Excitonic luminescence of hemiporphyrizines

Huber, Sabrina M; Seyfried, Martin S; Linden, Anthony; Luedtke, Nathan W

Abstract: Metal-free hemiporphyrizine (HpH2) is a notoriously insoluble material possessing interesting photophysical properties. Here we report the synthesis, structure, and photophysical properties of an octahedral zinc trans-ditriflate hemiporphyrizine complex “HpH2Zn(OTf)2” that contains a neutral hemiporphyrizine ligand. The photophysical properties of hemiporphyrizine are largely unaffected by introduction of zinc(II) triflate, but a dramatic increase in solubility is observed. HpH2Zn(OTf)2 therefore provides a convenient model system to evaluate the impact of aggregation on the photophysical properties of hemiporphyrizine. Soluble aggregates and crystalline materials containing planar hemiporphyrizines exhibit relatively strong absorbance of visible light (450–600 nm) and red luminescence (600–700 nm). Hemiporphyrizine monohydrate (HpH2·H2O), in contrast, has a nonplanar “saddle-shaped” conformation that exhibits very little absorbance of visible light in solution or in the solid state. Upon photoexcitation at 380 nm, HpH2Zn(OTf)2 and HpH2 exhibit multiwavelength emissions centered at 450 and 650 nm. Emissions at 450 nm are highly anisotropic, while emissions at 650 nm are fully depolarized with respect to a plane-polarized excitation source. Taken together, our results suggest that excitonic coupling of aggregated and crystalline hemiporphyrizines results in increased absorbance and emission of visible light from S0 → S1 transitions that are usually symmetry forbidden in isolated species. In contrast to previously proposed theories involving excited-state intramolecular proton transfer, we propose that the multiple-wavelength luminescent emissions of HpH2Zn(OTf)2 and HpH2 are due to emissive S1 and S2 states in aggregated and crystalline hemiporphyrizines. These results may provide a better understanding of the nonlinear optical properties of these materials in solution and in the solid state.

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**Excitonic Luminescence of Hemiporphyrazines**

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**Supporting Information**

**ABSTRACT:** Metal-free hemiporphyrazine (HpH₂) is a notoriously insoluble material possessing interesting photophysical properties. Here we report the synthesis, structure, and photophysical properties of an octahedral zinc trans-ditriflate hemiporphyrazine complex “HpH₂Zn(OTf)₂” that contains a neutral hemiporphyrazine ligand. The photophysical properties of hemiporphyrazine are largely unaffected by introduction of zinc(II) triflate, but a dramatic increase in solubility is observed. HpH₂Zn(OTf)₂ therefore provides a convenient model system to evaluate the impact of aggregation on the photophysical properties of hemiporphyrazine. Soluble aggregates and crystalline materials containing planar hemiporphyrazines exhibit relatively strong absorbance of visible light (450–600 nm) and red luminescence (600–700 nm). Hemiporphyrazine monohydrate (HpH₂·H₂O), in contrast, has a nonplanar “saddle-shaped” conformation that exhibits very little absorbance of visible light in solution or in the solid state. Upon photoexcitation at 380 nm, HpH₂Zn(OTf)₂ and HpH₂ exhibit multiwavelength emissions centered at 450 and 650 nm. Emissions at 450 nm are highly anisotropic, while emissions at 650 nm are fully depolarized with respect to a plane-polarized excitation source. Taken together, our results suggest that excitonic coupling of aggregated and crystalline hemiporphyrazines results in increased absorbance and emission of visible light from S₀ → S₁ transitions that are usually symmetry forbidden in isolated species. In contrast to previously proposed theories involving excited-state intramolecular proton transfer, we propose that the multiple-wavelength luminescent emissions of HpH₂Zn(OTf)₂ and HpH₂ are due to emissive S₁ and S₂ states in aggregated and crystalline hemiporphyrazines. These results may provide a better understanding of the nonlinear optical properties of these materials in solution and in the solid state.

