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Synthesis and low dimensional conductive behaviour of columnar bis(β-diketonato)copper(II) complexes with oligo(ethylene oxide) groups

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Several kinds of β-diketone with oligo(ethylene oxide) groups and their Cu-complexes were synthesized and characterized by ^{1}H NMR, IR, MS, and elemental analysis. The columnar mesomorphism of the bis[1-(*p*-ethoxy-di(ethyleneoxy)phenyl)-3-(*p*-*n*-hexyloxylphenyl)propane-1,3-dionato]copper(II) complex (abbreviated as C_6EDK-Cu) was studied by differential scanning calorimetry, polarizing optical microscopy and temperature variable X-ray diffraction. In comparison with the conductivity value of *c*. 10^{-8} S cm^{-1} of the pure columnar liquid crystal (C_6EDK-Cu), that of C_6EDK-Cu doped with $LiClO_4$ or iodine is increased by about three orders of magnitude and reaches 10^{-5} S cm^{-1} when heated to the columnar mesophase. It is noteworthy that the conductivity of C_6EDK-Cu doped with iodine is maintained when the sample is cooled from the mesophase to room temperature, while that of C_6EDK-Cu doped with $LiClO_4$ is decreased. The two kinds of conductive mechanism of C_6EDK-Cu doped with $LiClO_4$ or iodine are discussed.

1. Introduction

Because of their remarkable self-assembly properties, discotic liquid crystal materials are promising for realizing low dimensional conductivity and have been extensively studied [1]. Phthalocyanine and metallophthalocyanines are of interest as anisotropic conductive materials [2]. Upon doping metallophthalocyanines with iodine, the conductivity can rise to as high as about 0.7 S cm^{-1} or even 10^4 S cm^{-1} in the stacked direction of the single crystal. Overshadowing this remarkable property, however, is the fact that metallophthalocyanines are insoluble in common organic solvents and intractable due to their strong intermolecular interactions and the difficulty in obtaining single crystals. Ungar *et al.* [3] prepared several kinds of organized columnar molecular–salt and polymer–salt complexes based on a taper-shaped mesogen and crown ether groups, and achieved a conductivity of 10^{-6} S cm^{-1} in their columnar phases. Van Nostrum [4] reviewed the molecular design, synthesis, and supramolecular organization based on two kinds of discotic mesogenic units (electron rich units and hollow units) for one dimensional molecular materials capable of transporting charge, energy, ions or small molecules. Wendorff *et al.* [5–7] reported a remarkable improvement in light emitting diode (LED) properties using columnar triphenylenes as the hole transporting layer because of their exceptionally large hole mobility. The onset voltage for light emission was found to be unusually small and turned out to be strongly dependent on the orientation of the columns. Previous investigations of bis(β-diketonato)metal complexes had demonstrated that they exhibit characteristic columnar mesophases [8]. In the last few years, we have prepared a series of fishbone-like liquid crystalline polymers (FBLCPs) and their corresponding metal complexes [9–14]. These complexes with a high metal content exhibit a remarkably high isotropization temperature (T_i), a greatly broadened mesophase range and good film-forming ability. Until now, their conductive behaviour has not been reported. On the other hand, it is well known that poly(ethylene oxide) doped with lithium ions exhibits a high conductivity [15]. In this paper, we report the synthesis of columnar-like Cu-complexes of β-diketones with oligo(ethylene oxide) groups in order to combine the one dimensional columnar phase assembled by the discotic metal complex cores with the ordered ionic channel organized by the oligo(ethylene oxide) side groups. Their conductive behaviour and mechanism based on two kinds of doping conditions of the Cu-complexes, with iodine or $LiClO_4$, are also investigated.

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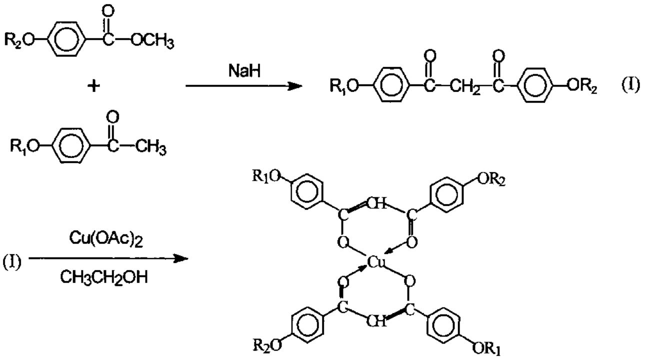
2. Experimental

2.1. *Materials*

The reagents and solvents were commercially available and of analytical purity. Dimethoxyethane was strictly dried by heating under reflux with sodium sand, using benzophenone as indicator. The synthetic route to the present β-diketone ligands and the corresponding copper(II) complexes is shown in the scheme.

