



Ionic Liquid Crystals with Hemicyanine Chromophores

K. BINNEMANS*, C. BEX and R. VAN DEUN

K.U. Leuven, Department of Chemistry, Coordination Chemistry Division, Celestijnenlaan 200F,
B-3001 Heverlee, Belgium

Abstract. The syntheses of (*E*)-*N*-alkyl-4-(2-(4-dimethylaminophenyl)ethenyl) pyridinium bromides (hemicyanine bromides) with C₁₄, C₁₆ and C₁₈ straight alkyl chains are described. The thermal behaviour of these compounds was investigated by differential scanning calorimetry (DSC) and by optical microscopy. The textures observed in polarised light revealed that these compounds exhibit a smectic A mesophase. A focal-conic fan texture was observed, together with regions showing homeotropic alignment. The phase behaviour of the compound with the C₁₆ chain can be summarized as: Cr₁·99·Cr₂·249·SmA·268·I (dec.). The transition temperatures are rather independent of the length of the alkyl chain. The compounds have a strong tendency to supercool to a glassy mesophase. A structural model for the mesophase is proposed. The bromide anion of the hemicyanine bromides can be replaced by the bulky tetrakis(β-diketonato)lanthanide(III) anion. As the β-diketone, 2,4-pentanedione (acetylacetone, acac) and 1,3-diphenyl-1,3-propanedione (dibenzoylmethane, DBM) are chosen. None of the lanthanide complexes containing the hemicyanine chromophore shows a mesophase. The complexes either melt directly to an isotropic liquid, or decompose without melting.

Key words: liquid crystals, hemicyanine, lanthanides, rare earths, β-diketone, metallomesogens, glassy mesophase.

1. Introduction

Compounds with a hemicyanine (aminostyrylpyridinium) chromophore are well-known as dyes [1]. Hemicyanine dyes exhibit a large charge separation between the ground state and the excited state. This charge separation is an indication for a large polarisability. The dyes have non-linear optical properties, such as generation of the second and third harmonics. These non-linear optical effects can be observed both in solution and in organised systems (in Langmuir–Blodgett films or in single crystals). The hemicyanine dyes are therefore candidates for the development of optical data storage systems or molecular switches [2, 3]. The non-linear optical properties of hemicyanine compounds with halogenide counter-ions were investigated by Bruce *et al.* [4], Lupo *et al.* [5] and by Grummt *et al.* [6]. Wang *et al.* [7]

* Author for correspondence. Tel.: +32 16 32 74 46; Fax: +32 16 32 79 92;
E-mail: Koen.Binnemans@chem.kuleuven.ac.be

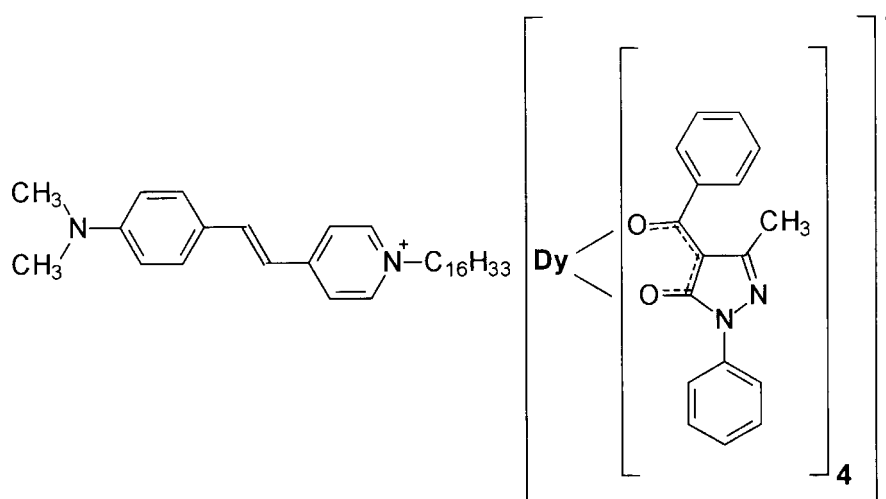


Figure 1. Structure of a hemicyanine compound with a dysprosium-containing coordination complex as the counter-ion [8].

synthesized a hemicyanine compound with a lanthanide coordination complex as the counter-ion instead of the halogenide (Figure 1).

The use of the dysprosium complex as the counter-ion not only improved the film-forming properties, but also resulted in a better charge separation in the hemicyanine chromophore. The Dy-complex has a high value for the hyperpolarisability β . Several examples of analogous lanthanide complexes with the hemicyanine chromophore are described in the literature [8–14]. In 1995, Wang *et al.* [15] reported the mesomorphic properties of the hemicyanine bromide (*E*)-*N*-hexadecyl-4-(2-(4-dimethylaminophenyl)ethenyl)pyridinium bromides and of the lanthanide complexes (*E*)-*N*-hexadecyl-4-(2-(4-(dimethylamino)phenyl)ethylen)pyridinium tetrakis(1-phenyl-3-methyl-4-benzoyl-5-pyrazolonato)lanthanide(III) (where the lanthanide(III) was La(III), Nd(III), Dy(III) or Yb(III)). Inspired by this work, we wanted to develop new lanthanide-containing metallomesogens. The basic idea was to substitute the bromide ion in the hemicyanine bromide by a negatively charged tetrakis(β -diketonato) lanthanide(III) complex (Figure 2). Since the type of β -diketone and the terminal alkyl groups of the hemicyanine can be varied, this approach seemed very promising for fine-tuning the mesomorphic properties of the lanthanide complexes. This could open the door for replacement of the tetrakis(β -diketonato) lanthanide(III) complex as the anion by other negatively charged lanthanide complexes.

