Siemens R3m/V diffractometer $Mo_{K\alpha}$ radiation, graphite monochromator. Because of their air sensitivity, the blue-black, rhombic crystals were mounted in silicon oil when removed from the mother liquor, and the measurement was performed at −85 °C. Since the cationic lattice is partly disordered, it is not possible to distinguish between H_2O and NH_4^+ centers. The overall number of both of these groups found in lattice positions is about 320 per formula unit; however, it must be assumed that some of those units are so disordered that they are not detectable by difference Fourier syntheses. Thus, for instance, no relevant lattice positions could be localized in the vicinity of the center of the cavity of the cluster. Results of model calculations revealed that a further 50–70 positions that should be occupied by H_2O units are present. Elemental analyses, redox titrations, and the determination of the NH_4^+ content by the Kjeldahl method yielded the quoted formula. As a result of the quite characteristic bond valence sums, the positions of protonation could be unequivocally located. The calculated values lie between 0.15 and 0.45 for the 70 doubly protonated and between 1.1 and 1.3 for the 28 singly protonated oxygen atoms. This corresponds to what we expected from our experience with numerous other relevant cluster anions. Furthermore, significantly lowered bond valence sums (average 5.66) for 70 Mo atoms without H_2O ligands, which lie in the equatorial plane or above and below it on the periphery of the tire-shaped anion, show that the 4d electrons (and likewise the "Mo^V" centers without consideration of the $\{Mo(NO)\}^{3+}$ units) are predominantly localized here. This correlates with the degree of reduction corresponding to the molecular formula, which was also determined by manganometric redox titration (see ref. [1]). (Calculation of bond valence sums according to I. D. Brown in *Structure and Bonding in Crystals, Vol. II* (Eds.: M. O'Keefe, A. Navrotsky), Academic Press, New York, 1981, p. 1.) Part of the $\{Mo(O_{br})_3(O_{term})_2(H_2O)\}$ and the $\{Mo(O_{br})_4(O_{term})(H_2O)\}$ octahedra (br = bridging, term = terminal) is disordered in such a way that the *trans* O_{term} and H_2O ligands exchange their positions (in each case unequivocally recognized in the individual octahedra through two Mo positions with apparent "distances" between 0.7 and 0.8 Å). Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (FRG) on quoting the depository number CSD-59058.

[3] Characterization of **4**: some characteristic IR bands (KBr disc prepared under argon): $\tilde{\nu}$ [cm^{-1}] = 1610 (m, br, $\delta(H_2O)$ and $\nu(NO)$), 1407 (m, $\delta_{as}(NH_4^+)$), 967 (m), 905 (m, $\nu(Mo{=}O)$), 812 (sh), 740 (s), 636 (s), 551 (s). Characteristic resonance Raman bands (solid/λ_e = 1064 nm): $\tilde{\nu}$ [cm^{-1}] = 806 (s, A_1), 536 (s), 462 (s), 326 (s), 221 (s). Vis/NIR (in H_2O): λ [nm] (ε_M [10^5 $L\,mol^{-1}\,cm^{-1}$]) = 750 (1.7, IVCT), 1080 (1.3, IVCT).

[4] The conditions required for the occurrence of D_{7d} symmetry were approximately fulfilled only for the Mo atoms. Deviations are observed mainly for the O_{term} and H_2O ligands of the $\{MoO_2(H_2O)(\mu_2\text{-}O)MoO_2(H_2O)\}$ units that are not transformed into each other by reflection across the dihedral planes.

