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ORIGINAL ARTICLE

Fluorescence signaling of aromatic oxoanion inclusion within metal-ion activated molecular receptor complexes formed from 2-(9-anthracenylmethylamino)ethyl-appended cyclen

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Abstract Our observations that 1-[2-[(9-anthracenylmethylamino)ethyl)-4,7,10-tris[(2*S*)-2-hydroxy-3-phenoxypropyl]-1,4,7,10-tetraazacyclododecane, L^1, complexes Cd(II) to form fluorescent $[CdL^1]^{2+}$ which undergoes a fluorescence change when it acts as an aromatic anion receptor complex has caused us to explore further the potential development of an interesting sequestration/sensor system. Accordingly, three new, octadentate, fluorescent, macrocyclic ligands, 1-[2-[(9-anthracenylmethyl)((2*S*)-2-hydroxy-3-phenoxypropyl)amino]ethyl]-4,7,10-tris[(2*S*)-2-hydroxy-3-phenoxypropyl]-1,4,7,10-tetraazacyclododecane, (L^2), 1-[2-[(9-anthracenyl-methyl)((2*S*)-2-hydroxy-3-(4′-methyl)phenoxypropyl)amino]ethyl]-4,7,10-tris[(2*S*)-2-hydroxy-3-(4′-methyl)phenoxypropyl]-1,4,7,10-tetraazacyclododecane, (L^3), and 1-[2-[(9-anthracenylmethyl)((2*S*)-2-hydroxy-3-(4′-*t*-butyl)phenoxypropyl)amino]ethyl]-4,7,10-tris[(2*S*)-2-hydroxy-3-(4′-*t*-butyl)phenoxypropyl]-1,4,7,10-tetraazacyclododecane, (L^4), have been prepared with a view to using their metal complexes to study aromatic anion sequestration. The eight-coordinate Cd(II) complexes of L^2 and L^3, $[CdL^2](ClO_4)_2{\cdot}5H_2O$ and $[CdL^3](ClO_4)_2{\cdot}2H_2O{\cdot}2Et_2O$ are both capable of acting as receptors for a range of aromatic oxoanions. This is demonstrated by perturbation of the anthracene derived fluorescence emission intensity as the guest aromatic oxoanion and the receptor complex combine. In 20% aqueous 1,4-dioxane the receptor complex/aromatic oxoanion association constants are in the range of $10^{3.2}$ M^{-1} (guest = *p*-hydroxybenzoate) to $10^{7.3}$ M^{-1} (guest = 3,4,5-trihydroxybenzoate).

Keywords Aromatic oxoanions · Cyclen derivatives · Fluorescence · Inclusion complex · Sensors

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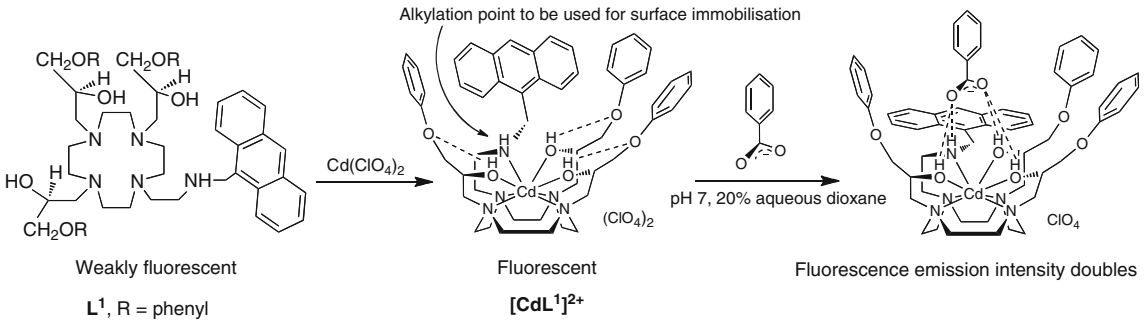
Introduction

In earlier work we have developed a family of molecular receptor complexes capable of sequestering aromatic oxoanions from aqueous and non-aqueous environments [1–5]. These molecular receptor complexes utilise an eight-coordinating metal ion, usually Cd(II), to form a metal complex with a hydrophobic cavity that is defined by the juxtapositioning of four aromatic moieties that are appended to the nitrogen atoms of a cyclen (1,4,7,10-tetraazacyclododecane) ligand. This cavity is fringed at its closed end with three or four hydrogen bond donor moieties that serve to retain aromatic oxoanions capable of acting as multiple hydrogen bond acceptors that enter the hydrophobic region. If one of the four pendant aromatic moieties is a fluorophore, such as the 2-(9-anthracenylmethylamino)ethyl moiety that forms part of the fluorescent receptor complex $[CdL^1]^{2+}$ shown in Scheme 1, the sequestration of an aromatic oxoanion triggers a fluorescence perturbation and the receptor complex functions as a sensor [6].

To develop sensors such as $[CdL^1]^{2+}$ into practical devices, in which the sensor is immobilised on the surface of a solid, we plan eventually to use the secondary amine in the 2-(9-anthracenylmethylamino)ethyl fluorophore (the anthracenylamine) as an alkylation point for covalently attaching the sensor to a 3-(glycidoxy)propyl-functionalised silica surface [7]. This converts the secondary anthracenylamine to a tertiary amine and reduces by one the



Scheme 1

maximum number of hydrogen bonds, albeit the one that is most likely to be the weakest [8], available for the retention of the aromatic oxoanion guest. It is, therefore, of importance to test the effect of alkylation at the anthracenylamine on the ability of this class of receptor complex to sequester aromatic oxoanions. This is the subject of this study. Previous study has shown that alkylation of the anthracenylamine in a similar ligand increases the strength of complexation of Cd(II) consistent with coordination of the anthracenylamine still occurring following alkylation [9].

