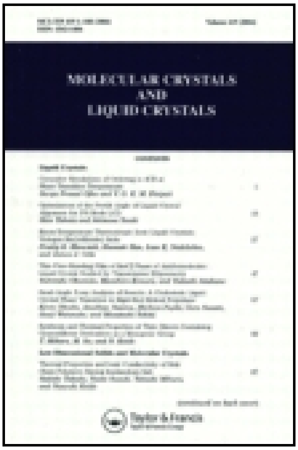

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# Very Unique Liquid Crystalline Phase Structures Having Two-Dimensional Silver Sheet for the Adducts of Phenazine and Silver Alkylsulfonates

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# Very Unique Liquid Crystalline Phase Structures Having Two-Dimensional Silver Sheet for the Adducts of Phenazine and Silver Alkylsulfonates

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*The silver ion–based supramolecular adducts bearing long alkyl chains (Cn-Phen: n (carbon number of alkyl chain) = 12, 14, 16, 18) were prepared by reaction of phenazine and silver alkylsulfonates. Their liquid crystalline behavior was studied by differential scanning calorimetry, polarizing microscopy, and temperature-dependent X-ray diffraction techniques. Each of the adducts exhibits three mesophases with layer structures; an unidentified smectic phase ($S_x$), smectic C ($S_C$), and smectic A ($S_A$) phases. Furthermore, it was found that each of the layers has a two-dimensional silver ion sheet sandwiched above and below by two aliphatic sheets.*

**Keywords:** liquid crystal; self-assembly; silver sheet

## 1. INTRODUCTION

Metal-based liquid crystals have been paid much attention in expectation of unique properties due to metals in addition to the intrinsic liquid crystalline properties of organic compounds [1–3]. On the other hand, metal-based supramolecular self-assembly provides a versatile strategy towards highly organized supramolecular systems [4–9]. Metal-based self-assembly is useful for obtaining the metal-containing mesogenic compounds because it is possible to control their structures by a careful and appropriate choice of the metal cation,

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counter anion, and organic ligand [10–12]. If alkyl chains are introduced to the metal-based supramolecular systems, novel liquid crystalline materials can be produced.

We have recently prepared the pyridazine-silver adducts with long alkyl chains obtained by reaction of pyridazine and silver alkylsulfonates [13]. The adducts exhibit two rectangular columnar mesophases. The introduction of long alkyl chains on the metal-based adducts has drastically provided them with thermotropic mesomorphism, indicating of new possibilities for the construction of metallomesogens.

In this report, we have prepared novel silver ion–based adducts with long alkyl chains by reaction of phenazine and silver alkylsulfonates (Scheme 1). The resulted adducts exhibited three mesophases with layer structures (unidentified smectic ($S_x$), smectic C ($S_C$), and smectic A ($S_A$) mesophases). Remarkably, each of the layers has a two-dimensional silver ion sheet with a rectangular arrangement sandwiched above and below by two aliphatic sheets. Herein we wish to report very unique liquid crystalline phase structures having two-dimensional silver sheet for the adducts of phenazine and silver alkylsulfonates.

## 2. EXPERIMENTAL

### 2.1. Materials

Phenazine (Phen) was purchased from Aldrich and used without further purification. Silver alkylsulfonates (silver dodecylsulfonate, silver tetradecylsulfonate, silver hexadecylsulfonate, and silver octadecylsulfonate) were prepared from the corresponding sodium alkylsulfonates and $AgNO_3$ [14].

The synthetic route for Cn-Phen (n = 12, 14, 16, and 18) is shown in Scheme 1. A typical preparation of $C_{18}$-Phen was as follows. A dimethylsulfoxide (DMSO) solution (4 mL) of Phen (0.046 g, $2.6 \times 10^{-4}$ mol) was added to a DMSO solution (25 mL) of silver octadecylsulfonate (0.25 g $5.7 \times 10^{-4}$ mol), and then the mixture was allowed to stand for a day at room temperature, giving the adduct ($C_{18}$-Phen) as yellow crystal in 28% isolated yield. The other Cn-Phen crystals were prepared in the same manner.

