A calix[4]arene receptor modified with 8-hydroxyquinoline for supramolecular energy transfer

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A new calix[4]arene receptor modified with 8-hydroxyquinoline has been synthesised, exhibiting luminescence and energy transfer properties in the presence of coordinated Eu^{3+} and Tb^{3+} ions.

Calixarene macrocyclic compounds have been exploited as building block systems[1] or for recognition of main group,[2] lanthanide[3] and actinide[4] metals by incorporating specific functions. Modified calixarene-based ligands with phosphino groups have been successfully employed in the preparation of transition metal catalysts, exhibiting well-defined cavities.[5,6] In addition, complexes of Eu^3 and Tb^{3+} ions with calixarene ligands incorporating chromophoric groups have also been pursued[7] because of their potential usefulness in fluoro-immunoassays. Luminescence of the metal ion in these complexes arises upon efficient light absorption by the ligand, followed by ligand-to-metal energy transfer.[8,9] Recently, a modified 8-hydroxyquinoline species[10] has been proposed as a versatile building block for supramolecular chemistry; however, the corresponding calixarene derivatives have never been reported in the literature. Here, we describe the novel bis(8-oxyquinoline)calix[4]arene ligand **3**, specially designed

for photophysical applications in metallo-supramolecular chemistry.

The synthesis (Scheme 1) was carried out by reacting *p-tert*-butylcalix[4]arene[11] with $Br(CH_2)_3Br$, in the presence of K_2CO_3, yielding the 5,11,17,23-tetra(*tert*-butyl)-25,27-bis(3-bromopropoxy)-26,28-(dihydroxy)calix[4]arene intermediate compound **1**[12]† as a white powder (85%). Treatment of **1** with K_2CO_3 and 8-hydroxyquinoline **2**, in acetonitrile, gave the new species **3**‡ as a white powder, with a yield of 25%, after chromatography ($R_f = 0.48$, cyclohexene–ethyl acetate 2 : 1, v/v). Microanalytical results were consistent with the formulation $C_{68}H_{78}N_2O_6 \cdot C_4H_8O_2$ (with 1 molecule of ethyl acetate) and the FAB MS spectrum revealed a molecular ion at 1019.9, consistent with $[C_{68}H_{78}N_2O_6]^+$.