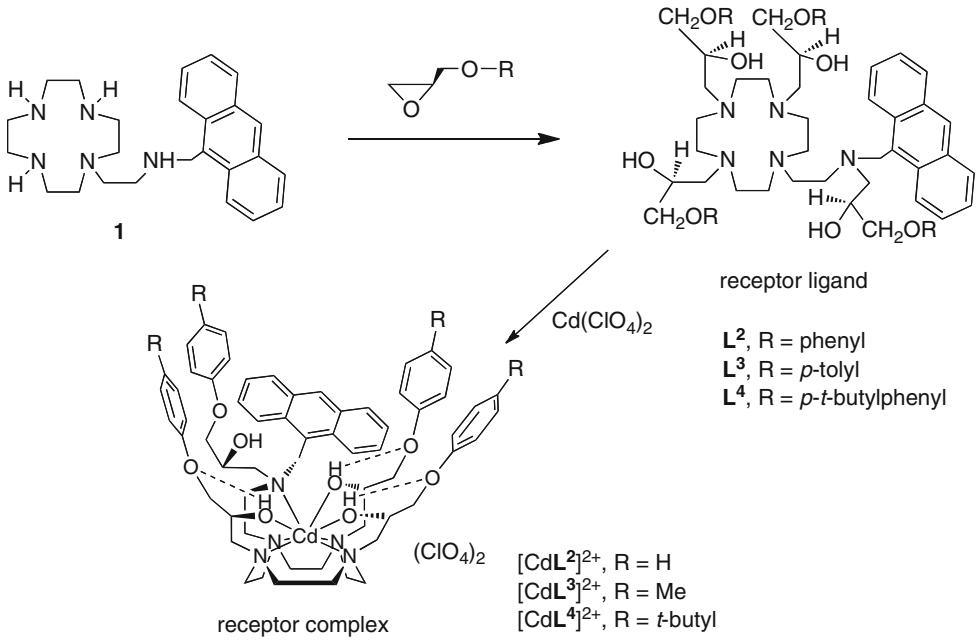
Results and discussion

Synthesis of the receptor ligands and complexes

A series of receptor complexes were prepared from ligands L^2–L^4, which are based on cyclen and bear an *N*-alkylated 2-(9-anthracenylmethylamino)ethyl fluorophore as one pendant arm and have corresponding alkylations at the macrocyclic secondary amines. L^2–L^4 were derived from the known compound 1-(2-(9-anthracenylmethylamino)ethyl)-1,4,7,10-tetraazacyclododecane, 1 [9, 10], using the procedure shown in Scheme 2. The epoxides chosen generate the required pendant arms on the receptor ligands that ultimately form the binding cavity necessary for aromatic oxoanion retention once the receptor complexes are formed through coordination to Cd(II). Use of enantiomerically pure epoxides is necessary to ensure that the reaction products are formed only as their homochiral diastereomer. Good yields of L^2–L^4 were obtained.

Cd(II) complexes of L^2–L^4 were readily formed as their diperchlorate salts by the addition of $Cd(ClO_4)_2$ to a solution of the respective ligand in hot ethanol and were characterised by NMR spectroscopy, microanalysis and their fluorescence behaviour. The structures of these complexes are expected to be broadly as shown in

Scheme 2



Schemes 1, 2 and similar to many other eight-coordinate Cd(II) complexes which have been formed from cyclen derived ligands that have four appended 2-hydroxyethyl, carboxymethyl, or carbomoylmethyl moieties where the structures have been determined by X-ray diffraction [2].

pH Dependence of the fluorescence emission of L^2–L^4

A preliminary inspection of the UV spectra of protonated L^2–L^4 in 20% aqueous 1,4-dioxane ($I = 0.1$ mol dm^{-3}, Et_4NClO_4) and their variation with pH during titration with Et_4NOH revealed almost identical spectra and the same minimal variation with pH as was seen previously with L^1 under the same conditions [6]. Accordingly, the same excitation frequency of 350 nm was used for the fluorescence studies described here. The variation of the fluorescence emission spectra for L^2–L^4 with pH differed from that seen with L^1, however. In particular, the pK_a value associated with the change from the more highly fluorescent, protonated form of the ligand, Fig. 1, to the less fluorescent form seen at high pH is lowered by about four

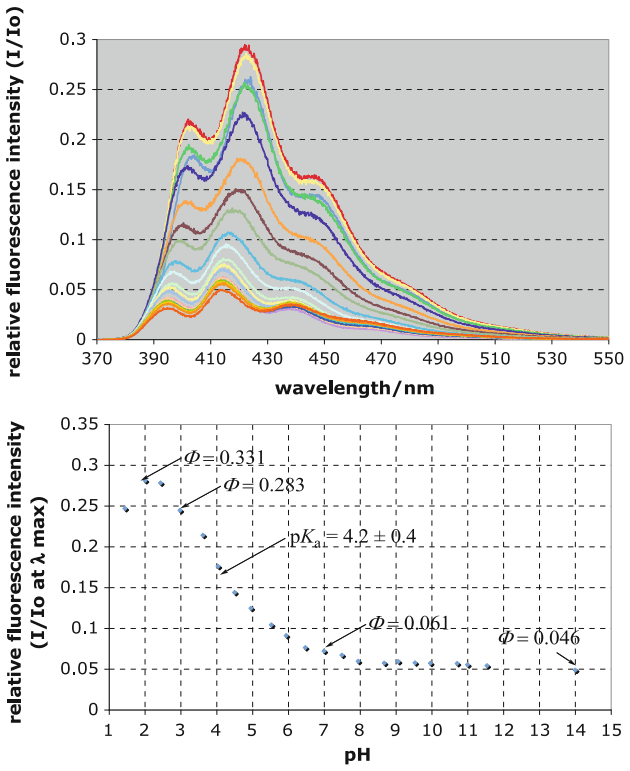


Fig. 1 *Top* fluorescence emission spectra ($\lambda_{ex} = 350$ nm) of protonated L^2 (protonated L^3 and L^4 behaved similarly), 10^{-6} mol dm^{-3} in 20% aqueous 1,4-dioxane ($I = 0.1$ mol dm^{-3}, Et_4NClO_4) during titration with Et_4NOH at 298 K. Emission maxima are at 403.2, 422.5, and 444.7 nm at pH 2 and at 394.5, 414.5, and 438.2 nm at pH 10. *Bottom* fluorescence emission intensity and quantum yields (Φ) of L^2 at λ_{max} plotted against pH. Intensities in both diagrams are relative to that of $[CdL^1]^{2+}$ at pH 7.0 under the same conditions

orders of magnitude; from *ca* 8.4 in L^1 and a close derivative [6], to 4.2 ± 0.4 for L^2–L^4. This pK_a almost certainly corresponds to the deprotonation of the anthracenylamine, since the consequent availability of a lone pair of electrons on this nitrogen atom is known to quench the fluorescence of anthracene via the photoinduced electron transfer (PET) effect [11]. The change from a secondary amine to a tertiary amine is expected to lower the basicity, due to weaker solvation of the protonated form [12], and so the lowering of the pK_a is not unexpected and is consistent with observations in related work [9]. The decrease in fluorescence at very low pH seen in Fig. 1 has been noted previously with anthracene derived fluorophores and is believed to be associated with protonation of the aromatic ring [13].

