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Short communication

Solid state photoluminescence of novel lanthanide complexes based on 4-benzoylpyrazolone Schiff base

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ABSTRACT

A novel, promising ligand for luminescent lanthanide complexes tris-((4-(3-methyl-1-phenyl-5-pyrazolonyl)-phenylmethylidene)-2-aminoethyl)amine (trenPMBP) was prepared and used as effective "antenna" for the ligand-sensitized photoluminescence of Tb^{3+}, Dy^{3+} and Sm^{3+} ions. All the complexes show surprisingly intensive photoluminescence in comparison with their simple 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone analogues. One of the reasons of such result can be a relatively high located triplet energy level of trenPMBP around 22675 cm^{-1}, which properly fits with the emissive energy levels of Tb^{3+} and Dy^{3+} (20430 cm^{-1} and 20830 cm^{-1}, respectively), thus avoiding back-energy transfer from the lanthanide to the ligand.

1. Introduction

Photoluminescent lanthanide complexes have been of significant interest as materials for biolabels, organic electronic materials, markers, OLED devices and photonic materials. The ligands play the role as sensitizers for the emission of lanthanide ion via light absorption-energy transfer-emission process. The most studied class of ligand is, so far, 1,3-diketones because of their commercial availability and/or relatively easy synthetic procedures. 1,3-Diketones, as ionizable ligands, form 1:3 neutral complexes with all lanthanide cations [1,2]. There are "analogues" of 1,3-diketones, such as 4-acyl (or aroyl)-pyrazolones [3–6], isoxazolones [7] and tetraarylimidodiphosphinates [8–12]. These classes of compounds possess one remarkable advantage over the 1,3-diketones – they are much less susceptible for oxidation with ambient oxygen, thus they would be more advantageous to be used in a variety of optoelectronic devices. On the other hand, their synthetic availability is much more laborious than that of 1,3-diketones.

So far there are many papers relevant to the Eu^{3+} and Tb^{3+} complexes with pyrazolones [5,13–15]. Only in very few cases the PL quantum yields for Eu^{3+} and Tb^{3+} pyrazolonate complexes in the solid state proved to be relatively high [5]. Two reviews on 4-acylpyrazolone metal complexes have appeared to date [3,4].

Current literature relevant to luminescent pyrazolonate complexes is mostly focused on 4-acyl derivatives of commercially available 3-methyl-1-phenyl-5-pyrazolone. It was found that for 4-acylpyrazolones their triplet states are located above the Tb^{3+} and Dy^{3+} emissive levels, thus allowing an efficient energy transfer from the ligand to the Ln(III). The triplet energy level in 4-aroylpyrazolones is lower, and the luminescence in such systems is much weaker in comparison with alkyl analogues or even it is not observable at all [16,17].

Some time ago a new dipodal Schiff base type complexes of pyrazolones with Cu^{2+}, Zn^{2+} and Cd^{2+} were prepared and characterized [18–22]. We decided to use tris(2-aminoethyl)amine (TREN) to provide the tris-pyrazolone ionizable ligand, capable of forming the neutral lanthanide complexes. TREN seems to be an interesting tool for preparing various lanthanide complexes including these designed for luminescence purposes [23–25] but it has not been applied to pyrazolones to date.

In this work we report on new pyrazolonate complexes with Tb^{3+}, Dy^{3+}, Sm^{3+} and Gd^{3+} cations.

2. Experimental

All chemicals were purchased form Aldrich. ^1H NMR spectra were recorded with a Varian Gemini 2000 BB spectrometer for solutions in $CDCl_3$ (internal Me_4Si). Mass spectra (ESI) were recorded with a Quattro LCT spectrometer. Elemental analysis was performed by in the Institute of Organic Chemistry PAS with a Vario EL

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III apparatus. IR spectra were recorded in KBr discs with a Nicolet Magna – IR® 560 E.S.P. Spectrometer.

