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Influence of Cation Size on the Fluorescent Properties of Bis-coronand Biphenyl-derived Complexes

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A new bis-coronand derived from biphenyl has been prepared and its complexing and sensing properties for alkaline, alkaline-earth and transition cations have been studied. Open and clamp complexes are formed depending on the cation size and complex stoichiometry. Both types of geometries can be distinguished due to their different fluorescent behaviour. Zn^{2+} gives rise to 1:1 and 1:2 complexes with a similar geometry.

Keywords: Sensing; Fluorescence; Conformational restriction; Biphenyl

INTRODUCTION

Molecular systems that combine binding ability and photochemical or photophysical properties are of great interest for designing chemosensors [1–4]. It has recently been established that conformational restriction is a viable mechanism for transducing ion binding into enhanced fluorescence emission in organic fluorophores [5–7]. Thus, biphenyl and bipyridyl derivatives which experiment fluorescence enhancement after complexation have been described in the literature [8,9]. However, studies carried out by Benniston *et al*. have demonstrated that fluorescence quantum yields for biphenyl polyethers are dependent on the torsion angle around the biphenyl group. Planar geometries favour higher yields and longer lifetimes [10]. For all these reasons, we have been interested in using the 4,4′-bis(N,N-dimethylamino)biphenyl (TMB, tetramethylbenzidine) subunit in the design and synthesis of red-ox and fluorescent sensors [11,12]. TMB-derivatives ligands show very peculiar fluorescent properties. Firstly, the presence of additional amino groups in substituents bound to the aromatic rings does not give rise to a quenching of the fluorescence whatever the spacer present. Normally, amines transfer one electron to the photoproduced vacancy in the HOMO of the fluorophore which quenches fluorescence. In these compounds, however, the diaminobiphenyl fluorophore has a rather high energy HOMO (owing to its easy oxidabizability), so PET from the amino is not probable. Secondly, an increment in the rigidity of these fluorophores makes them less fluorescent.

We now report the sensing behaviour of a new ligand that contains benzylamino coronands as binding units in order to study the influence that the size of different cations has in the fluorescent behaviour of the ligand. The most important difference would be related to the formation of open-like complexes of clamp-like complexes since the type of complexation is closely related to the dihedral angle between both aromatic rings and consequently to the fluorescent properties of the photo physical moiety (Scheme 1).

PHOTOPHYSICAL CHARACTERISTICS OF 2 AND EFFECT OF PROTONATION

Photophysical properties of **2** in CH_3CN were studied (Table I). As expected, they are not so different from those observed for the related compounds previously described [13,14]. Emission of fluorescence in **2** is remarkably blue-shifted in comparison to **TMB**, and is even more so when compared with its carbonylic counterpart **1** (Fig. 1). By contrast, **2** shows a similar behaviour to that observed for control compound **3**.

This behaviour is in agreement with the hypothesis of an excited state, in which both biphenyls

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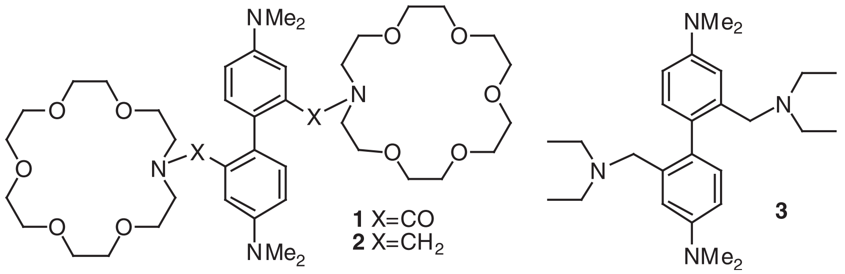

SCHEME 1

rings are coplanar and destabilised by the presence of substituents. Thus, S_1 is unfavoured by sterical repulsions and then, the energetic difference $S_1 \rightarrow S_0$ is enhanced in comparison with **TMB**. On the other hand, in the presence of a weak acid such as citric acid, a quenching of fluorescence was obtained (Fig. 2). Protonation of the azacrown nitrogen by the citric acid would induce the formation of an intramolecular hydrogen bond with the nitrogen in the opposite crown, forcing the dihedral angle in the biphenyl far from the coplanarity, which induces a quenching of the fluorescence. After addition of TFAA, the arylic nitrogens are also protonated, and then emission of fluorescence in **2** is strongly blue-shifted just as **TMB** is in the same acidic conditions.

