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Europium complex of 5-(4-dodecyloxyphenyl)-2,2′-bipyridine-6′-carboxylic acid

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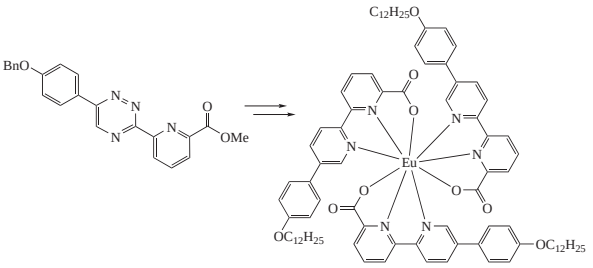
Based on '1,2,4-triazine' methodology, a new lanthanide(III) ligand, 5-(4-dodecyloxyphenyl)-2,2′-bipyridine-6′-carboxylic acid, was synthesized, and its luminescent europium(III) complex was prepared. The solubility in organic solvents for both the ligand and its europium complex was provided by the presence of a long aliphatic dodecyl moiety. The photophysical properties of the europium(III) complex were examined, the fluorescence quantum yield and the europium cation luminescence quantium yield were determined.



Luminescent lanthanide complexes are of significant interest for creation of phosphorescent labels for various bioimaging applications,[1] including the highly selective molecular probing of chiral molecules,[2] enantioselective recognition of *c*-type cytochromes and vitamin B_{12} in aqueous solutions[3] *etc*., for anion sensing applications,[4] and as electroluminescent materials for OLEDs.[5] In the latter case, to achieve a high emission intensity, it is necessary to exclude water molecules from the first coordination sphere of the lanthanide cation to prevent the possible quenching of the Ln^{III} ion emission *via* interaction with O–H oscillators.[6] The other necessary prerequisite is either high solubility of such complexes in organic solvents or their high volatility in the gas phase for the purposes of chemical doping or vacuum-deposition on the surface of semi-conductive polymers.

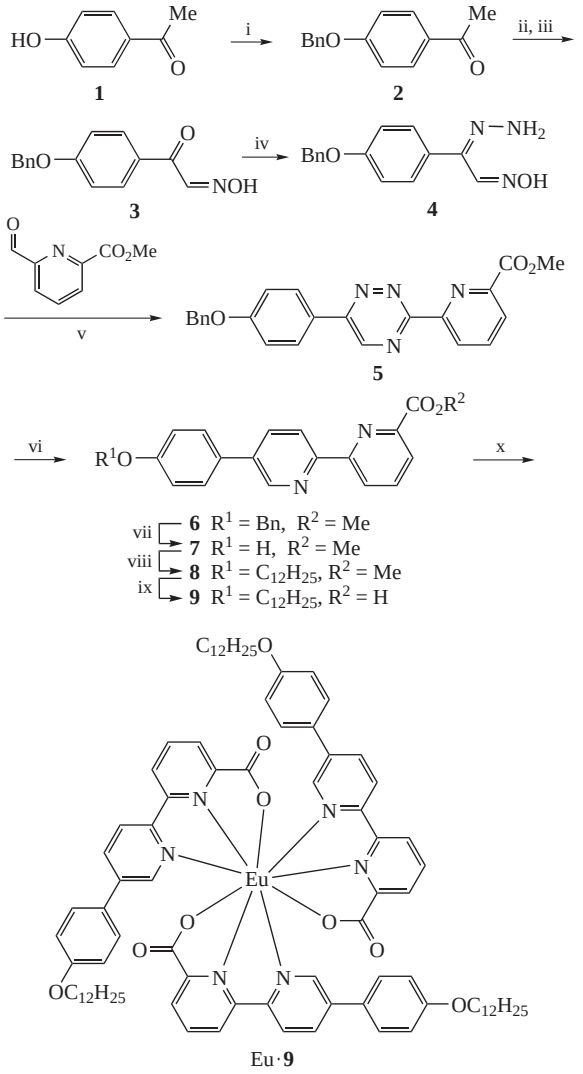
According to a literature, the β-diketonate Ln^{III} complexes are commonly used for OLED creation.[7] However, these complexes have a number of disadvantages, in particular, their photostability upon UV irradiation is very poor.[8] On the other hand, some complexes of 2,2′-bipyridine-6-carboxylic acids[9,10] or their aza-analogues[11] are potentially useful as components for OLEDs since they form neutral complexes $[Ln(L)_3]$ (L = 2,2′-bipyridine-6-carboxylate) with high quantum efficiency of a lanthanide luminescence. For some of these complexes the absence of water molecules in the first coordination sphere of the lanthanide cation was confirmed by X-ray diffraction analysis.[12,13] However, their major drawback is poor solubility in common organic solvents. Recently, we have demonstrated that solubility of such Ln^{III} complexes could be improved *via* the direct annulation of cyclopentene moiety into one of the pyridine moieties of the 2,2′-bipyridine system.[12,14] For their preparation, the 1,2,4-triazine inverse-electron-demand aza-Diels–Alder reaction was used. The thus obtained neutral europium complexes of 5-aryl-2,2′-bipyridine-6(6′)-carboxylic acids were soluble in dichloromethane in up to 10 g dm^{-3}, while the luminescence lifetime of the europium(III) complex was as high as 1.5 ms, and the luminescence quantum yield was up to 28%. In this paper, we report on the preparation of other soluble europium complexes of 5-aryl-2,2′-bipyridines (*i.e.* 5-aryl-2,2′-bipyridine-6′-carboxylic acid). The solubility was improved using another common approach,[15] namely, by introduction of an aryl substituent bearing long alkyl chain fragment into one of pyridine moieties of the 2,2′-bipyridine system.