Hemiporphyrazines (Hps) were discovered more than 50 years ago, but their photophysical properties remain enigmatic. Despite a relatively large body of computational results, few experimental photophysical studies have been published. This is due, in part, to the poor solubility properties of hemiporphyrazine free base (HpH₂) (Figure 1A) and its ability to bind water molecules to adopt nonplanar conformations with distinct photophysical properties. Together with its sensitivity to acid-catalyzed hydrolysis, tendency to form aggregates, and possibility of excited-state tautomerization, these properties make metal-free hemiporphyrazines like HpH₂ very difficult to fully characterize in solution. Despite these challenges, the recent discovery of large two-photon absorption cross sections of metal-free and metallo Hps will invigorate research aimed at characterizing the basic photophysical properties of hemiporphyrazines in the solid state and in solution.

In contrast to porphyrins and phthalocyanines, Hps have nonaromatic 20-electron π systems that readily adopt nonplanar conformations. As a result of symmetry-forbidden S₀ → S₁ transitions, planar Hps in solution exhibit relatively weak absorbance of visible light (ε₅₃₂nm = 16–2800 M⁻¹ cm⁻¹) but have relatively strong S₀ → S₂ transitions in the far UV (ε₃₅₀–₉₉₀nm = 20 300–36 800 M⁻¹ cm⁻¹). Interestingly, the metal-free, anhydrous hemiporphyrazine free base (HpH₂) can exhibit multiple emission maxima (430 and 650 nm) upon photoexcitation at 380 nm. This “dual emission” was previously ascribed to formation of an emissive HpH₂ tautomer having a fully conjugated 20-electron π system with the loss of aromaticity of each pyridine group (Figure 1B). Since free-base hemiporphyrazines have two sets of inequivalent inner nitrogen atoms, three tautomeric forms are theoretically possible (Figure 1A–C). Computational studies suggest that HpH₂ exists exclusively as tautomeric form “A” in the ground state, while emissive tautomers “B” and “C” are proposed to form as a result of excited-state intramolecular proton transfer (ESIPT) from S₀ to S₂. While light-induced tautomerization reactions are well-known phenomena in porphyrins and phthalocyanines, the possible role of ESIPT in hemiporphyrazine photophysics has remained conjecture for over 15 years. In light of other possible explanations for the multiwavelength emissions from HpH₂, such as the presence of excitons and/or triplet excited states, we became interested in the synthesis and characterization of a metallohemiporphyrazine containing a neutral HpH₂ ligand and a metal ion having a defined oxidation state to serve as a nontautomerizable analog of HpH₂. Such “neutral-ligand” complexes will have two theoretically possible tautomers where the exchangeable protons are located on the peripheral.
edge of the macrocycle (Figure 1D and 1E). Given the large
distances between the sites of potential exchange, these
tautomers will not undergo ESIP. It was hitherto unknown
if these types of metal complexes would exhibit multiple
wavelength emission properties similar to HpH2 and if so what
the true basis of this phenomenon might be.

Here we report the synthesis and characterization of an
crystallographically indistinguishable, spectroscopically
similar, and structurally analogous compound. HpH2
and HpH2·H2O, HpH2·MeOH, DMSO, and DMF due to the presence of axial ligands
in the solid state and in solution (Figure 1D). While one can
consider a zwitterionic representation of the HpH2 ligand in
this complex (Figure 1F), bond length analyses indicate that
the neutral representation (Figure 1D) is more informative.

Unlike HpH2 and HpH2·H2O, HpH2·Zn(OTf)2 is soluble in
MeOH, DMSO, and DMF due to the presence of axial ligands
on the zinc atom. The improved solubility of this complex
allows for concentration-dependent analyses of its photophysical properties. Interestingly, soluble aggregates and solid-
state samples of HpH2·Zn(OTf)2 exhibit multiple-wavelength
photoluminescence properties very similar to those of HpH2.