The effect of metal ion complexation on the fluorescence of L^2–L^4

Since the Cd(II) complexes of L^2–L^4 are to be used for aromatic oxoanion sequestration, it is their fluorescence emission intensities that constitute the baseline data against which any perturbations associated with aromatic oxoanion inclusion will be compared. These data were acquired under the same conditions that were used in the preceding section for L^2–L^4 by titrating 10^{-4} mol dm^{-3} solutions of each ligand with a 10^{-3} mol dm^{-3} solution of $Cd(ClO_4)_2$. To ensure that fluorescence changes due to metal binding were not confused with fluorescence changes due to pH change, arising from aquated Cd(II) hydrolysis, the ligand solutions were buffered at pH 7.0 using 0.01 mol dm^{-3} HEPES. It was found that for each ligand the fluorescence emission intensity increased up to the point where one equivalent of Cd(II) had been added and then plateaued, indicating, as was expected from the previous study of $[CdL^1]^{2+}$ [6], strong eight-coordinate binding of Cd(II) by each ligand. Coordination of the anthracenylamine is indicated because it is the donation of its lone pair electron density towards Cd(II) that causes the fluorescence emission increase by blocking the PET quenching of the fluorophore that otherwise occurs at pH 7.0 [14]. With L^2 the change in quantum yield upon complexation was from 0.061 to 0.251 (311%), for L^3 from 0.039 to 0.244 (526%) and for L^4 from 0.055 to 0.241 (338%). These are larger quantum yield changes than the 45% (from 0.471 to 0.684) increase seen during the formation of $[CdL^1]^{2+}$ and occur because L^1 is more strongly fluorescent at pH 7.0 due to its protonated anthracenylamine having a pK_a of ca. 8.4 rather than ca. 4.2. However, the relative fluorescence emission intensities at the wavelength of maximum emission (416 nm) of the Cd(II) complexes of L^2–L^4 compared with $[CdL^1]^{2+}$, are only 28, 27, and 26%, respectively, as may be seen for L^2 in Fig. 2, where the intensities are shown relative to that of $[CdL^1]^{2+}$ under the same conditions. This

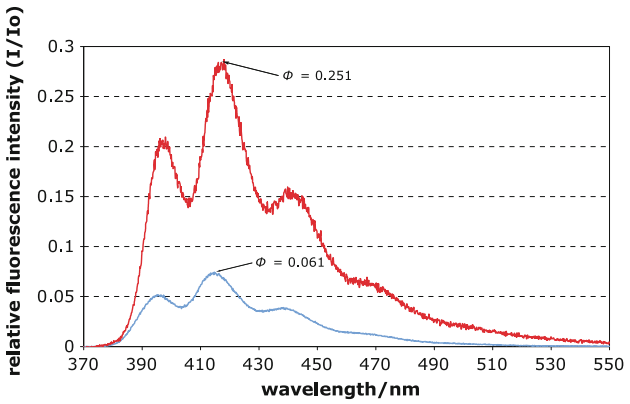


Fig. 2 Fluorescence emission spectra ($\lambda_{ex} = 350$ nm) and quantum yields (Φ) of L^2 alone, *lower trace*, 10^{-4} mol dm^{-3} in 20% aqueous 1,4-dioxane, $I = 0.1$ mol dm^{-3} (Et_4NClO_4) at pH 7.0 (0.01 mol dm^{-3} HEPES), and with 10^{-4} mol dm^{-3} Cd(II), *upper trace*. Intensities are relative to that of $[CdL^1]^{2+}$ under the same conditions

may be attributable to weaker binding of the alkylated anthracenylamine to the Cd(II), consistent with its lower basicity, which results in less effective suppression of the PET quenching. The fact that the Cd(II) complexes of L^2–L^4 have lower quantum yields than $[CdL^1]^{2+}$ renders them potentially more useful in terms of sensor behaviour since more scope remains for fluorescence enhancement upon aromatic oxoanion inclusion. Ligands L^2 and L^3 were also investigated with Pb(II), Zn(II), and Hg(II), in the same way, and found to show similar behaviour producing complexes with emission intensities at λ_{max}, compared with $[CdL^1]^{2+}$ of 27, 31 and 19%, and 27, 18 and 7%, respectively.

Fluorescence emission perturbation in $[CdL^2]^{2+}$ and $[CdL^3]^{2+}$ due to aromatic oxoanion sequestration

Studies of $[CdL^1]^{2+}$ in 20% aqueous 1,4-dioxane have shown that entry of an aromatic oxoanion into its binding cavity generally leads to a perturbation in its fluorescence emission intensity [6]. Overall, this may be positive or negative due to the interplay of several different quenching and enhancement effects. The principal effects of relevance to $[CdL^2]^{2+}$ and $[CdL^3]^{2+}$, when studied in a solvent that is partially aqueous, are likely to be, (1) displacement of hydrogen bonded water molecules from the binding cavity, which will enhance fluorescence [15, 16], (2) through space PET quenching, which can occur if the aromatic oxoanion has significant electron donor (e.g. *p*-dimethyaminobenzoate) or electron acceptor (e.g. *p*-nitrobenzoate) properties with respect to the anthracene moiety [17], and (3) hydrogen bonding to the fluorophore, (e.g. O–H$\cdots\pi$ hydrogen bonding to the anthracene moiety) which leads to quenching [18].

