A Cyclodextrin–Porphyrin Assembly as Chemosensor for Pentachlorophenol

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A quantitative change in the absorption profile of the assembly prepared from the torus-shaped 2-hydroxypropyl-cycloheptaamylose (hp-β-cyclodextrin, hp-β-CD) and planar porphyrin 4,4′,4″,4‴-(21*H*,23*H*-porphine-5,10,15,20-tetrayl)tetrakis(benzoic acid) (POR) occurs highly selectively in response to a guest–host complexation of pentachlorophenol.

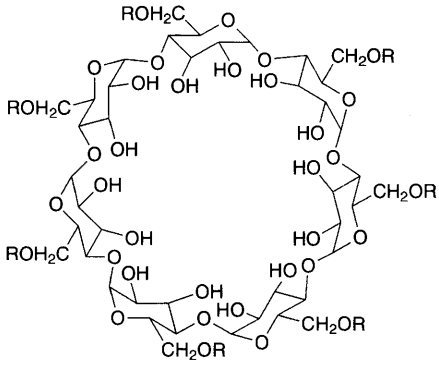
Development of spectrometric chemosensors able to recognize specific molecules is of importance for the quantification of target analytes in complex matrices.[1] In contrast to chemical derivatization commonly applied in spectrophotometric measurements of organic compounds to enhance both selectivity and sensitivity, the chemosensing approach is substantially less time-demanding and does not involve laborious procedures. In particular, a chemosensor is selective to the overall chemical structure of an analyte molecule rather than to only a specific functional group. For the measurement of small organic compounds, development of new chemosensing mechanisms is required and has attracted much recent attention.[2–5] We have designed and examined a novel chemosensing approach for the detection of pentachlorophenol (PCP), one of the most widespread recalcitrants in the environment. A cap-shaped molecular assembly prepared from the torus-shaped 2-hydroxypropyl-cycloheptaamylose (hp-β-CD) and planar 4,4′,4″,4‴-(21*H*,23*H*-porphine-5,10,15,20-tetrayl)tetrakis-(benzoic acid) (POR) was observed to exhibit an intense absorption peak at 420.5 nm, a feature inherited from porphyrin. A quantitative change in the absorption profile of the assembly occurred highly selectively in response to a guest–host complexation of PCP. Besides its inclusion into the hydrophobic cyclodextrin cavity of the assembly, PCP, to a certain extent, was conjugated with the chromogenic porphyrin moiety. Based on the experimental data, this study suggests a dual condition model for selectivity of recognition by the assembly. The first and necessary condition requires an inclusion of a target analyte inside the hydrophobic cavity of the assembly and a conjugation of the analyte to porphyrin fulfils the second and sufficient condition.

Hp-β-CD possesses a torus-shaped structure whose two edges are open with hydroxy groups on one and hydroxypropyl groups on the other (Fig. 1). Like its unmodified β-CD parent, hp-β-CD consists of seven glucopyranose units which are linked by α-(1–4) bonds. The open structure of hp-β-CD will form a semi-closed structure by closing one of the cavity edges with a 'cap' molecule, POR. POR is considered as a potential cap molecule since it consists of a planar porphyrin ring with four benzoxy groups on its edge (Fig. 1). On the formation of the cap-shaped assembly (Fig. 2 **A**), a POR molecule is assembled to hp-β-CD on the edge with the hydroxypropyl groups through hydrogen bonding between the four carboxylic groups of POR and the hydroxy groups of hp-β-CD, introducing an intense chromogenic component to the non-absorptive host molecule. The formation of hydrogen bonds between POR and hp-β-CD and the structure of the cap-shaped assembly were recently confirmed by NMR and UV–VIS spectrophotometry in our laboratory.[6]

A schematic sensing mechanism of the assembly is depicted in Fig. 2 **B**. The interior of the assembly is a hydrophobic cavity of high electron density, a distinct characteristic inherited from hp-β-CD. Although a variety of hydrophobic guest molecules with an appropriate size can be included into this cavity to form inclusion complexes, spectral changes will occur only when the guest molecule is conjugated to a certain extent with the POR moiety. The PCP molecule consists of two principal parts which fulfil this dual condition. The pentachlorinated benzene ring (*ca.* 5.8 Å) is a highly hydrophobic entity which can fit perfectly into the hp-β-CD cavity of the assembly (6.2 Å in diameter, 7.9 Å in depth) to form a water-soluble inclusion complex. Simultaneously, the hydroxy on the benzene ring is able to enter the central area of the porphyrin cycle and form hydrogen bonds with the porphyrin nitrogen. The interaction of the PCP hydroxy group with the porphyrin ring is expected to result in changes in the absorption characteristics of the assembly.

