

Lanthanide complexes of macrocyclic and macrobicyclic N-oxides; light-converting supramolecular devices

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ABSTRACT: Several ligands of various topology: macromonocyclic, macrobicyclic, cylindrical, acyclic, and pendant-type bearing photoactive units: 3,3'-biisoquinoline-2,2'-dioxide, methyl-2-pyridine and dibenzoylmethane display an efficient energy transfer from the excited triplet state of the ligand to the resonance level of the lanthanide cation. The lanthanide complexes are thus highly luminescent. The Eu(III) cryptate of 3 exhibits the highest quantum yield for the Eu(III) emission (0.17).

INTRODUCTION

Supramolecular photochemistry (ref. 1–3) is a rapidly expanding branch of supramolecular chemistry, covering area such as light-induced ionophore selectivity, charge separation, photoinduced energy migration, selective photochemical reactions, light conversion based on absorption-energy transfer-emission process, etc.

The latter process has been a focus of an extensive recent research. A combination of bicyclic molecular architecture with heterocyclic sensitizing units gave rise to the lanthanide cryptates (ref. 4) which displayed a range of desirable photophysical and photochemical features that might have been used in modern, time-resolved spectrofluorimetric immunoassays of unique sensitivity (ref. 5).

The nitrogen heterobiaryls such as 2,2'-bipyridine, are not very strong ligands for the lanthanide complexation, unless forming a three-dimensional cage molecule that binds lanthanides strongly, due to macrobicyclic effect. However, the literature data shows that the corresponding N-oxides are much more powerful ligands for the lanthanide complexation, as hard Lewis bases, and at the same time, more efficient sensitizers for the lanthanide emission (ref. 6). These characteristics led to the development of a family of photoactive ligands bearing heterocyclic N-oxides capable of binding the lanthanide cations and sensitizing their emission. Such complexes may be very attractive as fluorescent markers for modern medical diagnostics based on labelled monoclonal antibodies.

RESULTS AND DISCUSSION

The 1,1'-dimethyl-3,3'-biisoquinoline-2,2'-dioxide (1) (ref. 7) turned out to be particularly efficient sensitizer for the Eu(III) emission, and its 2:1 complex with europium chloride displayed an outstanding photochemical characteristics; its quantum yield was 0.25. The complex was not stable in water, however. This encouraged us to synthesize a range of macromonocyclic and macrobicyclic ligands incorporating one, two, or three such photoactive units (CHART).

Initially, we have obtained the ligand 3, bearing one 3,3'-biisoquinoline-2,2'-dioxide unit which displayed an excellent photophysical properties that are collected in the Table 1. It is noteworthy that the quantum yield of the Eu(III) luminescence depended

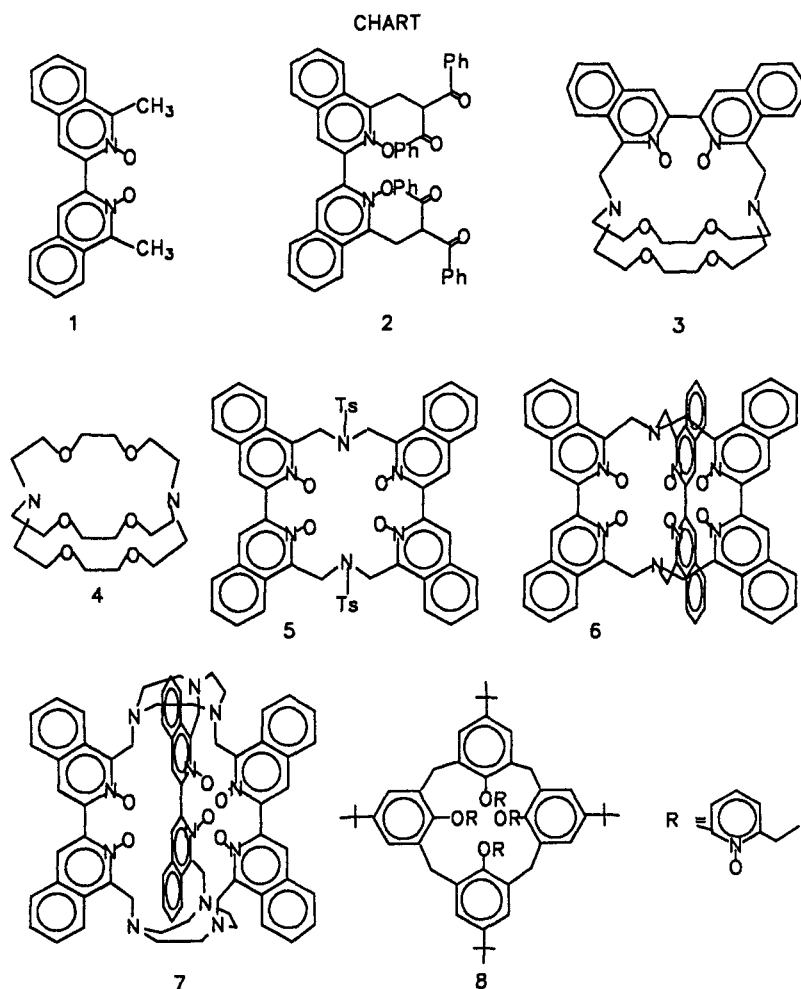


TABLE 1. Photophysical characteristics of the Eu(III) complexes in MeCN solution* at room temperature. $\lambda_{exc} = 337$ nm