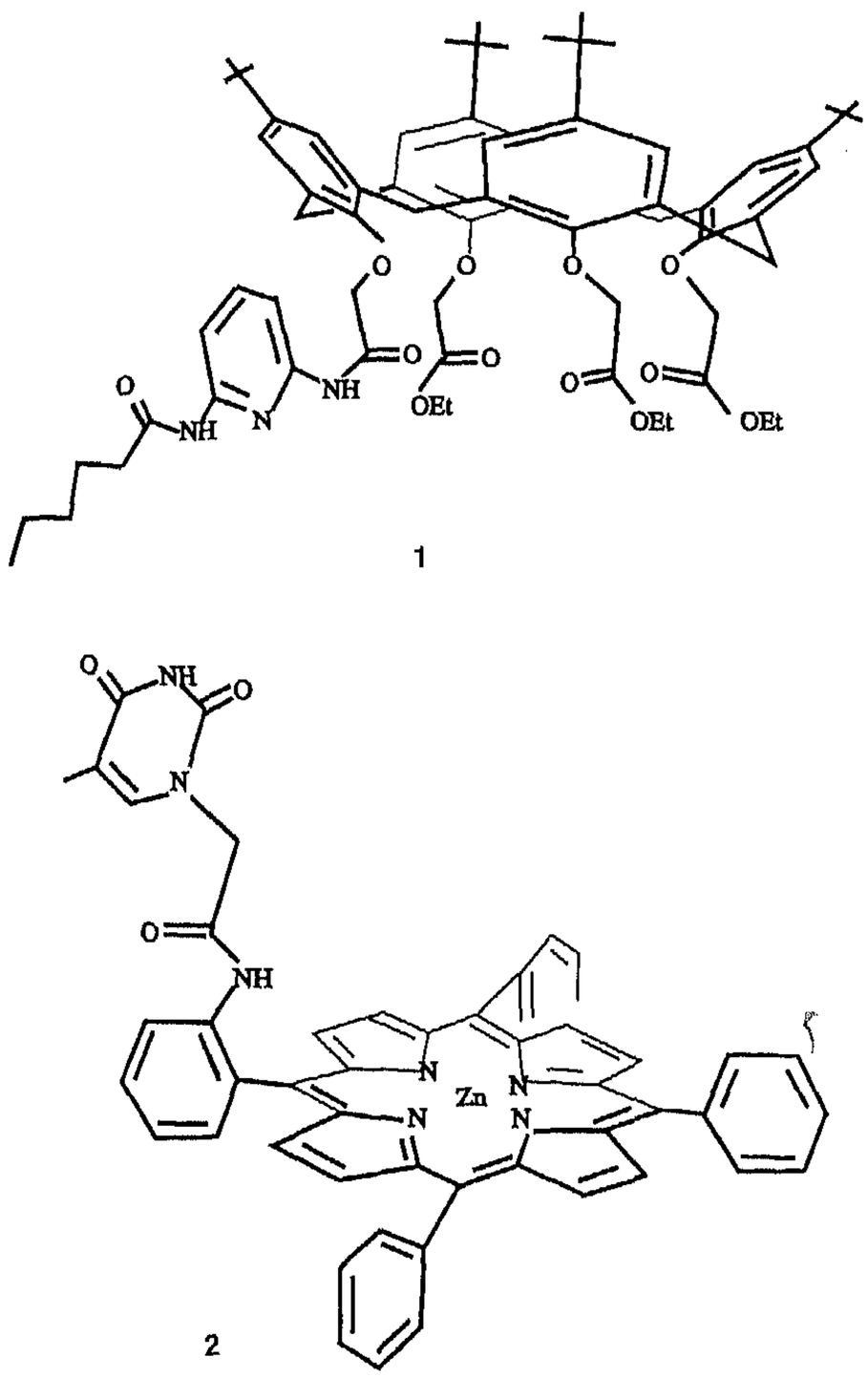
[5] The exciting process of nucleus formation in the case of ionic crystals with "giant ions" will, after thorough examination, be reported elsewhere. The relevant stochastic process in the present case leads not only to (large) crystals but also to a noncrystalline part or to material with a different degree of crystallization, the powder diagram of which corresponds to the envelope of that calculated from single crystal data. The Raman, IR, and UV/Vis/NIR spectra, and the analyses, are identical for the crystalline and noncrystalline parts.

A Self-Assembled Bifunctional Receptor

Dmitry M. Rudkevich,* Alexander N. Shivanyuk, Zbigniew Brzozka, Willem Verboom, and David N. Reinhoudt*

Molecular self-assembly is an important part of life processes and biological systems.[1] It results in a wide variety of complex structures such as double-stranded DNA, viral protein coatings, lipid membranes, and globular proteins. Self-assembling processes have also found applications in the design of nanostructures such as inorganic clusters, tubes and channels, monolayers, and hydrogen-bonded networks. The functions of such assemblies can be extrapolated from molecular properties.[2, 3] Recently, Sessler et al. reported photoinduced energy transfer in noncovalently linked photosynthetic systems.[4] Molecular recognition by encapsulation of small guest molecules in cavities assembled through noncovalent interactions has been achieved.[5] Self-assembled nanotubes constructed from cyclic peptide subunits can transport glucose across lipid bilayers.[6]

