Studies on Porphyrin−Quinhydrone Complexes: Molecular Recognition of Quinone and Hydroquinone in Solution

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Free-base and zinc(II) porphyrins bearing either one, two, or four hydroquinone entities at the meso positions are shown to bind quinones in solutions via a quinhydrone pairing mechanism. Electrochemical studies reveal that the quinhydrone complexes are stabilized by charge-transfer interactions between the donor (hydroquinone) and the acceptor (quinone). The redox potentials of the quinhydrone complexes are governed by the potentials of the quinones utilized to form quinhydrone. The ^{1}H NMR studies reveal that the quinhydrone complexes are stabilized by H-bonding in addition to the charge-transfer interactions. Singlet emission studies have shown that the fluorescence quenching of the porphyrin increases with an increase in the number of receptors, i.e., hydroquinone entities on the porphyrin macrocycle. Control experiments performed by using zinc porphyrin bearing a dimethoxyphenyl group, i.e., a receptor entity with no H-bonding ability, indicate that the H-bonding plays an important role in quinhydrone formation. Porphyrin−quinhydrone formed by using covalently linked porphyrin−quinone and hydroquinone present in solution shows fluorescence enhancement. The measured fluorescence quantum yields, ϕ_f, are found to depend on the metal ion in the porphyrin cavity and the oxidation potential of the employed hydroquinones. The present studies also reveal that the measured ϕ_f values depend on how the quinhydrone is linked to the porphyrin macrocycle, i.e., either through quinone or hydroquinone. Generally, porphyrin−quinhydrone formed by hydroquinone-appended porphyrins shows decreased ϕ_f values as compared to porphyrin−quinhydrone formed by quinone-appended porphyrins.

Introduction

There has been considerable research interest in the synthesis of porphyrins bearing receptor entities on the ring periphery for the development of new biomimetic model systems.[1−5] Among these, noncovalently linked electron-transfer donor−acceptor dyads featuring porphyrin and quinone are important to further our understanding of the naturally occurring photosynthetic electron-transfer reactions.[1−3] Though porphyrin−quinone dyads stabilized by noncovalent interactions, such as hydrogen bonds, ion pairing, cation complexation, or van der Waals interactions, are realized to be essential, studies on such models with well-defined binding mechanisms remain limited.[1−3] In addition, these noncovalently linked donor−acceptor dyads are highly useful for the development of new molecular electronic devices and optical sensors.[6]

Quinhydrone, a 1:1 quinone−hydroquinone, is a well-known molecular charge-transfer complex (Scheme 1).[7,8] In this complex, the charge-transfer interactions between the electron donor (hydroquinone) and the electron acceptor (quinone) primarily stabilize the complex while the

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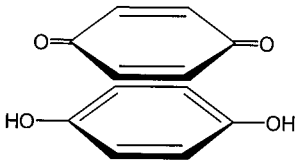
Scheme 1



hydrogen bonds provide additional stability both in the solid state and in solution.[7,8] The formation and importance of such quinhydrone type charge-transfer complexes involving electron-acceptor quinones and electron-donor biomolecules, such as purines, pyrimidines, amino acids, and proteins, is well-documented.[8b,c] Staab and coworkers have reported on the orientation dependence of charge-transfer interactions for intramolecular-type quinhydrone complexes in diastereomeric [2,2]paracyclophane and [3,3]paracyclophane molecular systems.[9]

Recently, we reported a novel molecular recognition route by using the quinhydrone pairing approach to form noncovalently linked porphyrin−acceptor complexes and fluorescent chemosensors.[10,11] In our approach, porphyrin−quinhydrone involving either hydroquinone-appended porphyrin and quinone present in solution[10] or quinone-appended porphyrin and hydroquinone present in solution were formed.[11] Quenching of singlet excited porphyrin was observed in a hydroquinone-linked zinc porphyrin after formation of hydroquinone−quinone complex.[10] Moreover, it was possible to control the extent of excited-state quenching by using a quinone-appended free-base porphyrin and hydroquinone present in solution.[11] In the present study, we have performed extensive studies on this molecular recognition approach by using porphyrins bearing one, two, or four hydroquinone or quinone entities (Schemes 2 and 3) and report on the mechanistic details of quinhydrone formation in porphyrin systems. The role of various quinones and the importance of hydrogen bonding in stabilizing the quinhydrone are also investigated. In contrast to the earlier reports,[8b,c] the present study demonstrates that the hydrogen bonding is a major factor in stabilizing quinhydrone in solution.

The rationale for the different compounds (Schemes 2 and 3) employed in the present study is as follows: Compounds **1a** and **1b** are employed to probe the effect of the metal ion in the porphyrin cavity on the free-energy change and the resulting fluorescence quenching of the excited porphyrin. The porphyrins bearing two and four hydroquinone receptors, **1c** and **1d**, are employed to visualize the effect of multiple receptors on a single porphyrin ring and its effect on fluorescence quenching. Compound **1e**, bearing a dimethoxyphenyl substituent, i.e., a substituent capable of forming quinhydrone stabilized only by charge-transfer interactions and not by H-bonding, is used to understand the role of H-bonding. Compound **1f**, *meso*-tetraphenylporphyrinatozinc(II), bearing no receptor hydroquinone or dimethoxyphenyl group, is utilized to quantitate the intermolecular interactions and the associated bimolecular quenching process.

The recognition of hydroquinone in solution is investigated by using covalently linked free-base porphyrin−quinone (**2a**) and zinc porphyrin−quinone (**2b**) dyads. Here, the quinone substituent on the porphyrin ring binds hydroquinone to form quinhydrone. Measurement of the fluorescence quantum yields of the porphyrin−quinhydrone complexes formed by various hydroquinones monitors the molecular recognition process.

Results and Discussion

Characterization of the Solid Porphyrin−Quinhydrone Complexes. It is found that the porphyrin−quinhydrone complexes slowly precipitate out in chloroform/hexane (1:1 v/v) solutions at −5 °C containing any of **1a**−**d** and quinones. The number of quinhydrone entities depends on the number of hydroquinone substituents on the porphyrin periphery. That is, **1a**, **1c**, and **1d** bearing one, two, and four hydroquinone substituents, respectively, result in the formation of porphyrins bearing one, two, and four quinhydrone entities. The positive ion electrospray mass spectrum of the isolated porphyrin−quinhydrone complexes in either acetonitrile or dichloromethane matrix under mild conditions exhibited the theoretically predicted molecular ion peaks. Under the same experimental conditions, the starting materials, i.e., **1a**−**d** and benzoquinone, revealed molecular ion peaks corresponding only to the mass of individual compounds.

Figure 1 shows the FT-IR spectrum of **1a** and **1a**−benzoquinone complex in a KBr matrix. The hydroquinone -OH groups of **1a** appear at 3430 cm^{-1}. After complexation of **1a** with benzoquinone, i.e., in the solid zinc porphyrin−quinhydrone, the -OH stretching frequency is lowered by about 200 cm^{-1} and appears at 3232 cm^{-1}. Similarly, the carbonyl stretching frequency of the bound quinone in zinc porphyrin−quinhydrone appears at 1632 cm^{-1} (Figure 1b). That is, it is lowered by 30 cm^{-1} as compared to the carbonyl stretching frequency of either benzoquinone or quinone-appended porphyrin, **2a**. Similar spectral trends have been observed for porphyrin−quinhydrone complexes formed by either **1c** or **1d** and hydroquinone as well as by **2a** and hydroquinone. These results indicate formation of quinhydrone that is quinone−hydroquinone complex[12] both in hydroquinone-appended porphyrins as well as quinone-appended porphyrins.