COMPLEXATION STUDIES WITH ALKALINE CATIONS

Titrations of **2** with perchlorates of Na^+, K^+, Cs^+ and Li^+ were performed in CH_3CN. Data of the titration with Na^+ were fitted by SPECFIT [15] to a 1:1 + 1:2 (L:M) stoichiometry model, where the complexation constants were $\log K_1 = 5.2 \pm 0.7$ and $\log K_2 = 11.5 \pm 0.2$. The theoretical spectra modelisation of the complexes (see Appendix A Figs. 9 and 10) suggested that the 1:1 complex would exhibit a lower quantum yield than **2**, while it should be higher for LM_2 than for the free ligand which was the experimentally observed behaviour (Fig. 3a). According to our previously reported results [13,14], a 1:1 clamp-type complex was proposed in which a more constrained angle in the biphenyl moiety would be translated in a quenching of the fluorescence. Evolution from the 1:1 clamp-complex to an open 1:2 complex will make both rings more coplanar, aided by the presence of charge repulsions between both cations. This modification in the dihedral angle would explain the enhancement of fluorescence observed.

TABLE I Data for absorption in the UV and emission of fluorescence for the ligands in CH_3CN

Ligand	Absorption λ_{max} (nm) (ε cm^{-1}M^{-1})	Emission λ_{max} (nm)	Quantum Yield (ϕ)
TMB	310 (34668)	401	0.13
1	295 (29600)	474	0.08
2	270 (42135)	363	0.057
3	269 (27781)	360	0.061

A good correlation was observed for K^+ with the model 1:1 + 1:2 (L:M), being the complexation constants of $\log K_1 = 7.3 \pm 0.5$ and $\log K_2 = 12.0 \pm 0.6$. In this case, the fluorescence of 1:1 complex is quite similar to the observed for the ligand which was also observed by the experimental data reflected in Fig. 3b. For this reason therefore, an open structure was proposed. LM_2 has much higher ϕ, which is in agreement with the coplanarity of the rings forced by the electrostatic repulsions of both cations. K^+(1.33 Å) has a suitable size to fit in the crown cavity and interacts properly with the six oxygen atoms. By contrast, Na^+(0.95 Å) is too small and does not interact

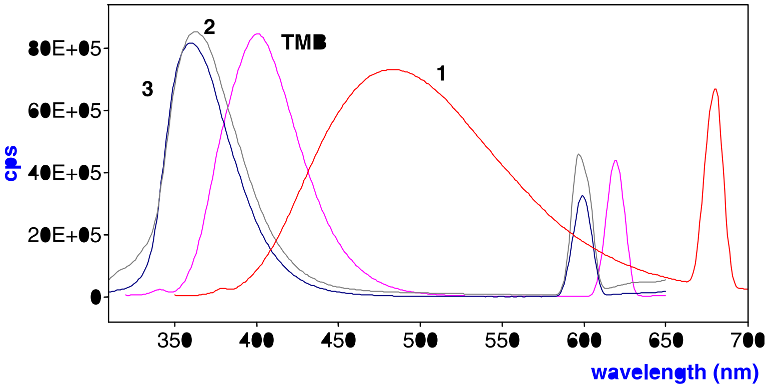

FIGURE 1 Fluorescence spectra for **TMB**, **1**, **2** and **3** in CH_3CN at 20°C. $\lambda_{exc} = 310$ nm, $\lambda_{exc} = 300$ nm, $\lambda_{exc} = 300$ nm and $\lambda_{exc} = 340$ nm respectively.

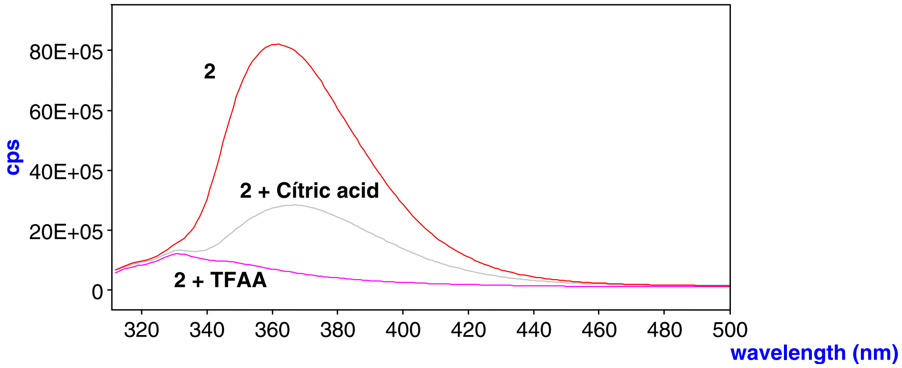

FIGURE 2 Fluorescence spectrum of **2** under different acid-base conditions in CH_3CN at 20°C, $\lambda_{exc} = 300$ nm and initial concentration of ligand of 2.30×10^{-6} M in CH_3CN. 2: ligand in CH_3CN or in 2.63×10^{-5} M of tetramethylamonnium hydroxide in CH_3CN. 2 + Cítric acid: ligand in 9.54×10^{-6} M of citric acid in CH_3CN. 2 + TFAA: ligand in a great excess of trifluoroacetic acid in CH_3CN.

