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Selective detection of resorcinol using a bis(benzothiazol-2-yl)pyridine based ditopic receptor

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ABSTRACT

1,6-bis(2,6-bis(benzothiazol-2-yl)pyridine-4-yloxy)hexane, ***bbh***, reported here, is the first specific ditopic receptor which selectively recognizes resorcinol among its structurally identical benzene metabolites like phenol, hydroquinone and catechol. Based on this molecule ***bbh***, an easy detection system for monitoring the supramolecular recognition via changes in photoluminescence has been devised and discussed. Host guest binding interactions have been characterized using simple spectroscopic techniques viz. UV–visible and NMR spectroscopy, which are in agreement with the details of photoluminescence based detection technique.

1. Introduction

Benzene-1,3-diol, commonly known as resorcinol, is a widely used reagent in manufacturing industries such as rubber, plastics, pharmaceuticals, dyes and cosmetics [1]. Effluents from these industries [2,3], cosmetic creams and lotions [4], oxidative hair dyes [5], tobacco leaves and smoke are major sources of resorcinol which pollute the environment [6–8]. Biological hazards of resorcinol are also well documented in literature. Suppression of thyroid hormone synthesis in human [9–11], induction of chromatid ruptures and exchanges in Chinese hamster ovary cells [12], carcinogenesis in the upper digestive tract induced by tobacco [13] and severe haematological abnormalities due to life time exposure [14] are some serious concerns where resorcinol was found responsible. Even fatal cases of resorcinol poisoning are reported for human fetus [15]. Serious implications of the detrimental effects of resorcinol exposure on human health and the corresponding emergency measures to be adopted have been discussed in a document by World Health Organization (WHO) [16].

Although hazards are well known, not many literatures are available that report simple detection methods for resorcinol. Techniques like inhibition of the chemiluminescence intensity using flow injection system [17], colorimetric method using silver nanoparticles [18], liquid chromatography [19,20], thin-layer chromatography [21], surface plasmon resonance [22] are not free from complicacy. For the reasons like reversible nature of weak binding and high selectivity, supramolecular host guest interactions are beneficial towards guest specific recognition [23–29]. Despite these established advantages, limited literatures are available on guest specific receptors which selectively recognize toxic molecules [30,31]. In fact very few receptors are reported for benzene metabolites even though it is urgent and highly relevant to biological toxicology [32,33]. Chetia et al. reported a synthetic receptor, namely 2,6-bis(benzimidazol-2-yl)pyridine, which recognizes benzene metabolites (phenol, catechol, hydroquinone and resorcinol) in general without selectivity [34]. Though adsorption based resorcinol removal processes have been proposed [35] crucial challenge remained unaddressed on selective detection of resorcinol as the other phenolic compounds hinder the process [36,37].

In this work a simple photoluminescence based resorcinol detection method is reported. A receptor, 1,6-bis(2,6-bis(benzothiazol-2-yl)pyridine-4-yloxy)hexane (***bbh***) (Fig. 1) was synthesized which contains 2,6-bis(benzothiazolyl)pyridine as the binding moiety. To achieve enhanced solubility in common organic

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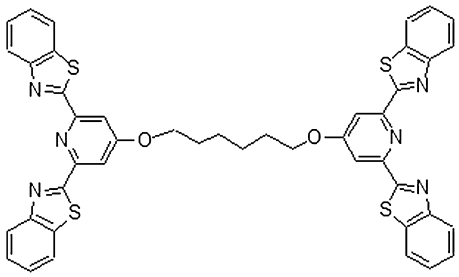

Fig. 1. 1,6-bis(2,6-bis(benzothiazol-2-yl)pyridine-4-yloxy)hexane (***bbh***).

solvents and to obtain greater host to guest ratio we designed the unique ditopic guest system with a flexible hexyl chain as a spacer. This receptor ***bbh*** is capable of recognizing resorcinol (guest) selectively among other benzene metabolites such as phenol, hydroquinone and catechol.

2. Experimental

2.1. Chemicals and solvents

All reagents (reagent grade or superior) were used as received without further purification unless mentioned. All solvents including acetonitrile and chloroform were used after purification.

2.2. Instrumentation

UV–visible spectra were recorded on a Perkin-Elmer Lambda 25 UV–visible spectrophotometer at room temperature. Fluorescence spectra were recorded on a Varian Cary Eclipse Fluorescence spectrophotometer. ^{1}H NMR spectra were obtained with a 400 MHz Varian FT spectrometer. FT-IR spectra were recorded using a Perkin Elmer spectrophotometer with samples prepared as KBr pellets.

2.3. Preparation of receptor ***bbh***

2,6-bis-benzothiazol-2-yl-pyridin-4-ol ligand (2.0 g, 5.5 mM), 1,6-dibromohexane (0.19 mL, 1.26 mM) and Na_2CO_3 (4.1 g) were dissolved in 10 mL solution of DMSO and stirred at 90 °C for 24 h (Scheme mentioned in supporting information). After that the mixture was poured into 200 mL of half-saturated NH_4Cl solution and washed with 100 mL of chloroform. The organics were collected and extracted again from a mixture of water and chloroform. The organics were evaporated and the residue was dried under vacuum. Pure compound was isolated as solid by column chromatography (100:0 $CHCl_3$:MeOH, 97:3 $CHCl_3$:MeOH) with an yield of 68% (0.8 g by weight).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, 4H, J = 8 Hz), 7.88 (s, 4H), 7.36–7.43 (m, 8 H), 4.24 (t, 4H, J = 6.1 Hz), 3.67–3.69 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.89, 151.25, 150.64, 142.66, 137.35, 123.72, 122.99, 120.34, 112.06, 110.10, 68.71, 29.43, 25.85.

