Supramolecular Porphyrin Assemblies through Amidinium–Carboxylate Salt Bridges and Fast Intra-Ensemble Excited Energy Transfer

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Abstract: Well-defined supramolecular assemblies of Zn and free-base porphyrins are constructed through the formation of amidinium–carboxylate salt bridges. A one-to-one donor–acceptor pair and a four-to-one antenna-type assembly are investigated. The steady-state and time-resolved fluorescence measurements unequivocally showed that efficient singlet–singlet excited energy transfer from the Zn–porphyrin complex to the free-base porphyrin takes place in these assemblies. Indeed, the observed energy-transfer rates in both types of assemblies are much faster than those the Förster mechanism would suggest, implying the involvement of an intermolecular through-bond mechanism.

Keywords: energy transfer • porphyrinoids • salt bridges • supramolecular chemistry • through-bond mechanism

Introduction

Photosynthetic antenna arrays found in nature funnel photoexcited energy into the reaction center.[1] Attempts have been made to mimic the antenna function by using artificial chromophores, porphyrins in particular, to better understand the energy-transfer processes and to create energy-harvesting devices. It has become increasingly apparent that noncovalent self-assembly is better suited to construct complex multichromophore assemblies.[2] Interactions that have been employed in constructing energy donor–acceptor porphyrin assemblies in this regard include metal coordination interactions,[3–6] hydrogen bonds,[6–8] and others.[9] The required properties for the intermolecular interaction joining chromophores include strength and directionality. Asymmetry is needed when a heterotopic supramolecule, such as a donor–acceptor pair, is desired. Another important issue, though often made light of, is whether the intermolecular interaction facilitates the energy-transfer process.

We here demonstrate that amidinium–carboxylate salt bridges, which have been used to construct *electron* donor–acceptor dyads[10] or a donor–spacer–acceptor triad,[11] can also be used to assemble an *energy* donor–acceptor dyad and pentad. The salt bridge consists of complementary double hydrogen bonds and electrostatic interaction, and, therefore, excels in directionality and strength.[10] We prepared the Zn–porphyrin complex with an amidine group (**ZnPA**) as the energy donor. This porphyrin was combined with the free-base porphyrins bearing either one (**FbPC**), and four (**FbPC$_4$**) carboxy groups to prepare the 1:1 donor–acceptor pair, **ZnPA·FbPC**, and the antenna-type 4:1 assembly, **(ZnPA)$_4$·FbPC$_4$**, respectively. The intra-ensemble singlet–singlet excited energy-transfer process was probed with steady-state and picosecond time-resolved fluorescence measurements. Fast excited energy transfer was observed in these supramolecules; this implies the involvement of a through-bond mechanism mediated by intermolecular bonds.

Results and Discussion

^{1}H NMR titration studies: The assembly of **ZnPA** with the two free-base porphyrins, that is, the free-base porphyrin with one (**FbPC**) and four (**FbPC$_4$**) carboxy moieties, was investigated with ^{1}H NMR titration experiments in [D$_6$]benzene/[D$_6$]DMSO (99:1). DMSO was added in order to dissolve enough of the free-base porphyrins, especially **FbPC$_4$**. The use of DMSO also simplifies the analysis of the assembly process. **ZnPA** aggregates with itself by axial coordination through the amidine group in non-coordinating solvents such as toluene; therefore, the ^{1}H NMR resonances are broadened and the electronic absorption spectrum exhibits

