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Photophysical and electrochemical properties of monoporphyrin rare earth liquid crystalline materials

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Abstract

The synthesis and characterization of [5-(p-alkacyloxy) phenyl-10,15,20-tri-phenyl] porphyrin (APTPP) and its lanthanide complexes(lanthanide ions: Ho(III), Dy(III), Er(III), Yb(III)) are reported. They form hexagonal columnar discotic columnar (Col_h) liquid crystals over an extended domain of temperature. Luminescence spectra of the compounds are discussed. Quantum yields of Q band are in the region 0.004570–0.05847. The electrochemical property is studied by cyclic voltammetry. The synthesized APTPP and its lanthanide complexes exhibit two one-electron reversible redox reactions and three redox reactions, respectively. The photovoltaic properties and charge-transfer process of the liquid crystalline compounds are investigated by surface photovoltage spectroscopy (SPS) and electric-field-induced surface photovoltaic spectroscopy (EFISPS) techniques, and the bands are analogous with the ultraviolet (Uv) –visible absorption spectra, which reveal that all compounds are P-type semiconductors. All of compounds are nonelectrolytes. \bigcirc 2007 Elsevier Ltd. All rights reserved.

Keyword: A. Organometallic compounds; A. Semiconductors; B. Chemical synthesis; C. Differential scanning calorimetry (DSC); C. X-ray diffraction

1. Introduction

Liquid crystal (LC) displays are known in which a single (liquid) crystal, $5 \mu m$ thick, covering an area of ca. 500 cm², is formed by simple capillary-filling of the isotropic material between two sheets of conducting glass (coated with the appropriate aligning agents) and cooling into the liquid crystalline phase [1]. LCs are one of the few classes of organic materials to have entered the field of sophisticated electronic applications, in particular as displays. This is due to the fact that they can be orientated in applied electric and magnetic fields [2]. Metallomesogens provide a number of new shapes and structures from which to test the limits of LC stability. Representative examples of these materials have been found for all major classes of rod- and disk-shaped LCs [3–5].

Porphyrin thin films have received considerable attention because of their interesting excited-state chemistry and catalytic behavior and because of Nature's ubiquitous of

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porphyrins in electron-transfer processes. Their photostability, high visible extinction coefficients, and low processing costs make them attractive candidates for electrophotographic, photovoltaic, and photoelectrochemical applications [6–10]. In this paper, we introduce two series of disk-shaped lanthanide porphyrin LCs. Their liquid crystalline phases are determined by X-ray diffraction at small angles region, and differential scanning calorimetry (DSC). We comprehensively study electrochemical, photophysical and semiconductor properties of the compounds by cyclic voltammetry, luminescence spectroscopy and surface photovoltaic spectroscopy. The structure of the compound is shown in Figs. 1 and 2.

2. Experimental section

2.1. Apparatus and measurements

Elementary analysis was measured by a Pekin-Elmer 240C auto elementary analyzer. Ultraviolet (Uv) –visible spectra were recorded on a shimadzu Uv-240 spectro-photometer in the range 350–700 nm using chloroform

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Fig. 1. Porphyrin liquid crystalline compounds: (a) [5-(p-alkacyloxy)phenyl-10,15,20-tri-phenyl] porphyrin, n = 8, 10 correspond to 10L, 12L, respectively; (b) [5-(p-alkacyloxy) phenyl-10,15,20-tri-phenyl] porphyrin lanthanide complex, n = 8, Ln = Er, Ho, Dy corresponding to 10ErOH, 10HoOH, 10DyOH, respectively; n = 10, Ln = Yb, Er, Ho corresponding to 12YbOH, 12ErOH, 12HoOH, respectively.



