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# Coordination chemistry of *N*-aminopropyl pendant arm derivatives of mixed N/S-, and N/S/O-donor macrocycles, and construction of selective fluorimetric chemosensors for heavy metal ions<sup>†</sup>

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The coordination chemistry of the *N*-aminopropyl pendant arm derivatives ( $L^{1c-4c}$ ) of the mixed donor macrocyclic ligands [12]aneNS<sub>2</sub>O, [12]aneNS<sub>3</sub>, [12]aneN<sub>2</sub>SO, and [15]aneNS<sub>2</sub>O<sub>2</sub> ( $L^{1a-4a}$ ) towards Cu<sup>II</sup>, Zn<sup>II</sup>, Cd<sup>II</sup>, Hg<sup>II</sup>, and Pb<sup>II</sup> in aqueous solution has been investigated. The protonation and stability constants with the aforementioned metal ions were determined potentiometrically and compared, where possible, with those of the unfunctionalised macrocycles. The measured values show that Hg<sup>II</sup> and Cu<sup>II</sup> in water have the highest affinity for all ligands considered, with the *N*-aminopropyl pendant arm weakly coordinating the metal centres. Crystals suitable for X-ray diffraction analysis were grown for the perchlorate salt ( $H_2L^{1c}$ )(ClO<sub>4</sub>)<sub>2</sub>·dmf, and for the 1 : 1 complexes [Cd( $L^{3a}$ )(NO<sub>3</sub>)<sub>2</sub>] (1), [Cu( $L^{4a}$ )(dmf)](ClO<sub>4</sub>)<sub>2</sub> (2), [Zn( $L^{1c}$ )(ClO<sub>4</sub>)]ClO<sub>4</sub> (3), [Cd( $L^{1c}$ )(NO<sub>3</sub>)]NO<sub>3</sub> (4), and [Hg( $L^{2c}$ )](ClO<sub>4</sub>)<sub>2</sub> (5). Their structures show the macrocyclic ligands adopting a folded conformation, which for the 12-membered systems can be either [2424] or [3333] depending on the nature of the metal ion.  $L^{1c-4c}$  were also functionalised at the primary amino pendant group with different fluorogenic subunits. In particular the *N*-dansylamidopropyl ( $L^{nd}$ , n = 1-4), and the *N*-(9-anthracenylmethyl)aminopropyl ( $L^{nc}$ , n = 1, 2, 4, Scheme 1) pendant arm derivatives of  $L^{1a-4a}$  were synthesised and their optical responses to the above mentioned metal ions were investigated in MeCN/H<sub>2</sub>O (4 : 1 v/v) solutions.

# Introduction

The design of artificial molecular sensors for the selective detection of different target species is a growing area of chemistry. The intense research interest in this field is driven by the great demand for extremely sensitive and selective analytical tools able to recognize, sense and evaluate at subnanomolar level the concentration of charged and neutral substrates in biological and environmental samples and in industrial waste effluent samples.

In this respect, fluorescent chemosensors have been widely studied in the past decade because of the low detection limits that can be achieved and relatively cheap equipment required.<sup>1-16</sup> These compounds are usually made of a fluorogenic fragment (signalling unit) covalently linked to a receptor unit. With such a supramolecular approach, the selective recognition of the target species by the receptor unit is converted into an

† Electronic supplementary information (ESI) available: Synthetic details including analytical and spectroscopic data for  $L^{1c-e}$ ,  $L^{2b-e}$ ,  $L^{3b-d}$ , and the isolated metal complexes. Protonation constants (log *K*) of  $L^{3a}$ ,  $L^{1c}$ ,  $L^{2c}$ ,  $L^{3c}$ , and  $L^{4c}$  (Table S1). Distribution diagrams for the systems  $Zn^{II}/L^{1c}$ , and  $Cd^{II}/L^{1c}$  (Fig. S1),  $Zn^{II}/L^{2c}$  (Fig. S2),  $Cu^{II}/L^{2c}$ , and  $Hg^{II}/L^{2c}$  (Fig. S3),  $Zn^{II}/L^{3c}$ , and  $Cd^{II}/L^{3c}$  (Fig. S4). Changes in the UV-Vis spectrum of  $L^{4d}$  (Fig. S5), and  $L^{2e}$  (Fig. S6) upon addition of increasing amounts of Hg<sup>II</sup>. See http://dx.doi.org/10.1039/b506785e

optical signal expressed as an enhancement or quenching of the fluorophore emission. The sensor performance can be improved by either increasing the selectivity of the host–guest interaction *via* an accurate design of the receptor unit, or by improving the transduction mechanism leading to a change of the fluorescence emission of the sensor. In this respect, a useful approach implies a direct interaction of the fluorophore with the target species.

By adopting a "receptor-spacer-fluorophore" model, many selective and sensitive sensors and switches for metal ions feature chromophores as anthracene, 8-hydroxyquinoline, dansylamide, or phenanthroline as signalling sites,1-9 either connected to a macrocyclic ligand as coordinating sidearms or inserted as a nonpendant integral part of a macrocyclic structure. In fact, macrocyclic receptors represent the first choice as receptor moieties for metal cations because of the extensive possibilities they can offer for modulation of host coordination environments, thereby allowing an easy route to achieving selective interactions with the substrate of interest. Many of the reported fluoroionophores feature polyoxa-,17,18 polyaza-,19-22 and aza/oxa-macrocycles<sup>23-26</sup> as the guest binding site, whereas the potential of mixed N/S-, and N/S/O-donating macrocyclic sites as selective receptors in molecular sensors remains more or less untapped.27-30

In this context, following our interest in both coordination chemistry of mixed thia-aza macrocycles,<sup>31-34</sup> and their

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(n = 1-4)

Scheme 1

analytical applications as selective ionophores towards heavy and transition metal ions, we describe here the coordination properties of the N-aminopropyl pendant arm derivatives ( $L^{1c-4c}$ ) of the NS<sub>2</sub>O-, NS<sub>3</sub>-, N<sub>2</sub>SO-, and NS<sub>2</sub>O<sub>2</sub>-donating macrocycles  $L^{{\scriptscriptstyle 1a}{\scriptscriptstyle -4a}}$  (Scheme 1) towards  $Cu^{{\scriptscriptstyle II}},~Zn^{{\scriptscriptstyle II}},~Cd^{{\scriptscriptstyle II}},~Hg^{{\scriptscriptstyle II}},$  and Pb<sup>II</sup>. The N-dansylamidopropyl ( $L^{nd}$ , n = 1-4), and the N-(9-anthracenylmethyl)aminopropyl ( $L^{ne}$ , n = 1, 2, 4) pendant arm derivatives of L<sup>1a-4a</sup> were also synthesised and their optical response to the above mentioned metal ions investigated in  $MeCN/H_2O(4:1 v/v)$  solutions. Although in these systems the fluorescent moiety is remote from the cavity of the macrocyclic receptor, the linker heteroatom of the fluorophore (*i.e.* the amine or amide nitrogen atom of the pendant arm/s) can participate in complexation to the metal ion, thereby possibly improving the signal transduction mechanism and leading to a reliable substrate-specific response by the sensor.

### Experimental

All melting points are uncorrected. Microanalytical data were obtained using a Fison EA CHNS-O instrument operating at 1000 °C. ESI mass spectra were recorded at the School of Chemistry of The University of Nottingham (UK). 1H and 13C NMR spectra were recorded on a Varian VXR300 or VXR400 spectrometer. Absorption spectra were recorded with a Varian Model Cary 5 UV-Vis-NIR spectrophotometer. Uncorrected emission, and corrected excitation spectra were obtained with a Varian Cary Eclipse Fluorescence spectrophotometer. In order to allow comparison among emission intensities, we performed corrections for instrumental response, inner filter effect, and phototube sensitivity.35 A correction for differences in the refraction index was introduced when necessary. Luminescence quantum yields (uncertainty  $\pm 15\%$ ) were determined using quinine sulfate in 1 M H<sub>2</sub>SO<sub>4</sub> aqueous solution ( $\Phi = 0.546$ ) as a reference. MeCN (Uvasol, Merck) and Millipore grade water were used as solvents for spectrophotometric measurements. Solutions of the ligands were  $2.5 \times 10^{-5}$  M. Other solvents and starting materials were purchased from commercial sources where available.

#### Synthesis of ligands and complexes

 $L^{1a}-L^{4a}$ , and  $L^{1b}$  were synthesised according to procedures reported in the literature.^{32,36,37} Here we report the procedure adopted for the synthesis of  $L^{4b-e}$  (see below). The same procedure has been adopted for the synthesis of  $L^{1c-e}, \ L^{2b-e},$  and  $L^{3b-d},$  for which spectroscopic and microanalytical data are supplied within the ESI.†

The complexes  $[Cd(L^{3a})(NO_3)_2]$  (1),  $[Cu(L^{4a})(dmf)](ClO_4)_2$ (2),  $[Zn(L^{1c})(ClO_4)]ClO_4$  (3),  $[Cd(L^{1c})(NO_3)]NO_3$  (4), and  $[Hg(L^{2c})](ClO_4)_2$  (5) were synthesized by following a standard procedure which includes mixing of the appropriate metal salt and the ligand in a 1 : 1 molar ratio in MeCN and the isolation of the product as crystals from the reaction mixture stirred for a few hours at room temperature by diffusion of Et<sub>2</sub>O vapor. In the case of **2** crystals were obtained by crystallization from dmf/Et<sub>2</sub>O of the product isolated from the reaction mixture by diffusion of Et<sub>2</sub>O vapor. Synthetic details including analytical data have been deposited as ESI.<sup>†</sup>

**Caution!** Most of the metal complexes synthesised were isolated in the solid state as  $ClO_4^-$  salts. We worked with these complexes on a small scale without any explosive incident. Despite these observations, the unpredictable behaviour of  $ClO_4^-$  salts necessitate extreme care in handling.