For both compounds in the solid state, emissions at 450 nm
retain their fluorescence polarization while emissions at 650 nm
are depolarized with respect to the excitation source. Taken
together, our results suggest that excitonic coupling of 90
aggregated hemiporphyrines causes increased absorbance
and emission of light from S0 ↔ S1 transitions that are
normally symmetry forbidden in the isolated species.4,9

While the participation of emissive triplet states cannot be excluded,
we anticipate that the multiwavelength luminescence properties
of HpH2·Zn(OTf)2 and HpH2 are a result of emissive S2 → S0
and S1 → S0 transitions. Given the growing interest in
hemiporphyrine-based materials as nonlinear optical devi-
ces,10,17,19 these results provide important design consider-
ations by revealing the presence of excitonic luminescence in
aggregated and crystalline hemiporphyrines.

### MATERIALS AND METHODS

**General Methods.** Phthalonitrile was purchased from Fluka; all
other reagents were obtained in the highest commercially available
grades from Sigma Aldrich. 1H NMR spectra were measured on a
Bruker ARX-300 spectrometer (Bruker, Karlsruhe, Germany). The
chemical shift values are given in ppm relative to the residual signal
from d6-DMSO (δ = 2.5 ppm) or MeOD (δ = 3.31 ppm). All data
processing was carried out with Topspin (Bruker). Mass spectra were
measured using an Esquire-LC from Bruker. Absorbance and fluorescence
spectra were measured using a Spectra Max M5 from Molecular

**Synthesis of HpH2·Zn(OTf)2 (1).** Phthalonitrile (500 mg, 3.90
mmol), 2,6-diaminopyridine (426 mg, 3.90 mmol), and
Zn(OTf)2·2H2O (710 mg, 1.95 mmol) were stirred in nitrobenzene (4 mL) at 22 °C
for 4 h under N2. The reaction mixture was cooled to room

temperature. The resulting precipitate was collected by vacuum
filtration, repeatedly washed with CH2Cl2 and acetone, and dried in
vacuo to yield red crystals (641 mg, 69%). 1H NMR (300 MHz,
MeOD): 

- δ 1H: 8.20 (s br, 2 H), 8.14 (t, J = 8.0, 2 H), 7.82 (m, 8 H), 7.71 (d, J = 8.0, 4 H). Anal. Calcd for C30H18F6N8O8S2Zn: C, 41.83; H, 2.01; N, 13.94. Found: C, 41.84; H, 2.18; N, 13.96.

**Synthesis of Hemiporphyrine Monohydrate (HpH2·H2O).** Phthalonitrile (500 mg, 3.90 mmol) and 2,6-diaminopyridine (426 mg, 3.90 mmol) in 1-
chloronaphthalene (3 mL) were heated to reflux. After 4 h the
solution was cooled to room temperature. The resulting precipitate
was isolated by filtration and repeatedly washed with cold methanol.

After recrystallization from nitrobenzene, red needles were obtained
(1.03 g, 60%). 1H NMR (300 MHz, d6-DMSO): 10.74 (s br, 2 H, NH), 7.99–7.96 (m, 4 H), 7.80–7.76 (m, 6 H), 6.84 (d, J = 7.8, 4 H). ESI MS (m/z): [M + H]+ calc for C28H16F6N8O8S2Zn: 441; found, 441.

**Synthesis of Hemiporphyrine Monohydrate (HpH2·H2O).** Phthalonitrile (500 mg, 3.90 mmol) and 2,6-diaminopyridine (426 mg, 3.90 mmol) in
1-
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value equal to 1.2 Ueq of its parent C atom (1.5 Ueq for the methyl groups). Data collection and refinement parameters are given in Table 1.

### Table 1. Summary of Crystallographic Data

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<tr>
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<th>HpH2Zn(OTf)2</th>
<th>HpH2</th>
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<tr>
<td>crystallized</td>
<td>MeOH</td>
<td>1-methylnaphthalene</td>
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<tr>
<td>empirical formula</td>
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<td>C26H16N8</td>
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<td>red, plate</td>
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<td>160(1)</td>
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<td>P21/n</td>
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<td>14.1690(4)</td>
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<td>b [Å]</td>
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<td>4.9988(1)</td>
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<tr>
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<td>15.0572(4)</td>
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<tr>
<td>refls used in refinement</td>
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<tr>
<td>params refined</td>
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<tr>
<td>wR(F) (all data)</td>
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<td>1.036</td>
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<td>Δρ (max: min) [e Å⁻³]</td>
<td>0.39: -0.35</td>
<td>0.27: -0.30</td>
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#### RESULTS