The spectra of the hp-β-CD–POR assembly and its PCP inclusion complex at pH 3.5 are shown in Fig. 3. At this pH, POR is protonated and shows a weak absorption in the VIS region [Fig. 3(*a*)] whereas the dissociated form of POR exhibits an intense absorption at 414 nm. The formation of its highly stable assembly[6] with hp-β-CD (formation constant *ca.* 6.9×10^5 dm^3 mol^{-1}) results in an intense characteristic absorption maximum at 420.5 nm [Fig. 3(*b*)]. Upon addition of PCP, the absorption spectrum of the assembly shifts to a longer wavelength with reduced absorption intensity [Fig. 3(*c–e*)]. The relationship of both spectral shift and absorption change to the PCP concentration is quantitative. Because of the high absorption coefficient of the assembly (3.1×10^5 dm^3 mol^{-1} cm^{-1}), changes in its spectrum caused by the inclusion of PCP provide a high sensitivity for the measurement of PCP.

To ascertain the selectivity of the sensing assembly for PCP, we have examined the spectral response of the assembly to all chlorophenols (tetra-, tri-, di- and mono-chlorophenols), benzene and its derivatives (toluene, xylene), polychlorinated benzenes (pentachlorobenzene and 2,3,5,6-tetrachlorobenz-



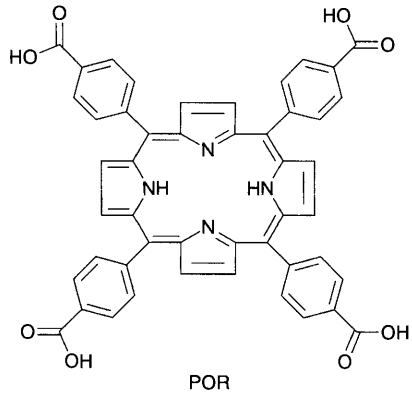


Fig. 1 The chemical structures of hp-β-CD and POR

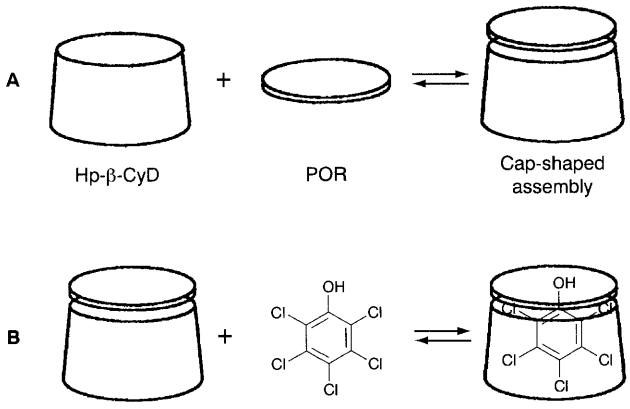


Fig. 2 Schematics of the formation of the hp-β-CD–POR assembly and the PCP assembly complex. The angular spacing of the seven hydroxypropyl groups on hp-β-CD is 51.4°, while that of the carboxy groups on POR is 90°. Because of their flexibility, the hydroxy groups on hp-β-CD are able to adjust their positions towards and approach the carboxyl groups on POR. NMR data[6] show that two of the carboxyl groups are at an angle different from that of the other two relative to the hydroxy groups with which they form hydrogen bonds. Therefore, the porphyrin cycle might not be perfectly centralized atop hp-β-CD. The orientation of PCP inside the assembly is based on the following convincing observations: (i) PCP does not affect the absorption spectrum of free POR; and (ii) similar to PCP, pentachlorobenzene has a strong affinity to the CD cavity but does not exhibit the characteristic effect on the absorption spectrum of the assembly.

