o-Benzoquinone appended zinc(II) porphyrin: a new fluorescent sensor for catechols

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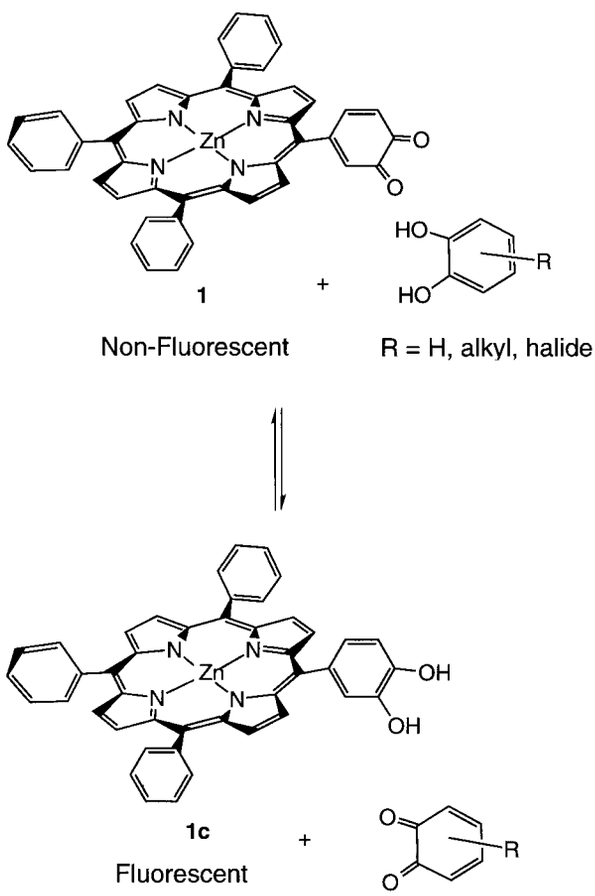
A newly synthesized, weakly fluorescent, *o*-benzoquinone appended zinc porphyrin is shown to undergo a redox equilibrium with catechols in solution resulting in the formation of a more fluorescent, catechol appended zinc(II) porphyrin.

Development of the novel macrocycle based fluorescent sensors and/or reagents is an area of active research because of the excellent sensitivity and good specificity they offer.[1] Among the different fluorophores utilized to develop sensor and/or reagents, porphyrins are attractive candidates due to their relatively high fluorescence quantum yields and emission in the red and near IR region.[2] Recently, we reported a fluorescence chemosensor for hydroquinone using a *p*-benzoquinone appended porphyrin.[3] In this system, a non-fluorescent *p*-benzoquinone appended porphyrin forms a quinhydrone type molecular complex with hydroquinone resulting in the formation of a fluorescent porphyrin. A similar strategy was also utilized earlier to develop a chemosensor for *p*-benzoquinone using a hydroquinone appended porphyrin.[4]

In order to develop a chemosensor and/or fluorescent reagent for catechol (1,2-dihydroxybenzene) and its substituted derivatives—a widely distributed molecular functionality in natural products—in the present study, for the first time, we have synthesized an *o*-benzoquinone appended zinc(II) porphyrin derivative. As demonstrated here, the weakly fluorescent *o*-benzoquinone appended porphyrin, **1**, undergoes a redox equilibrium with catechols to yield a more fluorescent, catechol appended zinc(II) porphyrin, **1c**, in solution according to Scheme 1.

The *o*-quinone appended zinc porphyrin, **1**, was synthesized by chemical oxidation of the *o*-catechol appended zinc porphyrin. The optical absorption spectrum of **1** revealed absorption bands characteristic of *meso*-aryl substituted zinc(II) porphyrins.[2] The peak maxima are found to be blue shifted by ~3–5 nm as compared to the catechol appended zinc(II) porphyrin, **1c**, an observation similar to that reported for *p*-benzoquinone and hydroquinone appended porphyrins.[3,4] Compound **1** is found to be weakly fluorescent with a net fluorescence quantum yield $\phi_f = 0.034$ as compared to $\phi_f = 0.102$ for **1c**. This low fluorescence of **1** could be ascribed to the occurrence of photoinduced electron transfer (PET) from the singlet excited zinc(II) porphyrin to the appended *o*-benzoquinone, similar to that reported for a number of *p*-benzoquinone appended porphyrin derivatives.[5] In order to verify the possibility of the occurrence of such a reaction, the free-energy change associated with a PET reaction was estimated by using the redox and emission data.