In this paper, we describe the synthesis and the mesomorphic properties of the (*E*)-*N*-alkyl-4-(2-(4-dimethylaminophenyl)ethenyl) pyridinium bromides (hemicyanine bromides) with C_{14} , C_{16} and C_{18} straight alkyl chains (**4–6**). The mesophases are studied by differential scanning calorimetry and by optical microscopy. It will be shown that these compounds show a different thermal behaviour than

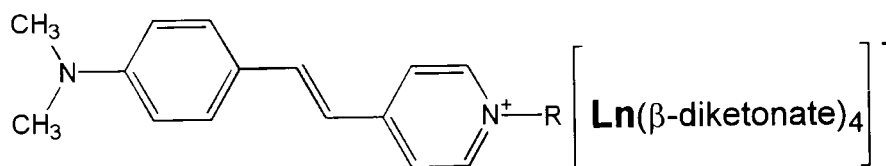


Figure 2. General structure of hemicyanine compounds with tetrakis(β -diketonato)-lanthanide(III) anions.

that described by Wang *et al.* [15]. In particular, the transition temperatures were interpreted incorrectly. The bromide anion of the hemicyanine bromides is replaced by the bulky tetrakis(β -diketonato)lanthanide(III) anions. As the β -diketone, 2,4-pentanedione (acetylacetone, acac) and 1,3-diphenyl-1,3-propanedione (dibenzoylmethane, DBM) are used. We have chosen elements of the middle of the lanthanide series (europium, gadolinium and terbium). The thermal behaviour of these lanthanide-containing coordination complexes is discussed.

2. Experimental

General: ^1H NMR spectra were recorded on either a Bruker WM 250 (250 MHz) or a Bruker AMX 400 spectrometer (400 MHz). ^{13}C NMR spectra were obtained on a Bruker AMX 400 spectrometer (100.6 MHz). CDCl_3 was used as the solvent and tetramethylsilane (TMS) as internal standard. The δ -values are expressed in ppm. IR spectra were recorded on a Bruker FTIR spectrometer IFS66. KBr-pellets of the samples were used for the FTIR-spectra. The following abbreviations are used for the IR band intensities: *w* = weak, *m* = medium, *s* = strong, *sh* = shoulder. Low resolution electron impact mass spectra were obtained on a Hewlett-Packard 5989A mass spectrometer (ionisation potential 70 eV). CHN microanalysis data were obtained at the Universities of Exeter (UK) or Sheffield (UK). Transition temperatures were determined by differential scanning calorimetry (DSC) with a Mettler-Toledo DSC821e module. The samples were sealed in 40 μL aluminium crucibles with a pierced lid. The thermograms were recorded in a dry nitrogen atmosphere. The samples were heated or cooled at a constant rate of 10 $^\circ\text{C min}^{-1}$. The DSC-apparatus was calibrated using an indium standard ($T_m = 156.6$ $^\circ\text{C}$; $\Delta H_m = 28.45$ J g^{-1}). Unless otherwise mentioned, onset temperatures are reported. Optical textures of the mesophases were observed with an Olympus BX60 polarising microscope with a Linkam TMS600 hot stage and a Linkam TMS93 temperature-controller. All chemicals were used as received, without further purification. Organic reagents were obtained from ACROS. Hydrated rare earth chlorides or nitrates were purchased from Aldrich.

2.1. SYNTHESIS

1-Tetradecyl-4-methylpyridinium bromide 1

Heat a mixture of 4-picoline (0.20 mol, 18.63 g) and 1-bromotetradecane (0.22 mol, 61.00 g) at reflux over 24 hours in absolute ethanol (30 mL). Cool the mixture to ambient temperature, filter on a Büchner funnel and wash with diethyl ether (75 mL). Recrystallize the crude product twice from diethyl ether: ethanol. Filter the purified product and wash with diethyl ether (2×100 mL). Dry in vacuo. Product **1** was obtained as white crystals in 83% yield (61.8 g). – ^1H NMR (δ , CDCl_3 , 400 MHz): 0.86 (t, 3H, CH_3), 1.27 (m, 22H, $(\text{CH}_2)_{11}$), 2.00 (quintet, 2H, CH_2), 2.67 (s, 3H, CH_3 -aryl), 4.92 (t, 2H, N^+CH_2 —), 7.89 (d, 2H, H-aryl, $J_0 = 6.5$ Hz), 9.31 (d, 2H, H-aryl, $J_0 = 6.5$ Hz). – ^{13}C NMR (δ , CDCl_3 , 100.6 MHz): 14.05 (CH_3), 22.21 (CH_3), 22.63 (CH_2), 26.03 (CH_2), 29.04 (CH_2), 29.29 (CH_2), 29.31 (CH_2), 29.46 (CH_2), 29.54 (CH_2), 29.58 (CH_2), 29.61 (CH_2), 31.81 (CH_2), 31.86 (CH_2), 61.29 (N^+CH_2), 128.76 (aryl-C), 144.21 (aryl-C), 158.72 (quat. C). – IR (cm^{-1} , KBr): 3018 (w), 2912 (s), 2845 (s), 1638 (s), 1570 (s), 1520 (m), 1472 (s), 1379 (m), 1320 (w), 1170 (m), 1044 (m), 827 (m), 721 (m), 551 (w). – m.p. 77 °C (diethyl ether: ethanol). – Anal. $\text{C}_{20}\text{H}_{36}\text{BrN}$ ($M_w = 370.42$ g mol $^{-1}$): Found C, 64.61; H, 10.22; N, 3.61%. Calc. C, 64.85; H, 9.80; N, 3.78%.