^{1}H NMR Studies. The ^{1}H NMR studies have been performed to verify the existence of H-bonding between the hydroquinone -OH groups of **1a** and the carbonyl groups of the quinone entity in solution. Representative spectral changes observed on addition of 2-methyl anthraquinone to a solution of **1a** in benzene-d_6 are shown in Figure 2. The solvent benzene-d_6 is used here to avoid any intermolecular coordination between the -OH groups and the zinc metal center.[13] In the studied solvent, the resonance peaks corresponding to the -OH protons of **1a**

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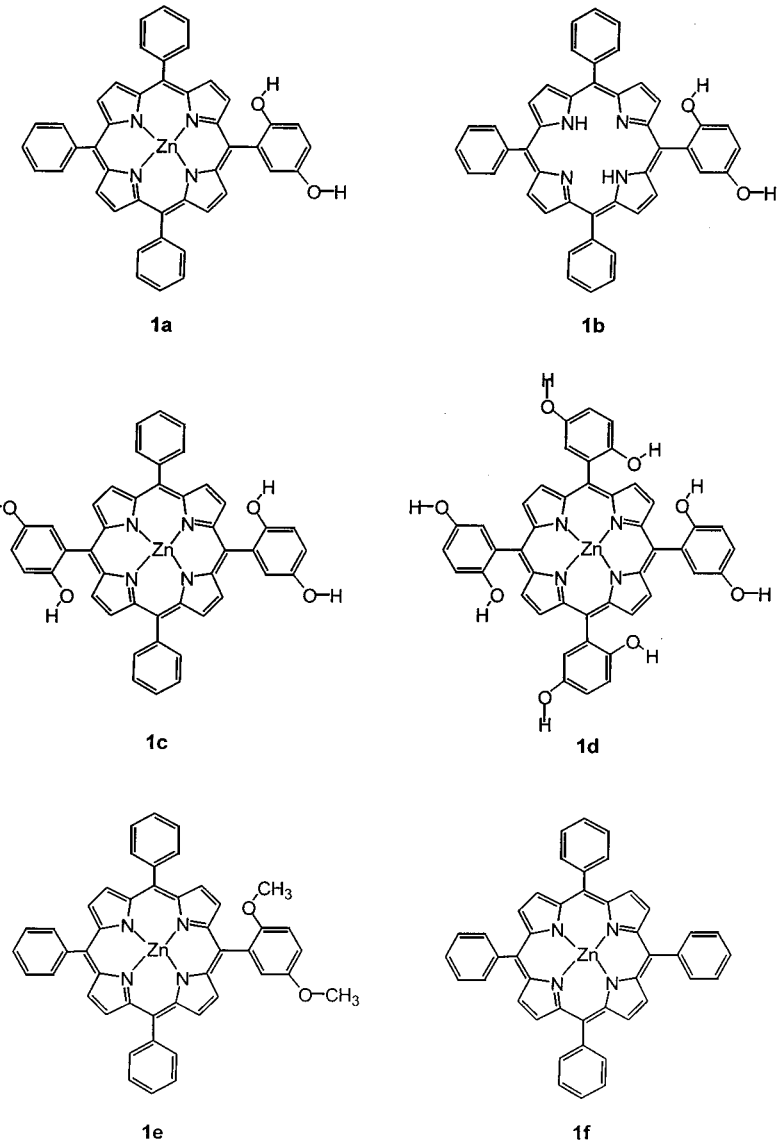
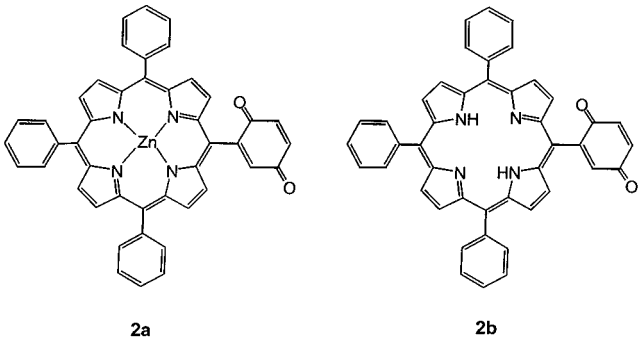
Scheme 2



Scheme 3



are located at 4.00 and 4.85 ppm, respectively. The positions of the resonance peaks corresponding to the three phenyl and the β-pyrrole protons of **1a** are located at positions not much different from that of *meso*-tetraphenylporphyrinatozinc(II).[10,11] After addition of quinone, the -OH peaks undergo a low field shift without perturbing appreciably the peak positions of the other porphyrin ring protons. Additionally, the resonance peak positions of 2-methyl anthraquinone protons reveal a small deshielding (<0.1 ppm). The larger downfield shift of both the -OH proton peaks and negligibly small shift of the porphyrin ring and the 2-methyl anthraquinone proton peaks suggests quinhydrone formation, most likely by forming two hydrogen bonds with the carbonyl groups of quinone.

Interestingly, for **1c** and **1d**, bearing two and four hydroquinone receptors, at least two types of binding are possible as shown in Scheme 4 for **1c**. The first type involves quinhydrone formation like in **1a** while the second involves porphyrin−quinone $\pi-\pi$ type stabilized by H-bonding between the quinone carbonyl groups and the hydroquinone ortho OH groups located at the opposite sides of the porphyrin ring (Scheme 4b). The latter type of binding is similar to that reported by Ogoshi et al. for 2-hydroxynaphthyl-derived porphyrins.[2c] If the second type of binding were to occur, then one would expect shielding of quinone protons due to porphyrin ring current effects[2c]. The optical absorption bands of the porphyrin are also expected to reveal spectral shifts under these conditions. The optical absorption and ^{1}H NMR studies involving **1c** or **1d** and quinones revealed spectral changes similar to that observed for titration of **1a** with quinones, indicating a quinhydrone type of

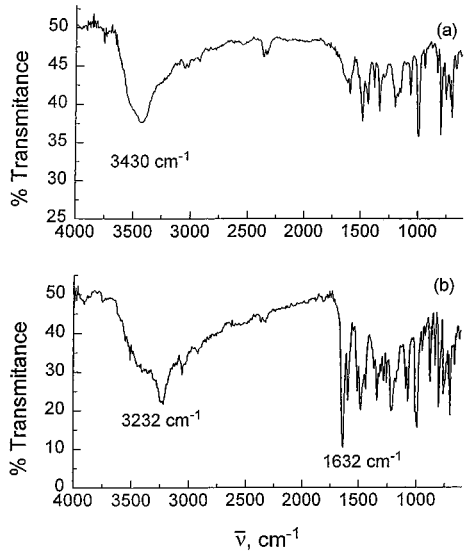


Figure 1. FT-IR spectrum of (a) **1a** and (b) isolated **1a**−benzoquinone complex in a KBr matrix.