2.1. Synthesis of the ligand

4-Benzoyl-3-methyl-1-phenyl-5-pyrazolone (**1**, 4.036 g; 14.5 mmol) was dissolved in toluene (50 mL) and it was heated to reflux. Tris(2-aminoethyl) amine was added dropwise and the resulting mixture was heated for additional 4 h. Then it was left at RT overnight. The precipitated solid was separated, washed with *n*-pentane (2 × 15 mL) and dried to give tris-((4-(3-methyl-1-phenyl-5-pyrazolonyl)-phenylmethylidene)-2-aminoethyl)amine (**2**, 3.36 g; 3.363 mmol, 75%) as light-brown amorphous solid which can be re-crystallized from chloroform. Mp = 145 °C (with decomposition), ^{1}H NMR (200 MHz, $CDCl_3$) δ: 11.19 (1H, t, $J_{NH,CH2}$ = 5.3 Hz, NH), 8.02–7.09 (2H, m), 7.54–7.30 (7H, m), 7.16–7.04 (1H, m), 3.20 (2H, dt, $J_{CH2,CH2}$ = 5.7 Hz), 1.15 (3H, s, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 165.7, 165.3 (C-5 and C-3 or C-4), 147.8, 138.9, 131.3 ($3 \times C_q$), 130.2, 128.8 (double intensity), 128.5 (double intensity), 127.5 (double intensity), 124.0, 119.4 (double intensity) (10 × C form Ph), 99.6 (C-3 or C-4), 53.5, 42.3 ($2 \times CH_2$), 15.0 (CH_3). FT-IR (KBr): υ 3060, 2959, 2922, 1628, 1591, 1537, 1500, 1481, 1458, 1444, 1409, 1384, 1357, 1158, 1027, 1010, 833, 757, 708, 694, 655 cm^{-1}; HRMS (ESI) calc. for $[C_{57}H_{54}N_{10}O_3]Na^+$ = 949.4272, found 949.4293; Anal. Calcd for $C_{57}H_{54}N_{10}O_3 \times 0.5CHCl_3 \times 1.5H_2O$: C, 68.12; H, 5.72; N, 13.82; found: C, 68.01; H, 5.50; N, 13.53.

2.2. General procedure for preparation of lanthanide complexes

To the solution of KOH (0.09 g, 1.62 mmol) in EtOH (25 mL) was added **2** (0.50 g, 0.54 mmol) and the reaction mixture was heated at reflux until all reagents were dissolved. Then a hot solution of appropriate lanthanide(III) nitrate (0.54 mmol) in EtOH (4 mL) was added dropwise and heating was prolonged for the next 2 h. Then reaction mixture was stirred at RT for 6 h and the precipitated solid was collected, washed with water (2 × 10 mL) and dried.

2.2.1. Tris-((4-(3-methyl-1-phenyl-5-pyrazolonyl)-phenylmethylidene)-2-aminoethyl)amine terbium(III) (*3a*)

0.490 g, 0.452 mmol, 84%, white amorphous solid. Mp > 325 °C (slow decomposition); FT-IR (KBr): υ 3423, 3060, 2926, 2854, 1603, 1568, 1523, 1489, 1457, 1435, 1367, 1349, 1158, 1028, 754, 731, 705, 691 cm^{-1}; HRMS (ESI) calc. for $[C_{57}H_{51}N_{10}O_3Tb]H^+$ = 1083.3472, found 1083.3507; Anal. Calcd for $C_{57}H_{51}N_{10}O_3Tb \times H_2O$: C, 62.18; H, 4.85; N, 12.72; found: C, 61.90; H, 4.78; N, 12.50.

2.2.2. Tris-((4-(3-methyl-1-phenyl-5-pyrazolonyl)-phenylmethylidene)-2-aminoethyl)amine dysprosium(III) (*3b*)

0.457 g, 0.421 mmol, 78%, white amorphous solid. Mp > 285 °C (slow decomposition), FT-IR (KBr): υ 3430, 3060, 2925, 2855, 1598, 1568, 1524, 1498, 1457, 1435, 1392, 1367, 1350, 1158, 1028, 755, 731, 705, 691 cm^{-1}; HRMS (ESI) calc. for $[C_{57}H_{51}N_{10}O_3Dy]H^+$ = 1088.3516, found 1088.3536; Anal. Calcd for $C_{57}H_{51}N_{10}O_3Dy$: C, 63.01; H, 4.73; N, 12.89; found: C, 62.81; H, 4.93; N, 13.05.