with all of them, thus, the lack of coordination with the oxygen atoms of one crown would be compensated for the interaction with the oxygen atoms in the other crown forming the clamp-type complex and inducing the quenching of fluorescence (Fig. 4).

Titration with Cs^+ was fitted to the model, and the best results were obtained with the 1:1 model, with a constant value of $\log K_1 = 7.3 \pm 0.9$. The quantum yield for **2**·Cs^+ was slightly lower than that for the free ligand (Table II). Cs^+ is too big to fit in a crown and might not interact with only one crown, but with both crowns. The size of Cs^+ would mean that the crowns might not approach so much as in the case of Na^+, and the complex would probably be formed with a small modification of dihedral angle; it is for this reason that the fluorescences of **2** and **2**·Cs^+ are so similar.

In the case of Li^+, data did not fit well to any complexation model. Slight quenching was observed after addition of Li^+ over **2**, probably owing to 1:1 (or higher) stoichiometries. In these complexes Li^+

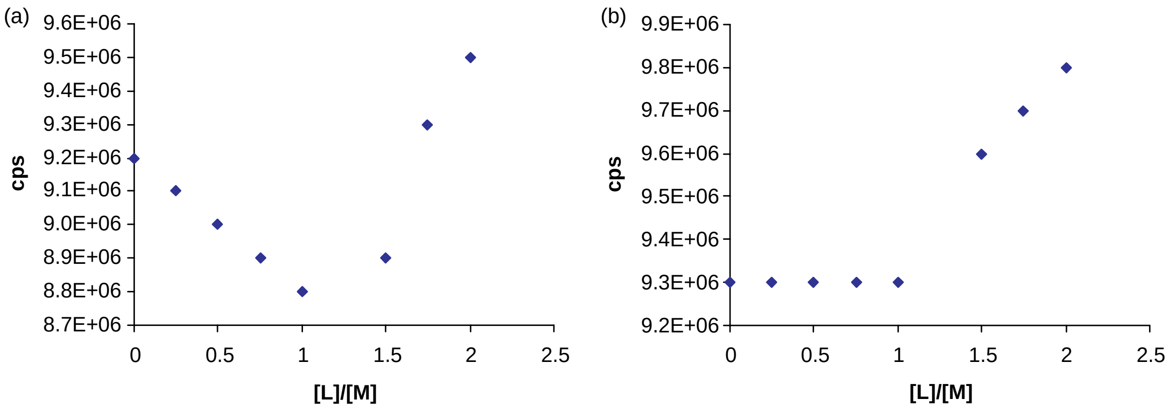

FIGURE 3 Fluorescence emission of **2** at $\lambda_{em} = 361$ nm in CH_3CN at 20°C, $\lambda_{exc} = 300$ nm in presence of increasing amounts of (a) sodium perchlorate and (b) potassium perchlorate.

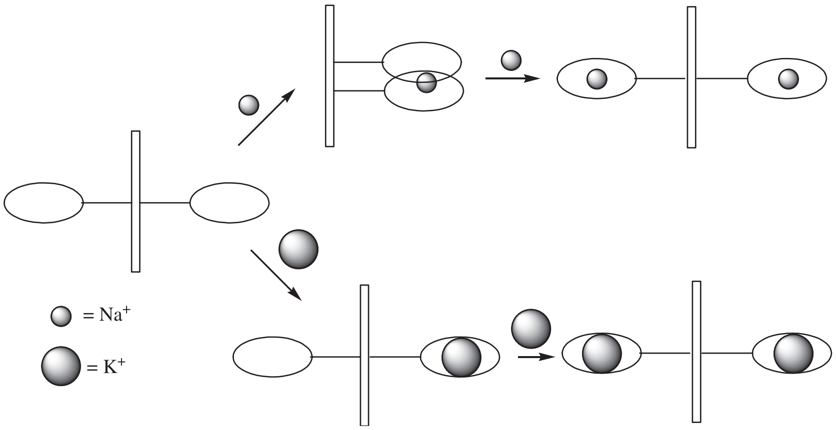

FIGURE 4 Complex 1:1 and 1:2 for **2** with Na^+ and K^+.

