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Calixarene[4]-Podands and Barrel-Shaped Calixarene[4]-Cryptands Based on 5,5'-substituted-2,2'-bipyridine Subunits

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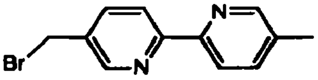
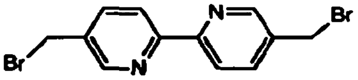
Abstract: The synthesis and preliminary lanthanides complexation studies of novel *syn*-1,3-*bis*-[(5-methyl-2,2'-bipyridine-5'-yl)methyl]-*p*-*tert*-calix[4]arene L_3 and *tetra*-[(5-methyl-2,2'-bipyridine-5'-yl)methyl]-*p*-*tert*-calix[4]arene L_4 podands and new *bis*-[(2,2'-bipyridine-5,5'-diyl)dimethyl]-*bis*-*p*-*tert*-calix[4]arene L_5 and *tetra*-[(2,2'-bipyridine-5,5'-diyl)dimethyl]-*bis*-*p*-*tert*-calix[4]arene L_6 cryptands with a barrel-shaped structure are described.

Molecular species capable of exhibiting strong luminescence are interesting from both a fundamental point of view and also because of their potential use for a variety of applications (photocatalysis, chemiluminescence and luminescent labels in fluoroimmunoassay). Recently, considerable efforts have been dedicated to the design and synthesis of lanthanides complexes in which an absorption-energy transfer-emission (A-ET-E) process has clearly been established. Among the numerous bipyridine-based macrobicyclic[1], macrocyclic[2-4], and cage-type[5-7] ligands it appears that one of the most promising compounds for the obtention of highly stable and strongly luminescent lanthanides complexes, contain four oligopyridine subunits (four bipy[3] or two bipy and two phen[4,8]) or two bipy subunits incorporated in a macrocycle and phosphinate esters in the side-arms[9] (bipy for 2,2'-bipyridine and phen for 1,10-phenanthroline).

To design a good ligand and emitting system based on lanthanide one has to take at least three prerequisites into account: (i) lanthanides ions must be shielded from the solvent; (ii) the ligand should not be sterically hindered in close proximity of the complexation site and finally (iii) the ligand must have the lowest excited-state sufficient high in energy to insure energy transfer to the lanthanides. Recent research has demonstrated that amide substituted calix[4]arenes can strongly encapsulated Eu^{3+} and Tb^{3+}. Interestingly, the latter complex exhibit a remarkably high luminescence quantum yield.[10] This, and previous findings from our laboratory, prompted us to investigate the synthesis of the novel podands L_3 and L_4 as well as new cryptands L_5 and L_6. 5,5'-substituted-2,2'-bipyridine precursors **1** and **2** were chosen as building blocks for the synthesis of the ligands presented in this communication.

