A novel porphyrin based fluorescent chemosensor using a molecular recognition approach

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Free-base porphyrin covalently linked to quinone exhibits enhanced fluorescence on coupling the quinone with hydroquinone, primarily due to the unfavourable conditions for an electron transfer reaction between the singlet excited porphyrin and the newly formed quinone–hydroquinone entity.

Fluorescent chemosensors are compounds with a fluorophore, binding site and a well-defined mechanism for communication. In general, these molecular systems possess binding ability coupled with photophysical–photochemical properties.[1] Two types of metal ion sensing chemosensors are known in literature:[1,2] (i) heterocycles bearing chelating arrays of donor atoms, the intrinsic chemosensors and (ii) systems in which the donor atoms remain insulated from the fluorophore π-system, the conjugate chemosensors. Some studies have also reported anion sensing fluorophores which often involve the inherent quenching property of the analyte.[1,3] On the other hand, neutral analyte sensing devices are found to be rare due to the limited availability of systems possessing complementary binding sites with an electrostatic handle on them.[4] Here we report a porphyrin based fluorescent chemosensor, where H-bonds and charge-transfer interactions are primarily responsible for stabilizing the quinone–hydroquinone complex (Fig. 1) and demonstrate enhanced fluorescence emission of porphyrin upon coupling the quinone with hydroquinone.

The quinone appended porphyrin, 5,10,15-triphenyl-20-(3,6-dioxocyclohexa-1,4-dienyl)porphyrin‡ **1a** was synthesized by the chemical oxidation of 5,10,15-triphenyl-20-(2,5-dihydroxyphenyl)porphyrin[5] using an excess of 2,6-dichloro-3,5-dicyano-1,4-benzoquinone (DDQ). The UV–VIS spectrum of **1a** in benzonitrile revealed spectral features similar to that reported for porphyrin–quinone systems in literature.[6] Addition of hydroquinone (10 equiv.) to the solution of **1a** revealed a small red shift of *ca*. 2 nm without any dramatic changes in the ε values, indicating the absence of any interactions between the added hydroquinone and the porphyrin ring. ^{1}H NMR studies revealed quinone–hydroquinone coupling. The singlet peak corresponding to the aromatic protons of the free hydroquinone exhibited a multiplet pattern with a net deshielding of nearly 0.1 ppm on forming the quinone–hydroquinone complex, while the porphyrin ring protons experience a small shielding. The binding constant calculated from the ^{1}H NMR data is found to be 13.1 dm^3 mol^{-1} in $CDCl_3$ at 25 °C.

Compound **1a** is found to be weakly fluorescent ($\phi_f < 0.01$) and this has been ascribed to the photoinduced intramolecular electron transfer from the excited singlet-state porphyrin, the donor, to the appended quinone, the acceptor.[7] Interestingly, as shown in Fig. 2, addition of 1,4-hydroquinone to the solution of **1a** exhibits a drastic enhancement of the porphyrin fluorescence intensity§ and the two bands at 652 and 720 nm correspond to the free-base porphyrin emission.[8] After addition of 8 equiv. of 1,4-hydroquinone, the fluorescence emission reaches a maximum and further addition results in no appreciable changes. At the saturation point, the calculated fluorescence quantum yield,¶ ϕ_f is found to be 0.25 and is nearly twice that of the unsubstituted meso-tetraphenylporphyrin,[8] H_2TPP (ϕ_f = 0.13).‖

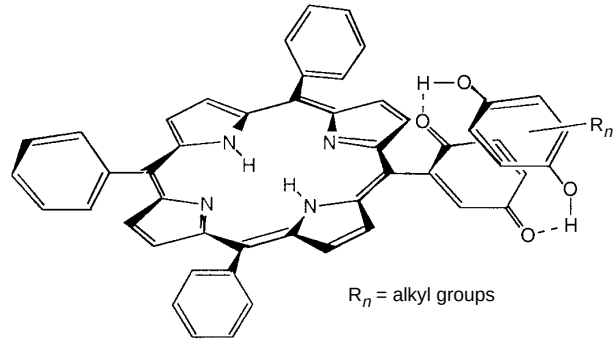

Fig. 1

Recently, we demonstrated a hydroquinone–quinone complexation in hydroquinone appended zinc porphyrin with intermolecularly added quinones.[5] Efficient fluorescence quenching of the zinc porphyrin was observed upon coupling the hydroquinone with substituted quinones. Electrochemical studies demonstrated that the reduction potential of the hydroquinone–quinone complexes are negatively shifted by 500–800 mV compared to that of the free quinones used for pairing. Based on the electrochemical reduction potentials of the newly formed hydroquinone–quinone redox couple, the optimum concentration of quenchers needed to saturate the fluorescence intensity and the calculated free-energy change, an excited-state electron transfer was suggested to be the quenching mechanism.[5] The present system, however, differs from the earlier one studied, in that the quinone entity is directly attached to the porphyrin π-system. In addition, it possesses a quinone–hydroquinone pair with a low reduction potential,** a free-base porphyrin with high oxidation potential†† and low energy of singlet-singlet emission compared to that of zinc porphyrin.[8] The net result of this redox tuning and altered photophysical property is the inhibition of fluorescence quenching due to intramolecular electron transfer. The calculated free energy change for an electron transfer from the excited free-base porphyrin to the quinone–hydroquinone complex, using the Rehm and Weller equation,[10] is found to be endergonic by *ca*. 0.33 V. As a result, the added hydroquinone upon complexing with quinone, inhibits the excited-state electron transfer in **1a** and consequently enhances the porphyrin fluorescence emission.[11]

Under normal conditions, one would expect the ϕ_f of **1a** in presence of hydroquinone to be close to that of the unsubstituted free-base porphyrin, H_2TPP; however, in the present study, the calculated ϕ_f is nearly two times that of H_2TPP [see Fig. 2(*h*)]. This additional fluorescence enhancement could be attributed to the mode of attachment of the quinone–hydroquinone to the porphyrin macrocycle and the nature of the charge-transfer interactions. Spectroscopic studies on the hydroquinone–quinone complexes have shown substantial charge-transfer interactions between the hydroquinone as a donor and benzo-

quinone as an acceptor.[12] This suggests that when the linkage is through quinone, the partial negative charge residing on the quinone would interact with the porphyrin π-system and might be responsible for fluorescence enhancement. If this is correct, then one would expect higher ϕ_f on fully reducing the quinone of **1a** instead of the partial negative charge of the quinone–hydroquinone complex. The following electrochemical studies suggest that this is more likely the case.

