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Formation of a Supramolecular Porphyrin-Spacer-Acceptor Ternary Complex and Intracomplex Electron Transfer

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A new ditopic spacer, *N*-propylisonicotinamidine, has been developed to assemble a ternary supramolecular complex, zinc-tetraphenylporphyrin (ZnTPP)-spacer-acceptor (3,4-dinitrobenzoic acid), via an axial coordination of the spacer to ZnTPP and a salt bridge interaction between the spacer and acceptor. Formation of this ternary complex was probed by ^{1}H HMR and UV−vis spectroscopy. The ternary complex is formed with an overall association constant of 1.9×10^8 M^{-2} in dichloromethane. The fluorescence is nearly completely quenched by the electron acceptor in the ternary complex as confirmed by the steady-state fluorescence measurements. The triplet excited state of ZnTPP is also quenched by the electron acceptor in the ternary complex. The ternary complex is also formed in acetonitrile, where fluorescence quenching is observed with an intracomplex quenching rate constant of 1.9×10^9 s^{-1}. Photoinduced intracomplex electron transfer is invoked as a likely mechanism of the fluorescence quenching and triplet bleaching.

Introduction

The use of designed intermolecular interactions to construct supramolecular donor−acceptor assemblies, in which photoinduced electron transfer takes place, has received considerable attention, since this approach has significant advantages over the covalent counterparts for construction of complex multicomponent structures.[1−3] A number of supramolecular donor-acceptor dyads have so far been reported,[3,4] where a recognition site has been introduced in a donor or/and an acceptor in order to bind the two partners with suitable intermolecular binding modes, including inclusion-type interactions,[5,6] electrostatic association,[7] coordination interactions,[8−12] hydrogen bonding,[13−19] and rotaxane formation.[20] The use of an independent spacer molecule having two recognition sites rather than single recognition site, which can bind both donor and acceptor molecules to form a ternary complex, merits special attention, since each component in such a ternary complex can be readily replaced by a different molecule which is optimized independently, keeping the other part unaltered. In addition, such a ternary complex system can be expanded to more complex systems consisting of multicomponents of electron donors and acceptors. In biological systems, particularly in the photosynthetic reaction center, proteins can be regarded as spacers which are able to organize the donor and acceptor components via noncovalent interactions. A macrocyclic spacer molecule with convergent and divergent recognition sites has been developed, which can bind two cofactors, a quinone and a porphyrin via hydrogen bond and coordination interaction, respectively.[21] However, such a ternary complex can only be formed in a relatively nonpolar solvent, since the hydrogen bonding interaction is too weak to compete with the strong solvation with polar solvents which are normally employed for photoinduced electron transfer reactions. Thus, occurrence of photoinduced electron transfer in a supramolecular ternary complex consisting of an electron donor, a spacer and an electron acceptor has yet to be confirmed or to be fully examined.

Here we report a different strategy for the construction of a supramolecular donor-spacer-acceptor ternary complex involving zinc-tetraphenylporphyrin (ZnTPP or P) as a donor and 3,4-dinitrobenzoic acid (DNBA or A) as an acceptor using a new ditopic spacer, *N*-propyl-isonicotinamidine (**1**), as shown in Figure 1. This spacer has two recognition sites: one is the amidinium-carboxylate salt bridge between the spacer and DNBA and the other is an axial coordination interaction between the pyridine moiety of the spacer and ZnTPP which is known to accept only one axial ligand.[8−11,22] The complexation can be conveniently monitored since the coordination results in significant changes in the ^{1}H NMR and UV−vis spectra. The amidinium-carboxylate salt bridge is characterized by large association constants. This strong interaction has been extensively employed in the studies of proton-coupled electron-transfer processes.[18,19]

Results and Discussion

Formation of a Supramolecular Ternary Complex in Dichloromethane. Complex formation from various combinations of the three components, i.e., ZnTPP, **1**, and DNBA, and reference compounds was studied by ^{1}H NMR and UV−vis absorption spectroscopy in dichlromethane. ^{1}H NMR provides

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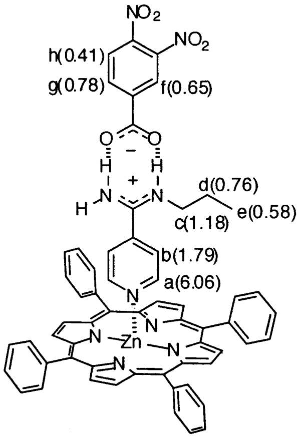

