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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 1.08×10^{-8} 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.

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 π–π stacking interaction, which eventually discouraged the non-radiative inactivation channel through stinted 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}H NMR spectra were recorded on a Mercury-600BB spectrometer at 600 MHz and ^{13}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, δ 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), K_2CO_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 CH_2Cl_2. Column chromatography (silica gel; petroleum ether:ethyl acetate = 50:1) afforded a white solid (3.4 g, 65%), m.p.45 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 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}C NMR (151 MHz, $CDCl_3$) δ 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 $CHCl_3$ (150 mL) and the insoluble part was filtered off. The resulting solid dissolved in $CHCl_3$ and washed twice with H_2O (100 mL). The organic layer was dried over anhydrous Na_2SO_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}H NMR (600 MHz, $CDCl_3$) δ 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}C NMR (151 MHz, $CDCl_3$) δ 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 CH_2Cl_2. The resultant solution was washed with H_2O, after the solid was filtered afforded a white solid **PQ5** (0.70 g, 90%), mp. 108–112 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 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}C NMR (151 MHz, $CDCl_3$) δ 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: $[M + H]^+$, calcd for 936; found 936.4.

2.2.4. Compound **2**

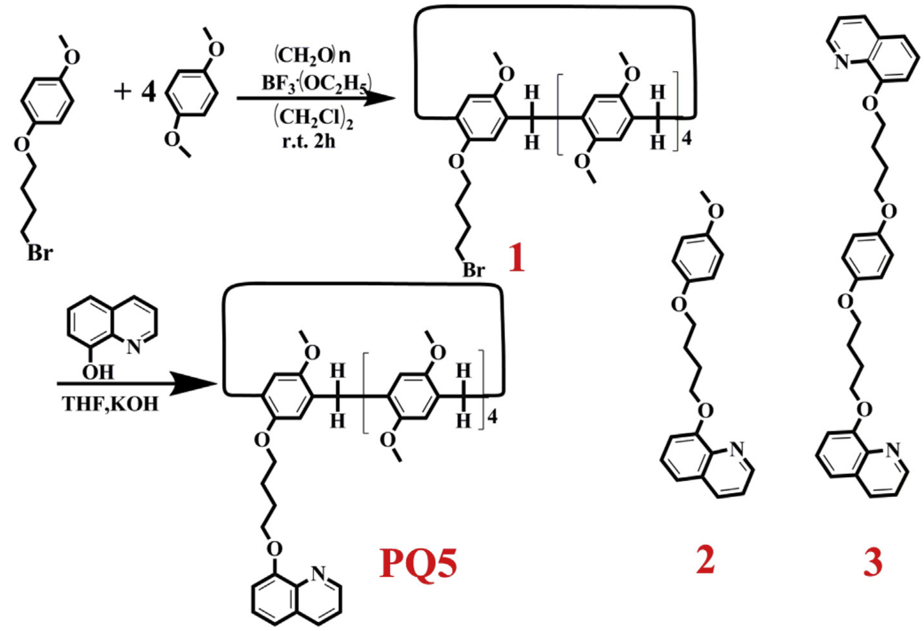
1-(4-Bromobutoxyl)-4-methoxybenzene (1.32 g, 5 mmol), and 8-hydroxyquinoline (0.726 g, 5 mmol) was dissolved in THF (80 mL). KOH (0.28, 5 mmol) was added and the reaction mixture was stirred at room temperature for 2 days. After the solvent was evaporated column chromatography (silica gel; petroleum ether:ethyl acetate = 20:1) afforded a white solid (1.68 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (151 MHz, $CDCl_3$) δ 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), K_2CO_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 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 CH_2Cl_2. Column chromatography (silica gel; petroleum ether:CH_2Cl_2 = 10:1) afforded a white solid (3.0 g, 40%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 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}C NMR (151 MHz, $CDCl_3$) δ 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}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J = 2.6 Hz, 2H), 8.13 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 16.9, 13.2,



Scheme 1. Synthesis of the copillar[5]arene **PQ5** linked 8-hydroxyquinoline and the chemical structure of the acyclic monomeric analog **2** and **3**.

8.0 Hz, 6H), 7.08 (d, $J = 7.5$ Hz, 2H), 6.82 (s, 4H), 4.33 (t, $J = 6.7$ Hz, 4H), 4.03 (t, $J = 6.2$ Hz, 4H), 2.26–2.17 (m, 4H), 2.09–1.99 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.75 (s), 153.10 (s), 149.29 (s), 140.44 (s), 135.83 (s), 129.49 (s), 126.64 (s), 121.51 (s), 119.49 (s), 115.40 (s), 108.70 (s), 68.53 (s), 68.13 (s), 26.18 (s), 25.77 (s).