1-Hexadecyl-4-methylpyridinium bromide 2

Same procedure as for **1**, but with 1-bromohexadecane (0.22 mol, 67.17 g). Product **2** was obtained as white crystals in 85% yield (67.8 g). – ^1H NMR (δ , CDCl_3 , 250 MHz): 0.89 (t, 3H, CH_3), 1.26 (m, 26H, $-(\text{CH}_2)_{13}$), 2.04 (m, 2H, CH_2), 2.69 (s, 3H, CH_3 -aryl), 4.92 (t, 2H, N^+CH_2 —), 7.94 (d, 2H, H-aryl, $J_0 = 6$ Hz), 9.39 (d, 2H, H-aryl, $J_0 = 6$ Hz). IR (cm^{-1} , KBr): 3009 (m), 2913 (s), 2846 (s), 1639 (s), 1568 (w), 1519 (m), 1470 (s), 1383 (w), 1322 (w), 1176 (m), 1045 (w), 974 (w), 821 (m), 713 (m), 555 (w). – m/z (EI, $M^+ = \text{C}_{22}\text{H}_{40}\text{N}^+$): 319 ($[\text{M} + 1]^+$, 4), 318 (M^+ , 25), 317 ($M^+ - 1\text{H}$, 97), 316 ($M^+ - 2\text{H}$, 44), 107 ($M^+ - \text{C}_{15}\text{H}_{31}$, 100). – m.p. 83 °C (diethyl ether: ethanol). – Anal. $\text{C}_{22}\text{H}_{40}\text{BrN}$ ($M_w = 398.47$ g mol $^{-1}$): Found C, 66.20; H, 10.32; N, 3.37%. Calc. C, 66.31; H, 10.12; N, 3.52%.

1-Octadecyl-4-methylpyridinium bromide 3

Same procedure as for **1**, but with 1-bromooctadecane (0.22 mol, 73.35 g). Product **3** was obtained as white crystals in 95% yield (81.4 g). – ^1H NMR (δ , CDCl_3 , 400 MHz): 0.86 (t, 3H, CH_3), 1.26 (m, 30H, $-(\text{CH}_2)_{15}$), 2.10 (quintet, 2H, CH_2), 2.67 (s, 3H, CH_3 -aryl), 4.92 (t, 2H, N^+CH_2 —), 7.90 (d, 2H, H-aryl, $J_0 = 6.5$ Hz), 9.34 (d, 2H, H-aryl, $J_0 = 6.5$ Hz). – ^{13}C NMR (δ , CDCl_3 , 100.6 MHz): 14.03 (CH_3), 22.19 (CH_3), 22.60 (CH_2), 26.01 (CH_2), 29.03 (CH_2), 29.27 (CH_2), 29.31 (CH_2), 29.45 (CH_2), 29.53 (CH_2), 29.58 (CH_2), 29.62 (CH_2), 31.80 (CH_2), 31.84 (CH_2), 61.21 (N^+CH_2), 128.77 (aryl-C), 158.68 (quat. C). – IR (cm^{-1} , KBr): 3041 (w), 2910 (s), 2845 (s), 1640 (s), 1574 (w), 1516 (m), 1467 (s), 1370 (w), 1317 (w), 1171 (m), 1042 (w), 825 (m), 715 (m), 546 (w). – m/z (EI, $M^+ = \text{C}_{24}\text{H}_{44}\text{N}^+$): 347 ($[\text{M} + 1]^+$, 6), 346 (M^+ , 32), 345 ($M^+ - 1\text{H}$, 100), 344 ($M^+ - 2\text{H}$, 53), 93 ($M^+ - \text{C}_{18}\text{H}_{37}$,

16). – m.p. 93 °C (recrystallized from diethyl ether: ethanol). – Anal. C₂₄H₄₄BrN (M_w = 426.52 g mol⁻¹): Found C, 67.34; H, 10.31; N, 3.23%. Calc. C, 67.58; H, 10.40; N, 3.28%.