Elemental analysis (%) found (calc.): $C_{12}$-Phen = $C_{36}H_{58}N_2O_6S_2Ag_2$: C, 47.85 (48.33); H, 6.75 (6.53); N, 3.00 (3.13). $C_{14}$-Phen = $C_{40}H_{66}N_2O_6S_2Ag_2$: C, 50.36 (50.53); H, 7.06 (6.70); N, 2.79 (2.95). $C_{16}$-Phen = $C_{44}H_{74}N_2O_6S_2Ag_2$: C, 52.26 (52.48); H, 7.75 (7.41); N, 2.68 (2.78). $C_{18}$-Phen = $C_{48}H_{82}N_2O_6S_2Ag_2$: C, 53.95 (54.23); H, 8.22 (7.78); N, 2.60 (2.64).

## 2.2. Measurements

The samples (Cn-Phen) were identified by elemental analysis (Perkin Elmer elemental analyzer 2400). The phase transition behavior of the samples was observed with a polarizing microscope, Olympus BH-2, equipped with a heating plate controlled by a thermoregulator (Mettler FP82HT hot stage, Mettler FP90 Central Processor), and measured with a differential scanning calorimeter (DSC), Shimadzu DSC-50. Temperature-dependent X-ray diffraction measurements were performed with Cu-K$\alpha$ radiation by using a Rigaku RAD X-ray diffractometer equipped with a hand-made heating plate [15] controlled by a thermoregulator.

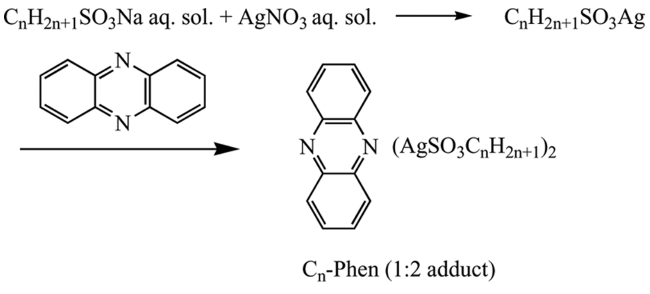
## 3. RESULTS AND DISSUSSION

### 3.1. Phase Transition Behavior

The reaction of phenazine (Phen) and silver alkylsulfonate in DMSO gave yellow crystalline solids (Cn-Phen). The coordination bonding of phenazine and silver ion was confirmed by fourier transform infrared (FT-IR) spectra. From elemental analysis, the stoichiometry of Cn-Phen was shown to be Phen:silver alkylsulfonate = 1:2, confirming that phenazine and silver alkylsulfonate form a 1:2 adduct, as shown in Scheme 1.

The phase transition sequences of the Cn-Phen (n = 12, 14, 16, and 18) adducts established by DSC measurements and polarizing microscopic observations are summarized in Table 1. Since each of them shows the same transition sequence, a representative $C_{12}$-Phen is described here.

When the virgin crystals of Cr (Fig. 1(e)) were heated from room temperature, they melt to an $M_1$ mesophase at 128.1°C, followed by an $M_2$ mesophase and an $M_3$ mesophase at 199.1°C and 243.0°C, respectively. On further heating, the sample decomposed at ca. 260°C without



**SCHEME 1** Synthetic route for adducts composed of phenazine and silver alkylsulfonates.

**TABLE 1** Phase transition temperatures and enthalpy changes of $C_n$-Phen (n = 12, 14, 16, and 18)

| Compound | Phase $\xrightarrow{\mathrm{T(^\circ C)[\Delta H(kJ/mol)]}}$ Phase |
|---|---|
| $C_{12}$-Phen | $\mathrm{Cr} \overset{128.1\ [20.6]}{\rightleftarrows} \mathrm{M_1} \overset{199.1\ [37.0]}{\rightleftarrows} \mathrm{M_2} \overset{243.0\ [35.0]}{\rightleftarrows} \mathrm{M_3} \xrightarrow{ca.\ 260^\circ\mathrm{C}} \mathrm{Decomp.}$ |
| $C_{14}$-Phen | $\mathrm{Cr} \overset{119.6\ [15.3]}{\rightleftarrows} \mathrm{M_1} \overset{188.0\ [42.2]}{\rightleftarrows} \mathrm{M_2} \overset{235.5\ [36.1]}{\rightleftarrows} \mathrm{M_3} \xrightarrow{ca.\ 260^\circ\mathrm{C}} \mathrm{Decomp.}$ |
| $C_{16}$-Phen | $\mathrm{Cr} \overset{117.9\ [14.8]}{\rightleftarrows} \mathrm{M_1} \overset{175.6\ [40.2]}{\rightleftarrows} \mathrm{M_2} \overset{235.6\ [30.3]}{\rightleftarrows} \mathrm{M_3} \xrightarrow{ca.\ 260^\circ\mathrm{C}} \mathrm{Decomp.}$ |
| $C_{18}$-Phen | $\mathrm{Cr} \overset{119.6\ [18.1]}{\rightleftarrows} \mathrm{M_1} \overset{166.2\ [49.3]}{\rightleftarrows} \mathrm{M_2} \overset{234.4\ [39.0]}{\rightleftarrows} \mathrm{M_3} \xrightarrow{ca.\ 260^\circ\mathrm{C}} \mathrm{Decomp.}$ |