3. Results and discussion

3.1. Design, synthesis and characterization

In view of this, and as a part of our research interest in pillararenes chemistry and molecular recognition [53–62], we designed and synthesized a novel copillar[5]arene-based anion receptor **PQ5** linked 8-hydroxyquinoline at one sites (Scheme 1). The key precursor 1 was achieved by only a one-step condensation reaction of compound 1-(4-bromobutoxyl)-4-methoxybenzene, 1, 4-dimethoxybenzene and para-formaldehyde under Lewis acid catalyzed conditions to obtain. Subsequent etherification reaction of the resulting 1 with 8-hydroxyquinoline in THF at room temperature, which was further applied NaOH to obtain the desired compound **PQ5** in a 90% isolated yield (Scheme S1). The acyclic monomeric pattern **2** and **3** were also prepared as a control for comparison (Schemes S2 and S3). The target molecules and intermediates were characterized by ^1H NMR spectrum, ^{13}C NMR spectrum and ESI-MS (Figs. S1–S13).

3.2. Fluorescence properties in DMSO/H_2O (8:2, v/v) solution

In order to investigate the CN^- recognition abilities of the sensor **PQ5** in DMSO/H_2O (8:2, v/v) solution, a series of host–guest recognition experiments were carried out. The recognition profiles of the sensor **PQ5** toward various anions (including F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, CN^- and SCN^-) were ready to research using fluorescence spectroscopy. In the fluorescence spectrum, the maximum emission of **PQ5** appeared at 456 nm in DMSO/H_2O (8:2, v/v) while excited at $\lambda_{ex} = 360$ nm. When 2.0 equiv. of CN^- was added to the solution of the sensor **PQ5**, the fluorescence emission band was red-shifted to 518 nm, and an approximate 3.5-fold fluorescence enhancement was observed (Fig. 1). In addition, a strong chartreuse fluorescence appeared (Fig. 1 Inset). From here, We are be easily detected cyanide ions through the sensor **PQ5**, cyanide was added dropwise towards the sensor **PQ5**, by color of the solution transformation from colorless to yellow–green under the UV lamp. The fluorescence spectral properties of sensor **PQ5** with CN^- were also carried out in the solution of DMSO/H_2O (0.01 M HEPES buffer, pH = 7.24, 80% DMSO) (Fig. S14), which we got the same experiment phenomenon with the above situation.

To validate the selectivity of sensor **PQ5**, the same tests were applied using F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, CN^- and SCN^- anions, and only CN^- have significant changes in the fluorescence spectrum of the sensor (Fig. 2), and none of those other

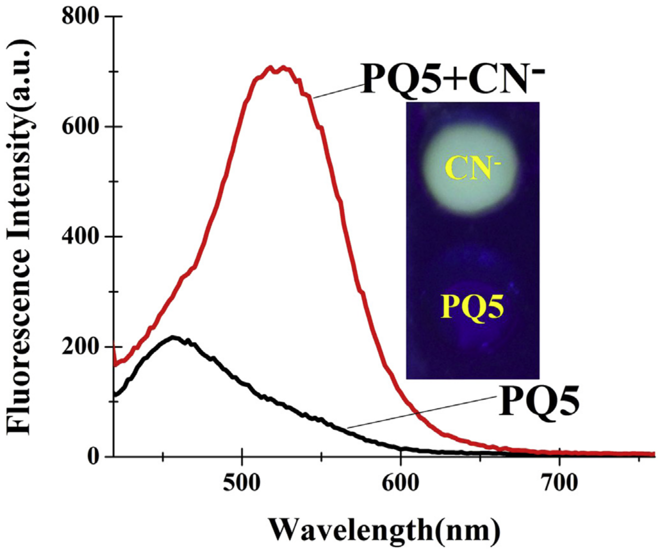


Fig. 1. Fluorescence spectral response of **PQ5** (1.0 mM) in DMSO/H_2O (8:2, v/v) upon addition of 2.0 equiv. of CN^- ($\lambda_{ex} = 360$ nm). Inset: photograph of **PQ5** (1.0 mM) upon addition of 2.0 equiv. of CN^-, which was taken under a UV–lamp (365 nm).

