Structurally Homologous β- and *meso*-Amidinium Porphyrins

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Introduction

Porphyrins bearing hydrogen-bond synthons provide an efficient method for the assembly of supramolecular architectures. Such systems underlie efforts directed at unraveling the effect of hydrogen bonds on energy and electron transfer.[1,2] Porphyrins featuring directional and complementary hydrogen-bond functionality are especially pertinent to energy and electron-transfer investigations because the donor−acceptor (D−A) pair is formed exclusive of homodimers (i.e., D−D and A−A pairs).[3] A rigid electron/energy transfer pathway, which possesses maximum electronic communication, is created when the hydrogen-bond synthon can be directly attached to the porphyrin macrocycle. We have exploited these basic design elements in the development of hydrogen-bonded networks for the study of proton-coupled electron transfer.[1,4,5] In particular, our work has focused on porphyrins modified with the amidinium group,[6−9] which is able to associate with carboxylate to form a salt bridge. This resultant amidinium−carboxylate interface models the arginine−aspartate salt bridge, an important stabilizing structural element in many biological systems.[10−13] The amidinium−carboxylate salt bridge combines the dipole of an electrostatic ion-pair interaction with a hydrogen-bonding scaffold, thus allowing us to investigate how proton motion within a hydrogen-bond interface affects the charge, energetics, and polarity of an electron transport chain. An amidinium−carboxylate structural motif is not only convenient for the assembly of donor−acceptor pairs but may also be employed in the construction of extended supramolecular structures.[14] Despite these advances, the utility of the directional, two-point hydrogen bond that amidinium provides to porphyrin supramolecular design has been heretofore limited because of the difficulty attendant to appending the hydrogen-bond synthon directly to the porphyrin macrocycle. Indeed, the only previous synthesis of a porphyrin bearing an amidinium directly appended to a porphyrin ring was elaborate and arduous.[15] Our interest in generalizing amidinium porphyrins for a variety of applications has led us to explore new strategies to affix amidiniums to porphyrin macrocycles. We now report a modular and facile methodology for the synthesis of a porphyrin modified with amidinium in the β position. In addition, we have extended this methodology to prepare the first example of a porphyrin bearing an amidinium group directly attached at the *meso* position, thus providing a homologous pair of porphyrin building blocks with electronically altered properties. We also describe the propensity of the structurally homologous β- and *meso*-amidinium porphyrins to form salt bridge complexes and the effects of salt bridge association on the excited-state properties of these novel architectures.

Experimental Section

Materials. Silica gel 60 (70−230 and 230−400 mesh, Merck) and Merck 60 F254 silica gel (precoated sheets, 0.2 mm thick) were used for column and analytical thin-layer chromatography, respectively. Solvents for synthesis were of reagent grade or better and were dried according to standard methods.[16] Spectroscopic experiments employed dichloromethane (spectroscopic grade, Burdick & Jackson). Mass spectral analyses were performed in the MIT Department of Chemistry Instrumentation Facility (DCIF). Nickel(II) 5,10,15,20-tetramesitylporphyrin (**1**) and nickel(II) 5,10,15-trimesitylporphyrin (**8**) were prepared using published procedures.[17,18]

Nickel(II) 2-Formyl-5,10,15,20-tetramesitylporphyrin (2). A suspension of **1** (420 mg, 0.5 mmol) in 300 mL of 1,2-dichloroethane was added over a period of 10 min under a nitrogen atmosphere to a warm solution (50−60 °C) of Vilsmeier reagent, prepared from dimethylformamide (DMF) (19.4 mL, 250 mmol) and $POCl_3$ (23.3 mL, 250 mmol). The solution was stirred at 70 °C under nitrogen for 3 h and quenched with aqueous Na_2CO_3; the resulting solution was stirred in air overnight. The organic layer was decanted, washed with water, and dried over Na_2SO_4, and the solvent was removed. Purification by column chromatography (silica gel, 1:1 CH_2Cl_2/hexanes) afforded porphyrin **2** (335 mg, 77% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.33 (s, 1H), 9.20 (s, 1H), 8.58−8.47 (m, 6H), 7.24 (s, 6H), 7.21 (s, 2H), 2.60 (s, 6H), 2.59 (s, 6H), 1.88 (s, 12H), 1.87 (s, 6H), 1.84 (s, 6H). ESIMS $[M + H]^+$, *m*/*z*: calcd for $C_{57}H_{52}N_4NiO$, 867.74. Found, 867.35.