To obtain the target ligand, the 1,2,4-triazine-based methodology[16] was used. Taking into account published data[17,18] and retrosynthetic considerations (see Online Supplementary Materials), the target ligand was prepared starting from 4-hydroxyacetophenone **1** (Scheme 1). For the protection of the aromatic 4-hydroxy group, benzylation was carried out to yield compound **2**.[19] Keto oxime **3** was obtained by further nitrosation under the slightly modified conditions,[20] *viz*., in benzene, particularly, due to low solubility of compound **2** in ethanol (a common solvent for the nitrosation of acetophenones[21]). The subsequent reaction of compound **3** with hydrazine hydrate was performed upon heating (*cf*. ref. 22). Then, according to a reported procedure,[12] the reaction between hydrazone **4** and 6-(methoxycarbonyl)pyridine-2-carbaldehyde[23] followed by aromatization afforded the 1,2,4-triazine **5**. The aza-Diels–Alder reaction[12] between crude compound **5** and 2,5-norbornadiene in boiling *o*-xylene furnished the 2,2′-bipyridine **6**, which was isolated analytically pure after recrystallization from acetonitrile. Finally, debenzylation of **6** with ammonium formate over Pd/C, alkylation of phenol moiety of **7** with dodecyl benzenesulfonate[24] in DMF, and the alkaline hydrolysis of ester **8** yielded the desired ligand **9**.

The europium complex Eu·**9** was prepared as described recently.[12] Since terbium complexes of 5-aryl-2,2′-bipyridine-6(6′)-carboxylic acids were reported to exhibit extremely low luminescence intensity,[12,14] the synthesis of Tb·**9** complex was considered to be inappropriate.

The stoichiometry of the Eu·**9** complex has been determined by elemental analysis and mass spectrometry, which is sufficient according to the previous reports.[10] Unfortunately, we failed to grow single crystals of Eu·**9** complex for X-ray diffraction measurements. Meantime, the data obtained for complex Eu·**9** correlate with those[12] for similar chelates lacking long aliphatic chains, whose structures were confirmed by X-ray studies.