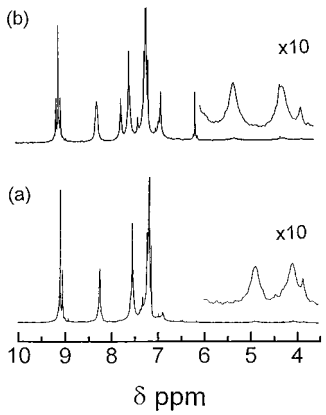


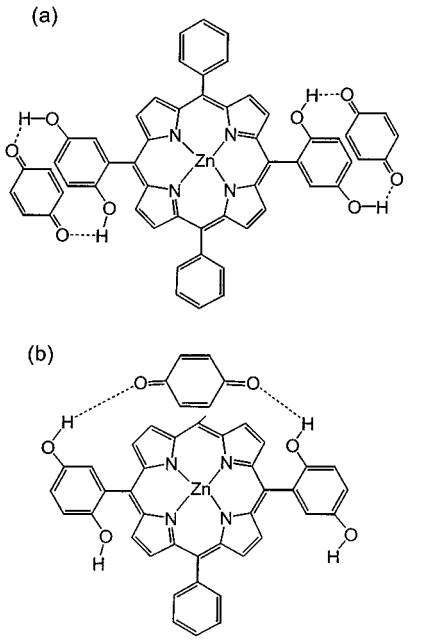
Figure 2. ^{1}H NMR spectrum of **1a** (a) in the absence and (b) in the presence of 1 equiv of 2-methyl anthraquinone in benzene-d_6. The origin of the spikelike peak at 3.9 ppm is not clear.

binding. The observed deshielding of both the -OH protons of the hydroquinone entities further supports the quinhydrone-type binding as shown in Scheme 4a.

Electrochemistry of Porphyrin−Quinhydrone Complexes. The redox potentials of the charge-transfer stabilized quinhydrone govern the overall stability and energetics of the porphyrin−quinhydrone complexes. Therefore, electrochemical study of the porphyrin−quinhydrone complexes leading to determination of the redox potentials is important. Quinhydrone undergoes a two-electron, two-proton electrochemical reduction ultimately resulting in the formation of hydroquinone (Scheme 5).[7] A complete characterization of the intermediates involved in the electrochemical process is difficult due to the associated electrochemical and chemical complications.[7] In the present investigation, however, it has been possible to determine the formal redox potentials of a few quinhydrone complexes by performing a systematic study involving control experiments.

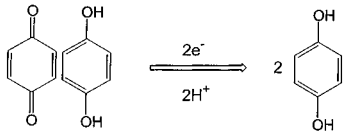
The quinones used to form quinhydrone with hydroquinone-appended porphyrins are listed in Table 1. They undergo two one-electron reversible electroreductions in nonaqueous solvent solutions.[14] In benzonitrile containing 0.1 M (TBA)ClO_4, values of the first redox potential

Scheme 4



(one of the *meso* phenyl ring is not shown for clarity)

Scheme 5



of the employed quinones varies between 0.56 V for dichlorodicyanobenzoquinone (DDQ) and −0.97 V vs SCE for 2-ethyl anthraquinone, covering a wide potential range of 1.53 V (Table 1). The hydroquinones used to form quinhydrone with quinone-appended porphyrins undergo a two-electron irreversible electrooxidation process.[14] The values of the electrooxidation peak potential vary between 0.71 V for 2-methoxyhydroquinone and 1.0 V vs Ag/AgCl for tetrachlorohydroquinone (Table 2).

Figure 3 shows cyclic voltammograms of **1a**, **1a** in the presence of DDQ (1.2 equiv), and **2a** in benzonitrile containing 0.1 M (TBA)PF_6. The two ring-centered electrooxidations of the porphyrin macrocycle of **1a** are located at $E_{1/2} = 0.89$ and 1.21 V vs SCE along with a third one at $E_{pa} = 0.83$ V, corresponding to the electrooxidation of the hydroquinone substituent of **1a**.[10] Addition of an easily reducible quinone, DDQ, to the solution of **1a** decreases the anodic peak current of the hydroquinone oxidation accompanied by a new anodic process located at $E_{1/2} = 1.40$ V vs SCE. During the negative potential scan, two new redox processes located at $E_{pa} = -0.31$ and −0.49 V vs SCE, corresponding to electroreduction of the quinhydrone, are also observed. To confirm that these processes are due to the quinhydrone reduction and not to quinone formed by chemical oxidation of the hydroquinone of **1a** by DDQ, control experiments involving **2a**, i.e., quinone-appended zinc porphyrin, are performed. As shown in Figure 3c, the voltammograms of **2a** are different from those seen in Figure 3a,b. That is, only two reversible anodic processes corresponding to the

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Table 1. Steady-State Fluorescence-Quenching Data for Functionalized Porphyrins by Various Quinones[a]

quinone	reduction potential Q/Q•−	reduction potential Q•−/Q2−	V vs SCE[b] [QQ′H2]/[QQ′H2]−	[Q1/2][c], mM 1a	1b	1c	1d	1e	1f
dichlorodicyanobenzoquinone	0.56	0.25	−0.31	0.026	0.198	0.023	0.015	1.86	19
tetrafluorobenzoquinone	−0.03	−0.72	−0.49	0.078	1.15	0.092	0.028	5.57	62
tetrachlorobenzoquinone	−0.05	−0.73	−0.47	0.082	1.16	0.099	0.032	5.85	68
dichloronaphthaquinone	−0.47	−1.09	−0.82	0.255	1.60	0.013	0.035	18.20	241
1,4-benzoquinone	−0.55	−1.12	−1.26	0.302	2.37	0.134	0.046	21.56	288
methyl-1,4-benzoquinone	−0.56	−1.10	−1.33	0.333	2.55	0.148	0.060	23.77	350
naphthaquinone	−0.72	−1.20		0.534	6.06	0.365	0.185	38.12	540
2-methyl-1,4-naphthaquinone	−0.73	−1.16		0.566	6.82	0.417	0.212	40.40	585
duroquinone	−0.84	−1.42		0.776	8.11	0.521	0.266	55.39	800
2-methyl anthraquinone	−0.92	−1.43		1.018	10.65	0.659	0.354	72.67	1050
2-ethyl anthraquinone	−0.97	−1.45		1.100	11.47	0.735	0.478	78.52	1180

[a] 20 μM porphyrin in deaerated benzonitrile, λ_{max} = 556 nm. [b] In benzonitrile; 0.1 M (TBA)PF_6; 0.1 V s^{-1}. [c] [$Q_{1/2}$] represents the concentration of quinone required to decrease the initial emission intensity of porphyrin by 50% according to the Stern−Volmer method; error = +6%.

Table 2. Emission Properties of Porphyrin−Quinhydrone Complexes Formed between Benzoquinone-Appended Porphyrins[a] and Hydroquinone

hydroquinone, H_2Q	E_{pa}[b], V vs Ag/AgCl	ϕ_f for **2a**:H_2Q	ϕ_f for **2b**:H_2Q
2-methoxy hydroquinone	0.71	0.053	0.266
2,3-dimethyl hydroquinone	0.80	0.051	0.239
2-methyl hydroquinone	0.82	0.046	0.256
hydroquinone	0.92	0.041	0.249
2-chlorohydroquinone	0.96	0.022	0.129
2-phenyl hydroquinone	0.98	0.026	0.110
tetrachlorohydroquinone	1.0	0.019	0.096
ZnTPP		0.103[c]	
H_2TPP			0.130[c]

[a] Porphyrin concentration = 20.0 μM in deaerated benzonitrile. [b] In 0.1M (TBA)PF_6 benzonitrile; scan rate = 0.1 V s^{-1}. [c] From ref 19.

