

Available online at www.sciencedirect.com



Inorganic Chemistry Communications 7 (2004) 1273-1276

INORGANIC CHEMISTRY COMMUNICATIONS

www.elsevier.com/locate/inoche

Zinc porphyrin with phenoxy-bridged pentacoordinate bis(8-hydroxyquinaldinate)gallium lateral pendants: synthesis and photophysical characterization

Massimo La Deda, Mauro Ghedini *, Iolinda Aiello, Irene De Franco

Centro di Eccellenza CEMIF.CAL, LASCAMM, Unità INSTM della Calabria, Dipartimento di Chimica, Università della Calabria, I-87030 Arcavacata (CS), Italy

> Received 28 July 2004; accepted 24 September 2004 Available online 30 October 2004

Abstract

This communication reports the synthesis of polymetallic species formed by a zinc-tetraphenolporphyrinate core $(ZnTPP(OH)_4, 1)$ and peripheral gallium-quinaldinate (Q'_2Ga) fragments. The photophysical analysis of 1 and of the model compound Q'_2GaOPh , **R**, shows an appreciable overlap between the absorption spectra of 1 and the emission spectra of **R**, suggesting the presence of a donor-acceptor energy-transfer process. Contrarily, the obtained results indicated that energy transfer does not occur, hence these polymetallic complexes work as double emitting species, for which the colour of luminescence depends on the excitation energy.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Metalloporphyrin; Gallium quinaldinate complexes; Photophysics; Energy transfer; Fluorescence

The pentacoordinated gallium complexes formed by two equivalents of the chelating 8-hydroxyquinaldine (HQ') and a monodentate ligand, such as substituted phenols or carboxylic acids, are chemically stable coordination compounds which have been studied with reference to their potential applications as molecular emitting materials [1]. The available literature data concerning these species show that their photophysical properties are fairly insensitive to the nature of the monodentate ligand [1a,c], being the active electronic states localized on the quinaldinate fragment [2].

In order to better exploit both the chemistry and the photophysical properties of the "Q'₂Ga" fragment, a protocol for the preparation of polymetallic complexes was established wherein the "Q'₂Ga" emitting features can be combined with those carried by an additional metal centre such as metalloporphyrins. Porphyrins are well known chromophores, which are used in a number of light-operating materials [3]; moreover, several supramolecular architectures, built with porphyrin cores, have been reported [4]. Thus, $ZnTPP(OH)_4$ (1), the zinc derivative which quantitatively forms (IR, NMR and MALDI/TOFMS data) upon addition of the stoichiometric amount of zinc acetate to the symmetrically substituted 5,10,15,20-tetrakis(4-hydroxyphenyl)-21H, 23H-porphyrin, H₂TPP(OH)₄, has been selected to be tested in reactions for the synthesis of mixed Ga/Zn complexes.

^{*} Corresponding author. Tel.: +39 984 492062; fax: +39 984 492066. *E-mail address:* m.ghedini@unical.it (M. Ghedini).

^{1387-7003/\$ -} see front matter © 2004 Elsevier B.V. All rights reserved. doi:10.1016/j.inoche.2004.09.025





We hereby describe the product which was formed upon reacting HQ', $Ga(NO_3)_3 \cdot xH_2O$ and **1** in a 8:4.5:1 molar ratio, respectively [5]. The dark blue solid residue, **2**, recovered after solvent distillation and repeated washing with water, ethanol and chloroform, was highly insoluble in most of the common solvents. The IR spectrum (KBr pellets) of the product displayed the expected absorptions in the 1610–1390 cm⁻¹ range, which are typical for the metal chelated Q' [1a]. Moreover, MALDI/TOFMS data [6] identified a mixture of ZnTPP(OH)₄ and of the polymetallic species $ZnTPP(OGaQ'_2)_4$, $ZnTPP(OH)(OGaQ'_2)_3$, $ZnTPP(OH)_2(OGaQ'_2)_2$, and $ZnTPP(OH)_3(OGaQ'_2)$, whereas elemental analysis gave experimental values which indicated that the product was not a pure species [7].