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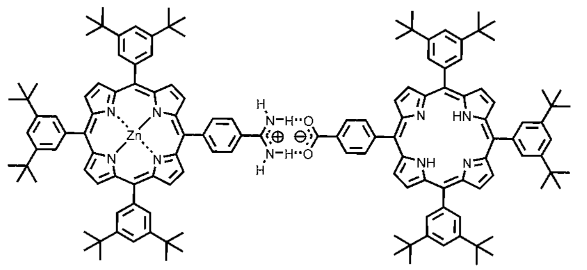
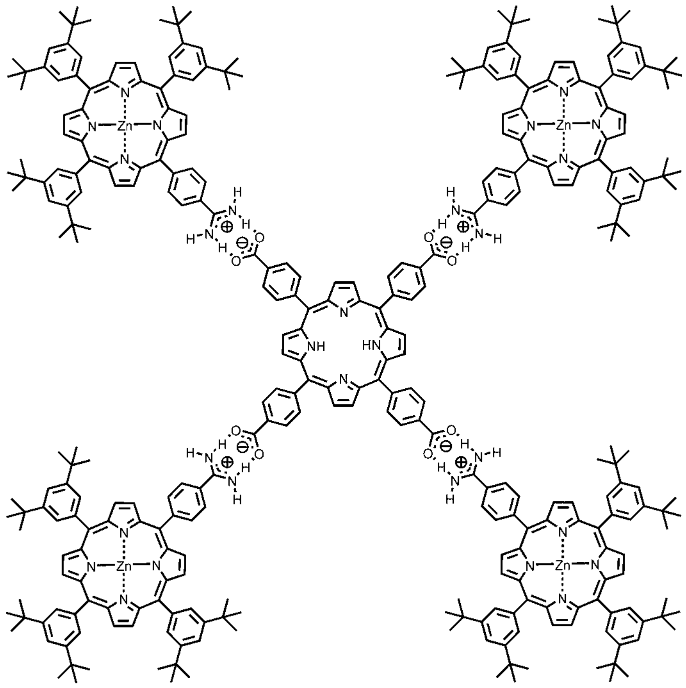


ZnPA • FbPC



(ZnPA)$_4$ • FbPC

red-shifted Q-band peaks relative to the Zn–tetraphenylporphyrin (ZnTPP) complex (data not shown). DMSO itself coordinates to the Zn ion in the macrocycle to prevent **ZnPA** from assembling with itself.

Incremental amounts of **ZnPA** were added into a solution of **FbPC** in [D$_6$]benzene/[D$_6$]DMSO (99:1), and the chemical shifts of the **FbPC** protons were recorded. The shifts changed on addition of up to one equivalent of **ZnPA** and then saturated as shown in Figure 1a. The formation of the 1:1 complex, **ZnPA·FbPC**, was clearly established by this ^{1}H NMR titration experiment. The downfield shifts indicate that two porphyrin rings lie in a side-by-side fashion, considering the large ring-current effect of porphyrin macrocycles.[12] The fact that protons closer to the carboxylate group experience larger shifts is consistent with the formation of the carboxylate–amidinium salt bridge. As for the mixtures of **FbPC$_4$** and **ZnPA**, similar chemical shift changes were observed as shown in Figure 1b. The formation of the 4:1 complex, **(ZnPA)$_4$·FbPC$_4$**, was also clearly proven from the abrupt halt of the chemical shift changes at this stoichiometry.

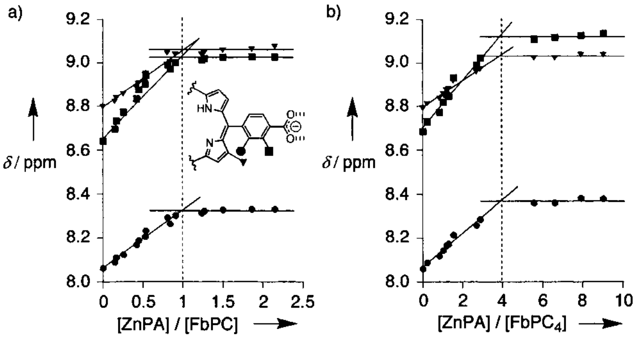


Figure 1. ^{1}H NMR chemical shifts of selected protons in free-base porphyrins in [D$_6$]benzene/[D$_6$]DMSO (99:1) as a function of the ratio of added **ZnPA** to the free-base porphyrin concentration: a) **FbPC** (5.6 mM); b) **FbPC$_4$** (0.11 mM).