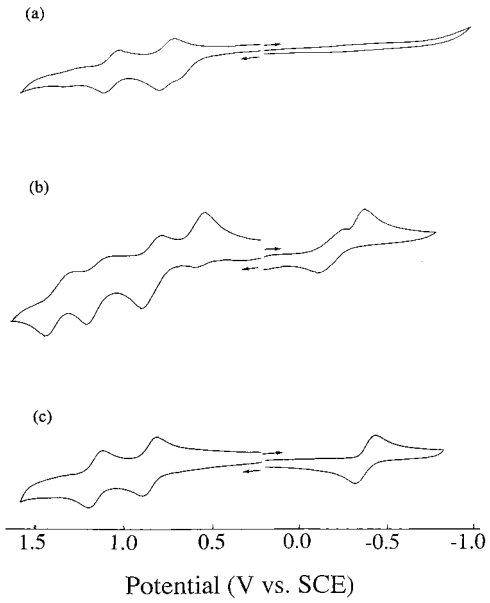

Figure 3. Cyclic voltammograms of (a) **1a**, (b) **1a** + DDQ (1.2 equiv), and (c) **2a** in 0.1 M (TBA)ClO_4 containing benzonitrile.

porphyrin ring oxidations and a reversible reduction process located at $E_{1/2}$ = −0.51 V vs SCE corresponding to the reduction of the appended quinone are observed. These results suggest that the electrode processes located at E_{pa} = −0.31 and −0.49 V in Figure 3b correspond to the reduction of the newly formed quinhydrone. On the basis of electrochemical redox potentials of simple quinhydrone in benzonitrile,[10] the redox couple located at $E_{1/2}$ = 1.40 V has tentatively been assigned to the oxidation of the newly formed quinhydrone, although it is difficult to obtain spectral evidences because of the occurrence of electrochemical processes prior to this redox process.

Similar electrochemical behavior has been observed during the titration of **1a** in the presence of other quinones. However, voltammetric peaks corresponding to the quinhydrone reduction are not well-developed, especially for quinhydrones formed by quinones of higher reduction potentials. Additional difficulties are also encountered due to the overlapping porphyrin ring reductions at more negative potentials and large amounts of quinone needed to produce measurable quantities of quinhydrone. It may also be mentioned here that in the presence of excess amounts of easily reducible quinones (such as DDQ, tetrafluorobenzoquinone, or tetrachlorobenzoquinones), a slow oxidation of the hydroquinone of **1a** occurs to yield **2a**. Therefore, determination of the potential corresponding to the reduction of quinhydrone has been possible only for the first six complexes (Table 1). The measured potentials exhibit a direct correlation with the reduction potential of the employed quinones. Generally, the quinhydrones are difficult to reduce by 200−500 mV as compared to the redox potentials of the corresponding free quinones.

Excited-State Emission Studies. Quenching of the porphyrin emission by quinones under inter- and intramolecular reaction conditions is very well-known.[4,15] Both steady-state and time-resolved emission studies have confirmed that the quenching mainly involves electron transfer from photoexcited porphyrin to quinones.[1−4,15] By using a variety of covalently linked porphyrin−quinone dyads, mutual orientation of the donor−acceptor entities and relevant geometrical factors necessary for efficient electron transfer have been evaluated by several research groups.[4]

The fluorescence quenching of **1f** (a donor bearing no receptor site) in the presence of quinones follows an intermolecular bimolecular quenching process.[15] The data of such quenching can be analyzed by using the Stern−Volmer equation.[16]

$$I_o/I = 1 + K_{sv}[Q] \quad (1)$$

where I_o and I represent fluorescence emission intensities

(15) Harriman, A.; Porter, G.; Searle, N. *J. Chem. Soc., Faraday Trans 2* **1979**, *75*, 1515.
(16) Natarajan, L. V.; Blankenship, R. E. *Photochem. Photobiol.* **1983**, *37*, 329.

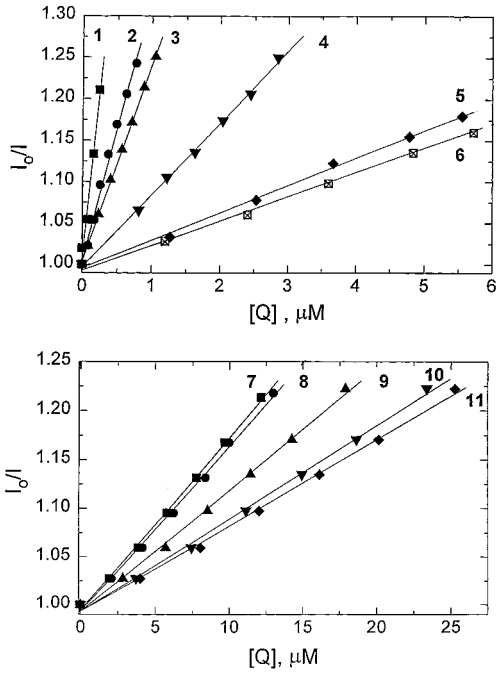

Figure 4. Stern−Volmer plots for the fluorescence quenching of **1a** in benzonitrile by different quinones: (1) DDQ, (2) tetrafluorobenzoquinone, (3) tetrachlorobenzoquinone, (4) dichloronaphthaquinone, (5) benzoquinone, (6) methyl benzoquinone, (7) naphthaquinone, (8) 2-methyl naphthaquinone, (9) duroquinone, (10) 2-methyl anthraquinone, and (11) 2-ethyl anthraquinone.

of porphyrin in the absence and the presence of the quencher, [Q], respectively; and K_{sv} is the Stern−Volmer quenching constant. K_{sv} is equal to the product of the bimolecular quenching constant, k_q, and the excited-state lifetime, τ, of the donor porphyrin in the absence of a quencher. The lifetime of **1f** in deareated benzonitrile solutions by using time-correlated singlet-photon counting technique is found to be 2.4 ns.[10] The calculated k_q values for the bimolecular reactions involving **1f** and quinones, determined from the slopes of the Stern−Volmer plots, are found to depend on the redox potentials of the quenchers. The magnitude of k_q varies between 21.9×10^9 M^{-1} for DDQ and 3.5×10^8 M^{-1} for 2-ethylanthraquinone and are close to that expected for diffusion-controlled processes.[6e]

Interestingly, an efficient quenching is observed when porphyrins bearing hydroquinone receptors are employed. The Stern−Volmer plots constructed for the fluorescence quenching of **1a**−**d** by quinones are linear, indicating absence of appreciable amounts of ground-state complexation between the porphyrin π-ring and the quinone, a result consistent with the ^{1}H NMR results. Representative Stern−Volmer plots for the donor **1a** and various quinones are shown in Figure 4. The quencher concentration necessary to reduce the fluorescence intensity to a minimum value is found to be nearly 2 orders of magnitude smaller than that needed for **1f**, suggesting an intramolecular-type quenching process. To quantitate this, we have calculated the concentration of quinones required to quench 50% of the original fluorescence intensity of the donor porphyrins, $[Q_{1/2}]$, from the Stern−Volmer plots. The calculated values are listed in Table 1 for all the porphyrins shown in Scheme 1.