Figure 1. The supramolecular ternary complex self-organized from ZnTPP, **1**, and DNBA. The proton labels show correspondence with Figure 2. The numbers in parentheses indicate limiting values of upfield shifts in ^{1}H NMR induced by complexation with ZnTPP.

precise information concerning supramolecular structures involving porphyrins, since the large porphyrin aromatic ring-current makes the chemical shifts of the protons highly sensitive to the spatial relationship with the porphyrin π-electron system.[23]

The addition of **1** to a solution of DNBA (4 mM) in CD_2Cl_2 up to an equivalent amount caused uniform downfield shifts by 0.12 ppm for all aromatic protons in DNBA. The shifts were nearly proportional to the amount of added **1**. Further addition of **1** caused little shifts. These results indicate that the association constant ($K_{1\cdot A}$) between **1** and DNBA is very large beyond a range ($\gg \sim 10^3$ M^{-1}) which can determined by the NMR method. Such a strong binding is ascribed to carboxylate-amidinium interactions, which involve not only complementary double hydrogen bonds involving doubly favorable secondary interactions but also electrostatic interaction.[18,19,24]

Then a mixed solution of equimolar **1** (4 mM) and DNBA (4 mM) in CD_2Cl_2 was titrated with ZnTPP. Practically, all molecules are in the associated form, **1**·DNBA, at these concentrations. The chemical shifts of protons in **1**·DNBA are plotted as a function of ZnTPP concentration in Figure 2. All protons experience upfield shifts upon addition of ZnTPP. An especially large change is induced for pyridine-H2 in **1**. A nonlinear curve-fitting procedure[25] was applied to the plots in Figure 2 and the association constant between ZnTPP and **1**·DNBA ($K_{P\cdot(\mathbf{1}\cdot A)}$) was determined as 550 M^{-1}, which is smaller than the values of typical pyridine derivatives, which are around 10^4 M^{-1}.[9] The positive charge developed in the pyridine ring upon protonation of the amidine moiety seems to render the pyridine-*N* less basic. The good agreement between the observed and calculated data in Figure 2 indicates formation of a well-defined ternary complex under these experimental conditions (note that all the plots are simulated with the same association constant). Since the carboxylate-amidinium salt bridge is much stronger than the amidine-zinc coordination interaction, ZnTPP can interact only with the pyridine-*N* of the spacer.

The limiting values of the complexation-induced upfield shifts are shown in Figure 1. The magnitudes of the shifts of protons in **1** agree well with those of pyridine derivatives found in the literature.[23a] The magnitudes of the shifts for the other protons are also well correlated with the separation distances from ZnTPP. If an assumption is made that **1** and DNBA align upright in perpendicular to ZnTPP, a center-to-center distance between ZnTPP and DNBA in the ternary complex is estimated to be 15 Å, using known distances for intermolecular bonds of ZnTPP-pyridine[11b,26] and a carboxylate-amidinium salt bridge.[19b]

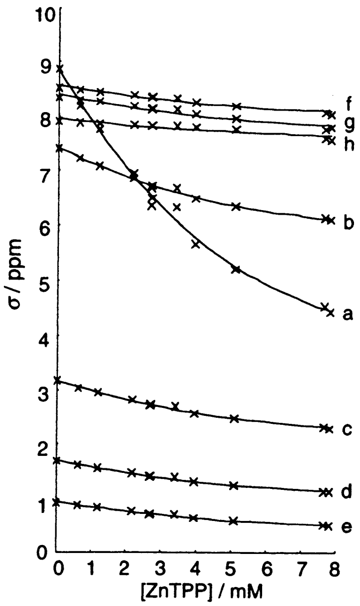

Figure 2. Changes in chemical shifts of protons in **1** (4 mM) and DNBA (4 mM) upon addition of ZnTPP in CD_2Cl_2. The labels indicate protons shown in Figure 1.

A red shift of the UV−vis spectrum is observed upon addition of axial ligands to ZnTPP, with which one can clearly differentiate axially ligated ZnTPP from free ZnTPP.[27] Upon addition of the spacer **1** to a dichloromethane solution of ZnTPP, the Q-bands in the UV−vis spectrum exhibited a red shift by ca. 15 nm. The association constant for the complex ZnTPP·**1** ($K_{P\cdot\mathbf{1}}$) was determined to be 8100 ± 120 M^{-1} by UV−vis titration in dichloromethane at 298 K. This value is more than 10 times larger than $K_{P\cdot(\mathbf{1}\cdot A)}$, indicating that the binding strength between ZnTPP and **1** is reduced by the association of DNBA to **1**. In contrast to **1**, no change in the absorption spectrum was observed when DNBA was added to a solution of ZnTPP in dichloromethane. This indicates that there is no direct association of ZnTPP and DNBA.

