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Luminescence of ytterbium in binuclear bis(porphyrin) complexes

Yurii V. Korovin,*[a] Natalia V. Rusakova,[a] Zinaida I. Zhilina,[b] Yurii V. Ishkov,[b] Sergey V. Vodzinsky[b] and Vladimir P. Dotsenko[a]

[a] *A. V. Bogatsky Physico-Chemical Institute, National Academy of Sciences of Ukraine, 65080 Odessa, Ukraine. Fax: +38 0482 652 012; e-mail: physchem@paco.net*

[b] *I. I. Mechnikov Odessa National University, 65026 Odessa, Ukraine. Fax: +38 0482 235 214; e-mail: jvi@te.net.ua*

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Binuclear complexes of ytterbium with four asymmetric bis(porphyrins) have been obtained, and their spectral and luminescence properties have been investigated.

Ytterbium porphyrins are promising IR-luminescence probes in biomedical practice.[1,2] However, there is almost no data on lanthanide complexes with covalently bound dimeric (or bis) porphyrins.[3] Synthetic dimeric porphyrins are good model systems for studying electron-transfer processes and the redox, catalytic and optical properties of the porphyrin chromophore as a main constituent of important biological systems.[4] We studied the spectral and luminescence properties of binuclear ytterbium complexes with four asymmetric bis(porphyrins) (Figure 1). The synthesis of the complexes was described previously.[5]

The complexes were prepared by a modified method[6] through the interaction of a 15 to 20-fold excess of Yb(acac)$_3$ (acac is acetylacetone as an extra ligand) and free porphyrin base **1**–**4** in 1,2,4-trichlorobenzene on boiling under argon for 20–25 h depending on porphyrin. The purity of the compounds was controlled by UV, IR and ^{1}H NMR spectroscopy. The complexation with two metal centres was confirmed by the absorption spectra and elemental analysis data. The spectra of metal-free porphyrins (Specord M40 UV-VIS spectrophotometer) were characterised by the presence of an intense split Soret band and four *Q*-bands (I–IV) (Table 1). The ratio of the intensities of the *Q*-bands allowed us to assign these spectra to the etio type: IV > III > II > I. It is known that the splitting (*i.e.*, the ratio between the intensities of short-wave and long-wave components) of the Soret band in dimeric porphyrins can give qualitative information on their structure.[7] The above ratios in the considered dimers are practically equal. This fact suggests an isotropic (intermediate between parallel and perpendicular) interlocation of porphyrins chromophores.[7] Almost synchronous changes in the spectra of all complexes were observed as compared to the spectra of free bases. Thus, the spectra of complexes consist of two *Q*-bands different in intensity and a broadened Soret band with no splitting.

Luminescence was excited with a Xe-150 xenon lamp and a Nd^{3+}:YAG laser (a SDL-1 spectrofluorimeter equipped with a photon-counting system and an attachment for phosphorescence measurements was used). The relative quantum yields of luminescence (Φ) of Yb$^{\text{III}}$ ions in complexes (Zn tetraphenylporphyrin as a standard compound, $\Phi = 0.03$ in ethanol) and luminescence lifetime (τ) were determined as described elsewhere.[8]

Table 1 Absorption spectra of bis(porphyrins) **1**–**4** and their ytterbium complexes in DMF solutions ($c = 2\times10^{-5}$ mol dm^{-3}).

Ligand/ Complex	$\lambda_{\max}$/nm (log ε)				
	Soret band	*Q*-bands			
		I	II	III	IV
1	419 (5.25)/ 425 (5.27)	646 (3.91)	590 (3.99)	550 (4.08)	514 (4.30)
(Yb)$_2$-**1**	423 (5.30)		595 (426)	557 (4.72)	
2	419 (5.80)/ 426 (5.85)	646 (4.33)	591 (4.40)	550 (4.57)	515 (4.89)
(Yb)$_2$-**2**	424 (5.86)		598 (4.71)	559 (5.23)	
3	414 (5.54)/ 427 (5.53)	645 (3.92)	589 (4.05)	549 (4.27)	514 (4.53)
(Yb)$_2$-**3**	426 (5.56)		596 (4.42)	558 (4.90)	
4	415 (5.64)/ 426 (5.63)	644 (4.01)	588 (4.14)	548 (4.28)	513 (4.60)
(Yb)$_2$-**4**	423 (5.70)		597 (4.39)	558 (4.95)	

Table 2 Luminescence characteristics of the binuclear bis(porphyrins) complexes of ytterbium (295 K).

Complex[a]	Position of T-levels, *E*/cm^{-1}	$\Phi\times10^3$ [b]	τ/μs[c]	$\Phi\tau^{-1}/10^{-3}$ s^{-1}
(Yb)$_2$-**1**	12980	4.1	5.1	0.80
(Yb)$_2$-**2**	12950	5.4	6.0	0.81
(Yb)$_2$-**3**	12995	2.7	3.7	0.73
(Yb)$_2$-**4**	12960	3.5	4.6	0.76
Yb-TPP	12890	4.2	5.1	0.82
Yb-T3PyP	12935	7.8	8.9	0.88
Yb-T4PyP	12920	10.1	10.9	0.93

[a] DMF solutions ($c = 2\times10^{-5}$ mol dm^{-3}). [b] $\lambda_{\text{exc}} = 425$ nm; luminescence spectra were corrected with a standard lamp. [c] Errors are ±10%.