Phase nomenclature: Cr = crystal and M = mesophase.
$M_1(S_x)$ = unidentified smectic mesophase + Ag. rec($C_2$/m); $M_2$ = Smectic C + Ag. rec($C_2$/m); $M_3$ = Smectic A + Ag.rec($C_2$/m).

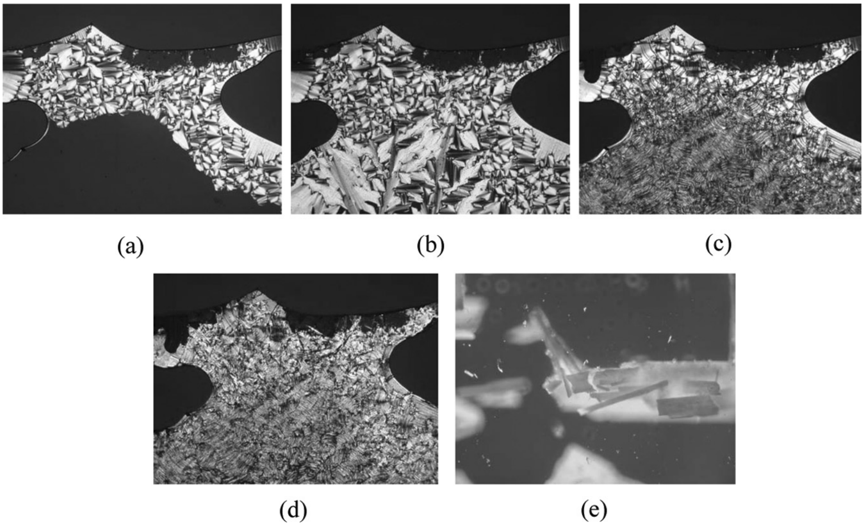


**FIGURE 1** Photomicrographs of the phases of $C_{12}$-Phen: (a) $M_3$ at 260°C; (b) $M_2$ at 225°C; (c) $M_1$ at 180°C; (d) Cr at room temperature (nonvirgin sample); (e) Cr at room temperature (virgin sample).

clearing into an isotropic liquid. Therefore, it was impossible to observe the natural textures. However, by putting the virgin sample on heating plate heated to 260°C in advance and cooling down gradually, it was possible to observe the textures and characterize the mesophases from the textures without the influence of thermal decomposition. Figure 1(a) shows a photomicrograph of the $M_3$ mesophase at 260°C. The $M_3$ mesophase exhibited a focal conic texture characteristic to a smectic mesophase. When the $M_3$ mesophase was cooled down to 225°C in the $M_2$ mesophase temperature region, the focal conic texture spread in a dark part of the $M_3$ mesophase (Fig. 1(b)). This result suggests that homeotropic alignment could be achieved in the dark part of the $M_3$ mesophase. Therefore, the $M_3$ mesophase and $M_2$ mesophase were tentatively assigned as a $S_A$ mesophase and $S_C$ mesophase, respectively. On further cooling to 180°C in the $M_1$ mesophase region, a fingerprint texture (Fig. 1(c)) appeared in the focal conic texture. The texture was held even in the crystal state cooled to room temperature (Fig. 1(d)).