(E)-N-tetradecyl-4-(2-(4-dimethylaminophenyl)ethenyl) pyridinium bromide 4

Add piperidine (5 mL) to a mixture of **1** (0.05 mol, 18.52 g) and 4-dimethylaminobenzaldehyde (0.05 mol, 7.46 g) in absolute ethanol (75 mL). Reflux for 4 hours with stirring and under dry nitrogen atmosphere. Cool the mixture to ambient temperature and chill in a salted ice bath. Filter the precipitate and wash with cold absolute ethanol (2 × 50 mL). Recrystallize twice from a ethanol:heptane (1 : 1) mixture, filter and wash with cold absolute ethanol (2 × 20 mL). Product **4** was obtained as an orange-red crystalline powder in 58% yield (14.5 g). – ¹H NMR (δ, CDCl₃, 400 MHz): 0.88 (t, 3H, CH₃), 1.28 (m, 22H, (CH₂)₁₁), 1.92 (quintet, 2H, CH₂), 3.06 (s, 6H, (CH₃)₂N), 4.64 (t, 2H, N⁺CH₂), 6.67 (d, 2H, aryl-H, J₀ = 9 Hz), 6.85 (d, 1H, —CH=, J_{trans} = 16 Hz), 7.51 (d, 2H, H-aryl, J₀ = 9 Hz), 7.67 (d, 1H, —CH=, J_{trans} = 16 Hz), 7.87 (d, 2H, aryl-H, J₀ = 7 Hz), 8.94 (d, 2H, H-aryl, J₀ = 7 Hz). – ¹³C NMR (δ, CDCl₃, 100.6 MHz): 14.14 (CH₃), 22.72 (CH₂), 26.17 (CH₂), 29.15 (CH₂), 29.39 (CH₂), 29.43 (CH₂), 29.56 (CH₂), 29.64 (CH₂), 29.68 (CH₂), 29.72 (CH₂), 31.68 (CH₂), 31.95 (CH₂), 40.14 ((CH₃)₂N), 60.37 (N⁺CH₂), 112.02, 116.49, 122.44, 122.82, 130.73, 143.03, 143.48, 152.40 (quat. C), 154.20 (quat. C). – IR (cm⁻¹, KBr): 3019 (w), 2912 (s), 2848 (s), 1639 (s, alkene C=C), 1569 (w, aryl C=C), 1517 (m, aryl C=C), 1466 (s), 1376 (w), 1319 (w), 1179 (m), 1042 (m), 826 (m), 708 (m), 553 (w). – m/z (EI, M⁺ = C₂₉H₄₅N₂⁺): 423 ([M + 2]⁺, 27), 422 ([M + 1]⁺, 92), 421 (M⁺, 80), 420 (M⁺-1H, 18), 224 (M⁺-C₁₄H₂₉, 100). Anal. C₂₉H₄₅BrN₂ (M_w = 501.59 g mol⁻¹): Found C, 69.05; H, 9.38; N, 5.20%. Calc. C, 69.44; H, 9.04; N, 5.58%.

(E)-N-hexadecyl-4-(2-(4-dimethylaminophenyl)ethenyl) pyridinium bromide 5

Same procedure as for **4**, but now starting with **2** (0.05 mol, 19.92 g). Product **5** was obtained as a orange-red crystalline powder in 71% yield (18.8 g). – ¹H NMR (δ, CDCl₃, 400 MHz): 0.87 (t, 3H, CH₃), 1.26 (m, 26H, (CH₂)₁₃), 1.93 (quintet, 2H, CH₂), 3.06 (s, 6H, (CH₃)₂N), 4.64 (t, 2H, N⁺CH₂), 6.68 (d, 2H, aryl-H, J₀ = 9 Hz), 6.86 (d, 1H, —CH=, J_{trans} = 16 Hz), 7.52 (d, 2H, H-aryl, J₀ = 9 Hz), 7.62 (d, 1H, CH=, J_{trans} = 16 Hz), 7.88 (d, 2H, aryl-H, J₀ = 7 Hz), 8.94 (d, 2H, H-aryl, J₀ = 7 Hz). – ¹³C NMR (δ, CDCl₃, 100.6 MHz): 14.10 (CH₃-), 22.60 (CH₂), 26.10 (CH₂), 29.05 (CH₂), 29.30 (CH₂), 29.35 (CH₂), 29.50 (CH₂), 29.55 (CH₂), 29.60 (CH₂), 29.65 (CH₂), 31.60 (CH₂), 31.9 (CH₂), 40.1 ((CH₃)₂N), 60.2 (N⁺CH₂), 111.9, 116.3, 122.2, 122.7, 130.6, 142.9, 152.2 (quat. C), 154.0 (quat. C). – IR (cm⁻¹, KBr): 3000 (w), 2912 (s), 2852 (m), 1641 (m, alkene C=C), 1591 (s, aryl C=C), 1526 (s, aryl C=C), 1467 (m), 1430 (m), 1362 (m), 1330 (m), 1161 (s), 827 (w), 717 (w), 518 (w). – m/z (EI, M⁺ = C₃₁H₄₉N₂⁺): 451 ([M + 1]⁺, 7), 450 (M⁺, 5), 448 (M⁺-1H, 2), 225 (M⁺-C₁₆H₃₂, 18), 224 (M⁺-C₁₆H₃₃, 100), 223 (M⁺-C₁₆H₃₄,

52). – Anal. $C_{31}H_{49}BrN_2$ ($M_w = 529.65$ g mol⁻¹): Found C, 69.94; H, 9.75; N, 4.88%. Calc. C, 70.30; H, 9.32; N, 5.29%.