In fact, the obtained complex Eu·**9** demonstrated the enhanced solubility in non-polar solvents (*e.g.*, CH_2Cl_2), as compared to



Scheme 1 *Reagents and conditions*: i, $PhCH_2Br$, K_2CO_3, 80 °C, 12 h; ii, EtONa, then Pr^iONO, benzene, 20 °C, ~18 h; iii, AcOH, H_2O, 20 °C, 30 min; iv, $NH_2NH_2 \cdot H_2O$, EtOH, 70 °C, 3 h, then H_2O, 20 °C; v, EtOH, 20 °C, 10 h, then AcOH, 118 °C, 5 min; vi, 2,5-norbornadiene, *o*-xylene, 143 °C, 19 h; vii, $HC(O)NH_4$, Pd/C, THF–MeOH (1:1), reflux, 50 min; viii, $PhSO_2OC_{12}H_{25}$, K_2CO_3, DMF, 100 °C, 10 h; ix, NaOH, EtOH, 65 °C, 30 min, then 20 °C, 3 h, then HCl, 20 °C; x, NaOH, MeOH, 65 °C, 5 min, then $EuCl_3 \cdot 6H_2O$, 20 °C.

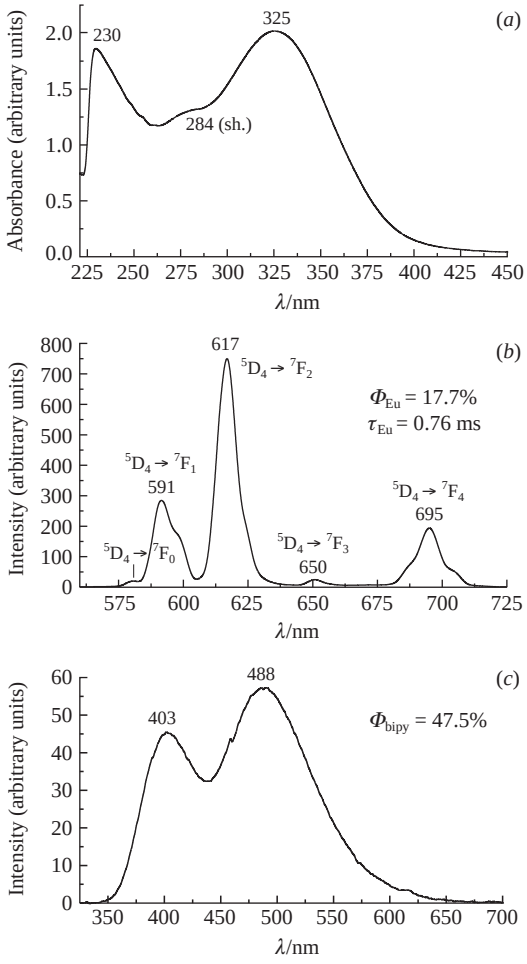


Figure 1 (*a*) Absorption, (*b*) europium cation luminescence and (*c*) fluorescence spectra of complex Eu·**9** in CH_2Cl_2 solution at room temperature (the excitation wavelength is 325 nm).

described complexes lacking long alkyl chains.[12] Absorption, europium cation luminescence and fluorescence spectra of complex Eu·**9** and its photophysical characteristics are shown in Figure 1.†

The photophysical studies of Eu·**9** revealed a significantly higher quantum yield of Eu^{3+} luminescence (17.7%) compared with those for a number of complexes (15–26%),[12] while the emission maxima positions were the same. The luminescence lifetime value of Eu·**9** (0.76 ms) was a little lower than those (typically 0.9–1.2 ms[12,14]) for the similar lanthanide complexes of the ligands lacking long alkyl chains. The $^5D_0 \rightarrow {}^7F_2$ emission band at 617 nm is dominating over the $^5D_0 \rightarrow {}^7F_1$ band (591 nm) that correlates well with the published emission spectra of similar chelates.[9,12–14] Meanwhile, the Eu·**9** complex demonstrated a highly intensive residual fluorescence of arylbipyridine chromophore corresponding to its π–π*-transitions (the fluorescence quantum yield was 47.5%). In other words, the introduction of an electron-donating alkoxy group into the aromatic substituent of the bipyridine ligand causes the significant lowering of the energies of excited states of the chromophore, which may hamper the energy transfer from the ligand T_1 level to the $^5D_0$ level of the europium cation.[6] Structurally close 5-(4-methoxyphenyl)-2,2′-bipyridine exhibited very intense fluorescence in acetonitrile solution (the fluorescence quantum yield was as high as 89%).[21] However, the residual fluorescence of 5-aryl-2,2′-bipyridine ligands in such complexes was completely eliminated in solid state. In this case only luminescence of europium cation was observed and no residual fluorescence was detected.[12] Thus, such a drawback of the Eu·**9** complex as the residual fluorescence could be eliminated under certain conditions.