^{1}H as well as ^{13}C NMR spectra clearly indicated a twofold molecular symmetry for the ligand **3**, confirming the bonding of quinolinic oxygen to the propoxy fragment of calix[4]arene. The ^{1}H NMR spectrum exhibited a large shift of the CH_2 signals (qui-$OCH_2CH_2CH_2OAr$) from 4.02 (compound **1**) to 4.55 ppm. The assignment of the signals of the quinoline fragments of **3** was based on the corresponding two-dimensional ^1H–^1H COSY NMR spectra (Fig. 1). The
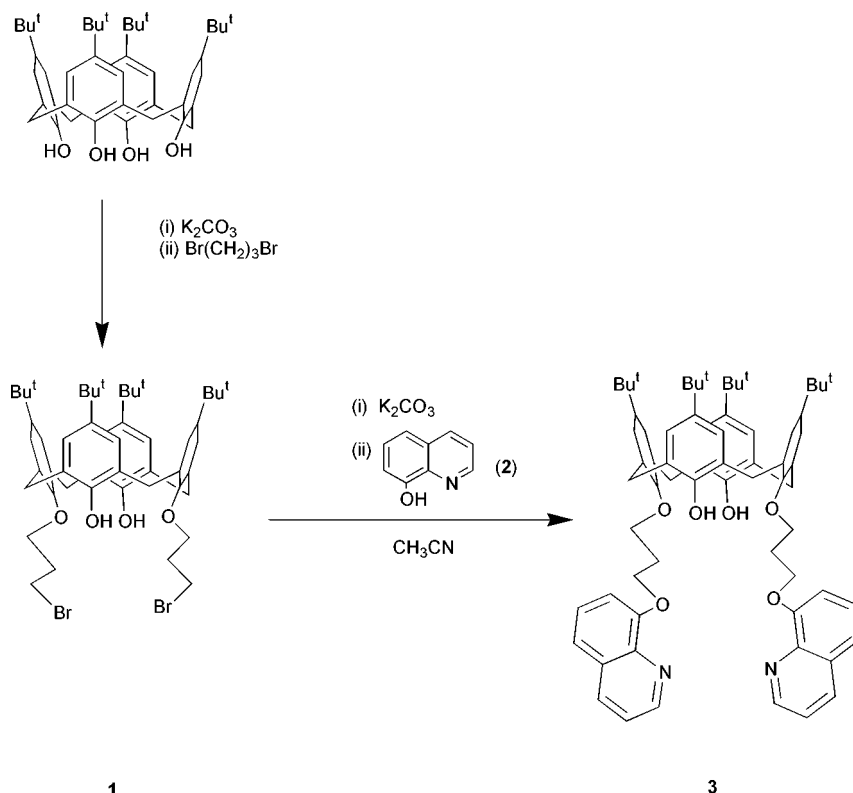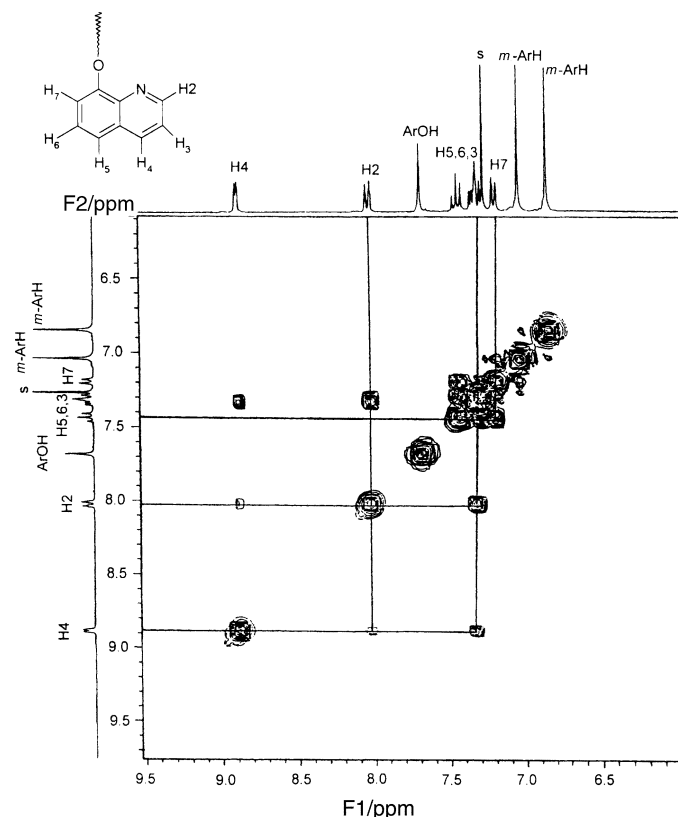

Scheme 1 Synthesis of ligand **3**.

Fig. 1 ^1H–^1H COSY NMR spectrum of the aromatic rings of **3**, in the range 6.0 to 9.5 ppm, in CDCl$_3$.

infrared spectrum showed characteristic bands of this ligand (in dry KBr) at 3350 [ν(O$\cdots$H) intermolecular hydrogen bond], 3046 ν(C–H$_{ar}$), 2957 ν_{as}(CH$_3$), 2905 ν(CH$_2$), 2868 ν_s(CH$_3$), 1615 ν(C=N), 1596 ν(C=C), 1570 ν(C=C), 1424 δ(CH$_2$), 1362 δ(O–H$_{phenol}$), 1262 and 1195 δ(Ar–O–C) cm^{-1} (Fig. 2). The assignment was carried out in comparison with the spectra of 8-hydroxyquinoline and ligand **1** precursors, and using the aromatic-heteroaromatic ring infrared tables.[13] Normally, the OH stretch in phenols gives rise to a strong absorp-

Fig. 2 IR spectra in KBr pellets of ligand **3**, [Eu·**3**]$^{3+}$ and [Tb·**3**]$^{3+}$ complexes.

tion near 3300 cm^{-1} due to O–H$\cdots$O bonds, while the corresponding deformation vibrations occur at 1390–1330 cm^{-1}. The bands found at 1615, 1570 and 1262 cm^{-1} have been observed in the quinoline moiety, but not in aromatic rings related to ligand **1**. The other bands correspond to the calix[4]arene **1**.