## 3.2. Mesophase Structures of Cn-Phen

The $M_1$, $M_2$, and $M_3$ mesophases were identified by temperature-dependent X-ray analyses. The X-ray data of all the mesophases of Cn-Phen are listed in Table 2. As can be seen from Table 1, Cn-Phen

**TABLE 2** X-ray diffraction data of $C_{12}$-Phen, $C_{14}$-Phen, $C_{16}$-Phen, and $C_{18}$-Phen

| | | | Spacing (γ) | | |
|---|---|---|---|---|---|
| Compound | Mesophase lattice constants (γ) | | Observed | Calculated | Miller indices (h k l) |
| $C_{12}$-Phen | $M_1$ at 160°C | $S_X$ | 32.7 | 33.6 | (0 0 1) |
| | $S_X$ c = 32.3 | | 16.6 | 16.8 | (0 0 2) |
| | | | 11.1 | 11.2 | (0 0 3) |
| | | | 4.47 | – | # |
| | Ag layer | Ag | 2.36 | 2.36 | (1 1 0) |
| | a = 4.10 | | 2.05 | 2.05 | (2 0 0) |
| | b = 2.90 | | 1.45 | 1.44 | (0 2 0) |
| | Rec($C_2$/m) | | 1.23 | 1.24 | (3 1 0) |
| | | | 1.18 | 1.18 | (2 2 0) |
| | $M_2$ at 210°C | $S_C$ | 28.7 | 29.3 | (0 0 1) |
| | $S_C$ c = 29.2 | | 14.6 | 14.7 | (0 0 2) |
| | | | 9.77 | 9.77 | (0 0 3) |
| | Ag layer | Ag | 2.37 | 2.37 | (1 1 0) |
| | a = 4.10 | | 2.05 | 2.05 | (2 0 0) |
| | b = 2.90 | | 1.45 | 1.45 | (0 2 0) |
| | Rec($C_2$/m) | | 1.24 | 1.24 | (3 1 0) |
| | | | 1.18 | 1.18 | (2 2 0) |
| | $M_3$ at 250°C | $S_A$ | 27.8 | 28.2 | (0 0 1) |
| | $S_A$ c = 28.2 | | 14.1 | 14.1 | (0 0 2) |
| | | | 9.40 | 9.40 | (0 0 3) |
| | Ag layer | Ag | 2.37 | 2.37 | (1 1 0) |
| | a = 4.10 | | 2.05 | 2.05 | (2 0 0) |
| | b = 2.90 | | 1.45 | 1.45 | (0 2 0) |
| | Rec($C_2$/m) | | 1.24 | 1.24 | (3 1 0) |
| | | | 1.18 | 1.18 | (2 2 0) |
| $C_{14}$-Phen | $M_1$ at 147°C | $S_X$ | 38.7 | 40.4 | (0 0 1) |
| | $S_X$ c = 41.0 | | 20.5 | 20.2 | (0 0 2) |
| | | | 13.5 | 13.5 | (0 0 3) |
| | | | 4.47 | – | # |
| | Ag layer | Ag | 2.36 | 2.36 | (1 1 0) |
| | a = 4.10 | | 2.05 | 2.05 | (2 0 0) |
| | b = 2.90 | | 1.45 | 1.44 | (0 2 0) |
| | Rec($C_2$/m) | | 1.23 | 1.24 | (3 1 0) |
| | | | 1.18 | 1.18 | (2 2 0) |
| | $M_2$ at 216°C | $S_C$ | 31.3 | 31.5 | (0 0 1) |
| | $S_C$ c = 31.4 | | 15.7 | 15.8 | (0 0 2) |
| | | | 10.5 | 10.5 | (0 0 3) |
| | Ag layer | Ag | 2.36 | 2.36 | (1 1 0) |
| | a = 4.10 | | 2.05 | 2.05 | (2 0 0) |
| | b = 2.90 | | 1.45 | 1.44 | (0 2 0) |
| | Rec($C_2$/m) | | 1.24 | 1.24 | (3 1 0) |

(*Continued*)

