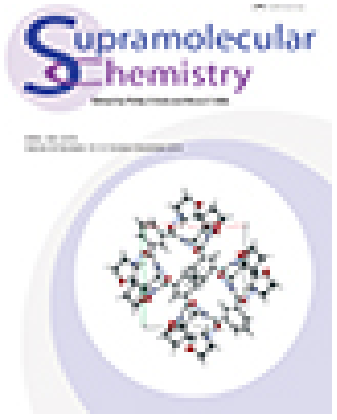

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Highly sensitive detection of mercury (II) in aqueous media by tetraphenylporphyrin with a metal ion receptor

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We provide a highly sensitive and selective assay to detect Hg^{2+} in aqueous solutions using a novel β-functionalised porphyrin-based chemosensor 5 at room temperature. The binding properties of the chemosensor 5 for cations were examined by UV–vis spectroscopy and ^{1}H NMR. The results indicate that a 1:1 stoichiometric complex is formed between chemosensor 5 and mercury (II) ion. The recognition mechanism between chemosensor 5 and metal ion was discussed based on their absorbance changes and the chemical shift changes when they interact with each other. Control experiments revealed that chemosensor 5 has a selective response to mercury (II) ion compared with other metal ions.

Keywords: porphyrin; chemosensor; mercury; relaxivity

Introduction

The design of artificial chemosensors for selective and sensitive quantification of biologically and environmentally important ion species, especially transition-metal ions, has attracted wide-spread interests of chemists, biologists, clinical biochemists and environmentalists in recent years. Because of their advantages of simple instrumentation, high sensitivity and facile analysis, many efficient chemosensors for transition-metal ions have been developed during the last two decades (*1–6*).

Magnetic resonance imaging (MRI) is one of the most popular diagnostic techniques used in clinic, and allows imaging of the body in a non-invasive manner (*7*, *8*). Exploiting the differences in longitudinal or transverse relaxation times (T_1 or T_2) among different tissues, MRI provides not only morphological, but also physiological and functional information about the subject being imaged (*9*). Currently, about one-third of the clinical MRI scans are accompanied by administration of a contrast agent (*10*). Gadolinium and manganese complexes are widely used as MRI contrast agents. Porphyrins are a unique class of metal chelating agents which may chelate paramagnetic metal.

Chemosensors that can highly sensitively and selectively detect transition metal ions such as Zn^{2+}, Cu^{2+}, Ni^{2+} and Hg^{2+} are especially important (*11–15*). To illustrate the invoked strategy, Hg^{2+} was chosen as the target guest for optimising the complementary structural characteristics of the β-porphyrin-based chemosensor. Mercury is considered as a prevalent toxic metal in the environment because both elemental and ionic mercury can be converted by bacteria in the environment to methyl mercury, which subsequently bioaccumulates through the food chain (*16–18*). When absorbed in the human body, mercury causes damage to the central nervous, DNA, mitosis, and endocrine system (*19–21*). As a result, developing new and practical multisignalling chemosensors for Hg^{2+} is still a challenge (*22–26*).

Among all well-explored molecular sensor scaffolds, porphyrins stand out elegantly as a judicious choice in this particular application (*27–29*). The covalent or non-covalent binding motifs bearing the porphyrin scaffold have gained importance in view of the crucial role of porphyrin assemblies in biological pigment systems. On the one hand, porphyrin scaffold offer an access to a variety of functionalisation possibilities. On the other hand, the intriguing photophysical properties associated with porphyrins warrant their exploitations in colorimetric sensing. As a result, we have witnessed in recent years that numerous designs of porphyrin-based chemosensors have been known for the detection of cations, anions and biologically relevant small organic molecules. For instance, Chan et al. (*30*) reported the development of 5,10,15,20-tetraphenylporphyrin (TPP) as a mercury ion-selective optical sensor, while Luo et al. (*31*) exploited porphyrin-appended terpyridine as a chemosensor for cadmium. To expedite the synthesis, most porphyrin-based sensory materials were assembled invariantly with four phenyl moieties incorporated into the C-5, 10, 15, 20 of the host (*30–35*). Discriminative introduction of different phenyl moieties onto the meso-positions of a porphyrin