The cyclic voltammogram†† of **1a** in PhCN exhibits four well separated one-electron reductions (Fig. 3). The first two processes corresponding to the reduction of the appended benzoquinone are located at $E_{1/2} = -0.51$ and -0.93 V respectively[13] while the latter two processes corresponding to the porphyrin ring reductions[14] are located at $E_{1/2} = -1.41$ and $E_{pc} = -1.83$ V *vs.* SCE respectively at a scan rate of 0.1 V s^{-1}. In order to generate a neutral free-base porphyrin linked to quinone anion radical, bulk electrolysis of **1a** was carried out at an applied potential of -0.75 V, a potential slightly more negative than the first reduction potential of the appended benzoquinone. After completion of the electrolysis, the fluorescence spectrum of the one-electron reduced product was recorded [see Fig. 2(*i*)]; the emission intensity was nearly 10% more than that observed for **1a** in the presence of excess of hydroquinone, suggesting that the interactions between the partially or fully reduced quinone and the porphyrin macrocycle could be responsible for additional fluorescence enhancement. However, further studies are needed to fully understand the mechanistic details of fluorescence enhancement in this novel system and these studies are in progress.

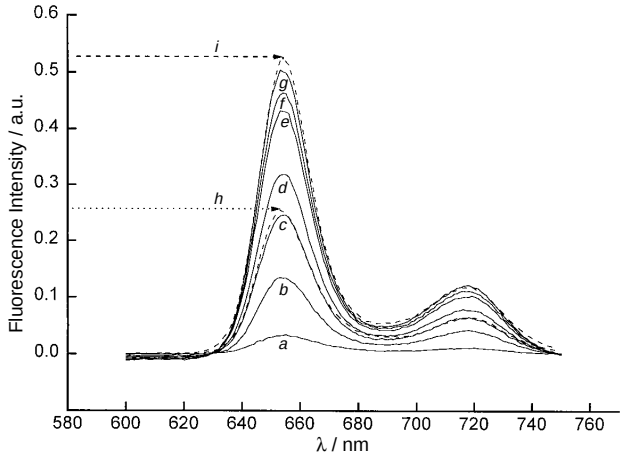

Fig. 2 Fluorescence emission spectrum of (*a*) compound **1a** (1 μm) in PhCN, λ_{ex} = 514 nm. Spectra (*b*)–(*g*) represent the emission spectrum of **1a** on increasing addition of hydroquinone (1 μm aliquots). Spectra (*h*) and (*i*) represent the emission spectrum of H_2TPP and the one-electron reduced product of **1a** in PhCN.

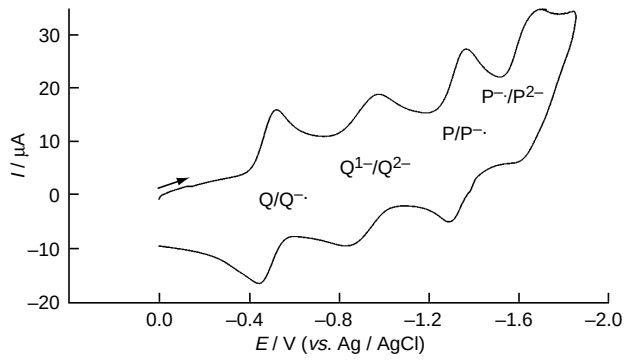

Fig. 3 Cyclic voltammogram of compound **1a** in benzonitrile, 0.1 m TBAP, scan rate = 0.1 V s^{-1}

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Footnotes

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‡ $\delta_H(CDCl_3)$ 8.90 (m, 8 H, pyrrole-H), 8.20 (s, 6 H, *ortho*-H of the triphenyl entity), 7.75 (m, 9 H, *meta*- and *para*-H), 7.29, 7.60, 8.38 (d, d and s, 3 H, quinone-H) and −2.78 (s, 2 H, imino-H). λ_{max} (PhCN)/nm (log ε) 414.6 (5.85), 511.6 (4.31), 542.2 (3.77), 590.3 (3.75) and 649.8 (3.66).

§ Addition of excess of hydroquinone to a solution of H_2TPP resulted in no appreciable changes in the fluorescence emission.

¶ Fluorescence quantum yields were calculated using the method described in ref. 9.

‖ Use of other alkyl substituted hydroquinones resulted in a similar fluorescence enhancement.

** Reduction of the quinone–hydroquinone complex in PhCN occurs at $E_{1/2} = -1.26$ V *vs.* SCE.

†† The first reversible oxidation of **1a** in PhCN, 0.1 m TBAP occurs at $E_{1/2}$ = 1.01 V *vs.* SCE.

‡‡ Cyclic voltammograms were obtained on a EG & G Model 263 A potentiostat using a three-electrode system. A glassy carbon electrode was used as the working electrode. A platinum wire served as the counter electrode, and Ag/AgCl was used as the reference electrode.

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