(E)-N-octadecyl-4-(2-(4-dimethylaminophenyl)ethenyl) pyridinium bromide 6

Same procedure as for **4**, but now starting with **3** (0.05 mol, 21.33 g). Product **6** was obtained as a orange-red crystalline powder in 74% yield (20.6 g). – ¹H NMR (δ , CDCl₃, 400 MHz): 0.88 (t, 3H, CH₃), 1.24 (m, 30H, (CH₂)₁₅), 1.95 (quintet, 2H, CH₂), 3.06 (s, 6H, (CH₃)₂N), 4.65 (t, 2H, N⁺CH₂), 6.67 (d, 2H, aryl-H, $J_0 = 9$ Hz), 6.85 (d, 1H, —CH=, $J_{trans} = 16$ Hz), 7.52 (d, 2H, H-aryl, $J_0 = 9$ Hz), 7.67 (d, 1H, —CH=, $J_{trans} = 16$ Hz), 7.88 (d, 2H, aryl-H, $J_0 = 7$ Hz), 8.94 (d, 2H, H-aryl, $J_0 = 7$ Hz). – ¹³C NMR (δ , CDCl₃, 100.6 MHz): 14.05 (CH₃-), 22.62 (CH₂), 26.08 (CH₂), 29.05 (CH₂), 29.30 (CH₂), 29.34 (CH₂), 29.47 (CH₂), 29.56 (CH₂), 29.60 (CH₂), 29.65 (CH₂), 31.58 (CH₂), 31.86 (CH₂), 40.04 ((CH₃)₂N), 60.27 (N⁺CH₂), 111.92, 116.39, 122.35, 122.71, 130.63, 142.93, 143.38, 152.3 (quat. C), 154.09 (quat. C). – IR (cm⁻¹, KBr): 3009 (w), 2912 (s), 2852 (m), 1641 (m, alkene C=C), 1592 (s, aryl C=C), 1530 (m, aryl C=C), 1469 (m), 1434 (w), 1368 (m), 1328 (m), 1161 (m), 831 (w), 716 (w), 549 (w). – m/z (EI, M⁺ = C₃₃H₅₃N₂⁺): 478 ([M + 1]⁺, 100), 477 (M⁺, 77), 476 (M⁺-1H, 14), 237 (M⁺-C₁₇H₃₆, 14), 225 (M⁺-C₁₈H₃₆, 31), 224 (M⁺-C₁₈H₃₇, 81), 223 (M⁺-C₁₈H₃₈, 47). – Anal. C₃₃H₅₃BrN₂ ($M_w = 557.70$ g mol⁻¹): Found C, 70.29; H, 9.81; N, 4.98%. Calc. C, 70.07; H, 9.58; N, 5.02%.

(E)-N-hexadecyl-4-(2-(4-dimethylaminophenyl)ethenyl) pyridinium tetrakis(1,3-diphenyl-1,3-propanedionato) europium(III) 7

Add an aqueous NaOH solution (8 mmol) to a stirred hot ethanolic solution (70 mL) of 1,3-diphenyl-1,3-propanedione (8 mmol, 1.79 g) and EuCl₃ · 6H₂O (2 mmol, 0.73 g) and hemicyanine bromide **2** (2 mmol, 1.06 g). A crystalline precipitate is formed. Reflux for 30 min with stirring. Cool the mixture to ambient temperature and chill in a salted ice bath. Filter the precipitate and wash the precipitate with cold ethanol (2 × 50 mL). Recrystallize the product from ethanol:water (1 : 1). Dry in vacuo. Yield: 78% (2.34 g). – IR (cm⁻¹, KBr) 3065 (w), 2922 (m), 2845 (m), 1648 (w, alkene C=C stretch), 1592 (s, C=O stretch), 1553 (s, aryl C=C stretch), 1514 (s, C=C stretch of β -diketone), 1467 (s), 1423 (s), 1367 (m), 1307 (m), 1285 (m), 1216 (m), 1160 (m), 1064 (m), 1025 (m), 948 (w), 723 (m), 688 (m), 606 (m), 507 (w). – Anal. C₉₁H₉₃N₂O₈Eu ($M_w = 1494.62$ g mol⁻¹): Found C, 72.62; H, 6.04; N, 1.81; Eu 10.67%. Calc. C, 73.12; H, 6.27; N, 1.87; Eu, 10.17%.

(E)-N-hexadecyl-4-(2-(4-dimethylaminophenyl)ethenyl) pyridinium tetrakis(1,3-diphenyl-1,3-propanedionato) gadolinium(III) 8

Some procedure as for **7**, but using Gd(NO₃)₃·5H₂O (2 mmol, 0.87 g). Yield: 72% (2.20 g). – IR (cm⁻¹, KBr) 3057 (w), 2928 (w), 2850 (w), 1645 (w, alkene C=C stretch), 1592 (s, C=O stretch), 1554 (s, aryl C=C stretch), 1516 (s, C=C stretch of β -diketone), 1463 (s), 1424 (s), 1367 (w), 1309 (w), 1286 (w), 1214 (w), 1165

(m), 1065 (w), 1022 (w), 955 (w), 720 (m), 680 (m), 604 (w), 513 (w). – Anal. $C_{91}H_{93}N_2O_8Gd$ ($M_w = 1499.91 \text{ g mol}^{-1}$): Found C, 72.87; H, 5.99; N, 1.73%. Calc. C, 72.47; H, 6.25; N, 1.87%.

(E)-N-hexadecyl-4-(2-(4-dimethylaminophenyl)ethenyl) pyridinium tetrakis(1,3-diphenyl-1,3-propanedionato) terbium(III) 9

Some procedure as for **7**, but using $TbCl_3 \cdot 6H_2O$ (2 mmol, 0.75 g). Yield: 54% (1.61 g). – IR (cm^{-1} , KBr) 3056 (w), 2923 (m), 2855 (m), 1641 (w, alkene C=C stretch), 1595 (s, C=O stretch), 1556 (s, aryl C=C stretch), 1517 (s, C=C stretch of β -diketone), 1466 (s), 1426 (s), 1405 (m), 1308 (w), 1283 (w), 1218 (w), 1163 (m), 1060 (w), 1022 (w), 942 (w), 719 (m), 692 (m), 605 (w), 511 (w). – Anal. $C_{91}H_{93}N_2O_8Tb$ ($M_w = 1501.58 \text{ g mol}^{-1}$): Found C, 72.44; H, 5.98; N, 1.76; Tb 11.05%. Calc. C, 72.79; H, 6.24; N, 1.87; Tb, 10.58%.

