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Design and Synthesis of a Self-Assembled Photochemical Dyad Based on Selective Imidazole Recognition

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The unique recognition properties of phenanthroline-strapped zinc porphyrin **1**, which displays extremely high affinity for *N*-unsubstituted imidazoles, has been used as the driving force for the assembly of a photochemical dyad involving a zinc(II) porphyrin as energy donor and a free base porphyrin as energy acceptor. The synthesis of the imidazole-substituted porphyrin is described together with the assembly of the dyad. ^{1}H NMR titrations confirm the formation of a 1/1 complex between **1** and **6**, as well as insertion of the imidazole of the acceptor within the phenanthroline strap of the donor. Preliminary fluorescence quenching measurements show that efficient energy transfer occurs between the self-assembled components.

Introduction

The light harvesting (LH) antenna systems of photosynthetic bacteria are responsible for photon absorption and subsequent tunneling of this energy via excited-state energy transfer to a photochemical reaction center. The rapidity and efficiency of the energy migration reflects the high degree of organization of the numerous bacteriochlorophylls within the antenna complexes.[1,2] In the LH1 and LH2 antenna complexes of photosynthetic bacteria, the light-harvesting chromophores are held in close spatial arrangement by noncovalent attachment to a protein scaffolding. These beautifully organized antenna complexes have inspired the design and synthesis of porphyrin arrays aimed at mimicking photosynthetic processes. Numerous donor−acceptor systems containing metallo- and free-base porphyrins, designed to study energy transfer processes, have been constructed by both covalent and noncovalent means.[3] Although the covalent assembly of multi-porphyrin structures provides the most precise topographical control, the synthesis of such systems can be both limiting and challenging.[4] By using noncovalent interactions, a building block approach may be taken to

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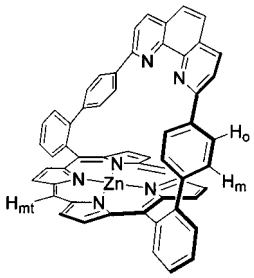

Figure 1. Zn−Porphen receptor **1**.

assemble several simple porphyrin components into more complex, yet spatially well-defined architectures. One of the major drawbacks of noncovalent assembly is that the resulting ensemble may be less stable than covalent counterparts. To overcome this potential problem, multiple metal−ligand interactions,[5,6] hydrogen bonds,[7] coordination chemistry,[8] or a combination of interactions[9] has been employed. Despite the variety of noncovalently assembled porphyrin arrays, relatively few consisting of zinc(II) porphyrin donors and free-base porphyrin acceptors have been reported.[10]

We have previously described the selective axial base binding displayed by the zinc(II) Porphen receptor **1** (Figure 1).[11] Coordination of *N*-unsubstituted imidazoles within the phenanthroline strap is enhanced by cooperative metal−ligand binding and hydrogen bond formation, leading to complexes with unprecedented stability (K_{ass} 19 500 000 M^{-1} for 2-methyl imidazole in CH_2Cl_2). Inclusion of imidazole within the phenanthroline strap has been clearly established

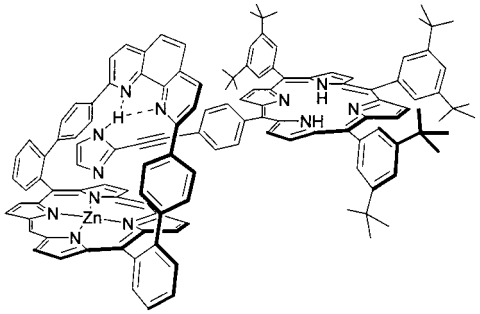

Figure 2. Assembly of a photochemical dyad via selective imidazole binding.

both in solution and in the solid state.[11] We have now taken advantage of the unusual axial binding to construct a self-assembled photochemical dyad from zinc(II) Porphen **1** (energy donor) and an imidazole-substituted free base porphyrin (**6**) (energy acceptor) (Figure 2). The synthesis, ^{1}H NMR titration studies, and preliminary fluorescence quenching measurements are described hereafter.

