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A bis(*m*-phenylene)-32-crown-10-based fluorescence chemosensor for paraquat and diquat

Jinqiang Zhang, Chunxi Zhai, Feng Wang, Chuanju Zhang, Shijun Li, Mingming Zhang, Ning Li, Feihe Huang *

Department of Chemistry, Zhejiang University, Hangzhou 310027, PR China

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ABSTRACT

A bis(*m*-phenylene)-32-crown-10-based host to which are covalently attached two pyrene groups as fluorescence chromophores was designed and synthesized. Its complexations with paraquat (**PQ**) and diquat (**DQ**) were studied by proton NMR, ESI mass spectrometry, and UV–vis spectroscopy. Its chemosensor behavior to **PQ** and **DQ** was revealed by fluorescence emission spectroscopy. This new host can function as a fluorescence chemosensor for **PQ** and **DQ** due to the inhibition of photoinduced electron transfer between the bis(*m*-phenylene)-32-crown-10 moiety and the pyrene groups by the addition of **PQ** (or **DQ**).

Paraquat (**PQ**) and diquat (**DQ**) are non-selective, effective, and quick acting herbicides.[1] They have been widely used in agriculture and horticulture. For their highly toxic effects on humans, numerous methods, such as electrophoresis, chromatography, photometric, and immunoassay, have been developed to monitor and control these herbicides in the environment, water, food, and clinical samples.[1] However, these methods usually are time-consuming and often require expensive and sophisticated instrumentation and/or sample preparation.[1,2] Fluorescence chemosensors based on molecular recognition, for their high sensitivity and selectivity, are one of the most active research areas in the detection and determination of cations and anions.[3] Crown ethers and related compounds have been widely used for molecular recognition of **PQ** and **DQ** by us and others.[4] Swager et al. prepared conducting polymers with crown ether side groups to detect **PQ** based on conductivity changes on **PQ** binding.[5] Willner et al. reported that the formation of the complexes between **PQ** and a series of dialkoxybenze- and dialkoxyarene-capped Zn(II)–porphyrins resulted in effective static quenching of the excited chromophores at very low quencher concentrations.[6] Yagi et al. developed a novel dual-mode porphyrinic receptor which can bind **PQ** derivatives to achieve the supramolecular control of photoinduced electron transfer (PET).[7] However, fluorescence chemosensors for **PQ** and **DQ** based on molecular recognition have been rarely reported up to date.

Pyrene is one of the most widely used fluorogenic units. Molecules with two (or more) pyrene groups can be used as excimer sensors because of the sensitivity of the intensity ratio of the monomer to the excimer emission to subtle conformational changes of the pyrene-attached receptors. The ratio change of monomer to excimer emission intensities is an informative parameter in a variety of sensing systems.[8] To explore the application of the crown ether/**PQ** (or **DQ**) molecular recognition motif in the detection of **PQ** (or **DQ**), we designed a bis(*m*-phenylene)-32-crown-10 (**BMP32C10**) derivative host, **1**, which has two pyrene groups covalently linked to its two ends as the fluorescent chromophores. In previous reports, it was found that **BMP32C10** derivatives can bind both **PQ** and **DQ**,[4g,l,r,9] so here the **BMP32C10** moiety can function as the recognition part and the fluorescence intensities of two pyrene groups can be measured as the parameters for sensing. Here we report the synthesis of **1**, and its complexations and sensing behavior with **PQ** and **DQ**.

To synthesize the fluorescent host **1**, bis(5-bromomethyl-*m*-phenylene)-32-crown-10[10] was synthesized by the literature procedure. Then, this intermediate was reacted with (1-hydroxymethyl)-pyrene[11] to afford **BMP32C10** derivative **1** in 78% yield (Scheme 1).[12]

Then, the complexation between **1** and **PQ** (or **DQ**) was studied. Job plots[13] (e.g., for **1**·**PQ** in Fig. 1) based on UV–vis absorbance data of the charge-transfer band ($\lambda = 420$ nm) demonstrated that the two complexes were of 1:1 stoichiometry in solution. The 1:1 stoichiometry of complexation between **1** and **PQ** (or **DQ**) was also confirmed by electrospray ionization mass spectrometric characterization of an equimolar solution of **1** and **PQ** (or **DQ**) in acetone.

* Corresponding author. Tel./fax: +86 571 87953189.
E-mail address: fhuang@zju.edu.cn (F. Huang).