Synthesis of L<sup>4b</sup>. A mixture of L<sup>4a</sup> (4.4 g, 17.5 mmol) and acrylonitrile (31.5 mL) was refluxed for 24 h under N<sub>2</sub>. After cooling, the excess acrylonitrile was removed under reduced pressure. The crude product was purified by flash silica gel chromatography using CH<sub>2</sub>Cl<sub>2</sub> : MeOH (90 : 10 v/v) as eluant. A white solid was obtained (2.7 g, 8.87 mmol, 51% yield). Mp: 40–42 °C. Elem. Anal.: found (calc. for C<sub>13</sub>H<sub>24</sub>N<sub>2</sub>S<sub>2</sub>O<sub>2</sub>): C, 51.10 (51.28); H, 8.04 (7.95); N, 9.55 (9.20); S, 21.21 (21.06). <sup>1</sup>H-NMR (400 MHz, 298 K, CDCl<sub>3</sub>):  $\delta_{\rm H}$  2.44 (2H, t, J = 7.2 Hz), 2.70–2.83 (14H, m), 3.60 (4H, s), 3.74 (4H, t, J = 5.2 Hz). <sup>13</sup>C-NMR (400 MHz, 298 K, CDCl<sub>3</sub>):  $\delta_{\rm C}$  16.90, 30.19, 31.18, 50.89, 54.36, 70.62, 73.57, 118.72.

Synthesis of L<sup>4c</sup>. A mixture of L<sup>4b</sup> (2.54 g, 8.34 mmol) and BH<sub>3</sub>. THF 1 M (250 mL) was refluxed for 48 h under N<sub>2</sub>. After cooling, water (150 mL) was added and the solvent was removed under reduced pressure. The residue was taken up in 2 M HCl (150 mL) and the resulting mixture was refluxed for 2 h. The solvent was then removed under reduced pressure and the resulting white solid was dissolved in water and passed through a Dowex 1 × 8–200 ion-exchange resin. A colourless oil was obtained (2.23 g, 7.25 mmol, 87% yield). <sup>1</sup>H-NMR (400 MHz, 298 K, CDCl<sub>3</sub>):  $\delta_{\rm H}$  1.55–1.58 (2H, m), 2.44 (2H, t, J = 6.8 Hz), 2.60–2.73 (10H, m), 3.32 (2H, br s), 3.53–3.55 (10H, m), 3.67 (2H, t, J = 5.4 Hz). <sup>13</sup>C-NMR (300 MHz, 298 K, CDCl<sub>3</sub>):  $\delta_{\rm c}$  29.80, 31.08, 40.27, 53.07, 54.13, 62.10, 70.63, 73.37.

Synthesis of L<sup>4d</sup>. A solution of dansyl chloride (0.19 g, 0.713 mmol) in anhydrous MeCN (25 ml) was added drop-wise to a mixture of L<sup>4c</sup> (0.2 g, 0.648 mmol) and  $K_2CO_3$  (0.29 g,

2.139 mmol) in anhydrous MeCN (25 ml). This mixture was stirred at room temperature for 48 h under N2. After filtration, the solvent was removed under reduced pressure. The residue (a yellow oil) was dissolved in CHCl<sub>3</sub> and washed with water. The organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure to yield a yellow oil. The product was purified by flash chromatography on silica gel using  $CH_2Cl_2$ : MeOH (90 : 10 v/v) as eluant to afford a yellow solid (0.27 g, 0.5 mmol, 77% yield). Mp: 88-89 °C. Elem. Anal.: found (calc. for C<sub>25</sub>H<sub>39</sub>N<sub>3</sub>S<sub>3</sub>O<sub>4</sub>): C, 55.54 (55.42); H, 7.88 (7.26); N, 7.60 (7.76); S, 17.99 (17.75).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$  1.50–1.52 (2H, m), 2.38 (2H, t, J = 5.6 Hz), 2.58–2.73 (12H, m), 2.84 (6H, s), 2.93-2.96 (2H, m), 3.59 (4H, s), 3.70-3.72 (4H, m), 6.59 (1H, br s), 7.14 (1H, d, *J* = 7.6 Hz), 7.44–7.55 (2H, m), 8.19 (1H, d, J = 7.6 Hz), 8.31 (1H, d, J = 8.4 Hz), 8.47 (1H, d, J =d, J = 8.4 Hz). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$  25.53, 29.26, 31.06, 43.04, 45.24, 53.66, 54.07, 70.61, 73.43, 114.93, 118.88, 122.97, 128.02, 129.28, 129.50, 129.65, 129.92, 134.80, 151.67. Mass Spectrum EI<sup>+</sup>: m/z 542 ([C<sub>25</sub>H<sub>39</sub>N<sub>3</sub>S<sub>3</sub>O<sub>4</sub>]<sup>+</sup>).

Synthesis of L<sup>4e</sup>. 9-anthraldehyde (0.21 g, 1.0 mmol) was added in portions to a solution of L<sup>4c</sup> (0.31 g, 1.0 mmol) in dry EtOH : MeCN (1 : 1 v/v, 24 mL). The mixture was stirred at room temperature for 24 h under N2. The solvent was removed under reduced pressure. The residue was dissolved in dry EtOH (50 mL) and NaBH<sub>4</sub> (1.44 g, 38 mmol) and NaBH<sub>3</sub>CN (2.39 g, 38 mmol) were added to the resulting solution. The mixture obtained was stirred at room temperature for 48 h under N<sub>2</sub>. The solvent was removed under reduced pressure and the residue was taken up in water and basified to pH = 14 with 5 M NaOH. The product was extracted with CH<sub>2</sub>Cl<sub>2</sub>, the organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent removed under reduced pressure. The crude product was purified by flash silica gel chromatography using  $CH_2Cl_2$  : MeOH (90 : 10 v/v) as eluant. A yellow solid was obtained (0.199 g, 0.40 mmol, 40% yield). Elem. Anal.: found (calc. for C<sub>28</sub>H<sub>38</sub>N<sub>2</sub>S<sub>2</sub>O<sub>2</sub>): C, 66.99 (67.43); H, 7.91 (7.68); N, 5.40 (5.62); S, 12.83 (12.86).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$  2.36–2.88 (20H, m), 3.37–3.50 (4H, m), 3.59-3.62 (2H, m), 4.12 (1H, br s), 4.72 (2H, s), 7.38-7.52 (4H, m), 7.92 (2H, d, J = 8.4 Hz), 8.26 (2H, d, J = 8.4 Hz), 8.33 (1H, s). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$  28.30, 29.32, 31.04, 44.93, 48.64, 53.68, 53.73, 70.64, 73.31, 123.85, 124.98, 126.46, 127.43, 129.60, 130.12, 131.33. Mass Spectrum EI+: m/z 499  $([C_{28}H_{38}N_2S_2O_2]^+).$ 

#### Potentiometric measurements

All pH-metric measurements were carried out in degassed 0.1 M NMe<sub>4</sub>NO<sub>3</sub> water solutions, at 298.1 K, using the equipment and procedure described elsewhere.<sup>38</sup> The combined Ingold 405 S7/120 electrode was calibrated as a hydrogen concentration probe by titrating amounts of HCl with CO<sub>2</sub>-free NMe<sub>4</sub>OH solutions and determining the equivalent point by Gran's method<sup>39</sup> which allows the determination of the standard potential  $E^{\circ}$ , and the ionic product of water (p $K_w = 13.83(1)$  at 298.1 K in 0.1 M NMe<sub>4</sub>NO<sub>3</sub>). Ligand and metal ion concentrations of  $1.0 \times 10^{-3}$  M and  $0.5 \times 10^{-3}$  to  $1.0 \times 10^{-3}$  M, respectively, were employed in the potentiometric measurements, which involved performing three titration experiments, each of *ca.* 100 data points, in the pH range 2–10.5. The relevant e.m.f. data were analysed by means of the computer program HYPERQUAD.<sup>40</sup>

## Crystallography

Crystal data and refinement details of all structure determinations appear in Table 1. Only special features of the analyses are mentioned here. Single crystal data collection for  $(H_2L^{1c})(ClO_4)_2 \cdot dmf$ ,  $[Cd(L^{3a})(NO_3)_2]$  (1),  $[Cu(L^{4a})(dmf)](ClO_4)_2$ (2),  $[Zn(L^{1c})(ClO_4)]ClO_4$  (3), and  $[Hg(L^{2c})](ClO_4)_2$  (5) was performed on a Bruker SMART CCD diffractometer using  $\omega$ scans. For  $[Cd(L^{1c})(NO_3)]NO_3$  (4) data were acquired on a