From Table 1, it follows that the $[Q_{1/2}]$ values depend on the redox potential of the acceptor, the quinone, and

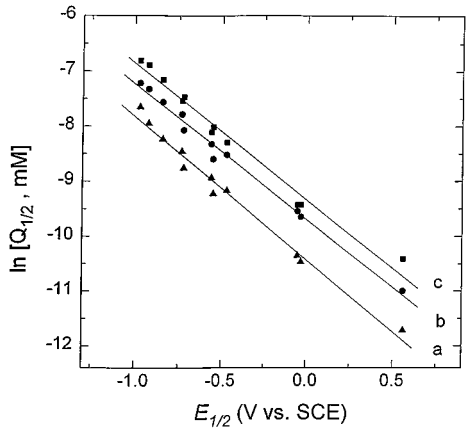

Figure 5. Dependence of $\ln[Q_{1/2}]$ on the first reduction potential of the quinones for (a) **1a**, (b) **1c**, and (c) **1d**.

the number of hydroquinone receptors on the porphyrin ring. Plots of $\ln[Q_{1/2}]$ vs $E_{1/2}$ of the quenchers are found to be linear (Figure 5). Generally, porphyrins bearing a higher number of receptor hydroquinones undergo efficient quenching, and this has been ascribed to the available higher number of binding sites. The dependence of $\ln[Q_{1/2}]$ on $E_{1/2}$ also suggests that the primary quenching mechanism involves photoinduced electron transfer (PET).[10,17] The PET quenching mechanism is also supported by a comparison between the $[Q_{1/2}]$ values obtained for **1a** and **1b**. Here, the zinc porphyrin in **1a** is a better donor as compared to the free-base porphyrin in **1b** because of its lower oxidation potential[18] and higher energy of the singlet−singlet emission.[19] The free-energy change, ΔG, for PET, calculated by using the oxidation potential of the donor, the reduction potential of the acceptor, and the energy corresponding to the singlet−singlet emission of the donor porphyrin, according to the Rehm and Weller method,[17] is found to be more exergonic for reactions involving **1a** than that involving **1b**. Hence, lower values of $[Q_{1/2}]$ are expected for **1a** as compared to **1b**. The calculated $[Q_{1/2}]$ values in Table 1 show such a trend and support the PET-quenching mechanism.

Role of Hydrogen Bonding. The importance of hydrogen bonding in quinhydrone formation and its role in governing the fluorescence-quenching process has been examined in the present study by using **1e** bearing a dimethoxyphenyl receptor entity. The results of fluorescence quenching, performed by using **1e**, are given in Table 1. The determined $[Q_{1/2}]$ values for **1e** are 1 order of magnitude smaller than that obtained for **1f** (which involves bimolecular quenching) and are 1 order of magnitude higher than that of **1a**. These results clearly indicate that employing **1a**, possessing both charge-transfer and H-bonding abilities, markedly increases the quenching ability of the porphyrin. Hence, the H-bonding ability of the hydroquinone receptor is borne out to be an important factor for efficient quenching of the porphyrin singlet state in the studied self-assembled via quinhydrone pairing, donor−acceptor dyads.

Formation of Quinhydrone in Quinone-Appended Porphyrins. The covalently linked dyads (**2a** and **2b)**

(17) Rehm, D.; Weller, A. *Isr. J. Chem*. **1970**, *8*, 529.
(18) Kadish, K. M.; Van Caemelbecke, E.; Royal, G. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000; Vol. 55, Chapter 1.
(19) (a) Seybold, P. G.; Gouterman, M. *J. Mol. Spectrosc.* **1969**, *31*, 1. (b) Quimby, D. J.; Longo, F. R. *J. Am. Chem. Soc.* **1975**, *97*, 5111.

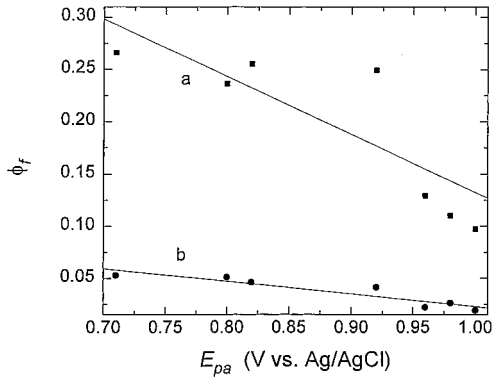

Figure 6. Dependence of ϕ_f on the oxidation potential, E_{pa}, of the hydroquinones for (a) **2a** and (b) **2b**.

employed to investigate the quinhydrone formation are found to be weakly fluorescent due to the occurrence of PET from the singlet excited porphyrin to the covalently linked quinone.[11,20] Free-energy calculations have indicated that the electron-transfer quenching is more favored in **2a** than in **2b** by about 0.42 eV. Addition of hydroquinone to solutions of either **2a** or **2b** increases the porphyrin fluorescence. Table 2 lists the fluorescence quantum yield,[21] ϕ_f, determined for **2a** and **2b** in the presence of different hydroquinones at their saturation point. For comparison, the fluorescence quantum yields for *meso*-tetraphenylporphyrin, H_2TPP, and ZnTPP, **1f**,[19] are also listed. From Table 2 and Figure 6, it follows that the ϕ_f depends on the type of porphyrin (free-base or zinc porphyrin) and on the oxidation potential, E_{pa}, of the employed hydroquinones. The higher scattering in the plots may be due to the steric effects caused by the hydroquinone substituents and the irreversible oxidation potentials of hydroquinones. For **2b**−hydroquinone, the ϕ_f value is twice as much as H_2TPP. However, the maximum ϕ_f for **2a**−hydroquinone is about 50% of that of ZnTPP. It may also be mentioned here that the addition of 1,4-dimethoxybenzene to a solution of **2a** or **2b** does not increase the ϕ_f appreciably.

The above observations can be rationalized as follows: The charge-transfer interactions of the quinone−hydroquinone complexes [$Q^{\delta-}$:$H_2Q^{\delta+}$] increase in the presence of easily reducible quinones or easily oxidizable hydroquinones or both. The quinhydrone is a weak electron acceptor as compared to the quinone employed to form the quinhydrone (Table 1). As a result, the ϕ_f of **2a**−hydroquinone and **2b**−hydroquinone is expected to be larger than that of the starting materials, **2a** and **2b**. In addition, the free-energy calculations[17] suggest that the electron-transfer quenching is more exergonic in the **2a**−hydroquinone complex than in the **2b**−hydroquinone complex. Hence, a lower ϕ_f is obtained for **2a**−hydroquinone as compared to **2b**−hydroquinone (Table 2).