Abstract in Japanese:
アミジニウム－カルボキシラート間の塩橋形成によって，亜鉛およびフリーベースポルフィリンからなる構造のはっきりした超分子会合体を構築した．１：１のドナー・アクセプターペアと４：１のアンテナタイプの会合体を検討した．定常光および時間分解蛍光測定によって，これらの会合体内で亜鉛ポルフィリンからフリーベースポルフィリンへの効率のよいエネルギー移動がおこることが確実に示された．実際，両タイプの会合体内で観察されたエネルギー移動速度はフェルスター機構から考えられるよりもかなり早く，分子間のスルーボンド機構の関与が示唆される．

Absorption and fluorescence spectra: Absorption and fluorescence spectra were recorded for these porphyrins in toluene/DMSO (99:1) at 25 °C. Table 1 lists the Soret- and Q-band absorption maxima (λ_{abs}) with their molar extinction coefficients, as well as the fluorescence maxima (λ_{fl}). The λ_{abs}'s of **ZnPA** are practically identical to those of the model Zn–tetrakis(3,5-di-*tert*-butyl)porphyrin complex (**ZnP**). This indicates that substitution with the amidine group does not perturb the electronic properties of Zn–porphyrin com-

Table 1. Absorption and fluorescence data in toluene/DMSO (99:1) at 25 °C.

	Soret band region		Q-band region		Fluorescence[a]
	λ_{abs} [nm]	ε [M^{-1}cm^{-1}]	λ_{abs} [nm]	ε [M^{-1}cm^{-1}]	λ_{fl} [nm]
ZnP	430	6.0×10^{5}	561	2.3×10^{4}	606, 658
			600	1.2×10^{4}	
ZnPA	430	6.0×10^{5}	561	2.5×10^{4}	606, 656
			601	1.2×10^{4}	
FbP	421	5.0×10^{5}	517	2.0×10^{4}	652, 710
			551	1.1×10^{4}	
			593	5.8×10^{3}	
			649	6.4×10^{3}	
FbPC	422	4.1×10^{5}	517	1.7×10^{4}	651, 713
			551	8.6×10^{3}	
			593	4.7×10^{3}	
			650	4.0×10^{3}	
FbPC$_4$	422	4.0×10^{5}	515	2.0×10^{4}	653, 710
			551	1.0×10^{4}	
			592	6.6×10^{3}	
			649	4.5×10^{3}	

[a] λ_{ex} = 560 nm.

plexes. Therefore, the D_{4h} symmetry of the metalloporphyrin is considered as being maintained as far as the electronic transitions are concerned. This is also the case for the carboxy derivatives of porphyrin; the λ_{abs}'s of **FbPC** and **FbPC$_4$** are practically identical to those of the model free-base porphyrin, tetrakis(3,5-di-*tert*-butyl)porphyrin (**FbP**). Thus, these porphyrins retain the D_{2h} symmetry electronically. The fact that the electronic structures are not perturbed by substitution in the porphyrins used in this study is an important point when the value of the orientation factor in the Förster mechanism is estimated (vide infra). The λ_{fl}'s of **ZnP**, **FbPC**, and **FbPC$_4$** are also nearly identical to those of the respective model porphyrins.

Then, self-assembly of **ZnPA** with **FbPC** and excited energy transfer therein have been examined by steady-state electronic absorption and fluorescence spectra. The absorption spectrum for an equimolar mixture (4 μM) of **FbPC** and **ZnPA** in toluene/DMSO (99:1) was virtually identical to the sum of those for component porphyrins, as shown in Figure 2a; this not only indicates that there is little ground-state interaction between the two porphyrin chromophores, but also excludes the possibility that simple aggregation of porphyrins occurs. One the other hand, fluorescence from the mixture was completely different from the sum of component spectra. Basically, the fluorescence from **ZnPA** was diminished and that from **FbPC** increased. The fluorescence intensity at 712 nm (λ_{ex} = 560 nm), at which only the free-base porphyrin fluorescence is observed, increased upon addition of **ZnPA** as shown in Figure 3, indicating that energy transfer from **ZnPA** to **FbPC** occurred. Assuming that this sensitization is due to the formation of the **ZnPA·FbPC** complex, the association constant was found to be 2.9(± 0.1) × 10^5 M^{-1}; as determined from the fluorescence intensity data by using a least-squares curve-fitting procedure. The need of the carboxy group in efficient sensitization is evident, since **FbP** showed only a little increase in fluorescence intensity, due to diffusional encounters, see Figure 3.