A mixed solution of ZnTPP (10 μM) and **1** (1.5 mM) was then titrated with DNBA as shown in Figure 3. The changes in the spectrum show that some dissociation of **1** from ZnTPP takes place upon addition of DNBA. The equilibria among the three components in solution are represented in eqs 1−3.

$$\mathrm{P} + \mathbf{1} \rightleftharpoons \mathrm{P}\cdot\mathbf{1} \qquad K_{\mathrm{P}\cdot\mathbf{1}} = [\mathrm{P}\cdot\mathbf{1}]/[\mathrm{P}][\mathbf{1}] \tag{1}$$

$$\mathbf{1} + \mathrm{A} \rightleftharpoons \mathbf{1}\cdot\mathrm{A} \qquad K_{\mathbf{1}\cdot\mathrm{A}} = [\mathbf{1}\cdot\mathrm{A}]/[\mathbf{1}][\mathrm{A}] \tag{2}$$

$$\mathrm{P} + \mathbf{1} + \mathrm{A} \rightleftharpoons \mathrm{P}\cdot\mathbf{1}\cdot\mathrm{A} \qquad K_{\mathrm{P}\cdot\mathbf{1}\cdot\mathrm{A}} = [\mathrm{P}\cdot\mathbf{1}\cdot\mathrm{A}]/[\mathrm{P}][\mathbf{1}][\mathrm{A}] \tag{3}$$

The values of $K_{\mathbf{1}\cdot A}$ and $K_{P\cdot\mathbf{1}\cdot A}$ were determined to be 2.2×10^5 M^{-1} and 1.9×10^8 M^{-2}, respectively, by applying a least-squares curve-fitting procedure as shown in the inset of Figure 3. The ratio of $K_{P\cdot\mathbf{1}\cdot A}$ to $K_{\mathbf{1}\cdot A}$, which should be equal to $K_{P\cdot(\mathbf{1}\cdot A)}$, becomes 860 M^{-1}, being consistent with the independently obtained value of 550 M^{-1} within the experimental uncertainty.

Fluorescence Quenching in the Supramolecular Ternary Complex in Dichloromethane. Having established the ternary complex formation as described above, steady-state fluorescence spectra of ZnTPP in the presence of various combinations of **1**, DNBA, and reference compounds were studied. In accord with a red shift in the UV−vis absorption spectrum, fluorescence emanating from coordinated ZnTPP is also red-shifted. Thus it is possible to distinguish fluorescence of coordinated ZnTPP

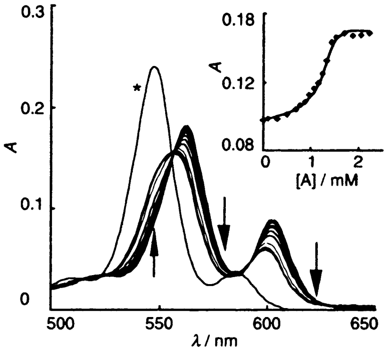

Figure 3. Absorption spectra of ZnTPP (10 μM) in dichloromethane at 298 K upon incremental addition of DNBA (0−2.2 mM) in the presence of **1** (1.5 mM). The arrows indicate the direction of change. The asterisked spectrum is of ZnTPP alone. The inset shows the absorbance change at 548 nm. The solid line is calculated based on the association constants described in the text.

from that of free ZnTPP. Fluorescence intensities in the following refer to integrated values obtained by integration through the whole spectrum.

The fluorescence of ZnTPP was perturbed by the axial coordination in the complex ZnTPP·**1**; the peaks were red-shifted by 15 nm and the intensity slightly reduced as compared with uncomplexed ZnTPP: $\phi_{P\cdot 1}/\phi_P = 0.86$. Upon addition of DNBA in the absence of **1**, the fluorescence of ZnTPP was gradually decreased due to diffusional quenching as shown in Figure 4a (diamond). No shift in the fluorescence maxima was observed, supporting that the quenching is not caused by static association but by diffusional encounter. The Stern−Volmer constant was determined to be 73 M^{-1}.