Previously we have described bifunctional receptors having in the same molecule covalently connected cation and anion binding sites.[7] In this communication we describe the molecular recognition of ionic species by a bifunctional receptor system, in which a cation and an anion binding site are positioned in close proximity by means of self-assembly. Such a system is able to bind simultaneously both cationic and anionic guest species. The strategy applied is based on the assembly of known receptors through hydrogen bonding. The cation receptor calix[4]arene **1**, which contains one amide and three ester groups,



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2

complexes alkali metal cations with a high selectivity for Na^+.[8] This calixarene was prepared in 78% yield from the corresponding triester monocarboxylic acid chloride[9] and 2-amino-6-(hexanamido)pyridine. The anion receptor porphyrin **2** was obtained in 49% overall yield by reaction of thymine with the appropriate bromoacetamidoporphyrin[10] in DMSO in the presence of K_2CO_3 as a base, followed by metalation with $Zn(OAc)_2 \cdot 2H_2O$. The Zn center in porphyrin **2** is expected[11] to bind anions in aprotic solution. For the assembly through hydrogen bonding, compounds **1** and **2** are functionalized with complementary diamidopyridine and thymine units, respectively.[12, 13]

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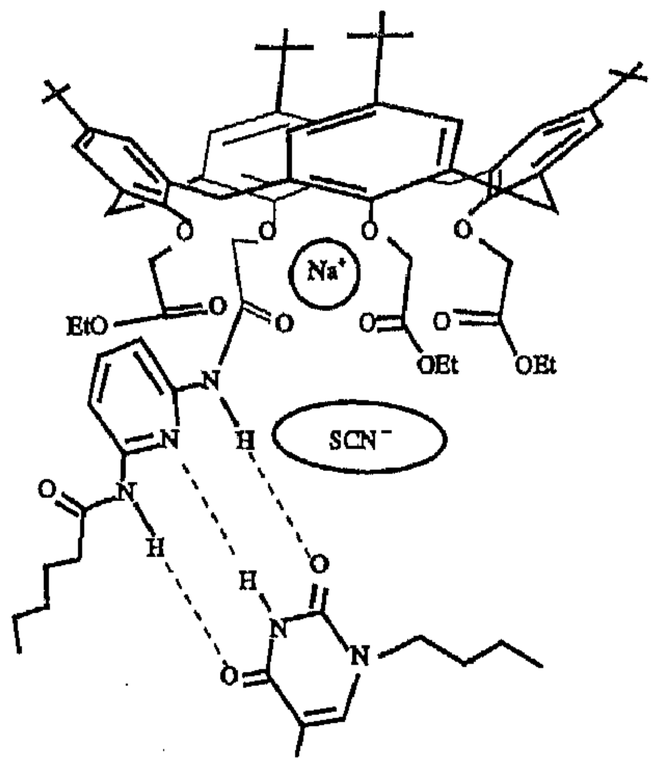
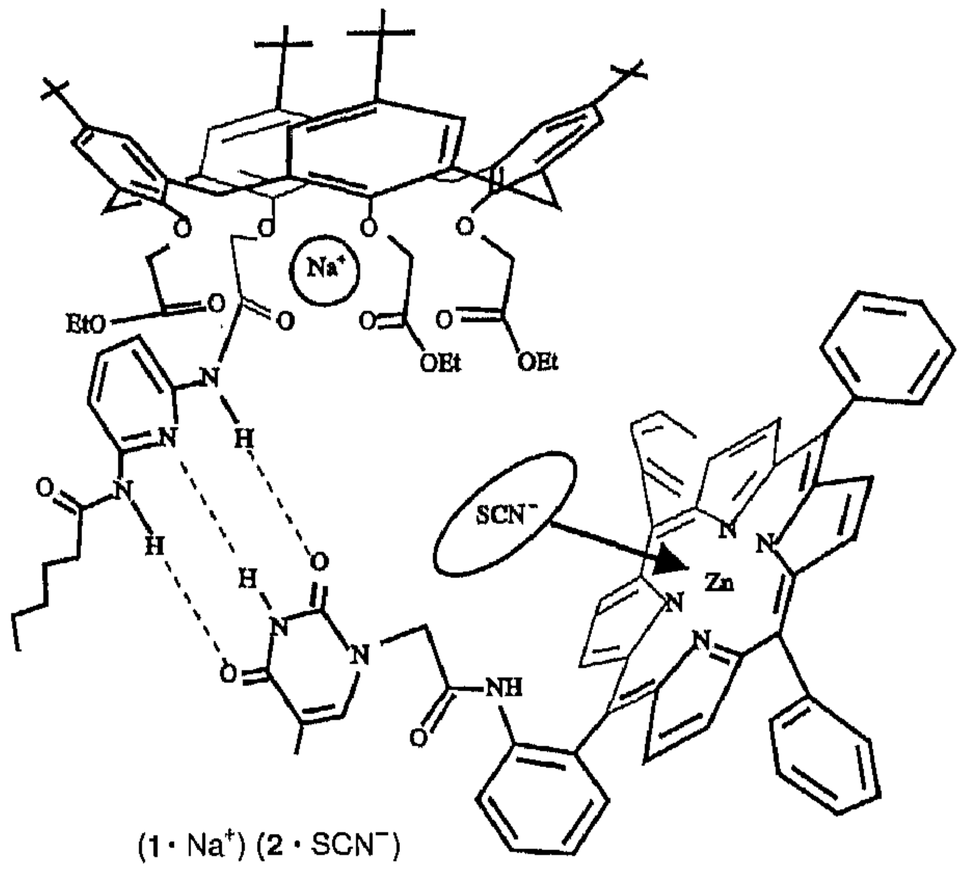
Calix[4]arene **1** strongly complexes Na^+ in $CDCl_3$, $[D_3]$MeCN, and $[D_8]$toluene solutions; from dilution experiments in $[D_3]$MeCN with $NaNO_3$ an association constant (K_{ass}) of $5.0 \times 10^4\,mol^{-1}$ was found. Calixarene **1** could be converted easily to the corresponding lipophilic complexes $(\mathbf{1}\cdot Na^+)ClO_4^-$, $(\mathbf{1}\cdot Na^+)I^-$, and $(\mathbf{1}\cdot Na^+)SCN^-$ by stirring a CH_2Cl_2 solution of **1** with saturated aqueous solutions of the appropriate sodium salts for three to five hours. With the more hydrophilic salts NaF and NaH_2PO_4 no complexes could be obtained.

