Effect of the inclusion of sodium cations on the binding properties of a switchable diporphyrin receptor†

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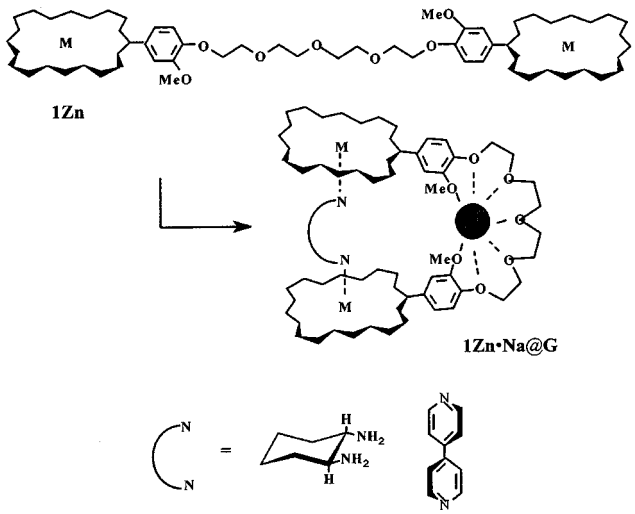
The nestling of Na^+ within the oligooxaethylene frame of the switchable diporphyrin receptor 1Zn results in an allosteric effect on the binding of ditopic amines, and remarkably influences the ligand-induced chiroptic properties of the assembly upon inclusion of chiral ditopic guests.

Diporphyrin and oligoporphyrin systems are regarded as excellent tools for the molecular recognition of organic guest molecules.[1] In particular, chiral diporphyrin systems have been successfully employed in the enantiomeric discrimination of amino acid derivatives.[2] Moreover, diporphyrin tweezers constitute interesting devices for the determination of the absolute configuration of amines, amino acids and derivatives.[3]

We recently reported[4] that simple oligooxaethylene-spacered diporphyrin arrays undergo a conformational change toward a cofacial geometry upon coordination of alkali metal ions within the ether framework of the receptor. We surmised that this geometrical variation would result in a change of the binding properties of a related zinc derivative toward the inclusion of bifunctional guests (G). In this paper we wish to report on the effect of the inclusion of Na^+ [5] on the binding features of the above mentioned diporphyrin receptor toward some bidentate amines, *i.e. trans*-1,2-diaminocyclohexane (1,2-DACy, racemic mixture), and 4,4′-bipyridyl (bpy). The results obtained evidence the presence of an allosteric effect exerted by the complexed metal ion, which promotes the attainment of a more rigid structure (**1Zn** · Na@G, Scheme 1). These studies have been extended to the chiral (+)- and (−)-1,2-DACy stereoisomers evidencing an interesting effect on the ligand-induced chiroptic properties of the resulting supramolecular assemblies.

Diporphyrin derivative **1Zn**, and its monotopic counterpart **2Zn**, have been synthesised by following a previously published procedure.[5,6] The derivative **1Zn** has been found to be a good receptor for several ditopic amines.[7] We focused our attention on bpy and 1,2-DACy owing to their different structural and coordination properties.[8] The formation of the host–guest inclusion complexes was carried out in CH_3CN–$CHCl_3$ (90 : 10, v/v). The formation of **1Zn** · Na@G adducts was conveniently monitored by following the typical red-shift of the Q visible bands of the porphyrin macrocycles.‡ The titration plots were analysed by fitting the experimental points to a 1 : 1 binding isotherm[9] to give the corresponding values of the association constants. The binding studies have been carried out with **2Zn** for comparison. The results are reported in Table 1. As expected, receptor **1Zn** binds to the considered ligands more strongly than its monotopic **2Zn** counterpart. On inspection of Table 1 the overwhelming effect of the donor ability of the ligands[10] on the strength of the binding is evident, the relative K values being 7.3×10^4 and 2.6×10^5 M^{-1} for bpy and 1,2-DACy respectively. The corresponding values of effective molarity (EM)[11a] are 2×10^{-2}



Scheme 1 Schematic structure of the **1Zn** · Na@G supramolecular ternary complex. Phenyl rings have been emitted for clarity.