Then, a mixed solution of ZnTPP (10 μM) and **1** (1.5 mM) was titrated with DNBA (the same experiment as in Figure 3). Fluorescence spectra were recorded during this titration as shown in Figure 4b. In the presence of **1**, the initial fluorescence maxima were red-shifted as compared to that of uncomplexed ZnTPP (asterisked in Figure 4). As the concentration of DNBA was increased, the fluorescence intensity declined significantly and, at the same time, the spectral shape returned to those of uncomplexed ZnTPP. Since the relevant association constants are all known, the distribution of species in a given solution can be calculated. For example, ZnTPP, ZnTPP·**1**·DNBA, and ZnTPP·**1** exist in a ratio of 46:51:3 in a solution containing 1.5 mM of **1** and 2 mM of DNBA. The fluorescence intensity for this solution is less than 40% of that of ZnTPP alone. This suggests that the fluorescence from this solution is predominantly from isolated ZnTPP, which accounts for 46% of porphyrin species, leading to the conclusion that fluorescence from the ternary complex ZnTPP·**1**·DNBA is negligibly small, or nearly completely quenched. Supporting this contention, the shape of this residual fluorescence is exactly the same as that of free ZnTPP; compare the asterisked spectrum and the final spectrum in Figure 4b.

A couple of model experiments were performed to confirm the unique feature of the ternary complex, ZnTPP·**1**·DNBA. First, when *N*-propylbenzamidine (**2**), which has no binding sites with ZnTPP, was used instead of **1**, little quenching was observed upon addition of DNBA (Figure 4a, circle). Second, when PhCOOH was added in place of DNBA, the fluorescence intensity did decline but to a lesser extent than that effected by DNBA (Figure 4a, square). The fluorescence lifetime was measured in an attempt to determine the electron-transfer rate. However, only one long lifetime component (1.82 ns) with a much weaker intensity was observed even in the presence of **1** (4 mM) and DNBA (4 mM). We infer that the short component is too fast to be detected in our instrument (see Experimental Section) on the basis of the very efficient steady-state fluorescence quenching (<20 ps).[28]

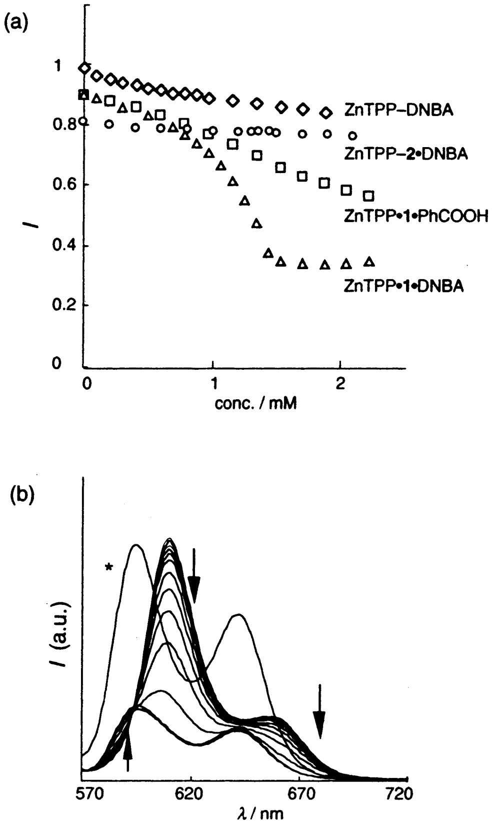

Figure 4. Titration experiments on a ZnTPP solution in dichloromethane (10 μM) at 298 K. (a) Integrated fluorescence intensities as a function of additive concentration (λ_{ex}, isosbestic 556 nm). The additives are DNBA alone (diamond), DNBA in the presence of **2** (1.5 mM) (circle), PhCOOH in the presence of **1** (1.5 mM) (square), and DNBA in the presence of **1** (1.5 mM) (triangle). (b) Fluorescence spectra upon addition of DNBA (0−2.2 mM) in the presence of **1** (1.5 mM). The arrows indicate the direction of change. The asterisked spectrum is of ZnTPP alone.