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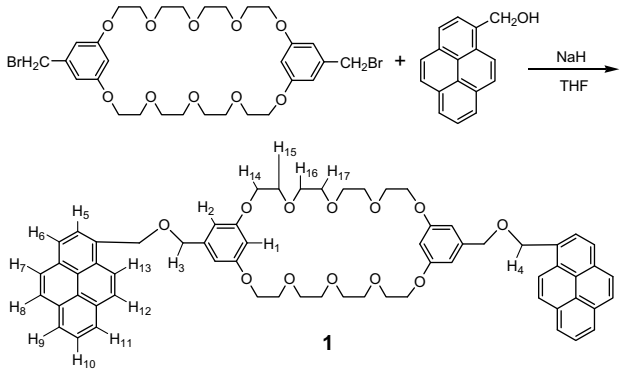

Scheme 1. Synthesis of bis(*m*-phenylene)-32-crown-10 derivative **1**.

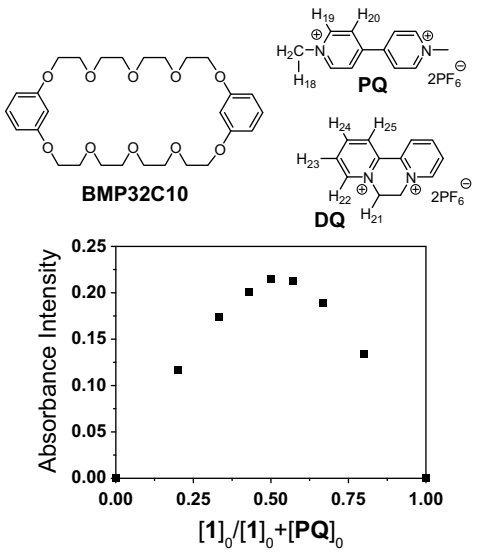

Figure 1. Job plots showing the 1:1 stoichiometry of the complex between **1** and **PQ** in acetone by plotting the absorbance intensity at $\lambda = 420$ nm (the host–guest charge transfer band) against the mole fraction of **1**. $[\mathbf{1}]_0$ and $[\mathbf{PQ}]_0$ are initial concentrations of **1** and **PQ**. $[\mathbf{1}]_0 + [\mathbf{PQ}]_0 = 2.00$ mM.

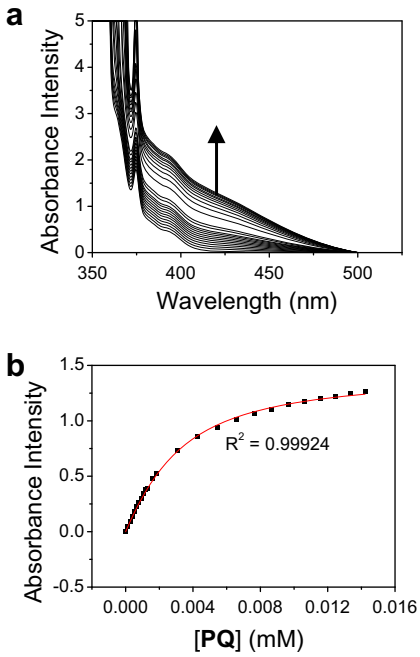

Figure 2. (a) The absorption spectral changes of **1** (2.00 mM) upon addition of **PQ** and (b) the absorbance intensity changes at $\lambda = 420$ nm upon addition of **PQ** (from 0 to 14.2 mM) in acetone. The red solid line was obtained from the non-linear curve-fitting.

Two relevant peaks were found for **1**·**PQ**: *m*/*z* 605.2 (27%) $[\mathbf{1}\cdot\mathbf{PQ}–2PF_6]^{2+}$ and 1355.4 (100%) $[\mathbf{1}\cdot\mathbf{PQ}–PF_6]^{+}$. One related peak was found for **1**·**DQ**: *m*/*z* 1207.3 (30%) $[\mathbf{1}\cdot\mathbf{DQ}–PF_6–HPF_6]^{+}$, with the base peak at *m*/*z* 1047.4, corresponding to $[\mathbf{1}+Na]^{+}$. No peaks were found for complexes with other stoichiometries.

The association constants (K_a) of **1**·**PQ** and **1**·**DQ** were determined by probing the charge-transfer bands of the complexes by UV–vis spectroscopy employing a titration method. Progressive addition of an acetone solution with high guest (**PQ** or **DQ**) concentration and low host (**1**) concentration to an acetone solution with the same host (**1**) concentration results in an increase of the intensity of the charge-transfer band of the complex (Fig. 2). Treatment of the collected absorbance data with a non-linear curve-fitting program afforded the corresponding K_a values, 487(±16) M^{-1} for **1**·**PQ** and 315(±19) M^{-1} for **1**·**DQ**,[14] close to the reported K_a values 550 M^{-1} and 390 M^{-1},[4b,9a] respectively, for **BMP32C10**·**PQ** and **BMP32C10**·**DQ**. This is reasonable considering that the CH_2OCH_2Ar has a Hammett σ value of zero[15] and thus is not expected to influence the complexation of **1** with **PQ** or **DQ** electronically.