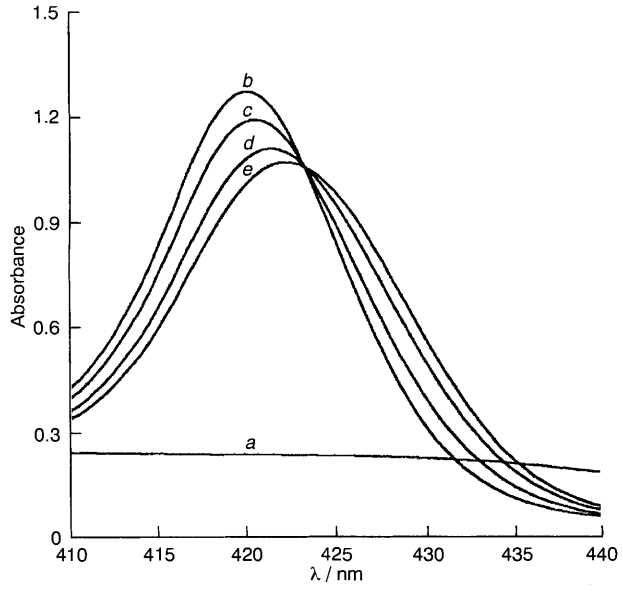


Fig. 3 Spectra of the hp-β-CD–POR assembly and the PCP assembly complex. Buffer solution: pH 3.5, 0.1 mol dm^{-3} potassium phosphate. (*a*) 5 μmol dm^{-3} POR, (*b*) 0.5 mmol dm^{-3} hp-β-CD; (*c*) 10 μmol dm^{-3}; (*d*) 30 μmol dm^{-3} and (*e*) 50 μmol dm^{-3} PCP added. The formation of the hp-β-CD–POR assembly at pH 3.5 requires about 15 min to reach equilibrium. However, the inclusion of PCP into the assembly cavity is effected instantaneously.

ene), 2,3,5,6-tetrachloroaniline, 2,3,5,6-tetrachloropyridinethiol and polynuclear aromatic hydrocarbons (naphthalene, anthracene, pyrene). Only 2,3,5,6-tetrachlorophenol was observed to exhibit the characteristic absorption shift shown in Fig. 3. However, the response sensitivity of 2,3,5,6-tetrachlorophenol was only about one fifth of that of PCP. Neither poorly polarized chlorophenols with low chlorination nor highly chlorinated benzenes without a phenolic hydroxy group gave a response to the chemosensing assembly (Fig. 4), although they all form inclusion complexes with the CD component of the assembly.[7] These observations for PCP selectivity thus verify

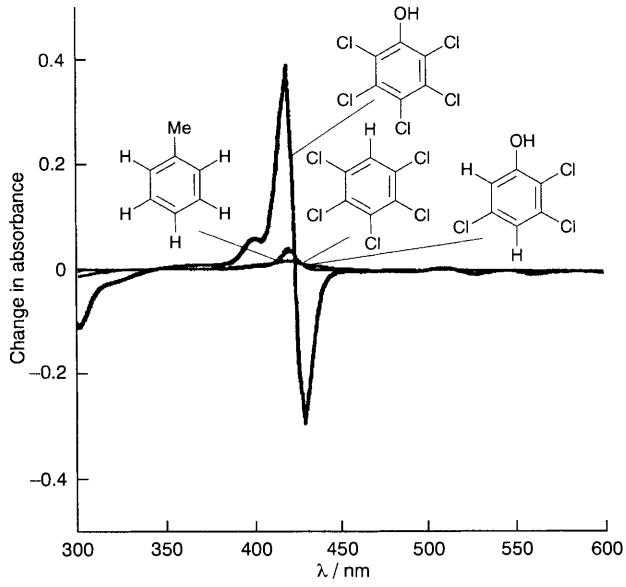


Fig. 4 Differential spectra of the hp-β-CD–POR assembly upon the addition of PCP, pentachlorobenzene, 2,3,5-trichlorophenol and toluene. Buffer solution: pH 3.5, 0.1 mol dm^{-3} potassium phosphate, 5 μmol dm^{-3} POR and 0.5 mmol dm^{-3} hp-β-CD. The differential spectra were obtained by subtracting the final spectrum from that before addition of 40 μmol dm^{-3} of each analyte.

the foregoing concept of the dual condition in the design of the chemosensor. A target analyte will only be recognized if it can be included into the CD cavity and at the same time it forms hydrogen bonds with the porphyrin moiety. In addition, the spectral response that signals the interaction between the prophyrin cycle and the guest molecule further depends on the strength of the hydrogen bond between the hydroxy group and the nitrogen and, in turn, the polarity of the hydroxy group.[8]

In principle, α-, β- and γ-CDs with different cavity sizes and their derivatives are all suitable for the formation of cap-shaped assemblies with POR and other planar large chromogenic molecules, *e.g.* crown ethers. If necessary, new interaction properties and sensing selectivity could also be created by introducing small species such as metal ions into the structure of the porphyrin or crown ether cycles. For the detection of a particular analyte, it is of paramount importance to select an appropriate cap molecule which is responsive to the functional group of the analyte, provided this compound can fit into the hydrophobic cavity of the assembly to fulfil the dual condition suggested. This communication, it is hoped, has called attention to the great need for future endeavours in fundamental research in cyclodextrin chemistry and chemosensing mechanisms for the development of a new class of sensing device.

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