In order to investigate the influence that the gallium and zinc centres mutually exert on the photophysical properties of **2**, the pentacoordinate reference complex Q'_2 GaOPh, **R**, was synthesized [8], characterized and compared with **1** and **2**. Table 1 presents the photophysical data, in which the relative luminescence intensities were evaluated from the area (on an energy scale) of the luminescence spectra and with reference to a luminescence standard [Ru(bpy)₃]Cl₂ ($\phi = 0.028$ in air-equilibrated water [9]).

The absorption spectrum of **1** (Fig. 1 and Table 1) displayed a strong transition to the second excited state $(S_0 \rightarrow S_2)$ at about 420 nm (the Soret or B band) and two weak vibronic transitions to the first excited state $(S_0 \rightarrow S_1)$ at about 560 and 600 nm (the Q bands). Remarkably, such a spectrum closely resembles that of the unsubstituted zinc porphyrin [10], thus indicating that, probably because of the steric influence [11], the phenols at the *meso* positions form a large dihedral angle with the porphyrin ring, preventing significant π -electron delocalization. With reference to the emitting properties of **1**, it should be pointed out that the internal conversion from S₂ to S₁ is rapid so fluorescence can only be detected from S₁ ($\lambda_{max} = 610$ nm, ϕ



Fig. 1. Overlap of the absorption spectrum of 1 (solid line) with the emission spectrum of R (dashed line).

Table 1					
Photophysical data ^a	of complexes	1,	2	and	R

Compound	Absorption, $\lambda_{\max}/nm(\epsilon/M^{-1} \text{ cm}^{-1})$	Emission ^b λ_{max}/nm	ϕ	τ/ns
1	424(555000), 559(18500), 600(11500)	610	0.018	1.2
2	256(210000), 352(33000), 424(931000), 559(29500), 600(18500)	500, 605	0.040	12.4 ^c ; 1.2 (64%) ^d , 11.7 (36%) ^d
R	256(67000), 358(4500)	510	0.106	12.5

^a In methanol at room temperature.

^b $\lambda_{ex} = 350$ nm.

^c $\lambda_{\rm em} = 500$ nm.

^d $\lambda_{\rm em} = 605$ nm.

= 0.018, and τ = 1.2 ns). Moreover, it should be noted that the molecular conformation of **1** prevents the intermolecular π - π interactions among porphyrin cores which, for unsubstituted porphyrins, usually quench the fluorescence emission, as demonstrated by the fact that, at high concentrations, **1** showed appreciable fluorescence [12].

The absorption spectrum of the reference complex **R** (Table 1) parallels that of previously reported similar quinaldinate gallium derivatives [13]. In particular, an intense band centred at 256 nm and a less intense absorption at 358 nm were observed and both were assigned to $\pi\pi^*$ transitions localized on the quinaldinate fragment [13]. The luminescence spectrum, reported in Fig. 1, exhibits a maximum at 510 nm, that can be safely attributed to a fluorescence deactivation ($\tau = 12.5$ ns) from the lowest excited electronic state [13].

Comparing the spectral pattern of 1 and \mathbf{R} , it is worthy of note that the absorption spectrum of 1 at the wavelengths corresponding to the excitation of the lowest excited state overlaps closely with the emission spectrum of \mathbf{R} (Fig. 1). Such features suggest that energy transfer (ET) from the donor (D) \mathbf{R} to the acceptor (A) 1 could be expected in 2, as it is a polymetallic species wherein the D and A chromophores are covalently linked.

