

SOLVATOCHROMISM OF LANTHANIDE COMPLEXES CONTAINING THE HEMICYANINE CHROMOPHORE

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Dedicated to Professor M. CHEMLA upon his Emeritat position being bestowed.

ABSTRACT

The solvatochromic properties of a hemicyanine bromide with a long alkyl chain and of the corresponding hemicyanine compounds with lanthanide containing anions are described. The anions are the tetrakis(pyrazolonato)lanthanide(III) and the tetrakis(β -diketonato)lanthanide(III) complexes. The syntheses of the compounds are described. Absorption spectra in 16 different organic solvents were recorded. Strong solvent effects are observed for the hemicyanine bromide and for the lanthanide compounds. A color change of the solutions from yellow to orange red is observed, depending on the solvent used. The solvatochromism is explained taking dipolar interactions between the solvent and the complexes into account.

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1. INTRODUCTION

Dyes based on the hemicyanine (aminostyryl pyridinium) chromophore have been thoroughly investigated in the past to establish the relation between molecular structure and color and for their solvatochromism (dependence of the color on the solvent used to dissolve the product [1]). Recently, the compounds regained new attention, not only because of the effect of solvent polarity on their optical properties [2], but also because of possible applications in the field of non-linear optics and of physiology/biochemistry.

Halogen containing hemicyanine dyes are used in physiology for the research on transport phenomena through cell membranes. Depending on the electric potential inside and outside the cell, charge separation can occur in the hemicyanine dyes bonded to the cell membrane. This charge movement results in a change of the optical properties [3].

Hemicyanine dyes exhibit a significant charge displacement when the molecules are excited from the ground state to an excited state. This large charge displacement is an indication for a large polarisability. The dyes show non-linear optical effects, such as generation of the second and third harmonics. These non-linear optical effects can be observed both in solution and in organised systems such as Langmuir-Blodgett (LB) films. Therefore, hemicyanine dyes are candidates to be used in optical data storage systems and

optical switches [4,5]. The non-linear optical properties of hemicyanine compounds with halogen counter-ions have been investigated by Bruce *et al.* [6], Lupo *et al.* [7], and by Grummt *et al.* [8].

Wang *et al.* [9] synthesised hemicyanine compounds with an anionic lanthanide coordination complex as the counter-ion, instead of a halogenide. The use of a tetrakis(pyrazolonato)dysprosium(III) complex as the anion not only improved the film forming properties (important for the preparation of LB films), but improved also the non-linear optical properties. The authors discussed the synthesis of the compound and the generation of the second harmonic. Because of a more pronounced delocalisation of the charge in the hemicyanine chromophore of the compound with the complex anion, this compound shows a larger value for the second-order molecular hyperpolarisability β .

The group of Huang prepared several analogous hemicyanine compounds [10-13]. For the pyrazolonato complexes, the rare-earth ions have been restricted to La, Nd, Dy and Yb. Structural changes of the hemicyanine chromophore include changing the two methyl groups of the amino-nitrogen by ethyl groups, or by changing the $C_{16}H_{33}$ chain by a $C_{18}H_{37}$ chain. Additionally, the authors prepared complexes in which the C=C linking group has been replaced by an azo group (N=N) [14]. Instead of the pyrazolone ligand, the β -diketones thenoyltrifluoroacetone (TTA) [15] and β -naphthyltrifluoroacetone (NTA) were also used in the complexes [16].

Zhao *et al.* [17] investigated the influence of a gas atmosphere (vapours of chloroform, acetic acid and isopropyl alcohol) on the generation of the second harmonic (SHG) in LB films of these compounds. Because of the dependence of the SHG signal on the composition of the gas atmosphere, the authors suggested application of the LB films as gas sensor. Pavier *et al.* [18] studied the luminescence of LB films containing the Dy and Nd complexes. The authors observed photoluminescence in the visible spectral region.

In this paper we report the solvatochromic properties of a hemicyanine bromide (figure 1) and of hemicyanine compound with tetrakis(pyrazolonato)lanthanide(III) complexes as the anion (figure 2) and of a hemicyanine compound with a tetrakis(β -diketonato)lanthanide(III) counter-ion. The synthesis of the compounds is described. Absorption spectra were recorded for the compounds dissolved in 16 different organic solvents. The solvatochromic effect originates from interactions between the complex and solvents of various polarities. For polar molecules this shift of the position of the absorption bands can be related to changes of the dipole moment upon excitation [19,20].