Similar experiments were done with **FbPC$_4$** in place of **FbPC**. Again, the absorption spectrum for a mixture of **ZnPA** and **FbPC$_4$** is identical to the sum of component spectra, as shown in Figure 2b. The result of a sensitization experiment is included in Figure 3. The increase of fluorescence in this case is nearly four times larger than that for **FbPC**, in agreement with more molecules (up to four) of **ZnPA** associating with **FbPC$_4$**. The fluorescence intensity dependence on **ZnPA** concentration was best fitted by assuming four independent, identical binding sites, that is, carboxy groups, on **FbPC$_4$** leading to the formation of the 4:1 complex, **(ZnPA)$_4$·FbPC$_4$**. The association constant between **ZnPA** and one of the sites on **FbPC$_4$** was determined as 2.2(± 0.2) × 10^6 M^{-1}.

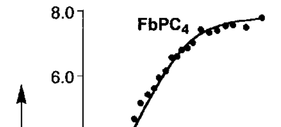


Figure 3. Fluorescence intensities of free-base porphyrins (4 μM) monitored at 712 nm as a function of **ZnPA** concentration in toluene/DMSO (99:1) at 25 °C (λ_{ex} = 560 nm). Dots are observed intensities, while lines are calculated curves based on the association constants as described in the text.

Time-resolved studies on excited energy transfer: Time-resolved fluorescence measurements were undertaken to determine the rates of energy transfer. For a pure sample, the fluorescence lifetime (τ_{ZnPA}) of **ZnPA** was 1.92 ns in toluene/DMSO (99:1). For the 1:1 mixture, **ZnPA·FbPC** (0.1:0.1 mM), the decay of the excited state of **ZnPA** monitored at 590–610 nm, at which the Zn-porphyrin fluorescence dominates, was biexponential with components of 0.22 and 1.92 ns (Figure 4a). The longer lifetime is the same as that of **ZnPA** alone, and the fast component (τ) is attributed to the energy transfer within the complex. Indeed, the fraction of the faster component increased with increasing **ZnPA** concentration, as shown in Figure 5. The energy-

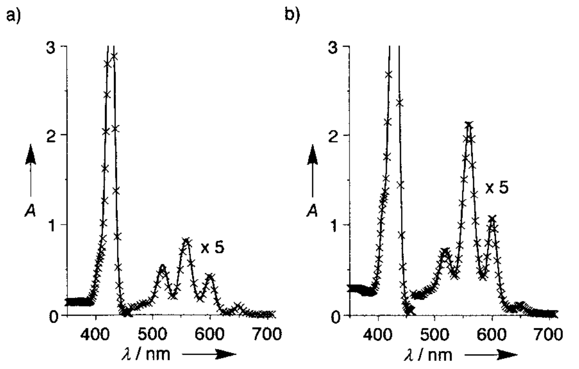


Figure 2. Comparison of observed (lines) and calculated (crosses) absorption spectra for the mixtures of Zn and free-base porphyrins in toluene/DMSO (99:1) at 25 °C. The calculated spectra are obtained simply by adding the component spectra: a) **ZnPA** and **FbPC** (5 μM each); b) **ZnPA** (16 μM) and **FbPC$_4$** (4 μM).