2.1.1. *Synthesis of 1-(p-ethoxy-di(ethyleneoxy)phenyl)-3-(p-n-hexoxylphenyl)propane-1,3-dione, C_6EDK*

C_6EDK was synthesized by the method derived from Ohta *et al.* [16]. A mixture of 3.00 g (1.19×10^{-2} mol) of *p*-ethoxy-di(ethyleneoxy)acetophenone and 2.80 g (1.18×10^{-2} mol) of methyl *p*-*n*-hexyloxybenzoate was dissolved in dimethoxyethane and heated under reflux for 3 h in the presence of 0.948 g of 60% sodium hydride (2.37×10^{-2} mol). The resulting brown–yellow solution was cooled to room temperature and stirred overnight. Small portions of ethanol and then water were added carefully to the resulting orange mixture. After acidifying the mixture with dilute hydrochloric acid, the product was extracted into ether. Crude C_6EDK ligand was obtained by evaporating the solvent; this was purified by chromatography on silica eluted with a mixed solvent of hexane and ethyl acetate in the volume ratio 2:1 to give 3.23 g of pale yellow crystals (yield 60%). 1,3-Bis[*p*-ethoxy-di(ethyleneoxy)phenyl]propane-1,3-dione (abbreviated as EEDK) and 1-(*p*-*n*-dodecyloxyphenyl)-3-(*p*-*n*-undecenyloxyphenyl)propane-1,3-dione (abbreviated as $C_{11}C_{12}$DK) were synthesized by similar procedures.



(I) C_6EDK: $R_1 = CH_3CH_2OCH_2CH_2OCH_2CH_2$ $R_2 = C_6H_{13}$

EEDK: $R_1 = R_2 = CH_3CH_2OCH_2CH_2OCH_2CH_2$

$C_{11}C_{12}$DK: $R_1 = C_{12}H_{25}$ $R_2 = C_{11}H_{23}$

Scheme. Synthetic route to the β-diketone ligands and the corresponding copper(II) complexes.

2.1.2. *Synthesis of the bis[1-(p-ethoxy-di(ethyleneoxy)-phenyl)-3-(p-n-hexyloxyphenyl)propane-1,3-dionato]copper(II) complex, C_6EDK-Cu*

A mixture of 2.41 g (5.28×10^{-3} mol) of C_6EDK and 0.527 g (2.64×10^{-3} mol) of anhydrous copper(II) acetate and 50.0 ml of anhydrous ethanol was stirred for 3 h at room temperature. The pale green solid which precipitated was washed with ethanol and recrystallized from ethyl acetate to give 2.30 g (yield 90%) of pale green crystals. EEDK-Cu and $C_{11}C_{12}$DK-Cu were prepared by similar procedures.

2.2. *Characterization*

The β-diketones and their copper(II) complexes were characterized by ^{1}H NMR, IR, MS and elemental analysis. The data are illustrated in table 1.

The phase behaviour of these copper(II) complexes was investigated by using a polarizing optical microscope (POM, Xintian, XP1A, China) equipped with a heating stage, differential scanning calorimetry (DSC, Perkin-Elmer DSC 7) and temperature-variable X-ray diffraction (XRD, PW1710 BASED).

2.3. *Determination of conductivity*

The doped samples were prepared by mixing C_6EDK-Cu with iodine or $LiClO_4$ and the conductivity was measured as a function of temperature. The sample

Table 1. Characterization data for the β-diketones with oligo(ethylene oxide) or alkoxy groups and their Cu(II) complexes.