Surprisingly, the diamidopyridine fragment in free **1** does not form hydrogen-bonded aggregates with complementary molecules such as *N*-butylthymine. In the ^1H NMR spectra no characteristic shifts[12] of C(O)NH signals were observed upon addition of *N*-butylthymine to $CDCl_3$, $[D_3]$MeCN, or $[D_8]$toluene solutions of **1**. The diamidopyridine moiety in **1** is apparently involved in intramolecular hydrogen bonding with the ethyl carboxylate groups, because the C(O)NH signals of **1** are shifted roughly $\Delta\delta = 0.3$ and 0.8 downfield in comparison with those of the $(\mathbf{1}\cdot Na^+)ClO_4^-$ complex in $CDCl_3$ and $[D_3]$MeCN, respectively. The Na^+ complexes of **1**, in which the carbonyls from the ester groups and the amide group are coordinated to the cation, do form hydrogen bonds with complementary molecules as indicated by the downfield shifts for the diamidopyridine C(O)NH protons of approximately $\Delta\delta = 0.5-0.6$ in $CDCl_3$, $[D_3]$MeCN, and $[D_8]$toluene upon addition of *N*-butylthymine to a solution of the $(\mathbf{1}\cdot Na^+)ClO_4^-$ complex. From dilution experiments in $[D_8]$toluene K_{ass} values of $1.5 \times 10^3\,mol^{-1}$ ($-\Delta G = 17.8\,kJ\,mol^{-1}$) and $1.7 \times 10^3\,mol^{-1}$ ($-\Delta G = 18.1\,kJ\,mol^{-1}$) were calculated for $(\mathbf{1}\cdot Na^+)ClO_4^-$ and $(\mathbf{1}\cdot Na^+)SCN^-$, respectively.[14, 15] This provides an interesting possibility of "switching on" the hydrogen bonding ability of **1** by complexation with Na^+ ions.[16] It means that anion receptor **2** can in principle be assembled with $(\mathbf{1}\cdot Na^+)ClO_4^-$ or $(\mathbf{1}\cdot Na^+)SCN^-$ complexes through a diamidopyridine–thymine interaction. UV/Vis experiments with porphyrin **2** show that it complexes I^- and SCN^- ions (introduced as tetrabutylammonium salts) in apolar solvents (CH_2Cl_2 and toluene). A bathochromic shift of the Soret band of 8–10 nm was found upon addition of $Bu_4N^+I^-$ and $Bu_4N^+SCN^-$ to a toluene solution of **2**, which is in agreement with the data published for simple tetraphenylporphyrins.[11] This binding is not strong; from dilution experiments a K_{ass} value of roughly $10\,mol^{-1}$ ($-\Delta G = 5.6\,kJ\,mol^{-1}$) was calculated for both I^- and SCN^- ions in toluene. No indication for complexation of the ClO_4^- ion was observed. Addition of *free* calix[4]arene **1** to a toluene solution of porphyrin **2** did not change the anion binding properties of **2**; K_{ass} values of roughly $10\,mol^{-1}$ for the complexation of I^- and SCN^- ions were found. Interactions between the hydrogen bonding sites of **1** and **2** were not observed in the ^1H NMR spectra upon mixing.