Fig. 2. Uv/visible spectra of 12L (—) and 12HoOH ($\ldots\ldots$) in a solution of CHCl3.

as solvent. IR spectra were recorded on a Nicolet 5PC-FT-IR spectrometer using KBr pellets in the region 400-4000 cm⁻¹. The ¹H NMR spectra were recorded in deuterated chloroform using a Varian-Unity-400 NMR spectrometer and employing tetramethylsilane as internal reference. Molar conductances of 10⁻³ mol dm⁻³ chloroform solution at 25° were measured on a DDX-111A conductometer. differential scanning calorimetry (DSC) was recorded on a NETESCH DSC 204. The optical microscopical properties were observed by a XinTian XP1 (CCD: TOTA-500II) polarized light microscope equipped with a variable temperature stage (Linkam TMS 94). X-ray diffraction was recorded by a Shimadzu XRD-6000. Excitation and emission spectra at room temperature in the region 300-800 nm using $10^{-5} \text{ mol dm}^{-3}$ chloroform solution were measured by FS920 steady-state fluorescence spectrometer. The SPS and EFISPS were recorded with Asokid junction photovoltaic cell ITO/sample/ITO (ITO: idium tin oxide) using light source-monchromator-lock-in diction technique. Redox potentials of the porphyrins in DMF containing 0.1 M TBAP as a supporting electrolyte

at room temperature were determined by cyclic voltammetry using a three-electrode system under deaerated conditions and a CHI 6000A electrochemical analyzer.

2.2. Synthesis of the compounds

2.2.1. 12L

[5-(*p*-hydroxy)phenyl-10,15,20-tri-phenyl]porphyrin was prepared by the literature method [11]. This product (2.00 g) was dissolved in 150 ml of benzene and dodecannoyl chloride (2.0 ml) in 20 ml benzene was added dropwise to the above solution within 2 h at 70° . The reaction solution was refluxed for 2 h and cooling to room temperature. Benzene was removed under reduced pressure. Then 150 ml distilled water was added to the reaction mixture and extracted four times with 150 ml chloroform. The chloroform solution was applied to chromatography aluminum oxide column. The first band containing 12L was collected, the elution solution concentrated and the product dried under vacuum. 10L was prepared by the similar method.

2.2.2. 12 YbOH

A mixture of 12L (300 mg, 0.4 mmol) and hydration $YbCl_3 \cdot 6H_2O$ (600 mg, 1.5 mmol) were heated in an imidazole (10.0 g) melt at 210° under the protection and stirring of a dry nitrogen stream for 2h. The extent of the reaction was followed by measuring the Uv-visible spectra of the reaction solution at 10 min intervals. After cooling the reaction mixture to 100° , 150 ml distilled water was added and the solution filtered, washed several times with distilled water in a separating funnel, and finally the product was dried under vacuum. The crude product was dissolved in chloroform (200 ml). The solution was shaken with 100 ml 0.1% aqueous AgNO₃ and the chloroform layer was separated. The mixture of chloroform (30 ml) and methanol (20 ml) were added to the separated chloroform. The mixture was again shaken with 100 ml 0.1% aqueous AgNO₃. This procedure was repeated until no more AgCl precipitated. The chloroform solution was concentrated and applied to chromatography aluminum oxide column. The first band containing a small amount ligand, 12L, was eluted by chloroform. The second band eluted by chloroform containing 20% methanol, obtained the solution of the complex. The product was crystallized by concentrated the solution and finally product was dried under vacuum. The title compound was obtained as a purple solid. Other complexes (12ErOH, 12HoOH, 10ErOH, 10HoOH, 10DyOH) were prepared by the similar method.

3. Results and discussion

3.1. Composition of the compounds

The elemental analyses for carbon, hydrogen, nitrogen, empirical formulae, yields and the decomposition temperatures are given in Table 1.

3.2. IR spectra

The main spectral band frequencies of the porphyrin compounds are presented in Table 2. The spectral bands at 966 and 3319 cm^{-1} in the ligands porphyrin are assigned to the N–H bending and stretching vibrations of the porphyrin core. The two vibration bands of complexes

Table 1

Table 2

Characterization data of compounds

disappear, since the hydrogen atoms of the porphyrin core are replaced by the lanthanide ion to form Ln–N bond. Existence of the Ln–OH bend vibration band in the region 1065–1068 cm⁻¹ shows that the hydrogen atoms of hydroxyl group is bonded to lanthanide ion. Assignments of other absorption bands are also presented in Table 2.