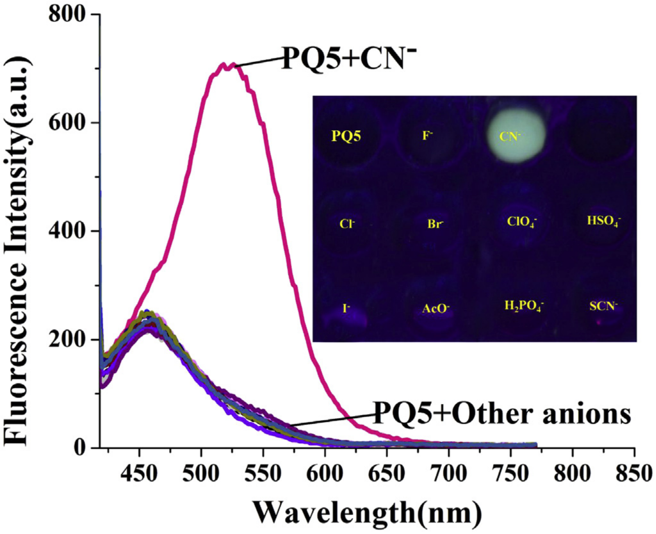


Fig. 2. Fluorescence emission data for **PQ5** and each of the various anions as the tetrabutylammonium salts, in the DMSO/H_2O (v/v = 8:2) solution. Inset: color changes observed for **PQ5** upon the addition of F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4{}^-$, $HSO_4{}^-$, $ClO_4{}^-$, CN^- and SCN^- in DMSO/H_2O (v/v = 8:2) solution on a spot plate. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

anions induced any significant changes in the fluorescent spectrum of the sensor. Upon addition of CN^- ions, the band was red-shifted accompanied with its absorption significantly enhanced at 518 nm. The apparent color change from colorless to chartreuse could be distinguished under the UV lamp.

So as to investigate the binding properties of the receptor **PQ5** towards CN^- ion, we implemented of the fluorescence titration of **PQ5** with CN^- in DMSO/H_2O (8:2, v/v) solution. The emission spectral variation of **PQ5** upon gradual addition of CN^- ion is shown in Fig. 3. In the fluorescence spectrum, upon addition of increasing amounts of CN^- ions (0–2.0 equiv.) to the solution of **PQ5** in DMSO/H_2O (8:2, v/v), the fluorescence emission at 456 nm is gradually red-shifted to 518 nm, directly leading to a strong chartreuse emission. The detection limit of the fluorescent spectrum changes calculated on the basis of 3σ/S is 1.08×10^{-8} mol L^{-1} for CN^- (Fig. S15), which is far lower than the WHO guideline of 1.9 μmol L^{-1} cyanide. Besides, while the amount of CN^- ion is beyond 2.0 equiv., the emission at 518 nm tends to saturation, which reveals the possible formation of a 2:1 complex between **PQ5** and CN^- (Fig. S16).

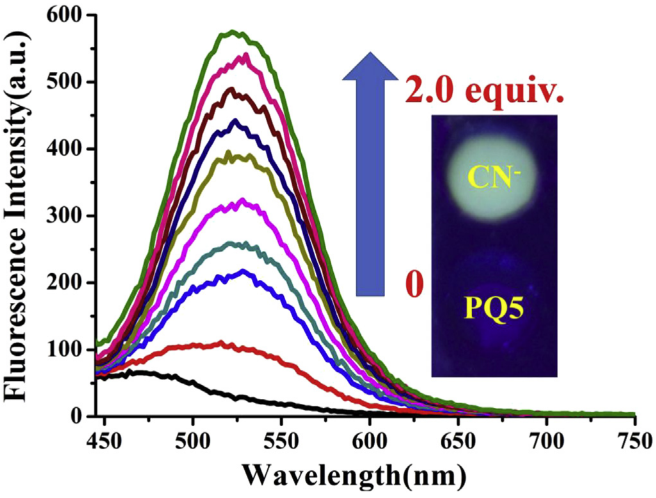


Fig. 3. Fluorescence spectra of **PQ5** (0.4 μM) in the presence of different concentration of CN^- in DMSO/H_2O (8:2, v/v) solution. Inset: color changes observed for **PQ5** upon the addition of CN^-. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