	Elemental analysis/%									
	C		H		Cu		NMR, δ/ppm			
Compound	calc	found	calc	found	calc	found	enol =CH	enol OH	IR ($\nu_{c=o}$)/cm^{-1}	MS (m/e)/M$^+$
EEDK	66.37	63.11	7.40	7.43			6.75	17.10	1675 (s)	489
EEDK-Cu	62.44	62.89	6.79	6.91	6.11	6.01				
C_6EDK	71.02	69.54	7.94	7.78			6.75	17.15	1681 (s)	457
C_6EDK-Cu	66.54	66.80	7.24	7.70	6.50	6.61				
$C_{11}C_{12}$DK	79.10	79.01	9.78	9.81			6.75	17.10	1600 (s)	577
$C_{11}C_{12}$DK-Cu	75.21	75.10	9.19	9.15	5.55	5.60				

was introduced into a sandwich cell which was composed of two parallel ITO-covered glass plates as shown in figure 1. The two plates were separated by a polycarbonate (PC) spacer with thickness about 50 µm. All samples were efficiently dried in vacuum overnight and the cell was further dried in a vacuum container prior to measurements. The conductivity was measured by using an electrometer operating in a constant frequency mode (1 kHz) (HIOKILCR 3520 Hi TESTER).

3. Results and discussion

3.1. *Columnar mesomorphism of the bis(β-diketonato)copper(II) complexes*

The phase transition temperatures (T_t) and enthalpies (ΔH_t) of three bis(β-diketonato)copper(II) complexes are summarized in table 2. DSC thermographs and POM photographs are shown in figure 2 and figure 3, respectively. C_6EDK-Cu exhibits two endothermic transitions (figure 2 *a*) at 103.37°C ($\Delta H_t = 4.16$ kcal mol^{-1}) and 146.17°C ($\Delta H_t = 8.18$ kcal mol^{-1}) which represent T_m and T_i, respectively, see figure 2(*a*). The phase between 103.37°C and 146.17°C is a columnar mesophase. The texture is a star-burst texture as shown in figure 3(*a*). The same texture can also be observed for $C_{11}C_{12}$DK-Cu [DSC in figure 2(*c*)], but EEDK-Cu [DSC figure 2(*b*)] does not show such a texture and is not mesomorphic. This may be due to its highly symmetric molecular structure.

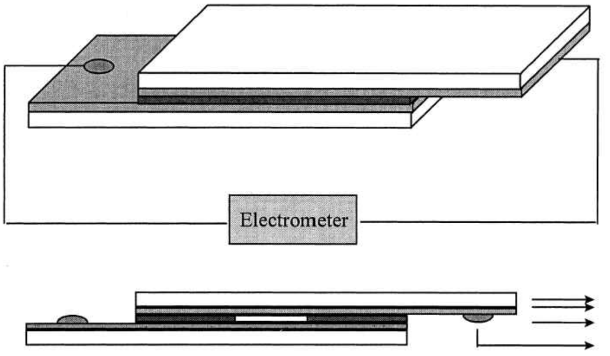


Figure 1. Side view and overview of the conductivity measurement cell; 1. glass substrate, 2. ITO surface, 3. PC spacer, 4. conductive gum.

Table 2. The phase transition temperatures, enthalpies and optical textures of the metal chelates. Phase nomenclature: Cr = crystal; Col = columnar liquid crystal; I = isotropic state.

Sample	T_t/°C ΔH_t/kcal mol^{-1}	Texture
C_6EDK-Cu	Cr $\xrightarrow[4.16]{103.37}$ Col $\xrightarrow[8.18]{146.17}$ I	star-burst
EEDK-Cu	Cr $\xrightarrow[18.49]{122.0}$ I	none
$C_{11}C_{12}$DK-Cu	Cr $\xrightarrow[7.4]{71.1}$ Col $\xrightarrow[35.84]{154.36}$ I	star-burst

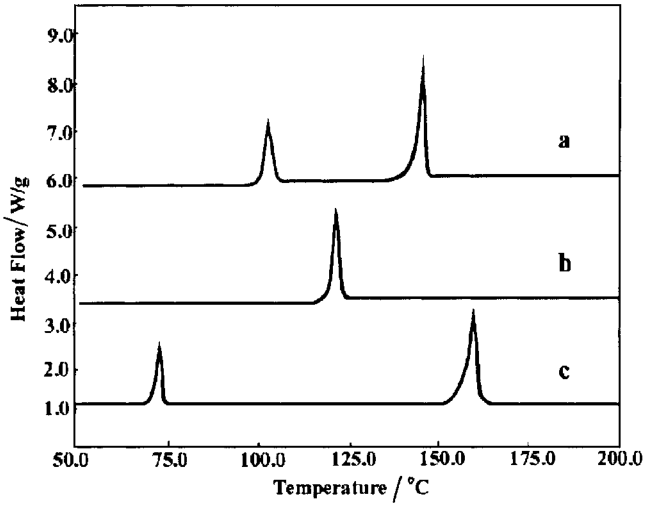


Figure 2. DSC traces for bis(β-diketonato)copper(II) complexes (heating rate 20°C min^{-1}): (*a*) C_6EDK-Cu; (*b*) EEDK-Cu; (*c*) $C_{11}C_{12}$DK-Cu.