When solutions of receptor complexes $[CdL^2]^{2+}$ and $[CdL^3]^{2+}$ at 10^{-4} or 10^{-6} mol dm^{-3} in 20% aqueous 1,4-dioxane, buffered at pH 7.0 (0.02 mol dm^{-3} lutidine, $I = 0.1$ mol dm^{-3} (Et_4NClO_4)) were titrated with the sodium salts of the aromatic oxoanions indicated in Table 1 perturbations of the fluorescence emission intensity (ΔI) were seen in most cases. These ranged from −66% with *p*-dimethylaminobenzoate to 250% with *m*-hydroxybenzoate. A typical titration curve, that for $[CdL^3]^{2+}$ and monosodium gallate is shown in Fig. 3. Since no perturbations of fluorescence intensity were seen in blank titrations where the uncomplexed receptor ligands L^2 and L^3 were used, the perturbations in the fluorescence of the receptor complexes were taken as being indicative of inclusion of the aromatic oxoanion within the binding cavity of the receptor complex in the manner shown in Scheme 1, but without the hydrogen bonding contribution from the anthracenylamine that is now alkylated. Non-linear least squares regression analysis of each titration curve gave the aromatic oxoanion association constants also shown in Table 1. Since the fluorescence perturbations span both negative and positive values it should be appreciated that no fluorescence emission perturbation does not necessarily imply that there is no aromatic oxoanion inclusion, although obviously log K_{assoc} cannot be determined in such instances.

The magnitude of the fluorescence perturbation that occurs on aromatic oxoanion inclusion within $[CdL^2]^{2+}$ is in some cases larger, both in the positive and negative sense, than that seen for the receptor complex $[CdL^1]^{2+}$, which lacks alkylation at the anthracenylamine. This indicates that the potential that the $[CdL^2]^{2+}$–$[CdL^4]^{2+}$ receptor complexes have as sensors is not diminished by anthracenylamine alkylation. Neither do the association constant values for aromatic oxoanions with $[CdL^2]^{2+}$ and $[CdL^3]^{2+}$ show a general pattern of diminution that might be anticipated due to the loss of the contribution from the secondary anthracenylamine to the group of hydrogen bond donors at the base of the binding cavity. In some cases the association constants are higher for aromatic oxoanions with $[CdL^2]^{2+}$, most noticeably with benzoate and benzenesulfonate, which have no *para*-substituent to project from the binding cavity, and which perhaps benefit more fully than some of the other aromatic oxoanions studied from the deepening and fuller enclosure of the cavity by the fifth pendant arm, attached to the anthracenylamine.

Conclusion

Alkylation of the anthracenylamine in receptor complexes formed from 2-(9-anthracenylmethylamino)ethyl-appended

Table 1 Association constants determined from fluorescence intensity monitored titrations[a], expressed as log (K_{assoc}/M^{-1}), and fluorescence intensity perturbations at 416 nm (ΔI)[b] for the inclusion of guest aromatic oxoanions within the receptor complexes $[CdL^1]^{2+}$, $[CdL^2]^{2+}$, and $[CdL^3]^{2+}$

Guest	Receptor complex					
	$[CdL^1]^{2+c}$		$[CdL^2]^{2+}$		$[CdL^3]^{2+}$	
	log K_{assoc}	ΔI (%)	log K_{assoc}	ΔI (%)	log K_{assoc}	ΔI
Benzoate	2.3	117	5.2 ± 0.1[d]	192	e	e
p-Hydroxybenzoate	4.5	27	3.2 ± 0.2	75	3.3 ± 0.3	35%
m-Hydroxybenzoate	5.3	21	5.2 ± 0.1[d]	250	e	e
Gallate (3,4,5-trihydroxybenzoate)	7.1	10	7.3 ± 0.5[d]	8	6.9 ± 0.3[d]	37%
p-Nitrobenzoate	4.9	−13	3.4 ± 0.1	−48	4.7 ± 0.3	−9%
p-Aminobenzoate	6.5	59	6.4 ± 0.1[d]	174	e	5%
p-Dimethylaminobenzoate	4.1	−30	3.2 ± 0.1	−66	–	0%
p-Toluenesulfonate	4.6	8	3.3 ± 0.2	91	4.2 ± 0.2	13%
Benzene sulfonate	3.4	39	5.6 ± 0.2	17	3.2 ± 0.3	25%

[a] [Receptor complex] = 10^{-4} mol dm^{-3}, measured at pH 7.0 (0.02 mol dm^{-3} lutidine) in 20% aqueous 1,4-dioxane, at 298 K, I = 0.1 mol dm^{-3} (Et_4NClO_4). Uncertainties are taken as one SD

[b] Values calculated as $(I_{Host–Guest}-I_{Host})/I_{Host}) \times 100$ where $I_{Host–Guest}$ is calculated together with K from non-linear least squares regression analysis of the titration curve

[c] Data taken from [6]

[d] [Receptor complex] = 10^{-6} mol dm^{-3}

[e] Not measured

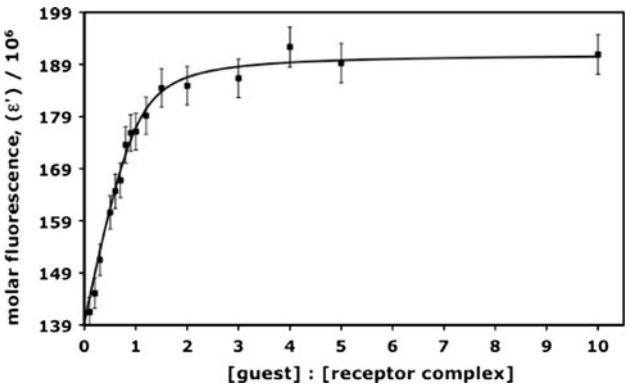


Fig. 3 Molar fluorescence changes (ε') at 416 nm for 10^{-6} mol dm^{-3} $[CdL^3](ClO_4)_2$ in 20% aqueous 1,4-dioxane at pH 7.0 (0.02 mol dm^{-3} lutidine, I = 0.1 mol dm^{-3} (Et_4NClO_4)) as it is titrated with monosodium gallate. *Squares* indicate the experimental points and the *curve* indicates the theoretical ε' values for the calculated values of K and $\varepsilon'_{Host–Guest}$. *Error bars* are ±2%

cyclen derived ligands, as may be used in future work for the purpose of attaching these sensors to a solid supporting material such as silica, has insignificant deleterious effects on the ability of the receptor complex to sequester aromatic oxoanions. The signalling ability of the sensor is slightly improved in some cases through the lower basicity of the alkylated anthracenylamine giving rise to a more weakly fluorescent receptor complex.