Compound **3** exhibits absorption bands at 283 and 320 nm associated with $\pi \rightarrow \pi^*$ transitions in the calix[4]arene and 8-oxyquinoline moieties, respectively [Fig. 3(a)]. A mixture of equimolar amounts of Eu(CF$_3$SO$_3$)$_3$ or Tb(CF$_3$SO$_3$)$_3$ and the ligand **3** in CH$_2$Cl$_2$ resulted in a pale yellow solution of the corresponding [Eu·**3**]$^{3+}$ or [Tb·**3**]$^{3+}$ complexes. As one can see in Fig. 3(b), there is a significant broadening of the 8-oxyquinoline absorption band in the near UV region, accompanied by a bathochromic shift, reflecting the coordination of this group to the lanthanide ions. The [Eu·**3**](CF$_3$SO$_3$)$_3$ and [Tb·**3**](CF$_3$SO$_3$)$_3$ complexes were also isolated in solid form and exhibited consistent elementary analysis.

Coordination of the lanthanide ions was readily evidenced in the IR spectra of the complexes (Fig. 2). Marked shifts of the ν(C=N) and ν(C=C) peaks of the quinoline moiety of **3** at 1615 and 1570 cm^{-1}, to 1634 and 1555 cm^{-1} in both the Eu(II) and Tb(III) complexes, indicates the involvement of the aromatic N atom in the binding process. Furthermore, the observed shifts in the δ(Ar–O–C) vibrations at 1262 and 1195 cm^{-1} to 1252 and 1165 cm^{-1} reflect the coordination of oxygen atoms of the quinoline and calixarene units. The bands at 1285 and 1032 cm^{-1} are ascribed to the CF$_3$SO$_3$$^-$ ion.[14] The shift from 3350 to 3437 cm^{-1} can be associated with the rupture of the intermolecular hydrogen bonds in the lower-rim oxygen atoms, due to their participation in the coordination process. Preliminary MM$^+$ molecular mechanics calculations revealed that the 8 coordination model is feasible, involving 4 oxygen atoms at the lower rim and the two bidentate 8-oxyquinoline arms, as illustrated in Fig. 4.

The fluorescence spectrum of ligand **3** (10 µmol dm^{-3} in MeCN, λ_{exc} = 283 or 320 nm) showed a characteristic emission band at 488 nm (ϕ_q = 0.0079) associated with the 8-
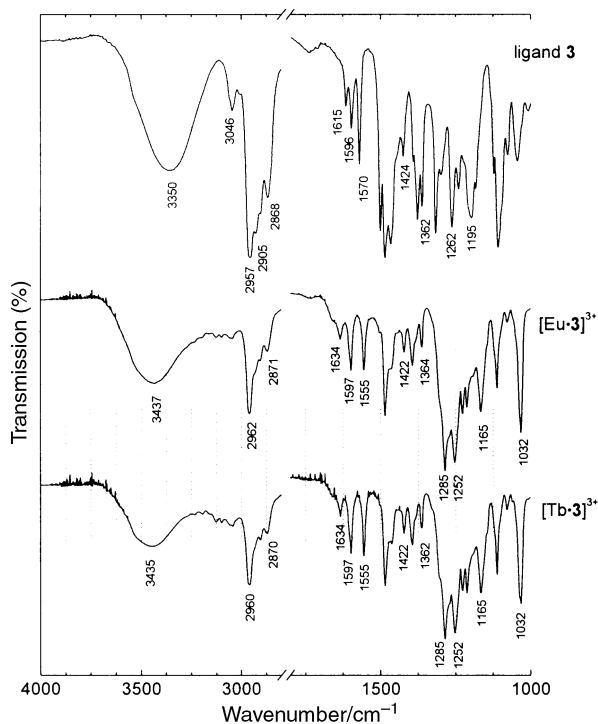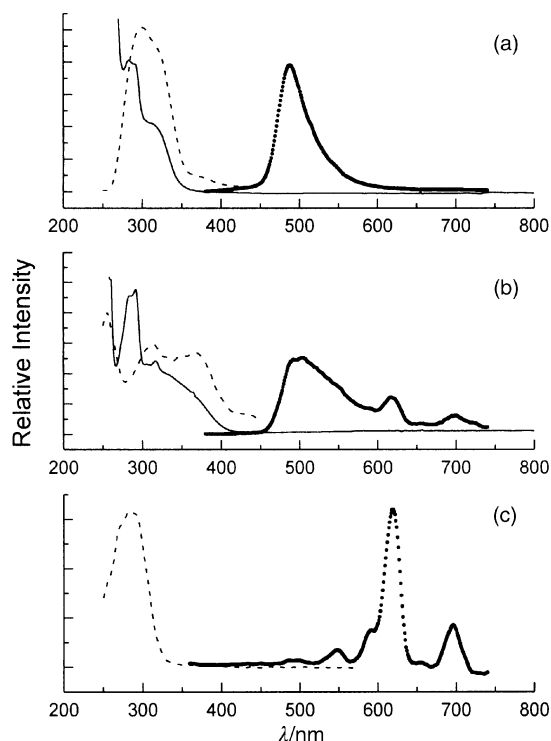
Fig. 3 UV–Vis and room temperature luminescence spectra of **3** and $[Eu \cdot 3]^{3+}$ (10 μmol dm^{-3} in MeCN). (*a*) Absorption spectrum of **3** (——) showing the calix[4]arene $\pi \rightarrow \pi^*$ band at 283 nm and the 8-oxyquinoline bands in the 300–400 nm range; fluorescence spectrum ($\cdots$) with $\lambda_{exc} = 283$ nm or 320 nm and excitation spectrum (– – –) with $\lambda_{em} = 490$ nm. (*b*) Absorption spectrum of $[Eu \cdot 3]^{3+}$ (——) and its corresponding fluorescence spectrum ($\cdots$) with $\lambda_{exc} = 283$ nm or 320 nm, showing the 8-oxyquinoline emission at 490 nm and the narrow Eu^{3+} $^5D_0 \rightarrow {}^7F_n$ bands; excitation spectrum (– – –) with $\lambda_{em} = 490$ nm. (*c*) Phosphorescence spectrum of $[Eu \cdot 3]^{3+}$ ($\cdots$) with $\lambda_{exc} = 283$ nm and 320 nm, showing the Eu^{3+} $^5D_0 \rightarrow {}^7F_n$ bands, and the corresponding excitation spectrum (– – –) with $\lambda_{em} = 619$ nm.