3.3. Molar conductances

The molar conductance values of the ligand 10L and its complexes 10ErOH, 10HoOH, 10DyOH are at 0.135, 0.522, 0.036 and $0.032 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, respectively. Those of the ligand 12L and its complexes 12YbOH, 12ErOH, 12HoOH are at 0.125, 0.036, 0.051 and $0.042 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, respectively. It indicates that the ligands and all complexes show nonelectrolytic behavior [12].

3.4. ¹H NMR spectra

The ¹H NMR chemical shift values in deuterated chloroform (δ , ppm) for the ligand 10L and complexes 10ErOH are collected in Table 3. Compared with the ligand 10L, the signal of the complex 10ErOH disappears

Compounds	Emperical formula	C (%)	N (%)	H (%)	Yields (%)	Dec. temp. (°)
10L	C ₅₄ N ₄ H ₄₈ O ₂	82.58 (82.62)	7.16 (7.14)	6.14 (6.16)	70	>400
12L	$C_{56}N_4H_{52}O_2$	82.66 (82.72)	6.90 (6.89)	6.46 (6.45)	68	>400
10ErOH	ErC ₅₄ N ₄ H ₄₇ O ₃	67.05(67.08)	5.81 (5.80)	4.87 (4.89)	83	>200
10HoOH	HoC ₅₄ N ₄ H ₄₇ O ₃	67.16 (67.22)	5.82 (5.81)	4.90 (4.88)	84	>200
10DyOH	DyC ₅₄ N ₄ H ₄₇ O ₃	67.40 (67.43)	5.81 (5.83)	4.90 (4.89)	88	>200
12YbOH	YbC56N4H51O3	67.16 (67.20)	5.58 (5.60)	5.12 (5.10)	82	>200
12ErOH	$ErC_{56}N_{4}H_{51}O_{3}$	67.65 (67.61)	5.60 (5.63)	5.11 (5.13)	84	>200
12НоОН	$HoC_{56}N_4H_{51}O_3$	67.69 (67.74)	5.64 (5.65)	5.15 (5.14)	86	>200

Theoretical values in parenthesis.

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Infrared	spectral	frequencies	(cm^{-1})) of	com	oounds

Compounds	O–H	С–Н	N-H (pyrrole)	C=O	C-C (benzol ing)	C-H (pyrrole)	Ln–OH	С–О	N-H (pyrrole)
10 L		2926	3319	1761	1597	1471		1199	966
		2855							
12 L		2920	3319	1765	1597	1466		1199	966
		2851							
10ErOH	3424	2922		1763	1596	1468	1068	1199	
	2852								
10HoOH	3420	2922		1763	1596	1466	1068	1199	
		2851							
10DyOH	3422	2922		1762	1596	1464	1067	1198	
		2853							
12YbOH	3430	2922		1762	1597	1465	1065	1198	
		2852							
12ErOH	3429	2922		1760	1598	1466	1065	1198	
		2850							
12HoOH	3431	2922		1762	1597	1465	1066	1198	
		2850							

at -2.74 ppm, since the hydrogen atom in the N–H bond is replaced by the rare earth ion and the signal at 0.20 ppm appears. The latter being due to hydroxyl group coordinated to the rare earth ion. The disappearance of the signal at -2.74 ppm and the appearance of the signal peak at 0.20 ppm indicate that the porphyrin ligand and hydroxyl group are coordinated to the lanthanide ion.

3.5. Uv-visible spectra

The maximum absorption values (λ_{max}) of the ligand and complexes are shown in Table 4. Characteristic Q and B (Soret) bands of porphyrins and metal porphyrins in visible and near-ultra violet ranges are assigned as the transitions from ground state (S₀) to the lowest excited singlet (S₁) and second lowest excited singlet state (S₂), respectively. The absorption spectra of all complexes are very similar. Compared with the ligands, the number of the absorption bands of the complexes decrease, it is attributed to symmetry increase of the complexes. Soret bands exhibit small shifts to longer wavelengths. The absorption bands in the Q-band region are designed as I, II, III, IV from red to blue. These are similar with the results of literatures [13,14].