[able 1	Crystallographic data for $(H_2L^{1c})(ClO_4)_2$ .	dmf, [Cd(L <sup>3a</sup> )(NO <sub>3</sub> ) <sub>2</sub> ] (1), [C	$U(L^{4a})(dmf)](ClO_4)_2$ (	(2), [Zn(L <sup>1c</sup> )(ClO <sub>4</sub> )]ClO <sub>4</sub> (3)	ı, [Cd(L <sup>1c</sup> )(NO <sub>3</sub> )]NO <sub>3</sub> (4), a	and $[Hg(L^{2c})](ClO_4)_2$ (5)	
	Compound	$(H_2L^{1c})(ClO_4)_2\cdot dmf$	1	2	3	4	5
	Formula	$C_{14}H_{33}Cl_2N_3O_{10}S_2$	$\mathbf{C}_8\mathbf{H}_{18}\mathbf{CdN}_4\mathbf{O}_7\mathbf{S}$	$\mathbf{C}_{13}\mathbf{H}_{28}\mathbf{C}\mathbf{I}_{2}\mathbf{C}\mathbf{u}\mathbf{N}_{2}\mathbf{O}_{11}\mathbf{S}_{2}$	$C_{11}H_{24}Cl_2N_2O_9S_2Zn$	$\mathbf{C}_{11}\mathbf{H}_{24}\mathbf{CdN_4O_7S_2}$	$\mathrm{C_{I1}}\mathrm{H_{24}}\mathrm{Cl_{2}HgN_{2}}\mathrm{O_{8}S_{3}}$
	Crystal system	Orthorhombic	Triclinic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
	Space group	<i>Pnma</i> (no. 62)	<i>P</i> -1 (no. 2)	$P2_12_12_1$ (no. 19)	$Pca2_1$ (no. 29)	<i>Pbca</i> (no. 61)	$Pca2_1$ (no. 29)
	W	538.45	426.72	586.93	528.71	500.86	629.99
	a/Å	11.535(1)	9.775(9)	7.6926(14)	15.788(2)	13.128(2)	13.586(1)
	$b/\dot{A}$	12.242(1)	10.351(5)	10.479(2)	9.698(1)	16.559(9)	16.156(1)
	$c/\text{\AA}$	17.296(2)	14.610(7)	28.649(5)	13.262(1)	16.951(2)	18.833(2)
	$a/^{\circ}$		94.195(9)				
	$\beta/^{\circ}$		94.010(8)				
	y /°		93.062(8)				
	$V/Å^3$	2442.4(4)	1472.5(17)	2309.4(7)	2030.6(4)	3685 (2)	4133.8(6)
	Ζ	4	4	4	4	8	8
	T/K	293(2)	150(2)	150(2)	293(2)	293(2)	293(2)
	$D_{ m c}/{ m g~cm^{-3}}$	1.464	1.925	1.688	1.729	1.806	2.185
	$\mu/\text{mm}^{-1}$	0.489	1.663	1.414	1.724	1.453	8.049
	Unique reflections, $R_{\rm int}$	3230, 0.038	7514, 0.049	5182, 0.027	3084, 0.031	3225, 0.013	8106, 0.076
	Observed reflections $[I > 2\sigma(I)]$	1656	6308	4481	1721	2354	5580
	Absorption correction	SADABS <sup>41</sup>	SADABS <sup>41</sup>	SADABS <sup>41</sup>	SADABS <sup>41</sup>	w-scans	SADABS <sup>41</sup>
	$T_{ m min}, {ar T_{ m max}}$	0.624, 1.000	0.726, 1.000	0.668, 1.000	0.732, 1.000	0.839, 1.000	0.683, 1.000
	$R_1$	0.0745	0.0441	0.0397	0.0491	0.0258	0.0360
	$wR_2$ [all data]	0.254	0.0959	0.0838	0.1402	0.0713	0.0799

Enraf-Nonius CAD-4 diffractometer using  $\omega$  scans. All data sets were corrected for Lorentz, polarization and absorption effects as specified in Table 1. All structures were solved by direct methods using SHELXS97<sup>42</sup> followed by difference Fourier syntheses and refined with full-matrix least squares using SHELXL97.<sup>43</sup> All non-H atoms were refined anisotropically and H atoms were introduced at calculated positions and thereafter incorporated into a riding model with  $U_{iso}(H) = 1.2 U_{eq}(C)$ . In **2**, **3**, and **5** some of the oxygen atoms in perchlorato anions display slightly high displacement parameters which might be indicative of partial disorder. However, any attempt to split these atoms into two components offered no advantage.

CCDC reference numbers 271763-271768.

See http://dx.doi.org/10.1039/b506785e for crystallographic data in CIF or other electronic format.

# **Results and discussion**

# Synthesis of $L^{rc}$ (n = 1-4) and their coordination properties towards $Cu^{II}$ , $Zn^{II}$ , $Cd^{II}$ , $Hg^{II}$ , and $Pb^{II}$

Mixed O/S-, N/S-, and N/O/S-donor macrocycles feature hard and soft binding sites in close proximity and, therefore, should ensure strong complexation to a great variety of metal ions. Compared to homoleptic thioether and polyaza macrocycles, the chemistry of these ligands, especially those containing three different donors, has been relatively neglected due to synthetic difficulties encountered in their preparation.<sup>36,37,44–48</sup> Recently, Reedijk et al. have developed a facile route for the synthesis of a range of mixed N/O/S-donor macrocycles which offers the advantage of an easier deprotonation step of the nitrogen atom after the cyclization reaction and a consequently higher overall yield.<sup>36</sup> This has prompted us to study mixed N/S-, and N/O/S-donor macrocycles as receptors in redox and fluorescence molecular sensors for heavy and transition metal (HTM) ions.<sup>32,33</sup> We surmised that a diversified donor set, featuring both hard and soft donor atoms, would confer selectivity to the recognition of HTM ions by the receptor, thus leading to a specific substrate-response of the signalling unit in a molecular sensor. According to the modular approach outlined in the introduction for the design and construction of fluorescence sensors, we linked the macrocycles L<sup>1a-4a</sup> to dansyl or 9-anthracenylmethyl fluorescent moieties via aminopropyl spacers.

Functionalisation of  $L^{1a-4a}$  to their *N*-aminopropyl pendant arm derivatives  $L^{1c-4c}$  was achieved *via* reaction of  $L^{1a-4a}$  with acrylonitrile and subsequent reduction of the isolated pendant arm nitrile derivatives,  $L^{1b-4b}$ , with BH<sub>3</sub>·THF.

Single crystals of  $(H_2L^{1c})(ClO_4)_2$ ·dmf were obtained by diffusion of  $Et_2O$  vapour into a dmf solution of the crude perchlorate salt of  $L^{1c}$  obtained by addition of concentrated  $HClO_4$  into a solution of  $L^{1c}$  in EtOH. An X-ray diffraction analysis (Fig. 1) reveals that the macrocyclic framework adopts a "butterfly" [2424] conformation with the plane of the ring folded along the S...S vector. This conformation is presumably determined by the intramolecular N(1)H...O(7) hydrogen bond [N(1)H...O(7) 2.05, N(1)...O(7) 2.909(5) Å, N(1)–H...O(7) 141°]. The protonated *N*-aminopropyl pendant arm points out of the ring cavity, and the terminal-NH<sub>3</sub><sup>+</sup> ammonium group forms three hydrogen bonds, one of which is with a molecule of dmf [N(16)H(16a)...O(2) 1.77, N(16)...O(2) 2.703(6) Å, N(16)–H(16a)...O(2) 179°].

Symmetry related  $(H_2L^{1c})^{2+}$  cations are bridged by two perchlorate ions *via* CH···O  $[C(3^{ii})H(3b^{ii})\cdots O(13)$  2.51,  $C(3^{ii})\cdots O(13)$  3.270(6) Å,  $C(3^{ii})-H(3b^{ii})\cdots O(13)$  135°, ii = 1 - x, -1/2 + y, -z] and NH···O hydrogen bonds at the terminal ammonium groups  $[N(16)H(16b/c)\cdots O(13) 2.23,$  $N(16)\cdots O(13) 2.995(6)$ Å,  $N(16)-H(16b/c)\cdots O(13) 140^{\circ}]$  thus forming undulating ribbons which propagate along the [010] direction. Ribbons of this type are connected *via* CH···O



**Fig. 1** Partial view of the packing diagram for  $(H_2L^{la})(ClO_4)_2$  dmf with the numbering scheme adopted. i = x, 3/2 - y, z; ii = 1 - x,  $-\frac{1}{2} + y$ , -z.

hydrogen bonds  $[C(2^{iii})H(2b^{iii})\cdots O(12) 2.47, C(2^{iii})\cdots O(12) 3.383(6) Å, C(2^{iii})-H(2b^{ii})\cdots O(12) 157^{\circ}, iii = -1/2 + x, 3/2 - y, 1/2 - z]$  to afford an extended 3D-network.