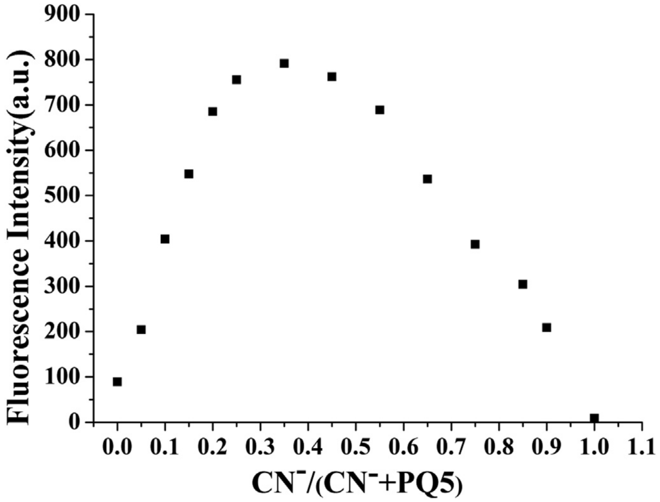


Fig. 4. The Job's plot examined between CN^- and **PQ5**, indicating the 1:2 stoichiometry, which was carried out by fluorescence spectra (λ_{ex} = 360 nm).

In order to quantify the complexation ratio between **PQ5** and CN^-, the fluorescence of Job's plot measurement (Fig. 4) was conducted by varying the concentration of both the sensor and the CN^-. The maximum point appears at the mole fraction of 0.33 which indicates that **PQ5** and CN^- were formed a 2:1 complex.

The selectivity of **PQ5** to CN^- was also examined over a wide range of pH values as shown in Fig. 5. The detection of CN^- can work well in the pH range of 3.0–14.0 in DMSO/H_2O (8:2, v/v).

To explore the utility of sensor **PQ5** as an ion-selective chemosensor for CN^-, competitive experiments were carried out in the presence of 2.0 equiv. of CN^- and 2.0 equiv. of various other ions (anions: F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4{}^-$, $HSO_4{}^-$, $ClO_4{}^-$, SCN^- and cations: Fe^{3+}, Hg^{2+}, Ag^+, Ca^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, Co^{2+}, Cr^{3+}, Mg^{2+}) in DMSO/H_2O (8:2, v/v). The results of these

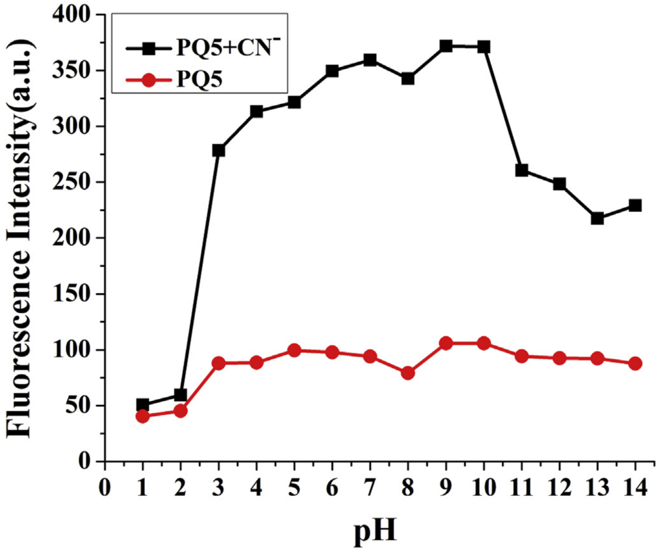


Fig. 5. Influence of pH on the fluorescence of **PQ5** (1.0 mM) in response to CN^- (2.0 equiv.) in DMSO–H_2O (8:2, v/v) solution.

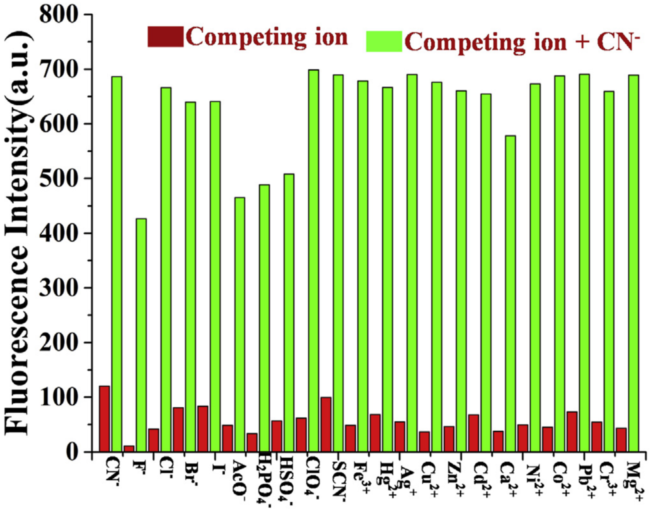


Fig. 6. Fluorescence intensities of **PQ5** (1.0 mM) in the presence of 2.0 equiv. of various ions containing 2.0 equiv. of CN^- in DMSO/H_2O (v/v = 8:2) solution (λ = 518 nm).