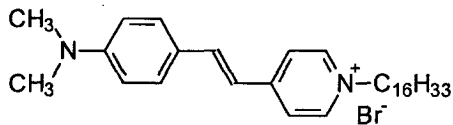


Figure 1. Hemicyanine bromide 2

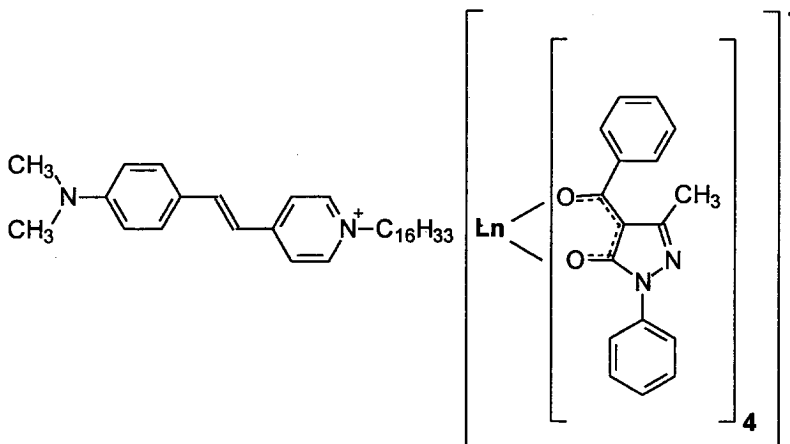


Figure 2. Pyrazolonato complexes of the lanthanides containing the hemicyanine chromophore (Ln = La (3), Gd (4), Lu(5)).

2. EXPERIMENTAL

2.1 General

^1H NMR spectra are recorded on a Bruker WM 250 spectrometer (250 MHz) or on a Bruker AMX 400 spectrometer (400 MHz). ^{13}C NMR spectra were obtained on a Bruker AMX 400 spectrometer (100.6 MHz). CDCl_3 is used as the solvent and tetramethylsilane (TMS) as internal standard. The δ -values are expressed in ppm. IR spectra are 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). Melting 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. Absorption spectra were recorded at room temperature on a Shimadzu UV-3100 spectrophotometer. In general, the absorption spectra were recorded between 700 nm and 300 nm. All chemicals were used as received, without further purification. Hydrated rare-earth chlorides or nitrates were purchased from Aldrich. For the solvents, spectroscopic grade was used when available, otherwise we used HPLC or analytical grade.

2.2 Synthesis

1-Hexadecyl-4-methylpyridinium bromide 1

Heat 4-picoline (0.20 mol, 18.63 g) and 1-bromohexadecane (0.22 mol, 67.17g) for 24 hours at reflux in absolute ethanol (30 mL). Cool the reaction mixture to room temperature, filter on a büchner and wash with diethyl ether (75 mL). Recrystallise the crude product twice from a mixture diethyl ether : ethanol. Filter the purified product on a büchner and wash with diethyl ether (2 × 100 mL). Dry in vacuo. Product **1** is obtained as white crystals in 85 % yield (67.8 g). — ¹H NMR (δ, CDCl₃, 250 MHz): 0.89 (t, 3H, CH₃), 1.26 (m, 26H, (CH₂)₁₃), 2.04 (m, 2H, CH₂), 2.69 (s, 3H, CH₃-aryl), 4.92 (t, 2H, N⁺CH₂), 7.94 (d, 2H, H-aryl, J_o = 6 Hz), 9.39 (d, 2H, H-aryl, J_o = 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⁺ = C₂₂H₄₀N⁺): 319 ([M+1]⁺, 4), 318 (M⁺, 25), 317 (M⁺-1H, 97), 316 (M⁺-2H, 44), 107 (M⁺-C₁₅H₃₁, 100). — m.p. 83 °C (diethyl ether : ethanol). — Anal. C₂₂H₄₀BrN (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 %.