**Solution studies.** Before proceeding with the synthesis of the target fluorescent sensors (Scheme 1) we investigated the protonation of  $L^{1c-4c}$  and complex formation with  $Cu^{II}$ ,  $Zn^{II}$ ,  $Cd^{II}$ ,  $Hg^{II}$ , and  $Pb^{II}$  by means of potentiometric measurements in aqueous solutions (298.1 K, 0.1 M NMe<sub>4</sub>NO<sub>3</sub>) in the pH range 2.0–10.5.

The protonation constants of the ligands are in the range generally observed for polyamine compounds and are supplied within ESI (Table S1).<sup>†</sup> The complexes formed and the corresponding stability constants are reported in Table 2, together with those previously reported for the complexes with L<sup>1a</sup>,<sup>32</sup> and those determined for the complexes with L<sup>3a</sup>. Precipitation at alkaline pHs of hydroxo complexes precluded the study of some systems in the alkaline pH region (Table 2), but since the process of complex formation generally takes place at acidic pH values, the relevant stability constants for the [ML]<sup>2+</sup> species were determined in all cases, with the only exceptions of the complexes of Pb<sup>II</sup> complexes with L<sup>1c</sup> and L<sup>2c</sup> and of Cd<sup>II</sup> with L<sup>4c</sup>. In fact, in these cases the low solubility of the complexes from acidic to alkaline pHs did not allow a speciation study by using potentiometric techniques.

The stability of the complexes with  $L^{3a}$ , which contains an N<sub>2</sub>SO-donor set within its cyclic framework, increases in the order  $Zn^{II} < Pb^{II} < Cd^{II} < Cu^{II} < Hg^{II}$ . Hg<sup>II</sup> and  $Cu^{II}$  form the most stable complexes, as generally observed in the case of polyamine ligands. The lower stability of the  $Zn^{II}$  complex with respect to the Cd<sup>II</sup> and Pb<sup>II</sup> ones is rather unusual for polyamine ligands, which generally show a similar binding ability for these three metal cations. This result could be explained by the presence in the donor set of a soft sulfur atom, which generally displays a higher affinity for the softer Cd<sup>II</sup> and Pb<sup>II</sup> metal ions.

A similar trend has also been observed in the case of other mixed N/O/S-donor tetradentate 12-membered macrocycles (see the stability constants of the metal complexes with  $L^{1a}$  and  $L^{2a}$  in Table 2).<sup>32,33</sup>

 $L^{lc}$  and  $L^{2c}$  contain an aminopropyl side arm attached respectively to a [12]aneNS<sub>2</sub>O or [12]aneNS<sub>3</sub> cyclic unit. Their

Table 2	Formation constants (log K	) of the metal compl	exes with L <sup>1a-3a</sup> , L <sup>1c-4c</sup>	$(I = 0.1 \text{ M}, 298.1 \text{ K})^{4}$
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			,		
Reaction	$Cu^{II}$	$Zn^{II}$	$Cd^{\Pi}$	Рвп	Hg <sup>II</sup>
$M^{2+} + L^{1a} \rightleftharpoons [ML^{1a}]^{2+}$	8.13 <sup>b</sup>	b	7.90 <sup>b</sup>	4.20 <sup>b</sup>	8.65(3) <sup>b</sup>
$M^{2+} + L^{2a} \rightleftharpoons [ML^{2a}]^{2+}$	$7.93(2)^{c}$	c,d	$5.8(1)^{c}$	$4.27(4)^{c}$	c,e
$M^{2+} + L^{3a} \rightleftharpoons [ML^{3a}]^{2+}$	9.81(6)	5.10(5)	8.10(5)	$6.93(5)^{g}$	$10.1(1)^{g}$
$[ML^{3a}]^{2+} + OH^{-} \rightleftharpoons [ML^{3a}(OH)]^{+}$	6.7(1)	ſ	f	f	3.7(1)
$M^{2+} + L^{1c} \rightleftharpoons [ML^{1c}]^{2+}$	9.67(1)	8.95(2)	8.08(3)	h	9.62(3)
$[ML^{1c}]^{2+} + H^{+} \rightleftharpoons [M(HL^{1c})]^{3+}$	5.25(3)	6.68(2)	5.02(8)		7.09(4)
$[ML^{1c}]^{2+} + OH^{-} \rightleftharpoons [ML^{1c}(OH)]^{+}$	6.11(5)	6.74(6)	2.98(8)		2.93(5)
$[ML^{1c}(OH)]^+ + OH^- \rightleftharpoons [ML^{1c}(OH)_2]$	2.91(6)	_ ``	_ `		_ ``
$M^{2+} + L^{2c} \rightleftharpoons [ML^{2c}]^{2+}$	9.23(3)	8.14(4)	8.20(3)	h	10.88(4)
$[ML^{2c}]^{2+} + H^+ \rightleftharpoons [M(HL^{2c})]^{3+}$	6.15(3)	6.68(2)	7.22(4)		6.05(5)
$[ML^{2c}]^{2+} + OH^{-} \rightleftharpoons [ML^{2c}(OH)]^{+}$	4.28(5)	6.63(2)	_		2.88(4)
$M^{2+} + L^{3c} \rightleftharpoons [ML^{3c}]^{2+}$	12.9(1)	7.5(1)	9.0(1)	9.2(1)	11.8(1)
$[ML^{3c}]^{2+} + H^+ \rightleftharpoons [M(HL^{3c})]^{3+}$	7.6(1)	8.3(1)	8.7(1)	8.7(1)	8.1(1)
$[M(HL^{3c})]^{3+} + H^{+} \rightleftharpoons [M(H_2L^{3c})]^{4+}$	5.3(1)	6.5(1)	6.3(1)	5.3(1)	6.7(1)
$[ML^{3c}]^{2+} + OH^{-} \rightleftharpoons [ML^{3c}(OH)]^{+}$	4.4(1)	4.3(1)	4.3(1)		3.7(1)
$M^{2+} + L^{4c} \rightleftharpoons [ML^{4c}]^{2+}$	6.9(1) <sup>f</sup>	5.4(1) <sup>f</sup>	i	6.0(1) <sup>f</sup>	7.8(1) <sup>f</sup>
$[\mathrm{ML}^{4\mathrm{c}}]^{2+} + \mathrm{H}^{+} \rightleftharpoons [\mathrm{M}(\mathrm{HL}^{4\mathrm{c}})]^{3+}$		_	_		7.3(1)

<sup>*a*</sup> For L<sup>4a</sup> it was not possible to study the complexation with the metal ions under consideration due to the impossibility to prepare a weighable salt of this macrocycle. <sup>*b*</sup> Values from reference 32. <sup>*c*</sup> Data for the complexation of L<sup>2a</sup> were provided by M. Schröder *et al.* as a private communication. <sup>*d*</sup> The stability of the complex is too low to be confidently determined. <sup>*e*</sup> Precipitation of the Hg<sup>II</sup> complex does not allow the determination of the stability of this complex. <sup>*f*</sup> Precipitation at slightly alkaline pH values of hydroxo complexes does not allow the study of the system in the alkaline pH region. <sup>*g*</sup> The Log *K* value for the Pb<sup>II</sup> and Hg<sup>II</sup> complexes are in good agreement with those previously found by Afshar *et al.* (Log *K* = 6.6 for [PbL<sup>3a</sup>]<sup>2+</sup> and Log *K* = 10.5 for [HgL<sup>3a</sup>]<sup>2+</sup>, see reference 37). <sup>*h*</sup> The low solubility of the Pb<sup>II</sup> complexes with L<sup>1c</sup> and L<sup>2c</sup> does not allow the potentiometric study of these system.

complexation to Cu<sup>II</sup>, Zn<sup>II</sup>, Cd<sup>II</sup> and Hg<sup>II</sup> occurs at acidic pH values, with the formation of  $[M(HL)]^{3+}$  species ( $M = Cu^{II}, Zn^{II}, Cd^{II}$  or Hg<sup>II</sup>,  $L = L^{1c}$  or  $L^{2c}$ ), followed by deprotonation to afford  $[ML]^{2+}$  complexes. Deprotonation of a coordinated water molecule takes place at neutral (Zn<sup>II</sup>) or alkaline (Cu<sup>II</sup> and Hg<sup>II</sup>) pH values to give hydroxo complexes, as shown in Fig. 2 for the Cu<sup>II</sup> and Hg<sup>II</sup> complexes with L<sup>1c</sup> (the distribution diagrams for the other complexes with L<sup>1c</sup> and L<sup>2c</sup> are supplied within ESI, Figs. S1, S2 and S3).† Cd<sup>II</sup> hydroxo-complexes with L<sup>2c</sup> were not detected in solution, due to their low solubility.