studies have revealed that these competing ions exerted little influence on the fluorescence emission spectra of sensor **PQ5** with CN^-, which further indicated that **PQ5** has specific selectivity to CN^- (Fig. 6).

3.3. The sensing mechanism

The proposed mechanism was also confirmed by ^1H NMR spectrum measurements. ^1H NMR spectrum displayed the chemical shift changes of **PQ5** upon the addition of 2.0 equiv. CN^- as shown in Fig. 7, all the signals related to the protons on **PQ5** shifted downfield obviously except that related to H_b, the ^1H NMR signals of quinoline ring protons (H_b) showed obvious upfield shifts. Which indicate that π−π stacking interactions between two molecules of quinoline ring and quinoline ring between pillar structures. When increasing the amount of cyanide, the chemical shift of all the protons are no longer changed (Fig. S17). Owing to sensor **PQ5** could take place an intramolecular rotation, the sensor is in the twisted intramolecular charge transfer state and show very weak fluorescence. Upon the gradual addition of CN^-, the sensor **PQ5** formed multiple hydrogen bonds with CN^-, which confined the intramolecular rotation of sensor **PQ5**, due to the intramolecular rotation was astrict by the multiple hydrogen bonds, the sensor shown a strong fluorescence emission at 518 nm.

The phenomenon that the conformation of **PQ5** changed from the columnar structure into the packing construction when **PQ5** interacted with CN^- was further validated by NOESY NMR spectroscopy. The NOESY spectrum (Fig. 8): strong correlations were observed between the quinoline ring protons H_a−H_f and the aliphatic hydrocarbons protons H_g as well as the bridging methylene protons H_i of the pillar[5]arene unit, suggesting that the quinoline ring was portion penetrate into the cavity of the pillar[5] arene. Furthermore, strong correlations were also observed between the H_h of the alkyl chain protons and quinoline ring protons H_d−H_f. Thus, the current measurements clearly pointed out that the formation of the alkyl chain rotational contraction, evidence that quinoline ring and pillar structure have strong interactions. Meanwhile, indicated that the distances between the quinoline ring extreme closer on average, supporting their participation in a common aggregate.

Meanwhile, the signal of the hydrogen atoms of quinoline ring protons (H_b) showed a significant upfield shift and the signal of