Experimental

General information

All syntheses were performed under dry nitrogen. Solvents were purified using literature methods [19]. Microanalyses were conducted at the University of Otago, New Zealand. NMR data were collected using a Varian Gemini 300 spectrometer operating at 300.075 MHz for protons and 75.462 MHz for ^{13}C. ^1H NMR chemical shifts were referenced to the residual protonated solvent peak taken as 7.26 ppm for $CDCl_3$, 2.60 ppm for DMSO-d_6, and 1.96 ppm for CD_3CN. For ^{13}C NMR spectra, chemical shifts were referenced to the central resonance of the solvent multiplet peak taken as 77.00 ppm for $CDCl_3$, 39.52 ppm for DMSO-d_6, and 118.10 ppm for CD_3CN (CN resonance). UV–visible absorbance spectra were measured on a Varian Cary 50 SCAN UV–Visible spectrophotometer. Flash chromatography was carried out using Brockman II basic alumina pH 10 ± 0.5 (particle size 100–290 mesh) as the stationary phase. Thin layer chromatography employed Merck no. 5551 aluminium-backed neutral (type T) alumina 150 F_{254} plates. (2*S*)-(+)-3-phenoxy-1,2-epoxypropane [1], (2*S*)-(+)-3-[4′-(methyl)phenoxy]-1,2-epoxypropane [5], and 1-(2-(9-anthracenylmethylamino)ethyl)-1,4,7,10-tetraazacyclododecane, 1, [9], were prepared by literature methods. (2*S*)-(+)-3-[4′-(*t*-butyl)phenoxy]-1,2-epoxypropane was prepared by

a method analogous to that used for (2*S*)-(+)-3-[4′-(methyl) phenoxy]-1,2-epoxypropane and was a gift from Prof. Xing-You Xu of the Huaihai Institute of Technology, China.

Syntheses

1-((N-(2-(9-Anthracenylmethyl)(N-(2S)-2-hydroxy-3-phenoxypropyl)aminoethyl))-4,7,10-tris((2S)-2-hydroxy-3-phenoxypropyl)-1,4,7,10-tetraazacyclododecane, L^2

1-(2-(9-anthracenylmethylamino)ethyl)-1,4,7,10-tetraaza-cyclododecane, 1, (366 mg, 0.9 mmol) was dissolved in dry EtOH (23 cm^3) and the solution stirred whilst warming it to boiling point. A solution of (2*S*)-(+)-3-phenoxy-1,2-epoxypropane (550 mg, 3.7 mmol) in dry EtOH (26 cm^3) was added dropwise. The reaction mixture was then stirred whilst refluxing for 7 d and monitored by TLC (alumina, MeOH/CH_2Cl_2 4:96). Upon disappearance of the epoxide, the reaction was cooled to room temperature and the solvent removed to leave a reddish-brown oil. This was purified on a basic alumina column (hexane/CH_2Cl_2 1:9) to remove three impurity bands, then flushed with MeOH to recover the product. Removal of solvent from the final fraction, and drying under vacuum gave the product as a reddish-brown oil (684 mg, 75%). UV–vis (20% aqueous 1,4-dioxane): λ_{max}/nm 386.4 (ε/dm^3 mol^{-1} cm^{-1} 7891), 366.5 (8562), 348.6 (5580), 332.4 (2947), 319.8 (sh) (1360). ^{1}H NMR (CD_3CN): δ 8.55 (2H, d, $J = 8$ Hz, Anth*H*); 8.39 (1H, s, Anth*H*); 8.00 (2H, d, $J = 8$ Hz, Anth*H*); 7.47 (4H, m, Anth*H*); 7.35 (8H, m, Ph*H*); 7.00 (10H, m, Ph*H*); 6.71 (2H, d, $J = 8$ Hz, Ph*H*); 4.8–1.8 (46H, br m, –O*H*, –C*H*–, and –CH_2–). ^{13}C NMR ($CDCl_3$): δ 157.8 (4C, Ph, *ipso*); 130.9 (2C, Anth, *ipso*); 130.8 (2C, Anth, *ipso*); 129.3 (1C, Anth, *ipso*); 129.0 (8C, Ph); 128.8 (2C, Anth); 127.4 (1C, Anth); 125.6 (2C, Anth); 124.5 (2C, Anth); 124.1 (2C, Anth); 120.4 (4C, Ph); 114.2 (8C, Ph); 71.1 (1C, OCH_2); 69.8 (1C, OCH_2); 69.4 (1C, OCH_2); 68.7 (1C, OCH_2); 68.4 (1C, methine); 67.2 (1C, methine); 66.6 (1C, methine); 65.8 (1C, methine); 65.2 (1C, exo-CH_2N); 60.1 (1C, exo-CH_2N); 58.2 (1C, exo-CH_2N); 57.5 (1C, exo-CH_2N); 55.0 (1C, exo-CH_2N); 54.2 (1C, exo-CH_2N); 52.8 (2C, cyclen CH_2); 51.8 (2C, cyclen CH_2); 51.4 (2C, cyclen CH_2); 50.1 (2C, cyclen CH_2); 46.0 (1C, Anth-CH_2N-). To obtain a sample for microanalysis L^2 was converted to its pentahydrochloride by taking a solution of it (960 mg, 1.12 mmol) in EtOH (14 cm^3), cooled in ice and treating it dropwise with 36% aqueous HCl (0.76 cm^3, 9.9 mmol). The mixture was allowed to stir overnight then the solvent was evaporated. The residue was triturated with ether. The white solid was collected by filtration, and dried under vacuum to yield the product as an off-white powder (866 mg, 55%), m.p. 121–123°. (Found: C, 61.6; H, 7.1; N, 5.6. $C_{61}H_{80}Cl_5N_5O_8$ requires C, 61.6; H, 6.8; N, 5.9%). $[\alpha]_D^{298} = -40.9°$ (c 0.005, EtOH).