We were interested in comparing the coordination properties of  $L^{1c}$  and  $L^{2c}$  with those of the corresponding macrocycles not bearing an *N*-aminopropyl side arm,  $L^{1a}$  and  $L^{2a}$ , respectively. As shown in Table 2,  $L^{1c}$  and  $L^{2c}$  form more stable [ML]<sup>2+</sup> complexes



**Fig. 2** Distribution diagrams for the systems  $Cu^{II}/L^{1c}$  (a), and  $Hg^{II}/L^{1c}$  (b)  $([M^{II}] = [L^{1c}] = 1 \times 10^{-3} \text{ M}, T = 298.1 \text{ K}, I = 0.1 \text{ M}).$ 

than  $L^{1a}$  and  $L^{2a}$ , indicating that in these species the amine group of the pendant arm is indeed involved in metal coordination. Furthermore, in contrast to the complexes with  $L^{1a}$  and  $L^{2a}$ , the complexes  $[ML^{1c}]^{2+}$  and  $[ML^{2c}]^{2+}$  display a marked tendency to bind a proton to afford monoprotonated  $[M(HL)]^{3+}$ species, as shown by the rather high values (Table 2) of the protonation constants of the  $[ML]^{2+}$  complexes ( $L = L^{1c}$  or  $L^{2c}$ ).

This suggests that protonation of these complexes takes place on the amine group of the pendant arm, with a consequent detachment of this nitrogen donor from the metal.

 $L^{3c}$  contains two aminopropyl pendant arms attached to a [12]aneN<sub>2</sub>SO moiety. Among the ligands investigated,  $L^{3c}$ forms the most stable complexes (Table 2), in agreement with the higher number of N-donors potentially available for metal coordination. Analogously to  $L^{1c}$  and  $L^{2c}$ , the presence of aminopropyl side arms gives rise to an increased stability of the [ML<sup>3c</sup>]<sup>2+</sup> complexes with respect to the corresponding complexes with the underivatised macrocycle  $L^{3a}$ . This suggests that at least one aminoalkyl pendant arm is involved in metal coordination.

At the same time, all metal complexes show a marked tendency to form mono- and di-protonated complexes, as shown in Fig. 3 for  $Cu^{II}$  and  $Hg^{II}$  (distribution diagrams for the systems  $Zn^{II}/L^{3c}$  and  $Cd^{II}/L^{3c}$  are supplied within ESI, Fig. S4).<sup>†</sup>

The fact that complexes with L<sup>3a</sup> do not show any tendency to bind protons indicates that protonation of [ML3c]2+ takes place on the primary amine group of the side arms. Furthermore, the constant for the addition of the first proton to the [ML<sup>3c</sup>]<sup>2+</sup> complexes  $([ML^{3c}]^{2+} + H^+ \rightleftharpoons [M(HL^{3c})]^{3+})$  ranges between 7.6 and 8.7 log units; these high values are generally attributed to protonation of amine groups not bound to metal cations.49 The second protonation constant is lower than the first one (5.3-6.7 log units), as expected for protonation of an aminopropyl group weakly involved in metal binding.49 Therefore, in the [ML<sup>3c</sup>]<sup>2+</sup> complexes only one aminopropyl side arm would be bound to the metal, while the other one would not be involved in any interaction with the metal. Consequently, binding of the first proton to the [ML3c]2+ complexes, observed at slightly alkaline pH values, takes place on the aminopropyl group not coordinated to the metal, while the second protonation step ( $[M(HL^{3c})]^{3+}$  + H<sup>+</sup>  $\rightleftharpoons$  [ $M(H_2L^{3c})]^{4+}$ ), at acidic pH values, occurs on the metal-bound aminopropyl side arm and causes its displacement from the metal.



**Fig. 3** Distribution diagrams for the systems  $Cu^{II}/L^{3c}$  (a) and  $Hg^{II}/L^{3c}$  (b)  $([M^{II}] = [L^{3c}] = 1 \times 10^{-3} \text{ M}, T = 298.1 \text{ K}, I = 0.1 \text{ M}).$ 

Among the N-aminopropyl pendant arm functionalised macrocycles under investigation, L4c displays the lowest binding ability for metal cations (Table 2). A tentative explanation of the lower stability of the complexes with L<sup>4c</sup> may involve the different molecular architecture of this ligand, which contains one nitrogen donor and four weakly coordinating sulfur or oxygen atoms within its 15-membered cyclic framework. Such a disposition could leave a sulfur or oxygen donor excluded from coordination to the metal in the [ML<sup>4c</sup>]<sup>2+</sup> complexes, thus generating a destabilising 8-membered chelate ring. At the same time, in contrast with the other macrocycles bearing an aminopropyl pendant arm reported here, the [ML<sup>4c</sup>]<sup>2+</sup> complexes  $(M=Cu^{{\scriptscriptstyle \rm II}},\,Zn^{{\scriptscriptstyle \rm I}}$  or  $Pb^{{\scriptscriptstyle \rm I}})$  do not display a particular tendency to form protonated species. Presumably, because of their low stability, protonation of the [ML4c]2+ species on the metalbound aminopropyl pendant arm (and consequent detachment from the metal) would lead to decomplexation rather than to the formation of a protonated [M(HL<sup>4c</sup>)]<sup>3+</sup> species. As a matter of fact, only the most stable complex, [HgL<sup>4c</sup>]<sup>2+</sup>, gives a monoprotonated species, [Hg(HL<sup>4c</sup>)]<sup>3+</sup>.

Solid state studies. A feature of 12-membered tetradentate macrocycles is their inability to host divalent transition metal ions within their cavity: it is not possible to achieve coplanarity between the four donor atoms and the guest metal. This is well documented for ligands with four identical donors, whereas structural data for mixed tetradentate N/S- and N/S/Odonor 12-membered macrocycles are sparse.<sup>37,44,45,50</sup> Recently, we reported the X-ray crystal structures for the 1:1 metal complexes of L1a with CuII, CdII, and HgII.32 L1a acts a tetradentate ligand and adopts folded [2424] or [3333] conformations resembling an open book with the spine along the S(4)-M-S(10) direction and N(1)-M-O(7) angles ranging from 81.50(12)° in  $[Cd(L^{1a})(NO_3)_2]$ to 111.2(4)° in [Hg(L<sup>1a</sup>)MeCN]<sup>+</sup>. In each case anionic ligands or solvent molecules complete the coordination sphere around the metal ion. Similar folded conformations are adopted by [12]aneN<sub>3</sub>S (1-thia-4,7,10-triazacyclododecane) in its complexes with Cu<sup>II</sup>, Zn<sup>II</sup>, Hg<sup>II</sup>, Pb<sup>II</sup>, and Ni<sup>II</sup>, with the more planar [3333] conformer being dominant for larger metal ions (Hg<sup>II</sup> and Pb<sup>II</sup>).50

Reaction of  $L^{3a}$  with  $Cd(NO_3)_2$  in MeCN afforded a colourless solution from which crystals suitable for X-ray

diffraction were obtained by diffusion of Et<sub>2</sub>O vapour. A single-crystal structure analysis confirmed the complex to be the species  $[Cd(L^{3a})(NO_3)_2]$  (1), the asymmetric unit consisting of two complexed macrocyclic molecules (1-I and 1-II). Due to the similarity of the two independent molecules in unit cell, only one (1-I) will be discussed (Fig. 4, Table 3). The coordination sphere around each metal centre consists of the N<sub>2</sub>SO-donor set of the macrocyclic framework, and two asymmetrically bidentate nitrato ligands (in 1-I, for one of the NO3<sup>-</sup> ions, one Cd-Onitrato distance is only slightly longer than those found for a clearly bidentate nitrato ligand (Fig. 4, Table 3),<sup>44</sup> whereas in 1-II this happens for both coordinated  $NO_3^-$  ions with short Cd– $O_{nitrato}$  distances of 2.308(4) and 2.325(4) Å, and longer ones of 2.704(5) and 2.678(4) Å). The Cd<sup>II</sup> ion is displaced out of the plane defined by the four donors of L<sup>3a</sup> (by 1.0 Å for both independent molecules 1-I and 1-II) and the macrocylic ligand adopts a [3333] conformation with N(1)-Cd-N(7) and S(4)-Cd-O(10) angles for 1-I of 114.8(2) [113.2(2) for 1-II] and 123.98(10) Å [122.63(10) Å for 1-II], respectively. A similar coordination sphere around the metal centres, and conformation for the macrocyclic ligands has been observed in the complexes  $[Hg(L^{3a})(NO_3)_2]$ ,<sup>37</sup>  $[Pb(L^{3a})NO_3)_2]$ ,<sup>37</sup>  $[Hg([12]aneNSO_2)(NO_3)_2]$  ([12]aneNSO\_2 = 1,7-dioxa-4-thia- $\begin{array}{l} 10\text{-azacyclododecane},^{45} \quad [Cd(\mathit{cis}\text{-}[12]\text{aneN}_2S_2)(NO_3)_2] \quad (\mathit{cis}\text{-}[12]\text{aneN}_2S_2 \quad = \quad 1,4\text{-dithia-7,10-diazacyclododecane},^{44} \quad \text{and} \quad \end{array}$ [Cd(L<sup>2a</sup>)(NO<sub>3</sub>)<sub>2</sub>],<sup>44</sup> thus confirming the inability of 12-membered mixed-donor tetradentate macrocycles to bind a metal in the plane of the donors, and their preference for a folded [2424] conformation with small metal ions such as Cu<sup>II</sup> and Zn<sup>II</sup>, or a more planar [3333] conformation with larger metals such as Cd<sup>II</sup>, Hg<sup>II</sup>, and Pb<sup>II</sup> that lack a particular stereochemical preference.