Electron transfer from the singlet excited-state of ZnTPP to DNBA is the most likely mechanism for the quenching of ZnTPP fluorescence, as is reported for other porphyrin-DNBA sets.[14,19] Relevant energetics have been examined by cyclic voltammetry measurements. The axial coordination of a base such as 4-ethylpyridine (EtPy) (3.0 mM) to ZnTPP (1.0 mM) in dichloromethane resulted in a negative shift of the one-electron oxidation potential of ZnTPP from E^0_{ox} vs SCE = 0.79 V to E^0_{ox} = 0.67 V. Similarly, the E^0_{ox} value of ZnTPP·**1**·DNBA in dichloromethane was determined as 0.63 V which is also negatively shifted due to the axial coordination of **1**·DNBA to ZnTPP. When DNBA was replaced by benzoic acid (PhCOOH) which can also form an amidinium-carboxylate salt bridge, the E^0_{ox} value of ZnTPP·**1**·PhCOOH was shifted slightly to 0.70 V in dichloromethane. On the other hand, the one-electron reduction potential of the DNBA moiety in ZnTPP·**1**·DNBA was shifted from E^0_{red} vs SCE = −0.83 V for DNBA alone to −0.77 V due to the formation of an amidinium-carboxylate salt bridge in ZnTPP·**1**·DNBA. Thus, the free energy changes of electron transfer (ΔG^0_{ET}) from ^{1}ZnTPP* and ^{3}ZnTPP* to DNBA in ZnTPP·**1**·DNBA are determined as −0.64 and −0.17 eV, respectively, in dichloromethane from the first oxidation potential of the porphyrin, the first reduction potential of the

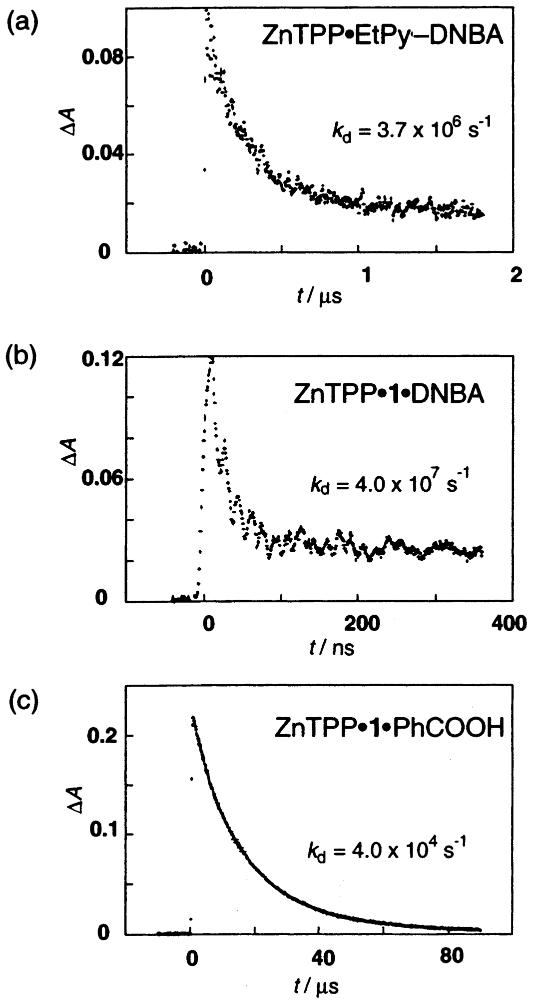

Figure 5. Decay dynamics of the triplet−triplet absorption due to ^{3}ZnTPP* at 470 nm after laser excitation at 433 nm in dichloromethane at 298 K. The first-order decay rate constants (k_d) are given in the figures. (a) ZnTPP (10 μM), EtPy (1.5 mM), and DNBA (2.0 mM). (b) ZnTPP (10 μM), **1**(1.5 mM), DNBA (2.0 mM). (c) ZnTPP (10 μM), **1**(1.5 mM), PhCOOH (2.0 mM).

acceptor, and the energy levels of the porphyrin excited states in the complex ($S_1 = 2.04$ eV and $T_1 = 1.57$ eV).[29−31] Similarly, the free energy changes of electron transfer without complex formation are calculated as −0.47 and 0.03 eV for the singlet and triplet processes, respectively, based on the excited-state energy levels of free ZnTPP ($S_1 = 2.09$ eV and $T_1 = 1.59$ eV). It should be noted here that the free energy changes become more negative by 0.17 and 0.20 eV for the singlet and triplet processes, respectively, thereby more favorable for electron transfer due to the formation of the supramolecular complex.

