Pergamon

Tetrahedron Letters, Vol. 38, No. 8, pp. 1381-1384, 1997
© 1997 Published by Elsevier Science Ltd
All rights reserved. Printed in Great Britain.
0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)00025-7

Sensitized Luminescence Emission of the Europium(III) Ion Bound to a Pyrene-Containing Triacid Ligand

Jean-Ernest Sohna Sohna, Frédéric Fages*

Photophysique et Photochimie Moléculaire, associé au CNRS, Université de Bordeaux I,
351 Cours de La Libération, 33405 Talence, France.[†]

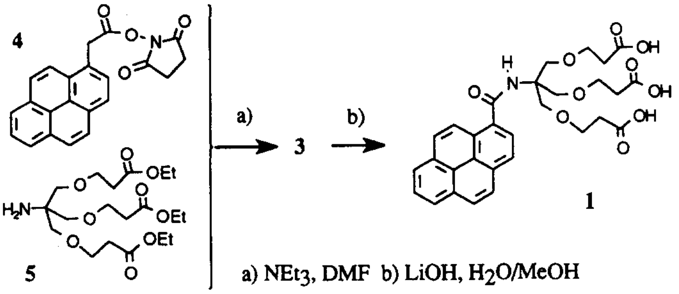
Abstract: A pyrene-tethered triacid receptor and its chelates with two lanthanide(III) metal cations have been synthesized. The first example of energy transfer taking place from the excited pyrene chromophore to the europium(III) metal is reported therein.

A research area of fascinating interest relies on the design and the engineering of supramolecular devices for artificial photosynthesis or information processing. In that connection, the conception of two-component systems combining a metal cation binding subunit and a light-sensitive aromatic chromophore occupies a central place.[1] Particularly this approach has found attractive applications in the field of lanthanide complexation chemistry.[2]

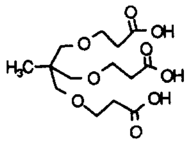
During the course of investigations on the synthesis of tripodal molecular receptors for first-row transition-metal ions,[3] it occurred to us that compound **1**, a pyrene-based carboxylic triacid building block, could be a promising precursor towards the preparation of a variety of fluorescent complexing agents.[4] The pyrene chromophore has been successfully used as reporter group in fluorescent chemosensors chemistry,[3,5] and represents also a versatile light-harvesting unit for the design of supramolecular metallosystems endowed with photoactive features.[6]

Recently, calix[4]arene-triacid derivatives,[7] and, particularly, tripodal triether-acid chelators[8] structurally related to **1** were shown to form electroneutral complexes with lanthanide(III) metal cations. We thus prepared the europium(III) chelate, [**1**,Eu], and investigated its photophysical properties. [**1**,Eu] enabled to observe the pyrene-sensitized luminescence emission of Eu^{III} in solution, which is, to our knowledge, the first example of an antenna effect between the pyrene chromophore and the europium(III) ion.

The synthetic route used for the preparation of **1** is as follows.



a) NEt_3, DMF b) LiOH, $H_2O/MeOH$



2

[†] E-mail: f.fages@lcoo.u-bordeaux.fr; FAX: +33 (0)5 56 84 66 45.

Compound **1** was obtained as a viscous oil in 35 % yield from **4** and **5**.[9,10] The structures of the compounds were confirmed by ^1H, ^{13}C NMR, mass spectrometry, and elemental analyses.[11] The chelate [**1**,Eu] was prepared by reaction of **1** with a stoichiometric amount of $Eu(NO_3)_3,5H_2O$ in water in the presence of slightly over 3 molar equivalents of NaOH.[8] The europium complex precipitated to give a white solid that was insoluble in most organic solvents. Attempts to obtain a FAB-MS were unsuccessful. Satisfactory C, H, N, and Eu elemental analyses were obtained, and the FT-IR spectrum[11] (KBr) showed spectral features consistent with those published[8] for analogous complexes. The terbium(III) chelate, [**1**,Tb], was prepared similarly from $TbCl_3,6H_2O$.[11]The europium neutral complex of the non-fluorescent triacid derivative, **2**, was also prepared and used as reference compound for photophysical investigations.