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

Add piperidine (5 mL) to a mixture of **1** (0.05 mol, 19.92 g) and 4-dimethylaminobenzaldehyde (0.05 mol, 7.46g) in absolute ethanol (75 mL). Heat at reflux for 4 hours, with stirring and under dry nitrogen atmosphere. Cool the mixture to room temperature and chill in a salted ice bath. Filter the precipitate and wash with cold absolute ethanol (2×50 mL). Recrystallise twice from a ethanol:heptane (1:1) mixture, filter and wash with cold absolute ethanol (2×20 mL). Product **2** is 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, J_o = 9 Hz), 6.86 (d, 1H, CH=, J_{trans} = 16 Hz), 7.52 (d, 2H, H-aryl, J_o = 9 Hz), 7.62 (d, 1H, -CH=, J_{trans} = 16 Hz), 7.88 (d, 2H, aryl-H, J_o = 7 Hz), 8.94 (d, 2H, H-aryl, J_o = 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 (m), 2912 (s), 2852 (s), 1641 (s, alkene C=C), 1591 (w, aryl C=C), 1526 (m, aryl C=C), 1467 (s), 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. C₃₁H₄₉BrN₂ (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-hexadecyl-4-(2-(4-dimethylaminophenyl)ethenyl)pyridinium tetrakis(4-benzoyl-3-methyl-1-phenyl-2-pyrazolonato)lanthanum(III) 3

Add compound **2** (2 mmol, 1.06 g), NaOH (8 mmol, 2M solution) and La(NO₃)₃·6H₂O (2 mmol, 0.88 g) to a solution of 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (8 mmol, 2.23 g) in absolute ethanol (40 mL). Heat at reflux for 30 min with stirring. Cool the reaction mixture to room temperature and chill in a salted ice bath. Filter the precipitate on a büchner and wash the precipitate with cold, absolute ethanol (2×50mL). Recrystallise the crude

product from ethanol:water (1:1). Dry in vacuo. A dark red solid is obtained in a yield of 53 % (1.78 g). — IR (cm^{-1} , KBr): 3060 (w), 2922 (m), 2853 (w), 1638 (m, alkene C=C), 1610 (s, C=O stretch), 1591 (s, C=N stretch), 1573 (s, aryl C=C stretch), 1527 (m, C=C stretch), 1475 (s, C=O stretching and CH bending), 1430 (m), 1397 (w), 1365 (m), 1323 (w), 1230 (w), 1156 (s), 1054 (m), 947 (m), 836 (m), 757 (m), 697 (m), 604 (m). — m.p. 141 °C — Anal. $\text{C}_{99}\text{H}_{101}\text{N}_{10}\text{O}_8\text{La}$ ($M_w = 1697.86 \text{ g mol}^{-1}$): Found C, 69.83; H, 6.09; N, 8.03 %. Calc. C, 70.04; H, 6.00; N, 8.25 %.

(E)-N-hexadecyl-4-(2-(4-dimethylaminophenyl)ethenyl)pyridinium tetrakis(4-benzoyl-3-methyl-1-phenyl-2-pyrazolonato) gadolinium(III) 4

Same procedure as for 3, but now using $\text{Gd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (2 mmol, 0.87 g). A dark red solid is obtained in a yield of 53 % (1.78 g). — IR (cm^{-1} , KBr): 3056 (w), 2927 (m), 2850 (w), 1643 (sh, alkene C=C), 1616 (s, C=O stretch), 1593 (s, C=N stretch), 1579 (s, aryl C=C stretch), 1533 (m, C=C stretch), 1496 (s, C=O stretching and CH bending), 1432 (m), 1395 (w), 1363 (m), 1327 (w), 1230 (w), 1160 (s), 1056 (m), 946 (m), 831 (m), 768 (m), 694 (m), 611 (m). — m.p. 162 °C — Anal. $\text{C}_{99}\text{H}_{101}\text{N}_{10}\text{O}_8\text{Gd}$ ($M_w = 1716.20 \text{ g mol}^{-1}$): Found C, 69.05; H, 6.07; N, 8.16; Gd, 8.90 %. Calc. C, 69.29; H, 5.93; N, 8.25; Gd, 9.16 %.