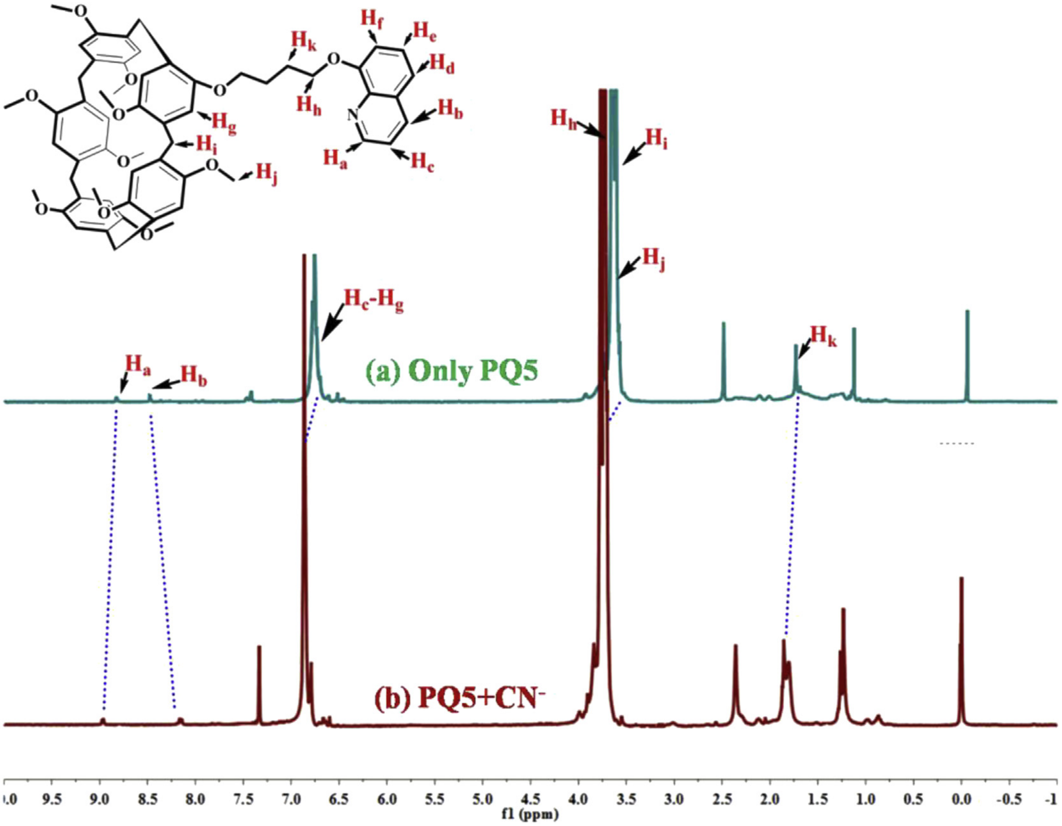


Fig. 7. ^1H NMR spectra (400 MHz, 0.4 mL $CDCl_3$ and 0.1 mL DMSO-d_6 (4:1 v/v).) of free **PQ5** and in the presence of CN^-.

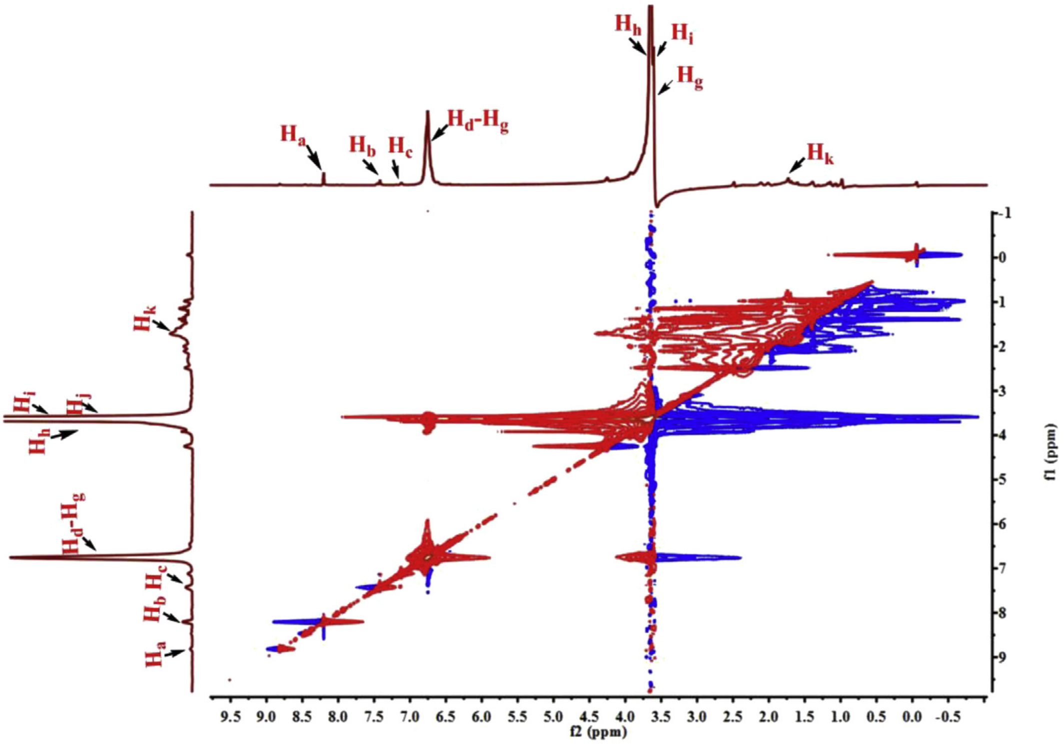


Fig. 8. 2D NOESY spectrum of **PQ5** in 0.4 mL $CDCl_3$ and 0.1 mL DMSO-d_6 (4:1 v/v) at 298 K after addition of 0.5 equiv. of CN^-.