The final assembly experiment was carried out between $(\mathbf{1}\cdot Na^+)SCN^-$ and **2**.[17] Addition of porphyrin **2** to a $[D_8]$toluene solution of $(\mathbf{1}\cdot Na^+)SCN^-$ resulted in a pronounced thymine–diamidopyridine interaction. From the ^1H NMR chemical shifts of the C(O)NH signals a K_{ass} value of $2.8 \times 10^4\,mol^{-1}$ ($-\Delta G = 24.9\,kJ\,mol^{-1}$) for $(\mathbf{1}\cdot Na^+)(\mathbf{2}\cdot SCN^-)$ was calculated. This is significantly higher than those of the interactions in $(\mathbf{1}\cdot Na^+)\cdot$*N*-butylthymine$\cdot SCN^-$ and $Bu_4N^+(\mathbf{2}\cdot SCN^-)$ separately. A Job plot confirmed the 1:1 stoichiometry of the complex (Fig. 1).[18, 19] The $(\mathbf{1}\cdot Na^+)(\mathbf{2}\cdot SCN^-)$ assembly in toluene was also confirmed by UV/Vis spectroscopy; the Soret band displayed a bathochromic shift of 8 nm thus reflecting the Zn–SCN^- interaction (Fig. 2). From these experiments a K_{ass} value of $2.5 \times 10^4\,mol^{-1}$ was calculated, indicating strong anion binding.



$(\mathbf{1}\cdot Na^+)\cdot$Thymine$\cdot SCN^-$



$(\mathbf{1}\cdot Na^+)\,(\mathbf{2}\cdot SCN^-)$

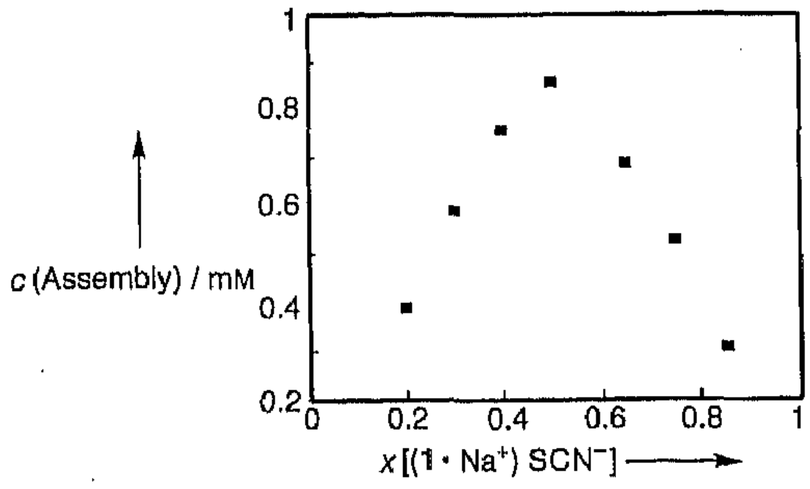


Fig. 1. Titration of 1 mmol of $(1\cdot Na^+)SCN^-$ with 1 mmol of **2** in $[D_8]$toluene with formation of the assembly $(1\cdot Na^+)(2\cdot SCN^-)$ (Job plot).