(E)-N-hexadecyl-4-(2-(4-dimethylaminophenyl)ethenyl)pyridinium tetrakis(4-benzoyl-3-methyl-1-phenyl-2-pyrazolonato) lutetium(III) 5

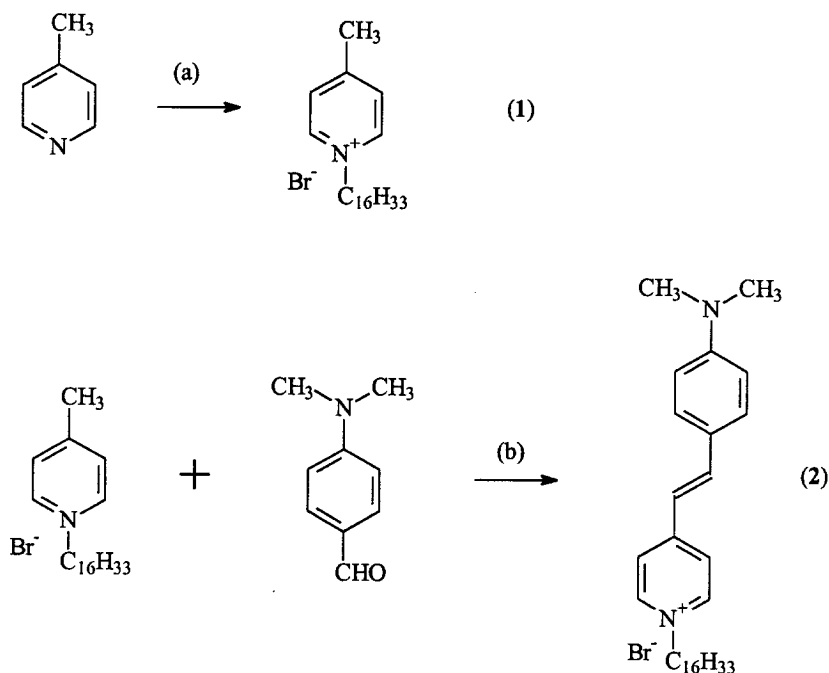
Same procedure as for 3, but now using $\text{Lu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (2 mmol, 0.78 g). A dark red solid is obtained in a yield of 65 % (2.26 g). — IR (cm^{-1} , KBr): 3060 (w), 2926 (m), 2853 (w), 1636 (sh, alkene C=C), 1614 (s, C=O stretch), 1592 (s, C=N stretch), 1577 (s, aryl C=C stretch), 1526 (m, C=C stretch), 1497 (s, C=O stretching and CH bending), 1435 (s), 1395 (w), 1369 (m), 1321 (m), 1234 (w), 1157 (s), 1058 (m), 948 (m), 839 (m), 758 (m), 700 (m), 612 (w). — m.p. 161 °C — Anal. $\text{C}_{99}\text{H}_{101}\text{N}_{10}\text{O}_8\text{Lu}$ ($M_w = 1733.91 \text{ g mol}^{-1}$): Found C, 68.47; H, 5.74; N, 7.88; Lu, 10.58 %. Calc. C, 68.58; H, 5.87; N, 8.08; Lu, 10.09 %.

(E)-N-hexadecyl-4-(2-(4-dimethylaminophenyl)ethenyl)pyridinium tetrakis(1,3-diphenyl-1,3-propanedionato) gadolinium(III) 6

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 $\text{Gd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (2 mmol, 0.87 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 room temperature and chill in a salted ice bath. Filter the precipitate and wash the precipitate with cold ethanol (2×50 mL). Recrystallise the product from 2-butanone:acetone (1:1). Dry in vacuo. 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. $\text{C}_{91}\text{H}_{93}\text{N}_2\text{O}_8\text{Gd}$ ($M_w = 1499.91 \text{ g mol}^{-1}$): Found C, 72.87; H, 5.99; N, 1.73 %. Calc. C, 72.47; H, 6.25; N, 1.87 %.