TABLE II Stoichiometry, topology of the complex and constant of complexation for the complexes with **2** with alkaline and earth-alkaline cations in CH_3CN, 298 K

Cation	Stoich. (L:M)	log K_1	geometry	log K_2	geometry
Na^+	1:1 + 1:2	5.2 ± 0.7	clamp	11.5 ± 0.2	open
K^+	1:1 + 1:2	7.3 ± 0.5	open	12.0 ± 0.6	open
Cs^+	1:1	7.3 ± 0.9	clamp	–	–

would be surrounded by 4 oxygen atoms in the same crown. Li^+ is a hard cation and is compatible with oxygen atoms, but it is too small to be surrounded by lot of them.

Finally, some tests of selectivity towards a cation in the presence of others were carried out. Titrations of **2** with mixtures of Na^+/Cs^+ and K^+/Cs^+ showed that, enhancements of fluorescence were obtained in all cases. This was expected, regarding the constants of complexation, and indicates that the LM_2 with Na^+ and K^+ complex are preferred by the ligand (Fig. 5).

STUDIES OF THE ABILITY TOWARDS TRANSITION AND POST-TRANSITION CATIONS BY 2

The complexation ability of ligand **2** was tested towards Zn^{2+}, Cd^{2+} and Cu^{2+} in CH_3CN (see Appendix A Figs. 11 and 12). Results with Zn^{2+} revealed that data fitted to a 1:1 + 1:2 (L:M) model where the calculated constants were $\log K_1 = 9.8 \pm 0.1$ and $\log K_2 = 17.8 \pm 0.2$ (Table III). The emission tendency in the presence of this cation is different to this observed with the alkaline cations. Whereas the 1:1 complex showed a ϕ similar to that observed for **2**·Na^+ or **2**·Cs^+, what suggest a clamp complex between **2** and Zn^{2+}, the 1:2 ($L:M_2$) complex showed a significant quenching of the fluorescence (Fig. 6).

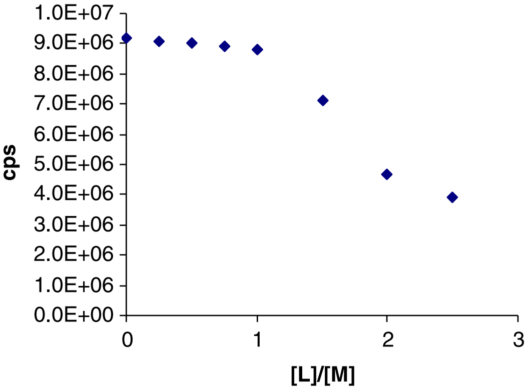

FIGURE 6 Fluorescence emission of **2** at $\lambda_{em} = 361$ nm in CH_3CN at 20°C, $\lambda_{exc} = 300$ nm in presence of increasing amounts of zinc triflate.

This behaviour was clearly different to that shown by the studied alkaline cations and suggests that both L:M and $L:M_2$ complexes have a clamp geometry. This type of geometry has been widely observed in binuclear zinc (II) complexes with different type of ligands [16–18]. In some of these complexes a decrease in the Zn···Zn separation *via* bridging contra ions or solvent molecules has been described [19,20].

In order to obtain more information about the way ligand **2** interacts with Zn^{2+}, several NMR experiments were carried out. ^1H NMR and ^{13}C NMR

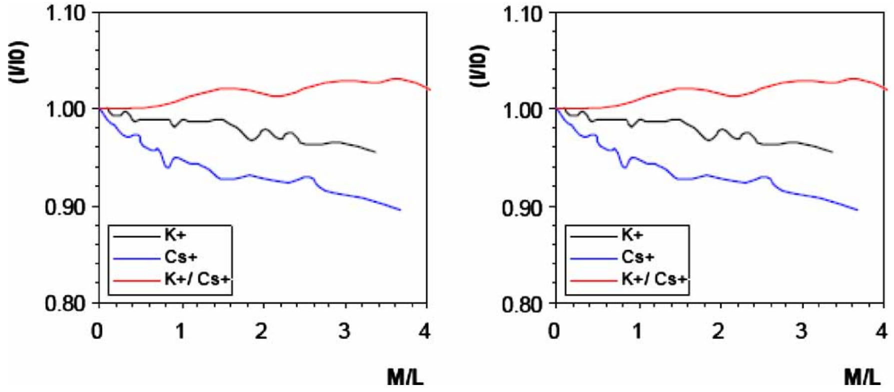

FIGURE 5 Experiments of competence between K^+/Cs^+ (left) and Na^+/Cs^+ (right). Experiments were performed in CH_3CN, at 298 K and $\lambda_{exc} = 300$ nm. Initial concentration of **2** was *circa* 2.5×10^{-6} M in all cases. Amounts of an equimolecular mixture of K^+/Cs^+ or Na^+/Cs^+ were added over the ligand, depending on the experiment. Represented relative intensity refers to the intensity at each point divided by the intensity at the beginning of the titration.