**Fig. 4** ORTEP view of one (1-I) of the two independent  $[Cd(L^{3a})(NO_3)_2]$  units in 1 with the adopted numbering scheme. Displacement ellipsoids are drawn at 30% probability. Hydrogen atoms have been omitted for clarity except those on the macrocyclic N-donors.

Even fewer structural data are available for metal complexes with 15-membered mixed N/S/O-donor pentadentate macrocycles such as L<sup>4a</sup> than for the smaller 12-membered macrocyclic ligands.<sup>44,47,51</sup> The greater flexibility and the larger cavity of these systems allows very different conformations to be adopted from a "butterfly" or folded geometry in  $[Cd(L^{4a})(NO_3)_2]$ ,<sup>44</sup>  $[Ni([15]aneN_2S_2O)(H_2O)](NO_3)_2$ ,<sup>47</sup>  $[Ag([15]aneN_2S_2O)(SCN)]$ ,<sup>51</sup>  $([15]aneN_2S_2O) = 1-0xa-7,10-dithia-4,13-diazacyclopentadecane),$  $[Ni([15]'aneN_2S_2O)(NO_3)]NO_3$ ,<sup>47</sup> and  $[Cu([15]'aneN_2S_2O)]-(ClO_4)_2$  ( $[15]'aneN_2S_2O = 1-0xa-4,13-dithia-7,10-diazacyclo$ pentadecane),<sup>47</sup> to a flattened geometry in  $[Cd([15]aneN_2S_2O)]-(NO_3)]NO_3$  ( $[15]aneN_2SO_2 = 1,4-dioxa-10-thia-7,13-diaza$ cyclopentadecane)<sup>44</sup> with the metal centres encapsulated within the ring cavity.

	$1-\mathbf{I}^b$	2	3	$4^{d}$	5′
M-N(1)	2.303(4)	1.979(3)	2.150(5)	2.441(3)	2.500(9) [2.505(9)]
M-S(4)	2.710(2)	2.4038(10)	2.486(4)	2.6681(10)	2.772(3) [2.737(3)]
M-X(7)	2.311(5)	2.347(2)	2.195(4)	2.666(2)	2.544(3) [2.563(3)]
M - S(10)			2.466(3)	2.5970(9)	2.697(3) [2.657(3)]
M - O(10)	2.511(4)	2.433(3)			
M-S(13)		2.4069(10)			
M-Y(1)	2.409(4) [2.522(4)]	1.925(2)	2.030(5)	2.239(3)	2.190(9) [2.169(8)]
M-Y(2)	2.297(4) [2.778(5)]		2.362(7)	2.334(2) [2.838(3)]	
N(1)-M-S(4)	78.88(13)	86.79(9)	90.3(4)	76.94(7)	77.5(2) [76.0(2)]
N(1)-M-X(7)	114.8(2)	95.17(10)	97.5(2)	94.37(8)	126.7(2) [129.2(2)]
N(1)-M-S(10)			84.3(4)	80.22(6)	77.6(2) [79.0(2)]
N(1)-M-O(10)	72.4(2)	93.75(10)			
N(1)-M-S(13)		88.67(8)			
N(1)-M-Y(1)	90.73(15) [137.26(15)]	176.97(11)	102.5(2)	90.20(10)	94.0(3) [95.8(3)]
N(1)-M-Y(2)	122.9(2) [73.9(2)]		174.6(5)	159.37(9) [152.02(8)]	
S(4) - M - X(7)	77.93(13)	78.35(6)	79.1(3)	70.23(5)	80.33(10) [82.22(10)]
S(4) - M - S(10)			156.61(7)	133.23(3)	132.63(9) [132.16(10)]
S(4)–M–O(10)	123.98(10)	146.55(6)			
S(4) - M - S(13)		134.58(3)			
S(4) - M - Y(1)	153.83(11) [143.83(11)]	93.52(8)	101.2(4)	103.88(7)	105.0(3) [106.9(2)]
S(4) - M - Y(2)	86.76(12) [75.59(10)]		91.7(8)	82.47(7) [127.06(6)]	
X(7) - M - S(10)			79.1(3)	71.50(5)	83.29(9) [82.97(9)]
X(7) - M - O(10)	72.4(2)	68.28(8)			
X(7) - M - S(13)		147.06(7)			
X(7) - M - Y(1)	128.0(2) [82.80(15)]	81.95(9)	160.1(2)	171.43(8)	138.6(3) [134.7(2)]
X(7) - M - Y(2)	115.6(2) [149.8(2)]		78.0(2)	79.66(9) [83.01(8)]	
O(10) - M - S(13)		78.84(6)			
O(10) - M - Y(1)	73.95(14) [77.30(15)]	84.33(9)			
O(10) - M - Y(2)	149.03(15) [135.64(14)]				
Y(1) - M - S(10)		02.24(7)	102.2(4)	116.51(7)	116.4(3) [115.7(2)]
Y(1) - M - S(13)		93.24(7)	01.0(0)	115 72(7)	
Y(2) - M - S(10)	51 72(12) [40 04(12)]*		91.9(8)	115./3(/)	
$\Upsilon(1) - M - \Upsilon(2)$	$51./3(13) [48.94(13)]^{c}$		82.1(2)	93.33(10) [96.31(10)] <sup>e</sup>	

**Table 3** Selected bond distances (Å) and angles (°) for  $[Cd(L^{3a})(NO_3)_2]$  (1),  $[Cu(L^{4a})(dmf)](ClO_4)_2$  (2),  $[Zn(L^{1c})(ClO_4)]ClO_4$  (3),  $[Cd(L^{1c})(NO_3)]NO_3$  (4), and  $[Hg(L^{2c})](ClO_4)_2$  (5)<sup>*a*</sup>

<sup>*a*</sup> X(7) = N (1), O (2, 3, and 4), S (5); Y(1) = N(2)O<sub>3</sub> (1), O(1S) (2), N(16) (3, 4, and 5); Y(2) = N(3)O<sub>3</sub> (1), Cl(2)O<sub>4</sub> (3), N(2)O<sub>3</sub> (4). <sup>*b*</sup> Selected bond lengths (Å) and angles (°) for one of the two independent molecules of 1 are reported; where two values are reported, the first refers to the bond distances and angles involving O(21) or O(31), and the second to bond distances and angles involving O(22) or O(32) (see Fig. 4). <sup>*e*</sup> Y(1)–M–Y(2) = O(21)–Cd–O(22) [O(31)–Cd–O(32)] (see Fig. 4). <sup>*a*</sup> Where two values are reported, the first refers to the bond distances and angles involving O(22) (see Fig. 7). <sup>*e*</sup> Y(1)–M–Y(2) = N(16)–Cd–O(20) [N(16)–Cd–O(22)] (see Fig. 7). <sup>*f*</sup> Selected bond lengths (Å) and angles (°) for both independent molecules of 5 ([5-I] and [5-II]) are reported.

The X-ray crystal structure of the compound  $[Cu(L^{4a})(dmf)](ClO_4)_2$  (2) obtained by reacting  $L^{4a}$  with  $Cu(ClO_4)_2$  in MeCN followed by crystallization in dmf/Et<sub>2</sub>O, is not an exception. In this structure the stereochemical demands of the metal centre for an octahedral coordination environment results in a "butterfly" configuration of the macrocycle, with the plane of the ring folded at the S…S vector. The site in the *pseudo*-octahedral coordination sphere left free by  $L^{4a}$  is occupied by a molecule of dmf (Fig. 5, Table 3). The Cu<sup>II</sup> ion lies in the equatorial mean plane defined by the atoms S(4), S(13), O(7), and O(10), and the apical N(1) atom is hydrogen bonded to a perchlorato ion [NH…O 2.31, N…O 3.146(4) Å, N-H…O 147.5°].

Despite numerous attempts to isolate the solid state crystalline 1 : 1 complexes of  $L^{nc}$  (n = 1-4) with the metal ions under investigation, only for  $[Zn(L^{1c})(ClO_4)]ClO_4$  (3),  $[Cd(L^{1c})(NO_3)]NO_3$ (4), and  $[Hg(L^{2c})](ClO_4)_2$  (5) were crystals of diffraction quality grown. In 3, the coordination environment around the metal center is *pseudo*-octahedral with five positions occupied by the  $N_2S_2O$ -donor set of  $L^{1c}$ , and the remaining site taken up by a monodentate perchlorato ligand (Fig. 6, Table 3). The  $Zn^{II}$  ion is displaced 0.23 Å out of the equatorial mean plane defined by the atoms N(1), S(4), S(10), and O(20) towards the apical N(16) atom which is hydrogen bonded to a perchlorato ligand  $[NH \cdots O 2.24, N \cdots O 3.121(15) \text{ Å}, N-H \cdots O 168^{\circ}]$ , and provides the shortest Zn-donor interaction [Zn-N(16) 2.030(5) Å]. Despite the presence of a coordinating 3-aminopropyl pendant arm, the macrocyclic framework of L<sup>1c</sup> in 3 is folded along the S · · · S vector with a N(1)–Zn–O(7) folding angle of



**Fig. 5** ORTEP view of the  $[Cu(L^{4a})(dmf)]^+$  complex cation interacting with a perchlorato ion in **2** with the adopted numbering scheme. Displacement ellipsoids are drawn at 30% probability. Hydrogen atoms except that on the macrocyclic N-donor, and one perchlorato ion have been omitted for clarity.