A comparison of the emission behavior between the two types of porphyrin−quinhydrone complexes investigated here indicates that the mode of attachment of quinhydrone to the porphyrin macrocycle also affects the emission behavior. That is, the ϕ_f for **1a**−quinone complexes is 20−30% smaller than that of **2a**−hydroquinone complexes even though both have a zinc porphyrin and quinhydrone donor−acceptor entities. Similar trends are also observed for the free-base porphyrin containing **1b**−quinone and **2b**−hydroquinone complexes.[23] One possible explanation for this behavior could be the formation of intermediate charge-transfer states. It is likely that the interactions between the charge-transfer stabilized quinhydrone [$Q^{\delta-}$:$H_2Q^{\delta+}$] and porphyrin π-system alters the porphyrin emission behavior. In the case of **2a**−hydroquinone, the partial negative charge located on the quinone unit of the quinhydrone entity interacts with the porphyrin π-system thereby increasing the fluorescence intensity.[11] Similarly, when the linkage is through hydroquinone, like in the case of **1a**−quinone, the partial positive charge located on the hydroquinone of the quinhydrone entity interacts with the porphyrin π-system thereby decreasing the fluorescence intensity. These observations indicate that the mode of linking of quinhydrone to the porphyrin ring plays an important role in controlling the photophysical properties of the porphyrin complex.

Formation of Quinhydrone-Paired Porphyrin Dimer. Another interesting aspect of the present study is to verify whether the quinhydrone pairing mechanism can be utilized to form self-assembled supramolecular porphyrins. With this in mind, we have attempted to form a hetero porphyrin dimer containing porphyrins **1a** and **2b**. It is observed that the self-assembled dimer precipitates out in solution (in about 6 h) when stoichiometric amounts of **1a** and **2b** were allowed to interact in $CHCl_3$/hexane (1:1 v/v) solution at −5 °C. Positive ion electrospray mass spectrum of the dimer in CH_3CN matrix revealed the expected molecular ion peak. The ^{1}H NMR spectrum of **1a** revealed a net deshielding of the hydroquinone -OH protons on addition of increasing amounts of **2b**, a result similar to that observed for **1a** and quinone pairing (Figure 2), indicating the formation of a quinhydrone-paired porphyrin dimer (see Supporting Information for mass and ^{1}H NMR spectral details). Presently, we are engaged in the synthesis and physicochemical studies of other self-assembled via quinhydrone-pairing porphyrin dimers, trimers, and pentamers involving porphyrins **1a**, **1c**, and **1d** and porphyrins **2a** and **2b**.

Conclusion

It has been shown that both the free-base and the zinc(II) porphyrins bearing either one, two, or four hydroquinone receptors bind quinones via quinhydrone pairing. As shown by means of the electrochemical and ^{1}H NMR studies, the porphyrin−quinhydrone complexes are primarily stabilized by charge-transfer interactions between the electron donor (hydroquinone) and the electron acceptor (quinone) as well as by H-bonding interactions. The redox potentials of the quinhydrone are governed by the potential of the quinone utilized to form the quinhydrone. The fluorescence emission studies have indicated that the quenching ability of the donor, i.e., porphyrin, is larger the larger the number of receptors, i.e., hydroquinone substituents, on the macrocycle. The values of quenching efficiency, determined in terms of

(20) (a) Dalton, J.; Milgrom, L. R. *J. Chem. Soc., Chem. Commun.* **1979**, 609. (b) Chan, A. C.; Dalton, J.; Milgrom, L. R. *J. Chem. Soc., Perkin Trans 2* **1982**, 707. (c) Bergkamp, M. A.; Dalton, J.; Netzel, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 253.

(21) The ϕ_f values were calculated according to the method described in ref 22.

(22) Austin, A.; Gouterman, M. *Bioinorg. Chem*. **1978**, *9*, 281.

(23) This effect is seen in solutions of isolated solid porphyrin−quinhydrone complexes as well as in situ generated complexes.

[$Q_{1/2}$], follow the $E_{1/2}$ values of the quinones suggesting that electron transfer from the singlet excited state is the main quenching mechanism. Experiments performed by using dimethoxyphenyl-bearing zinc porphyrin have revealed the significance of the hydrogen bonding. Quinhydrone formed by using porphyrin covalently linked to a quinone and hydroquinone present in solution shows fluorescence enhancement. The measured ϕ_f values depend on the nature of the porphyrin and the redox potentials of hydroquinones. The mode of attachment of the quinhydrone to the porphyrin ring is also shown to affect the emission behavior of the porphyrin. Generally, porphyrin−quinhydrone complexes formed by hydroquinone-linked porphyrins show decreased ϕ_f values as compared to a porphyrin−quinhydrone complex formed by quinone-linked porphyrins. Finally, the present quinhydrone-pairing approach is shown to be a useful approach to obtain self-assembled supramolecular porphyrins.

Experimental Section

General Information. Benzonitrile (Aldrich) for spectral and electrochemical experiments was distilled over P_2O_5 under vacuum. Tetra-*n*-butylammonium perchloride, (TBA)ClO_4 (Kodak), and tetra-*n*-butylammonium hexafluorophosphate, (TBA)PF_6 (Aldrich), were recrystallized from ethyl alcohol. All other reagents were commercial chemicals of analytical grade. They were used without further purification, unless otherwise indicated. The newly synthesized compounds were freshly purified by column chromatography, and their purity was tested by TLC prior to spectral measurements.

Instrumentation. The UV−visible spectral measurements were carried out with a Shimadzu model 1600 UV−visible spectrophotometer. The fluorescence was monitored by using a Spex Fluorolog spectrometer. A right angle detection method was used. The ^{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 by using a conventional three-electrode system on a EG&G model 263A potentiostat. A platinum button electrode was used as the working electrode. A platinum wire served as the counter electrode. A KCl saturated calomel electrode (SCE) or an Ag/AgCl electrode, separated from the test solution by a fritted supporting electrolyte/solvent bridge, was used as the reference electrodes.

5,10,15-Triphenyl-20-(2,5-dihydroxyphenyl)porphyrinatozinc, 1a, and 5,10,15-Triphenyl-20-(2,5-dihydroxyphenyl)porphyrin, 1b. These were synthesized according to the earlier published methods with few modifications.[10,13] First, 5,10,15-triphenyl-20-(2,5-dimethoxyphenyl)porphyrin was synthesized by reacting 2,5-dimethoxybenzaldehyde (1 mM), pyrrole (4 mM), and benzaldehyde (3 mM) in 450 mL of propionic acid for 45 min. The propionic acid was removed under reduced pressure, and the solid mixture was washed with methanol and purified on a basic alumina column using toluene:hexane (1:1 v/v) as eluent. Yield 5.02%. ^{1}H NMR ($CDCl_3$): δ 8.83 (s, 8H, β-pyrrole), 8.21 (m, 6H, *o*-phenyl), 7.77−7.70 (m, 9H, *m*- and *p*-phenyl), 7.61−7.26 (d, d, s, 3H, dimethoxy phenyl), 3.91−3.52 (s, s, 6H, -OCH_3), −2.84 (s br, 2H, imino). UV−vis (benzonitrile) λ, nm (log ϵ): 415 (5.40), 512 (4.13), 546 (3.79), 587 (3.68), 645 (3.58). FAB-mass spectroscopy (*m*/*z*): calcd for CH_3CN, 674.76; found, 674.8.