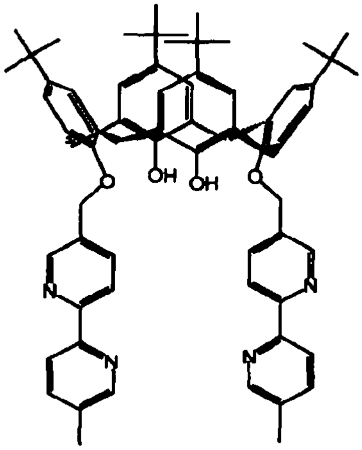


1

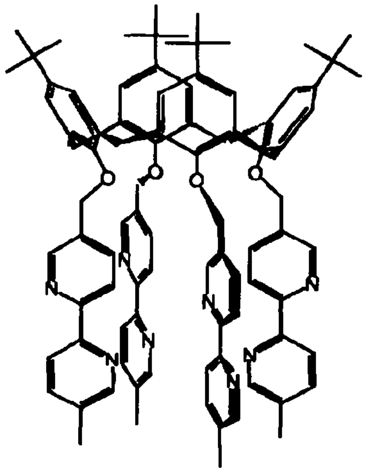


2

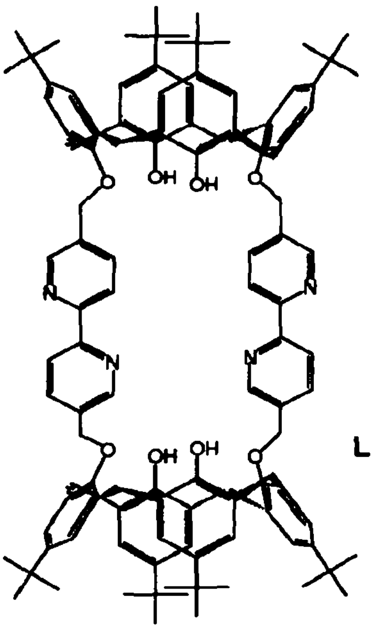
We now wish to report the first examples of *tetra*-bipy substituted calix[4]arenes together with double calix[4]arenes bridge by two- or four bipy subunits. Due to their barrel-shaped arrangement, these new multi-*käfigartige* molecules have been called *calix[4]barrelands*. Calixarenes functionalized by one bipy (substituted in the 5 position)[11] or by two bipy (substituted in the 6 position[12] or in the 4 position[13]) have previously been reported. Compounds L_3 and L_5 were respectively prepared by reaction of 5-methyl-5'-(bromomethyl)-2,2'-bipyridine **1** (2 equiv.) or 5,5'-(bromomethyl)-2,2'-bipyridine **2** (1 equiv.) with *p-tert*-butylcalix[4]arene (1 equiv.), using Na_2CO_3 as base.



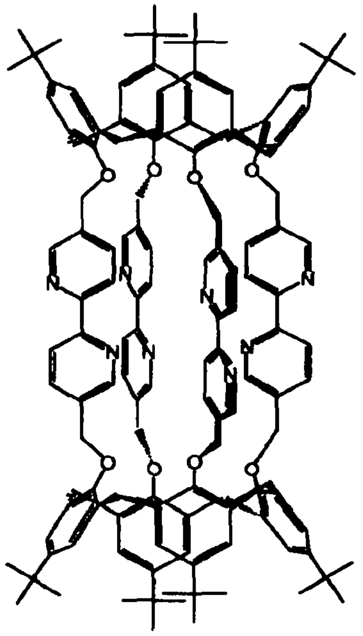
L_3



L_4



L_5



L_6

The ^1H NMR spectrum of L_3 and L_5 are similar and exhibits, as expected, a single AB system for the bridging methylene groups, a singlet for the methyl (only observed for L_3) and for the OH, a singlet for the OCH_2-bpy groups, two singlets for the phenyl protons and the *tert*-butyl substituents. The spectrum shows a dissymmetric bipy for ligand L_3 (six patterns) and a symmetric bipy for ligand L_5 (three patterns).

Compounds L$_4$ and L$_6$ were respectively prepared by reaction of NaH (4.4 equiv.) with *p-tert*-butylcalix[4]arene (1equiv.), or by reacting NaH (4.4 equiv.) with the crytand L$_5$ followed by subsequent reaction with the monobromo derivative **1** or the dibromo derivative **2**. The *calix[4]barreland* L$_6$ could not be prepared by a direct synthesis from the sodium tetraanion of *p-tert*-butylcalix[4]arene, but only from the sodium tetraanion of the conformationally rigid macrotricycle L$_5$, followed by a subsequent reaction with the compound **2**. It is noteworthy that high dilution conditions, are not needed for the synthesis of molecules L$_5$ and L$_6$. A template-effect of sodium could not be excluded; however, the sodium-free cryptand was isolated at the end of the reaction. A *transcoïde* conformation of the two pyridine rings of the bipy's is expected for all new ligands, in solution and in the solid state, in order to minimize the steric repulsion of the nitrogen doublets.