oxyquinoline group [Fig. 3(*a*)]. In the case of the $[Eu \cdot 3]^{3+}$ complex, a less intense 8-oxyquinoline fluorescence emission was observed at 490 nm ($\lambda_{exc} = 283$ or 320 nm), accompanied by a series of narrow bands associated with the lanthanide $^5D_{0,1}$ to ^7F_j transitions [Fig. 3(*b*)]. The strongest europium ion emission at 619 nm corresponds to the electric-dipole allowed $^5D_0 \rightarrow {}^7F_2$ hypersensitive transition while the shoulder at 590 nm [Fig. 3(*c*)] can be associated with the magnetic dipole transition, $^5D_0 \rightarrow {}^7F_1$. The intensity ratio of these two europium ion transitions is related to the symmetry of the coordination sphere.[15] A distortion of the symmetry causes an intensity enhancement of the hypersensitive transition. Typi-
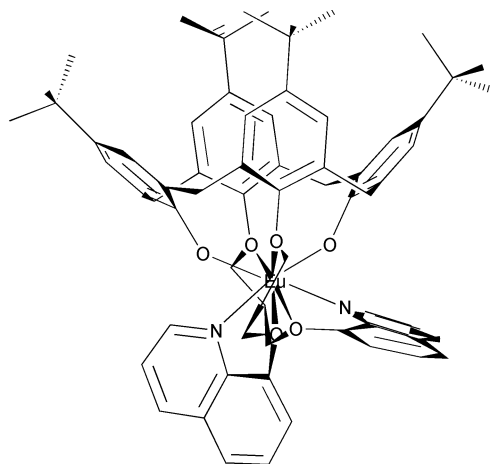
Fig. 4 Structural representation of the $[Eu \cdot 3]^{3+}$ complex from molecular mechanics calculations.

cally, intensity ratios ranging from 8 to 12 have been reported for complexes exhibiting an asymmetric coordination sphere, and this is probably the case for the $[Eu \cdot 3]^{3+}$ complex.

The excitation profile for the 8-oxyquinoline emission in the $[Eu \cdot 3]^{3+}$ complex is consistent with the absorption bands of the 8-oxyquinoline chromophore; however, the emission quantum yield was substantially smaller, $\phi_q = 0.0034$, in comparison with that of ligand **3** ($\phi_q = 0.0079$). These values are lower than those reported for Eu–bipyridine-calixarene systems,[7] but are comparable to those of lanthanide complexes containing triphenylene antenna groups.[16] Lifetime measurements for the 8-oxyquinoline emission were below the working limit of our Edinburgh flash photolysis instrument (<10 ns); however, as a reference, the reported lifetime for the related aluminium(III)–8-hydroxyquinoline complex[17] was 10 ns. In that case, the emission has been associated with the lowest $^1\pi\pi^*$ level, involving substantial charge transfer from the phenoxide part to the pyridyl site of the 8-hydroxyquinoline ligand.[18,19] Presumably, by means of the heavy metal effect, the lanthanide ion promotes efficient singlet–triplet intersystem crossing, lowering the emission quantum yields for the 8-oxyquinoline singlet state.