1-((N-(2-(9-Anthracenylmethyl)(N-(2S)-2-hydroxy-3-[(4′-methyl)phenoxy]propyl)aminoethyl))-4,7,10-tris((2S)-2-hydroxy-3-[(4′-methyl)phenoxy]propyl)-1,4,7,10-tetraazacyclododecane, L^3

1-(2-(9-anthracenylmethylamino)ethyl)-1,4,7,10-tetraaza-cyclododecane, 1, (320 mg, 0.789 mmol) was dissolved in dry EtOH (16 cm^3) and the solution stirred whilst heating it to boiling point. A solution of (2*S*)-(+)-3-[4′-methylphenoxy]-1,2-epoxypropane (532 mg, 3.24 mmol) in dry EtOH (16 cm^3) was added dropwise. The reaction was then stirred whilst refluxing for 10 days and monitored by TLC (alumina, 4% MeOH/CH_2Cl_2). Upon disappearance of the starting epoxide, the reaction was cooled to room temperature, and the solvent removed to leave an orange oil (0.91 g). This was purified on a basic alumina column (10% hexane/CH_2Cl_2) giving the product as a reddish-brown oil, (684 mg, 82%). UV–vis (20% aqueous 1,4-dioxane): λ_{max}/nm 388.7 (ε/dm^3 mol^{-1} cm^{-1} 9522), 368.7 (9941), 350.3 (6532), 334.0 (3607), 320.2 (2054). ^{1}H NMR ($CDCl_3$): δ 8.49 (2H, d, $J = 8.6$ Hz, Anth*H*); 8.38 (1H, s, Anth*H*); 7.97 (2H, distorted d, $J = 7.6$ Hz, Anth*H*); 7.46 (4H, m, Anth*H*); 7.03 (8H, br s, Ph*H*); 6.78 (8H, m, Ph*H*); 4.8–1.2 (46H, br m, –O*H*, –C*H*– and –CH_2–); 2.26 (12H, s, –CH_3). ^{13}C NMR ($CDCl_3$): δ 156.4 (4C, Ph, *ipso*); 131.8 (2C, Anth, *ipso*); 131.6 (1C, Anth, *ipso*); 130.0 (8C, Ph); 129.9 (4C, Ph); 129.0 (2C, Anth, *ipso*); 128.0 (2C, Anth); 127.9 (2C, Anth); 127.0 (2C, Anth); 126.0 (1C, Anth); 124.8 (2C, Anth); 114.4 (8C, Ph); 70.3 (4C, OCH_2); 67.9 (1C, methine); 66.9 (1C, methine); 65.5 (1C, methine); 65.3 (1C, methine); 60.4 (1C, exo-CH_2N); 58.3 (1C, exo-CH_2N); 58.0 (1C, exo-CH_2N); 57.8 (1C, exo-CH_2N); 56.3 (1C, exo-CH_2N); 53.8 (1C, exo-CH_2N); 53.2 (1C, cyclen CH_2); 53.0 (1C, cyclen CH_2); 52.3 (1C, cyclen CH_2); 52.1 (1C, cyclen CH_2); 51.8 (1C, cyclen CH_2); 50.3 (1C, cyclen CH_2); 50.0 (1C, cyclen CH_2); 49.8 (1C, cyclen CH_2); 47.8 (1C, Anth-CH_2N-); 20.1 (4C, CH_3). To obtain a sample for microanalysis L^3 was converted to its pentahydrochloride trihydrate by taking a solution of it (910 mg, 0.86 mmol) in EtOH (11 cm^3) cooled in ice. The stirred solution was treated dropwise with 36% aqueous HCl (0.6 cm^3, 7.6 mmol) and allowed to continue stirring overnight. The solvent was then evaporated and the residue triturated with ether. The brown solid was collected by filtration and dried under vacuum (800 mg, 94%). (Found: C, 60.06; H, 7.13; N, 5.60. $C_{65}H_{94}Cl_5N_5O_{11}$ requires C, 60.11; H, 7.29; N, 5.39%). $[\alpha]_D^{298} = -42.2°$ (c 0.007, EtOH).

1-((N-(2-(9-Anthracenylmethyl)(N-(2S)-(-)-2-hydroxy-3-[(4′-t-butyl)phenoxy]propyl)aminoethyl))-4,7,10-tris((2S)-(-)-2-hydroxy-3-[4′-(t-butyl)phenoxypropyl)-1,4,7,10-tetraazacyclododecane, L^4