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structure framework not only suffers from its poor efficiency but also requires extensive purification efforts to fish out the desired precursor for the subsequent sensor assemble. In contrast, direct preparation of symmetrical tetra-meso-arylated porphyrins is a simple synthetic preparation; however, the resultant host may contain too many functionalities which could distract the subsequent sensor design. A seemingly neglected alternative approach by selective functionalisation warrants attention in the arena of sensor development. As demonstrated by us and others, symmetrical TPP can be functionalised at the β-pyrrolic carbon of the porphyrin with high selectivity and diverse variants (*36–38*). In this context, we have recently reported a novel dicarboxylate receptor based on a β-pyrrolic functionalisation strategy (*39*). To our knowledge, there is scarce literature known on porphyrin-based chemosensor development involving the appendage of receptive sites at its β-pyrrolic carbons. In response to this challenge, we describe the design and construction of a porphyrin-based chemosensor by appending binding site via the β-pyrrolic functionalisation strategy (Figure 1), utilising a metal centre of the manganese porphyrin host as the paramagnetic centre in this report.

Experimental

Ethyl 2-(5-methyl-2-phenoxymethylcarboxylate)-5,10,15,20-tetraphenylporphyrin (3)

This compound was prepared according to the published procedure (*39*).

2-(5-Methyl-2-phenoxymethylcarboxy-(2,2′-(ethane-1,2-diylbis(oxy))dianiline))-5,10,15,20-tetraphenylporphyrin (4)

Compound 3 (100 mg) in THF (25 ml) was stirred and refluxed with aqueous NaOH solution (3 M, 10 ml) for 5 h. The reaction mixture was extracted with $CHCl_3$ (3 × 20 ml). The combined organic layers were washed with saturated brine solution and distilled water successively, and then dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure, and the residue was then subjected to column chromatography over silica gel, using $CHCl_3$–CH_3OH (100:2) as the eluent. The organic solution of the desired fractions was combined, condensed and the pH adjusted to 4 by diluted HCl solution. The organic layer was collected, dried and evaporated to