(E)-N-hexadecyl-4-(2-(4-dimethylaminophenyl)ethenyl) pyridinium tetrakis(2,4-pentanedionato) europium(III) 10

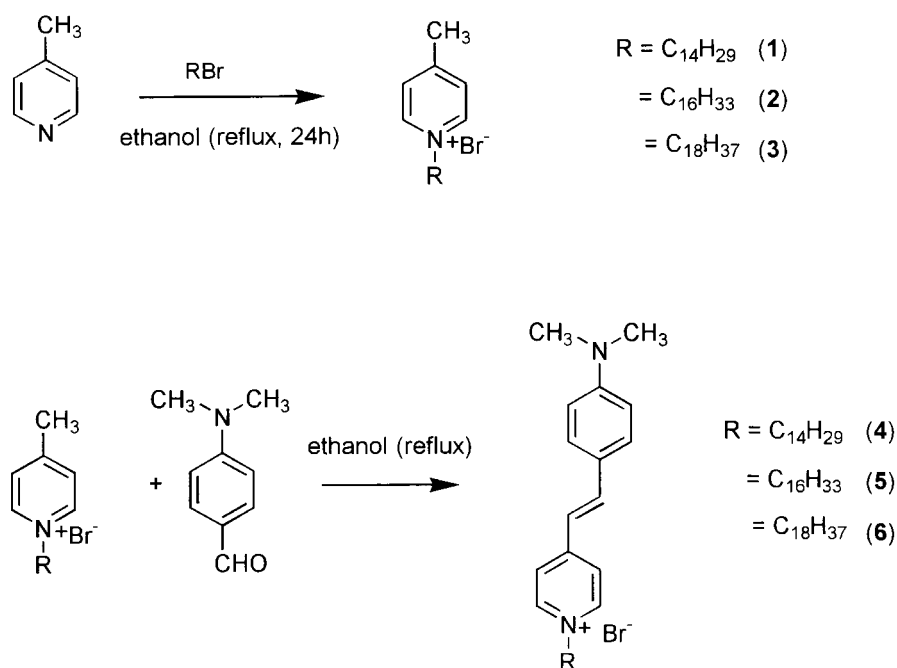
Add NaOH (8 mmol), hemicyanine bromide **2** (2 mmol, 1.06 g) and $EuCl_3 \cdot 6H_2O$ (2 mmol, 0.73 g) to a solution of 2,4-pentanedione (8 mmol, 0.80 g) in ethanol (40 mL). Reflux for 30 min with stirring. Cool the mixture to ambient temperature, and chill in a salted ice bath. Filter the precipitate on a Büchner funnel and wash the precipitate with cold absolute ethanol ($2 \times 20 \text{ mL}$) and with chloroform ($2 \times 20 \text{ mL}$). Dry in vacuo. Yield: 76% (1.51 g). \times IR (cm^{-1} , KBr): 3076 (w), 2998 (w), 2958 (w), 2919 (m), 2850 (m), 1647 (sh, alkene C=C stretch), 1598 (s, C=O stretch), 1551 (w, aryl, C=C stretch), 1520 (s, C=C stretch of β -diketone), 1467 (s), 1413 (s), 1258 (m), 1193 (w), 1167 (m), 1016 (m), 917 (m), 763 (w), 657 (w), 532 (w). Anal. $C_{51}H_{77}N_2O_8Eu$ ($M_w = 998.15 \text{ g mol}^{-1}$): Found C, 72.62; H, 6.04; N, 1.81; Eu 15.55%. Calc. C, 73.13; H, 6.27; N, 1.87; Eu 15.22%.

(E)-N-hexadecyl-4-(2-(4-dimethylaminophenyl)ethenyl) pyridinium tetrakis(2,4-pentanedionato) terbium(III) 11

The same procedure as for complex **10**, but using $Tb(NO_3)_3 \cdot 5H_2O$ (2 mmol, 0.87 g). Yield: 67% (1.35 g). – IR (cm^{-1} , KBr): 3078 (w), 2990 (w), 2962 (w), 2921 (w), 2852 (w), 1647 (sh, alkene C=C stretch), 1603 (s, C=O stretch), 1552 (m, aryl, C=C stretch), 1521 (s, C=C stretch of β -diketone), 1471 (s), 1407 (s), 1257 (s), 1197 (w), 1161 (w), 1015 (s), 920 (s), 761 (m), 660 (w), 528 (m). – Anal. $C_{51}H_{77}N_2O_8Tb$ ($M_w = 1005.11 \text{ g mol}^{-1}$): Found C, 72.44; H, 5.98; N, 1.76%. Calc. C, 72.79; H, 6.24; N, 1.87%.

3. Synthesis

The hemicyanine bromides **4–6** were synthesized by a two-step reaction (Scheme 1). During the first step, 4-Picoline was refluxed with the *n*-bromoalkane in ethanol. The crude products were recrystallized twice from a diethyl ether: ethanol



Scheme 1.

mixture. The 1-alkyl-4-methylpyridinium bromides **1–3** were condensed with 4-dimethylamino-benzaldehyde via a Knoevenagel-type reaction. The reagents were heated in absolute ethanol with piperidine as the catalyst. The crude hemicyanine bromide was recrystallized twice from an ethanol : hexane mixture. Only the trans-product (*E*) was formed. There is no evidence for the formation of the cis-isomer, probably because of steric hindrance by the aromatic groups. The 1-alkyl-methylpyridinium bromides are white powders; whereas, the hemicyanine bromides have a very intense orange-red colour. The products were characterized by NMR, IR-spectroscopy, mass spectrometry and by CHN microanalysis.