These results prove the formation of the *noncovalently* organized bifunctional receptor system $(1\cdot Na^+)(2\cdot SCN^-)$ (Fig. 3).[20] The Na^+ ion is complexed by calixarene **1**, the SCN^- ion coordinates to the Zn-porphyrin **2**, and these cation and anion receptors are connected through hydrogen-bonded aggregation. The (significant) enhancement of the hydrogen bonding as well as the anion complexation points to a *coopera-*

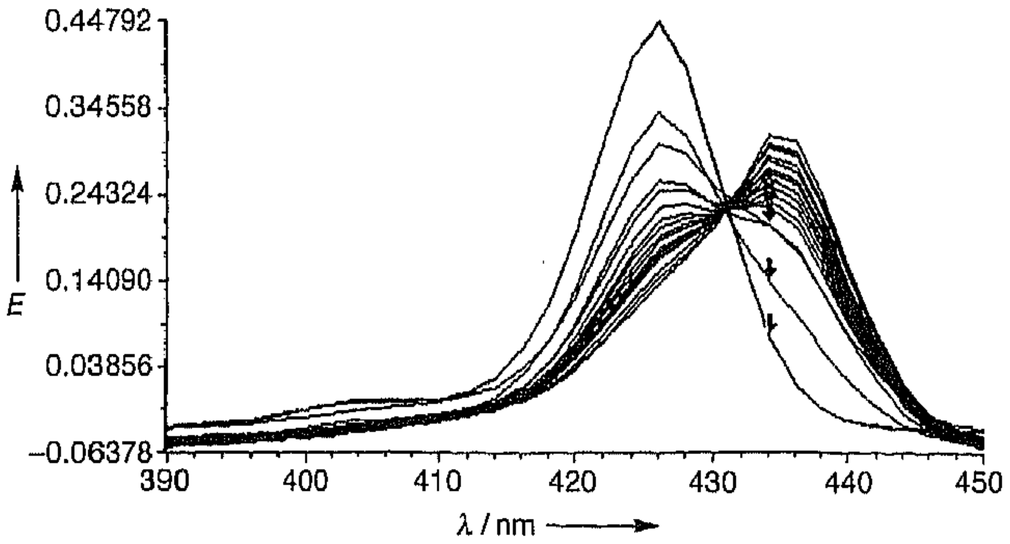


Fig. 2. Complexation of $(1\cdot Na^+)SCN^-$ with **2** in toluene. The assembly was monitored by UV/Vis spectroscopy between 390 and 450 nm (E = extinction). [**2**] = 1×10^{-3} mM; the concentration of $(1\cdot Na^+)SCN^-$ ranges from 5×10^{-4} to 1×10^{-1} mM.