Experimental Section

General. Compounds **1** and **2** were prepared according to refs 12 and 13, respectively. Reagents and solvents of reagent grade were purchased and used without further purification. NEt_3 was distilled under argon over KOH prior to use. Anhydrous Na_2SO_4 was used as drying agent after aqueous workup. Evaporation and concentration in vacuo were carried out at H_2O-aspirator pressure. Column chromatography was performed with silica gel (0.063−0.200 mm) from Merck. Melting points are uncorrected. Mass spectra were recorded using a nitrobenzyl alcohol matrix. Elemental analyses were performed by le Service de Microanalyze de l'Institut de Chimie, Université Louis Pasteur, and by le Service d'Analyze Elementaire de l'Institut Universitaire de Technologie, Strasbourg, Sud.

1-[[2-(Trimethylsilyl)ethoxy]methyl]-2-[2-(trimethylsilyl)ethynyl]imidazole (3a). To a degassed solution of **2** (5.00 g, 15.4 mmol) in freshly distilled NEt_3 (50 mL) in a flame-dried flask under argon was added $Pd(PPh_3)_2Cl_2$ (0.22 g, 0.31 mmol) and CuI (0.03 g, 0.15 mmol). This mixture was degassed again, and then trimethylsilylacetylene (2.55 mL, 18.5 mmol) was added via syringe. The reaction mixture was degassed and then heated at 60° for 6 h. Solvents were removed under reduced pressure. The residue was taken in CH_2Cl_2, washed with saturated NH_4Cl (aq) and brine, dried, filtered, and evaporated to dryness. Purification by column chromatography (SiO_2, EtOAc/hexane: 1/4) afforded **3a** as a colorless oil (3.86 g, 13.1 mmol, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.07 (s, 1H); 7.04 (s, 1H); 5.37 (s, 2H); 3.52 (t, J = 8 Hz, 2H); 0.90 (t, J = 8 Hz, 2H); −0.26 (s, 9H); −0.02 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 131.60; 129.52; 119.70; 98.77; 92.80; 74.62; 65.89; 17.12; −0.88; −1.90. Anal. Calcd for $C_{14}H_{26}N_2OSi_2$: C, 77.01; H, 8.90; N, 9.51. Found: C, 77.51; H, 9.13; N, 9.44.

1-{[2-(Trimethylsilyl)ethoxy]methyl}-2-ethynylimidazole (3b). Eight pipet drops of 2 M NaOH (aq) were added to a solution of **3a** (2.00 g, 6.80 mmol) in MeOH (20 mL). The reaction mixture was stirred at rt, and progress of the deprotection was monitored

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by TLC. After 1 h, the solvents were removed under vacuum, and the resulting residue was taken in CH_2Cl_2, washed with brine, dried, filtered, and evaporated to dryness. Column chromatography (SiO_2, EtOAc/hexane: 1/1) gave **3b** as an oil (1.36 g, 6.13 mmol, 90%). This product was used immediately, without further purification, for the subsequent coupling reaction. ^{1}H NMR (300 MHz, $CDCl_3$): 7.09 (s, 1H); 7.07 (s, 1H); 5.38 (s, 2H); 3.53 (t, J = 8 Hz, 2H); 3.32 (s, 1H); 0.89 (t, J = 8 Hz, 2H); −0.02 (s, 9H).