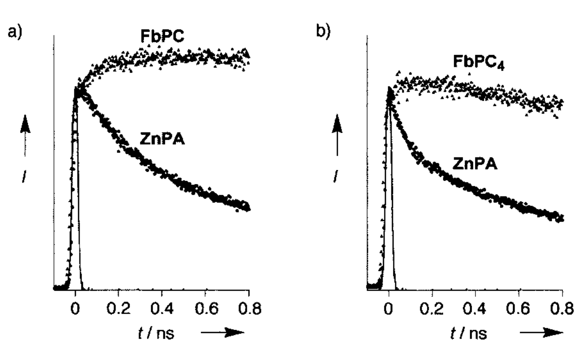


Figure 4. Time-resolved fluorescence traces in toluene/DMSO (99:1) (Ti:sapphire laser, λ_{ex} = 400 nm). Solid line: excitation laser; round dots: **ZnPA** fluorescence (582–617 nm); triangles: free-base porphyrin fluorescence (720–770 nm): a) **ZnPA** (0.1 mM) and **FbPC** (0.1 mM); b) **ZnPA** (0.4 mM) and **FbPC$_4$** (0.1 mM).

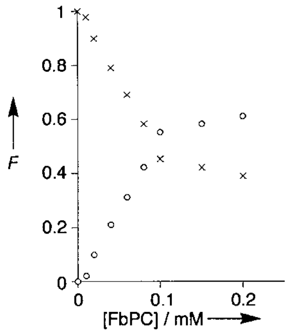


Figure 5. Fractions of the longer (crosses) and shorter (circles) components of **ZnPA** (0.1 mm) fluorescence as a function of added **FbPC** concentration in toluene/DMSO (99:1).

transfer rate (k_{ET}) was determined from this fast component from Equation (1) as 4.0×10^9 s^{-1}.

$$k_{ET} = \tau^{-1} - \tau_{ZnPA}^{-1} \quad (1)$$

These fluorescence lifetimes also give a quantum yield for the energy transfer (Φ_{ET}) as 0.89. The occurrence of energy transfer in this supramolecular dyad is clearly indicated by a delayed increase in fluorescence monitored at 720–770 nm, at which only the **FbPC** moiety emits, as shown in Figure 4a.

Similar analysis was also conducted for the 4:1 complex, **$(ZnPA)_4 \cdot FbPC_4$** (0.4:0.1 mm). The time trace of **ZnPA** fluorescence can be fitted with a superposition of two exponential functions with lifetimes of 0.08 ns (72%) and 1.2 ns (28%). The fast component may be attributed to energy-transfer processes within the supramolecular complex. With this value, the energy-transfer rate constant and the quantum yield were determined as 1.2×10^{10} s^{-1} and 0.96, respectively. However, the slower component is substantially slower than that for free **ZnPA**; this might reflect a complicated equilibrium in solution involving Fb, ZnFb, Zn_2Fb, Zn_3Fb, and Zn_4Fb complexes.[13] A delayed rise in fluorescence from **$FbPC_4$** is also apparent from Figure 4b, providing direct evidence for the energy transfer.

The mechanism of excited energy transfer: The through-space Förster energy-transfer rates ($k^{Förster}$)[14] for the dyad and pentad are estimated to be 5.1×10^8 and 6.8×10^8 s^{-1}, respectively, from Equation (2), whereby κ^2 is an orientation factor, Φ_{ZnPA} is the fluorescence quantum yield of **ZnPA** in the absence of the acceptor, J_F is the spectral overlap term (in M^{-1}cm^3), n is the solvent refractive index, τ_{ZnPA} is the fluorescence lifetime of **ZnPA** in the absence of the acceptor (in s), and r is the donor–acceptor center-to-center distance (in cm).[2c]

$$k^{Förster} = \frac{8.81 \times 10^{-25} \kappa^2 \Phi_{ZnPA} J_F}{n^4 \tau_{ZnPA} r^6} \quad (2)$$