1-(2-(9-anthracenylmethylamino)ethyl)-1,4,7,10-tetraazacyclododecane, 1, (268 mg, 0.66 mmol) was dissolved in dry EtOH (20 cm^3) and stirred. (2*S*)-(+)-3-[4′-(*t*-butyl) phenoxy]-1,2-epoxy propane (541 mg, 2.61 mmol) was added in EtOH (20 cm^3). The reaction mixture was heated under reflux for 10 days, whilst monitoring by TLC (CH_2Cl_2/hexane, 9:1). Upon loss of starting material the reaction was cooled to room temperature, filtered and the filtrate was evaporated to leave the product as a reddish oil (700 mg, 86%). UV–vis (20% aqueous 1,4-dioxane): λ_{max}/nm 388.6 (ε/dm^3 mol^{-1} cm^{-1} 7753), 368.5 (8159), 350.2 (5350), 334.1 (2786), 319.0 (sh) (1444). ^{1}H NMR (CD_3CN): δ 8.51 (2H, d, $J = 5.8$ Hz, Anth*H*); 8.43 (1H, d, $J = 5.8$ Hz, Anth*H*); 7.99 (2H, d, $J = 6.4$ Hz, Anth*H*); 7.45 (4H, br s, Anth*H*); 7.4–7.1 (8H, m, Ph*H*); 7.0–6.4 (8H, m. Ph*H*); 4.62 (4H, br s, –O*H*); 4.50–1.80 (42H, br m, –C*H*- and –CH_2–); 1.27 (36H, br s, –CH_3). ^{13}C NMR (CD_3CN): δ 157.7 (3C, Ph, *ipso*); 157.5 (1C, Ph, *ipso*); 144.3 (4C, Ph, *ipso*); 135.3 (2C, Anth, *ipso*); 132.4 (2C, Anth, *ipso*); 131.4 (1C, Anth, *ipso*); 130.0 (2C, Anth); 128.6 (2C, Anth); 127.8 (1C, Anth); 127.2 (6C, Ph); 127.0 (2C, Ph), 126.1 (2C, Anth); 124.5 (2C, Anth); 118.3 (4C, Ph); 115.0 (4C, Ph); 72.5 (1C, O*C*H_2); 71.3 (1C, O*C*H_2); 70.5 (1C, O*C*H_2); 70.2 (1C, O*C*H_2); 69.8 (1C, methine); 68.6 (1C, methine); 67.3 (1C, methine); 67.2 (1C, methine); 66.6 (1C, exo-N*C*H_2); 64.1 (1C, exo-*C*H_2N); 61.5 (1C, exo-*C*H_2N); 58.8 (1C, exo-*C*H_2N); 57.7 (1C, exo-*C*H_2N); 54.4 (1C, exo-*C*H_2N); 52.9 (2C, cyclen *C*H_2); 52.6 (2C, cyclen *C*H_2); 52.3 (2C, cyclen *C*H_2); 51.7 (2C, cyclen *C*H_2); 47.4 (1C, Anth-*C*H_2N-); 34.7 (4C, -*C*$(CH_3)_3$); 31.8 (12C, -*C*H_3). To obtain a sample for microanalysis L^4 was converted to its pentahydrobromide monohydrate by taking a solution of it (100 mg, 0.08 mmol) in EtOH (5 cm^3) and treating it with 48% HBr (100 μL) and allowing it to stir for 1 h. The solvent was evaporated and the residue was triturated with ether. The light brown solid was collected by filtration and dried under vacuum. Yield:(94 mg, 71%). (Found C, 55.8; H, 7.2; N, 4.15. $C_{77}H_{114}Br_5N_5O_9$ requires C, 55.94; H, 6.95; N, 4.24%). $[\alpha]_D^{298} = -29.3°$ (c 0.008, EtOH).

Safety note: perchlorate salts are potentially explosive. Although no problems were encountered in the synthesis or use of the following compounds extreme care should be taken when handling them.

$[CdL^2](ClO_4)_2 \cdot 5H_2O$

A solution of cadmium(II) perchlorate hexahydrate (106 mg, 0.26 mmol) in dry EtOH (5 cm^3) was added dropwise over 5 min to a refluxing solution of L^2 (232 mg, 0.23 mmol) in dry EtOH (5 cm^3). A white precipitate formed instantly. The suspension was left refluxing for 1 h, then cooled to room temperature. The solvent was concentrated by rotary evaporation and then the residue was triturated with ether to produce a light cream powder. This was collected by filtration, washed with ice-cold water (1 cm^3) and dried under vacuum to give the product, (252 mg, 83%). (Found: C, 51.85; H, 5.98; N, 4.97. $C_{61}H_{85}CdCl_2N_5O_{21}$ requires C, 52.05; H, 6.09; N, 4.98%). UV–vis (20% aqueous 1,4-dioxane): λ_{max}/nm 388.7 (ε/dm^3 mol^{-1} cm^{-1} 9481), 368.7 (9935), 350.3 (6423), 334.4 (3364), 320.2 (sh) (1763). ^{1}H NMR (DMSO-d_6):δ 8.61 (3H, br s, Anth*H*); 8.09 (2H, br s, Anth*H*); 7.52 (4H, br s, Anth*H*); 7.28 (8H, br m, Ph*H*); 7.0–6.4 (12H, br m, Ph*H*); 5.1–1.8 (46H, br m, –O*H*, –C*H*– and –CH_2–). ^{13}C NMR (DMSO-d_6):δ 158.5 (1C, Ph, *ipso*); 158.2 (3C, Ph, *ipso*); 131.0 (2C, Anth); 130.9 (1C, Anth); 130.3 (8C, Ph); 129.6 (2C, Anth); 127.6 (2C, Anth); 126.8 (1C, Anth); 126.1 (2C, Anth); 125.1 (2C, Anth); 124 (2C, Anth); 121.3 (3C, Ph); 121.0 (1C, Ph); 115.6 (8C, Ph); 71.0 (1C, O*C*H_2); 70.6 (1C, O*C*H_2); 70.3 (2C, O*C*H_2); 67.7 (1C, methine); 67.0 (1C, methine); 66.2 (1C, methine); 64.4 (1C, methine); 61.5 (1C, exo-*C*H_2N); 60.0 (1C, exo-*C*H_2N); 57.5 (1C, exo-*C*H_2N); 56.1 (1C, exo-*C*H_2N); 54.2 (1C, exo-*C*H_2N); 52.0 (1C, exo-*C*H_2N); 51.3 (2C, cyclen *C*H_2); 50.2 (2C, cyclen *C*H_2); 49.0 (2C, cyclen *C*H_2); 48.2 (2C, cyclen *C*H_2); 44.8 (1C, Anth-*C*H_2-N-).

$[CdL^3](ClO_4)_2 \cdot 2Et_2O \cdot 2H_2O$

A solution of cadmium(II) perchlorate hexahydrate (1.152 g, 3.0 mmol) in EtOH (20 cm^3) was added dropwise over 5 min to a refluxing solution of L^3 (1.911 g, 2.5 mmol) in EtOH (63 cm^3). A white precipitate formed instantly. The suspension was left refluxing for 1 h, then cooled to RT. The solvent was evaporated and trituration of the residue with ether produced a light cream powder. This was collected by filtration, washed with water (1 cm^3) and dried under vacuum to give the pure product (1.831 g, 74%). (Found: C, 56.09; H, 7.09; N, 4.20. $C_{73}H_{107}CdCl_2N_5O_{20}$ requires C, 56.28; H, 6.92; N, 4.50%). UV/vis (20% aqueous 1,4-dioxane): λ_{max}/nm 388.7 (ε/dm^3 mol^{-1} cm^{-1} 9596), 368.7 (10120), 350.3 (6678), 334.1 (3644), 320.4 (sh) (2038). ^{1}H NMR (DMSO-d_6): δ 8.90 (3H, br s, Anth*H*); 8.39 (2H, br s, Anth*H*); 7.81 (4H, br s, Anth*H*); 7.35 (8H, br m, Ph*H*); 7.4–6.6 (8H, br m, Ph*H*); 5.6–2.0 (58H, br m, –O*H*, –C*H*–, –CH_2– and CH_2 of ether); 2.30 (12H, br s, –CH_3); 1.10 (6H, m, CH_3 of ether). ^{13}C NMR (DMSO-d_6): δ 156.5 (2C, Ph, *ipso*); 156.2 (2C, Ph, *ipso*); 131.1 (2C, Anth, *ipso*); 131.0 (2C, Anth, *ipso*); 130.0 (8C, Ph); 129.1 (4C, Ph); 128.6 (2C, Anth, *ipso*); 127.6 (2C, Anth); 127.1 (2C, Anth); 126.2 (2C, Anth); 125.2 (2C, Anth); 114.5 (8C, Ph); 72.0 (2C, O*C*H_2);