2-Cyano-5,10,15,20-tetramesitylporphyrin (4). The diacid of freebase **3** was obtained by using 15% H_2SO_4 in trifluoroacetic acid (TFA) (30 mL) to demetalate **2** (87 mg, 0.1 mmol). Without further purification of the diacid, hydroxylamine hydrochloride (34 mg, 0.5 mmol) was added to a mixture of porphyrin **3** in TFA (1 mL) and formic acid (30 mL). The resulting solution was refluxed for 24 h under nitrogen and then concentrated under reduced pressure. The residue was taken up in CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ and water, dried over Na_2SO_4, and taken to dryness. Column chromatography (silica

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gel, 1:1 CH_2Cl_2/hexanes) afforded porphyrin **4** (66 mg, 82% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.26 (s, 1H), 8.79 (d, J = 5.4 Hz, 2H), 8.72 (d, J = 5.4 Hz, 2H), 8.57 (s, 2H), 7.35 (s, 2H), 7.31 (s, 6H), 2.68 (s, 3H), 2.65 (s, 9H), 1.89 (s, 12H), 1.88 (s, 6H), 1.86 (s, 6H). ESIMS $[M + H]^+$, *m*/*z*: calcd for $C_{57}H_{53}N_5$, 808.06. Found, 808.43. Nickel(II) was inserted into porphyrin **4** using standard methods[19] to yield **5**. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.08 (s, 1H), 8.60−8.48 (m, 6H), 7.25 (s, 2H), 7.21 (s, 6H), 2.60 (s, 3H), 2.58 (s, 9H), 1.84 (s, 18H), 1.82 (s, 6H). ESIMS $[M + H]^+$, *m*/*z*: calcd for $C_{57}H_{51}N_5Ni$, 864.74. Found, 864.05.

Nickel(II) 2-Amidinium-5,10,15,20-tetramesitylporphyrin Chloride (6). To a toluene solution (300 mL) of nickel(II) porphyrin **5** (400 mg, 0.462 mmol) was added chloromethylaluminum amide (19.3 mL, 1.2 M in toluene) under a nitrogen atmosphere. The reaction solution was heated at 90 °C under nitrogen for 7 d. The resulting mixture was cooled to room temperature, poured slowly onto silica gel (80 g) in $CHCl_3$ (200 mL), and stirred for 10 min. The slurry was filtered, and the filtercake that was collected was washed with a mixture of $CHCl_3$ and methanol until the filtrate was colorless. The solvent was removed. Purification by column chromatography (silica gel, 10:1 $CHCl_3$/CH_3-OH) followed by recrystallization from CH_2Cl_2 and methanol gave amidinium porphyrin **6** (288 mg, 68% yield). ^{1}H NMR (300 MHz, 3% CD_3OD in $CDCl_3$, 25 °C): δ = 8.78 (s, 1H), 8.54−8.42 (m, 6H), 7.18 (s, 6H), 7.14 (s, 2H), 2.54 (s, 12H), 1.80 (s, 12H), 1.79 (s, 6H), 1.78 (s, 6H). HRFABMS (M^+), *m*/*z*: calcd for $C_{48}H_{45}N_6Zn$, 881.3842. Found, 881.3863.