The IR spectral bands at 966 and 3319 cm⁻¹ in the ligand porphyrin are assigned to the N–H bending and stretching

Table 3	
¹ H NMR spectral	bands of ligand and complex

Compounds	Proton numbers	Position of the protons	δ (ppm)
10L	8	Pyrrole, ring	8.85
	19	Phenyl, ring	7.24, 7.50, 7.78, 8.22
	2	-OOC(CH ₂)-	2.72-2.76
	16	-(CH ₂) _n -	1.25-1.90
	3	-CH ₃	0.88-0.93
	2	N–H	-2.74
10ErOH	8	Pyrrole, ring	8.41
	19	Phenyl, ring	7.99, 7.63, 7.27
	2	-OOC(CH ₂)-	2.40
	16	-(CH ₂) _n -	1.33
	3	-CH ₃	0.90
	1	–OH	0.20

vibrations of the porphyrin core. When the lanthanide complexes formed, the two bands disappeared. Which indicate the hydrogen atoms of the porphyrin core are replaced by the lanthanide ion to form Ln–N bond. Existence of the Ln–OH bend vibration band in the region 1065–1068 cm⁻¹ shows that the hydrogen atoms of hydroxyl group is bonded to lanthanide ion. The elemental analytical experimental data for carbon, hydrogen, nitrogen consistent with theoretical values. The molar conductance values of the complexes are lower. They are all nonelectrolyte.

It may be concluded from the results mentioned above that (a) porphyrin ligand is coordinated to a lanthanide ion in a tetradentate fashion and (b) the coordination number of central earth ion is 5. The lanthanide ion would be outside of the porphyrin molecular plane.

3.6. Luminescence spectra

Table 5 gives the emission spectral data of the ligands and complexes. The emission spectra of ligand 12L and complex 12HoOH are shown in Fig. 3.

The near 651 nm bands of two ligands disappear. Other spectral bands undergo only a small change. There are fluorescence of the S_2 (B, Soret band) and S_1 (Q band) in porphyrin complexes. Fluorescence of the B (Soret) band is attributed to transition from the second excited singlet state S_2 to ground state $S_0, S_2 \rightarrow S_0$. The Soret fluorescence

 Table 5

 Emission spectral data of ligands and compounds

Compounds	Peak valu	ues (nm)	Quantum yields $(\Phi_{\rm f})$		
	Q(0-0)	Q(0-1)	Q(0-2)		
10L	601	651	717	0.02201	
12L	601	652	717	0.05847	
10ErOH	605	653	714	0.01661	
10HoOH	604	653	709	0.004570	
10DyOH	604	653	716	0.01306	
12YbOH	608	655	713	0.01075	
12ErOH	601	653	714	0.008707	
12HoOH	605	652	715	0.05605	

Table 4

Uv-visible spectral data of compounds

Compounds	λ_{\max} (nm)							
	B (Soret)	Ι	II	III	IV			
10L	417 (2.8 \times 10 ⁵)	516 (1.6×10^4)	550 (7.6×10^3)	590 (4.9×10^3)	$647 (3.9 \times 10^3)$			
12L	418 (2.5×10^5)	$515(9.6 \times 10^3)$	$550(4.9 \times 10^{3})$	590 (2.7×10^3)	$647(1.9 \times 10^{3})$			
10ErOH	$423(2.5 \times 10^5)$	$519(1.2 \times 10^{3})$	$552(8.7 \times 10^4)$	590 (2.3×10^4)	· · · · · · · · · · · · · · · · · · ·			
10HoOH	$421(2.9 \times 10^5)$	$516(4.0 \times 10^4)$	$552(1.6 \times 10^5)$	591 (4.2×10^4)				
10DyOH	418 (3.0×10^5)	516 (1.9×10^4)	$552(2.6 \times 10^4)$	591 (1.2×10^4)				
12YbOH	$422(2.7 \times 10^5)$	$515(8.1 \times 10^3)$	552 (1.8×10^4)	590 (8.0×10^3)				
12HoOH	421 (1.9 × 105)	515 (6.7 × 103)	552 (1.4 × 104)	591 (7.0 × 103)				