SEM-Imidazole H_2Porphyrin (5). To a degassed solution of **4** (285 mg, 0.25 mmol) in triethylamine (20 mL) in a flame-dried flask under argon was added $Pd(PPh_3)_2Cl_2$ (3.5 mg, 0.05 mmol) and copper(I) iodide (1 mg, 0.005 mmol). This mixture was degassed again, before adding a solution of ethynyl imidazole **3b** (61 mg, 0.27 mmol) in toluene (10 mL). This degassed mixture was stirred at 50 °C for 24 h, and then solvents were removed under vacuum. The residue was dissolved in CH_2Cl_2, washed with saturated NH_4Cl (aq), dried, filtered, and evaporated to dryness. The resulting blue-violet solid (**Zn-5**) was taken in CH_2Cl_2 (50 mL), and five drops of CF_3CO_2H were added. After 30 min of stirring, the green solution was washed with H_2O and then basified with 10% Na_2CO_3 (aq). The pink organic layer was collected, dried, filtered, and evaporated to dryness in vacuo. The crude product was purified by column chromatography (SiO_2/CH_2Cl_2/EtOAc: 4/1) to yield **5** (260 mg, 0.22 mmol, 89%) that was used without further purification for the next step. ^{1}H NMR (300 MHz, $CDCl_3$): 8.91 (s, 6H); 8.83 (d, J = 4.8 Hz, 2H); 8.26 (d, J = 7.8 Hz, 2H); 8.09 (s, 6H); 7.96 (d, J = 7.8 Hz, 2H); 7.81 (s, 3H); 7.24 (s, 1H); 7.21 (s, 1H); 5.62 (s, 2H); 3.74 (t, J = 8 Hz, 2H); 1.04 (d, J = 8 Hz, 2H); 1.53 (s, 54H); 0.05 (s, 9H); −2.69 (s, 2H).

HIm-H_2Porphyrin (6). A 1 M solution of TBAF (8 mL) in THF was added to a degassed solution of **5** (260 mg, 0.22 mmol) in dry THF (20 mL). The solution was stirred at 50−55 °C under argon for 3 h, and then solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2, washed with H_2O, Na_2CO_3 (aq), and brine, dried, filtered, and evaporated to dryness. Purification by column chromatography (SiO_2, CH_2Cl_2/EtOAc: 4/1) afforded **6** (138 mg, 0.13 mmol, 60%) as a violet solid. Mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 9.50 (br s, 1H); 8.91 (s, 6H); 8.83 (d, J = 4.8 Hz, 2H); 8.25 (d, J = 8.1 Hz, 2H); 8.09 (d, J = 1.8 Hz, 4H); 8.07 (s, 2H); 7.93 (d, J = 7.7 Hz, 2H); 7.80 (s, 2H); 7.79 (s, 2H); 7.22 (s, 1H); 7.06 (s, 1H); 1.53 (s, 54H); −2.69 (s, 2H). UV−vis (CH_2Cl_2): 298 (29 000); sh 406 (83 900); 422 (456 200); 454 (49 700); 518 (17 900); 554 (11 400); 592 (5700); 648 (5900). UV−vis (hexane): 262 (24 300); 291 (28 100); sh 403 (74 000); 418 (383 000); 482 (5200); 515 (15 800); 548 (9900); 592 (4300); 649 (3700). FAB$^+$ MS Calcd for $C_{73}H_{80}N_6$: 1041.5. Found: 1041.7 (100%). Anal. Calcd for $C_{73}H_{80}N_6 \cdot 2H_2O$: C, 81.38; H, 7.86; N, 7.79. Found: C, 81.56; H, 7.52; N, 8.04.

1-{[2-(Trimethylsilyl)ethoxy]methyl}-2-[2-(phenyl)ethynyl]-imidazole (7a). This compound was prepared, with an unoptimized yield, according to the procedure described for the synthesis of **3a**, using the following: **2** (0.648 g, 0.002 mol), dry NEt_3 (10 mL), $Pd(PPh_3)_2Cl_2$ (0.070 g, 0.10 mmol), CuI (0.038 g, 0.19 mmol), and phenylacetylene (0.44 mL, 0.004 mol). This mixture was stirred at rt for 5 days, and then $Pd(PPh_3)_2Cl_2$ (0.019 g, 0.03 mmol), CuI (0.009 g, 0.05 mmol), and phenylacetylene (0.11 mL, 0.001 mol) were added and heated at 60 °C for 20 h. Workup and purification by column chromatography (SiO_2, CH_2Cl_2, then CH_2Cl_2/EtOAc: 10/75) afforded **7a** (239 mg, 0.8 mmol, 40%) as a yellow oil that was used without further purification for the subsequent deprotection step. ^{1}H NMR (300 MHz, $CDCl_3$): 7.57−7.54 (m, 2H); 7.39−7.36 (m, 3H); 7.15 (d, J = 1.2 Hz, 1H); 7.11 (d, J = 1.2 Hz, 1H); 5.46 (s, 2H); 3.58 (t, J = Hz, 2H); 0.93 (t, J = Hz, 2H); −0.04 (s, 9H). ^{13}C NMR (50.3 MHz, $CDCl_3$): 131.75; 130.53; 129.28; 128.89; 128.54; 121.67; 120.31; 92.88; 78.44; 75.25; 66.57; 17.70; −1.44.