Table 1 Binding constant values (K) for the interaction of amine guests with porphyrin receptors, in CH_3CN–$CHCl_3$ (90 : 10, v/v) at $T = 25\,°C$

Entry	Receptor	Guest	K/M^{-1} (EM[a]/M)
1	**1Zn**	bpy	7.3×10^4 (2.0×10^{-2})
2		bpy[b]	1.1×10^4 (3.0×10^{-3})
3		bpy[c]	7.3×10^4 (2.0×10^{-2})
4		1,2-DACy	2.6×10^5 (3.0×10^{-4})
5		1,2-DACy[b]	4.5×10^5 (5.0×10^{-4})
6	**2Zn**	bpy[d]	9.0×10^2
7		1,2-DACy[d]	1.5×10^4

[a] Effective molarity values are reported in parentheses. [b] In the presence of $NaClO_4$ 0.05 M. [c] In the presence of Bu_4NClO_4 0.05 M. [d] The values of K obtained in the presence of $NaClO_4$ 0.05 M were identical within experimental error.

† Electronic supplementary information (ESI) available: full experimental details, NMR labelling scheme for the porphyrin derivatives and UV-visible spectra of **1Zn**@G in the presence of added $NaClO_4$. See http://www.rsc.org/suppdata/nj/b1/b102904p/

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and 3×10^{-4} M. The EM value estimated§ in the case of the binding of bpy lies fairly well within the calculated range for a strainless ring closure reaction,[11b,c] whereas the corresponding value for the interaction of 1,2-DACy is about two orders of magnitude lower than that expected. This may indicate that the formation of the latter pseudo-cyclic assembly, owing to the shorter N–N distance of the guest, occurs with some degree of ring strain.[12] The complexation studies were also performed in the presence of added Na^+,¶ which is known to promote a conformational change of the resulting supramolecular complex toward a pseudo-cyclic structure (**1Zn** · Na).[4,5,13] This affects the binding of a given guest by virtue of the tuned preorganisation of the receptor. This is indeed the case for the inclusion of 1,2-DACy, which features a two-fold increase of the binding constant K in the presence of the added cation.[14] Conversely, in the case of the inclusion of the "longer" guest, *i.e.* bpy, a negative allosteric effect is found. A decrease in K by nearly one order of magnitude is in fact observed, and this can be interpreted in terms of a less favourable interaction of bpy within the less flexible cavity of the host.‖ The magnitude of these effects is in line with other reports which have recently appeared in the literature,[15] in which the inclusion of some alkali metal ions results in a positive effect on the binding of halides to some ditopic receptors. The allosteric effect is also nicely evident in the CD experiments relative to the binding of chiral diamine guests such as (1*R*,2*R*)-(−)-1,2-diaminocyclohexane, and (1*S*,2*S*)-(+)-1,2-diaminocyclohexane [(±)G*] stereoisomers. The binding results in the formation of extrinsically chiral supramolecular host–guest complexes [**1Zn**@(±)G*] as evidenced by the exciton-coupled CD of the interacting porphyrin chromophores.[16] The chiroptic properties of the resulting assemblies are modulated by the absolute configuration of the guest. The inclusion of the (−) isomer, for example, results in a negative bisignate CD spectrum, whereas in the case of the (+) enantiomer a mirrored positive spectrum is observed. Remarkably, the presence of Na^+ results in an increased CD amplitude of the spectra (Fig. 1), as witnessed by the relative $\Delta\varepsilon$ values for the complex with (−)G* of −415 and −620 L mol^{-1} cm^{-1} for **1Zn** and **1Zn** · Na, respectively, at 436 nm.[17] This finding confirms the hypothesis of the formation of a tighter supramolecular structure, which features a higher degree of ellipticity.[18] Finally, the inclusion of Na^+, resulting in a more rigid system, promotes an appreciably increased stability of the supramolecular complex toward the presence of an excess (up to 100 equivalents) of the title diamine.**

The cation-induced conformational change of a flexible diporphyrin host results in an allosteric effect toward the binding of ditopic amine ligands, which is dependent on the structural properties of the guests. The interaction with chiral diamines results in the formation of a supramolecular chiral complex, which features increased ellipticity and stability in the presence of Na^+. This would have promising application in the construction of receptors and sensors for substrates with biological activity. Further studies on the effect of the inclusion of different metal ions toward the binding of a larger class of ditopic guests are currently under investigation in our laboratories.

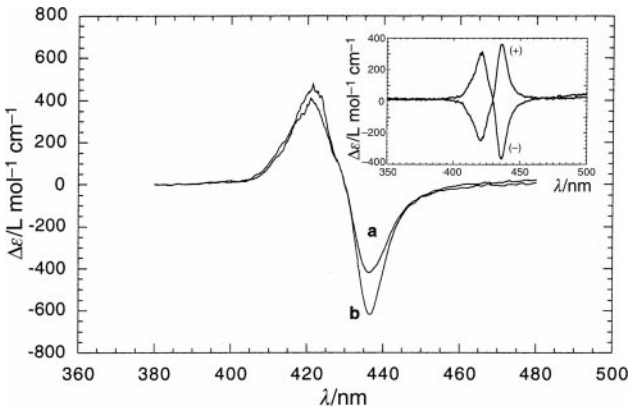

Fig. 1 CD spectra of **1Zn**@(−)G* ([**1Zn**] = 1.8×10^{-6} M, CH_3CN–$CHCl_3$, 90 : 10, v/v), in the presence of added $NaClO_4$. (a) $[Na^+] = 0$ M, (b) $[Na^+] = 0.05$ M. The inset shows the CD spectra for the **1Zn**@(±)G* complexes (see text).