We then examined the dynamics of the triplet excited state formed by intersystem crossing from the singlet excited state. The triplet−triplet absorption of ZnTPP (10 μM) at 470 nm in dichloromethane decayed obeying first-order kinetics with the first-order decay rate constant (k_d) of 2.2 × 10^4 s^{-1} which corresponds to the triplet lifetime of 45 μs.[29] This means that the triplet−triplet annihilation is negligible under the present experimental conditions. The decay rate constant remained virtually unchanged (2.4 × 10^4 s^{-1}) in the presence of EtPy (1.5 mM). The addition of DNBA (2.0 mM) to the ZnTPP·EtPy system resulted in a significant increase in the decay rate constant (3.7 × 10^6 s^{-1}), which is ascribed to an intermolecular electron transfer from ^{3}ZnTPP*·EtPy to DNBA, as shown in Figure 5a. The decay rate constant increased with increasing

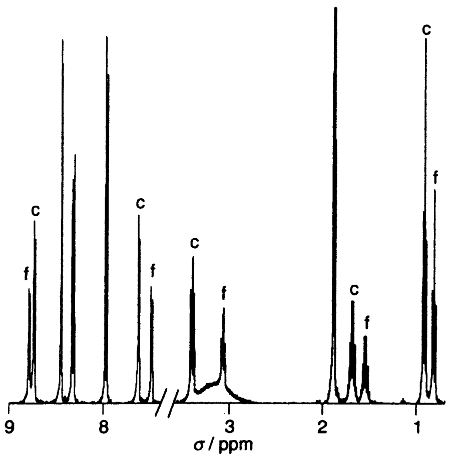

Figure 6. Proton NMR of a mixture of **1** (20 mM) and DNBA (25 mM) in CD$_3$CN. Protons in free **1** and complexed **1** are marked with "f" and "c", respectively.

DNBA concentration. When EtPy (1.5 mM) is replaced by **1** (1.5 mM) to form a supramolecular ternary complex, ZnTPP·**1**·DNBA, in the presence of DNBA (2.0 mM), the triplet decay rate constant becomes about 10 times larger (4.0 × 10^7 s^{-1}) than the corresponding value of the ZnTPP·EtPy-DNBA system (3.7 × 10^6 s^{-1}) as shown in Figure 5b. The residual absorbance in Figure 5b decays in a prolonged time with a rate constant which is the same as that in the absence of DNBA. When DNBA in ZnTPP·**1**·DNBA is replaced by PhCOOH (2.0 mM), which cannot act as an electron acceptor, the triplet decay rate constant (4.0 × 10^4 s^{-1}) is much smaller than the value of ZnTPP·**1**·DNBA (4.0 × 10^7 s^{-1}), as shown in Figure 5c. These results clearly indicate that an efficient intracomplex quenching of ^{3}ZnTPP* by DNBA occurs in the ternary complex. Given the very efficient fluorescence quenching in the ZnTPP·**1**·DNBA complex, the origin of the triplet porphyrin must be free ZnTPP, which accounts for 46% of all porphyrin species under the experimental conditions (vide supra). Therefore, complex formation after photoexcitation has to be assumed to explain the observed decaying behavior. Thus, the much enhanced triplet decay rate constant corresponds to the rate constant of complex formation of ^{3}ZnTPP* and **1**·DNBA.[32]

The nanosecond transient absorption spectra observed upon laser excitation of a dichloromethane solution of ZnTPP·**1**·DNBA at 433 nm exhibited only the triplet−triplet absorption due to ^{3}ZnTPP*. This indicates that back electron transfer from DNBA$^{\bullet-}$ to ZnTPP$^{\bullet+}$ in the ternary complex is too fast to detect the radical ion pair, ZnTPP$^{\bullet+}$·**1**·DNBA$^{\bullet-}$ in dichloromethane.

Formation of a Ternary Complex and Fluorescence Quenching in Acetonitrile. The strong binding by the amidinium-carboxylate salt bridge between the spacer and DNBA and by an axial coordination of the pyridine moiety of the spacer with ZnTPP in ZnTPP·**1**·DNBA enables us to examine formation of the supramolecular ternary complex in a more polar solvent than dichloromethane, such as acetonitrile.

The ^{1}H NMR for the mixture of **1** and DNBA in CD$_3$CN showed two distinct sets of resonances for **1**, corresponding to free **1** and the complex **1**·DNBA as shown in Figure 6. The integration of these resonances directly gave the ratio of these species and the association constant was obtained as 120 M^{-1} at 298 K. This value is significantly smaller than the association constant in dichloromethane due to the strong solvation to **1** and DNBA. Nonetheless, the salt bridge interaction between and DNBA is strong enough to form an appreciable amount of the complex in acetonitrile.

