



## A pillar[5]arene-based cyanide sensor bearing on a novel cyanide-induced self-assemble mechanism



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### ABSTRACT

We have designed and synthesized a novel copillar[5]arene-based chemosensor, which employ 8-hydroxyquinoline group as a binding site and signal group. By a novel cyanide-induced self-assemble mechanism, the pillar[5]arene-based chemosensor shown high sensitivity and selectivity for cyanide in aqueous media. When cyanide was added to the solution of the chemosensor, a strong chartreuse fluorescence appeared. The detection limit of the fluorescent spectrum is  $1.08 \times 10^{-8} \text{ mol L}^{-1}$  for cyanide. Moreover, test strips based on the sensor were fabricated, the chemosensor is a good cyanide test kits. In addition, we made life applications of cyanide detected, the chemosensor is also could detect cyanide in aqueous extracts from sprouting potatoes. It is worth mentioning that cyanide-induced self-assemble mechanism is a novel strategy for the design of pillararene based chemosensor. Moreover, to the best of our knowledge, it's the first example of pillararene based cyanide chemosensors.

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### 1. Introduction

Pillar[5]arenes [1], as a new type of macrocyclic hosts are linked by methylene bridges at contrapuntal of 2, 5-dialkoxybenzene rings, forming a distinctive rigidity pillar structure [2–6]. Functional groups modified on pillararenes often gives rise to distinctive properties that greatly stimulates the interest of chemists of this area [7–10]. The idiographic structure and easy functionalization of pillar[5]arenes carries them excellent capability to selectively bind different types of guests and provide a beautiful terrace for the construction of various receptors with different modifying groups [11,12]. Despite excessive reports on complexation of organic species, the use of host–guest interactions involving pillararenes and inorganic anions remains very limited [13,14]. Given this, Cao reported the design and preparation of a novel copillar[5]arene [15–18] and its application in anion-binding. So far, only a few publications involve copillararene [19–24]. It is worth mentioning that recognition of cyanide by pillararene as receptors has been unexplored to date [25–28].

The recognition of anions have received concern by many chemists for their important roles in biological, industrial, and

environmental processes [29–32]. Especially, cyanide is a virulent anion causing poisoning in organism and the environment [33–35]. Industrially discharged cyanide are widespread in the surroundings and do harm to biology by absorption through the skin, gastrointestinal tract and lungs, bringing about loss of awareness, vomiting, convulsion, and even death [36,37]. Therefore, highly selective sensors for cyanide have been received widespread attention for their applicability to circumstance and the pathological imaging of the anions [38]. Among the less conventional methods designed for sensing cyanide ions, those which exploit chemical reactions that produce fluorometric and colorimetric responses have considered to be the most ease and efficient methods to sensing cyanide owing to their briefness, high sensitivity and cherished nature [39–41].

Furthermore, processes like aggregation induced excitation or aggregation induced excitation strengthen have been applied in the development of specific fluorescent sensors [42,43]. The polymerization course assisted such molecules to bind efficiently through  $\pi$ – $\pi$  stacking interaction, which eventually discouraged the non-radiative inactivation channel through stunted within the molecule rotations [44,45]. This can explain the strengthened fluorescent excitation in the polymerization, In view of this, we thought of the quinoline compounds. As one of these, 8-hydroxyquinoline is one of the most important complexing agent for ions in its fluorescence upon ions binding [46–48]. Therefore, 8-hydroxyquinoline has

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been used to construct highly sensitive fluorescent sensors for ions of important biological and environmental significance [49–51], we envisaged that this shall be probable through introducing an efficient enhancing pathway in the 8-hydroxyquinoline ethers that can be raised its fluorescence characteristics upon anions complex [52]. As a consequence, we envisaged that tethering quinoline section, which are recognized as an excellent fluorophores for anion sensors. With our continued interest in recognition of anions, we report herein on the design and synthesis of a novel copillar[5]arene, which showed a fluorescent sensing for cyanide and proposed cyanide-induced self-assemble mechanism. Up until now, pillararene-based fluorescent sensors have been developed only for organic and neutral guests, and no literature on functionalized pillararenes designed for fluorescent sensors towards cyanide has been published and this is the first example of selective fluorescent recognition towards cyanide in the field of pillararene chemistry.