Zinc(II) 2-Amidinium-5,10,15,20-tetramesitylporphyrin Chloride (7). Concentrated H_2SO_4 (5 mL) was added to **6** (92 mg, 0.1 mmol). The mixture was stirred at room temperature for 5 min, and ice was then added. The suspension was neutralized with solid Na_2CO_3 and filtered to give the crude free base porphyrin, which was not further purified. $ZnCl_2$ (136 mg, 1.0 mmol) was added to a solution of the free-base porphyrin in DMF (20 mL). The mixture was heated at 60 °C for 30 min and concentrated under vacuum, and water was added. The resulting precipitate was collected by filtration and washed with water. The solid, which was purified by column chromatography (silica gel, 10:1 $CHCl_3$/CH_3OH), was dissolved in 20% methanol in $CHCl_3$. The solution was cooled to 0 °C after which 5 mL of a 0.1 N methanolic KOH solution was added. The reaction was stirred at 0 °C for 5 min and concentrated under reduced pressure; addition of 10 mL of a 1 N aqueous KOH solution resulted in the formation of a suspension. The solid collected from filtration was taken up in 20% methanol in $CHCl_3$ (20 mL) and added to 30 mL of a 1 N aqueous NaCl solution containing HCl (adjusted to pH 1−2). The organic solvent was removed, and the mixture was filtered and washed with water. Purification by preparative TLC (silica gel, 10:1 $CHCl_3$/CH_3OH) afforded **7** (37 mg, 40% yield). ^{1}H NMR (300 MHz, 5:1 CD_3OD/$CDCl_3$, 25 °C): δ = 8.80 (s, 1H), 8.60−8.50 (m, 6H), 7.22 (s, 6H), 7.15 (s, 2H), 2.58 (s, 12H), 1.82 (s, 6H), 1.81 (s, 6H), 1.78 (s, 12H). HRFABMS (M^+), *m*/*z*: calcd for $C_{48}H_{45}N_6Zn$, 887.3780. Found, 887.3752. The hexafluorophosphate salt of **7** was prepared from metathetical exchange with $TlPF_6$ in methanol. ^{1}H NMR (300 MHz, 5:1 CD_3OD/$CDCl_3$, 25 °C): δ = 8.78 (s, 1H), 8.54−8.42 (m, 6H), 7.16 (s, 6H), 7.09 (s, 2H), 2.52 (s, 9H), 2.50 (s, 3H), 1.77 (s, 6H), 1.76 (s, 6H), 1.74 (s, 6H), 1.73 (s, 6H).

Nickel(II) 5-Formyl-10,15,20-trimesitylporphyrin (9). Porphyrin **8** (400 mg, 0.69 mmol), which was suspended in 1,2-dichloroethane (100 mL), was added over a 10 min period under a nitrogen atmosphere to a warm solution (50−60 °C) of a Vilsmeier reagent, prepared from DMF (2.7 mL, 34.5 mmol) and $POCl_3$ (2.7 mL, 34.5 mmol). The solution was stirred at 70 °C under nitrogen for 3 h, quenched with aqueous NaOAc, and stirred in air overnight. The organic layer was separated, washed with water, and dried over Na_2SO_4, and the solvent layer was removed. Purification by column chromatography (silica gel, 1:1 CH_2Cl_2/hexanes) afforded porphyrin **9** (378 mg, 73% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 12.10 (s, 1H), 9.80 (d, J = 5.4 Hz, 2H), 8.69 (d, J = 5.4 Hz, 2H), 8.46 (d, J = 5.4 Hz, 2H), 8.41 (d, J = 5.4 Hz, 2H), 7.22 (s, 4H), 7.18 (s, 2H), 2.59 (s, 6H), 2.56 (s, 3H), 1.86 (s, 12H), 1.85 (s, 6H). ESIMS $[M + H]^+$, *m*/*z*: calcd for $C_{48}H_{42}N_4$-NiO, 749.57. Found, 749.27.

Nickel(II) 5-Cyano-10,15,20-trimesitylporphyrin (12). Nickel(II) porphyrin **9** (69 mg, 0.1 mmol) was demetalated by TFA (20 mL) containing 15% H_2SO_4 to give the diacid of free-base **10**. The diacid, which was not further purified, was dissolved in a mixture of formic acid (20 mL) and TFA (0.5 mL); hydroxylamine hydrochloride (34 mg, 0.5 mmol) was added to this solution. The mixture was refluxed for 24 h under a nitrogen atmosphere and concentrated under reduced pressure. The residue was taken up in CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ and then water, dried over Na_2SO_4, and taken to dryness. Column chromatography (silica gel, 1:1 CH_2Cl_2/hexanes) gave pure **11** (54 mg, 75% yield). Nickel(II) was inserted using standard methods to yield **12**.[19] ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.44 (d, J = 4.8 Hz, 2H), 8.78 (d, J = 4.8 Hz, 2H), 8.60 (d, J = 4.8 Hz, 2H), 8.57 (d, J = 4.8 Hz, 2H), 7.27 (s, 4H), 7.23 (s, 2H), 2.62 (s, 6H), 2.60 (s, 3H), 1.85 (s, 18H). ESIMS $[M + H]^+$, *m*/*z*: calcd for $C_{48}H_{41}N_5$-Ni, 746.57. Found, 746.26.