The Förster calculation is based on values of $\kappa^2 = 1.01$, $\Phi_{ZnPA} = 0.021$ (measured with reference to $\Phi_{ZnTPP} = 0.030$[15]), $J_F = 3.4 \times 10^{-14}$ (**ZnPA·FbPC**) and 4.5×10^{-14} M^{-1}cm^3 (**$(ZnPA)_4 \cdot FbPC_4$**), $n = 1.51$ (toluene), $\tau_{ZnPA} = 1.92 \times 10^{-9}$ s, and $r = 2.23 \times 10^{-7}$ cm. The center-to-center separation, r, is based on data from the X-ray structures of ZnTPP,[16] free-base TPP,[17] and an amidinium–carboxylate complex.[18] The value of the orientation factor, κ^2, is for parallel Zn–porphyrin/free-base porphyrin arrays. This value is based on the Jablonski's symmetrical planar oscillator model for Zn–porphyrin,[19] which requires that the D_{4h} symmetry must not be severely perturbed by substitution. It is most likely that this requirement is fulfilled, as the absorption spectrum of **ZnPA** is virtually identical to that of the model porphyrin, **ZnP** (vide supra; Table 1). The value of κ^2 is also based on another assumption that the transition dipoles of **FbPC** is oriented along the imidazole NH–NH and N–N axes.[20] This assumption may also be justified, since the absorption spectrum of **FbPC** is virtually identical to that of **FbP**, showing again that perturbation is minimum. The value of $\kappa^2 = 1.01$ gives an upper limit, since the two porphyrin groups can rotate about the center-to-center axis in fluid solutions, giving a lower averaged κ^2 value.

The obtained Förster rates are certainly too small to account for the observed rates of energy transfer, even if structural uncertainties are taken into account. If the observed energy-transfer rate of 4.0×10^9 s^{-1} for the dyad were accounted for by the Förster mechanism, the center-to-center separation would have to be ~16 Å, which is improbably short; the center-to-center separation between two porphyrins connected with the diarylethyne bridge, $-Ph-C{\equiv}C-Ph-$, is already 20 Å.[15] Some sort of aggregation of the porphyrins, which might give a close contact between the Zn–porphyrin complex and free-base porphyrin is excluded from the fact that the absorption spectra of the mixture is identical with the sum of the component absorption spectra (vide supra).

These considerations infer that a through-bond mechanism[21] is in operation in the excited energy transfer in these Zn/Fb porphyrin assemblies through the amidinium–carboxylate salt bridges. Thus, it is suggested that hydrogen bonds, augmented by electrostatic attraction in this particular case, can mediate through-bond energy transfer. Although there have already been many examples of noncovalent energy transfer involving porphyrins,[2–9] as described in the introduction, there seems to be no report on through-bond energy transfer involving intermolecular bonds. In many reports in which energy-transfer rates are measured, the observed rates are consistent with the Förster mechanism.[4a,5f,5h,7,9c] Thus, it is unusual that a faster rate is observed than that estimated from the Förster mechanism; this may warrant further studies on this system to clarify the mechanism of the fast singlet–singlet intra-ensemble excited energy transfer.

Conclusion

We have constructed a supramolecular porphyrin dyad and pentad through amidinium–carboxylate salt bridges, in which energy transfer occurs efficiently. The observed rates of energy transfer are much faster than expected from the Förster mechanism. Hence, a through-bond mechanism is implicated involving the hydrogen-bond interface. It is worth noting that although through-bond *electron* transfer mediated by intermolecular interactions, such as coordination bonds and hydrogen bonds, has been widely recognized,[10,22,23] the involvement of a through-bond mechanism in *energy* transfer in well-defined supramolecular architectures has received little attention so far. It would be important to shed more light on intermolecular through-bond energy transfer to understand natural energy transfer and, ultimately, to create efficient artificial energy transfer systems.

Experimental Section

Physical measurements: ^{1}H NMR spectra were recorded on a JEOL JNM-GX400 spectrometer. Proton peak positions were referenced to tetramethylsilane. Laser desorption ionization time-of-flight MS (LDI-TOFMS) spectra for porphyrins were taken on an Applied Biosystems Voyager RP-PRO without using a matrix. Elemental analyses were performed by the Chemical Analysis Center of the College of Science and Technology, Nihon University. FAB-HRMS measurements were conducted by I. Yoshikawa of University of Tokyo.

Steady-state absorption and fluorescence measurements (except for the fluorescence quantum yield determination) were conducted in air-equilibrated toluene/DMSO (99:1), using Shimadzu RF-2400PC and UV-5300PC spectrometers, respectively. The samples were maintained at 25 °C in constant temperature units. It was confirmed that the spectroscopic behavior described herein is not appreciably affected by small variations of the DMSO content. Picosecond time-resolved fluorescence lifetimes were measured for samples purged with Ar by using an argon-ion pumped Ti:sapphire laser (Tsunami) ($\lambda_{ex}=400$ nm) and a streak scope (Hamamatsu Photonics).