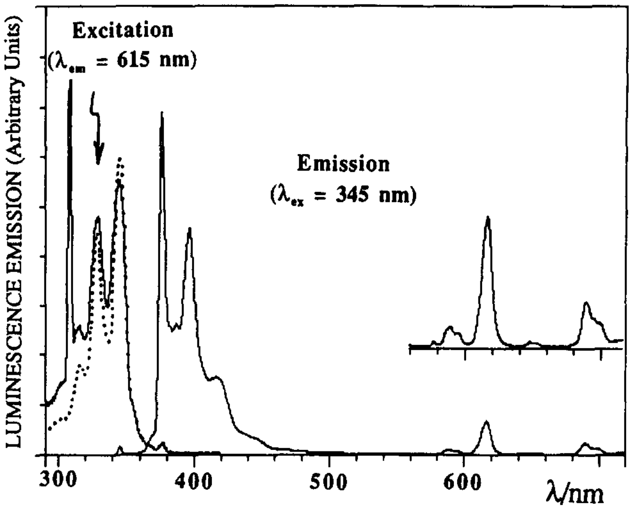


Figure. Luminescence emission and excitation spectra of [1,Eu] in DMF (containing 0.2 % DMSO) at room temperature (10^{-5} M). Dotted line: ^1L_a absorption band of the pyrene chromophore in the complex.

The electronic absorption spectra of **1** and [**1**,Eu] in the DMF/DMSO 99.8/0.2 (v/v) solvent mixture (*ca.* 10^{-5} M) were found identical, which indicated the absence of ground state interactions between the pyrene nucleus and the chelated metal. Upon light excitation at 345 nm (^1L_a band of pyrene), a solution of [**1**,Eu] exhibited a dual spectrum, composed of the pyrene fluorescence emission band (370-500 nm), and, at longer wavelength, the characteristic europium metal luminescence contribution (Figure). While the former could be detected at concentrations lower than 10^{-6} M, the latter could only be recorded for more concentrated solutions, typically around 10^{-5} M. Similar features were observed when the excitation wavelength was scanned over the whole absorption spectrum of the pyrene group, particularly at 280 nm which corresponds to the strong ^1B_b electronic transition. Luminescence excitation spectra monitored at the metal emission closely matched the absorption bands of pyrene. Under the same experimental conditions, a solution (*ca.* 10^{-5} M) of the reference complex, [**2**,Eu], did not show any luminescence emission. These results are indicative of the occurrence of an energy transfer process from the sensitizing aromatic chromophore to the metal ion. The spectroscopic data for **1** and its Eu^{III} chelate are collected in the Table.[12]

Energy transfer between a series of excited arenes as energy donors and lanthanides(III) has already been reported, intermolecularly[16] in fluid solution or in micellar media, as well as intramolecularly[7,17] in the case of chromophore-appended receptors. Yet the efficient quenching of pyrene singlet excited state by the oxidizing Eu^{3+} ion has been shown to proceed *via* photoinduced electron transfer processes.[18] Such mechanism would be of rather low efficiency in the case of [**1**,Eu], with regard to the observed weak quenching of the pyrene fluorescence emission (Table).

Table: Electronic Absorption and Luminescence Emission Data for Receptor **1**, and its Eu^{III} and Tb^{III} Chelates.

	Absorption	Emission			
	λ_{max} (ε_{max}) ^{a}	Pyrene chromophore ^{b}		M^{III} centre ^{a}	
	nm (M^{-1} cm^{-1})	Φ_F	τ (ns)	Φ_F	τ (ms)
1	346 (37300)	0.1 (ND)		-	-
		0.49 (D)	180 (D)	-	-
[**1**,Eu]	346 (37100)	0.08 (ND)		0.002 (ND)	0.92 (ND)
		0.43 (D)	150 (D)	0.009 (D)	
[**1**,Tb]	346 (37 350)	0.1 (ND)		None	-

In DMF/DMSO (99.8/0.2 v/v); 25 °C. ^{a} *ca.* 10^{-5} M. ^{b} *ca.* 10^{-6} M. ND = non-degassed. D = degassed.