Molar extinction coefficient in parenthesis.

is about two orders of magnitude weaker than the $S_1 \rightarrow S_0$ of Q band emission. Its quantum yield is so low that sometimes fluorescence becomes unobservable. This fluor-



Fig. 3. Emission spectrum of 12L (--) and 12HoOH (.....).

escence emission does not occur yet at room temperature in our experimental excited wavelength, 415 nm. Q (0–0) fluorescence bands of the complexes are in the region 601–608 nm. Q (0–1) fluorescence bands of the complexes are in the region 651–655 nm and Q (0–2) bands 709–717 nm. They are mirror symmetric to the absorption spectra. Quantum yields (Φ_f) of Q band for the complexes are in the range 0.0045–0.056 and ligands 0.022–0.058. The S₁→S₀ quantum yield depends on the relative rates of the radiative process S₁→S₀ and two radiationless processes S₁MM→S₀ and S₁MM→Tn.

Compared the complexes with their ligands, quantum yields of complexes are much less than ligands. The fluorescence quantum yields of our complexes are much less than 0.20. Thus, the excited state of the complexes S_1 is primarily deactivated by radiationless decay. Therefore, spin-forbidden process S_1 was Tn is the predominant route for radiationless deactivation of S_1 in the complexes.

The mentioned above quantum yields (Φ_f) were calculated by the following equation:

$$\Phi_{\rm f} = \Phi_{\rm fs} n^2 A_{\rm s} I_{\rm f} / (n_{\rm s}^2 A I_{\rm fs}),$$



Fig. 4. SPS and EFISPS of 12L and 12HoOH. (a) EFISPS of 12HoOH. (b) SPS of 12HoOH. (c) EFISPS of 12L. (d) SPS of 12L.

where $n_{\rm s}$, $A_{\rm s}$ and $I_{\rm fs}$ are the refractive index, absorbance and integrated intensity of standard sample at excited wavelength, respectively. Meso-tetraphenylporphyrin Zinc, ZnTPP was used as standard sample, $\Phi_{\rm fs} = 0.033$ [15].

3.7. Surface photovoltaic spectroscopy (SPS) and electric field induced surface photovoltaic spectroscopy (EFISPS)

The SPS and EFISPS of the compounds 12L and 12HoOH are shown in Fig. 4. Their photovoltaic spectral bands are given in Table 6. It is found that the photovoltaic action spectra follow the absorption spectra response well, indicating that they are corresponding to similar electron transition process. Porphyrin molecule is of the conjugate π bonding system. The π -orbitals in porphyrins are analogous to valance of organic semiconductor, and its π^* orbital to the conduction band. Photogenerated charge carriers in the π system are non-localized, their motion is free in the valance band, while photo-generated electrons in the conduction band. In this kind of system, the band to band transition is characterized as a $\pi - \pi^*$ transition, exhibiting chiefly Soret (B) $(a_{2u}(\pi) \rightarrow e_g(\pi^*)$ transition) and Q $(a_{1u}(\pi) \rightarrow e_g(\pi^*)$ transition) bands. The surface photovoltaic (SPV) response band at 300-400 nm (P band) is corresponding to the higher energy level transition process, $b_{2u}(\pi) \rightarrow e_{\sigma}(\pi^*)$.

The photoexcitation and photogenerated charge transfer processes of the compounds are shown in Fig. 5, where $E_{\rm C}$, $E_{\rm v}$ and $E_{\rm f}$ are the minimum energy of the conduction band, the maximum energy of the valence band and the Fermi energy level, and $E_{\rm g}$ is the forbidden bandwidth, respectively [16]. The signal detected by surface photovoltage spectroscopy is equivalent to the change in the surface potential barrier on illumination: $\delta v_{\rm s} = v_{\rm s}^* - v_{\rm s}^0$, where $v_{\rm s}^*$ and $v_{\rm s}^0$ are the surface potential heights before and after illumination, respec-