The cyclic voltammogram of **1** in 0.1 M $(TBA)PF_6$ in benzonitrile exhibits two one-electron oxidations, with the half-wave potentials located at $E_{1/2} = 0.80$ and 1.20 V *vs.* Ag/AgCl respectively (Fig. 1). Spectroelectrochemical studies confirmed that these two anodic waves correspond to the formation of a porphyrin π-cation radical and a dication species respectively. During the negative scan of the potential, an irreversible wave located at $E_{pc} = -0.20$ V *vs.* Ag/AgCl is observed corresponding to the reduction of the appended *o*-quinone entity.[6] Extending



Scheme 1

the potential scan beyond the first reduction, additional waves corresponding to the reduction of the porphyrin macrocycle have been observed (data not shown). A comparison between the reduction potential of *o*-quinone in **1** and that reported for *p*-quinone in *p*-quinone appended porphyrin[3] suggests that the *o*-quinone is easier to reduce by more than 300 mV and, hence, is a better electron acceptor. The calculated free-energy change for the electron transfer (ΔG_{ET}) from the singlet excited porphyrin to the appended *o*-quinone, according to the method of Rahm and Weller,[7] is found to be exergonic by 0.9 ± 0.1 V. These results suggest that PET is the most likely mechanism of fluorescence quenching of **1**.

Addition of catechols to the solution of **1** increases the fluorescence intensity of **1**. Fig. 2 shows such a behavior for **1** in the presence of different equivalents of added 4-methylcatechol. The enhancement of fluorescence intensity could take place according to the redox equilibrium shown in Scheme 1 or by forming a quinhydrone type complex involving the *o*-quinone and catechol derivatives, as shown earlier for the case of *p*-quinone appended porphyrin derivative.[3] However, in the present study, we have no convincing spectral evidence for a

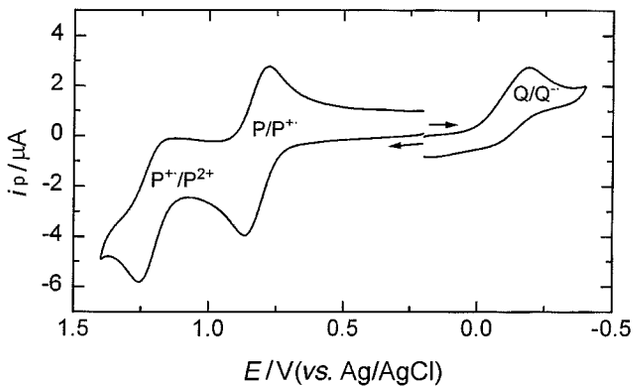


Fig. 1 Cyclic voltammogram of **1** in 0.1 M $(TBA)PF_6$ in benzonitrile. Scan rate = 0.1 V s^{-1}.

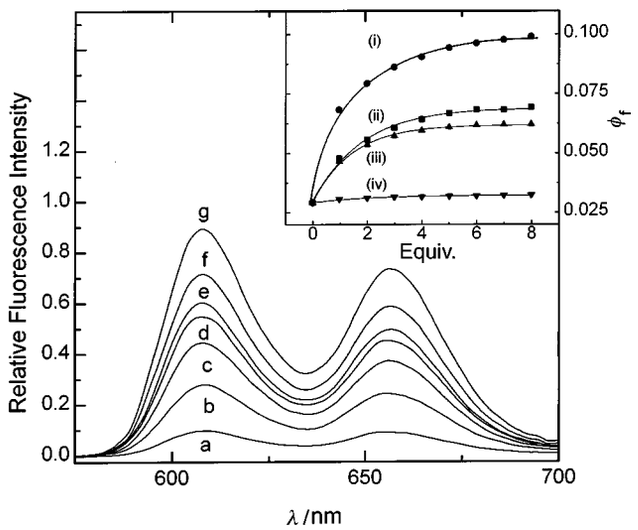


Fig. 2 Fluorescence emission spectrum of (a) **1** (2.3 μM) in PhCN, λ_{ex} = 556 nm. Spectra (b)–(f) represent the emission spectrum of **1** on increasing addition of 4-methylcatechol (1, 2, 3, 5 and 7 equiv. respectively). Spectrum (g) represents emission spectrum of **1c** (2.3 μM). The inset figure shows the change in fluorescence quantum yield of **1** in the presence of various amounts of (i) 4-methylcatechol, (ii) catechol, (iii) *tert*-butylcatechol and (iv) tetrachlorocatechol.