Nickel(II) 5-Amidinium-10,15,20-trimesitylporphyrin Chloride (13). To a solution of **12** (69 mg, 0.1 mmol) in toluene (50 mL) was added chloromethylaluminum amide (5.0 mL, 1.0 M in toluene) under a nitrogen atmosphere. The resulting solution was heated at 80 °C under nitrogen for 7 d. The mixture was cooled to room temperature, poured slowly into silica gel (20 g) in $CHCl_3$ (50 mL), and stirred for 10 min. The slurry was filtered, and the resulting filtercake was washed with a mixture of $CHCl_3$ and methanol until the filtrate was no longer colored. The solvent was removed, and purification by column chromatography (silica gel, 10:1 $CHCl_3$/CH_3OH) followed by recrystallization from dichloromethane and methanol afforded amidinium porphyrin **13** (56 mg, 70% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.21 (d, J = 4.8 Hz, 2H), 8.77 (d, J = 4.8 Hz, 2H), 8.61 (d, J = 4.8 Hz, 2H), 8.58 (d, J = 4.8 Hz, 2H), 7.22 (s, 6H), 2.58 (s, 9H), 1.81 (s, 6H), 1.79 (s, 12H). HRFABMS (M^+), *m*/*z*: calcd for $C_{48}H_{45}N_6Zn$, 763.3059. Found, 763.3079.

Zinc(II) 5-Amidinium-10,15,20-trimesitylporphyrin Chloride (14). Concentrated H_2SO_4 (5 mL) was added to **13** (80 mg, 0.1 mmol). After stirring the mixture at room temperature for 5 min, ice was added. The suspension was neutralized with solid Na_2CO_3 and filtered to give the crude free-base porphyrin. Without further purification, the free-base porphyrin was dissolved in DMF (20 mL) and $ZnCl_2$ (136 mg, 1.0 mmol) was added. The mixture was heated at 60 °C for 30 min and then concentrated under vacuum. The precipitate that was formed upon water addition to the concentrate was collected by filtration and washed with water. The solid was purified by column chromatography (silica gel, 10:1 $CHCl_3$/CH_3OH), reisolated, and dissolved in 20% methanol in $CHCl_3$. The solution was cooled to 0 °C to which 5 mL of a 0.1 N methanolic KOH solution was added. The reaction was stirred at 0 °C for 5 min and concentrated under reduced pressure, and an additional 10 mL of a 1 N aqueous KOH solution was added to the concentrate to produce a suspension, which was filtered. The solid was taken up in 20% methanol in $CHCl_3$ (20 mL) and added to 30 mL of a 1 N aqueous NaCl solution containing HCl (adjusted to pH 1−2). The organic solvent was removed, and the mixture was then filtered and washed with water. Purification by preparative TLC (silica gel, 10:1 $CHCl_3$/CH_3OH) afforded **14** (28 mg, 35% yield). ^{1}H NMR (300 MHz, 1:20 CD_3OD/$CDCl_3$, 25 °C): δ = 9.26 (br s, 2H), 8.80 (br s, 2H), 8.64 (d, J = 4.8 Hz, 2H), 8.60 (d, J = 4.8 Hz, 2H), 7.25 (s, 4H), 7.23 (s, 4H), 2.60 (s, 6H), 2.59 (s, 3H), 1.81 (s, 6H), 1.78 (s, 12H). HRFABMS (M^+), *m*/*z*: calcd for $C_{48}H_{45}N_6Zn$, 769.2997. Found, 769.3240.