3. RESULTS AND DISCUSSION

The hemicyanine bromide **2** is synthesised by a two-step reaction (Scheme 1). During the first step, a hexadecyl chain is attached to the nitrogen atom of 4-picoline (4-methylpyridine). 4-Picoline is heated at reflux with *n*-bromohexadecane in ethanol. The crude product is recrystallised twice from a mixture diethyl ether:ethanol. The 1-hexadecyl-4-methylpyridinium bromide **1** is condensed with 4-dimethylaminobenzaldehyde via a *Knoevenagel type* reaction. The reagents are heated in absolute ethanol, with piperidine as the catalyst. The crude hemicyanine bromide is recrystallised twice from a mixture ethanol:hexane. Only the *trans*-product (*E*) is formed. There is no evidence for the formation of the *cis*-product, probably because of steric hindrance by the aromatic groups. The 1-hexadecyl-methylpyridinium bromide **1** is a white powder, whereas the hemicyanine bromide **2** has a very intense orange-red colour. The products are characterised by NMR, IR-spectroscopy, mass spectrometry and by CHN microanalysis.



Scheme 1. Synthesis of compounds **1** and **2**

Conditions: (a) $C_{16}H_{33}Br$, ethanol (reflux, 24h); (b) piperidine (catalyst), ethanol (reflux, 4h).

The lanthanide complexes 3-6 are synthesised by reaction of the hemicyanine bromide 2 with the pyrazolone 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one or with the β -diketone 1,3-diphenyl-1,3-propanedione (dibenzoylmethane, DBM). First the pyrazolone or the β -diketone is deprotonated by an equivalent amount of NaOH. Then, the hemicyanine bromide and a lanthanide salt are added to the deprotonated pyrazolone or β -diketone. The molar ratio pyrazolone (or β -diketone): hemicyanine bromide : lanthanide salt is 4:1:1. For the lanthanide salt, one can either use the hydrated nitrate or the hydrated chloride salt. All the reactions are done in ethanol. The lanthanide complexes were characterised by CHN microanalysis and by IR spectroscopy. The lanthanide content was determined gravimetrically as the 8-hydroxyquinoline complex. The analysis results revealed that the complexes are anhydrous and that four pyrazolone or β -diketone ligands and one hemicyanine group are present for each lanthanide ion.

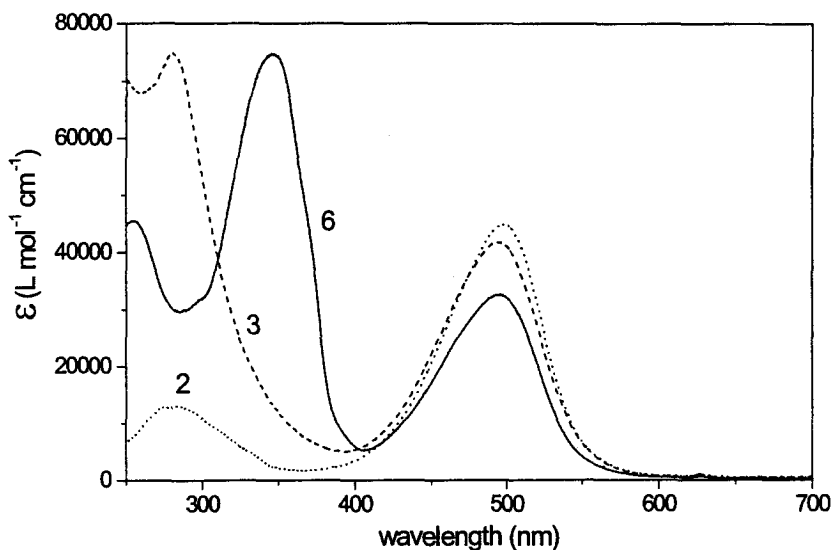


Figure 3. Absorption spectra of compounds 2, 3 and 6 in chloroform (conc. 1.0×10^{-5} M).

The absorption spectra of the hemicyanine bromide ligand 2 and of the lanthanide complexes 3-6 were recorded in different organic solvents. The solvents were chosen in such a way that both polar and apolar, protic and aprotic solvents are present: acetone, acetonitrile, 1-butanol, 2-butanone, chlorobenzene, chloroform, 1,2-dichloroethane, dichloromethane, 1,4-dioxane, dimethylsulphoxide (DMSO), ethanol, methanol, 1-pentanol, 1-propanol, pyridine, tetrahydrofuran (THF). None of the compounds was soluble in water or in toluene. Different

solutions were prepared with a concentration between 2.5×10^{-6} M and 2.0×10^{-5} M. The colour of the solutions ranges from yellow to intense orange red, depending on the solvent used (yellow in THF, orange red in DCM). This is an evidence for the solvatochromic properties of the compounds containing the hemicyanine chromophore. The peak maxima of the absorption bands were determined, together with the corresponding molar absorptivities ϵ . The ϵ values were obtained by plotting the absorbances in function of the concentration of the solutions and by constructing a straight line through the data points using a linear least-squares fitting procedure. According to the law of Lambert-Beer, the slope is ϵL , where L is the path length (1 cm in our case).