quinhydrone type complex formation. Moreover, the separation of the reaction products obtained after the fluorescence titration, revealed the formation of catechol appended porphyrin, **1c**, indicating the conversion of *o*-quinone to catechol in **1** according to Scheme 1. Importantly, the increase in the fluorescence intensity depends upon the employed catechol derivatives. When tetrachlorocatechol, a catechol with higher oxidation potential, is employed, no reaction involving an increase in fluorescence intensity is observed [plot (iv) in the inset of Fig. 2], thus confirming the occurrence of a redox equilibrium reaction.

Studies performed on the fluorescence enhancement of **1** in the presence of other dihydroxybenzene derivatives revealed selectivity of **1** towards catechol. Fig. 3 shows the fluorescence spectrum of **1** in the presence of 6 equiv. of catechol, resorcinol and hydroquinone respectively. It is evident that the fluorescence enhancement of **1** in the presence of catechol is at least four times larger than that observed for **1** either in the presence of resorcinol or hydroquinone. Further studies to probe the mechanistic details of PET in **1** and fluorescence enhancement process are in progress.

Experimental

Benzonitrile (Aldrich) for spectral and electrochemical experiments was distilled over P_2O_5 under vacuum. Tetra-*n*-butylammonium hexafluorophosphate, $(TBA)PF_6$, (Aldrich) was

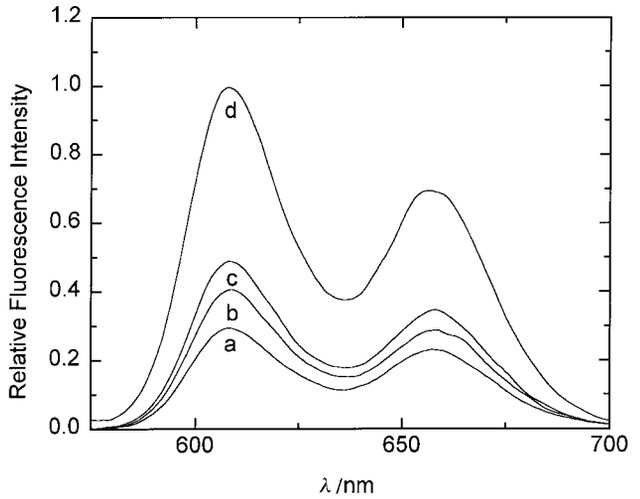


Fig. 3 Fluorescence emission spectrum of (a) **1** (2.3 μM) in PhCN, λ_{ex} = 556 nm. Spectra (b)–(d) represent the emission spectrum of **1** in the presence of 6 equiv. of hydroquinone, resorcinol and catechol respectively.

recrystallized from ethyl alcohol and dried at 40 °C for at least one week prior to use. All other reagents were of analytical grade and used without further purification, unless otherwise indicated.

Synthesis of 5-(*o*-benzoquinone)-10,15,20-triphenylporphyrinato-zinc(II), 1

The synthesis of **1** was carried out as follows: the precursor porphyrin, 5-(3,4-dimethoxyphenyl)-10,15,20-triphenylporphyrin, **1a**, was synthesized by reacting 3,4-dimethoxybenzaldehyde (18 mmol), pyrrole (72 mmol) and benzaldehyde (54 mmol) in 400 mL refluxing propionic acid for 1 h. The precipitate obtained after evaporating propionic acid was washed several times with methanol to remove the tars and the residue was air-dried. Compound **1a** was purified over a basic alumina column using toluene–hexane (65:35) mixture as eluent. The second fraction was found to contain the desired compound (yield = 8.6%). ^{1}H NMR in $CDCl_3$: δ_H 8.74 (m, 8H, pyrrole-H), 8.21 (m, 6H, *ortho*-H of the triphenyl entity), 7.63 (m, 9H, *meta*- and *para*-H of the triphenyl entity), 7.30, 7.23 (d, s, 3H, substituted phenyl-H), 3.83 (d, 6H, methoxy-H), −2.77 (s, 2H, imino-H).