**TABLE 2** Continued

| Compound | Mesophase lattice constants (γ) | Spacing (γ) | | | Miller indices (h k l) |
|---|---|---|---|---|---|
| | | | Observed | Calculated | |
| | $M_3$ at 250°C | $S_A$ | 30.0 | 30.0 | (0 0 1) |
| | $S_A$ c = 30.2 | | 15.1 | 15.0 | (0 0 2) |
| | | | 10.0 | 10.0 | (0 0 3) |
| | Ag layer | Ag | 2.37 | 2.37 | (1 1 0) |
| | a = 4.10 | | 2.05 | 2.05 | (2 0 0) |
| | b = 2.90 | | 1.45 | 1.45 | (0 2 0) |
| | Rec($C_2$/m) | | 1.24 | 1.24 | (3 1 0) |
| | | | 1.19 | 1.18 | (2 2 0) |
| $C_{16}$-Phen | $M_1$ at 142°C | $S_X$ | 39.1 | 42.1 | (0 0 1) |
| | $S_X$ c = 43.0 | | 21.5 | 21.1 | (0 0 2) |
| | | | 14.0 | 14.0 | (0 0 3) |
| | Ag layer | Ag | 2.37 | 2.37 | (1 1 0) |
| | a = 4.10 | | 2.05 | 2.05 | (2 0 0) |
| | b = 2.90 | | 1.45 | 1.45 | (0 2 0) |
| | Rec($C_2$/m) | | 1.23 | 1.24 | (3 1 0) |
| | $M_2$ at 200°C | $S_C$ | 32.0 | 34.0 | (0 0 1) |
| | $S_C$ c = 32.2 | | 16.1 | 17.0 | (0 0 2) |
| | | | 11.9 | 11.3 | (0 0 3) |
| | Ag layer | Ag | 2.37 | 2.37 | (1 1 0) |
| | a = 4.10 | | 2.05 | 2.05 | (2 0 0) |
| | b = 2.90 | | 1.45 | 1.45 | (0 2 0) |
| | Rec($C_2$/m) | | 1.24 | 1.24 | (3 1 0) |
| | | | 1.18 | 1.18 | (2 2 0) |
| | $M_3$ at 250°C | $S_A$ | 31.5 | 31.9 | (0 0 1) |
| | $S_A$ c = 32.0 | | 16.0 | 16.0 | (0 0 2) |
| | | | 10.6 | 10.6 | (0 0 3) |
| | | Ag | 2.37 | 2.37 | (1 1 0) |
| | Ag layer | | 2.05 | 2.05 | (2 0 0) |
| | a = 4.10 | | 1.44 | 1.45 | (0 2 0) |
| | b = 2.90 | | 1.24 | 1.24 | (3 1 0) |
| | Rec($C_2$/m) | | 1.18 | 1.18 | (2 2 0) |
| $C_{18}$-Phen | $M_1$ at 140°C | $S_X$ | 34.5 | 34.6 | (0 0 1) |
| | $S_X$ c = 34.6 | | 17.3 | 17.3 | (0 0 2) |
| | Ag layer | Ag | 2.36 | 2.36 | (1 1 0) |
| | a = 4.10 | | 2.05 | 2.05 | (2 0 0) |
| | b = 2.90 | | 1.45 | 1.45 | (0 2 0) |
| | Rec($C_2$/m) | | 1.24 | 1.24 | (3 1 0) |
| | | | 1.18 | 1.18 | (2 2 0) |
| | $M_2$ at 191°C | $S_C$ | 32.5 | 32.8 | (0 0 1) |
| | $S_C$ c = 32.8 | | 16.4 | 16.4 | (0 0 2) |
| | Ag layer | Ag | 2.37 | 2.37 | (1 1 0) |
| | a = 4.10 | | 2.04 | 2.05 | (2 0 0) |

(*Continued*)

**TABLE 2** Continued

| | | Spacing (γ) | | | |
|---|---|---|---|---|---|
| Compound | Mesophase lattice constants (γ) | | Observed | Calculated | Miller indices (h k l) |
| | b = 2.90 | | 1.45 | 1.44 | (0 2 0) |
| | Rec($C_2$/m) | | 1.23 | 1.24 | (3 1 0) |
| | | | 1.18 | 1.18 | (2 2 0) |
| | $M_3$ at 250°C | | 31.5 | 32.0 | (0 0 1) |
| | $S_A$ c = 31.8 | $S_A$ | 15.9 | 16.0 | (0 0 2) |
| | | | 10.7 | 10.7 | (0 0 3) |
| | Ag layer | | 2.37 | 2.37 | (1 1 0) |
| | a = 4.10 | | 2.05 | 2.05 | (2 0 0) |
| | b = 2.90 | Ag | 1.45 | 1.45 | (0 2 0) |
| | Rec($C_2$/m) | | 1.24 | 1.24 | (3 1 0) |
| | | | 1.18 | 1.18 | (2 2 0) |

showed the same mesophases. Hence, the identification of these mesophases was described for a representative $C_{12}$-Phen.