Compound **1b** was synthesized by drop by drop addition of 5 mL of BBr_3/CH_2Cl_2 (1 M) to a solution of 0.2 g (0.3 mM) of 5,10,15-triphenyl-20-(2,5-dimethoxyphenyl)porphyrin dissolved in a minimum amount of CH_2Cl_2 at −78 °C. The solution was maintained at −78 °C for 1 h during which the addition was completed. This mixture was then allowed to attain rt and was stirred for another 12 h. At the end of this 12 h period, the mixture was again cooled to −5 °C, taking care that the temperature was maintained below 5 °C, and 5 mL of cold water was added to quench the reaction, followed by addition of saturated sodium bicarbonate solution. This combined solution was stirred for 0.5 h, followed by evaporation of the combined solution under reduced pressure. The solid was washed with water, dried, and then washed with chloroform. The solid thus obtained was purified on a basic alumina column using $CHCl_3$/MeOH (95:5 v/v) as eluent to yield **1b**. Yield 70.1%. ^{1}H NMR ($CDCl_3$): δ 8.81 (m, 8H, β-pyrrole), 8.19 (m, 6H, *o*-phenyl), 7.75 (m, 9H, *m*- and *p*-phenyl), 7.32−7.01 (s, d, d, 3H, hydroquinone ring), 4.65 (s, br, -OH), −2.74 (s, br, 2H, imino). UV−vis (benzonitrile) λ, nm (log ϵ): 416.5 (5.36), 513 (4.13), 546 (3.79), 588 (3.68), 646(3.58). FAB-mass spectroscopy (*m*/*z*): calcd for CH_3CN, 646.7; found, 646.9.

Compound **1a** was synthesized by metalation of **1b** with zinc acetate. To a solution of **1b** (0.2 g, 0.31 mM) in $CHCl_3$, excess of zinc acetate in methanol was added. This solution was stirred for 30 min. The solvent was removed under reduced pressure, and the crude product was dissolved in CH_2Cl_2, washed with water, and dried over sodium sulfate. The solution was concentrated and loaded on to a basic alumina column. The pure **1a** was eluted with 90:10 (v/v) $CHCl_3$:MeOH. Yield 94%. ^{1}H NMR ($CDCl_3$): δ 8.93−8.78 (m, 8H, β-pyrrole), 8.18−8.12 (m, 6H, *o*-phenyl), 7.77−7.66 (m, 9H, *m*- and *p*-phenyl), 6.89−6.65 (d, d, s, 3H, hydroquinone), 4.60 (s, br, 2H, -OH). UV−vis (benzonitrile) λ, nm (log ϵ): 422.5 (5.35), 553 (3.94), 592 (3.45). FAB-mass spectroscopy (*m*/*z*): calcd for CH_3CN 710.10; found, 709.9.

5,15-Diphenyl-10,20-bis(2,5-dihydroxyphenyl)porphyrinatozinc(II), 1c. This was synthesized according to Lindsey and Lee[24] with a few modifications. For this first, *meso*-phenyldipyrromethane was synthesized according to the following procedure. A solution of benzaldehyde (0.2 mL, 2 mM) and pyrrole (5.6 mL, 80 mM) was treated with trifluoroacetic acid (0.016 mL, 0.1 mM) at rt for 15 min. The mixture was diluted with CH_2Cl_2 (50 mL), washed with 0.1 M NaOH solution and water, and dried over sodium sulfate. The solvent and the unreacted pyrrole were removed by vacuum distillation at rt. The resulting yellow amorphous solid was dissolved in a minimum amount of ether and purified by flash chromatography on silica gel column with cyclohexane:ethyl acetate: triethylamine (80:19:1) as eluent. Yield 0.2 g, 45%. ^{1}H NMR ($CDCl_3$): δ 7.82 (s, br, 2H, NH), 7.31−7.12 (m, 5H, phenyl), 6.62 (q, 2H, pyrrole), 6.09 (q, 2H, pyrrole), 5.87 (m, 2H, pyrrole), 5.44 (s, 1H, *m*-H).

Next, 5,15-diphenyl-10,20-bis(2,5-demethoxyphenyl)porphyrin was synthesized by reacting 2,5-dimethoxybenzaldehyde (0.15 g, 0.9 mM) and *meso*-phenyldipyrromethane (0.2 g, 0.9 mM) in 90 mL of $CHCl_3$ under argon for 10 min. A solution of $BF_3{-}O(Et)_2$ (120 μL of 2.5 M stock solution in $CHCl_3$) was added, and the solution was stirred for 1 h at rt. At the end, DDQ (155 mg, 0.68 mM) was added, and the stirring was continued at rt for an additional 1 h. The solvent was removed under reduced pressure, and the crude porphyrin was dissolved in $CHCl_3$ and purified over a basic alumina column with $CHCl_3$:hexane (1:1 v/v) as eluent. Yield 0.2 g, 30%. ^{1}H NMR ($CDCl_3$): δ 8.79 (m, 8H, β-pyrrole), 8.19 (m, 4H, *o*-phenyl), 7.67 (m, 6H, *m*- and *p*-phenyl), 7.59−7.39 (d, d, s, 6H, bis-dimethoxyphenyl), 4.02−3.65 (s, s, 12H, −OCH_3), −2.78 (s, br, 2H, imino). UV−vis (benzonitrile) λ, nm (log ϵ): 415 (5.39), 512.4 (4.12), 546.2 (3.76), 587 (3.65), 645 (3.53). FAB-mass spectroscopy (*m*/*z*): calcd for CH_3CN 734.85; found, 734.8.

The 5,15-diphenyl-10,20-bis(2,5-dihydroxyphenyl)porphyrin was synthesized as follows. To a 5 mL solution of BBr_3/CH_2Cl_2 (1 M) at −78 °C, 0.2 g (0.27 mM) of 5,15-diphenyl-10,20-bis(2,5-dimethoxyphenyl)porphyrin in a minimum amount of CH_2Cl_2 was added. The solution was maintained at this temperature for 1 h during which the addition was completed. This mixture was then allowed to attain rt, and stirring was continued for another 12 h. At the end of this 12 h period, the mixture was again cooled to −5 °C, taking care that the temperature was maintained below 5 °C, and 5 mL of cold water was added to quench the reaction, followed by addition of saturated sodium bicarbonate solution. This combined

(24) Lee, C.-H.; Lindsey, J. S. *Tetrahedron* **1994**, *50*, 11427.

solution was stirred for 0.5 h, followed by evaporation of the combined solution under reduced pressure. The solid was washed with water, dried, and then washed with chloroform. The solid thus obtained was purified on a basic alumina column using $CHCl_3$/MeOH (90:10 v/v) as eluent. Yield 76.3%. ^{1}H NMR ($CDCl_3$): δ 8.81 (m, 8H, β-pyrrole), 8.16 (m, 4H, *o*-phenyl), 7.72 (m, 6H, *m*- and *p*-phenyl), 7.63−7.44 (d, d, s, 6H, bis-dihydroxyphenyl), 4.65 (s, br, 4H, -OH), −2.74 (s, 2H, imino). UV−vis (benzonitrile) λ, nm (log ϵ): 415 (5.40), 512 (4.13), 546 (3.79), 590 (3.68), 647 (3.58). FAB-mass spectroscopy (*m*/*z*): calcd for CH_3CN 678.7; found, 678.9.