The temperature-variable X-ray diffraction pattern for C_6EDK-Cu is shown in figure 4. In the small angle region, there are three diffraction peaks in the columnar mesophase. Moreover, the ratios of $d_1:d_2:d_3$ are 1 : 1/2 : 1/3, where *d* is the distance between two adjacent layers. According to Ohta *et al.* [17], these bis(β-diketonato)copper(II) complexes with long alkyl side groups, showing spacings exactly in the ratios of 1 : 1/2 : 1/3, exhibit a typical columnar mesophase. The X-ray diffraction curve shows a regular arrangement of metal chelates in the temperature range of the columnar phase. When the sample is heated to 150°C, the discotic phase is destroyed and the X-ray diffraction peaks at small angles disappear.

3.2. *Conductive behaviour of doped C_6EDK-Cu*

The conductivity of undoped C_6EDK-Cu is about 10^{-8} S cm^{-1} and there is no distinct increase when it is heated to give the mesophase. In order to improve the conductivity of C_6EDK-Cu and investigate the conductive mechanism, we mixed C_6EDK-Cu with $LiClO_4$ or iodine. The results and discussion are described below.

It can be seen from figure 5 that there is a sharp increase in conductivity of lithium ion-doped C_6EDK-Cu with a mol ratio of C_6EDK-Cu : $LiClO_4$ = 3 : 1 when it is heated to give the columnar mesophase. The conductivity (σ) rises abruptly from 10^{-8} to 10^{-5} S cm^{-1}. There is a similar result for the doping at a mol ratio of C_6EDK-Cu : $LiClO_4$ = 1 : 1. Meanwhile, when iodine is

Figure 3. Optical textures of three bis(β-diketonato)copper(II) complexes: (*a*) C_6EDK-Cu (140°C); (*b*) $C_{11}C_{12}$DK-Cu (120°C) (*c*) EEDK-Cu (94°C).

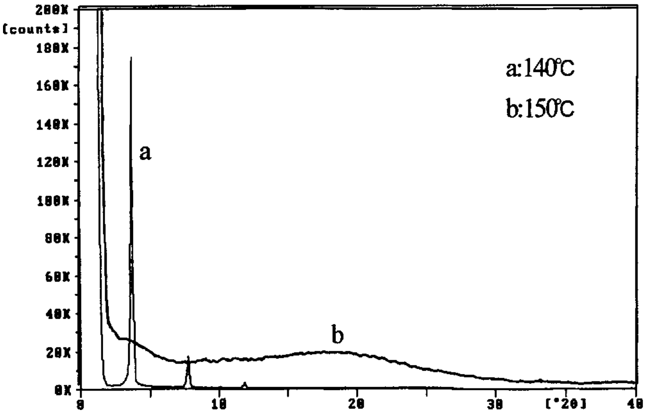


Figure 4. X-ray diffraction of C_6EDK-Cu at 140°C (columnar mesophase) and 150°C (isotropic state): *d* is the distance between two adjacent layers, and $d_1:d_2:d_3 = 1:1/2:1/3$ (d_1 = 2.273 nm, d_2 = 1.139 nm, d_3 = 0.7481 nm).

incorporated into C_6EDK-Cu with a mol ratio of 1:1, the conductivity increases continuously with increase in temperature, as shown in figure 6, and finally reaches 10^{-6} S cm^{-1}. The DSC curve of a pure and $LiClO_4$ doped sample is shown in figure 7. There is no significant change in the mesophase behaviour of the sample (apart from peak broadening), but there is an additional broad endothermic peak now centred at 84°C in the DSC curve of the $LiClO_4$-doped sample. A possible explanation for this transition is breakdown of the association linking the lithium ions and oligo(ethylene oxide) groups [15].