In the phosphorescence mode, it was possible to discriminate the emission of the lanthanide ion, as shown in Fig. 3(*c*). Surprisingly, the observed excitation spectra for the lanthanide phosphorescence emission matched the absorption band of the calixarene moiety at 280 nm, rather than the absorption band of the 8-oxyquinoline group at 320 nm. More than indicating that the Eu^{3+} emission is being promoted by the calixarene moiety, this result also implies that the lanthanide ion should be interacting with the lower-rim oxygen atoms, in agreement with the infrared spectra. According to the electronic spectra, the $^1\pi\pi^*$ and $^3\pi\pi^*$ levels of calixarene are higher in energy than those of the 8-oxyquinoline group. In this way, the efficient calixarene singlet–triplet conversion by the heavy metal effect would promote the energy transfer to the $^5D_0$ level of Eu^{3+}, thus accounting for the observed lanthanide phosphorescence emission and the corresponding excitation profile. On the other hand, since the $^1\pi\pi^*$ emission of 8-oxyquinoline occurs at 490 nm, the $^3\pi\pi^*$ level can be lower than the $^5D_0$ level of Eu^{3+}, and would not contribute to the antenna effect in the $[Eu \cdot 3]^{3+}$ complex.

In the case of the terbium complex, a similar, but much less intense 8-oxyquinoline luminescence ($\phi_q = 0.0018$) has been observed, using a typical concentration of 10 μmol dm^{-3} in MeCN and $\lambda_{exc} = 283$ or 320 nm. In this case, as reported for several terbium–bipyridyl complexes[20] and other similar terbium compounds, the weak luminescence may be due to efficient $^1\pi\pi^* \rightarrow {}^3\pi\pi^*$ intersystem crossing (heavy metal effect), as well as to a back-energy transfer process[7,20] from the excited metal to the 8-oxyquinoline $\pi\pi^*$ levels. In fact, from the corresponding bands at 545 and 619 nm, respectively, the $^5D_4$ level for Tb^{3+} is more energetic than the $^5D_0$ level for Eu^{3+}, practically coinciding with the $^1\pi\pi^*$ level of 8-oxyquinoline. Both mechanisms would decrease the fluorescence quantum yield from the 8-oxyquinoline singlet state.

From the results reported here, it is clear that the attachment of the 8-oxyquinoline groups to the calix[4]arene moiety does provide new effective binding sites for coordination of metal ions, facilitating their interaction with the calixarene lower-rim oxygen atoms and allowing, in this way, for efficient energy transfer from the organic host (calixarene) to the metal centre.

Notes and references

† Whilst this work was in progress, Li *et al.* reported[12] the synthesis of a new 5,11,17,23-tetra(*tert*-butyl)-25,27-bis(3-bromopropoxy)-26,28-(dihydroxy)calix[4]arene ligand, **1**.

‡ Consistent elemental analyses have been obtained for all compounds. Selected data for **3**. ^{1}H NMR (299.94 MHz): $\delta(CDCl_3) = 8.87$ (dd, 4-C*H*, 2H, $^3J = 4.3$ Hz and $^4J = 1.8$ Hz), 8.03 (dd, 2-C*H*, 2H, $^3J = 8.3$, $^4J = 1.8$ Hz), 7.63 (s, OH, 2H), 7.44–7.30 (m, 5,6,3-C*H*, 6H), 7.16 (d, 7-C*H*, 2H, $^3J = 6.6$ Hz), 7.00 and 6.81 (2 s, *m*-ArH, 4H each), 4.55 (t, quin–OC*H$_2$*CH$_2$CH$_2$OAr, 4H, $^3J = 6.7$ Hz), 4.24 (d + t, *AB* spin system + quin–OCH$_2$CH$_2$C*H$_2$*OAr, 8H, $^2J = 13.1$ Hz), 3.27 (d, A*B* spin system, 4H, $^2J = 13.1$ Hz), 2.55 (m, OCH$_2$C*H$_2$*CH$_2$O, 4H, $^3J = 6$ Hz), 1.27 and 0.97 (2 s, Bu^t, 18H each). ^{13}C{^{1}H} NMR (75.42 MHz): $\delta(CDCl_3) = 150.68$–126.90 (s, arom. Cq), 125.52 and 124.98 (2 s, arom. CH of calixarene), 121.30–109.38 (arom. CH of quinoline), 73.07 (s, ArOC*H$_2$*CH$_2$CH$_2$O–quin), 65.91 (s, quin–OC*H$_2$*CH$_2$CH$_2$OAr), 33.92 and 33.79 [2 s, Cq, *C*(CH$_3$)$_3$], 31.69 [s, Ar*C*H$_2$Ar + *C*(CH$_3$)$_3$], 30.99 [s, C(*C*H$_3$)$_3$], 29.87 (s, OCH$_2$*C*H$_2$CH$_2$O). FAB-MS: $m/z = 1019.9$ (100%) [M]$^+$. Anal. calc. for C$_{68}$H$_{78}$N$_2$O$_6 \cdot$ C$_4$H$_8$O$_2$: C 78.09, H 7.83, N 2.53; found: C 78.33, H 7.97, N 2.44.