Proton NMR characterization was also done to investigate the complexations of **1** with **PQ** and **DQ** (Fig. 3). The proton NMR spectra indicate that **1**·**PQ** and **1**·**DQ** are fast-exchange complexation systems. The chemical shift changes showed very similar characteristics after complexations of **1** with **PQ** and **DQ**. Significant upfield shifts of aromatic protons H_1 and H_2 and α-ethyleneoxy protons H_{14} of **1** were observed (Fig. 3b–d). Its benzyl protons H_3 and β-ethyleneoxy protons H_{15} have relatively small upfield changes, while γ- and δ-ethyleneoxy protons H_{16} and H_{17} moved downfield (Fig. 3b–d). The pyridinium protons, H_{19}, H_{20}, and H_{22}–H_{25}, of both **PQ** and **DQ**, methyl protons H_{18} of **PQ** and methylene protons H_{21} of **DQ** also had obvious upfield shifts (Fig. 3a, b, d, and e). Since protons H_4 of the methylene groups connected to the pyrene groups and aromatic protons H_5–H_{13} on the pyrene groups of **1** had only very small chemical shift changes (Fig. 3b–d), it is reasonable to think that these protons are not involved in non-covalent interactions between the host **1** and the guest **PQ** or **DQ** and that the molar ratio of the monomer to excimer changes a little after the complexation of **1** with **PQ** or **DQ**.

The chemosensor behavior of the new host **1** to **PQ** and **DQ** was investigated by fluorescence emission spectroscopy in acetone. Fluorescence spectra (Fig. 4) showed that there are two sets of peaks which display the characteristics of pyrene monomer ($\lambda_{max} = 389$ nm) and excimer ($\lambda_{max} = 479$ nm), although the intensities of both the monomer and excimer emissions are relatively small. This should be caused by PET from the **BMP32C10** moiety of the host to the pyrene groups.[16] The progressive addition of **PQ** into the acetone solution of the host which is at fixed concentration resulted in the small decrease of the intensity of the excimer emission peak and the drastic increase of the intensity of the monomer emission peak. Similar results were observed for the **DQ** titration. These indicated that the molar ratio of monomer to excimer increased a little after the complexation of **1** with **PQ** or **DQ** so the excimer peak decreased a little and that pyrene groups exist as monomers when host **1** molecules are complexed. The above proton NMR characterization also confirmed that the ratio of monomer to excimer changed only a little since the peaks corresponding to the aromatic protons on the pyrene groups shifted a little after complexation.[17] The main reason for the drastic increase of the fluorescence intensity of the monomer emission is that the

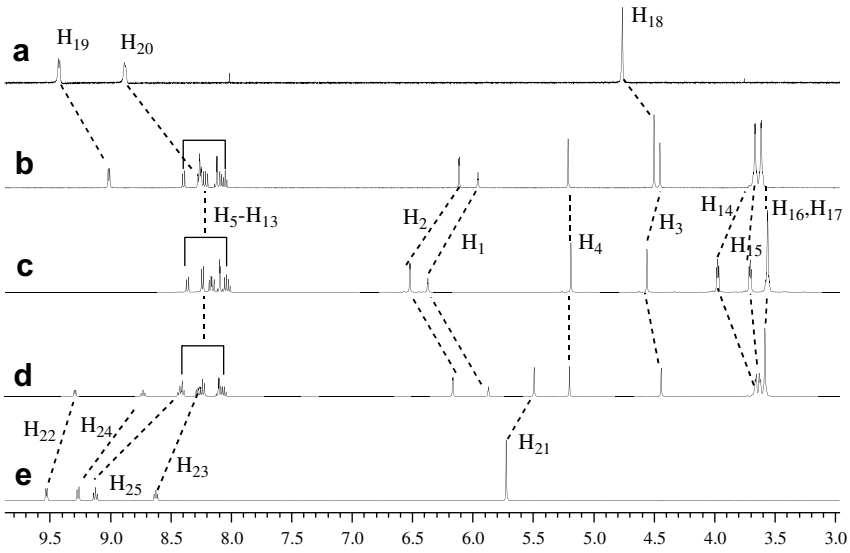

Figure 3. Partial proton NMR spectra (500 MHz, acetone-d_6, 22 °C) of (a) **PQ**, (b) 2.00 mM **1** and **PQ**, (c) **1**, (d) 2.00 mM **1** and **DQ**, and (e) **DQ**.