97.5(2)°, and adopts a [2424] conformation having the same distribution of the torsion angles observed in the  $1 : 1 \text{ Cu}^{II}$ 



**Fig. 6** ORTEP view of  $[Zn(L^{1c})(ClO_4)]ClO_4$  (**3**) with the adopted numbering scheme. Displacement ellipsoids are drawn at 30% probability. Hydrogen atoms except those on the pendant amino group have been omitted for clarity.

and Cd<sup>II</sup> complexes of the unfunctionalised ligand L<sup>1a</sup>.<sup>32</sup> In particular, the torsion angles at the C–N(1) and C–O(7) bonds assume *anti* arrangements [absolute values of the angles ranging from 158.7(14) to 174.4(14)°], whereas one of each pair of torsion angles about the C–S bonds is *gauche* [52.9(12), 77.8(11)°], the other two torsion angles assumes the values of 126.4(12), and 122.9(12)°. A *gauche* disposition is preferred at the C–C bonds [48.0(14)–70.0(12)°].

With respect to **3**, the coordination sphere around the metal centre in  $[Cd(L^{1c})(NO_3)]NO_3$  (**4**) is much more distorted (Fig. 7, Table 3). The Cd<sup>II</sup> ion is effectively six-coordinate with the macrocyclic moiety of L<sup>1c</sup> bound to one side of the metal ion *via* its NS<sub>2</sub>O-donor set, and with the *N*-aminopropyl pendant group and an essentially monodentate nitrato ligand completing the coordination environment [the Cd–O(22) bond distance of 2.838(3) Å is at the extreme upper end of the commonly accepted range where the nitrato ligand can be considered bidentate]. The Cd<sup>II</sup> ion is displaced well out of the ring cavity of the [12]aneNS<sub>2</sub>O framework [1.09 Å out of the mean plane defined by the atoms N(1), S(4), S(10), and O(7)] by the interaction with the 3-aminopropyl pendant group of L<sup>1c</sup> which is involved in the



Fig. 7 ORTEP view of  $[Cd(L^{1c})(NO_3)]NO_3$  (4) with the adopted numbering scheme. Displacement ellipsoids are drawn at 30% probability. Hydrogen atoms except those on the pendant amino group have been omitted for clarity.

shortest Cd-donor bound [Cd-N(16) 2.239(3) Å] in this complex, and is also hydrogen bonded to a nitrato ligand [NH · · · O 2.28, N····O 3.124(4) Å, N-H····O 160°]. As a consequence, the Cd-O(7) bond length [2.666(2) Å], although well within the range 2.36–2.84 Å reported for similar bonds in other Cd<sup>II</sup> complexes,45 is significantly longer than the corresponding bond distance [2.561(3) Å] observed in  $[Cd(L^{1a})(NO_3)_2]^{32}$  where the macrocylic ligand is not functionalised and a bidentate nitrato ligand formally occupies the position site of the 3-aminopropyl pendant group of L<sup>1c</sup> in 4. Furthermore, the conformation adopted upon coordination by the [12]aneNS<sub>2</sub>O moiety of L<sup>1c</sup> in 4 is neither [2424] nor [3333] as confirmed by the torsion angles at the C–N(1) bonds which are one *anti*  $[175.2(3)^{\circ}]$  and one gauche  $[67.5(4)^{\circ}]$  (absolute values) instead of both anti (see above for 3), and by the placements at the C-S(4) bonds which assume absolute values of  $95.5(3)^{\circ}$  and  $51.3(3)^{\circ}$ .

A genuine [3333] conformation characterised by pairs of consecutive gauche torsion angles separated by an anti angle is instead adopted upon coordination by the [12]aneNS<sub>3</sub> moiety of  $L^{2c}$  in both independent units of  $[Hg(L^{2c})](ClO_4)_2$  in 5. In this complex the coordination sphere around the metal center in both independent molecules is a distorted square-based pyramid (Fig. 8, Table 3) with the Hg<sup>II</sup> ions displaced about 0.9 Å from the mean basal coordination planes defined by the atoms N(1), S(4), S(7), and S(10), towards the apical N(16) atoms which provide the shortest Hg-donor interactions. The 3-aminopropyl pendant group of both independent [Hg(L<sup>2c</sup>)](ClO<sub>4</sub>)<sub>2</sub> molecules is hydrogen bonded to two perchlorato ligands as shown in Fig. 8 for **5-I** [NH(16a) · · · O(33) 2.37, N(16) · · · O(33) 3.042(16) Å, N–  $H(16a) \cdots O(33) \ 132^{\circ}; \ NH(16b) \cdots O(22) \ 2.39, \ N(16) \cdots O(22)$ 3.264(15) Å, N–H(16b) · · · O(22) 164°]. Hg–O distances ranging from 3.541(14) to 3.209(10) Å between the metal centers in both independent  $[Hg(L^{2c})](ClO_4)_2$  molecules and the O-atoms of the perchlorato ions are too long to be indicative for significant interactions.



**Fig. 8** ORTEP view of one (5-I) of the two independent  $[Hg(L^{2c})](ClO_4)_2$  units in 5 with the adopted numbering scheme. Displacement ellipsoids are drawn at 30% probability. Hydrogen atoms have been omitted for clarity except those on the pendant amino group.

Synthesis of  $L^{nd}$  (n = 1-4) and  $L^{nc}$  (n = 1, 2, 4) and optical response of these new fluorescent sensors in the presence of Cu<sup>II</sup>, Zn<sup>II</sup>, Cd<sup>II</sup>, Hg<sup>II</sup>, and Pb<sup>II</sup>.

 $L^{nd}$  (n = 1-4) were synthesized by reacting  $L^{nc}$  (n = 1-4) with a stoichiometric amount of dansyl chloride in MeCN.  $L^{nc}$  (n = 1, 2, 4) were instead synthesized by direct Schiff-base condensation of  $L^{nc}$  (n = 1, 2, 4) with 9-anthraldehyde in dry EtOH : MeCN (1 : 1 v/v) followed by the reduction of the

**Table 4** Photophysical properties of  $L^{nd}$  (n = 1-4) and  $L^{nc}$  (n = 1, 2, 4) in MeCN/H<sub>2</sub>O (4 : 1 v/v) at pH 7.0, and fluorescence intensity changes as a function of the metal  $(I_{rel}(\%))^a$ 

	Absorption		Fluorescence					
Ligand	λ/nm	$\epsilon/dm^3mol^{-1}cm^{-1}$	λ/nm	$\Phi$	$Cu^{\Pi}$	$Cd^{II}$	$\mathrm{Hg}^{\mathrm{II}}$	
$L^{1d}$	251	19960	534	0.24			11.0	
	338	4260						
$L^{2d}$	252	15530	532	0.24	39.0		1.9	
	338	4800						
$L^{3d}$	253	29770	530	0.17	22.0		27.0	
	338	8400						
$L^{4d}$	253	15150	528	0.16			5.6	
	339	4260						
$L^{1e}$	350	4260	416	0.065	21.0	$160.4^{b}$	8.0	
	367	6240						
	387	5550						
$L^{2e}$	350	4660	417	0.057	12.5		2.7	
	367	6760						
	387	5990						
$L^{4e}$	350	4620	416	0.086	64.9°		10.0	
	368	6650						
	388	5860						

"  $I_{rel}$  (%) represents the percentage of the residual fluorescence intensity for a L/M" molar ratio of 2; Zn" does not affect the fluorescence intensity of any of the ligands, while an insoluble precipitate forms upon addition of  $Pb^{II}$  to solutions of all ligands. <sup>*b*</sup> A smooth and monotonic increase of the luminescence intensity is observed upon addition of  $Cd^{II}$  to  $L^{Ie}$ . <sup>*c*</sup> A smooth and monotonic decrease of the luminescence intensity is observed upon addition of CuII to L4e.

crude products obtained with NaBH<sub>4</sub>/NaBH<sub>3</sub>CN (1 : 1) in dry EtOH. Unfortunately, despite many attempts we were unable to a prepare a pure sample of L<sup>3e</sup> (Scheme 1) using this synthetic procedure. The photophysical properties of these compounds  $(\lambda_{ex}, \varepsilon_{ex}, \lambda_{em},$  fluorescent quantum yield,  $\Phi)$  are reported in Table 4.

The optical response of  $L^{nd}$  (n = 1-4) and  $L^{ne}$  (n =1, 2, 4) to Cu<sup>II</sup>, Zn<sup>II</sup>, Cd<sup>II</sup>, Hg<sup>II</sup> and Pb<sup>II</sup> was studied in MeCN/H<sub>2</sub>O (4 : 1 v/v) solutions buffered with HEPES [4-(2hydroxyethyl)piperazine-1-ethanesulfonic acid] at pH 7.0.