### Synthesis and Structures. Unlike porphyrins and phthalocyanines, Hps have highly asymmetric coordination geometries. When coordinated to metals, the two nitrogen atoms from the isoindole moieties bind more tightly to the metal while the pyridine units retain much of their original character. Previous studies have focused on the synthesis of metallohemiporphyrines (HpMX₄) where the Hg ligand carries a −2 or −1 charge in complexes containing Pb(II), Cu(II), Co(II), Ni(II), Fe(II), Mn(II), and Sn(IV). In contrast, there are only a few small number of "neutral-ligand" metallohemiporphyrines of the type HpH₂MX₄ reported where M = Cu(II), Ni(II), or Zn(II) and X = Cl or Br. In these complexes, the charge of the metal ion is balanced by the axial ligands to give a neutral HpH₂ ligand. To the best of our knowledge, no crystal structure or solid-state luminescence properties of such a complex have previously been reported.

Reactions containing a 2:2:1 mixture of 2,6-diaminopyridine, phthalonitrile, and Zn(OTf)₂ in refluxing nitrobenzene give a red crystalline substance HpH₂Zn(OTf)₂. This new complex is soluble in MeOH, DMSO, and DMF, and it can be handled in the presence of oxygen and traces of water without decomposition. Crystals of HpH₂Zn(OTf)₂ suitable for crystallographic characterization were grown in solutions of methanol by slow diffusion of diethyl ether. Two types of crystals were obtained. The first was a relatively low-quality crystal type which gave a crystal structure consistent with elemental analysis and NMR data. The second crystal type gave very high-quality diffraction data and was found to be the methanolysis product of HpH₂Zn(OTf)₂ where methanol displacement of axial triflate ions from zinc. The resulting structure of HpH₂Zn(MeOH)₂(OTf)₂ is C₂ symmetry (Figure 2), where the two exchangeable N–H protons on the ligand are at diagonal meso nitrogen atoms. The triflate counterions (omitted for clarity in Figure 2) act as acceptors of O–H···O hydrogen bonds from methanol (H–O = 1.95(3) Å) and N–H···O hydrogen bonds from the meso nitrogen atoms (H–O = 2.13(2) Å). One might consider a zwitterionic representation for the HpH₂ ligand in this complex (Figure 2), but bond length analyses indicate the neutral representation (Figure 1D) is more informative, where the N1–C1 and N1–C4 bond lengths are highly asymmetric at 1.392(2) and 1.394(2) Å, respectively. Likewise, C1=N4 and C4=N2 are also asymmetric at 1.331(2) and 1.274(2) Å, respectively (Figure 2). These bond lengths reveal the presence of an alternating pattern of single and double bonds consistent with tautomer "D" (Figure 1D). In contrast, the structure of the free-base anhydrous ligand HpH₂ (presented below) has nearly identical N1–C1 and N1–C4 bond distances at 1.392(2) and 1.394(2) Å, respectively, and nearly identical C1=N4 and C4=N2 bond lengths at 1.282(2) and 1.320(2) Å, respectively (Figure 3).