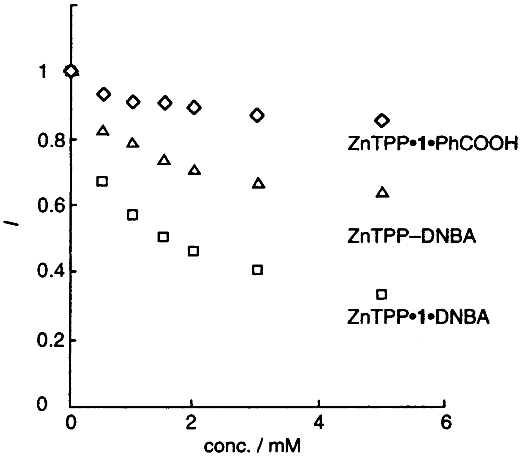

Figure 7. Integrated fluorescence intensities of ZnTPP in acetonitrile plotted as a function of additive concentration (λ_{ex}, isosbestic 559 nm) at 298 K. The additives are DNBA alone (triangle), an equimolar mixture of **1** and PhCOOH (diamond), and an equimolar mixture of **1** and DNBA (square).

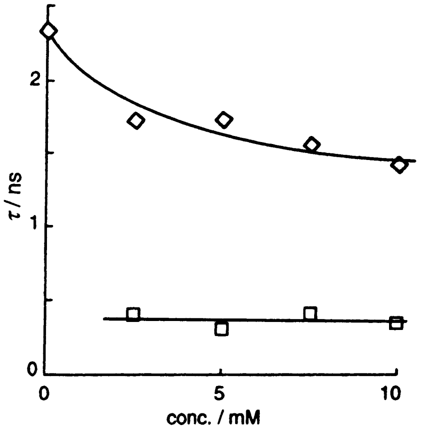

Figure 8. Plot of the short-component (square) and the long-component (diamond) of fluorescence lifetimes of ZnTPP (0.1 mM) against the concentration of equimolar **1** and DNBA in acetonitrile.

The evidence of axial coordination to the central zinc in the porphyrin macrocycle was obtained by UV−vis spectra. There are two major peaks in the Q-band of ZnTPP in acetonitrile at 555 and 595 nm. Upon incremental addition of an equimolar mixture of **1** and DNBA, the peaks showed a red shift with isosbestic points. The association constant is determined as 2400 M^{-1} at 298 K. This value is for the equilibrium between ZnTPP and the mixture of **1** and **1**·DNBA, since it is based solely on the change in the Q-band of ZnTPP and hence it does not reflect the equilibrium between **1** and DNBA.

The fluorescence intensity of ZnTPP decreased considerably upon addition of an equimolar mixture of **1** and DNBA, accompanied by the absorption changes, as shown in Figure 7 (square). The extent of decrease in the fluorescence intensity, when excited at an isosbestic point, upon addition of both **1** and DNBA exceeded that observed upon addition of only DNBA (triangle) or PhCOOH instead of DNBA (diamond). This indicates that an efficient fluorescence quenching occurs only in the ternary complex, ZnTPP·**1**·DNBA, in acetonitrile.

Decays comprising two-components were observed in picosecond fluorescence lifetime measurements for acetonitrile solutions of ZnTPP in the presence of **1** and DNBA. The lifetimes were plotted against the concentration of added equimolar mixture of **1** and DNBA (Figure 8). The lifetime of the long component decreased gradually as the additive concentration was increased, while that of the short component remained virtually unchanged at $\tau = 0.4$ ns. The fractional amplitude of the short component increased from 0 to over 30% as the concentration of **1** and DNBA was increased from 0 to 10 mM, being consistent with the amount of ZnTPP·**1**·DNBA calculated using the association constants as derived above. The long lifetime component is ascribed to the dynamic quenching process of free ZnTPP by DNBA, while the short component is due to the static intracomplex quenching. When an equimolar mixture of **1** and PhCOOH (5 mM each), instead of DNBA, was added, the fluorescence decayed monoexponentially with a lifetime of 1.59 ns (τ_0), showing that electron-withdrawing nitro groups are essential to the appearance of the short component. This strongly suggests the occurrence of photoinduced electron transfer from ^{1}ZnTPP* to DNBA in the supramolecular ternary complex. The rate of quenching k is determined using eq 4 as $k = 1.9 \times 10^9$ s^{-1}.

$$k = \tau^{-1} - \tau_0^{-1} \tag{4}$$

Our attempts to obtain unequivocal evidence for the ion pair formation via photoinduced electron transfer from picosecond transient absorption measurement have not been successful so far, probably due to fast back electron transfer.