2-[2-(Phenyl)ethynyl]imidazole (7b). This compound was prepared according to the procedure described for the synthesis of **6**, using the following: **7a** (146 mg, 0.49 mmol) in 1 M TBAF in THF (12 mL, 12 mmol). This mixture was refluxed for 45 min, and workup, purification by column chromatography (SiO_2, CH_2Cl_2/EtOAc: 2/1), and recrystallization from cold CH_2Cl_2 gave **7a** (47 mg, 0.28 mmol, 57%) as pale yellow needles. Mp 161 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 7.54−7.50 (m, 2H); 7.37−7.32 (m, 3H); 7.14 (s, 2H). Anal. Calcd for $C_{11}H_8N_2$: C, 78.55; H, 4.79; N, 16.66. Found: C, 78.52; H, 4.69; N, 16.27.

Results and Discussion

To take advantage of this strong binding as a connecting tool for the construction of a photochemical dyad, an imidazole has been covalently linked to a free base porphyrin according to Scheme 1. 2-Iodo-1-{[2-(trimethylsilyl)ethoxy]-methyl}imidazole,[13] **2**, was coupled with trimethylsilylacetylene (TMSA) via the Sonogashira cross-coupling method[14] to afford **3a** in excellent yield. The alkyne-protecting $SiMe_3$ group was removed quantitatively by reaction with NaOH (aq) in MeOH. Because of limited stability, the deprotected compound **3b** was used rapidly without further purification. The iodo tetraaryl zinc(II)−porphyrin **4** was obtained through an AB_3 Lindsey-type synthesis[15] and metalated with zinc to prevent copper insertion during the Sonogashira coupling with **2**. Palladium catalyzed coupling of porphyrin **4** with **3b** gave the SEM-protected imidazole zinc porphyrin **Zn-5**. This compound, characterized by ^{1}H NMR as a dimer[16] in dichloromethane solutions (see Supporting Information), proved to be difficult to purify. Treatment of the crude coupling product **Zn-5** with TFA, however, greatly facilitated purification, affording the free base porphyrin **5** in 89% yield. Subsequent treatment of this intermediate with tetra-*n*-butylammonium fluoride (TBAF)[17] in THF afforded **6** in 60% yield from **5** after purification by column chromatography and crystallization from cold methanol.

Insertion of the imidazole of **6** in the phenanthroline strap of Porphen receptor **1**, yielding the assembled dyad depicted in Figure 2, was monitored by ^{1}H NMR. Typical ^{1}H NMR data collected after addition of free base porphyrin **6** to zinc(II) Porphen receptor **1** provides evidence for insertion of the imidazole in the phenanthroline strap of the receptor (see Figure 3 and Supporting Information). Changes in the chemical shifts of the Porphen (**1**) protons are indicative of the inclusion complex topography. Insertion of the imidazole ring of **6** within the strap of the receptor results in a loss of symmetry of the porphyrin ring of **1** and, thus, a nonequivalence of the β-pyrrolic and methene protons. This is best