2.2.3. Tris-((4-(3-methyl-1-phenyl-5-pyrazolonyl)-phenylmethylidene)-2-aminoethyl)amine samarium(III) (*3c*)

0.390 g, 0.352 mmol, 65%, white amorphous solid. Mp > 320 °C (slow decomposition); FT-IR (KBr): υ 3429, 3058, 2925, 2852, 1597, 1568, 1521, 1457, 1435, 1392, 1367, 1348, 1158, 1028, 754, 729, 705, 691 cm^{-1}; HRMS (ESI) calc. for $[C_{57}H_{51}N_{10}O_3Sm]Na^+$ = 1098.3241, found 1098.3223; Anal. Calcd for $C_{57}H_{51}N_{10}O_3Sm \times 2H_2O$: C, 61.65; H, 4.99; N, 12.61; found: C, 61.35; H, 4.61; N, 12.70.

2.2.4. Tris-((4-(3-methyl-1-phenyl-5-pyrazolonyl)-phenylmethylidene)-2-aminoethyl)amine gadolinium(III) (*3d*)

0.507 g, 0.405 mmol, 75%, white amorphous solid. Mp > 320 °C (slow decomposition), FT-IR (KBr): υ 3447, 3060, 2962, 2854, 1603, 1570, 1521, 1457, 1436, 1384, 1370, 1027, 766, 707, 692 cm^{-1}; HRMS (ESI) calc. for $[C_{57}H_{51}N_{10}O_3Gd]H^+$ = 1083.3472, found 1083.3507; Anal. Calcd for $C_{57}H_{51}N_{10}O_3Gd \times 2.5H_2O$: C, 60.78; H, 5.01; N, 12.43; found: C, 60.72; H, 4.94; N, 12.17.

2.3. Spectroscopic characterization of novel complexes

Absorption spectra were recorded on Shimadzu UV-3100 UV-VIS-NIR Spectrophotometer in THF. For luminescence experiments, the samples were placed in fluorimetric 1-cm path cuvettes and, when necessary, purged from oxygen by bubbling with argon. Uncorrected emission spectra were obtained with an Edinburgh FLS920 spectrometer equipped with a peltier-cooled Hamamatsu R928 photomultiplayer tube (185–850 nm). An Edinburgh Xe900 450 W Xenon arc lamp was used as exciting light source. Corrected spectra were obtained *via* a calibration curve supplied with the instrument. Luminescence quantum yields (Φ_{em}) in solution obtained from spectra on a wavelength scale (nm) were measured according to the approach described by Demas and Crosby [26] using air-equilibrated $[Ru(bpy)_3Cl_2$ in water solution $\Phi_{em} = 0.028]$ as standard.

The luminescence lifetimes in the microsecond–millisecond scales were measured by using a Perkin-Elmer LS-50 spectrofluorimeter equipped with a pulsed xenon lamp with variable repetition rate and elaborated with standard software fitting procedures. For solid samples, Φ_{em} have been calculated by corrected emission spectra obtained from an apparatus consisting of a barium sulphate coated integrating sphere (4 or 6 inches), an He-Cd laser (λ_{exc}: 325 nm, 5 mW) or Xe900 450 W Xenon arc lamp as light sources and a CCD AVA-Spec2048 (or R928 photomultiplayer tube) as signal detector, following the procedure described by De Mello et al. [27] Experimental uncertainties are estimated to be ±8% for lifetime determinations, ±20% for emission quantum yields, ±2 nm and ±5 nm for absorption and emission peaks, respectively.

The phosphorescence spectra were measured on Fluorolog®-3 spectrofluorimeter at 77 K in 2-methyltetrahydrofuran which was distilled over $LiAlH_4$ prior to use.

3. Results and discussion

Treatment of 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone with TREN in toluene provides trenPMBP (**2**) which precipitates out from the reaction mixture in 75% yield (Scheme 1). Further reaction of **2** with the appropriate lanthanide(III) nitrates in refluxing KOH–ethanol solution led to the expected complexes, which also precipitated immediately. After simple washing with ethanol and water analytically pure samples were obtained in high yields. Upon irradiation by UV light Tb^{3+}, Dy^{3+}, and Sm^{3+} complexes exhibited green, yellow-white and deep red luminescence, respectively.

Absorption spectra for ligand and complexes (Fig. 1) were, as it might be expected, almost identical to dipodal ligand and its complexes reported previously [18], suggesting that no additional interactions between ligand's subunits take place. The free ligand exhibits strong absorption bands at 261, 304 and 350 nm. In complexes two major bands are located at 248 and 298 nm (see Table 1).

The emission spectrum of the Tb^{3+} complex (**3a**) recorded in the solid state shows typical signals, with maxima located at 487, 549,