Compound **1a** obtained above was converted to 5-(3,4-dihydroxyphenyl)-10,15,20-triphenylporphyrin, **1b**, by the reaction of BBr_3 in CH_2Cl_2 at −80 °C for 1 h, followed by stirring the reaction mixture at room temperature for another 12 h. At the end, the reaction mixture was cooled to −5 °C and quenched with the addition of water (50 mL) followed by 2 mL of triethylamine. The compound extracted in $CHCl_3$ was washed with saturated $NaHCO_3$ solution and dried over anhydrous Na_2SO_4. Compound **1b** was purified over a silica gel column using $CHCl_3$–CH_3OH (98:2) as eluent (yield = 90%). ^{1}H NMR in $CDCl_3$: δ_H 8.83 (m, 8H, pyrrole-H), 8.22 (m, 6H, *ortho*-H of the triphenyl entity), 7.75 (m, 9H, *meta*- and *para*-H of the triphenyl entity), 7.39, 7.00 (d, s, 3H, substituted phenyl-H), −2.72 (s, 2H, imino-H).

Compound **1b** (0.1 mmol) obtained from the previous step was reacted with zinc acetate tetrahydrate (1 mmol) in methanol (100 mL) and the progress of the metallation reaction was followed spectrophotometrically. After completion of the metallation reaction (~1 h), the solution was evaporated to dryness. The metallated porphyrin, 5-(3,4-dihydroxyphenyl)-10,15,20-triphenylporphyrinatozinc, **1c**, was purified over a silica gel column using $CHCl_3$–CH_3OH (95:5) mixture as eluent (yield = 92%). ^{1}H NMR in $CDCl_3$: δ_H 8.93 (m, 8H, pyrrole-H), 8.19 (m, 6H, *ortho*-H of the triphenyl entity), 7.73 (m, 9H, *meta*- and *para*-H of the triphenyl entity), 7.62, 7.08 (d, s, 3H, catechol-H). UV–VIS in PhCN: λ [log (ε/l mol^{-1} ml^{-1})] nm 429 (5.23), 556 (3.94), 598 (3.66).

Finally compound **1** was obtained by reacting **1c** (0.1 mmol) with *o*-chloranil (0.3 mmol) in methanol for 2 h. After evaporating the solvent, the residue was dissolved in a minimum amount of $CHCl_3$ and purified over a silica gel column using $CHCl_3$ as eluent (yield = 73%). ^{1}H NMR in $CDCl_3$: δ_H 9.11 (m, 8H, pyrrole-H), 8.22 (m, 6H, *ortho*-H of the triphenyl entity), 7.76 (m, 9H, *meta*- and *para*-H of the triphenyl entity), 8.12, 7.63 (s, d, 3H, *o*-quinone-H). λ [log (ε/l mol^{-1} ml^{-1})] nm 423 (5.19), 554 (3.88), 593 (3.53). The newly synthesized **1** was found to be highly light sensitive and, hence, was protected from light.

The UV–VIS spectral measurements were carried out on a Shimadzu Model 1600 UV–VIS spectrophotometer. The fluorescence was monitored by using a Spex Fluorolog spectrometer. A right angle detection method was used. The fluorescence quantum yield, ϕ_f, were measured according to the method of Austin and Gouterman.[8] ^{1}H NMR studies were carried out on a Varian 400 MHz spectrometer. Tetramethylsilane (TMS) was used as an internal standard. Cyclic voltammograms were obtained on a EG & G Model 263 A potentiostat using a three-electrode system. Platinum or glassy carbon disk electrodes were used as the working electrodes. A platinum wire served as the counter electrode. An Ag/AgCl electrode, separated from the test solution by a fritted supporting electrolyte/solvent bridge, was used as the reference electrode.

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Notes and references

† On leave from the Department of Studies in Chemistry, Mysore University, Manasagangothri, Mysore, 570 006, India.

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