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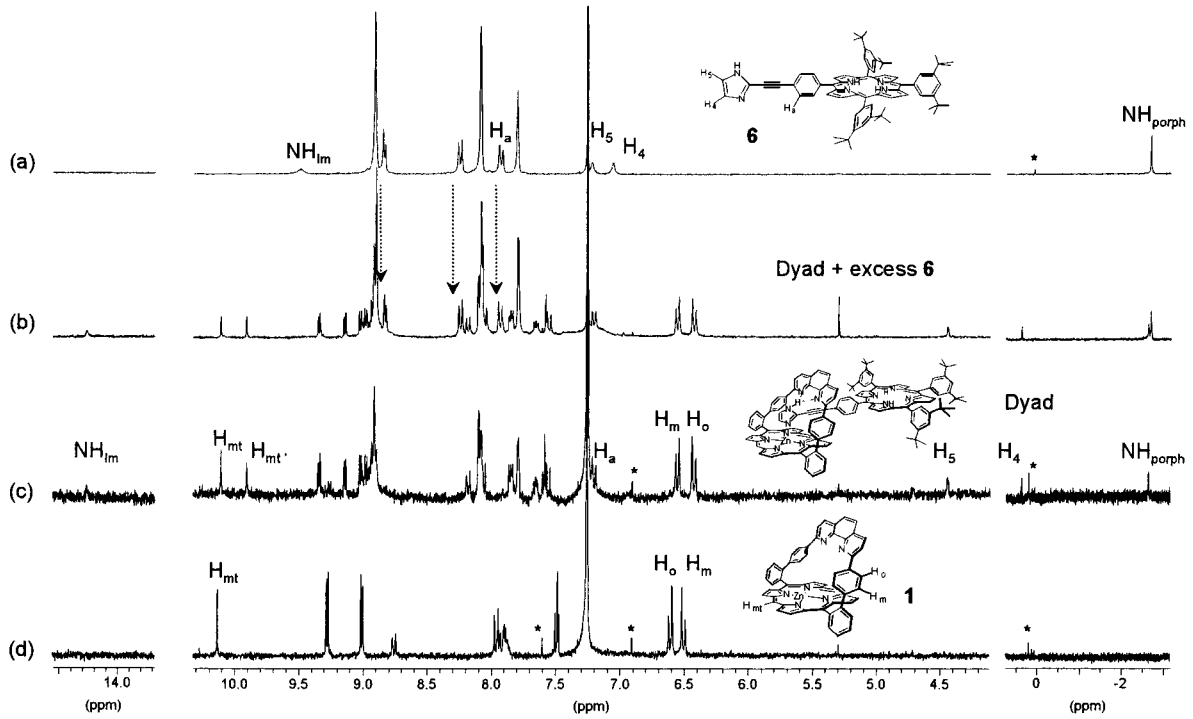
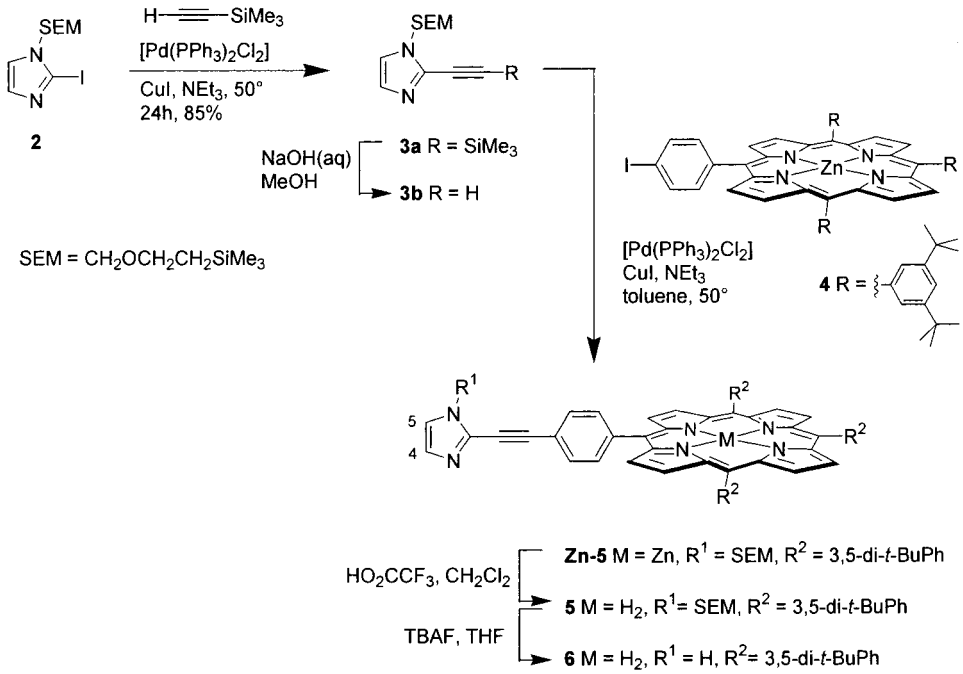


Figure 3. Representative ^{1}H NMR (300 MHz, $CDCl_3$) of the dyad and its components; * = sidebands.