In summary, a convenient synthesis of 5-(4-alkoxyphenyl)-2,2′-bipyridine-6′-carboxylic acids using the modified '1,2,4-triazine' methodology has been accomplished. The introduction of long alkyl chain in the aromatic substituent is crucial for improving the solubility in organic solvents of the resulting 2,2′-bipyridine ligands, as well as their neutral lanthanide(III) complexes. For neutral europium(III) complex of 5-(4-dodecyloxyphenyl)-2,2′-bipyridine-6′-carboxylic acid, the europium cation luminescence quantum yield and lifetime value were close to those reported previously for similar europium(III) complexes.[12,14]

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† Fluorescence quantum yield (Φ_{bipy}) in CH_2Cl_2 solution was determined using quinine bisulfate in 0.1 N solution of H_2SO_4.[25] Europium cation luminescence quantum yield (Φ_{Eu}) in CH_2Cl_2 solution was established using optically matching solution of $[Ru(bpy)_3]Cl_2$.[26] The excitation wavelength was 325 nm.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.07.026.

References

1 S. Faulkner, S. J. A. Pope and B. P. Burton-Pye, *Appl. Spectrosc. Rev.*, 2005, **40**, 1.
2 G. Muller, *Dalton Trans*., 2009, 9692.
3 S. C. J. Meskers and H. P. J. M. Dekkers, *J. Phys. Chem. A*, 2001, **105**, 4589.
4 (*a*) K.-C. Chang, S.-S. Sun, M. O. Odago and A. J. Lees, *Coord. Chem. Rev.*, 2015, **284**, 111; (*b*) S. Shinoda and H. Tsukube, *Analyst*, 2011, **136**, 431.
5 (*a*) Z.-Q. Bian and C.-H. Huang, in *Highly Efficient OLEDs with Phosphorescent Materials*, ed. H. Yersin, Wiley-VCH, Weinheim, 2008, p. 391; (*b*) H. Xu, R. Chen, Q. Sun, W. Lai, Q. Su, W. Huang and X. Liu, *Chem. Soc. Rev.*, 2014, **43**, 3259.
6 L. Armelao, S. Quici, F. Barigelletti, G. Accorsi, G. Bottaro, M. Cavazzini and E. Tondello, *Coord. Chem. Rev.*, 2010, **254**, 487.
7 (*a*) N. T. Kalyani and S. J. Dhoble, *Renew. Sustain. Energy Rev.*, 2012, **16**, 2696; (*b*) J. Kido and Y. Okamoto, *Chem. Rev.*, 2002, **102**, 2357; (*c*) A. de Bettencourt-Dias, *Dalton Trans.*, 2007, 2229; (*d*) Yu. S. Kudyakova, D. N. Bazhin, Ya. V. Burgart and V. I. Saloutin, *Mendeleev Commun*., 2016, **26**, 54.
8 (*a*) K. Binnemans, in *Handbook on the Physics and Chemistry of Rare Earths*, eds. K. A. Gschneidner, Jr., J.-C. G. Bünzli and V. K. Pecharsky, Elsevier, Amsterdam, 2005, vol. 35, pp. 107–272; (*b*) K. Binnemans, *Chem. Rev.*, 2009, **109**, 4283.
9 (*a*) S. Comby, D. Imbert, A.-S. Chauvin, J.-C. G. Bünzli, L. J. Charbonnière and R. F. Ziessel, *Inorg. Chem.*, 2004, **43**, 7369; (*b*) G. S. Kottas, M. Mehlstäubl, R. Fröhlich and L. De Cola, *Eur. J. Inorg. Chem.*, 2007, 3465.