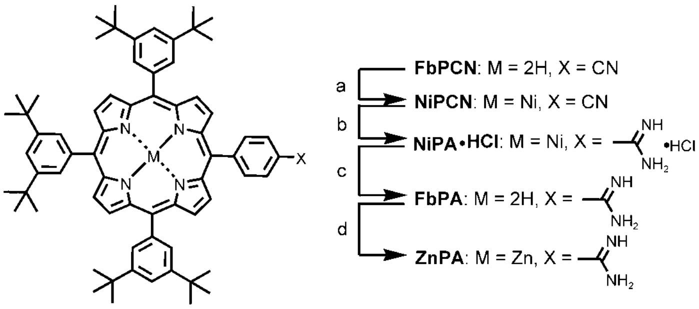
Materials: Toluene was purchased from Godo Solvents and distilled from Na. Spectroscopic grade DMSO was purchased from Kanto Kagaku. ZnTPP obtained from Aldrich was purified to remove chlorin.[24] **FbPC$_4$** was purchased from Aldrich and used as received. **FbPC** was prepared according to the literature.[25–27] **FbP** was obtained as a byproduct in the preparation of **FbPCN**,[28] to which Zn ion was incorporated to give **ZnP**.[29] **ZnPA** was prepared according to Scheme 1, as detailed in the following.

NiPCN: A solution of **FbPCN**[28] (200 mg, 0.21 mmol) in CHCl$_3$ (20 mL) and a solution of Ni(AcO)$_2$·4H$_2$O (315 mg, 1.26 mmol) in MeOH (10 mL) were mixed; and this solution was refluxed for 24 h in the dark. After the solvent was evaporated, the residue was dissolved in a small amount of CH$_2$Cl$_2$, was washed with aqueous NaHCO$_3$ (10 %), and was dried over Na$_2$SO$_4$. After the removal of Na$_2$SO$_4$ and then the solvent, the residue was purified by chromatography over silica gel with CH$_2$Cl$_2$/hexane (1:2) as eluent. The second fraction was collected to afford a purple solid (166 mg, 78 %). ^{1}H NMR (400 MHz, CDCl$_3$, TMS): $\delta=1.46$ (s, 54H; *t*BuH), 7.71–7.72 (m, 3H; *t*BuArH), 7.85–7.86 (m, 6H; *t*BuArH), 7.98 (d, $J=8$ Hz, 2H; NCArH), 8.15 (d, $J=8$ Hz, 2H; NCArH), 8.61 (d, $J=5$ Hz, 2H; porphyrin-β), 8.80–8.81 ppm (m, 6H; porphyrin-β); LDI-TOFMS (without matrix): *m/z*: 1031 [M^+]; elemental analysis calcd (%) for $C_{69}H_{75}N_5Ni{\cdot}0.5H_2O$ (1042.2): C 79.53, H 7.35, N 6.72; found: C 79.24, H 7.20, N 6.73.