Physical Measurements. ^{1}H NMR spectra were collected at the MIT DCIF on either a Varian XL-300, Unity 300, or Mercury 300 spectrometer. Spectra were recorded at 25 °C. All chemical shifts are reported using the standard δ notation in parts-per-million; positive chemical shifts are to higher frequency from the given reference. Absorption spectra were obtained using either a Cary-17 spectrophotometer modified by On-Line Instrument Systems (OLIS) to include computer control or a Spectral Instruments 440 Series spectrophotometer.

Luminescence lifetime measurements were obtained with a Hamamatsu C4334-0 Streak Camera, which was the detector on a previously

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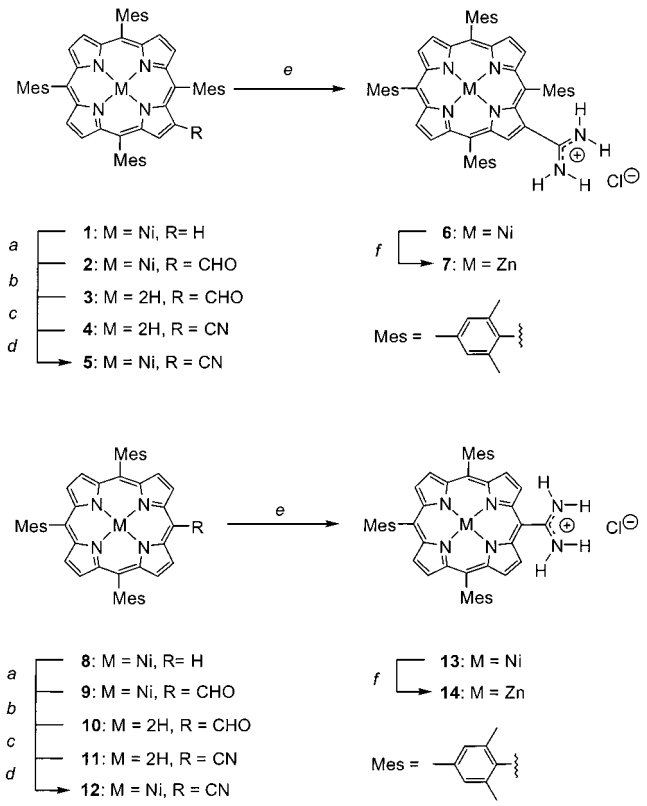
Scheme 1. Synthetic Routes for β- and *meso*-Amidinium Porphyrins[a]



[a] (a) Vilsmeier reagent, 1,2-dichloroethane; (b) 15% H_2SO_4 in TFA; (c) $NH_2OH{\cdot}HCl$, HCO_2H, and TFA (30:1); (d) $Ni(OAc)_2{\cdot}4H_2O$, DMF; (e) $AlCl(CH_3)(NH_2)$, toluene; (f) 1. H_2SO_4; 2. $ZnCl_2$, DMF.

described subpicosecond laser system.[20] Luminescence measurements were performed on solutions of porphyrin at concentrations of $\sim 2 \times 10^{-5}$ M, giving an optical density of 0.2−0.3 at the Q_{10} band (λ_{exc} = 550 nm). Samples for lifetime measurements were contained within a cell equipped with a solvent reservoir and a 1 cm clear fused-quartz cell (Starna Cells, Inc.). The two chambers were isolated from each other by a high-vacuum Teflon valve and from the environment with a second high-vacuum Teflon valve. Samples were subject to at least three freeze−pump−thaw cycles (10^{-3} Torr).