Scheme 1



illustrated by the splitting of the methene peak mt at 10.15 ppm of free **1** (Figure 3d) into two signals, mt and mt′ at 10.11 and 9.90 ppm, respectively, in the 1:1 dyad complex (Figure 3c). The shielding of the ortho protons, H_o ($\Delta\delta$ = −0.18 ppm), of the phenyl spacer of **1** provides further evidence for imidazole binding in the pocket of **1**. The most significant changes are observed for the chemical shifts of the imidazole NH, H_4 and H_5 protons. Upon complexation, the NH protons shifts downfield from 9.5 to 14.2 ppm. This shift is indicative of hydrogen bond formation between the NH proton of the imidazole and the nitrogen atoms of the phenanthroline. A drastic shielding of imidazole protons H_4 ($\Delta\delta$ = −6.0 ppm) and H_5 ($\Delta\delta$ = −2.8 ppm) is also observed, reflecting coordination of the imidazole to the zinc atom of **1**. Binding is complete once a 1:1 stoichiometry is reached, as no further changes are observed upon addition of excess substrate **6** (Figure 3b). At 2:1 stoichiometry, peaks corresponding to unbound guest **6** are observed, notably the imidazole H_4 and H_5 at 6.98 and 6.91 ppm, respectively, and the porphyrin NH singlet at −2.4 ppm. During the titration, the appearance of sharp signals corresponding to complexed imidazole−porphyrin **6** is observed together with

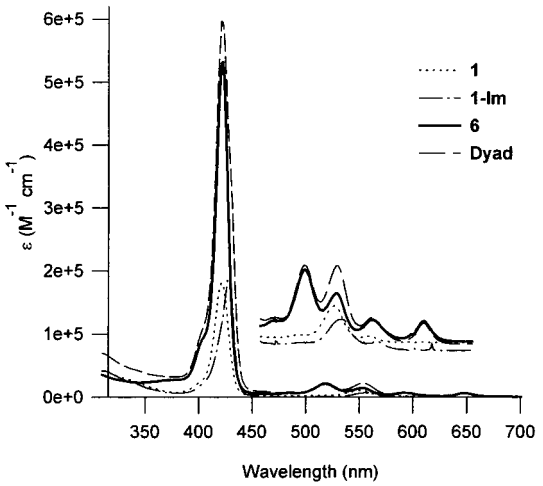


Figure 4. Absorption spectra of the dyad and its components in CH_2Cl_2 at 4×10^{-6} M.

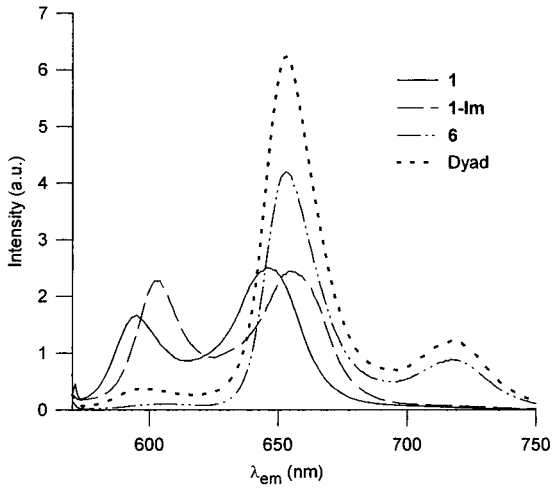
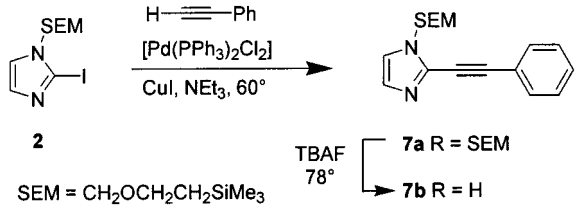


Figure 5. Fluorescence spectra (λ_{ex} = 556 nm) of the dyad and its components at 4×10^{-6} M in CH_2Cl_2 containing 0.01% of 2,6-lutidine.