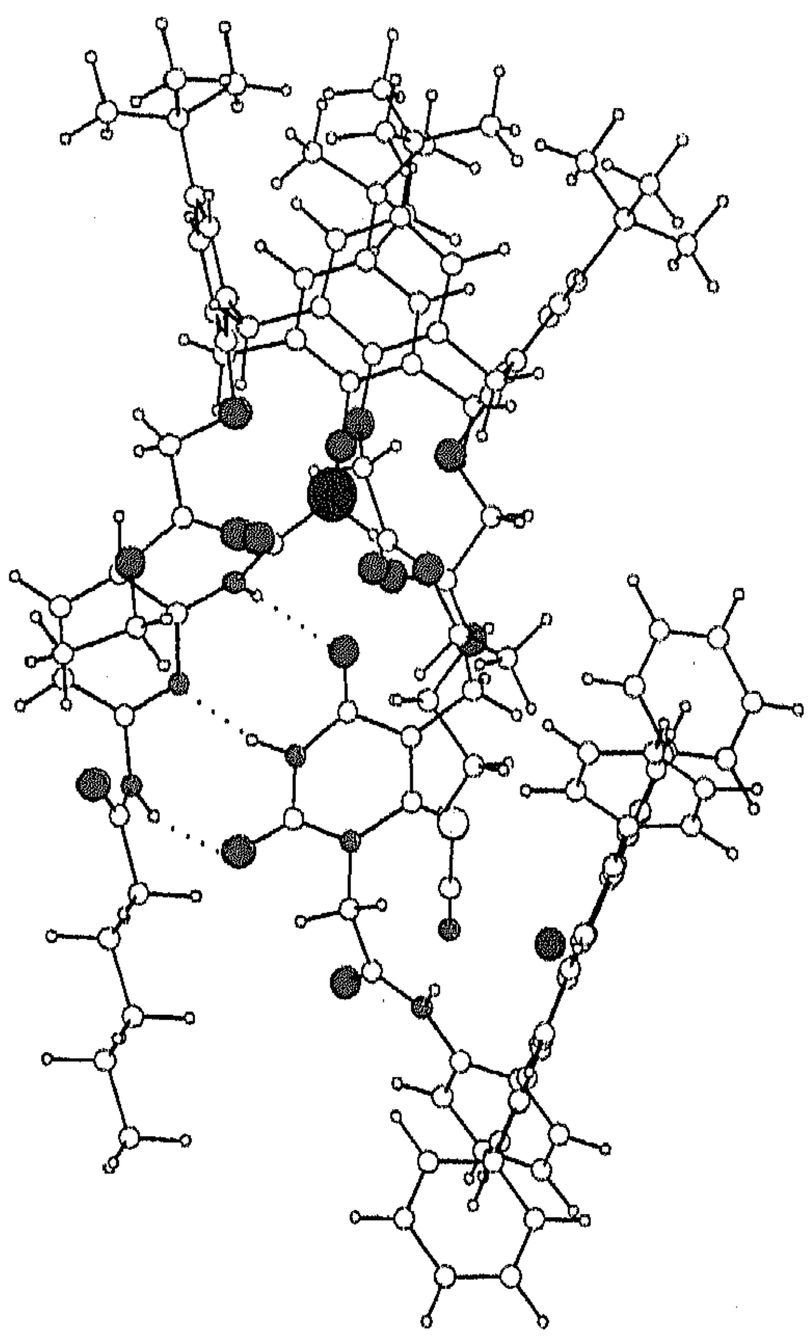


Fig. 3. Energy-minimized structure of the assembly $(1\cdot Na^+)(2\cdot SCN^-)$. Na = green, Zn = violet, S = yellow, O = red, N = blue, C,H = white.

tion of the individual interactions between calix[4]arene **1**, Zn-porphyrin **2**, and the Na^+ and SCN^- ions. The positions of all four components in the complex are fixed in solution by specific ion–dipole interactions and hydrogen bonding. The assembly can be "switched on" by complexation of the Na^+ ion with receptor **1**, and "switched off" by addition of MeOH, which is able to destroy hydrogen bonds.

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[13] Selected data for **1**: M.p. 88–89 °C (MeCN); ^{1}H NMR ([D$_8$]toluene): δ = 9.61, 8.61 (2 br s, 2H, NH), 8.25, 8.12 (2 d, ^3J(H,H) = 8.0 Hz, 2H, diamidopyridine), 7.19 (t, ^3J(H,H) = 8.0 Hz, 1H, diamidopyridine), 6.92, 6.82, 6.69 (3 s, 8H, arom.), 5.12, 4.78 (2 d, ^3J(H,H) = 14.0 Hz, 4H, $CH_2C(O)$), 4.98, 4.72, 3.17, 3.10 (4 d, ^3J(H,H) = 13.0 Hz, 8H, CH_2-calix), 4.78, 4.53 (2 s, 4H, $CH_2C(O)$), 4.9–4.5 (m, 6H, OCH_2), 2.45 (t, ^3J(H,H) = 7.5 Hz, 2H, $CH_2C(O)N$), 1.85–1.75, 1.4–1.3 (2 m, 6H, CH_2), 1.15 (s, 18H, *t*Bu), 1.09, 1.03 (2 s, 18H, *t*Bu), 0.91 (t, ^3J(H,H) = 7.2 Hz, 9H, CH_3), 0.80 (t, ^3J(H,H) = 7.5 Hz, 3H, CH_3); FAB-MS (NBA matrix): *m/z*: 1154.4 (M^+, calcd 1154.5). Selected data for **2**: M.p. 253–255 °C; UV/Vis (toluene): λ_{max} = 426 nm; ^{1}H NMR ([D$_8$]toluene): δ = 9.06 (d, ^3J(H,H) = 8.0 Hz, 1H, arom.), 8.98 (s, 4H, porphyrin), 8.88, 8.67 (2 d, ^3J(H,H) = 4.8 Hz, 4H, porphyrin), 8.3–8.0 (m, 8H, arom.), 7.80 (d, ^3J(H,H) = 8.0 Hz, 1H, arom.), 7.6–7.4 (m, 10H, arom. + NH), 7.09 (t, ^3J(H,H) = 7.2 Hz, 1H, arom.), 5.30 (s, 1H, thymine), 2.70 (s, 2H, $NCH_2C(O)$), 2.01 (s, 3H, CH_3); FAB-MS (NBA matrix): *m/z*: 859.1 (M^+, calcd 859.3). NBA = nitrobenzyl alcohol.