The absorption spectra of all free dansylamidopropyl derivatives,  $L^{1d-4d}$ , in MeCN/H<sub>2</sub>O (4 : 1 v/v) at pH 7.0 present a large, unstructured band around 338 nm and a more intense one around 252 nm, see Table 4. These species are also luminescent, exhibiting an emission band maximum in the range 528 (L<sup>4d</sup>)-534 nm (L<sup>1d</sup>). The highest fluorescent quantum yield is that measured for  $L^{1d}$  and  $L^{2d}$  ( $\Phi = 0.24$ ), while for  $L^{3d}$  and  $L^{4d}$  the values of  $\Phi$  measured are 0.17 and 0.16, respectively.

Changes in the absorption and emission spectra of the four ligands were only observed upon addition of Cu<sup>II</sup> or Hg<sup>II</sup> to MeCN/H<sub>2</sub>O (4 : 1 v/v) solutions of  $L^{nd}$  (n = 1-4) buffered at pH 7.0; an insoluble precipitate was formed in the case of Pb<sup>II</sup>. In particular, the bands at 338 nm for L<sup>1d</sup>-L<sup>3d</sup> and 339 nm for L<sup>4d</sup> shift to lower wavelengths (less than 6 nm) and increase slightly in intensity (see ESI Fig. S5 for the L<sup>4d</sup>/Hg<sup>II</sup> system<sup>†</sup>). However, the intensity increase was more evident upon addition of Cu<sup>II</sup>.

Interestingly, while the fluorescence of L<sup>2d</sup> and L<sup>3d</sup> was quenched by both Cu<sup>II</sup> ( $I_{rel}$  39.0 and 22.0% for L<sup>2d</sup> and L<sup>3d</sup>, respectively) and Hg<sup>II</sup> ( $I_{rel}$  1.9 and 27.0% for L<sup>2d</sup> and L<sup>3d</sup>, respectively, see Fig. 9a for the  $L^{3d}$ ), for  $L^{1d}$  and  $L^{4d}$  a quenching of the luminescence intensity was observed only upon addition of Hg<sup>II</sup> up to a Hg<sup>II</sup>/L<sup>nd</sup> (n = 1, 4) molar ratio of 1 ( $I_{rel}$  11.0 and 5.6%, respectively, Fig. 9b for the L<sup>4d</sup>). In all cases no shift of the emission bands was observed. The strong quenching effect observed for L<sup>2d</sup> and L<sup>3d</sup> with Cu<sup>II</sup> can be ascribed to either a dansyl-to-metal energy-transfer (ET) or to a metal-to-dansyl electron-transfer (eT) mechanism. Data obtained for similar complexes<sup>52</sup> have suggested that at least a contribution from the ET mechanism is operating. In the case of Hg<sup>II</sup>, a contribution to fluorescence quenching from the heavy-atom effect cannot be excluded, while the ET mechanism cannot be effective for this d10 ion.52

The free ligands  $L^{ne}$  (n = 1, 2, 4) showed in MeCN/H<sub>2</sub>O (4 : 1 v/v) at pH 7.0 the typical absorption and emission due to the presence of the anthracenyl group with the maximum in the absorption band at about 367 nm and the maximum in the fluorescence band at 416 nm (Table 4). The values measured for the fluorescence quantum yield ranged from 0.057 to 0.086 (Table 4). These values are remarkably lower than that observed for anthracene in MeCN (0.27) due to a photoinduced electron transfer process from the secondary nitrogen of the propylamino pendant arm to the  $\pi$  system of the fluorescent unit.53

Similar effects, and in general not dramatic, were observed on the absorption properties of  $L^{ne}$  (n = 1, 2, 4) as a consequence of metal ion complexation: a small decrease in extinction coefficients was observed only upon addition of Cu<sup>II</sup> or Hg<sup>II</sup> (a small increase of  $\varepsilon$  was noticed instead in the case of L<sup>4e</sup> with both metal ions) accompanied in some cases by very small red shifts (less than 4 nm for L<sup>1e</sup> and L<sup>2e</sup> with both metal ions); no changes were recorded upon addition of  $Zn^{II}$  and  $Cd^{II}$ , while an insoluble precipitate formed in the case of Pb<sup>II</sup> with all three anthracenyl derivatives. For the titrations of L<sup>1e</sup> with both Cu<sup>II</sup> and Hg<sup>II</sup>, and of L<sup>2e</sup> with Hg<sup>II</sup>, well defined isosbestic points were observed (see ESI Fig. S6 for the L<sup>2e</sup>/Hg<sup>II</sup> system<sup>†</sup>).

In contrast to L<sup>1d</sup> (see above), a quenching of the luminescence intensity was observed for L1e upon addition of both CuII and HgII ( $I_{\rm rel}$  21.0 and 8.0%, respectively). The plateau values were reached after the addition of about one, and two molar equivalents of Hg<sup>II</sup> and Cu<sup>II</sup>, respectively. A smooth monotonic increase of the luminescence intensity was also monitored upon addition of  $Cd^{II}$  ( $I_{rel}$  160.4% for a L<sup>1e</sup>/Cd<sup>II</sup> molar ratio of 2). The behavior of  $L^{2e}$  and  $L^{4e}$  is instead very similar to that observed for their structural analogous,  $L^{2d}$  and  $\dot{L}^{4d}$ , bearing the dansylamido moiety. In fact, a quenching of the fluorescence was caused by the addition of 1 molar equivalent of  $Cu^{II}$  and  $Hg^{II}$  ( $I_{rel}$  12.5 and 2.7%, respectively) in the case of L<sup>2e</sup> (Fig. 9c), whereas only the addition of Hg<sup>II</sup> determined a significant quenching  $(I_{rel})$ 10%) in the case of L<sup>4e</sup> (Fig. 9d). However, for L<sup>4e</sup>, a smooth and monotonic decrease of the luminescence intensity was also observed upon addition of  $Cu^{II}$  ( $I_{rel}$  64.9% for a L<sup>le</sup>/Cu<sup>II</sup> molar ratio of 2), see Fig. 9d and Fig. 9b for comparison with L<sup>4d</sup>. The decrease of fluorescence intensity upon addition of Cu<sup>II</sup> or Hg<sup>II</sup> ions to  $L^{ne}$  (n = 1, 2, 4), as described above, provides clear evidence that in these systems the quenching process due to



**Fig. 9** Fluorescent intensity/molar ratio plot for  $L^{3d}$  (a),  $L^{4d}$  (b),  $L^{2e}$  (c) and  $L^{4e}$  (d) (2.5 × 10<sup>-5</sup> M, MeCN/H<sub>2</sub>O (4 : 1 v/v), pH = 7.0) in the presence of increasing amounts of Cu<sup>II</sup> ( $\bullet$ ), Hg<sup>II</sup> ( $\bullet$ ), Zn<sup>II</sup> (+), and Cd<sup>II</sup> ( $\blacktriangle$ ). An insoluble precipitate formed upon addition of Pb<sup>II</sup> to solutions of all four ligands.

eT or ET mechanisms involving the metal ion prevails over the eT process among the secondary N-donor and the anthracene that would be interrupted upon complexation of the functionalised pendant arm to the metal ion with consequent switching on of the fluorescence. The fluorescence intensity changes are tabulated as a function of metal and sensor number in Table 4.

#### Conclusions

Following the "receptor-spacer-signalling unit" model, we have synthesised the fluorescent chemosensors  $L^{nd}$  (n = 1-4) and  $L^{ne}$ (n = 1, 2, 4, Scheme 1) in which mixed N/S- and N/S/O-donor macrocycles are connected through an aminopropyl linker to a dansyl or a 9-anthracenylmethyl fluorescent moiety. Their optical response towards the "borderline" and the "soft" metal ions Cu<sup>II</sup>, Zn<sup>II</sup>, Cd<sup>II</sup>, Hg<sup>II</sup> and Pb<sup>II</sup> which are of great importance from an industrial, biological, and environmental points of view, has been investigated at pH 7.0 in MeCN/H<sub>2</sub>O (4 : 1 v/v) solutions. As expected, and in line with our studies performed both in solution and in the solid state on the coordination chemistry of the N-aminopropyl pendant arm precursors  $L^{1c-4c}$  (Scheme 1), the presence of S-donor atoms in the macrocyclic frameworks can confer specificity and selectivity to the interaction of the present molecular sensors with the metal ions considered. In particular, L<sup>1d</sup> and L<sup>4d</sup> both containing a dansylamido fluorogenic fragment as signalling unit, and respectively, a NS<sub>2</sub>O- and a NS<sub>2</sub>O<sub>2</sub>-donor set in the cyclic receptor unit, respond selectively to Hg<sup>II</sup> by a quenching in the fluorescence emission. In particular, L<sup>1d</sup> has already found analytical application in the construction of a fluorimetric bulk optode membrane for selective subnanomolar detection of Hg<sup>II</sup>

in aqueous solutions (see ref. 54 for analytical details such as membrane preparation, response mechanism and measuring principle, measuring range and dynamic response time, and interference of co-existing cationic species). These results should aid further development and application of selective chemical sensors for "soft" metal cations which employ S-containing macrocycles as receptor units. In fact, there are only a few reports of fluorescent chemosensors for heavy metal ions which feature S-donor macrocycles as receptors units. Our results once more point out that within a supramolecular modular approach to the design of "soft" metal ions-selective fluorescent sensors, the choice of the "read-out" unit is critical to both sensorperformance and sensor-selectivity.<sup>33</sup>

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