Scheme 2



the disappearance of peaks of free Porphen receptor **1**, thus excluding fast exchange between bound and unbound species at this concentration (3.8×10^{-4} M).

The association constant for the binding of **6** within the phenanthroline strap of **1** is too high to be determined from ^{1}H NMR data. UV−vis titrations are also unsuitable in the present case because of an overlap of the species' individual spectra (Figure 4). To estimate an association constant for the binding of **1** and **6**, a model compound for **6**, namely 2-[2-(phenyl)ethynyl]imidazole (**7b**), was desirable. This compound was synthesized via an unoptimized Sonogashira coupling of **2** and phenylacetylene, affording **7a** which was subsequently treated with TBAF (Scheme 2). Binding studies of ZnPorphen **1** with **7b** could be carried out by UV−vis spectroscopy because of an 8 nm red shift of the Soret band of **1** upon complexation of **7b**. The calculated association constant of $(1.6 \pm 0.2) \times 10^6$ M^{-1} in CH_2Cl_2 is similar to that previously determined for binding of imidazole with **1** ($K_a = (1.3 \pm 0.1) \times 10^6$ M^{-1}).[11] During the course of these studies, it was found that free base porphyrin **6** was photosensitive in pure CH_2Cl_2.[18] This phenomenon was inhibited by the presence of 0.01% 2,6-lutidine in CH_2Cl_2. A nearly 10-fold decrease in the binding constant for **1** and **7b** was observed in 2,6-lutidine-stabilized dichloromethane ($K_a = (3.4 \pm 0.3) \times 10^5$ M^{-1}). It seems highly unlikely that 2,6-lutidine binds to the zinc porphyrin as no red shift was observed in the Soret band of **1** when comparing its absorption in pure CH_2Cl_2 and lutidine-stabilized CH_2Cl_2. An interaction, such as hydrogen bond formation, between the imidazole NH and the lutidine nitrogen atom might be considered as the possible reason for the observed decrease of the binding constant.

To investigate the photoinduced energy transfer from phenanthroline-strapped Zn(II)−porphyrin **1** to free base porphyrin **6**, fluorescence quenching experiments were performed in CH_2Cl_2 containing 0.01% 2,6-lutidine. In Figure 4, the electronic absorption spectra of **1**, **6**, and a Zn(II) Porphen−imidazole complex (**1-Im**) show that **6** can be selectively excited at 518 nm, but it is not possible to selectively excite **1** and **1-Im**. Fluorescence spectra of the individual dyad components (Figure 5) show that emission from **1**, **1-Im**, and **6** can selectively be monitored at 595, 602, and 719 nm, respectively.

Upon irradiation at 556 nm of the dyad, derived from a 1:1 mixture of **1** and **6**, emission at 595 nm from the zinc porphyrin, or 602 nm from the **1-Im** complex, clearly drops in intensity (Figure 5). Titration experiments show that the emission of the dyad at 595 nm continues to decrease upon addition of excess acceptor **6** to donor **1** (see Supporting Information), suggesting that at a concentration of 4×10^{-6} M association between **1** and **6** is incomplete. Using the association constant determined for **1** with **7b**, it was estimated that 56% of **1** and **6** is uncomplexed at 4×10^{-6} M.[19] Comparison of the excitation spectra at 595 nm of **1**, **1-Im**, and the dyad (Figure 6) shows excitation maxima at 548 nm for **1** and the dyad and at 556 nm for **1-Im**. This confirms that the emission observed at 595 nm for the 1:1 mixture of **1** and **6** in Figure 5 is due to uncomplexed Zn−Porphen **1** rather than to incomplete quenching of the excited state of the 1:1 complex. Quenching experiments at higher concentrations are precluded, as control experiments demonstrated excited-state interactions between **1-Im** and 5,10,-15,20-tetrakis-(3,5-di-*tert*-butylphenyl)porphyrin (**8**), a reference acceptor compound, at concentrations higher than 1×10^{-5} M.[20]

(18) In the absence of 2,6-lutidine, free base porphyrin **6** undergoes photoinduced protonation upon irradiation in CH_2Cl_2. The absorption spectrum of **6** in CH_2Cl_2 stabilized with 2,6-lutidine is identical to that observed in hexane, in which no photoinduced protonation has been observed. Further details of this phenomenon will be published elsewhere.