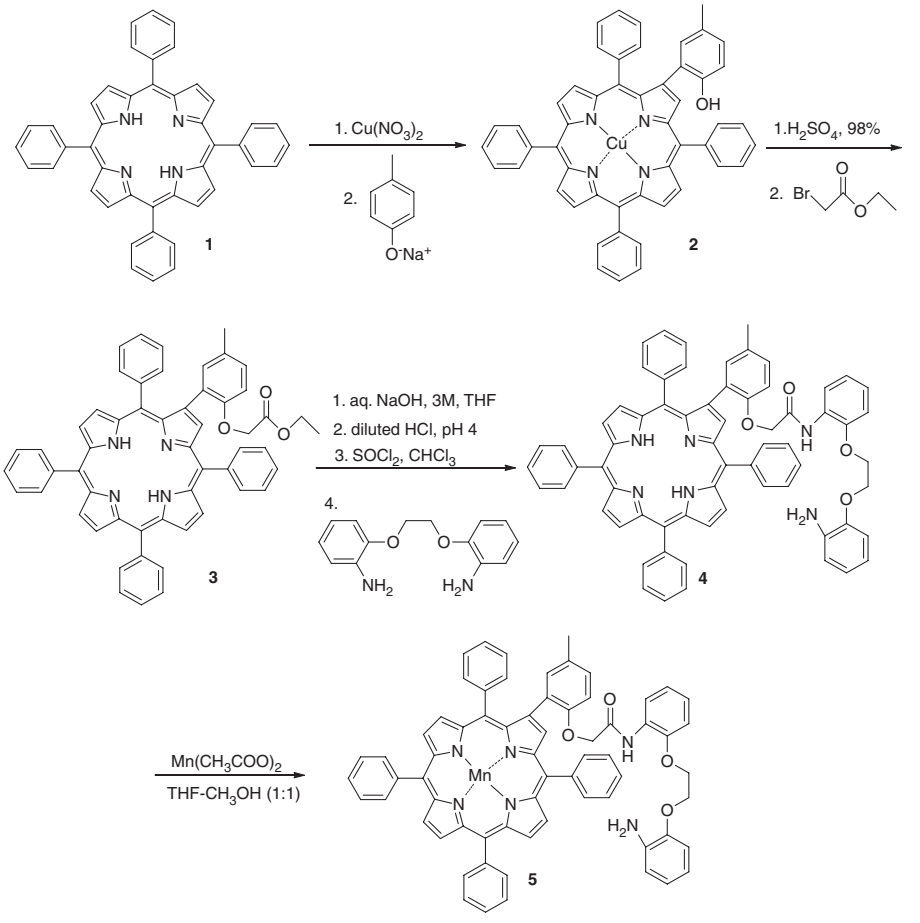


Figure 1. Synthetic route for chemosensor 5.

dryness to afford the free porphyrin as a solid. The solid was dissolved in dried $CHCl_3$ (30 ml) and refluxed with excess $SOCl_2$ for 3 h, then evaporated to dryness. The residue was dissolved in dried $CHCl_3$ (30 ml), then refluxed with 2,2′-(ethane-1,2-diylbis(oxy)) dianiline (35 mg) and dried Et_3N (1 ml) under N_2 protected from light for 7 h. The solvent was removed under reduced pressure, and the residue was then subjected to column chromatography over silica gel, using CH_2Cl_2–CH_3OH (100:2) as the eluent. The pure product was recrystallised from CH_2Cl_2–hexane to afford compound 4 (75 mg, 60%). ^{1}H NMR (500 MHz; $CDCl_3$) δ: 8.80–8.86 (m, 5H, 3-H, 7-H, 8-H, 17-H, and 18-H), 8.72–8.73 (d, $J = 4.5$ Hz, 1H, 12-H), 8.63–8.64 (d, $J = 4.5$ Hz, 1H, 13-H), 8.23–8.25 (m, 6H, 5-, 10- and 15-H_o), 8.04 (s, 1H, 20-H_o), 7.70–7.83 (m, 13-H, 5-, 10-, 15-$H_{m,p}$, and amide-$H_{o,m,p}$), 7.11 (s, 1H, 6′-H), 6.82–6.90 (m, 4H, aniline-Ho, m, p), 6.73–6.74 (dd, $J = 8.5$ Hz, 1H, 4′-H), 6.43–6.44 (d, $J = 8.5$ Hz, 1H, 3′H), 4.37 (br s, 2H, NH_2), 4.30 (s, 2H, CH_2), 3.84–3.93 (ABq, $J = 3.6$ Hz, 4H, CH_2), 2.26 (s, 3H, CH_3), −2.63 (br s, 2H, NH inner). MS (ESI) calcd for $C_{67}H_{52}N_6O_4$ $(M + 1)^+$requires 1005, found 1027 $(M + Na^+)$.

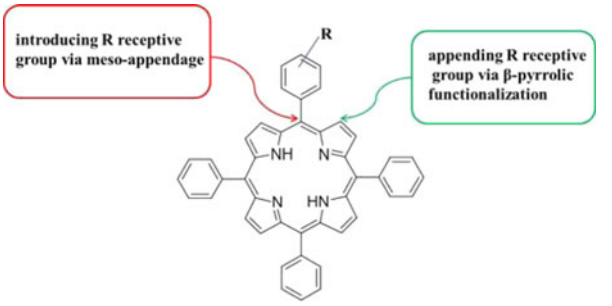
(2-(5-Methyl-2-phenoxymethylcarboxy-(2,2′-(ethane-1,2-diylbis(oxy))dianiline))-5,10,15,20-tetraphenylporphyrinato)Mn(II) (5)

Compound 4 (36.5 mg) was dissolved in THF–CH_3OH (1:1) and refluxed with excess $Mn(CH_3COO)_2{\cdot}4H_2O$ for 3 h. The mixture was washed with distilled water, and then dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure, and the residue was then recrystallised from $CHCl_3$–hexane to afford compound 5 (31 mg, 80%) as a purple solid. HR-MS (ESI) calcd for $C_{67}H_{50}N_6O_4Mn$ $(M + 1)^+$ requires 1057.3274, found 1057.3180.