Two mechanisms are generally operating in ET processes: the Dexter ET, which is a coherent transfer of exciton, from D to A sites, at a rate which is proportional to the orbital overlap of D and A. The second ET process is the Förster resonance energy transfer (RET), which consists of a through-space induced dipole energy exchange that is dependent on the D-A distance and on the orientation of the emission-transition dipole of D and the absorption-transition dipole of A (orientation factor, κ^2) [14]. In principle, the Dexter ET should be ineffective in 2, since, as previously mentioned, with respect to the porphyrin ring, the phenol rings adopt a tilted conformation which prevents large orbital overlap between the D and A sites. Indeed, as the luminescence spectrum of 2 shows a band at 500 nm ($\lambda_{ex} = 256$ nm; Table 1 and Fig. 2), which can be attributable to the emission of the D component (e.g., the " Q'_2Ga " fragment), a complete ET process from D to A can be excluded. Alternatively, taking into account the Förster mechanism, the transfer efficiency can be calculated according to the formula $E_{\text{RET}} = 1 - (\tau_{\text{DA}}/\tau_{\text{D}})$, wherein τ_{DA} and τ_{D} are the lifetimes of D, respectively, with and without A [14]. The lifetimes measured at the emission maxima, 500 nm for 2 ($\tau_{DA} = 12.4$ ns) and 510 nm for **R** ($\tau_{\rm D}$ = 12.5 ns) are reported in Table 1 and from these data E_{RET} was found to be 0.008. This low value suggests that, probably because of the unfavourable κ^2 factor, the RET mechanism practically does not work in 2.

0.5 0.4 0.4 0.1

Fig. 2. Absorption (solid line) and emission spectra ($\lambda_{ex} = 256$ nm, dashed line; $\lambda_{ex} = 424$ nm, dotted line) of complex **2** in methanol solution.

This study shows a possible synthetic protocol for the preparation of new Ga/Zn polymetallic complexes. In the experimental conditions here described the main product is Ga₄/Zn. As Ga₄/Zn is highly insoluble and very difficult to purify completely, traces of the homologous polymetallic species (e.g., Ga₃/Zn, Ga₂/Zn or Ga/ Zn) cannot be effectively removed. However, the above results suggest that the photophysical properties of the whole Ga_n/Zn series (n = 1-4) should be unaffected by the number of the gallium centres which surround the zinc-containing core. In particular, as reported for 2, a double emission wavelength, at 500 and 606 nm, was detected (Table 1). Therefore, as excitation on the quinaldinate fragment produces a bluish green emission and excitation on the porphyrin levels produces a red orange emission, the luminescence colour can be modulated by the selected excitation wavelength. In conclusion, these preliminary results suggest that polynuclear complexes formed by HQ' and H2TPP(OH)4 ligands and containing different metal ions may actually modulate the emission colour and/or improve the κ^2 factor. Further studies are therefore currently underway to investigate these complexes for both fundamental and applicative purposes.

Acknowledgement

This research was supported by the Italian Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR) through the Centro di Eccellenza CEMIF.CAL grant.

References

 (a) L.S. Sapochak, P.E. Burrows, D. Garbuzov, D.M. Ho, S.R. Forrest, M.E. Thompson, J. Phys. Chem. 100 (1996) 17776;
 (b) A. Elschner, H.W. Heuer, F. Jonas, S. Kirchmeyer, R. Wehrmann, K. Wussow, Adv. Mater. 13 (2001) 1811;
 (c) S. Tan, B. Zhao, Y. Zou, Z. Xiao, X. Wang, G. Yu, Y. Liu, D. Zhu, J. Mater. Sci. 39 (2004) 1405.



- [2] (a) C.H. Chen, J. Shi, Coor. Chem. Rev. 171 (1998) 161;
 - (b) Y. Qiu, Y. Shao, D. Zhang, X. Hong, Jpn. J. Appl. Phys. 39 (2000) 1151;

(c) J. Qiao, Y. Qiu, L. Wang, L. Duan, Y. Li, D. Zhang, Appl. Phys. Lett. 81 (2002) 4913;

(d) M. Ghedini, M. La Deda, I. Aiello, A. Grisolia, J. Chem. Soc., Dalton Trans. (2002) 3406;

(e) M. Ghedini, M. La Deda, I. Aiello, A. Grisolia, Synth. Met. 138 (2003) 189;

(f) M. Ghedini, M. La Deda, I. Aiello, A. Grisolia, Inorg. Chim. Acta 357 (2004) 33.