alkyl chain protons (H_h) showed a significant downfield shift, indicating that the electrostatic interaction between the two molecules of **PQ5** and the π–π stacking between the quinoline ring of pillar structure. More importantly, sensor **PQ5** is most likely to band with CN^- via its N atoms on pyridine and alkyl chain protons (H_h), and the hydrogen bond between pyridine N atoms and alkyl chain protons (H_h) on **PQ5** formed two six-membered rings and also two five-membered ring formed between cyanide and alkyl chain protons (H_h) as well as (H_a) on **PQ5** (Fig. S18), the molecules formed a supramolecular system by means of self-assemble when CN^- is added (Fig. 9). In sharp contrast, acyclic monomeric analog **2** and **3** even at a identical concentration with the linked 8-hydroxyquinoline functionality being equal to that of **PQ5**, but they both only shows very poor fluorescence under the same conditions (Figs. 10 and 11), highlighting the importance of the preorganization of the pillar[5]arene platform on the recognition of CN^- via the cooperative coordination in the supramolecular complex.

To further investigate the practical application of chemosensor **PQ5**, test strips were fabricated by immersing filter papers into DMSO/H_2O (v/v = 8:2) solution of **PQ5** (2×10^{-3} M) and then drying them in air. The test strips containing **PQ5** were utilized to sense CN^-. As shown in Fig. 12, when CN^- were added on the test strips, an obvious color change was observed with CN^- solution

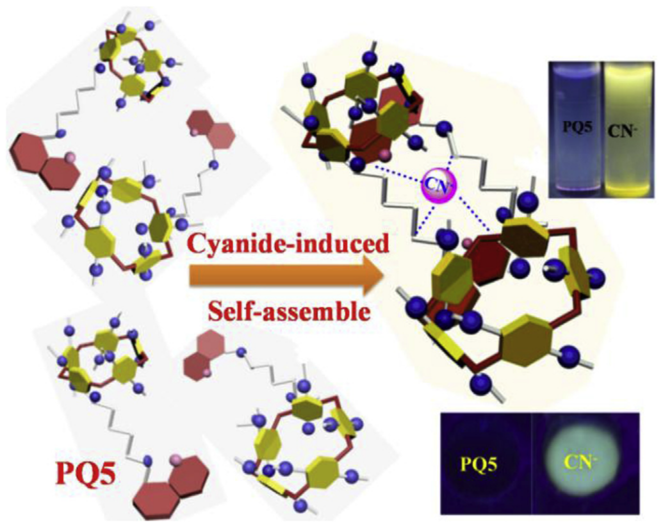


Fig. 9. The proposed structures of **PQ5** for CN^- anions.

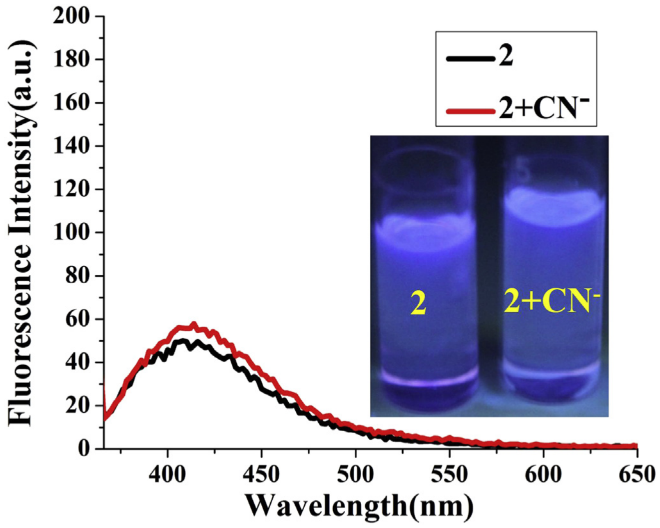


Fig. 10. Fluorescence spectral response of **2** (1.0 mM) in DMSO/H_2O (8:2, v/v) upon addition of 2.0 equiv. of CN^- (λ_{ex} = 360 nm). Inset: photograph of **2** (1.0 mM) upon addition of 2.0 equiv. of CN^-, which was taken under a UV-lamp (365 nm).