Table 6 Spectral bands of SPS and EFISPS of the compounds

Compounds	External field voltage (V)	Maximum peaks (λ_{max}/nm)						
		P band		Soret (B) band	Q band			
12L	0	349	424	516	556	596	658	
	0.25	348	424	516	556	595	651	
	0.50	346	424	517	557	597	670	
	-0.25	344	423	517	558	597	660	
	-0.50	340	422	521	557	599	656	
12HoOH	0	328	433	515	557	598		
	0.125	327	432	513	561	601		
	0.25	331	423	516	560	601		
	0.50	332	428	519	562	601		
	-0.25	334	431	514	561	598		
	-0.50	332	431	515	561	601		
	-1.0	332	431	514	562	601		



Fig. 5. Photoexcitation and photogenerated charge transfer processes in the compounds.

tively. As far as band-to-band transitions are concerned, a positive response of the surface photovoltage ($\delta v_s > 0$) means that the sample is characterized as a P-type semiconductor [16].

Compared the SPS and EFISPS of two compounds, it can be found that there are two characterizations. One is that the SPV response intensities of P band of complex is larger than ligand, which indicated that the P band of the complex exhibits higher photo-electric conversion efficiency. On the other hand, the number of SPV response peaks of Q band decrease when the complex forms. This is the similar with behavior of Uv-visible spectrum. Increasing a positive electric field on ITO (indium tin oxide), photovoltaic response intensities of the complex and ligand are all enhanced, which demonstrates the external electric field is of the same sign as the build-in field. On the contrary, when a negative electric field is applied, photovoltaic response intensities are all increased. It can be seen that the Q and Soret bands of the ligand and complex exhibit a "simultaneous response" with change of positive and negative electric field, this indicates that they are corresponding to an analogous transition characteristic, both belonging to the π - π * transition. However, the variation rate of B and Q bands with change of positive and negative electric field is different. From above discussion, it can be found that P band is different from B and Q bands. P band is transition from the next highest occupied molecular orbital (NHOMO) to the lowest unoccupied molecular orbital (LUMO) transition, while B and Q bands arise from coupling of the two transitions between the highest occupied molecular orbital (HOMO) and LUMO [17].

3.8. LCs

Small-angle X-ray diffraction of 10L at room temperature is observed. The *d* spacing of the first three reflections are $d_{100} = 34.7$ Å, $d_{110} = 20.8$ Å, $d_{200} = 17.4$ Å. The ratios of the *d* spacing are 1:1/ $\sqrt{3}$:1/2, which corresponds to the first three reflections of a hexagonal columnar structure. We conclude that the mesophase structure is probably a hexagonal columnar discotic columnar, Col_h. Wide-angle X-ray diffraction of the compounds gave a broad peak (centered at $2\theta = 20^{\circ}$) due to the commonly seen liquid-like packing of alkyl chains in the mesophase. The X-ray diffraction results of other compounds are similar to those of 10L. The liquid crystalline phase of the ligands and complexes were characterized by differential scanning calorimetry (DSC). The DSC results of the ligands and complexes are summarized in Fig. 6. The transition temperature and enthalpies of the various porphyrin compounds are given in Table 7. Compared 12L with its lanthanide complexes, the LC phase of the complexes tends to room temperature, but enthalpy smaller than the ligand.

3.9. Cyclic voltammetry

Porphyrin ring has higher HOMO $3a_{2u}(\pi)$ and lower LUMO4e_g(π^*). It can occur to oxidation reaction in

HOMO and reduction reaction in LUMO. Cyclic voltammetric studies have been performed to evaluate the redox portentials and determine the HOMO-LUMO energy level. The electrochemical properties of two ligands and 10HoOH were studied in 0.1 M tetrabutylammonium perchlorate (TBAP) in DMF by cyclic voltammetry (CV). Within the accessible potential window of the solvent, two quasi-reversible redox processes of 10L, 12L and 10HoOH have been observed, respectively. The first and second redox potentials corresponding to the porphyrin ring reaction of 10L and 12L are located at $E_{1/2} = -1.712$, -2.314 and -1.720, -2.189 V v_s Ag/Ag^+ , respectively [18,19]. The corresponding potentials for the porphyrin ring reaction of 10HoOH are located at $E_{1/2} = -2.201$. The first redox potentials of 10HoOH concerning lanthanide metal ion are located at $E_{1/2} = -1.384 \text{ V} v_s \text{ Ag/Ag}^+$. Fig. 7 gives the cyclic voltammogram of 10HoOH.