TABLE III Stoichiometry, topology of the complex and constant of complexation for the complexes with **2** with Zn^{2+} and Cd^{2+} in CH_3CN, 298 K.

Cation	Stoich. (L:M)	log k_1	geometry	log k_2	geometry
Zn^{2+}	1:1 + 1:2	9.8 ± 0.1	clamp	17.8 ± 0.2	clamp
Cd^{2+}	1:1 + 1:2	7.4 ± 0.2	clamp	14.2 ± 0.2	clamp

TABLE IV Chemical shifts for **2** and **2** with 1 equiv. and 2 equiv. of Zn^{2+} in CD_3CN at 298 K

^1H	H_a	H_b	H_c	H_d	H_e	H_f	H_g	H_h	H_i	H_j	H_k
2	7.01	6.62	6.84	3.24	2.56	3.38	3.47–3.55				2.93
2·Zn^{2+}	7.12	6.92	7.15	4.43/3.90	3.02–3.05		3.54–3.61				3.04
2·Zn_2^{4+}	7.23	6.92	7.13	4.43/3.70	2.72–3.01		3.37–3.73				3.02

^{13}C	C_d	C_e	C_f	C_g	C_h	C_i	C_j	C_k
2	58.49	55.10	70.66	71.02	71.17	71.21	71.30	40.97
2·Zn^{2+}	55.10	53.84/53.59	63.65/63.44	69.76	69.85	69.95	70.19	39.62
2·Zn_2^{4+}	54.42	54.10/54.18	69.58/63.40	69.66/69.61	69.86/69.76	70.20	70.24	39.96

spectra were registered for solutions in CD_3CN of free ligand and free ligand in the presence of 1 and 2 equiv of $Zn(tfl)_2$. Chemical shifts are shown for the most interesting signals in Table IV.

These data indicate that complexation with 1 equiv of Zn^{2+} gives rise to clear modifications in the area of the crown cavity close to the nitrogen atom (H_d, H_e, H_f and C_d, C_e and C_f). This fact is in accordance with the structural proposal for the 1:1 complex that involves both cavities in the cation complexation (see Fig. 7). The NMR spectra registered in the presence of a second equivalent of Zn^{2+} showed two important data. Firstly, no modification in the $N(CH_3)_2$ was observed, which indicates that these groups were not involved in complexation, and secondly the number of carbons of the cavity modified in this new complex extended from H_d to H_h which was in accordance with the complexation of one cation in each cavity. However, these experiments were not conclusive about the open or clamp geometry of the complex.

The same pattern is observed for Cd^{2+}(0.97 Å), i.e., a 1:1 clamp complex with a constant of complexation value of $\log K_1 = 7.4 \pm 0.2$ and an open nearly-quenched 1:2 complex ($\log K_2 = 14.2 \pm 0.2$).

A monotonic quenching throughout the addition of Cu^{2+} to **2** was observed. However, the same situation was observed in the titration of TMB with Cu^{2+}, so these results are not relevant. Cu^{2+} can quench both, by binding the N in the TMB subunit or by mere collision with the compound (Fig. 8).

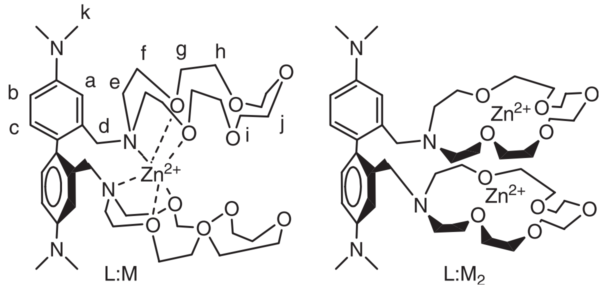

FIGURE 7 Structure proposed for the **2**·Zn^{2+} and **2**·2Zn^{2+} complexes.