- [3] (a) M.A. Baldo, D.F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M.E. Thompson, S.R. Forrest, Nature 395 (1998) 151;
 (b) R.C. Kwong, S. Sibley, T. Dubovoy, M. Baldo, S.R. Forrest, M.E. Thompson, Chem. Mater. 11 (1999) 3709;
 (c) J. Otsuki, A. Suka, K. Yamazaki, H. Abe, Y. Araki, O. Ito, Chem. Commun. (2004) 762.
- [4] (a) C.M. Drain, J.-M. Lehn, J. Chem. Soc., Chem. Commun. (1994) 2313;

(b) S. Leininger, B. Olenyuk, P.J. Stang, Chem. Rev. 100 (2000) 853.

- [5] The gallium salt was dissolved in the minimum amount of water and added to an ethanolic solution of 1 containing four equivalents of sodium hydroxide. To such a solution, HQ', in ethanol, was successively added and the resulting mixture heated under reflux overnight.
- [6] I. Aiello, L. Di Donna, M. Ghedini, M. La Deda, A. Napoli, G. Sindona, Anal. Chem. 76 (2004) 5985.
- [7] The calculated values of the elemental analyses do not differentiate significantly between the ZnTPP(OGaQ'_2)_4, ZnTPP(OH) (OGaQ'_2)_3ZnTPP(OH)_2(OGaQ'_2)_2 or ZnTPP(OH)_3(OGaQ'_2) species since the related C%, H% and N% values span the ranges

64.27–66.10, 4.26–3.72 and 7.25–7.22, respectively. Moreover, ZnTPP(OH)₄ analyses for C%, 71.21; H%, 3.80 and N% 7.55. In a typical preparation, the obtained product analyzed for C%, 63.99; H%, 4.17; N%, 7.68. Thus, although the MALDI/TOFMS data do not allow for a quantitative estimation of the relative abundance of the different metal complexes, on the bases of both the reproducibility of the preparation and the values of the data we obtained, we believe that the ZnTPP(OH)(OGaQ'_2)_3, ZnTPP(OH)_2(OGaQ'_2)_2, ZnTPP(OH)_3(OGaQ'_2) and ZnTPP(OH)_4 species are present in trace amounts only and do not affect the results of the photophysical measurements.

- [8] The complex Q'₂GaOPh was prepared by adapting the procedure described in Ref. [1a].
- [9] K. Nakamaru, Bull. Chem. Soc. Jpn. 55 (1982) 2967.
- [10] H.L. Anderson, Chem. Commun. (1999) 2323.
- [11] D.A. Fletcher, R.F. McMeeking, D. Parkin, J. Chem. Inf. Comput. Sci. 36 (1996) 746.
- [12] M.C. Lensen, S.J.T. van Dingenen, J.A.A.W. Elemans, H.P. Dijkstra, G.P.M. van Klink, G. van Koten, J.W. Gerritsen, S. Speller, R.J.M. Nolte, A.E. Rowan, Chem. Commun. (2004) 762.
- [13] (a) O. Popovych, L.B. Rogers, Spectrochim. Acta 16 (1960) 49;
 (b) O. Popovych, L.B. Rogers, Spectrochim. Acta 21 (1965) 1229;
 (c) L.S. Sapochack, P.E. Burrows, D. Garbuzov, D.M. Ho, S.R. Forrest, M.E. Thompson, J. Phys. Chem. 100 (1996) 17766;
 (d) L.S. Sapochack, A. Padmaperuma, N. Washton, F. Endrino, G.T. Schmett, J. Marshall, D. Fogarty, P.E. Burrows, S.R. Forrest, J. Am. Chem. Soc. 123 (2001) 6300;
 (e) A. Elschner, H.W. Heuer, F. Jonas, S. Kirchmeyer, R. Wehrmann, K. Wussow, Adv. Mater. 13 (2001) 1811.
- [14] J.R. Lakowicz, Principle of Fluorescent Spectroscopy, second ed., Kluwer Academic/Plenum Publishers, New York, 1999.