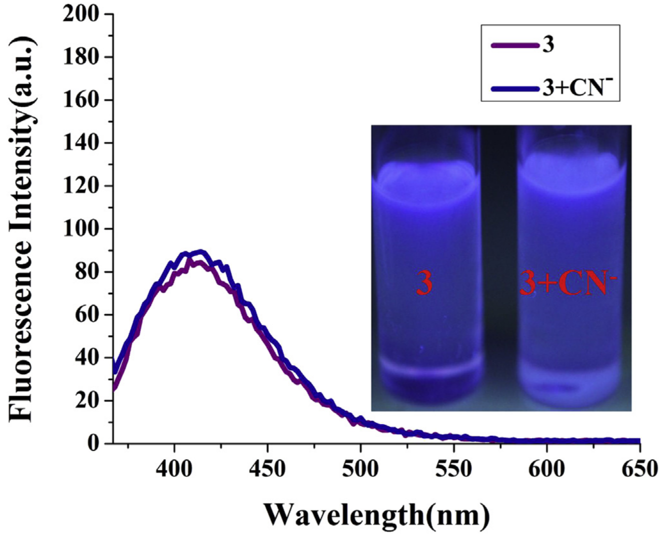


Fig. 11. Fluorescence spectral response of **3** (1.0 mM) in DMSO/H_2O (8:2, v/v) upon addition of 2.0 equiv. of CN^- ($\lambda_{ex} = 360$ nm). Inset: photograph of **3** (1.0 mM) upon addition of 2.0 equiv. of CN^-, which was taken under a UV-lamp (365 nm).

under a UV lamp. Therefore, the test strips could conveniently detect CN^- in water solutions.

We also investigated the practical utilities of the sense in our daily life, we selected the sprouting potatoes to carry out the below experiment. The sprouting potato (150 g) was first mashed before being soaked in water (200 mL) for 4 days until the extract became muddy. The mixture was filtered and the filtrate was washed with 100 mmol/L NaOH solution (100 mL) to get the cyanide-containing solution. As shown in Fig. 13, upon the addition cyanide-containing solution into **PQ5**, An obvious color change from colorless to yellow was observed under the UV lamp.

4. Conclusions

In conclusion, we have designed and synthesized a novel copillar[5]arene **PQ5**. It can sense cyanide by a novel cyanide-induced self-assemble mechanism with high selectivity and sensitivity. The detection limit of the fluorescent spectrum is 1.08×10^{-8} mol L^{-1} for CN^-. Moreover, test strips based on the sensor were fabricated, which served as convenient and efficient CN^- test kits and the sensor **PQ5** is a good way to detect cyanide aqueous extracts from sprouting potatoes. The work shown here not only presents the fact of using recognition towards cyanide, but more importantly, the cyanide-induced self-assemble mechanism reported here is a novel strategy for the design of pillararene based chemosensors.

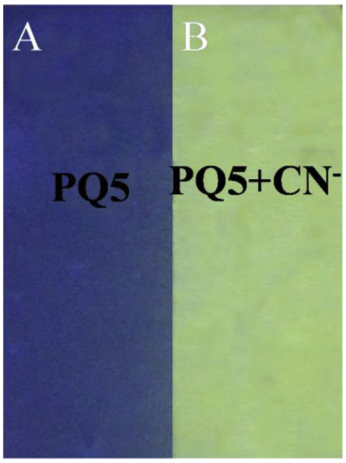


Fig. 12. Photographs of **PQ5** on test strips (A) only **PQ5**, (B) after immersion into water solutions with CN^-.

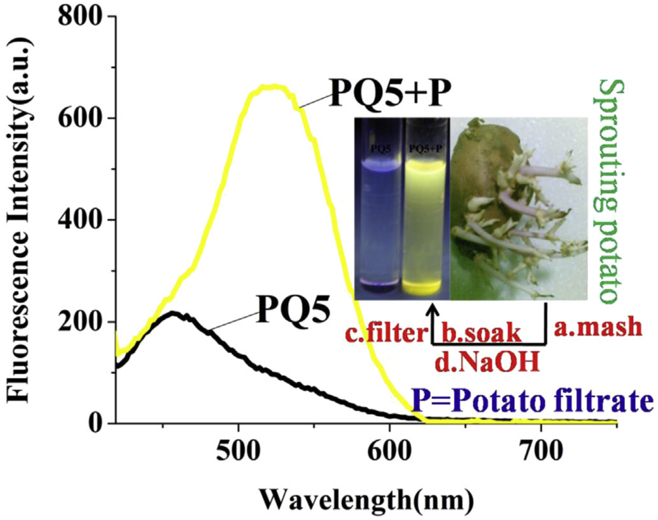


Fig. 13. Fluorescence emission data for the sensor **PQ5** to detect cyanide in sprouting potato. Inset: color changes observed for **PQ5** upon the addition of cyanide-containing under the UV lamp and photograph of sprouting potato. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2015.12.021.

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