Fig. 6. Differential scanning calorimetry of ligands and compounds. Black = solid phase, white = mesophase, gray = isotropic.

 Table 7

 Phase transition temperatures and enthalpy change of the porphyrin devirations

Compounds	$t/^{\circ}C (\Delta H/kJ mol^{-1})$						
10L	с —	35. 0(7.5)	17 9.0(16.0)				
121.	с —	63.3(67.4)	142. 0(6.0)				
10НоОН	с 🗕	42. 0(0.2)	55.3(1.4)				
122604	с 🗕	20. 0(0.3)	55. 3(7.6)				
125-04	с –	-77.0(3.2)	IL				
1221011		4.4(1.2)	37.9(0.2)				
12НоОН	С —	LC					

C = crystal, LC = liquid crystal, IL = isotropic liquid; Heating() crystal; Heating rate: 10°/min.



Fig. 7. Cyclic voltammogram of 10HoOH (DMF, room temperature, $[Bu_4N][ClO_4]$ as supporting electrolyte, Ag/Ag^+ electrode).

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Reference

- [1] B.A. Gregg, M.A. Fox, A.J. Bard, J. Am. Chem. Soc. 111 (1989) 3024.
- [2] D. Adam, P. Schuhmacher, J. Simmerer, et al., Nature 371 (1994) 141.
- [3] S.A. Hudson, P.M. Maitlis, Chem. Rev. 93 (1993) 861.
- [4] P. Espinet, M.A. Esteruelas, L.A. Oro, J.L. Serrano, E. Sola, Coord. Chem. Rev. 117 (1992) 215.
- [5] A.M. Giroud-Godquin, P.M. Maitlis, Angew. Chem., Int. Ed. Engl 30 (1991) 375.
- [6] J. Sokolnicki, R. Wiglusz, S. Radzki, A. Graczyk, J. Legendziewicz, Opt. Mater. 26 (2) (2004) 199.
- [7] R. Wiglusz, J. Legendziewicz, A. Graczyk, S. Radzki, P. Gawryszewska, J. Sokolnicki, J. Alloys Compounds 380 (1–2) (2004) 396.
- [8] J. Dargiewicz-Nowicka, M. Makarska, M.A. Villegas, J. Legendziewicz, St Radzki, J. Alloys Compounds 380 (1–2) (2004) 380.
- [9] M. Makarska, St Radzki, J. Legendziewicz, J. Alloys Compounds 341 (1–2) (2002) 233.
- [10] S. Radzki, J. Legendziewicz, J. Sokolnicki, R. Wiglusz, J. Alloys Compounds 300–301 (2000) 439.
- [11] L.N. Ji, X. Jia, Zhong Shan Da Xue Xue Bao 32 (1993) 1.
- [12] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.
- [13] G.F. Liu, T.S. Shi, Synth. React. Inorg. Met.-Org. Chem. 23 (1993) 1145.
- [14] G.F. Liu, T.S. Shi, Synth. React. Inorg. Met.-Org. Chem. 24 (1994) 1127.
- [15] D.J. Quimby, F.R. Longo, J. Am. Chem. Soc. 77 (1975) 5111.
- [16] D.J. Wang, W. Liu, L.Z. Xiao, J.T. Li, Chem. Bull. 10 (1989) 32.
- [17] Z.X. Zhao, T.F. Xie, G.F. Liu, Synth. Met. 33 (2001) 123.
- [18] R.H. Felton, H. Linschitz, J. Am. Chem. Soc. 88 (1966) 1113.
- [19] M.H. Qi, G.F. Liu, J. Phys. Chem. B, 107 (2003) 7640.