70.0 (1C, OCH_2); 69.1 (1C, OCH_2); 67.9 (2C, methine); 66.0 (2C, methine); 65.0 (1C, exo-CH_2N); 64.8 (1C, exo-CH_2N); 64.2 (1C, exo-CH_2N); 62.5 (1C, exo-CH_2N); 57.5 (4C, CH_2 of ether); 57.0 (1C, exo-CH_2N); 53.0 (1C, exo-CH_2N); 51.4 (2C, cyclen CH_2), 50.5 (2C, cyclen CH_2); 49.4 (2C, cyclen CH_2); 48.0 (2C, cyclen CH_2); 45.1 (1C, Anth-CH_2N-); 20.2 (4C, -CH_3); 15.3 (4C, CH_3 of ether).

[CdL^4](ClO$_4$)$_2$·CH$_3$CN

A solution of cadmium(II) perchlorate hexahydrate (0.183 g, 0.43 mmol) in dry EtOH (3.5 cm^3) was added dropwise over 5 min to a refluxing solution of L^4 (0.35 g, 0.39 mmol) in dry EtOH (11 cm^3). A white precipitate formed instantly. The suspension was left refluxing for 1 h, then cooled to room temperature. The solvent was evaporated and then trituration of the residue with ether produced a light cream powder. This was collected by filtration, washed with ice-cold MeCN, followed by drying under vacuum, to give the pure product (0.272 g, 45%). (Found C, 60.06; H, 7.13; N, 5.60. $C_{79}H_{110}CdCl_2N_6O_{16}$ requires: C, 59.94; H, 7.00; N, 5.31%.). UV–vis (20% aqueous 1,4-dioxane): λ_{max}/nm 388.2 (ε/dm^3 mol^{-1} cm^{-1} 4865), 367.8 (5565), 349.9 (3950), 333.2 (2335), 317.9 (sh) (1400). ^{1}H NMR (CD$_3$CN):δ 8.96 (3H, br s, Anth*H*); 8.52 (2H, br s, Anth*H*); 7.97 (4H, br s, Anth*H*); 7.29 (8H, br s, Ph*H*); 6.8–6.4 (8H, br s, Ph*H*); 4.9–2.0 (46H, br m, –O*H*, –C*H*– and –CH_2–); 2.30 (36H, br s, –CH_3); 1.96 (3H, s, CH_3 of CH_3CN). ^{13}C NMR (CD$_3$CN): δ 157.7 (3C, Ph, *ipso*); 157.5 (1C, Ph, *ipso*); 144.0 (4C, Ph, *ipso*); 135.6 (2C, Anth, *ipso*); 135.3 (1C, Anth, *ipso*); 132.4 (2C, Anth, *ipso*); 131.7 (1C, Anth); 130.0 (2C, Anth); 128.0 (2C, Anth); 127.8 (2C, Anth); 127.2 (8C, Ph); 126.0 (2C, Anth); 118.3 (1C, CH_3CN), 116.1 (2C, Ph); 115.0 (6C, Ph); 72.5 (1C, OCH_2); 71.3 (3C, OCH_2); 69.8 (1C, methine); 67.8 (1C, methine); 67.3 (1C, methine); 66.0 (1C, methine); 58.7 (2C, exo-CH_2N); 58.2 (2C, exo-CH_2N); 57.7 (2C, exo-CH_2N); 54.4 (1C, cyclen CH_2); 52.9 (1C, cyclen CH_2); 52.3 (1C, cyclen CH_2); 52.0 (1C, cyclen CH_2); 51.6 (1C, cyclen CH_2); 50.5 (1C, cyclen CH_2); 49.4 (1C, cyclen CH_2); 47.4 (1C, cyclen CH_2); 45.2 (1C, Anth-CH_2-N-); 34.7 (4C, -$C(CH_3)_3$); 30.2 (12C, -CH_3); 1.8 (CH_3CN).

Aromatic oxoanion association constant measurements

Titration of each receptor complex with the sodium salt of the various guest aromatic oxoanions, during which the fluorescence emission intensity at 416 nm was monitored, gave a titration curve that was analysed by non-linear least squares regression to yield the aromatic oxoanion association constants and the molar fluorescence ($\varepsilon'_{Host–Guest}$) of the receptor host–guest complexes. These titrations were conducted in 20% aqueous 1,4-dioxane (I = 0.1 M Et_4NClO_4) at pH 7.0 (0.02 M lutidine). The fluorescence emission spectra at 298 ± 0.1 K were recorded on a Varian Cary Eclipse fluorescence spectrophotometer, using stoppered 10 mm quartz cells, over a wavelength range of 370–550 nm at 0.15 nm intervals, with a scan rate of 40 nm min^{-1}. Both the excitation and emission monochromator slit widths were set at 5 nm, and due to the highly fluorescent nature of the compounds, a 1.5 absorbance attenuator was used for 10^{-4} mol dm^{-3} solutions, while 10^{-6} mol dm^{-3} solutions required no attenuation. All samples were purged with N_2 prior to use. Quantum yields were calculated with respect to quinine in 0.5 mol dm^{-3} H_2SO_4 according to the method of Demas [20], and are corrected for solvent refractive indices.

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