The lanthanide complexes **7–11** were formed by reaction of the hemicyanine bromides **4–6** with either the β -diketones 2,4-pentanedione (acetylacetone, acac) or 1,3-diphenyl-1,3-propanedione (dibenzoylmethane, DBM). First, the β -diketone was deprotonated by an equivalent amount of NaOH, then, the hemicyanine bromide and a lanthanide salt were added. The molar ratio β -diketone: hemicyanine bromide: lanthanide salt was 4 : 1 : 1. For the lanthanide salt, one can use the hydrated nitrate or chloride salt. All the reactions were done in ethanol. The complexes of DBM were recrystallized from either acetone:2-butanone (1 : 1) or ethanol:water (1 : 1). The acac complexes were washed twice with cold ethanol and then cold chloroform. The lanthanide complexes were characterized by CHN microanalysis and by IR-spectroscopy. The lanthanide content was determined gravimetrically as the 8-hydroxyquinoline complex. The analyses revealed that the

complexes are anhydrous and that four β -diketone ligands and one hemicyanine group are present for each lanthanide ion.

4. Mesomorphic Properties

Wang *et al.* [15] described the mesomorphic properties of the hemicyanine bromide **5**. According to these authors the compound melts at 96.3 °C and the clearing point is 246.3 °C, and that it is an enantiotropic liquid crystal. The focal conic texture indicated the presence of a smectic mesophase. The DSC-curve of **5** synthesized by us shows three endothermic peaks in the first heating cycle, at 99 °C, 249 °C and at 268 °C. After the second peak, an increase of the baseline is observed, due to decomposition of the product. No further peaks are observed in subsequent heating and cooling cycles. Investigation of the optical textures by polarising microscopy revealed that the transition at 99 °C is not the melting peak, but a crystal-crystal transition ($Cr_1 \rightarrow Cr_2$). No textural change of the solid compound could be observed. The second peak in the thermogram at 249 °C corresponds to the melting peak. The melt is anisotropic indicating the presence of a mesophase. The third peak at 268 °C is the clearing point. When cooling from the isotropic melt, a mesophase is again formed. The texture is the focal conic fan texture, typical for a smectic mesophase. Because the texture formed by a thin film of the mesophase between untreated microscope slides exhibits both extinct regions (homeotropic alignment) and regions with a fan-like texture (homogeneous alignment), we can conclude that the mesophase is a smectic A mesophase (SmA). At the clearing points, the formation of gas bubbles is observed in the melt, so that its decomposition is not only evident from the increase of the baseline in the DSC-thermogram, but also by visual observation under the microscope. When the melt is cooled, the texture formed in the mesophase is retained, even if the product has solidified. Thus, the mesophase is frozen into a glassy state. We would like to indicate that an anisotropic glass is formed. Ionic mesogens, and in particular ionic metallomesogens show a strong tendency to form glassy mesophases [16]. The other hemicyanine bromides have an analogous thermal behaviour with very comparable transition temperatures.

The metal complexes **7–11** formed by replacing the bromide ion of the hemicyanine bromides **4–6** by the bulky tetrakis(β -diketonato)lanthanide(III) anion do not show mesophases. The complexes with the DBM ligand (**7–9**) have a single melting point; whereas the complexes with acac decompose at the melting point (Eu-complex **10**) or decompose without melting (Tb-complex **11**). Ionic liquid crystals have a strong tendency to form smectic mesophases, because of the electrostatic attraction. Therefore, the formation of a smectic A mesophase by the hemicyanine bromides **4–6** is explainable. However, the lanthanide-containing anions are too bulky to maintain the organization of the cationic hemicyanine molecules in layers and with their molecular long axis parallel to each other. Because of the absence of the necessary conditions for molecular organization, no mesophase can be

Table I. Thermal behaviour of the hemicyanine bromides **4–6** and of the lanthanide complexes **7–11**

| Compound ^a | Transition temperatures (°C) (and enthalpies ΔH in kJ mol ⁻¹) ^b |
|--|--|
| 4 | Cr ₁ ·99 (28.4)·Cr ₂ ·251 (12.1)·SmA·265 (28.8)·I (dec.) |
| 5 | Cr ₁ ·99 (36.5)·Cr ₂ ·249 (13.4)·SmA·268 (10.6)·I (dec.) |
| 6 | Cr ₁ ·100 (32.7)·Cr ₂ ·255 (13.1)·SmA·271 (14.4)·I (dec.) |
| Eu(DBM) ₄ L ⁵ (7) | Cr ₁ ·112 (20.5)·Cr ₂ ·202 (46.8)·I |
| Gd(DBM) ₄ L ⁵ (8) | Cr ₁ ·112 (23.3)·Cr ₂ ·206 (51.8)·I |
| Tb(DBM) ₄ L ⁵ (9) | Cr ₁ ·116 (5.4)·Cr ₂ ·206 (43.0)·I |
| Eu(acac) ₄ L ⁵ (10) | Cr·226·I (dec.) |
| Tb(acac) ₄ L ⁵ (11) | (dec. without melting) |

^a L⁵: cation of compound **5**. acac = acetylacetone, DBM = dibenzoylmethane.