Results and Discussion

Amidinium functionalities were directly attached at either the β (**7**) or *meso* (**14**) positions of the mesityl porphyrin macrocycle according to the synthetic procedures outlined in Scheme 1. For the β-amidinium system, the readily available nickel(II) 5,10,-15,20-tetramesitylporphyrin (**1**) was chosen as the starting material due to the solubilizing properties of the ancillary methyl groups. Formylation of **1** proceeds smoothly by the Vilsmeier reaction to deliver **2**.[21] Demetalation with 15% H_2SO_4 in TFA and reaction with hydroxylamine hydrochloride in refluxing formic acid containing TFA gives nitrile **4**.[22] After nickel insertion, the nitrile is transformed to amidinium **6** by treatment with an excess of Weinreb's amide transfer reagent[23] under harsh conditions (90 °C, 7 d). It is noteworthy that the amide transfer reaction is not observed when the zinc(II) complex or free base of the nitrile is used. Demetalation of nickel followed by zinc insertion affords the amidinium porphyrin **7** after workup. The synthesis of the β-amidinium porphyrin **7** from **1** in just six steps represents a significant improvement over our previous synthesis of a β-amidinium porphyrin, which encompassed an arduous 26-step procedure.[15] The modular nature of the approach reported herein is highlighted by our successful preparation of the first porphyrin with an amidinium group directly attached to a *meso* position of the porphyrin superstructure, the analogous *meso*-amidinium porphyrin **14**, from nickel(II) 5,10,15-trimesitylporphyrin (**8**). To the best of our knowledge, **7** and **14** represent the first homologous porphyrin pair that features a hydrogen-bond donor group directly attached to the β and *meso* positions of a porphyrin ring.

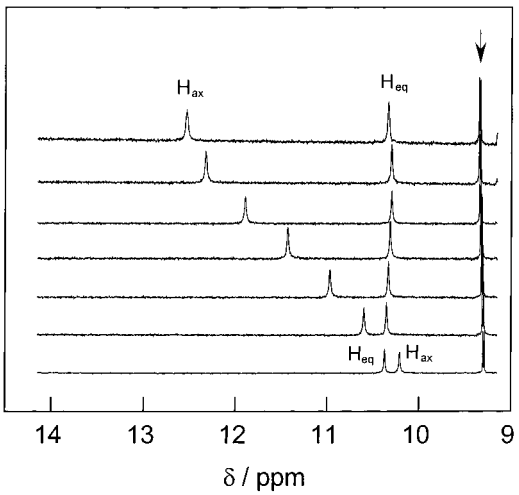


Figure 1. Selected ^{1}H NMR spectra of **13** (2.34 mM) in the absence of and in the presence of 0, 1.08, 2.50, 5.29, 11.05, 26.02, and 56.84 mM (bottom to top) tetrabutylammonium benzoate in DMSO-d_6. The spectral range captures the amidinium protons internal (NH_{ax}) and external (NH_{eq}) to the salt bridge interface. The arrow identifies the ^{1}H resonances of the β-pyrrole protons.

The two-point hydrogen bond of the amidinium−carboxylate interface features two favorable secondary interactions,[24] supported by electrostatic stabilization of proximate and opposite charges within the salt bridge. To assess the stability of the salt bridge for the homologous β- and *meso*-amidinium porphyrin systems, we undertook ^{1}H NMR measurements of the nickel-(II) forms of the porphyrins in the presence of benzoates.

Figure 1 displays the ^{1}H NMR spectral changes resulting from the association of *meso*-amidinium porphyrin **13** to 3,5-dinitrobenzoate in d_6-DMSO. Signatures of the salt bridge are the concentration-dependent downfield shift of the amidinium protons involved in hydrogen bonding and an insensitivity of the chemical shift for the amidinium protons external to the salt bridge. Such behavior has been observed previously for the complexation of bicyclic guanidinium to carboxylate[25] and amidinium to phosphate[26] and carboxylate.[6−9] The singlet at 10.20 ppm, corresponding to the internal amidinium proton (NH_{ax}), shifts downfield upon the addition of 3,5-dinitrobenzoate, whereas the chemical shift of the external amidinium proton (NH_{eq}) does not change significantly during the titration (<0.2 ppm). A nonlinear least-squares fit[27] of these chemical shift data for the hydrogen-bonded amidinium protons vs the

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carboxylate concentration yields a binding constant of $K_A = 236 \pm 5\ M^{-1}$. As has been observed for benzamidinium−benzoate[28] and other primary two-point hydrogen-bond systems,[29,30] a significantly higher binding constant ($K_A = 6860 \pm 420\ M^{-1}$) is observed when the 3,5-dinitrobenzoate is replaced by benzoate owing to the increased basicity of the carboxylate guest. β-Amidinium porphyrin **6** exhibits similar behavior to its *meso*-amidinium counterpart and gives comparable binding constants with benzoate ($K_A = 2450 \pm 130\ M^{-1}$) and 3,5-dinitrobenzoate ($K_A = 161 \pm 4\ M^{-1}$). These results establish the high stability of the amidinium−carboxylate interface, which persists in solution even when the dielectric constant of the solvent is high.