Noticeably, the europium emission in [**1**,Eu] is extremely low, which might indicate that energy transfer from pyrene to chelated Eu^{III} is rather difficult. This feature might be rationalized by considering that the lowest energy triplet state for compound **1**, lying at *ca.* 16800 cm^{-1}, is essentially isoenergetic with the lowest europium $^5D_0$ emitting state (*ca.* 17200 cm^{-1}), which could favour metal-to-chromophore back energy transfer. The pyrene triplet state was reasonably assumed to act as energy donor, by analogy with previous work.[16-18] The oxygen quenching effect (Table) on the europium luminescence in [**1**,Eu] may confirm this mechanism.[19] However, energy transfer processes from the pyrene singlet excited state[20] into either the ^5L manifold of complexed europium(III), which is spin allowed, or LMCT states can not be completely excluded, although the latter possibility is known not to lead to sensitized $^5D_0$—>^7Fj emission.[21]Anyway, the lowest energy level in the terbium chelate is the first triplet state of pyrene and this may account for the lack of metal lumiscence emission. Furthermore, addition of a small amount of water to a DMF solution of [**1**,Eu] led to the total suppression of the sensitized Eu^{III} emission whereas that of pyrene remained unchanged. Such effect could be due to the poor ability of that ligand unit to shield the bound metal ion from interaction with water molecules, although metal dissociation can not be completely ruled out. The detailed investigation of the photophysical properties of the lanthanide chelates of compound **1** is being actively pursued in order to obtain further insights into the mechanism of energy transfer between pyrene and Eu^{III} in these species.

Acknowledgements: The authors thank the CNRS, the University Bordeaux I, and La Région Aquitaine for financial support. Mrs. C. Belin and Dr. J.-C. Soulignac are gratefully acknowledged for their assistance in performing europium(III) lifetime measurements.

REFERENCES AND NOTES

1. Balzani,V.; Scandola, F. *Supramolecular Photochemistry*, Horwood, Chichester, 1991. Lehn, J.-M. *Supramolecular Chemistry*, VCH, Weinheim, 1995.
2. For a recent review, see: Parker, D.; Williams, J.A.G. *J. Chem. Soc., DaltonTrans.* **1996**, 3613-3628.