Ligand (L)	Eu(III) salt (S)	L/S ratio	λ_{em} (nm)	τ (ms)	Φ
1	EuCl ₃ ^a	2:1	592, 618, 700	0.65	0.25
1	Eu(DBM) ₃	1:1	594, 615, 653, 703	0.20	0.057
2	EuCl ₃	"	579, 594, 615, 622, 653, 703	0.64	0.05
2 ²⁻	EuCl ₃	"	592, 615, 653, 703	0.60	0.027
2 ²⁻	EuCF ₃ SO ₃	"	580, 594, 615, 653, 702	0.38	0.0279
3	EuCl ₃	"	580, 590, 600, 611, 618, 650	0.62	0.057
3	Eu(CF ₃ SO ₃) ₃	"	580, 590, 600, 611, 619, 650	0.70	0.17
3	Eu(CF ₃ SO ₃) ₂ Br ^a	"	580, 590, 600, 611, 619, 650	0.52	0.138
3	Eu(ClO ₄) ₃ Br ^a	"	579, 589, 598, 611, 618, 682	0.64	0.04
3	Eu(DBM) ₃	"	585, 613, 653, 703	0.26	0.023
4	Eu(DBM) ₃	"	594, 613, 653, 703	0.22	0.0331
5	Eu(ClO ₄) ₃	"	580, 590, 595, 614, 618, 650	0.25	0.064
6A**	Eu(CF ₃ SO ₃) ₃	"	580, 607, 613, 653, 703	0.25	0.0022
6B**	Eu(CF ₃ SO ₃) ₃	"	580, 594, 607, 652, 703	0.24	0.0015
7	Eu(CF ₃ SO ₃) ₃	"	594, 616, 653, 703	0.14	0.001
8	EuCl ₃	"	580, 592, 616, 700	-	0.003
8	TbCl ₃	"	490, 544, 587, 618	-	0.002

a): from ref. 7; *) spectra of 8 in MeOH; **) two diastereoisomers due to axial chirality of the 3,3'-biisoquinoline-2,2'-dioxide unit

very significantly on the counter ion involved. The highest quantum yield was obtained with trifluoromethanesulphonate as a counter ion, although we expected a better performance with bibenzoylmethane anion, which is also a good sensitizer for the lanthanide emission (ref. 8). It is worth of mentioning that the Eu(III) cryptate of 3 was stable in water solution. The ligands 5, 6, and 7 have been obtained in a hope to increase the quantum yield for the Eu(III) emission, due to "antenna effect", e. g. collective convergent light harvesting and energy transfer to the Eu(III) cation. It was a bit disappointing that more sensitizing units than one did not lead to enhanced quantum yield of the Eu(III) emission, as shown in the Table 1.

The photoactive calix(4)arene 8 bearing four methyl-2-pyridine units formed a photoactive Eu(III) and Tb(III) complexes which were not stable in water media, and the quantum yields for the emission were not particularly impressive (ref. 9).

The combination of a neutral photoactive binding sites (N-oxides) and ionizable photoactive groups, such as 1,3-diketonates, may lead to a collective cooperation in the energy transfer to the lanthanide cations. Furthermore, there is a chance to form heterobinuclear, or even heteropolynuclear lanthanide complexes which might have been of particular interest, both theoretical and practical.

Initially, we have investigated the complex of Eu(DBM)₃ (DBM = dibenzoylmethane) with 1,1'-dimethyl-3,3'-biisoquinoline, as a model compound for further bicyclic structures. In this case the quantum yield was not particularly satisfactory. Secondly, in order to see the interaction of the encapsulated lanthanide cation with the photoactive 1,3-diketonate, we have formed the Eu(III) cryptate 4, surrounded by three dibenzoylmethane anions. The quantum yield of the emission process of Eu(III) was enhanced by factor of ca. 1.5, comparing to Eu(DBM) chelate. This observation may be useful in the future work involving photoactive lanthanide cryptates, ion-paired with photoactive 1,3-diketonates.

The introduction of two dibenzoylmethane residues into the 3,3'-biisoquinoline-2,2'-dioxide skeleton led to the ligand 2 which can be doubly ionized. We have formed the neutral 1:1 complex of 2 with EuCl₃, and after double ionization of 2, two 1:1 complexes of the formula: 2.EuCl and 2.EuCF₃SO₃. In the two latter cases we expected a participation of the 1,3-diketonate side-arms in the coordination to the Eu(III) cation, and eventually enhanced quantum yield of the Eu(III) emission, but the experimental data show the lack of increased efficiency in the energy transfer to the Eu(III).

CONCLUSIONS

It seems from the experimental data that more photoactive units incorporated into the photoactive ligand may not increase the efficiency of the absorption-energy transfer-emission process. Bicyclic structures bearing three photoactive units (6, 7) were found to be less efficient than the cryptand 3. This fact may be interpreted in this way that the cavity of the compound 6 is too small to accommodate Eu(III) cation fully, and either the N-oxide units have to be distorted significantly to allow the Eu(III) cation to enter the cavity, or the Eu(III) forms an exclusive complex with 6. In both cases the energy transfer may not be remarkable. The ligand 7 may possess the cavity that is too large for Eu(III), and small water molecules may penetrate the cavity, quenching the fluorescence to a remarkable extent. Thus it seems that careful interplay with anions may do better job in order to enhance the quantum yields, than an introduction of more photoactive units, as demonstrated with the ligand 3.

The combination of photoactive neutral and ionizable groups may need a further work, since our preliminary results show no significant cooperativity in the energy transfer process in the model systems. Probably, both photoactive units should possess the lowest triplet excited state very close to each other to ensure the overall energy transfer very efficient.

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