(19) The concentrations of the dyad and its uncomplexed components **1** and **6** were calculated using the program HALTAFALL.

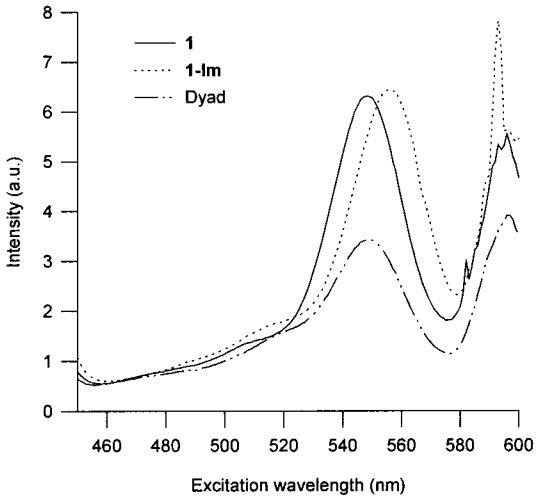


Figure 6. Comparison of the excitation spectra (λ_{em} = 595 nm) of the dyad, **1**, and **1-Im**.

Despite the incomplete binding at the concentration studied, evidence for energy transfer within the dyad is provided by the 38% increase in emission at 717 nm of the dyad compared to that of free base **6**.[21] To prove that this behavior is a property of the self-assembled dyad, several control experiments were carried out. When reference acceptor **8** was added to **1-Im** and irradiated at 554 nm, the intensity of the **1-Im** emission at 602 nm remained unchanged (see Supporting Information). In the reverse titration, adding **1-Im** to **8**, the emission at 717 nm, due only to the free base porphyrin **8**, remained unchanged. Furthermore, when donor **1** is added to acceptor **6** and irradiated at 518 nm, where only the acceptor absorbs, the emission spectrum of acceptor **6** is observed (see Supporting Information). The quenching at 602 nm observed in the 1:1 mixture of **1** and **6**, and the 38% increase in emission at 717 nm, can thus be attributed to photoinduced energy transfer within the assembled dyad. Other reports of energy transfer in noncovalently linked zinc(II) porphyrin and free base porphyrin assemblies[6,10c] also demonstrate that energy transfer from donor to acceptor is less efficient than in covalent multiporphyrin arrays.[22]

(20) At 1×10^{-5} M, upon excitation at 554 nm, ~6% energy transfer was observed between zinc(II) porphyrin **1-Im** and free base porphyrin **8**. No interaction was detected between these two porphyrins at 5×10^{-6} M.

(21) In a first approximation, the 38% emission increase is representative of the energy transfer efficiency and is in agreement with those (0.2−0.6) observed for similarly spaced zinc and free base porphyrins: Kilså, K.; Kajanus, J.; Mårtensson, J.; Albinsson, B. *J. Phys. Chem. B* **1999**, *103*, 7329. Detailed calculations including correction of absorption, emission, and excitation spectra will be published for a series of free base acceptors.

Conclusion

In conclusion, these results demonstrate that the highly selective binding of *N*-unsubstituted imidazoles in the phenanthroline-strapped receptor **1** is a powerful tool for the spontaneous assembly of rigid photonic devices. Time-resolved studies and Förster radii calculation for **1-Im** are necessary to determine the rate of the energy transfer responsible for the properties of the assembled dyad and the eventual contribution of electron transfer to the fluorescence quenching process. To examine the influence of the distance between **1** and **6**, changes in the phenyl acetylene spacer are in progress as well as efforts toward the assembly of energy tunneling polymers.

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Supporting Information Available: ^{1}H NMR spectrum of dimeric **Zn-5**, ^{1}H NMR titration for dyad formation, fluorescence titration of **1** with **6**, and fluorescence control experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

IC020043B

(22) Efficient energy transfer (>0.9) in a covalently linked multi-porphyrin array has been reported: Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759.