Experimental

Syntheses

Zinc[5-(4-hydroxy-3-methoxyphenyl)-10,15,20-triphenylporphyrinato], 2Zn. ^{1}H NMR ($CDCl_3$): δ 9.0–8.9 (m, 8H, β-H), 8.2 (br s, 6H, *o*-C_6H_5), 7.7 (br s, 6H, *m*-C_6H_5), 7.3–7.2 (m, 6H, C_6H_5 + aromatics), 3.97 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$): δ 150.5 (C-α), 150.2 (C-α), 142.9 (C-1″), 134.5 (C-2″, C-6″), 132.0 (C-β), 127.9 (C-4″), 127.5 (C-3″, C-5″), 126.6 (C-β), 121.1 (C-*meso*), 117.5 (C-5′), 112.6 (C-2′), 56.2 (CH_3O). UV-vis ($CHCl_3$), λ_{max}/nm (log ε): (Soret, 5.8), 490 (4.1), 552 (3.9). FAB-MS (NBA), m/z: 723 $[M]^+$.

1,11-Bis[zinc(2-methoxy-4-(10,15,20-triphenylporphyrinato)phenoxy]-3,6,9-trioxaundecane, 1Zn. ^{1}H-NMR ($CDCl_3$): δ 9.0–8.8 (m, 8H, β-H), 8.18 (br s, 6H, aromatics), 7.7–7.6 (m, 12H, aromatics), 7.65 (d, J = 8.4 Hz, 1H, aromatics), 4.33 (br t, J = 4.8 Hz, 2H, OCH_2CH_2O), 3.96 (br t, J = 4.8 Hz, 2H, OCH_2CH_2O), 3.89 (s, 3H, CH_3O), 3.7 (m, 4H, OCH_2CH_2O). ^{13}C-NMR ($CDCl_3$): δ 150.3 (C-α), 150.1 (C-α), 150.0 (C-α), 147.9 (C-3′), 147.3 (C-4′), 143.0 (C-1″), 136.1 (C-1′), 134.4 (C-2″), 131.8 (C-β), 127.3 (C-3″), 126.4 (C-β), 122.1 (C-6′), 120.8 (C-*meso*), 120.7 (C-*meso*), 118.7 (C-5′), 111.5 (C-2′), 70.9 (CH_2CH_2O), 70.7 (CH_2CH_2O), 69.8 (CH_2CH_2O), 68.6 (CH_2CH_2O), 56.0 (OCH_3). UV-vis ($CHCl_3$), λ_{max}/nm (log ε): 423 (6.1, Soret), 551 (4.3), 594 (4.1). FAB-MS (NBA), m/z: 1604 $[M]^+$.

Acknowledgements

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Notes and references

‡ Evidence for a 1 : 1 **1Zn**@G complex formation was given by the presence of several well-defined isosbestic points and by a continuous variation plot (Job plot) which shows a sharp inflection point at $\chi(G) = 0.5$.

§ The EM calculation has been made on the assumption that the cyclic complexes with bpy and 1,2-DACy posses 19 and 20 rotors (*i.e.* freely rotating single bonds), respectively.

¶ From the binding constant value for the interaction of Na^+ with the porphyrin receptor (K_{ass} = 500 M^{-1}, see ref. 4) it can be estimated that the predominant species is the complexed form (**1Zn** · Na) at the chosen cation concentration (0.05 M).

‖ The fact that, in a separate experiment, the addition of an excess (up to 0.05 M) of Bu_4NClO_4 does not influence the strength of the binding of 1,2-DACy to **1Zn**, safely rules out the occurrence of effects due to the increased ionic strength of the medium. Moreover, the invariance of the K values for the binding of bpy to the reference **2Zn** receptor in the presence of Na^+ (see entry 6, Table 1) excludes the possibility that the reduced degree of binding observed would be a mere consequence of a Lewis acid–base interaction of the ligand with the sodium cation.

** Related structures, in fact, are known to be unstable, in the presence of an excess of added ligands, toward the conversion into linear oligomers [see, for example, ref. 3(*a*)].

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