From the above mentioned results, there may exist two different kinds of conductive mechanism. When the sample is doped with $LiClO_4$ and is heated above the crystal to liquid crystal transition temperature, the rigid coplanar cores of the bis(β-diketonato)copper(II) complexes are gradually self-assembled into a columnar phase, while the oligo(ethylene oxide) groups are aggregated

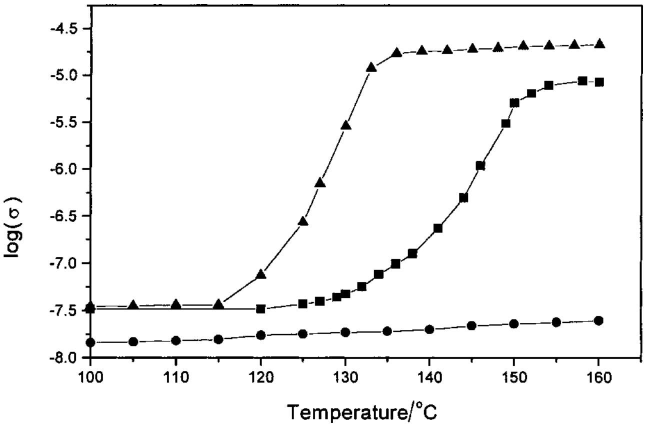


Figure 5. Conductivity (*σ*) of C_6EDK-Cu doped with $LiClO_4$: C_6EDK-Cu:$LiClO_4$ = 1:1 (■); undoped sample (●); C_6EDK-Cu:$LiClO_4$ = 3:1 (▲).

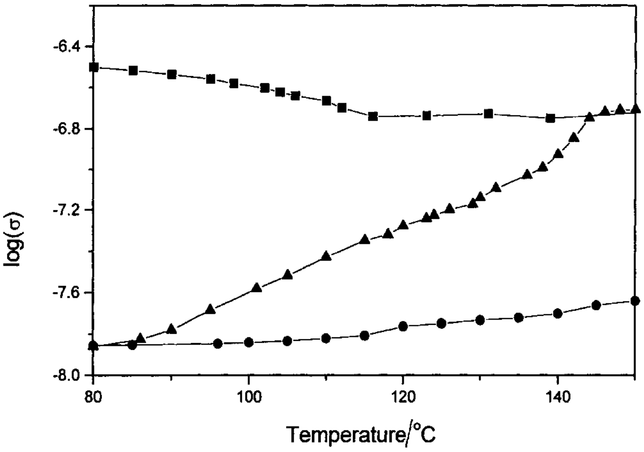


Figure 6. Conductivity (*σ*) of C_6EDK-Cu doped with iodine: C_6EDK-Cu:iodine = 1:1 (cooling) (■); undoped sample (●); C_6EDK-Cu:iodine = 1:1 (heating) (▲).

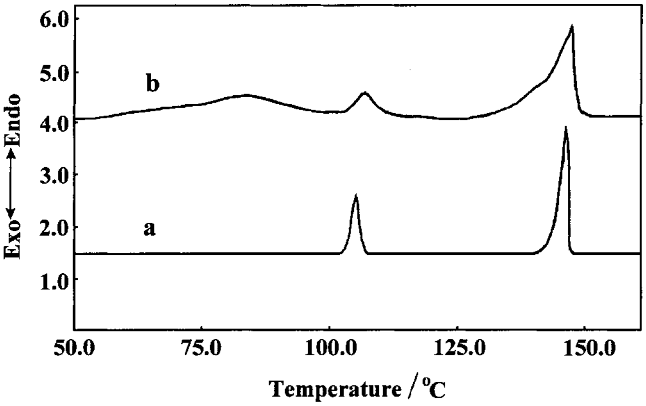


Figure 7. DSC Curves for undoped and $LiClO_4$-doped C_6EDK-Cu (heating rate 20°C min^{-1}): (*a*) undoped sample; (*b*) $LiClO_4$-doped sample.