Notably, the C4=N2 "double" bonds and N1−C4...
“single” bonds have nearly identical lengths in both HpH2 and HpH2Zn(MeOH)2·2(OTf). These results are consistent with the neutrality of the Hp ligand in both structures. This conclusion is further supported by the similar photophysical properties exhibited by these materials as well as the lack of acidity exhibited by HpH2Zn(OTf)2 (1) in methanol/water mixtures. For all experiments reported here, deprotonation of HpH2Zn(OTf)2 in solution to give an anionic ligand can be excluded, because this reaction is accompanied by a characteristic color change from red to green and the loss of solubility.11 Despite many decades of research, only a single, relatively low-quality crystal structure of the anhydrous hemiporphyrin ligand (HpH2) was available, apparently refined without hydrogen atoms (R = 0.115).29 HpH2 was therefore prepared according to modified published procedures,30 and red crystals of HpH2 suitable for single crystal X-ray diffraction were grown by slow cooling (180−25 °C) of a saturated solution in 1-methylnaphthalene under an inert atmosphere (Figure 3). The resulting structure at 160 K (R = 0.049) was found to have different unit cell parameters than the previously published structure.29 Aside from some small distortions similar to those observed in HpH2Zn(MeOH)2·2(OTf), HpH2 adopts a nearly planar structure. Despite the presence of repulsive interactions between the isoindole hydrogen atoms in the center of the macrocycle (N−H···H−N distance = 2.12(3) Å), tautomer “A” of HpH2 is present in our crystal structure (Figures 1A and 3). The nitrogen atoms of the isoindole moieties are separated by 3.867(2) Å, while the distance between the two pyridyl nitrogen atoms is 4.506(2) Å (Figure 3). These distances are similar to those observed in HpH2Zn(MeOH)2·2(OTf) at 3.939(2) and 4.461(2) Å, respectively. Given the small but significant differences in bond lengths in these compounds (discussed in greater detail in the previous paragraph), it was hitherto unknown if HpH2 and HpH2Zn(OTf)2 would exhibit similar or diverse photophysical properties. To provide a nonplanar hemiporphyrin for comparison, we also synthesized hemiporphyrin monohydrate (HpH2·H2O),1 for which a good crystallographic analysis has already been reported (Figure 4, R = 0.068).15 This structure is characterized by a nonplanar, “saddle”-shape conformation. Interestingly, the N2−C9 bond lengths in HpH2·H2O of 1.411(4) Å are slightly longer than the corresponding N2−C9 bonds of 1.394(2) Å in both HpH2 and HpH2Zn(MeOH)2·2(OTf). This is consistent with a greater extent of π conjugation across the pyridine units in HpH2 and HpH2Zn(MeOH)2·2(OTf) as compared to HpH2·H2O. This conclusion is supported by trends in the absorbance and fluorescence properties of these compounds.

Photophysical Properties in Solution. Solutions of 56 μM HpH2Zn(OTf)2 (1) in MeOH exhibit multiple emissions centered at 430 and 630 nm upon photoexcitation at 380 nm (Figure 5). A similar phenomenon was reported for the anhydrous, metal-free ligand HpH2 in DMF.7 In our experience and those of others, crystalline HpH2 is an insoluble material that readily converts into the nonplanar, yellow monohydrate (HpH2·H2O) in solvents containing even small traces of H2O.1,11 This has a profound influence on its photophysical properties4,9 and furthermore complicates any rigorous analysis of the concentration-dependent luminescence properties of anhydrous HpH2 in solution. In contrast, HpH2Zn(OTf)2 provides a highly soluble model complex for the neutral...
Serial dilutions of HpH₂Zn(OTf)₂ conducted at room temperature in MeOH revealed concentration-dependent absorbance and fluorescence spectra. With increasing concentrations of HpH₂Zn(OTf)₂, increased molar extinction coefficients from 430 to 500 nm were observed (Figure 6).

**Photophysical Properties: Solid State.** The limited solubility of HpH₂ and its tendency to bind water molecules prevent reliable concentration-dependent characterization of its photophysical properties in solution.¹,⁴,⁹,¹¹ We therefore prepared samples in the solid state by grinding each crystalline substance with KBr and pressing pellets. Both HpH₂ and HpH₂Zn(OTf)₂ exhibit relatively strong absorbances between 450 and 600 nm in the solid state with distinct features at 500 and 550 nm (Figure 7). The saddle-shaped compound.

![Figure 6. Absorbance spectra of HpH₂Zn(OTf)₂ as a function of concentration (reported in micromolar) in MeOH.](image)

![Figure 7. Absorbance spectra of HpH₂Zn(OTf)₂, HpH₂, and HpH₂·H₂O prepared in pressed KBr pellets at 0.3 mg/200 mg KBr with an optical path length of 1 mm. See Supporting Information Figure S7 for raw data including KBr blank.](image)

HpH₂·H₂O, in contrast, lacks these absorbance features (Figure 7 and Supporting Information, Figure S7).