Figure 2 shows the X-ray diffraction patterns of $C_{12}$-Phen in the crystal, $M_1$, $M_2$, and $M_3$ phases. All the mesophases of $C_{12}$-Phen gave less than ten sharp reflections with a halo at $2\theta \cong 20°$. The conventional broad halo of liquid crystals can be observed at $2\theta \cong 20°$, which generally corresponds to the molten long alkyl chains. Therefore, the broad halo may correspond to the melting of alkyl chains of alkylsulfonate anions. The spacings of peak nos. 1–3 for the $M_1$, $M_2$, and $M_3$ mesophases are in a ratio of 1:1/2:1/3, which indicates that these mesophases have a smectic (layer) structure with the layer thickness = 32.3 Å, 29.2 Å, and 28.2 Å, respectively. These results are compatible with the focal conic textures (Fig. 1(a)–(c)). A peak (no. 4), unassignable to the smectic structure, was observed in the $M_1$ mesophase. The peak can also be seen in the X-ray data of $C_{14}$-Phen. The peaks seem to originate from the stacking distance of phenazine cores in the $M_1$ mesophase.

It is noteworthy that all the mesophases exhibit the same five peaks in the high-angle region ($2\theta > 35°$) and the peaks are also observed in the crystal. Judging from these facts, the peaks come not from the mesophase structure, but from an arrangement of inorganic components ($Ag^+$ ions). The peaks could be assigned as reflections from a two-dimensional rectangular lattice, and the lattice constants (a) and (b) could be calculated to be 4.10 Å and 2.90 Å, respectively. Moreover, it was clarified from the extinction rules for rectangular lattices that

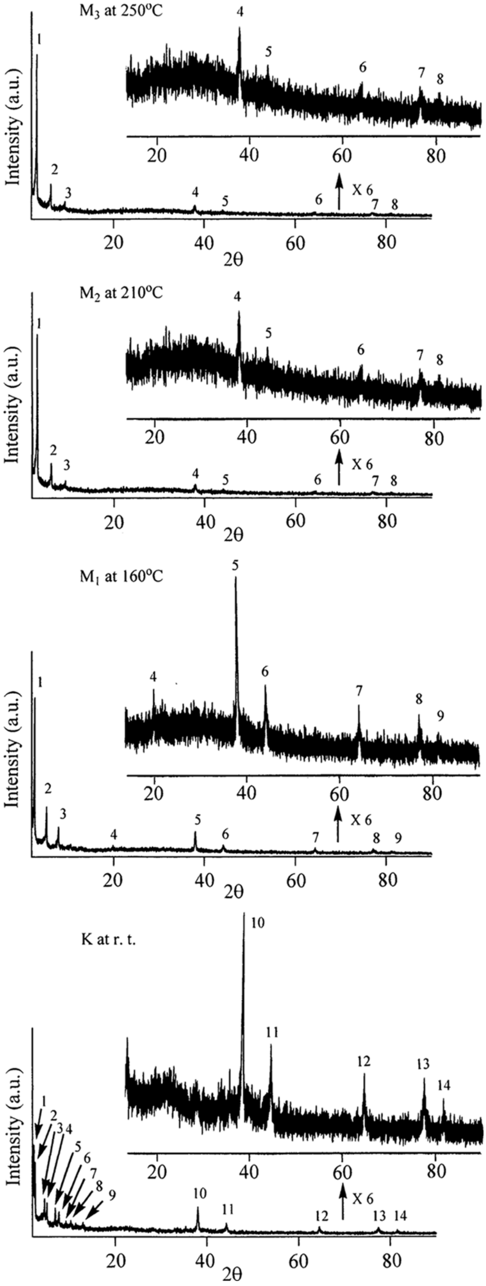


**FIGURE 2** X-ray diffraction patterns of $C_{12}$-Phen in the mesophases and crystalline state.

the lattice has $C_2$/m symmetry. If the rectangular lattice is regarded as a two-dimensional silver sheet, the number of $Ag^+$ ions (Z) in a unit is 2. In fact, the Z value could be calculated to be 1.75 nearly equal to 2 by using the lattice constant $a = 4.10$ Å, $b = 2.90$ Å, $c = 2.52$ Å (the diameter of $Ag^+$) and an assumed density $p = 10.449\ gcm^{-3}$ (the density of Ag). Therefore, the X-ray diffraction data suggest that a two-dimensional silver sheet can be self-organized by the reaction of phenazine and silver dodecylsulfonate and that the silver sheet forms a layer mesophase structure. Similar two-dimensional metal sheet has also been observed for the mesophase of "flying-seed-like" alkali metal carboxylates by K. Ohta et al. [16].