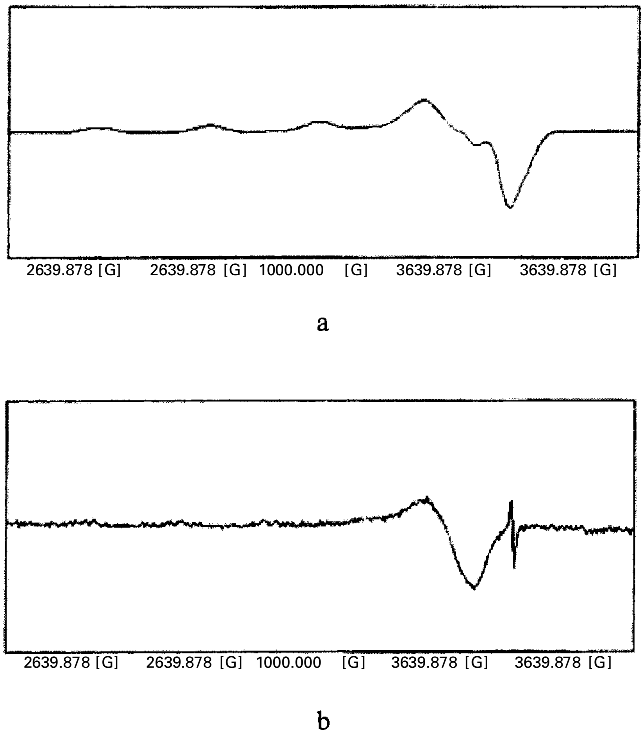


Figure 8. ESR spectra of undoped and iodine-doped C_6EDK-Cu (at room temperature): (*a*) undoped sample; (*b*) iodine-doped sample.

between adjacent stacked columns and form ionic channels in which the lithium ions are transported. This high ion conductivity is therefore attributed to the supramolecular self-assembled columnar phase and the oriented channel between the columns. When the sample is cooled below the mesophase to Cr temperature (< 80°C), the high conductivity cannot be maintained due to the damage to the ionic channel caused by crystallization of the oligo(ethylene oxide) groups. However, the conductive behaviour can be reproduced when the sample is heated again.

When an iodine-doped sample is heated, the rigid disk-shaped core which is partially oxidized by iodine is gradually assembled into a columnar phase. The quasi-planar macrocycles with central copper(II) ions are close to each other, which is favourable for π-orbital overlap and the conduction band. Partial oxidation of the macrocycles by iodine will generate charge carriers leading to quasi-one dimensional conductivity. ESR measurements were made at room temperature by using an X-band high frequency modulation spectrometer [18, 19], and a strong ESR signal corresponding to the radical cation was found, as shown in figure 8. The ESR spectral line width is about 4 Gauss. This demonstrates that the sample doped with iodine can form 'charge transfer' molecular complexes and give rise to a radical cation which can act as a charge carrier and eventually result in a stable conductive state even at room temperature. In addition, It is noteworthy that the dipole–dipole interaction and delocalization of unpaired electrons have smeared out the hyperfine structures of the ESR signal.

As previously reported [20], bis(β-diketonato)metal complexes consist of distorted coplanar macrocyclic units. As the macrocycle conjugation is weaker than in metallophthalocyanines, the conductivity of C_6EDK-Cu doped with iodine is not very high. But it is noteworthy to mention that oxidation of the C_6EDK-Cu rigid core by iodine can lead to a stable semiconductivity. The rigid coplanar core may be assembled into a low-dimensional structure with a chain of iodine counterions located in channels parallel to the columnar central axis. The conductivity of C_6EDK-Cu doped with iodine is supposed to be that of a *p*-type electronic conductor as has been reported previously for phthalocyaninatocopper(II) (PcCu) [2].

4. Conclusion

Several β-diketones with oligo(ethylene oxide) groups and their Cu-complexes were synthesized. The columnar mesophase of C_6EDK-Cu was confirmed by DSC, POM and temperature-variable X-ray diffraction. The conductivity of C_6EDK-Cu doped with $LiClO_4$ or iodine is increased by about 2–3 orders of magnitude and reaches 10^{-5} S cm^{-1} when the sample is heated to the columnar mesophase. The conductivity of C_6EDK-Cu doped with iodine can be maintained when the sample is cooled from the mesophase to room temperature, while that of C_6EDK-Cu doped with $LiClO_4$ cannot be maintained. Investigations on the conductivity of C_6EDK-Cu doped with $LiClO_4$ or iodine have demonstrated that there are two kinds of conductive mechanism. Although on crystallization of the oligo(ethylene oxide) groups, the ionic conductivity is destroyed, polymerization and suitable crosslinking may disfavour crystallization and lead to a stable conductivity state. Further investigations aimed at improving and stabilizing the conductivity of columnar metal complexes are in progress.

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