Results and discussion

Porphyrin receptor synthesis

The readily accessible TPP was chosen as the starting material for building up chemosensor 5 (Scheme 1). Employing the synthetic protocol developed by us, the β-pyrrolicfunctionalised 2-substituted cresol Cu porphyrin 2 was obtained in about 50% overall yield from TPP (*36*). Demetallation of 2 by treatment with concentrated sulphuric acid followed by alkylating the appended phenol with ethyl bromoacetate and potassium carbonate gave rise to the corresponding ethyl ester 3 in 40% yield. Liberation of the free carboxylic acid was achieved by base hydrolysis and subsequent careful acidification with dilute hydrochloric acid. The 2,2′-(ethane-1,2-diylbis(oxy))dianiline could interact with many metal ions (*40*), which was combined to the porphyrin as the binding site by amide condensation reaction. Insertion of manganese metal to make the paramagnetic centre was achieved by refluxing the metal-free β-substituted porphyrin with manganese acetate in 1:1 methanol–THF for 3 h, affording chemosensor 5 in 80% overall yield.



Scheme 1. (Colour online) Meso-appendage versus β-pyrrolic functionalisation strategy to assemble the porphyrin framework for the chemosensor design.

In the present study, we have successfully designed a porphyrin-based optical chemosensor for detection of transition metal ions. On the other hand, the paramagnetic centre of the Mn(II)–porphyrin may suggest a way to use the chemosensor as a contrast agent in biological environment.

Binding characteristics of chemosensor 5

The binding of the Zn^{2+}, Cu^{2+}, Ni^{2+} and Hg^{2+} to the newly synthesised chemosensor 5 was examined by UV–vis absorption spectral method. The UV–vis absorption titration binding experiments were performed at room temperature. As shown in Figure 2, an obvious absorption of chemosensor 5 appeared at 378, 405, 480, 584 and 621 nm, respectively, in toluene solution, and all of those absorption intensities changed gradually with an increase of metal ion concentration.

At the end of the UV–vis titration, obvious blue shifts of the absorption bands can be observed, and all of the absorption intensities of the bands were increased except the absorption band at 480 nm, which was the most typical absorption band of the porphyrin-based compound chemosensor 5 named soret band. The changes of the soret band around 480 nm decreased at first and then blue shifted to about 475 nm and increased gradually with the metal ions concentration increasing, as shown in Figure 3.

Through the UV–vis titration experiments, blue shifts of 4, 4, 4 and 5 nm for the soret band were found when Zn^{2+}, Cu^{2+}, Ni^{2+} and Hg^{2+} were introduced with the concentration change from 1.67×10^{-6} mol/l to 4.17×10^{-5} mol/l, respectively. New soret bands appeared at 476, 476, 476 and 475 nm at the end of the UV–vis titrations between chemosensor 5 and Zn^{2+}, Cu^{2+}, Ni^{2+} and Hg^{2+}. Two clear isosbestic points (around 479 nm and