Due to high background emissions and light scattering by KBr pellets, fluorescence emission data were collected using thick layers of neat, microcrystalline materials randomly deposited on polystyrene surfaces. Upon excitation at 350 nm, HpH₂, HpH₂Zn(OTf)₂, and HpH₂Zn(MeOH)₂·2(OTf) exhibit nearly identical emission spectra, with multiple emission peaks centered at 450, 480, 650, and 720 nm (Figure 8).

![Figure 8. Fluorescence emission spectra of randomly deposited microcrystalline materials using excitation at 350 nm and a long-pass emission filter at 420 nm.](image)

HpH₂·H₂O, in contrast, exhibits multiple emission peaks centered at 450, 480, and 530 nm. Crystal packing effects have a limited influence on the photophysical properties reported here. These crystalline materials exhibit highly diverse packing geometries (Supporting Information, Figures S2 and S8–S10), but crystals of HpH₂Zn(MeOH)₂·2(OTf) and HpH₂ exhibit absorbance, emission, and polarization spectra nearly identical to HpH₂Zn(OTf)₂ (1) (Figures 7–9). The relative emission intensities from crystalline samples of HpH₂ and...
The aggregation of HpH2Zn(OTf)2 has a profound impact on its photophysical properties. Upon aggregation in solution, luminescent emissions at 600–650 nm become apparent while the emissions at 400–450 nm are diminished (Figure 5 and Supporting Information, Figure S6). Previous studies have speculated that the multiple-wavelength emissions from HpH2Zn(OTf)2 are a result of excited-state intramolecular proton transfer reactions (ESIPT). However, HpH2Zn(OTf)2 is incapable of ESIPT and yet exhibits absorbance, multil wavelength emissions, and polarization spectra very similar to those of HpH2 (Figures 7–9). Our results therefore disprove ESIPT as the basis of the “dual-emission” properties of these compounds in the solid state. The exact mechanism for the multiple-wavelength emissions from aggregated and crystalline hemiporphyrines remains an open question. One possible explanation is the presence of short-lived triplet states.

We were unable, however, to detect any O2 sensitivity or longlived emissions (greater than 10 ns) from soluble aggregates of HpH2Zn(OTf)2 in solution. Another explanation is that S2 → S0 (~450 nm) and S1 → S0 (~650 nm) transitions are responsible for multil wavelength emissions from hemiporphyrines. In isolation, S0 ↔ S1 transitions are normally symmetry forbidden in hemiporphyrines, but excitonic coupling present in aggregated and crystalline hemiporphyrines may increase the oscillator strength of this transition due to its coupling with S0 → S2 transitions. Porphyrins and phthalocyanines have also been shown to undergo redistribution of transition dipole strengths between their “B bands” (~400 nm) and “Q bands” (500–650 nm) upon aggregation in solution due to excitonic coupling between these transition dipoles. Similar effects may be present for HpH2Zn(OTf)2, where dilute solutions exhibit strong absorbance centered at 370 nm and little, if any, absorbance at 450 nm, and aggregated samples exhibit increased extinction coefficients at 300 and 450 nm and decreased extinction coefficients from 330 to 400 nm (Figure 6). Interestingly, these changes are accompanied by the emergence of isotropic fluorescent emissions at 650–700 nm (Figures 6 and 8). Taken together, these results suggest the presence of enhanced S0 ↔ S1 transitions in aggregated hemiporphyrines due to the presence of excitonic coupling with S0 ↔ S2 transitions. Given the growing interest in hemiporphyrine-based materials as nonlinear optical devices, these results provide important new design considerations by highlighting the differences in photophysical properties of planar versus nonplanar hemiporphyrines as well as the presence of excitonic luminescence from aggregated and crystalline hemiporphyrines.
Notes
The authors declare no competing financial interest.

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