## 2. Experimental

### 2.1. Materials and instruments

All reagents for synthesis were of analytical grade, commercially and were used without further purification. All the anions were added in the form of tetrabutylammonium (TBA) salts. Which were purchased from Sigma–Aldrich Chemical, stored in a vacuum desiccator. Melting points were measured on an X-4 digital melting point apparatus and were uncorrected. UV–vis spectra were recorded on a Shimadzu UV-2550 spectrometer. Fluorescence spectra were recorded on a Shimadzu RF-5310.  $^1\text{H}$  NMR spectra were recorded on a Mercury-600BB spectrometer at 600 MHz and  $^{13}\text{C}$  NMR spectra were recorded on a Mercury-600BB spectrometer at 150 MHz with DMSO- $d_6$  as solvent. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS,  $\delta$  scale with solvent resonances as internal standards). Mass spectra were performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer.

### 2.2. Synthesis

#### 2.2.1. 1-(4-Bromobutoxyl)-4-methoxybenzene

In a 500 mL round-bottom flask, 4-methoxyphenol (2.48 g, 20 mmol),  $\text{K}_2\text{CO}_3$  (8.4 g, 60 mmol), KI (3.3 g, 20 mmol), 1, 4-dibromobutane (17.3 g, 80 mmol) and acetone (400 mL) were added. The reaction mixture was stirred at reflux for 2 days. After the solid was filtered off, the solvent was evaporated and the residue was dissolved in  $\text{CH}_2\text{Cl}_2$ . Column chromatography (silica gel; petroleum ether:ethyl acetate = 50:1) afforded a white solid (3.4 g, 65%), m.p.45 °C.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  6.83 (s, 4H), 3.94 (t,  $J$  = 6.1 Hz, 2H), 3.83–3.69 (s, 3H), 3.48 (t,  $J$  = 6.7 Hz, 2H), 2.11–2.00 (m, 2H), 1.97–1.84 (m, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  153.83 (s), 153.00 (s), 115.42 (d,  $J$  = 4.8 Hz), 114.64 (d,  $J$  = 2.5 Hz), 67.46 (s), 55.73 (s), 33.52 (s), 30.24 (d,  $J$  = 7.2 Hz), 29.51 (s), 28.01 (s), 26.11 (s), 6.49 (s).

#### 2.2.2. Copillar[5]arene 1

1-(4-Bromobutoxyl)-4-methoxybenzene (1.32 g, 5 mmol) and 1, 4-dimethoxybenzene (2.76 g, 20 mmol) in 1, 2-dichloroethane (80 mL), paraformaldehyde (0.75 g, 25 mmol) was added. Then, boron trifluoride diethyl etherate (3.2 mL, 25 mmol) was added to the solution and the mixture was stirred at room temperature for 1 h. The solution was poured into methanol and the resulting precipitate was collected by filtration. The solid was dissolved in  $\text{CHCl}_3$  (150 mL) and the insoluble part was filtered off. The resulting solid dissolved in  $\text{CHCl}_3$  and washed twice with  $\text{H}_2\text{O}$  (100 mL). The

organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated to afford the crude product, which was isolated by flash column chromatography using petroleum ether/ethyl acetate (50:1). The fractions containing the product were combined and concentrated under vacuum to give a kind of copillar[5]arene (1.5 g, 30%) as a white solid, m.p. 116–119 °C. The proton NMR spectrum of a copillar[5]arene.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  6.93–6.63 (m, 10H), 3.89 (d,  $J$  = 6.5 Hz, 1H), 3.83 (t,  $J$  = 6.0 Hz, 1H), 3.81–3.75 (m, 10H), 3.75–3.55 (s, 27H), 3.42 (d,  $J$  = 130.4 Hz, 2H), 1.92 (s, 1H), 1.81 (s, 1H), 1.25 (s, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  150.50 (s), 128.17 (d,  $J$  = 5.5 Hz), 113.59 (s), 67.19 (s), 55.63 (d,  $J$  = 20.2 Hz), 39.58 (s), 33.45 (s), 31.77 (s), 30.74–30.25 (m), 29.42 (d,  $J$  = 6.9 Hz), 28.39 (s).

