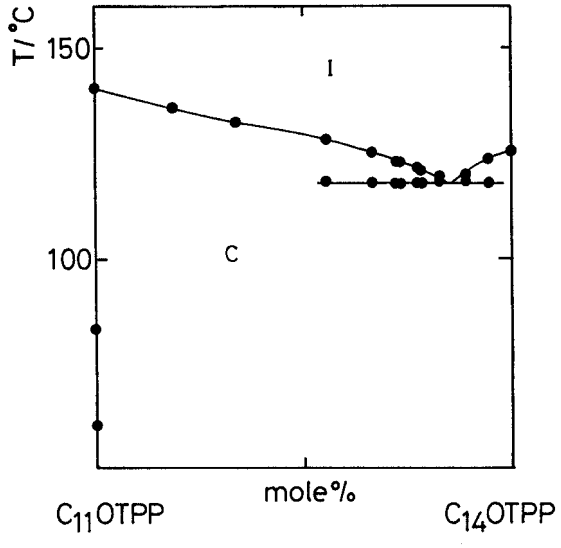


Figure 6. Binary phase diagram for C_{11}OTPP–C_{14}OTPP.

Table 3. Phase transition temperatures, enthalpies and entropies of the (5, 10, 15, 20-tetrakis (4-*n*-dodecylphenyl)porphynato)metals (C_{12}TPPM).

	C→D'_L or D_L			D'_L→D_L			D_L→I		
M	T/°C	ΔH/kJ mol^{-1}	ΔS/JK^{-1} mol^{-1}	T/°C	ΔH/kJ mol^{-1}	ΔS/JK^{-1} mol^{-1}	T/°C	ΔH/kJ mol^{-1}	ΔS/JK^{-1} mol^{-1}
Co	28	39	132	50	13	39	161	30	69
Ni	44	51	162				129	22	56
Cu	32	51	170	56	14	44	188	32	70
Zn	37	85	276	52	5·4	17	220†	—	—
Pd	30	42	137	60	13	39	186	29	63

†With decomposition.

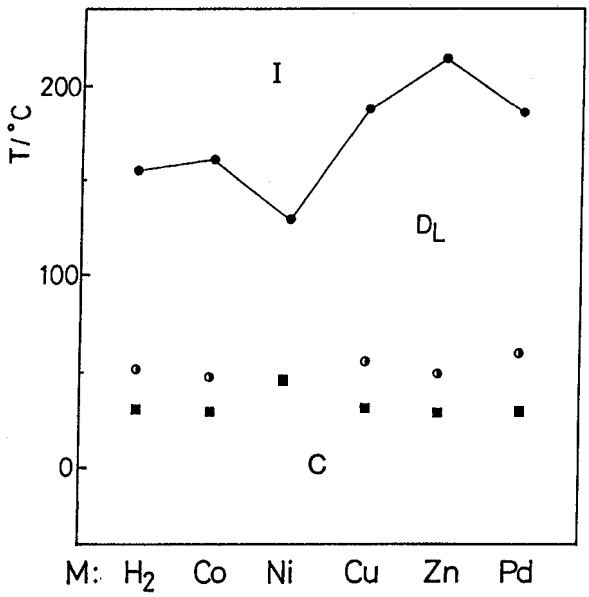


Figure 7. Phase transition temperatures of C_{12}TPPM (M: H_2, Co, Ni, Cu, Zn, and Pd). ●, D_L–I; ◑, D'_L–D_L; ■, C–D'_L or D_L.

structure, though other mesomorphic porphyrins and phthalocyanines typically exhibit discotic hexagonal columnar phases [12].

On the other hand, the central metals can contribute importantly to the mesomorphic properties and the order of enhancement of mesophase thermal stability was revealed to be Zn > Cu, Pd > Co > (H_2) > Ni for the complexes.

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