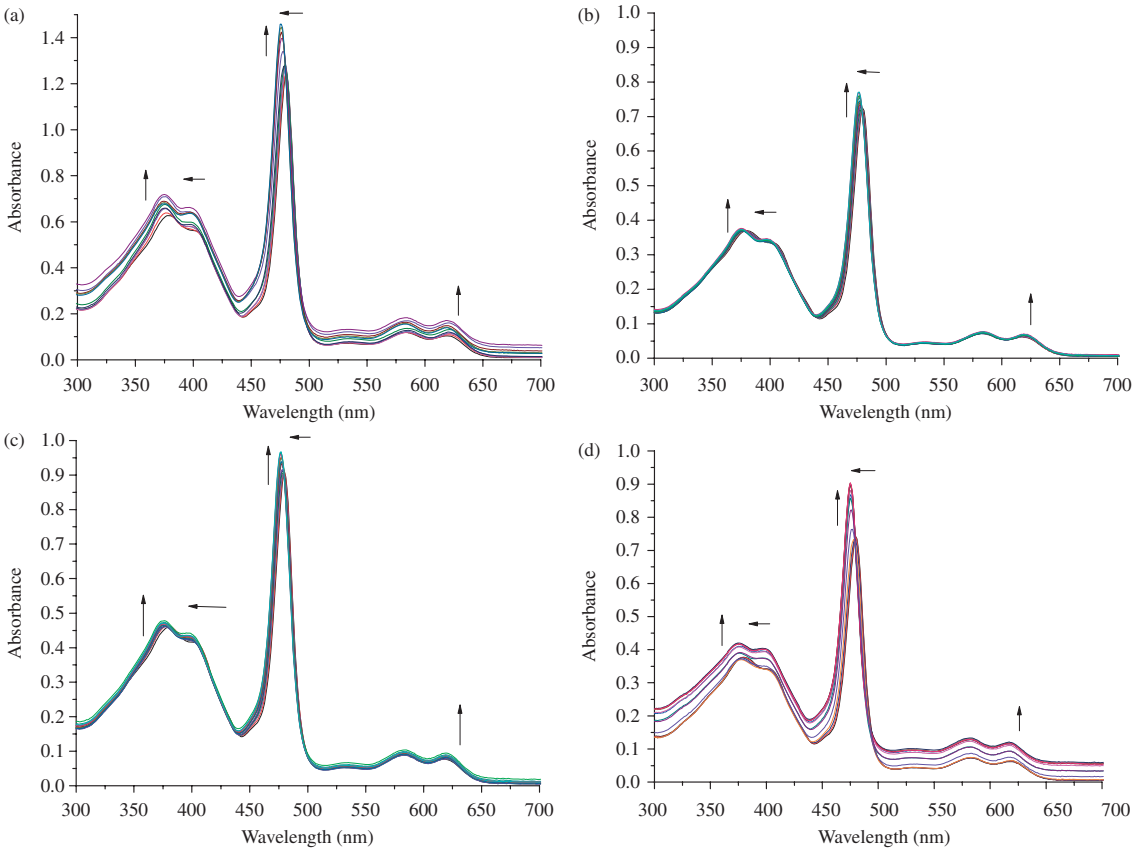


Figure 2. (Colour online) UV absorbance spectra of chemosensor 5 (6.0×10^{-6} mol/l) upon the addition of various amounts of (a) Zn^{2+}, (b) Cu^{2+}, (c) Ni^{2+} and (d) Hg^{2+}.

493 nm) were observed, which is indicative of the existence of two states through the formation of a 1:1 complex.

When the chemosensor 5 binds with the metal ions, the electron cloud of the porphyrin ring should be moved towards the metal ions. As a result, the electron density of the porphyrin ring should be decreased, which causes the absorbance intensity at 480 nm to decrease at first. When the concentration of the metal ions increased continually, the configuration of the dianiline moiety of the chemosensor 5 may be changed to bind the metal ion more stably, which turned the terminal phenyl groups of the dianiline moiety more closely to the porphyrin ring. As a result, a possible $\pi-\pi$ conjugation took place between the phenyl group and the porphyrin ring, which turned the conjugated system larger. So the electron density of the conjugated-system in the chemosensor 5 increased and the chromophore became larger, which could explain the reason of the absorbance intensity of the chemosensor 5 at about 475 nm increased to build a new soret band of it in certain degree. The rigidity of the molecule of chemosensor 5 could be enhanced by the configuration change, and as a result, the binding between chemosensor 5 and metal ions would be more stable.