Soret (B) and Q absorption bands for the zinc(II) amidinium porphyrins **7** and **14** are characteristic of a standard four orbital model for porphyrin spectra.[31] The absorption spectra for the compounds are similar. For **7**: $\lambda_{abs,max}(B) = 429$ nm ($\epsilon = 2.57 \times 10^5\ M^{-1}\ cm^{-1}$); $\lambda_{abs,max}(Q_{1,0}) = 556$ nm ($\epsilon = 7.76 \times 10^3\ M^{-1}\ cm^{-1}$); $\lambda_{abs,max}(Q_{0,0}) = 594$ nm ($\epsilon = 3.94 \times 10^3\ M^{-1}\ cm^{-1}$). For **14**: $\lambda_{abs,max}(B) = 424$ nm ($\epsilon = 3.05 \times 10^5\ M^{-1}\ cm^{-1}$); $\lambda_{abs,max}(Q_{1,0}) = 565$ nm ($\epsilon = 1.66 \times 10^4\ M^{-1}\ cm^{-1}$); $\lambda_{abs,max}(Q_{0,1}$, sh) $= 596$ nm ($\epsilon = 4.88 \times 10^3\ M^{-1}\ cm^{-1}$); $\lambda_{abs,max}(Q_{0,0}) = 611$ nm ($\epsilon = 5.92 \times 10^3\ M^{-1}\ cm^{-1}$). Excitation into the absorption manifold of **7** and **14** results in intense luminescence with features that are typical of Q(0,0) and Q(0,1) transitions ($\lambda_{em,max}(Q_{0,0}) = 611$ and 615 nm; $\lambda_{em,max}(Q_{0,1}) = 655$ and 670 nm for **7** and **14** in CH_2Cl_2, respectively). Time-resolved measurements reveal a monophasic and exponential luminescence decay; lifetimes are typical of a singlet excited state (τ_{obs}(**7**) = 1.80 ns, τ_{obs}(**14**) = 2.58 ns). The same luminescence experiments were carried out on the salt-bridge complexes, formed by the addition of 10 equiv of tetrabutylammonium benzoate to solutions of the respective porphyrins. Whereas the fluorescence maxima and decay rate of *meso*-substituted porphyrin **14** remain essentially unchanged upon salt-bridge formation (**14**·benzoate: $\lambda_{em,max}(Q_{0,0}) = 611$ nm and $(Q_{0,1}) = 670$ nm, $\tau_{obs} = 2.64$ ns), the photophysics of **7** are considerably perturbed (**7**·benzoate: $\lambda_{em,max}(Q_{0,0}) = 604$ and $(Q_{0,1}) = 653$ nm, $\tau_{obs} = 2.04$ ns). These results suggest that the amidinium group is more strongly coupled to the porphyrin π-system when attached at the β position than at the *meso*-position. This differential perturbation of electronic structure by site substitution about the porphyrin periphery has been observed for covalent networks;[32] the results reported here show similar behavior in a noncovalent networks, thus providing a convenient means to tune the electronic properties of hydrogen-bonded amidinium porphyrin assemblies.

In summary, the bottleneck created by laborious synthesis of porphyrin macrocycles directly appended with amidinium has been circumvented with a facile and efficient synthesis. The new methodology affords both β- and *meso*-substituted architectures. The congeners readily form supramolecular assemblies by their association to carboxylates with high binding constants. The β- and *meso*-substituted amidinium porphyrins are spectroscopically similar, but emission data indicate that amidinium interacts more strongly with the porphyrin ring when attached at the β position as opposed to the *meso* position. This observation invites the possibility of investigating the role of hydrogen-bond-mediated coupling on the rates of proton-coupled electron transfer. More generally, comparative studies of β- and *meso*-substituted amidinium porphyrins should advance our understanding of the spectroscopic and electron/energy transfer properties of hydrogen-bonded porphyrin supramolecules.

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