EXPERIMENTAL SECTION

General Methods

All commercially available reagents were used without further purification. Benzene was dried over sodium. Water sensitive reactions were performed under argon. Column chromatography was carried out on SDS activated neutral aluminium oxide (0.05–0.2 mm; activity degree 1). Melting points were measured with a Cambridge Instrument and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1750 FT-IR and a Bruker Equinox 55 FT-IR. NMR spectra were recorded with Bruker Avance 300/500 and Varian Unity-300/400 spectrometers. Chemical shifts are reported in parts per million downfield from TMS. Spectra were referenced to residual undeuterated solvent. High resolution mass spectra were taken with a Fisons VG-AUTOSPEC and those using the eletrospray ionizing technique were recorded on an HPLC-MS with ion trap Bruker 3000-Esquire Plus. UV spectra were run at 20°C (thermostated) either on a Shimadzu UV-2102 PC or on a Biotech Instruments XL spectrometer. Steady-state fluorescence measurements were carried out using an Instruments SA (Jobin-Yvon) Fluoromax-2, equipped with a red sensitive Hamamatsu R928 photomultiplier tube and a Varian Cary Eclipse Fluorimeter. Spectra were corrected for the wavelength dependence of the detector using a calibration curve generated with a standard lamp.

Synthesis of 2,2′-Bis(1-aza-18-crown-6-methylen)-4,4′-bis(dimethylamino) Biphenyl (2)

Compound **1** [11] (193 mg, 0.23 mmol) was dissolved in dry THF (20 ml) in a round bottom flask provided with a stirrer and under an argon atmosphere. BH_3–THF (ca. 1.0 M in THF) (10 ml, 10 mmol) was dropped to the stirred solution at room temperature. After 24 hours, more BH_3–THF (10 ml, 10 mmol) was added and the reaction was stirred for a further 24 hours. H_2O was cautiously dropped until effervescence was over. HCl (6 M) (2 ml) was added

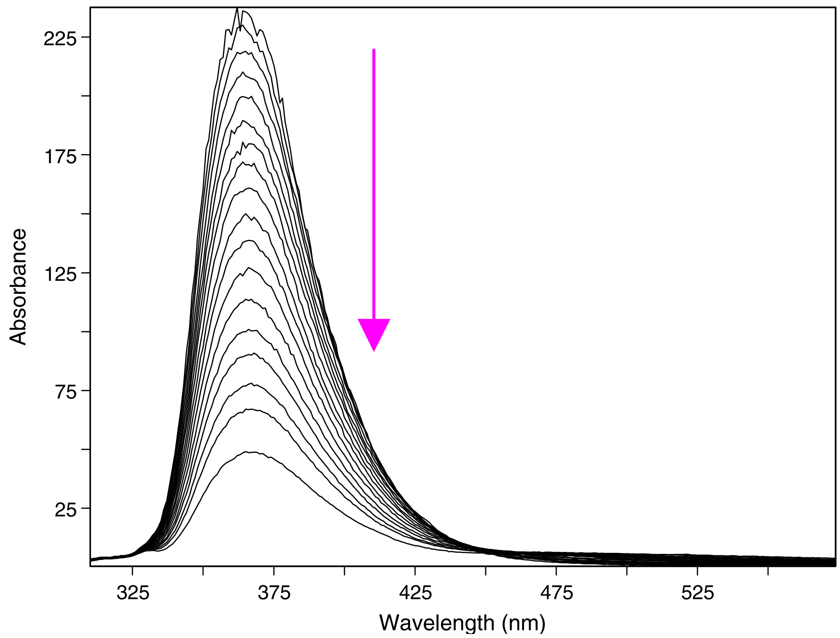

FIGURE 8 Emission of fluorescence spectra in the titration of **2** with Cu^{2+} in CH_3CN, 298 K. Initial concentration of **2** was 2.15×10^{-6} M. 0 to 5.46 equivalents of Cu^{2+} were added. It was no possible to fit any model from SPECFIT to these data.

afterwards and the solution was stirred for 4 hours at room temperature. NaOH in pellets was added then until pH was *ca*. 9 and the latter solution was extracted in a continuous mode with $CHCl_3$ for 48 hours. After drying over sodium sulphate and the distillation of solvent the product (98 mg, 54%) was obtained. IR (KBr) $\bar{\nu}_{max}$ (cm^{-1}): 2940 (CH), 2870, 1607 (Ar), 1495 (CN), 1352 (CN), 1113 (CO), 807 ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.09 (2H, d, $J = 2.8$ Hz, Ar–H), 6.91 (2H, d, $J = 8.4$ Hz, Ar–H), 6.62 (2H, dd, $J = 8.4$ Hz, $J = 2.8$ Hz, Ar–H), 3.69–3.64 (24H, m, OCH_2), 3.60 (8H, m, OCH_2), 3.51 (8H, m, NCH_2CH_2O), 3.33 (4H, d, $J = 8.0$ Hz, $ArCH_2N$), 2.99 (12H, s, $N(CH_3)_2$), 2.69 (8H, t, $J = 5.9$ Hz, $N\mathit{CH_2}CH_2O$). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 147.9 (s), 137.7 (s), 129.9 (d), 128.4 (s), 111.8 (d), 109.5 (d), 69.8–69.1 (t), 56.7 (t), 53.1 (t), 39.7 (q), 29.3 (t). HRMS (EI): M^+ found 790.5064. $C_{42}H_{70}O_{10}N_4$ requires 790.5092. **UV** (CH_3CN) $\lambda_{max} = 270$ nm, $\varepsilon = 42135$; shoulder at $\lambda = 310$ nm. Emission of fluorescence (CH_3CN): $\lambda_{em} = 362$ nm at $\lambda_{exc} = 300$ nm. Quantum yield (CH_3CN): 0.057 (quinine sulphate in 1 M H_2SO_4).