To study the binding rate of the chemosensor 5 towards Zn^{2+}, Cu^{2+}, Ni^{2+} and Hg^{2+}, the different hyperchromicities and slopes of soret band of the chemosensor 5 were investigated, shown in Table 1.

The UV–vis absorbance changes of chemosensor 5 showed that chemosensor 5 can interact with Zn^{2+}, Cu^{2+}, Ni^{2+} and Hg^{2+} in the solution. As summarised in Table 1, Hg^{2+} made 34.2% hyperchromicity of the soret band of chemosensor 5, which was larger than the Zn^{2+}, Cu^{2+} and Ni^{2+} made. When investigated the slope of the absorption increasing, the slope Hg^{2+} leading to was 15251.3, while the Zn^{2+}, Cu^{2+} and Ni^{2+} caused were 5143.9, 8687.0, 5808.3 respectively, which were much smaller than Hg^{2+} caused. This result indicated the binding between chemosensor 5 and Hg^{2+} in the solution was stronger and faster than the Zn^{2+}, Cu^{2+} and Ni^{2+}, which suggested the selectivity of chemosensor 5 towards these metal ions.

Binding mechanism and molecular structure change certification of chemosensor 5

Since the chemosensor 5 contained Mn(II) in the molecule, which was paramagnetic, compound 4 was chosen for