1 V. Böhmer, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 713; C. D. Gutsche, *Calixarenes*, The Royal Society of Chemistry, Cambridge, UK, 1989; S. Shinkai, *Tetrahedron*, 1993, **49**, 8933.
2 P. D. Beer, M. G. B. Drew, P. B. Leeson, K. Lyssenko and M. I. Ogden, *J. Chem. Soc., Chem. Commun.*, 1995, 929.
3 M. P. O. Wolbers, F. C. J. M. van Veggel, B. H. M. Snellink–Ruël, J. W. Hofstraat, F. A. J. Geurts and D. N. Reinhoudt, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2141.
4 K. Araki, N. Hashimoto, H. Otsuka, T. Nagasaki and S. Shinkai, *Chem. Lett.*, 1993, 829.
5 C. Loeber, C. Wieser, D. Matt, A. De Cian, J. Fischer and L. Toupet, *Bull. Soc. Chim. Fr.*, 1995, **132**, 166.
6 I. A. Bagatin, D. Matt, H. Thönessen and P. Jones, *Inorg. Chem.*, 1999, **38**, 1585.
7 N. Sabbatini, M. Guardigli, I. Manet, R. Ungaro, A. Casnati, R. Ziessel, G. Ulrich, Z. Asfari and J.-M. Lehn, *Pure Appl. Chem.*, 1995, **67**, 135.
8 J.-A. Yu, R. B. Lessard, L. E. Bowman and D. G. Nocera, *Chem. Phys. Lett.*, 1991, **187**, 263.
9 C. M. Rudzinski, D. S. Engebretson, W. K. Hartmann and D. G. Nocera, *J. Phys. Chem. A*, 1998, **102**, 7442.
10 M. Albrecht, O. Blau, E. Wegelius and K. Rissanen, *New J. Chem.*, 1999, **23**, 667.
11 C. D. Gutsche, *Org. Synth.*, 1989, **68**, 234.
12 Z. T. Li, G.-Z. Ji, C.-X. Zhao, S.-D. Yuan, H. Ding, C. Huang, A.-L. Du and and M. Wei, *J. Org. Chem.*, 1999, **64**, 3573.
13 N. B. Colthup, L. H. Daly and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York, 1964.
14 E. L. Varetti, *Spectrochim. Acta, Part A*, 1988, **44**, 733.
15 A. F. Kirby and F. S. Richardson, *J. Phys. Chem.*, 1983, **87**, 2544.
16 S. I. Klink, L. Grave, D. N. Reinhoudt, F. C. J. M. van Veggel, M. H. Werts, F. A. J. Geurts and J. W. Hofstraat, *J. Phys. Chem. A*, 2000, **104**, 5457.
17 C. W. Tang and S. A. VanSlyke, *J. Appl. Phys.*, 1989, **65**, 3610.
18 W. Stampor, J. Kalinowski, G. Marconi, P. Di Marco, V. Fattori and and G. Giro, *Chem. Phys. Lett.*, 1998, **283**, 373.
19 W. Humbs, E. van Veldhoven, H. Zhang and M. Glasbeek, *Chem. Phys. Lett.*, 1999, **304**, 10.
20 B. Alpha, R. Balhardini, V. Balzani, J.-M. Lehn, S. Perathoner and N. Sabbatini, *Photochem. Photobiol.*, 1990, **52**, 299.