[14] All K_{ass} values were obtained at 293 K using a constant concentration of the $(1\cdot Na^+)$ complex of 1.00 mM and a varying concentration of a guest of 0.25–5.00 mM. The values were calculated by nonlinear regression according to the procedure described in: J. A. A. de Boer, D. N. Reinhoudt, S. Harkema, G. J. van Hummel, F. de Jong, *J. Am. Chem. Soc.* **1982**, *104*, 4073–4076. The estimated error is 5%.

[15] The complex $(1\cdot Na^+)I^-$ appeared to be very light-sensitive and decomposed upon titration.

[16] A similar phenomenon has recently been reported, see: H. Murakami, S. Shinkai, *J. Chem. Soc. Chem. Commun.* **1993**, 1533–1535.

[17] Porphyrin **2** complexes F^- ions (as the tetrabutylammonium salt) very strongly; a K_{ass} value of 2.3×10^4 mol^{-1} in toluene was calculated. Since the complex $(1\cdot Na^+)F^-$ could not be obtained, a toluene solution of the complex $(1\cdot Na^+)(2\cdot ClO_4^-)$ was titrated (UV/Vis, ^{1}H NMR) with $Bu_4N^+F^-$. Despite the very strong interaction ($K_{ass} \approx 3.0\times10^4$ mol^{-1}) initially detected, fast precipitation of NaF from the toluene solution followed, which prevented further assembly .

[18] K. A. Connors, *Binding Constants*, Wiley, New York, **1987**, p. 24.

[19] ^{1}H NMR spectrum of $(1\cdot Na^+)/2\cdot SCN^-)\cdot$([D$_8$]toluene): δ = 10.29, 10.18 (2 br s, 2H, NH), 8.99 (s, 4H, porphyrin), 8.95, 8.26 (2 d, ^3J(H,H) = 8.0 Hz, 2H, arom.), 8.83 (q, ^3J(H,H) = 4.8 Hz, 4H, porphyrin), 8.50 (d, ^3J(H,H) = 8.0 Hz, 2H, arom.), 8.2–8.0, 7.8–7.5 (2 m, 18H, arom. + NH), 7.38 (t, ^3J(H,H) = 8.0 Hz, 1H, arom.), 7.25, 7.17 (2 s, 8H, arom.), 5.60 (s, 1H, thymine), 4.60, 4.22 (2 s, 4H, $CH_2C(O)$), 4.55, 4.49, 3.30, 3.25 (4 d, ^3J(H,H) = 13.0 Hz, 8H, CH_2-calix), 4.38, 4.11 (2 d, ^3J(H,H) = 14.0 Hz, 4H, $CH_2C(O)$), 4.0–3.8 (m, 6H, OCH_2), 3.28 (s, 2H, $NCH_2C(O)$), 2.53 (t, ^3J(H,H) = 7.5 Hz, 2H, $CH_2C(O)N$), 2.01 (s, 3H, CH_3), 1.85–1.75, 1.4–1.1 (2 m, 6H, CH_2), 1.21 (s, 36H, *t*Bu), 1.03, 1.00 (2 t, ^3J(H,H) = 7.2 Hz, ^3J(H,H) = 7.5 Hz, 6H, CH_3), 0.80 (t, ^3J(H,H) = 7.2 Hz, 6H, CH_3).

[20] The proposed structures were additionally confirmed by molecular mechanics calculations performed with Quanta/CHARMm Version 3.3. Energy minimizations (conjugate gradient) were carried out (Steepest Descents followed by Adopted Based Newton Raphson) until the root mean square of the gradient was less than 0.01 kcal mol^{-1} Å^{-1}.

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