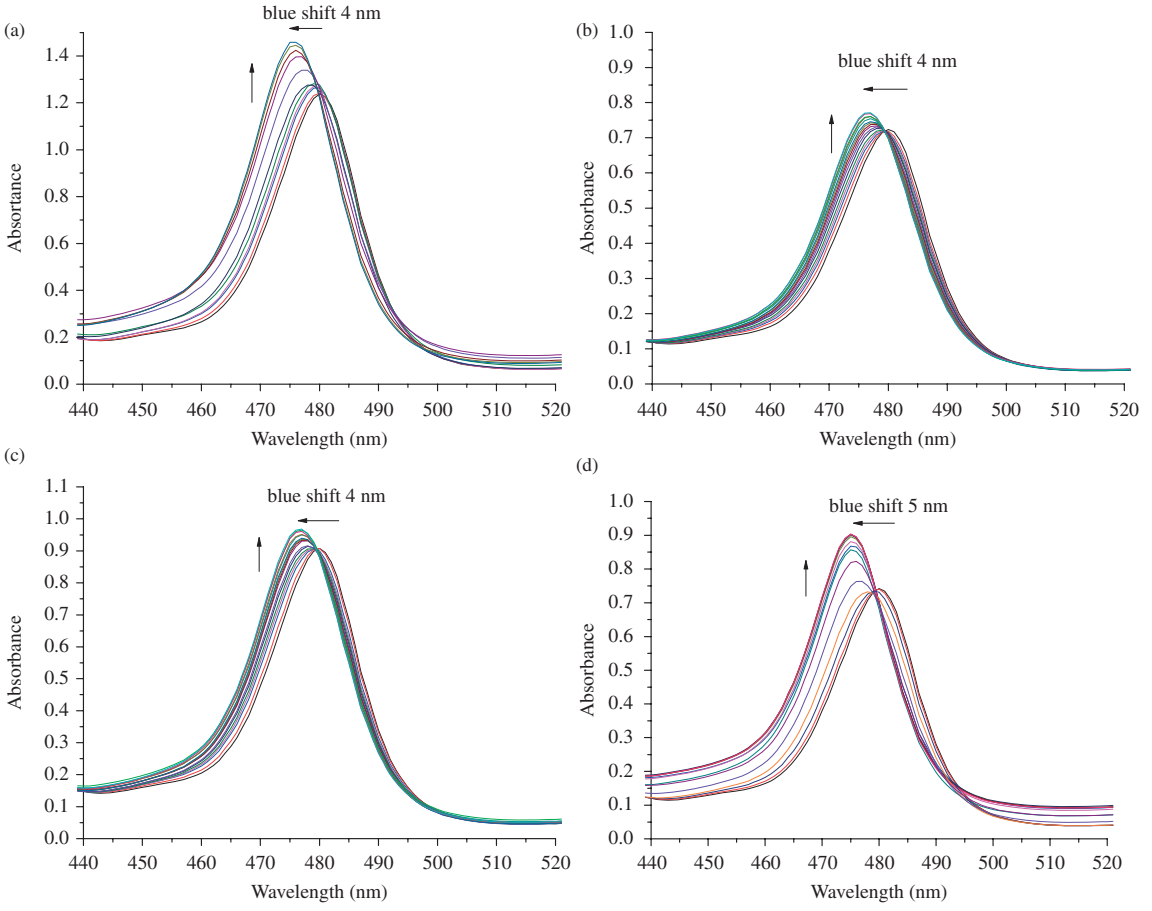


Figure 3. (Colour online) UV absorbance spectra of the soret band of chemosensor 5 (6.0×10^{-6} mol/l) upon the addition of various amounts of (a) Zn^{2+}, (b) Cu^{2+}, (c) Ni^{2+} and (d) Hg^{2+}.

^{1}H NMR experiment to check the binding site and the molecular structure change instead. As shown in the ^{1}H NMR spectra of Figure 4(a,b), treatment of 1 equivalent of Hg^{2+} resulted in a slight upfield shift of ether-methylene protons by δ 0.1 ppm, and this signal split into two. There was also a slight upfield shift of the phenyl moiety at the terminal dianiline moiety protons by δ 0.2 ppm. When excess Hg^{2+} was added to the solution, no further change of the spectra can be observed. The ^{1}H NMR results suggest that Hg^{2+} coordinated with the amino and the amide of the dianiline forms Hg—N bonding and that O atoms of ethermethylene form Hg—O bonding.

On the basis of the ^{1}H NMR spectroscopy, the plausible binding mechanism of chemosensor 5 in the present system was also schematically depicted in Figure 4. The transformation into folded conformation might be partly attributed to the participation of the N atoms of the dianiline and O atoms of ethermethylene in the complex formation with the guest metal ions. The phenyl moiety at the terminal dianiline moiety maybe $\pi-\pi$ conjugated with one of the meso-phenyl groups, which, on the one hand, can enhance the rigidity of the host and, on the other hand, can increase the electron density of the conjugated system to bind the metal ion more stably.

T_1 *experiment of chemosensor 5*

To investigate whether the chemosensor 5 can be used as a contrast agent, the T_1 experiment was studied at room temperature in the mixed solution that contained 95% Acetone-d6 and 5% H_2O at 500 MHz. The results are given in Table 2.

When calculated by the data given in Table 2, the relaxivity (R) of chemosensor 5 was fitted by the linear equation.

Table 1. Compared date of the interaction of Zn^{2+}, Cu^{2+}, Ni^{2+} and Hg^{2+} with chemosensor 5.

Metal ion	Hyperchromicity (%)	Blue shift (nm)	Slope
Zn^{2+}	27.1	4	5143.9
Cu^{2+}	26.6	4	8687.0
Ni^{2+}	25.2	4	5808.3
Hg^{2+}	34.2	5	15251.3