Finally, **1c** was synthesized by metalation of 5,15-diphenyl-10,20-bis(2,5-dihydroxyphenyl)porphyrin with zinc acetate.[25] To a solution of 5,15-diphenyl-10,20-bis(2,5-dihydroxyphenyl)-porphyrin (0.2 g, 0.3 mM) in $CHCl_3$, excess zinc acetate in methanol was added, and the solution was stirred for 30 min. The solvent was removed under reduced pressure, and the crude product was dissolved in CH_2Cl_2, washed with water, and dried over sodium sulfate. The solution was concentrated and loaded on to a basic alumina column. Pure **1c** was eluted with $CHCl_3$:hexane (90:10 v/v). Yield 94%. ^{1}H NMR ($CDCl_3$): δ 8.93−8.88 (m, 8H, β-pyrrole), 8.17−8.16 (m, 6H, *o*-phenyl), 7.74−7.72 (m, 6H, *m*- and *p*-phenyl), 7.44−7.09 (d, d, s, 6H, dihydroxyphenyl), 4.57 (s, 4H, -OH). UV−vis (benzonitrile) λ, nm (log ϵ): 422 (5.35), 553 (3.92), 592 (3.42). FAB-mass spectroscopy (*m*/*z*): calcd for CH_3CN 742.13; found, 742.3.

5,10,15,20-Tetrakis(2,5-dihydroxyphenyl)porphyrinatozinc(II), 1d. For this, first 5,10,15,20-tetrakis(2,5-dimethoxyphenyl)porphyrin was synthesized by reacting 2 g (30 mM) of pyrrole and 4.95 g (30 mM) of 2,5-dimethoxy benzaldehyde in 500 mL of propionic acid for 1 h. The propionic acid was evaporated under reduced pressure. The solid was then dissolved in a minimum amount of chloroform and purified on a basic alumina column using $CHCl_3$/hexane (75:25) as eluent. Yield 22%. ^{1}H NMR ($CDCl_3$): δ 8.76 (s, 8H, β-pyrrole), 8.07 (d, 4H, *m*-phenyl), 7.62 (d, 4H, *p*-phenyl), 7.41 (s, 4H, *o*-phenyl), 4.12−3.74 (s, s, 24H, $-OCH_3$), −2.89 (s, br, 2H, imino). UV−vis (benzonitrile) λ, nm (log ϵ): 415 (5.36), 512 (4.12), 546 (3.76), 587 (3.62), 645 (3.58). FAB-mass spectroscopy (*m*/*z*): calcd for CH_3CN 854.95; found, 854.9.

Next, 0.2 g (0.23 mM) of 5,10,15,20-tetrakis(2,5-dimethoxyphenyl)porphyrin in a minimum amount of CH_2Cl_2 was treated with 5 mL of BBr_3/CH_2Cl_2 (1 M) at −78 °C follwed by stirring for 12 h at rt. The mixture was cooled again to −5 °C, and 5 mL of cold water was added to quench the reaction, followed by addition of saturated sodium bicarbonate solution. This combined solution was stirred for 0.5 h, followed by evaporation of the combined solution under reduced pressure. The solid was washed with water, dried, and then washed with chloroform. The solid thus obtained was purified over a basic alumina column using $CHCl_3$/MeOH (80:20) as eluent to yield 5,10,15,20-tetrakis(2,5-dihydroxyphenyl)porphyrin. Yield 64%. ^{1}H NMR ($CDCl_3$:DMSO, 90:10 v/v): δ 8.96 (s, 8H, β-pyrrole), 8.17 (d, 4H, *m*-phenyl), 7.81 (d, 4H, *p*-phenyl), 7.62 (s, 4H, *o*-phenyl), 4.74 (s, br, 8H, -OH), −2.72 (s, br, 2H, imino). UV−vis (benzonitrile) λ, nm (log ϵ): 415 (5.40), 512 (4.12), 549 (3.76), 592 (3.62), 648 (3.56). FAB-mass spectroscopy (*m*/*z*): calcd for CH_3CN 742.74; found, 742.7.

Finally, **1d** was synthesized by metalation of 5,10,15,20-tetrakis(2,5-dihydroxyphenyl)porphyrin with zinc acetate.[25] To a solution of 5,10,15,20-tetrakis(2,5-dihydroxyphenyl)porphyrin (0.2 g, 0.3 mM) in methanol, an excess of zinc acetate in methanol was added. This solution was stirred for 30 min. The solvent was removed under reduced pressure, and the crude product was suspended in water and filtered. The product was dissolved in acetone, adsorbed on silica gel, and loaded on to a silica gel column. The pure **1d** was eluted with $CHCl_3$:MeOH (85:15 v/v). Yield 94%. ^{1}H NMR ($CDCl_3$): δ 8.95−8.89 (m, 8H, β-pyrrole), 8.19−8.17 (m, 4H, *o*-phenyl), 7.75−7.73 (m, 8H, *m*- and *p*-phenyl), 5.74 (s, br, 8H, -OH). UV−vis (benzonitrile) λ, nm (log ϵ): 424 (5.20), 553 (3.95), 592 (3.47). FAB-mass spectroscopy (*m*/*z*): calcd for CH_3CN 806.13; found, 805.3.

5,10,15-Triphenyl-20-(3,6-dioxocyclohexa-1,4-denyl)-porphyrin, 2b. This was synthesized by chemical oxidation of **1b**. To a solution of 0.2 g (0.31 mmol) of **1b** in 50 mL of $CHCl_3$, 0.176 g (0.774 mmol) of DDQ was added, and the solution was stirred for 2 h. The solution was then concentrated and loaded on a basic alumina column. Using a mixture of chloroform/hexane, pure **2b** was eluted. Yield 68%. ^{1}H NMR ($CDCl_3$): δ 8.90 (m, 8H, β-pyrrole), 8.20 (s, 6H, *o*-phenyl), 7.75 (m, 9H, *m*- and *p*-phenyl), 7.29, 7.60, 8.38 (d,d,s, 3H, quinone), −2.78 (s, 2H, imino). UV−Vis (benzonitrile) λ, nm (log ϵ): 413 (5.29), 511 (3.89), 545 (3.44), 588 (3.44), 646 (3.32). FAB-mass spectroscopy (*m*/*z*): calcd for CH_3CN 644.74; found, 644.1.

5,10,15-Triphenyl-20-(3,6-dioxocyclohexa-1,4-denyl)-porphyrinatozinc(II), 2a. To 0.1 g (0.14 mM) of **1a** in 50 mL of CH_2Cl_2, 0.08 g (0.352 mM) of DDQ was added, and the solution was stirred for 2 h. The solution was then concentrated under reduced pressure, loaded on a basic alumina column, and eluted with $CHCl_3$. Yield 50%. ^{1}H NMR ($CDCl_3$): δ 8.99 (d, 8H, β-pyrrole), 8.17 (m, 6H, *o*-phenyl), 7.74 (m, 9H, *m*- and *p*-phenyl), 7.43−7.41 (m, 3H, quinone). UV−vis (benzonitrile) λ, nm (log ϵ): 418 (5.38), 549 (3.92), 618 (3.42). FAB-mass spectroscopy (*m*/*z*): calcd for CH_3CN 708.13; found, 709.0.

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Supporting Information Available: The mass spectra of selected porphyrin−quinhydrone complexes and the porphyrin dimer as well as the ^{1}H NMR spectral data of the porphyrin dimer. This material is available free of charge via the Internet at http://pubs.acs.org.

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