3. Fages, F.; Bodenant, B.; Weil, T. *J. Org. Chem.* **1996**, *61*, 3956-3961.
4. This compound allowed the preparation of a fluorescent tripodal trisbipyridine ligand and its ruthenium(II) complex. Sohna Sohna, J.-E.; Fages, F. unpublished results.
5. Aoki, I.; Kawabata, H.; Nakashima, K.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1991**, 1771-1773.
6. Bodenant, B.; Fages, F. *Tetrahedron Lett.* **1995**, *36*, 1451-1454. Wilson, G. J.; Sasse, W. H. F.; Mau, A. W.-H. *Chem. Phys. Letters* **1996**, *250*, 583-588.
7. Steemers, F. J.; Verboom, W.; Reinhoudt, D. N.; van der Tol, E. B.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 9408-9414.
8. Dupraz, A.; Guy, C.; Dupuy, C. *Tetrahedron Lett.* **1996**, *37*, 1237-1240.
9. The activated ester, **4**, was obtained by DCC-mediated condensation of 1-pyreneacetic acid with *N*-hydroxysuccinimide. The amino-triester compound, **5**, was prepared according to published procedures.[10]
10. Newkome, G. R.; Lin, X.; Young, J. K. *Synlett* **1992**, 53-54. Dandliker, P. J.; Diederich, F.; Gross, M.; Knobler, C. B.; Louati, A.; Sanford, E. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1739-1742.
11. Selected analytical data. **1**: 250-MHz ^{1}H NMR δ (acetone-d_6): 2.44 (t, 6H), 3.59 (t, 6H), 3.70 (s, 6H), 4.28 (s, 2H), 6.84 (s, 1H), 8.0-8.4 (m, 9H) ppm. Anal. calcd for $C_{31}H_{33}NO_{10},0.5H_2O$: C 63.25, H 5.82, N 2.34; found C 63.53, H 5.83, N 2.69. [**1**,Eu]: m.p.> 250 °C. FT-IR ν (KBr): 1553 (ν_a), 1444 (ν_s) cm^{-1}. Anal. calcd for $C_{31}H_{30}NO_{10}Eu,4.5H_2O$: C 45.99, H 4.85, N 1.73, Eu 18.76; found C 45.99, H 4.54, N 2.20, Eu 18.01. [**1**,Tb]: m.p.> 250 °C.Anal. calcd for $C_{31}H_{30}NO_{10}Tb,4H_2O$: C 46.10, H 4.74, N 1.73, Tb 19.67; found C 45.84, H 4.46, N 1.81, Tb 21.18.
12. The fluorescence quantum yields of the pyrene and lanthanide(III) chromophores were determined by comparison with quinine sulfate[13] in 1N sulfuric acid (0.55 at 25 °C), and Eu aquo ions[14] (0.0074 for 394 nm excitation), respectively. Fluorescence decay of the pyrene chromophore were obtained using the single-photon counting technique.[15] Eu^{III} luminescence decay measurements were performed with a SPEX Fluorolog spectrofluorimeter. Solutions were degassed by repeated freeze-pump-thaw cycles.
13. Hanai, S.; Hirayama, F. *J. Phys. Chem.* **1983**, *87*, 83-89.
14. Haas, Y.; Stein, G. *J. Phys. Chem.* **1971**, *75*, 3668-3677.
15. Fages, F.; Desvergne, J.-P.; Bouas-Laurent, H. *J. Am. Chem. Soc.* **1989**, *111*, 96-102.
16. Darwent, J. R.; Flint, C.D.; Sharpe, N. W. *J. Chem. Soc., Chem. Commun.* **1988**, 747-748. Mwalupindi, A. G.; Blyshak, L. A.; Ndou, T. T.; Warner, I. M. *Anal. Chem.* **1991**, *63*, 1328-1332. Marciniak, B.; Hug, G. L. *J. Photochem. Photobiol. A: Chem.* **1994**, *78*, 7-13. Escabi-Perez, J. R.; Nome, F.; Fendler, J. H. *J. Am. Chem. Soc.* **1977**, *99*, 7749-7754.
17. Murru, M.; Parker, D.; Williams, G.; Beeby, A. *J.Chem. Soc., Chem. Commun.* **1993**, 1116-1118. Sato, N.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 2* **1993**, 621-624. Parker, D.; Williams, J. A. G. . *J. Chem. Soc., Perkin Trans. 2* **1995**, 1305-1314. Abusaleh, A.; Meares, C. F. *Photochem. Photobiol.* **1984**, *39*, 763-769.
18. Sabbatini, N.; Indelli, M. T.; Gandolfi, M. T.; Balzani, V. *J. Phys. Chem.* **1982**, *86*, 3585-3591, and references therein.
19. Darwent, J. R.; Dong, W.; Flint, C. D.; Sharpe, N. W. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 873-880.
20. Concerning the possibility of a ligand-to-metal energy transfer taking place from the $^1\pi\pi^*$ level of bipyridine moieties, see: Prodi, L.; Maestri, M.; Ziessel, R.; Balzani, V. *Inorg. Chem.* **1991**, *30*, 3798-3802.
21. Sabbatini, N.; Guardigli, M.; Lehn, J.-M. *Coord. Chem. Rev.* **1993**, *123*, 201-228.

(*Received in France* 20 *November* 1996; *accepted* 24 *December* 1996)