The spectrum in the visible region is very comparable for both the hemicyanine bromide and the lanthanide complexes. In figure 3, the absorption spectrum of the hemicyanine bromide 2 and of the lanthanide complexes 3 and 6 in chloroform are shown. The colour of the solutions is due to an intense charge transfer band between 467 nm (in THF) and 527 nm (in 1,2-dichloroethane) for the hemicyanine bromide 2, and between 471 nm (in 1,4-dioxane) and 520 nm (in 1,2-dichloroethane) for the lanthanide complexes 3-6. Thus depending on the solvent, the peak maximum can move over more than 50 nm. The charge transfer band originates from charge transfer from the anionic lanthanide complex to the cationic hemicyanine chromophore. The discussion concerning the solvatochromism of the compounds will be largely restricted to this charge transfer band. The ϵ values of the charge transfer peak in the hemicyanine bromide 2 are between 39200 (in DMSO) and 48300 (in chloroform) $L \text{ mol}^{-1} \text{ cm}^{-1}$.

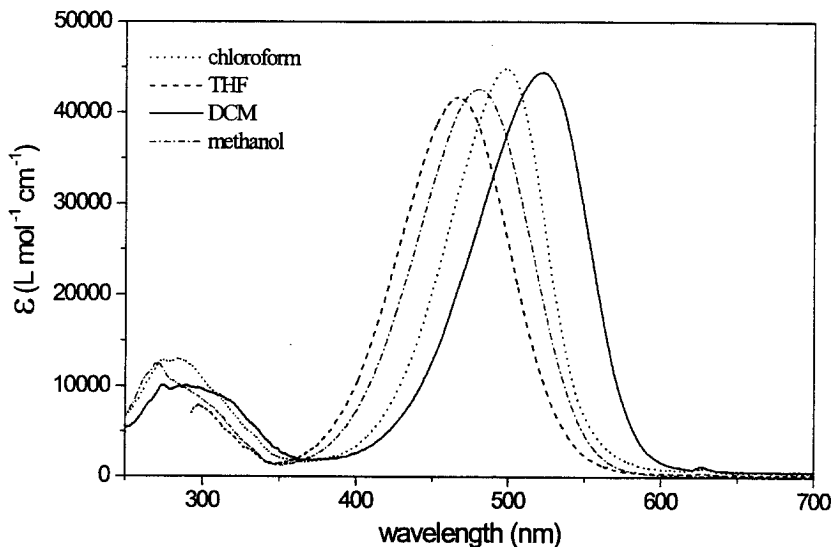


Figure 4. Absorption spectra of hemicyanine bromide 2 in chloroform, THF, dichloromethane (DCM) and methanol (conc. 1.0×10^{-5} M).

Table 1

Influence of the solvent on the peak maximum (nm) of the charge transfer band in the hemicyanine bromide **2** and in the lanthanide complexes **3-6***.

	2	3	4	5	6
acetone	477	476	477	478	477
acetonitrile	476	475	476	475	474
1-butanol	491	492	490	491	---
2-butanone	481	482	481	481	---
chlorobenzene	494	502	500	496	482
chloroform	497	494	494	493	496
1,2-dichloroethane	527	518	518	517	518
dichloromethane	522	517	516	512	499
1,4-dioxane	---	471	473	472	---
DMSO	477	476	477	477	477
ethanol	485	486	485	486	486
methanol	480	480	480	481	480
1-pentanol	492	491	492	492	---
1-propanol	488	490	488	489	488
pyridine	499	498	499	498	498
tetrahydrofuran	466	472	478	482	---

* The concentration of the solutions was 1.00×10^{-5} M.