IR (KBr) 722, 737, 756, 1241, 1036, 1514, 1591, 1564, 1557, 2993–2830 cm^{-1}.

HR-MS(ESI): 804.1502 Analysis: C, 67.42; H, 4.80; N, 9.53; S, 13.78 λ_{max}: 320 nm.

$\lambda_{Emission\ Max}$: 378 nm (ex. 330 nm).

2.4. Methods

Both UV–visible and photoluminescence studies of ***bbh*** were performed in solution phase using 1:1 (v/v) acetonitrile and chloroform mixed solvent. Concentrations were maintained at 6.67×10^{-5} M for UV–visible studies and at 6.90×10^{-7} M for photoluminescence studies. Same ratio of solvents (1:1, v/v) was maintained for preparation of resorcinol solutions. To monitor the gradual changes in UV–visible absorption and quenching of photoluminescence intensity, solutions of ***bbh*** were titrated with aliquots of resorcinol in increments of 0.1 equivalents each time. NMR titration was also performed in solution phase. Solution of ***bbh***, was prepared using d-acetonitrile/d-chloroform (1:9, v/v) mixed solvent. Gradual changes in NMR spectra of ***bbh*** upon addition of resorcinol were monitored by titrating resorcinol aliquots (in 1:9, v/v d-acetonitrile/d-chloroform) in increments of 0.5 equivalents at a time.

3. Results and discussion

Receptor ***bbh*** was synthesized by simple condensation of 2,6-bis-benzothiazol-2-yl-pyridin-4-ol with 1,6-dibromohexane. 2,6-bisbenzothiazol-2-yl-pyridin-4-ol was prepared by a known Phillips condensation methodology [38,39]. Boca et al. reported characteristic valence vibration of the thiazole ring in 2,6-bis(benzthiazol-2-yl)pyridine ligand was reported at 1514 cm^{-1} [40]. Three other peaks at 719, 737 and 756 cm^{-1} were also assigned (either belongs to deformation vibrations of aromatic rings, out-of-plane vibrations of C–H, or the plane deformation vibrations of the thiazole). Peaks at 1584, 1564 and 1559 cm^{-1} were reported as valence vibration bands of pyridine ring in the same literature. FTIR spectroscopic investigation on ***bbh*** was found to be in agreement with these reported observations. The characteristic peak of valence vibration of thiazole was observed exactly at 1514 cm^{-1} for ***bbh***. Three peaks at 722, 737, and 756 cm^{-1} corresponding to deformation vibrations of aromatic rings, out-of-plane vibrations of C–H, or the plane deformation vibrations of the thiazole ring were also observed. Valance vibrations of pyridine rings were observed at 1591, 1564 and 1557 cm^{-1}. The aryl–O and O–CH_2 stretching bands that should appear at 1240 cm^{-1} and in the range 1050–1010 cm^{-1} [41] were observed at 1241 and 1036 cm^{-1}. Presence of both the significant bands of aryl–O and O–CH_2 together in FTIR spectra establishes the attachment of the hexyl spacer to the 2,6-bis(benzothiazolyl)pyridine binding moiety in ***bbh***. Aliphatic C–H stretching absorption band that normally appear just below 3000 cm^{-1} [42] was prominent on FTIR spectra of ***bbh*** in the range 2993–2830 cm^{-1}. (The FTIR spectra of ***bbh***, is placed in the supporting information).

UV–visible spectroscopy was utilized as a tool to ascertain the binding ability of receptor ***bbh*** towards resorcinol. Gradual changes in UV–visible absorption spectra of ***bbh*** were followed while titrating aliquots of resorcinol in increments of 0.1 equivalents at a time. Absorption maxima of receptor ***bbh***, associated with the π–π^* transition, was observed at 320 nm initially. With gradual increase of resorcinol equivalence, two distinct modifications were observed on the otherwise simple UV–visible spectra. Firstly, the absorbance of the peak at 320 nm started decreasing significantly and secondly a new peak at 282 nm with a shoulder started growing gradually. The absorbance of the new peak picked up a gradual growth and its shoulder finally came up as a distinct peak at 277 nm. Significantly, all individuals of the family of spectra crossed each other on a common point at 287 nm. Presence of such a common point, called an isosbestic point, implies existence of at least one species at equilibrium with the other [43]. This observation implied gradual formation of a ***bbh***-resorcinol supramolecular complex which was at equilibrium with ***bbh.*** A weak interaction between ***bbh*** and resorcinol molecule, like the kind of hydrogen bond, must be responsible for this supramolecular complexation. Another crucial observation was that the change in absorbance of the peak at 320 nm came to a limit while equivalence of resorcinol became double than that of ***bbh***. A plot of absorbance of ***bbh*** at 320 nm against equivalence of resorcinol clarified the results (inset of Fig. 2) and helped to verify