#### 2.2.3. Compound PQ5

A copillar[5]arene 1 (0.71 g, 1 mmol), and 8-hydroxyquinoline (0.073 g, 1 mmol) was dissolved in THF (60 mL). KOH (0.056, 1 mmol) was added and the reaction mixture was stirred at room temperature for 3 days. The solvent was evaporated and the residue was dissolved in  $\text{CH}_2\text{Cl}_2$ . The resultant solution was washed with  $\text{H}_2\text{O}$ , after the solid was filtered afforded a white solid PQ5 (0.70 g, 90%), mp. 108–112 °C.  $^1\text{H}$  NMR (600 MHz, DMSO- $d_6$ )  $\delta$  8.94 (s, 1H), 7.58 (s, 1H), 6.85–6.81 (m, 14H), 4.37 (d,  $J$  = 48.6 Hz, 4H), 3.71 (s, 27H), 1.95 (d,  $J$  = 82.4 Hz, 10H), 1.80 (s, 4H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  201.54, 150.52, 150.48, 150.46, 150.41, 150.37, 149.56, 128.46, 128.30, 128.26, 128.19, 114.30, 113.59, 113.47, 113.44, 113.36, 98.41, 68.01, 67.37, 67.26, 55.75, 55.65, 55.61, 55.52, 55.50, 55.49, 55.47, 55.45, 55.41, 28.45, 27.77. ESI-MS  $m/z$ :  $[\text{M} + \text{H}]^+$ , calcd for 936; found 936.4.

#### 2.2.4. Compound 2

1-(4-Bromobutoxyl)-4-methoxybenzene (1.32 g, 5 mmol), and 8-hydroxyquinoline (0.726 g, 5 mmol) was dissolved in THF (80 mL). KOH (0.28, 5 mmol) was added and the reaction mixture was stirred at room temperature for 2 days. After the solvent was evaporated column chromatography (silica gel; petroleum ether:ethyl acetate = 20:1) afforded a white solid (1.68 g, 82%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.01–8.95 (m, 1H), 8.16 (d,  $J$  = 8.3 Hz, 1H), 7.51–7.39 (m, 3H), 7.11 (d,  $J$  = 7.5 Hz, 1H), 6.89–6.83 (m, 4H), 4.37 (t,  $J$  = 6.6 Hz, 2H), 4.07 (t,  $J$  = 6.2 Hz, 2H), 3.80 (s, 3H), 2.27–2.21 (m, 2H), 2.11–2.04 (m, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  154.74 (s), 153.71 (s), 153.13 (s), 149.28 (s), 140.41 (s), 135.86 (s), 129.50 (s), 126.65 (s), 121.51 (s), 119.50 (s), 115.43 (s), 114.60 (s), 108.71 (s), 68.53 (s), 68.15 (s), 55.72 (s), 26.18 (s), 25.77 (s).

#### 2.2.5. 1, 4-Bis (4-bromobutoxyl) benzene

Hydroquinone (2.3 g, 20.0 mmol),  $\text{K}_2\text{CO}_3$  (16.6 g, 120 mmol), KI (6.6 g, 40 mmol), 1, 4-dibromobutane (34.6 g, 160 mmol) and acetone (400.0 mL) were added in a 500 mL round-bottom flask stirred at 60 °C under  $\text{N}_2$ . The reaction mixture was stirred at reflux for 2 days. After the solid was filtered off, the solvent was evaporated and the residue was dissolved in  $\text{CH}_2\text{Cl}_2$ . Column chromatography (silica gel; petroleum ether: $\text{CH}_2\text{Cl}_2$  = 10:1) afforded a white solid (3.0 g, 40%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  6.83 (d,  $J$  = 0.8 Hz, 4H), 3.96 (t,  $J$  = 6.0 Hz, 4H), 3.52–3.25 (m, 4H), 2.10–1.88 (m, 8H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  153.07 (s), 115.40 (s), 67.35 (d,  $J$  = 30.2 Hz), 33.52 (s), 30.25 (s), 30.21 (s), 29.50 (s), 28.00 (s).

#### 2.2.6. Compound 3

1, 4-Bis (4-bromobutoxyl) benzene (1.9 g, 5 mmol), and 8-hydroxyquinoline (1.452 g, 10 mmol) was dissolved in THF (80 mL). KOH (0.56, 10 mmol) was added and the reaction mixture was stirred at room temperature for 3 days. After the solvent was evaporated column chromatography (silica gel; petroleum ether:ethyl acetate = 10:1) afforded a white solid (1.0 g, 30%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.95 (d,  $J$  = 2.6 Hz, 2H), 8.13 (d,  $J$  = 8.3 Hz, 2H), 7.42 (d,  $J$  = 16.9, 13.2,

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