The 4*f* luminescence of Yb$^{\text{III}}$ ions in the test complexes is observed at 960–1010 nm ($\lambda_{\max} = 980$ nm, $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition) on the excitation in a wide spectral range (~300–600 nm). The highest efficiency was detected on excitation at the maximum of the Soret band. The similarity of the excitation spectra of the 4*f* luminescence of Yb$^{\text{III}}$ in porphyrin complexes to their absorption spectra [Figure 2, (Yb)$_2$–**1** complex as an example] indicates that ytterbium ions take energy from the organic

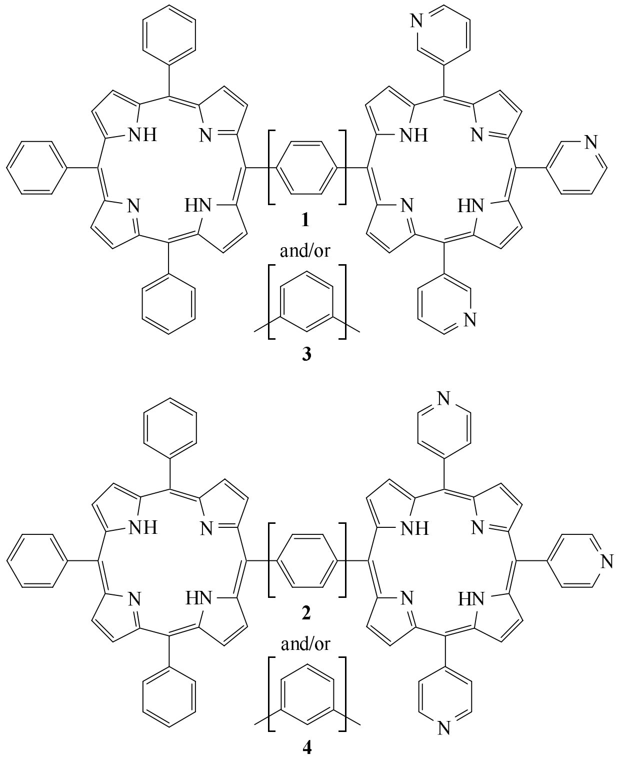

Figure 1 Structure of the ligands.

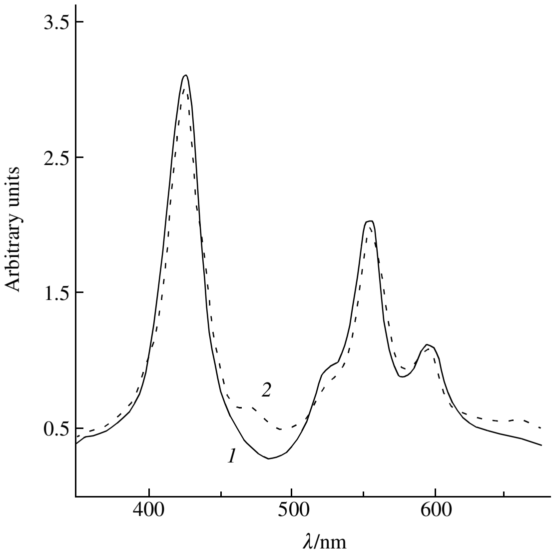

Figure 2 Electronic (*1*) absorption and (*2*) excitation spectra of $(Yb)_2$-**1** (2×10^{-5} mol dm^{-3} in DMF; λ_{an} = 980 nm).

moiety of the complex molecule [the energies of the triplet levels (*T*) of dimeric porphyrins are ~13000 cm^{-1}].

The characteristics of the 4*f* luminescence of Yb^{III} in the complexes are given in Table 2. For comparison, data for complexes with *meso*-tetraphenylporphyrin (TPP) and *meso*-tetra[3(4)-pyridil]porphyrin (T3PyP and T4PyP) are given. The data suggest that the luminescence in monomeric and dimeric complexes is somewhat higher in *p*-pyridil derivatives [*e.g.*, Yb–T4PyP, $(Yb)_2$–**2**, $(Yb)_2$–**4**] than in *m*-pyridil derivatives [*e.g.*,Yb–T3PyP, $(Yb)_2$–**1**, $(Yb)_2$–**3**]. However, we believe that the fact that 4*f* luminescence efficiency in dimers is somewhat lower than that in monomeric complexes is more important. The reason is the resonance Yb–Yb interaction, which manifests itself in spite of a rather long distance between two lanthanide centres. With the use of molecular mechanics calculations (the MM$^+$ method, the HYPERCHEM 5.1 program) we found that the Yb–Yb distance in *m*-phenylene derivatives $(Yb)_2$–**3** and $(Yb)_2$–**4** is equal to 10.8±0.1 Å. The Yb–Yb distance in *p*-phenylene derivatives $(Yb)_2$–**1** and $(Yb)_2$–**2** is 12.0±0.1 Å. These results are in good agreement with data obtained by other methods for structurally similar complexes.[9] Evidently, the difference in distances explains the higher luminescence characteristics of *p*-phenylene derivatives. Note that analogous energy-transfer processes were observed before in dinuclear lanthanide complexes with *p*-*tert*-butylcalix[8]arene[10] at almost the same metal–metal distances. It should be noted that the value of Φ/τ indicates that the quantum efficiency of intramolecular energy transfer in the test complexes is high (higher than that in Yb crown-porphyrins[8]). The almost quenched molecular luminescence (manifested in non-metal porphyrins as two weakly structured bands in the regions 610–645 nm and 690–720 nm) proves this fact. Moreover, the quantum yields of the 4*f* luminescence of Yb^{III} ions and the luminescence lifetime are the highest.[11]

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