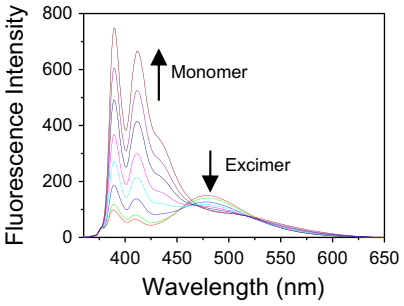

Figure 4. Fluorescence emission intensity changes of **1** (6.96×10^{-6} M) upon addition of **PQ** (from 0 to 0.18 mM) in acetone. The excitation wavelength was 350 nm.

addition of **PQ** (or **DQ**) inhibited PET between the **BMP32C10** moiety and pyrene groups.

Interestingly, we found that after addition of **PQ** (or **DQ**), the fluorescence emission color of the solution changed from cyan to purple due to the change of the ratio of the monomer fluorescence emission intensity to the excimer fluorescence emission intensity (Fig. 5).

In summary, we designed and synthesized a **BMP32C10**-based fluorescence chemosensor for **PQ** and **DQ**.[18] Its fluorescence chemosensor behavior to **PQ** and **DQ** was investigated using fluorescence spectroscopy. We showed that the new host could act as a fluorescence chemosensor due to the inhibition of PET between the **BMP32C10** moiety and the pyrene groups by the addition of **PQ** (or **DQ**). The studies presented here provide a new potential method for detection of **PQ** and **DQ**.

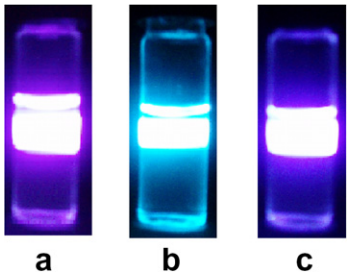

Figure 5. Photography of the fluorescence emissions of (a) **1** in the presence of **PQ**, (b) **1**, and (c) **1** in the presence of **DQ** in acetone under irradiation at 350 nm.

Acknowledgment

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Supplementary data

^{1}H and ^{13}C NMR spectra of **1**, ESI spectra of equimolar acetone solutions of **1** with either of **PQ** and **DQ**, determination of the association constants of **1**·**PQ** and **1**·**DQ**, fluorescence emission intensity changes of **1** upon addition of **DQ**, and fluorescence emission spectra of **PQ** and **DQ** are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.06.062.

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12. Synthesis of **1**: To a suspension of NaH (80 mg, 60% in mineral oil, 2.7 mmol) in THF (20 mL) was added (1-hydroxymethyl)-pyrene (348 mg, 1.50 mmol) in THF (20 mL) at 0 °C under nitrogen. After stirring for 30 min, bis(5-bromomethyl-*m*-phenylene)-32-crown-10 (361 mg, 0.50 mmol) in THF (20 mL) was added. Then the mixture was stirred at rt for 20 h. The reaction was quenched with H_2O. The residue was concentrated in vacuo and redissolved in dichloromethane. The solution was washed with H_2O two times and dried over anhydrous sodium sulfate. The solvent was removed and the residue was purified by column chromatography with ethyl acetate as the eluent to afford **1** as a white solid (400 mg, 78%), mp 238 °C dec. ^{1}H NMR (500 MHz, acetone-d_6, room temperature) δ (ppm): 8.38–8.36 (d, 2H J = 9.0 Hz), 8.25–8.23 (m, 4H), 8.19–8.15 (m, 4H), 8.12–8.08 (m, 4H), 8.06–8.01 (m, 4H), 6.52 (d, 4H, J = 2.0 Hz), 6.37 (t, 2H, J = 2.0 Hz), 5.20 (s, 4H), 4.57 (s, 4H), 3.98 (dd, 8H, J_1 = 4.5 Hz, J_2 = 5.0 Hz), 3.72–3.70 (m, 8H), 3.59–3.55 (m, 16H). ^{13}C NMR (125 MHz, acetone-d_6, room temperature) δ (ppm): 160.3, 141.1, 132.1, 131.2, 130.9, 129.3, 127.5, 127.4, 127.3, 127.2, 126.1, 125.3, 125.2, 124.6, 123.8, 106.1, 100.3, 71.9, 70.7, 70.6, 70.3, 69.4, 67.5. HRESIMS m/z calcd for $[M+Na]^+$ $C_{64}H_{64}O_{12}Na$, 1047.4295; found 1047.4211, error 8.0 ppm.
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18. Here our studies were done in acetone. However, since acetone is miscible with water, the chemosensors reported here can also be used to detect **PQ** and **DQ** in water. Recently, Anslyn pointed out 'Even if the target analytes are in water to start, as long as the solvent system is miscible with water these analytes can be studied'. See: Anslyn, E. V. *J. Org. Chem.* **2007**, *72*, 687–699.