^b Abbreviations: Cr₁, Cr₂: solid state phases; SmA: smectic A mesophase; I: isotropic liquid; dec.: decomposition.

formed. Even with small β -diketones, e.g., acac and DBM the anionic tetrakis (β -diketonato) lanthanide(III) complexes are too voluminous and no mesophases are observed. Therefore, it is bizarre that Wang *et al.* [15] describe mesophases formed by complexes where the pyrazolon 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one is used as the ligand instead of a smaller β -diketone. However, we were able to show that the lanthanide complexes synthesized by Wang *et al.* do not form mesophases. These results were published elsewhere [17]. The thermal behaviour of the hemicyanine bromides **4–6** and of the lanthanide complexes **7–11** are summarized in Table I.

5. Conclusions

The (*E*)-*N*-alkyl-4-(2-(4-dimethylaminophenyl)ethenyl) pyridinium bromides (hemicyanine bromides) with C₁₄, C₁₆ and C₁₈ straight alkyl chains (**4–6**) show a smectic A (SmA) mesophase. The transition temperatures are virtually independent of the length of the alkyl chain. The transition temperatures of hemicyanine bromide with C₁₆-chain (**5**) differ from the temperatures reported earlier by Wang *et al.* [15]. Their disadvantage is that they melt at high temperature (ca. 250 °C) and that they decompose in the mesophase stability range when heated for too long a time. However, the mesophase can be frozen into a glassy state. The lanthanide complexes (**7–11**) formed by replacing the bromide anion of the hemicyanine bromide by a tetrakis(β -diketonato)lanthanide(III) anion do not exhibit a mesophase. The complexes melt directly to the isotropic liquid or decompose without melting.

Acknowledgements

KB is Postdoctoral Fellow of the F.W.O.-Flanders (Belgium). He thanks the F.W.O. for a “Krediet aan Navorsers” and Prof. C. Görrler-Walrand for providing laboratory facilities (GOA 98/03 and F.W.O. research grant G.0124.95). RVD (specialisatiebursaal IWT) is indebted to the “Flemish Institute for the Encouragement of Scientific and Technological Research in the Industry (IWT)” for financial support. We wish to thank Prof. W. D’ Olieslager for the use of his FTIR-spectrometer.

References

1. F. Lehmann, G. J. Mohr, P. Czerny, and U. W. Grummt: *Dyes and Pigments* **29**, 85 (1995).
2. G. Marowsky, L. F. Chi, D. Möbius, R. Steinhoff, Y. R. Chen, D. Dorsch, and B. Rieger: *Chem. Phys. Lett.* **147**, 420 (1988).
3. S. R. Marder and J. W. Perry: *Science* **263**, 1706 (1994).
4. D. W. Bruce, R. G. Denning, M. Grayson, R. Le Lagadec, K. K. Lai, B. T. Pickup, and A. Thornton: *Adv. Mater. Optics Electron.* **4**, 293 (1994).
5. D. Lupo, W. Prass, U. Scheunemann, A. Laschewesky, H. Ringsdorf, and I. Ledoux: *J. Opt. Soc. Am. B* **5**, 300 (1988).
6. U. W. Grummt, K. H. Feller, F. Lehmann, R. Colditz, R. Gadonas, and A. Pugzlys: *Thin Solid Films* **284–285**, 904 (1996).
7. K. Z. Wang, C. H. Huang, G. X. Xu, Y. Xu, Y. Q. Liu, D. B. Zhu, X. S. Zhao, X. M. Xie, and N. Z. Wu: *Chem. Mater.* **6**, 1986 (1994).
8. K. Z. Wang, C. H. Huang, G. X. Xu, X. S. Zhao, X. H. Xia, N. Z. Wu, L. Xu, and T. K. Li: *Thin Solid Films* **252**, 139 (1994).
9. D. J. Zhou, C. H. Huang, K. Z. Wang, G. X. Xu, X. S. Zhao, X. M. Xie, L. G. Xu, and T. K. Li: *Langmuir* **10**, 1910 (1994).
10. Y. J. Xiao, X. X. Gao, C. H. Huang, and K. Z. Wang: *Chem. Mater.* **6**, 1910 (1994).
11. K. Z. Wang, N. Z. Wu, C. H. Huang, G. X. Xu, Y. Xu, Y. Q. Liu, D. B. Zhu, L. Y. Liu, and W. C. Wang: *Chem. J. Chinese Univ.* **16**, 1 (1995).
12. H. Li, C. H. Huang, D. Zhou, L. Xu, T. K. Li, X. S. Zhao, and X. Xie: *Prog. Natural Sci.* **6**, 96 (1996).
13. M. A. Pavier, M. S. Weaver, D. Lidzey, T. Richardson, T. M. Searle, D. D. C. Bradley, C. H. Huang, H. Li, and D. Zhou: *Thin Solid Films* **284–285**, 644 (1996).
14. M. S. Weaver, D. G. Lidzey, M. A. Pavier, H. Mellor, S. L. Thorpe, D. D. C. Bradley, T. Richardson, T. M. Searle, C. H. Huang, H. Liu, and D. Zhou: *Synth. Metals* **76**, 91 (1996).
15. K. Z. Wang, C. H. Huang, G. X. Xu, and Q. F. Zhou: *Solid State Comm.* **95**, 223 (1995).
16. F. Neve: *Adv. Mater.* **8**, 277 (1996).
17. K. Binnemans, C. Bex, and D. W. Bruce: *Liq. Cryst.* **26**, 771 (1999).