10 M. B. S. Botelho, M. D. Gálvez-López, L. De Cola, R. Q. Albuquerque and A. S. S. de Camargo, *Eur. J. Inorg. Chem.*, 2013, 5064.
11 N. M. Shavaleev, S. V. Eliseeva, R. Scopelliti and J.-C. G. Bünzli, *Inorg. Chem.*, 2010, **49**, 3927.
12 D. S. Kopchuk, A. P. Krinochkin, D. N. Kozhevnikov and P. A. Slepukhin, *Polyhedron*, 2016, **118**, 30.
13 N. M. Shavaleev, F. Gumy, R. Scopelliti and J.-C. G. Bünzli, *Inorg. Chem.*, 2009, **48**, 5611.
14 A. P. Krinochkin, D. S. Kopchuk and D. N. Kozhevnikov, *Polyhedron*, 2015, **102**, 556.
15 (*a*) N. M. Shavaleev, S. V. Eliseeva, R. Scopelliti and J.-C. G. Bünzli, *Chem. Eur. J.*, 2009, **15**, 10790; (*b*) N. M. Shavaleev, S. V. Eliseeva, R. Scopelliti and J.-C. G. Bünzli, *Inorg. Chem.*, 2015, **54**, 9166.
16 (*a*) R. A. A. Foster and M. C. Willis, *Chem. Soc. Rev.*, 2013, **42**, 63; (*b*) A. Rykowski, D. Branowska and J. Kielak, *Tetrahedron Lett.*, 2000, **41**, 3657; (*c*) D. L. Boger, *Tetrahedron*, 1983, **39**, 2869; (*d*) D. S. Kopchuk, A. F. Khasanov, I. S. Kovalev, G. V. Zyryanov, V. L. Rusinov and O. N. Chupakhin, *Mendeleev Commun*., 2013, **23**, 209; (*e*) N. V. Chepchugov, D. S. Kopchuk, I. S. Kovalev, G. V. Zyryanov, V. L. Rusinov and O. N. Chupakhin, *Mendeleev Commun*., 2016, **26**, 220.
17 A. M. Prokhorov, V. N. Kozhevnikov, D. S. Kopchuk, H. Bernard, N. Le Bris, R. Tripier, H. Handel, B. Koenig and D. N. Kozhevnikov, *Tetrahedron*, 2011, **67**, 597.
18 (*a*) S. Lepri, F. Buonerba, L. Goracci, I. Velilla, R. Ruzziconi, B. D. Schindler, S. M. Seo, G. W. Kaatz and G. Cruciani, *J. Med. Chem.*, 2016, **59**, 867; (*b*) S. Zhu, X. Hao, S. Zhang, X. Qin, X. Chen and C. Zhu, *Bioorg. Med. Chem. Lett.*, 2016, **26**, 2880.
19 J. E. Bakali, F. Klupsch, A. Guédin, B. Brassart, G. Fontaine, A. Farce, P. Roussel, R. Houssin, J.-L. Bernier, P. Chavatte, J.-L. Mergny, J.-F. Riou and J.-P. Hénichart, *Bioorg. Med. Chem. Lett.*, 2009, **19**, 3434.
20 H. M. Priestley and E. Moness, *J. Org. Chem.*, 1940, **5**, 355.
21 V. N. Kozhevnikov, O. V. Shabunina, D. S. Kopchuk, M. M. Ustinova, B. König and D. N. Kozhevnikov, *Tetrahedron*, 2008, **64**, 8963.
22 B. B. Dey, *J. Chem. Soc., Trans.*, 1914, **105**, 1039.
23 C. Platas-Iglesias, M. Mato-Iglesias, K. Djanashvili, R. N. Muller, L. Vander Elst, J. A. Peters, A. de Blas and T. Rodríguez-Blas, *Chem. Eur. J.*, 2004, **10**, 3579.
24 A. A. Fernandez, M. J. A. van Dongen, D. Blanco-Ania and P. H. J. Kouwer, *RSC Adv.*, 2014, **4**, 30267.
25 W. H. Melhuish, *J. Phys. Chem.*, 1961, **65**, 229.
26 K. Nakamaru, *Bull. Chem. Soc. Jpn*., 1982, **55**, 2697.

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