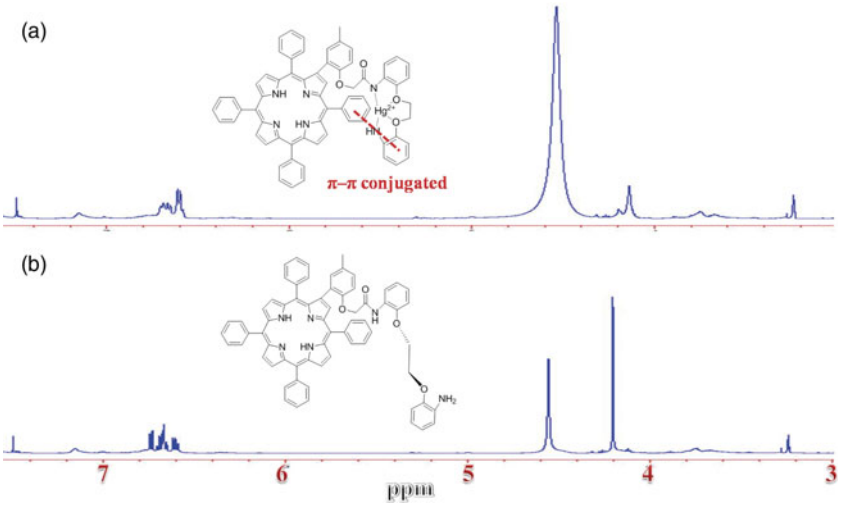


Figure 4. (Colour online) ^{1}H NMR spectra of compound 4 (3×10^{-2} M) (a) and in the presence of Hg^{2+} (b) in $CD_3OD/CDCl_3$ (1:1).

As shown in Figure 5, the relaxivity (R) of chemosensor 5 was 14.06 $mM^{-1} s^{-1}$, and the linearly dependent coefficient square was 0.97018, which was so close to 1 and indicates that the result matched perfectly. These results suggest that the chemosensor 5 had the possible capability to be a contrast agent.

Table 2. The change of the T_1 of the solution upon the addition of various amounts of chemosensor 5.

$C_{chemosensor5}$ (mM)	C_{Mn} (mM)	T_1 (ms)	$1/T_1$ (s^{-1})
0	0	660	1.51515
0.51	0.51	91.93	10.87784
1.02	1.02	44.12	22.66546
2.55	2.55	20.49	48.80429
5.1	5.1	13.04	76.68712

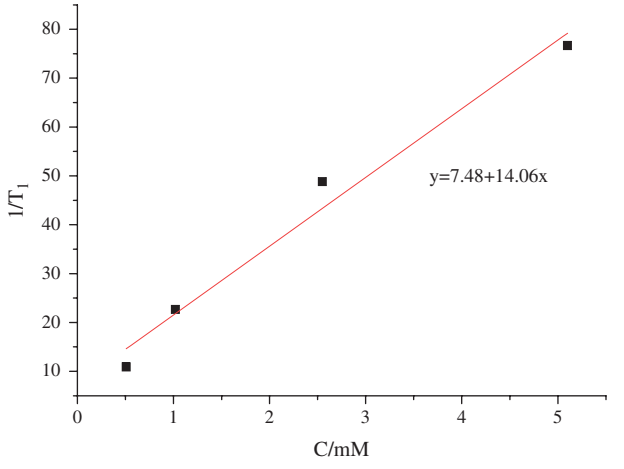


Figure 5. (Colour online) The linear fitting of the relaxivity (R) of chemosensor 5.

Conclusion

In contrast to the traditional meso-functionalisation approach, in this study, we report the expeditious construction of a porphyrin-based chemosensor by incorporating a receptor at its β-pyrrolic carbon. A selective Hg^{2+} chemosensor is efficiently developed. Interestingly, the phenyl moiety at the terminal dianiline moiety may be π−π conjugated with one of the meso-phenyl groups, which, on the one hand, can enhance the rigidity of the host and, on the other hand, can increase the electron density of the conjugated system to bind the metal ion more stably. The chemosensor also showed a good relaxivity, which suggested the possible capability to be a contrasting agent. The strategy is proven to be highly efficient and potentially versatile. In principle, other substituted water-soluble functional groups can be appended on the tetraphenylporphyrin scaffold of the chemosensor at its other three β-pyrrolic positions to improve its solubility in water solution. So it may exhibit its versatile capability to get metal ion resonance image in biological environment, such as *in vivo*. Exploration along this direction in chemosensor development is in progress.

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