NiPA·HCl: A solution of AlMe$_3$ in hexanes (2 M, 0.80 mL) was added to a suspension of NH$_4$Cl (86 mg, 1.6 mmol) in dry toluene (10 mL), and the mixture was stirred for 2 h at room temperature under Ar. A solution of **NiPCN** (166 mg, 0.16 mmol) in dry toluene (10 mL) was added, and the resulting solution stirred at 80 °C for 46 h in the dark. The reaction mixture was poured into a suspension of silica gel in CHCl$_3$ (10 g, 50 mL). The mixture was well stirred and filtered. The solvents were evaporated from the filtrate. The residue was purified by chromatography (silica, CHCl$_3$/MeOH, 2:1) and the second band gave a purple solid (160 mg, 91 %) as the amidinium chloride. ^{1}H NMR (400 MHz, CDCl$_3$, TMS): $\delta=$ 1.46 (s, 54H; *t*BuH), 7.71–7.72 (m, 3H; *t*BuArH), 7.85–7.86 (m, 6H; *t*BuArH), 8.17 (d, $J=8$ Hz, 2H; amidinium-ArH), 8.31 (d, $J=8$ Hz, 2H; amidinium-ArH), 8.61 (d, $J=5$ Hz, 2H; porphyrin-β), 8.81–8.82 ppm (m, 6H; porphyrin-β); LID-TOFMS (without matrix): *m/z*: 1050 [M+H]$^+$; FAB-HRMS: *m/z*: calcd for $C_{69}H_{79}N_6Ni$ ([M+H]$^+$): 1049.5719; found: 1049.5719; elemental analysis calcd (%) for $C_{69}H_{79}ClN_6Ni{\cdot}1.5H_2O$ (1113.7): C 74.42, H 7.42, N 7.55; found: C 74.51, H 7.26, N 7.53.

FbPA: Concentrated HCl (4 mL) and TFA (4 mL) were added to a solution of **NiPA**·HCl (306 mg, 0.28 mmol) in CH$_2$Cl$_2$ (150 mL), and the mixture was stirred at room temperature for 24 h in the dark. The reaction mixture was washed with aqueous NaOH (10 %) and dried over Na$_2$SO$_4$. Evaporation of the solvent gave a purple solid (258 mg, 99 %). ^{1}H NMR (CDCl$_3$, 400 MHz, TMS): $\delta=-2.71$ (s, 2H; pyrrole-NH), 1.51–1.52 (m, 54H; *t*BuH), 7.78–7.80 (m, 3H; *t*BuArH), 8.00 (d, $J=8$ Hz, 2H; amidine-ArH), 8.06–8.08 (m, 6H; *t*BuArH), 8.30 (d, $J=8$ Hz, 2H; amidine-ArH), 8.80 (d, $J=5$ Hz, 2H; porphyrin-β), 8.90 ppm (s, 6H; porphyrin-β); LDI-TOFMS (without matrix): *m/z*: 993 [M+H]$^+$.

ZnPA: A solution of Zn(AcO)$_2$·2H$_2$O (270 mg, 1.2 mmol) in MeOH (20 mL) was added to a solution of **FbPA** (270 mg, 0.29 mmol) in CH$_2$Cl$_2$ (60 mL). The mixture was stirred at room temperature for 24 h in the dark. The reaction mixture was washed with aqueous NaHCO$_3$ (10 %) and dried over Na$_2$SO$_4$. Evaporation of the solvent gave a residue, which was crystallized from MeOH to afford a purple solid (221 mg, 78 %). ^{1}H NMR: (CD$_3$OD, 400 MHz, TMS): $\delta=1.45$ (s, 54H; *t*BuH), 7.77–7.78 (m, 3H; *t*BuArH), 7.89–8.00 (m, 6H; *t*BuArH), 8.08 (d, $J=8$ Hz, 2H; amidine-ArH), 8.36 (d, $J=8$ Hz, 2H; amidine-ArH), 8.69 (d, $J=4$ Hz, 2H; porphyrin-β), 8.73–8.76 ppm (m, 6H; porphyrin-β); LDI-TOF (without matrix): *m/z*: 1057 ([M+2H]$^+$); elemental analysis calcd (%) for $C_{69}H_{78}N_6Zn{\cdot}0.5H_2O$ (1065.9): C 77.76, H 7.47, N 7.89; found: C 77.66, H 7.38, N 7.70.



Scheme 1. a) CHCl$_3$/MeOH, Ni(AcO)$_2$·4H$_2$O, reflux, 24 h (78 %); b) toluene, MeAl(Cl)NH$_2$, 80 °C, 46 h (91 %); c) CH$_2$Cl$_2$, HCl/TFA (1:1), room temperature, 24 h (99 %); d) CH$_2$Cl$_2$/MeOH, Zn(AcO)$_2$·2H$_2$O, room temperature, 24 h (78 %).

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