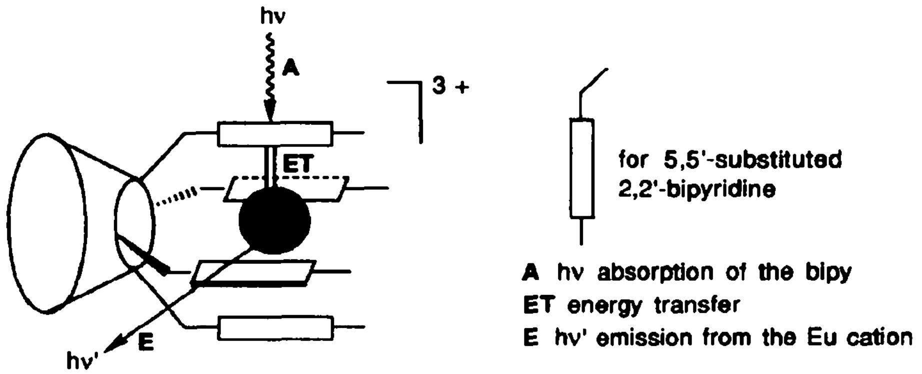
Table: Selected data for compounds depicted in Scheme

Product	Isolated yield (%) a)	IR (cm^{-1}) b)	^{1}H NMR δ_{AB}(ppm) J_{AB}; $\Delta\nu$(Hz) c)	UV-Vis. λ_{max} (nm) ε (M^{-1}cm^{-1}) d)	Mass spectra e)
L$_3$	78	3398, 1599	3.75 13.1; 193.6	290(44900) 230(36300)	1013
L$_4$	29	–, 1600	3.51 12.3; 242.7	290(69500) 230(56200)	1377
L$_5$	23	3402, 1600	3.87 13.0; 184.7	290(68400) 231(66900)	1657
L$_6$	4	–, 1600	4.00 12.9; 230.1	284(63100) 230(72100)	2018

a) averaged isolated yield obtained from at least two reactions; b) $\nu_{O\text{-}H}$ and ν_{bipy} measured in KBr pellets; c) measured in CDCl$_3$ solutions at room-temperature, data was referenced relative to the residual protitated solvent (7.25 ppm); d) measured in CH$_2$Cl$_2$ solutions at room-temperature; e) obtained by FAB$^+$ using (m-NBA) as matrix and correspond to [M+H]$^+$.

The *calix[4]barreland* L$_6$ exhibits a first order NMR spectrum, showing a highly symmetric molecule with a C$_4$ rotation axis along the center of the two calixarenes and a plane of symmetry crossing the middle of the carbon-carbon bonds of the bipy subunits. Based on their proton and carbon NMR spectra all four novel ligands adopt a fixed cone conformation in solution at room-temperature, with the bipy pendant subunits on the same side with respect to an ideal plane containing the bridging methylene groups of the macrocycle in podands L$_3$ and L$_4$.

Finally, preliminary Eu^{3+} complexation studies with ligands L$_3$ and L$_4$ show the straightforward synthesis of new fluorescent complexes.[14] Due to the presence of four chromophores in podand L$_4$ the light harvesting is quite high (antenna effect) and the A-ET-E principle illustrated in the Scheme has been clearly established. The complex [EuL$_4$]$^{3+}$ has a high molar extinction coefficient and a high luminescence quantum yield. The efficiency of the incident light-emitted light conversion defined as the product of the absorption efficiency and the luminescence quantum yield, is the highest value (1.3 %) found up till now for a luminescent europium complex. Further development of this synthetic work will be directed toward the preparation of polymeric *supramolecular devices* and their use for dual emitting systems and as amperometric sensors, thanks to the presence of two or four phenolic groups, respectively in compounds L$_3$ and L$_5$. The photophysical studies of these novel ligands as well as their lanthanide complexes is currently in progress and will be published elsewhere.



Acknowledgments

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14. $[Eu(L_3)](NO_3)_3 \cdot 4H_2O$ 91%; FAB^+ (m-NBA) 1289 $[M-NO_3]^+$; elemental analysis: Found: C, 75.09; H, 7,68; N, 4.99, Calc. for $C_{68}H_{76}N_4O_4 \cdot 4H_2O$ (M_r = 1013.388 + 72.061): C, 75.25; H, 7.80; N, 5.16.
$[Eu(L_4)](Cl)_3 \cdot 6H_2O$ 68%; FAB^+(m-NBA) 1564 $[M-2Cl]^+$, 1528 [M-3Cl-H]; elemental analysis: Found: C, 74.16; H, 7.25; N, 7.41, Calc. for $C_{92}H_{96}N_8O_4 \cdot 6H_2O$ (M_r = 1377.842 + 108.092): C, 74.37; H, 7.33; N, 7.54.

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