General Procedure for Fluorometric Studies

Fluorimetric titrations were carried out in 1 cm pathlength quartz fluorescence cells at 20°C (thermostatted). The concentration of ligand was *ca*. $5 \cdot 10^{-6}$ M in acetonitrile (Spectroscopic grade). An approximately constant ionic strength was maintained by adding the inert salt $N(Bu)_4PF_6$ (*ca*. 30 mol per mol of ligand). Measurements were recorded in the presence of the corresponding metal triflates (metal-to-ligand ratio between 0.25 to 12 equivalents). Quantum yields were measured using quinine sulphate monohydrate in H_2SO_4 (1 M, aq) as the standard ($\Phi = 0.546$). Complexation constants were determined from the analysis of the spectral assembly, regarding LM_2, LM and L_2M as possible stoichiometries by fitting the data to one of the general models (specified in each case).

Acknowledgements

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APPENDIX A

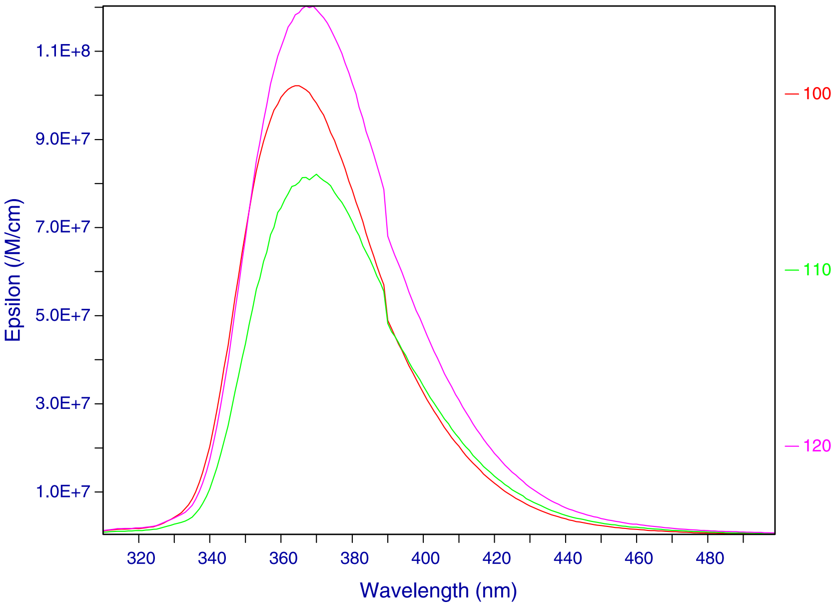

FIGURE 9 Model of SPECFIT for the titration of **2** with Na^+. Fitting to LM + LM_2 stoichiometries. Simulated emission spectra for the formed complexes.