In the UV part of the spectrum, a $\pi \rightarrow \pi^*$ transition due to the aromatic groups is observed. This $\pi \rightarrow \pi^*$ transition is much intenser for the lanthanide complexes than for the hemicyanine bromide. Depending on the solvent, the ϵ values of this transition range between 8700 and 12200 L mol⁻¹ cm⁻¹ for the hemicyanine bromide **2** and between 68400 and 84500 L mol⁻¹ cm⁻¹ for the La-complex **3**. This increase is due to the aromatic groups of the pyrazolone or of the β -diketone ligand. Thus, the $\pi \rightarrow \pi^*$ transition is more intense than the charge transfer band in the lanthanide complexes, but not in the hemicyanine bromide **2**. For the complex with the β -diketone ligand, the $\pi \rightarrow \pi^*$ transition is shifted to longer wavelengths in comparison to the complexes with the pyrazolone ligand. In solvents which are transparent to wavelengths smaller than 250 nm, a third transition can be observed in the solution spectra of the complexes. This transition is assigned to a $n \rightarrow \pi^*$ transition within the carbonyl groups. Depending on the solvent, the ϵ values of this transition range between 61400 and 77500 L mol⁻¹ cm⁻¹ for the La-complex **3** and between 45400 and 66300 L mol⁻¹ cm⁻¹ for the Gd-complex **6**. Figure 4 shows the absorption spectra of the hemicyanine bromide **2** in different solvents and figure 5 shows the corresponding spectra of the La-compound **3**.

The nature of the lanthanide ion has a negligible influence on the spectral behaviour: La³⁺ can be replaced by Gd³⁺ or Lu³⁺ without changing the spectroscopic properties significantly. La³⁺ has an empty 4f-shell and Lu³⁺ has a full 4f-shell, so that no f-f transitions can be observed for these ions. The intraconfigurational f-f transitions of Gd³⁺ are in the UV part of the spectrum (between 270 and 320 nm). But these transitions have a very low intensity, and are not observed in the presence of the intense $\pi \rightarrow \pi^*$ transitions. In general, the ϵ values of f-f transitions are less than 10 L mol⁻¹ cm⁻¹ [21].

In all the solvents, both the hemicyanine bromide and the lanthanide complexes behave according to the law of Lambert-Beer: a linear behaviour between the absorbance and the concentration is observed. Dilution has only a very small effect on the position of the absorption peaks. However, dilution shifts the position of the charge transfer band significantly to longer wavelengths in the case of dichloromethane as the solvent. For instance in the 2.00×10^{-5} M solution the absorption maximum of the charge transfer band of the La-complex 3 is found at 512.5 nm, but at 525.2 nm in the 2.50×10^{-6} M solution. The strongest effect is observed for the Gd-complex 6: a shift from 494.9 to 516.5 nm. The shift is less pronounced in the case of the hemicyanine bromide: from 517.2 to 525.0 under the same conditions. Moreover, the effect was observed every time we remade the solution. At present, we don't have an explanation for this phenomenon.

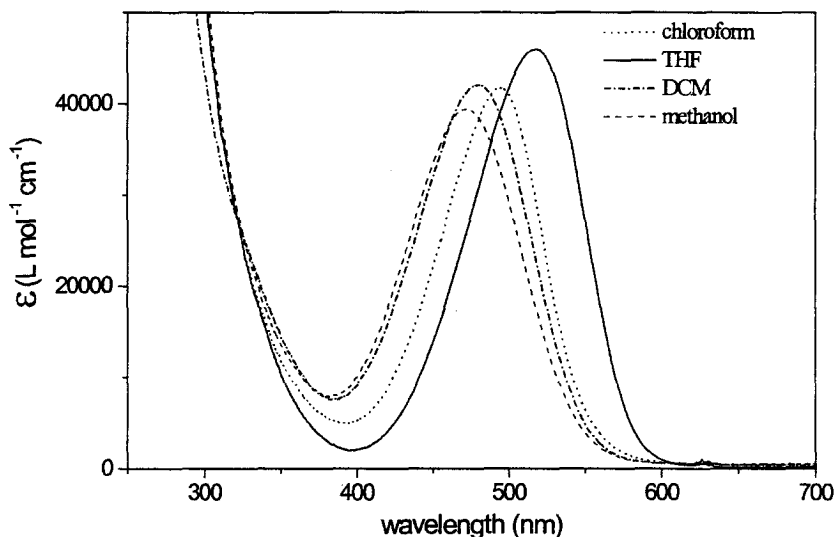


Figure 5. Absorption spectra of the La-complex 3 in chloroform, THF, dichloromethane (DCM) and methanol (conc. 1.0×10^{-5} M).