Layer structures composed of the silver sheet were also observed in the $M_2$ and $M_3$ mesophases of the other $C_{14}$-, $C_{16}$-, and $C_{18}$-Phen adducts. As can be seen from Table 2, the layer thickness increases little by little, when the alkyl chain length gets longer.

## 3.3. Model of Mesophases

Figure 3 illustrates a phase structure model of the $M_3$ ($S_A$) mesophase. Each of the layers may have a two-dimensional silver sheet sandwiched above and below by two aliphatic sheets. In the aliphatic sheets, the alkyl groups may freely rotate to form the soft part. In the silver sheet, $Ag^+$ ions are disposed in a rectangular lattice with C2/m symmetry. The lattice constant $a = 2.90$ Å of the rectangular lattice is almost compatible with the diameter of $Ag^+$ (2.52 Å). The repulsion among $Ag^+$ ions may be depressed due to the binding

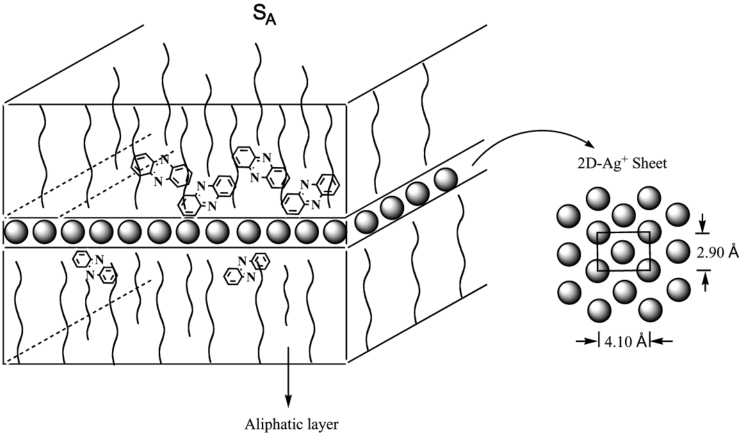


**FIGURE 3** Proposed mesophase structure model of the $M_3$ ($S_A$).

of alkylsulfonate ion to $Ag^+$ ion. The exact location of phenazine molecules remains unclear, but the molecules seem to interact with $Ag^+$ ion through coordination bonding and to be distributed above and below the silver sheet. As the molecular length of dodecylsulfonate anion could be estimated from CPK model to be ca. 16 Å, the layer thickness of the $M_3$ mesophase of $C_{12}$-phen is ca. 34–35 Å when the aliphatic sheets form a bilayer structure. However, the layer thickness was determined as 28.2 Å from the X-ray diffraction study, as mentioned above. This suggests that the alkyl chains interdigitate between layers in part. From similar comparison between the molecular length of alkylsulfonate anion and the observed layer thickness for the corresponding Cn-Phen adducts, it is clear that the longer the chain becomes, the more an interdigitated overlap of the alkyl chains becomes.

If the conditions of the overlap of the alkyl chains in the $M_3$ and $M_2$ mesophases are identical, the layer thickness in the $M_2$ ($S_C$) mesophase should be smaller than that in the $M_3$ ($S_A$) mesophase due to tilting of alkyl chains to the silver sheet. But the results are opposite, suggesting that the overlap of the alkyl chains in the $M_2$ mesophase decreases in comparison with in the $M_3$ mesophase.

As mentioned above, a part of the $M_3$ texture showed a homeotropic alignment. As pointed out by Ujiie, ionic liquid crystals themselves work as a surface treatment reagent like a silane coupling reagent [17]. The present ionic liquid crystal containing silver cation and alkylsulfonate anion may also work as a surface treatment reagent to show the homeotropic alignment.

## 4. CONCLUSION

Phenazine reacted with silver alkylsulfonates through a self-assembling process. The resulting adducts organized to form a very unique two-dimensional rectangular silver sheet in the mesophases. The adducts exhibited three smectic mesophases (unidentified smectic ($S_x$), smectic C ($S_C$), and smectic A ($S_A$) mesophases). In the $S_A$ mesophase, the adducts partly homeotropically aligned. These results represent a significant example that the introduction of long alkyl chains into metal-based self-assembling system can provide a useful strategy to form liquid crystalline metal-organic nanostructures.

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