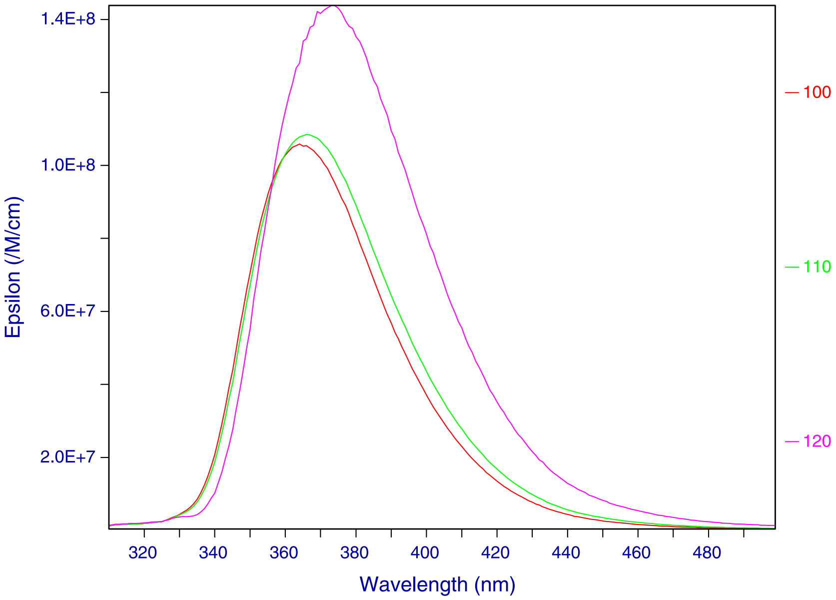

FIGURE 10 Model of SPECFIT for the titration of **2** with K^+. Fitting to LM + LM_2 stoichiometries. Simulated emission spectra for the formed complexes.

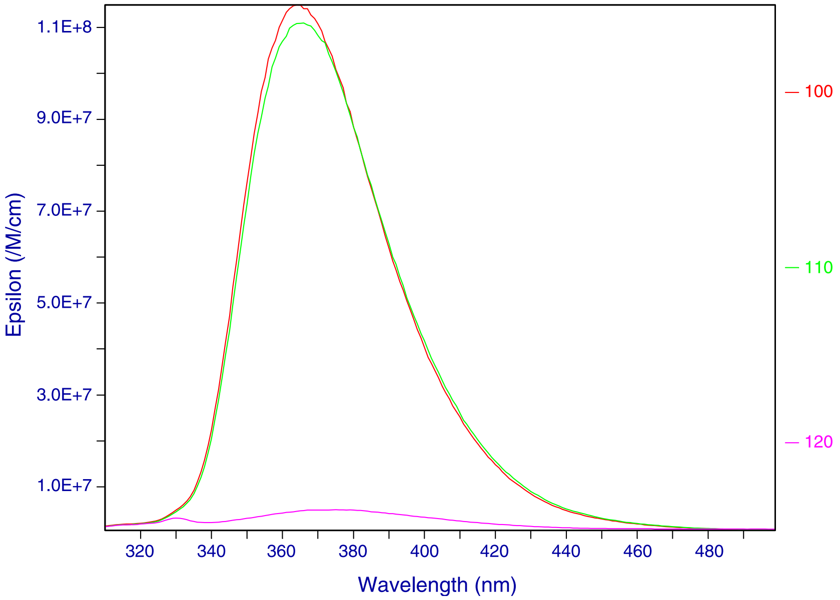

FIGURE 11 Model of SPECFIT for the titration of **2** with Zn^{2+}. Fitting to LM + LM_2 stoichiometries. Simulated emission spectra for the formed complexes.

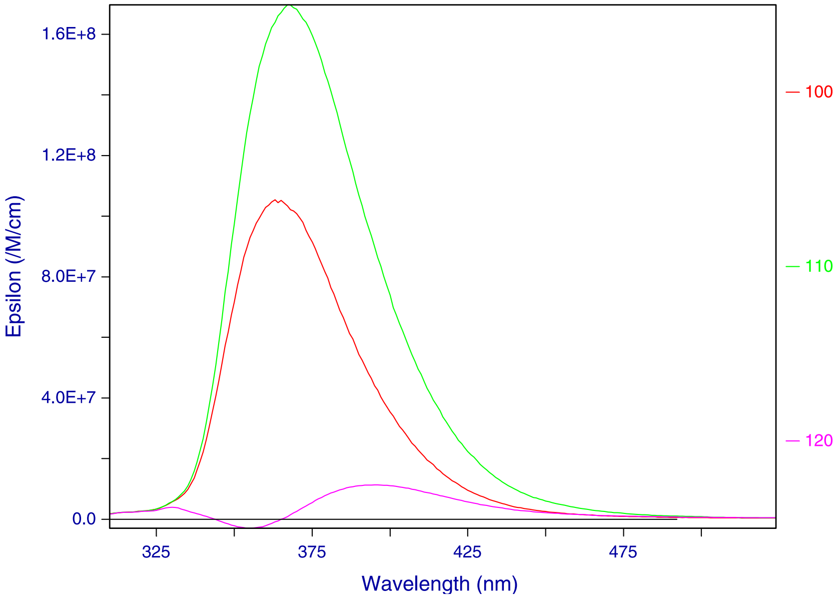

FIGURE 12 Model of SPECFIT for the titration of **2** with Cd^{2+}. Fitting to LM + LM_2 stoichiometries. Simulated emission spectra for the formed complexes.