Conclusion

It has been demonstrated that compound **1**, bearing pyridine and amidine (or amidinium) functions, acts as a spacer that can hold tightly a donor (ZnTPP) and an acceptor (DNBA) together via an axial coordination of the spacer to ZnTPP and a strong salt bridge interaction between the spacer and acceptor to form the ternary complex, ZnTPP·**1**·DNBA, in dichloromethane as well as in acetonitrile. Much more efficient intracomplex quenching of ^{1}ZnTPP* and ^{3}ZnTPP* by DNBA occurs in the supramolecular ternary complex than intermolecular processes between the uncomplexed molecules. The mechanism of the quenching is most likely electron transfer to DNBA in the ternary complex, based on the energetics of the relevant species and the comparison with the related porphyrin-DNBA systems.[14,19] The use of such multitopic receptor molecules in constructing multicomponent assemblies facilitating electron transfer among the components provides a powerful method to construct systems with increasing complexity involving many components, keeping their structures and functions under control. The ditopic spacer molecule **1** developed in this study is a start in this direction.

Experimental Section

Chemicals. *N*-Propylbenzamidinium chloride was prepared according to a literature procedure.[33,34] The hydrochloride salt was converted to the neutral species **2** with aqueous NaOH, which was then extracted with $CHCl_3$, and dried over $MgSO_4$. Evaporation of the solvent gave an oily residue, which was freeze-dried from benzene under vacuum to afford a white powder.

Synthesis of *N*-Propylisonicotinamidinium Chloride, 1·HCl. The compound **1** was synthesized following the procedure of Singh and Lesher.[35] After a solution of $NaOCH_3$ (56 mg, 1.04 mmol) and isonicotinonitrile (1.05 g, 10.1 mmol) in dry CH_3OH (10 mL) was stirred at room temperature for 1.5 h, $PrNH_3Cl$ (1.00 g, 10.4 mmol) was added to it. This solution was further stirred at room temperature for 26 h. The solution was evaporated and the obtained residue was crystallized from EtOH to afford white crystals (0.58 g, 28%), mp. 151−153 °C.

^{1}H NMR (400 MHz, CD_3OD): $\delta = 0.97$ (3H, t, $J = 7.3$ Hz), 1.70 (2H, sextet, $J = 7.3$ Hz), 3.36 (2H, t, $J = 7.3$ Hz), 7.64 (2H, d, $J = 3.0$ Hz), 8.73 (2H, d, $J = 3.0$ Hz). EI−HRMS, *m/z*: calcd for $C_9H_{12}N_3$ $[M-H_2Cl]^+$, 162.1031; found, 162.1029; calcd for $C_9H_{13}N_3$ $[M-HCl]^+$, 163.1109; found, 163.1116. Elemental analysis: calcd for $C_9H_{14}ClN_3$ (%), C, 54.14; H, 7.07; N, 21.04; found, C, 54.18; H, 6.94; N, 21.12.

Spectral and Electrochemical Measurements. All UV−Vis and fluorescence spectroscopic measurements were conducted in air-equilibrated dichloromethane or acetonitrile solutions. The cyclic voltammetry measurements were performed on a BAS 100 W electrochemical analyzer in a deoxygenated dichloromethane solution containing 0.10 M *n*-Bu_4NClO_4 as a supporting electrolyte at 298 K using Pt working and counter electrodes and Ag wire reference electrode. Ferrocene was used as an internal standard. For fluorescence spectroscopy (Shimadzu RF-5300PC spectrofluorophotometer), ZnTPP was excited at an isosbestic point. The fluorescence intensity I was obtained by integrating the whole spectrum against the wavenumber and reported with respect to that of ZnTPP so that the values are in proportion to fluorescence quantum yields. The picosecond time-resolved fluorescence lifetimes were measured at 600 nm using an argon-ion pumped Ti:sapphire laser (Tsunami) ($\lambda_{ex} = 410$ nm) and a streak scope (Hamamatsu Photonics).

The picosecond transient absorption spectra were observed by the pump and probe method using a femtosecond Ti:sapphire regenerative as laser light ($\lambda_{ex} = 388$ nm) and a dual MOS linear image sensor (Hamamatsu Photonics, C6140) as a detector. Nanosecond transient absorption measurements were carried out using a Nd:YAG laser (Continuum, SLII-10, 4−6 ns fwhm) at 355 nm with the power of 10 mJ as an excitation source. Photoinduced events were estimated by using a continuous Xe-lamp (150 W) and an InGaAs-PIN photodiode (Hamamatsu 2949) as a probe light and a detector, respectively. The output from the photodiodes and a photomultiplier tube was recorded with a digitizing oscilloscope (Tektronix, TDS3032, 300 MHz). The transient spectra were recorded using fresh solutions in each laser excitation. All experiments were performed at 298 K for air-free solutions purged with Ar.

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