If we compare the absorption spectra of the compounds dissolved into a homologous series of straight-chain alcohols, we notice that the absorption maximum of the charge transfer peak shifts to longer wavelengths (a bathochromic shift) in the order methanol < ethanol < 1-propanol < 1-butanol < 1-pentanol. This trend can be related to the decrease of the relative electric permittivity ϵ_r when going from methanol ($\epsilon_r = 33$) to 1-pentanol ($\epsilon_r = 15.1$). The shift is very pronounced for a change of the solvent from methanol to ethanol ($\Delta\lambda$ is ca. 6 nm). The differences are less for the higher members of the homologous series. This can also

be explained on the basis of the relative electric permittivity ϵ_r : when going from methanol to ethanol, the ϵ_r value decreases from 33 to 25.3, whereas from 1-butanol to 1-pentanol the ϵ_r values only decrease from 17.8 to 15.1. The same trend as for the alcohols is observed for the ketones: the peak maximum of the charge transfer band shifts to longer wavelengths when acetone ($\epsilon_r = 21.0$) as the solvent is replaced by 2-butanone ($\epsilon_r = 18.6$). The correlation between the peak maximum of the charge transfer band and relative electric permittivity of the solvent is valid for homologous series, but not for all different types of solvents. Although acetone ($\epsilon_r = 21.0$) and 1-propanol ($\epsilon_r = 20.8$) have very comparable ϵ_r values, a large wavelength shift is observed for the charge transfer band of the compounds in these two solvents. The reason is that the alcohols are protic solvents and the ketones polar aprotic solvents.

A general polarization red shift due to the solvent polarisation by the transition dipole and which depends on the solvent refractive index, is observed in the electronic spectra of all organic molecules in solution (polarisation red shift) [22]. When the solute is polar, other effects to dipole-dipole and dipole-polarisation forces come into operation [23].

The compounds we study in this paper are ionic dyes which exhibit a dipolar character in the ground state. During light absorption, an electron is transferred from the anion to the positive pyridine ring. This transition gives rise to the charge transfer band. The anion is converted into a neutral atomic group and so is the cation. In the excited state, only a weak dipole remains in the plane of the pyridine ring. The strong electric dipole is transformed by the charge transfer into a weak dipole. A molecule which possesses a strong electric dipole will be in a solvent cage with strong polar solvent molecules. The solvent molecules are oriented in such a way as required by the dipolar character of the host molecule. During the transition, which occurs within a very small time interval, only the electrons have the time to change position. The excited molecules, in which the electric dipole has been weakened and has been reoriented, are now within a solvent cage which is no longer adapted to the electronic requirements of the excited molecule, since the solvent cage is suitable for the electronic distribution in the ground state molecule. Thus, a polar solvent creates a stabilizing solvent cage around these ionic dyes in the ground state, but a destabilizing solvent cage for the excited state. The transition energy increases with increasing solvent polarity. An increase in solvent polarity results in a hypsochromic shift of the charge transfer band, i.e. to shorter wavelengths. This is equivalent to state that a decrease in the solvent polarity results in a bathochromic shift of the charge transfer band, i.e. to longer wavelengths. Besides the dipolar effect, the hydrogen bonding has an effect too on the solvatochromic properties of the compounds dissolved in the homologous series of n-alcohols.

4. CONCLUSIONS

Strong solvent effects are observed for lanthanide complexes containing the hemicyanine chromophore. This indicates that the complexes undergo a strong dipole change during the absorption process. The solvent effects result in a color change of the solutions of the complexes from yellow to orange red, depending on the solvent used (= solvatochromism). A qualitative explanation could be given for the solvatochromic behaviour of solutions of the complexes dissolved in a homologous series of the n-alcohols, taking dipolar interactions between the solvent and the complexes into account. The explanation of the solvent effects in the other solvents proved to be more difficult.

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