

## A Giant Supramolecular Light-Harvesting Antenna–Acceptor Composite

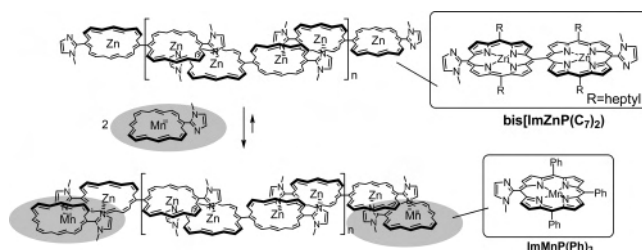
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A giant light-harvesting antenna–acceptor composite was constructed by heterodimerization of imidazolylmanganese(III)porphyrin to molecular terminals of the zinc porphyrin array composed of *meso–meso* linked bis(imidazolylzincporphyrin). Fluorescence quenching titration indicated that the terminal imidazolylmanganese(III)porphyrin quenched excited zinc porphyrin separated by a large number of intervening porphyrins and that the *meso–meso* linked bis(imidazolylzincporphyrin) array was an efficient light-harvesting antenna.

In natural photosynthetic systems, light energy absorbed by one of the chromophores in the antenna complexes is transferred through intra- and interantenna complexes until it reaches the reaction center with almost quantitative yields.<sup>1</sup> Photoinduced charge separation then transfers an electron to the acceptor to initiate oxidation/reduction reactions. Various designs of porphyrin-based artificial antenna,<sup>2</sup> such as star,<sup>3</sup> windmill,<sup>4</sup> macroring,<sup>5</sup> dendrimer,<sup>6</sup> and linear array,<sup>7</sup> have been reported. Introduction of acceptor molecule(s) to the antenna at appropriate position(s) is essential for the conversion of captured light energy. Covalently linked<sup>8</sup> and sup-



**Figure 1.** Formation of a light-harvesting antenna–acceptor composite by heterocomplementary coordination.

ramolecular<sup>9</sup> antenna–acceptor composites for mimicking the light-harvesting function have been reported. The synthetic burden of covalent approaches increases sharply with the number of antenna molecules. We describe here a supramolecular strategy for constructing a composite of a giant linear antenna and terminal acceptors. This system was used to ascertain the number of porphyrins capable of carrying excitation energy.

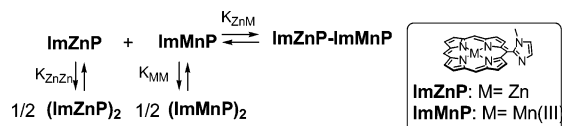
A *meso–meso*-linked bis(imidazolylzincporphyrin) **bis[ImZnP(C<sub>7</sub>)<sub>2</sub>]** array was used as a linear antenna motif. Since this linear antenna has two free zinc imidazolyl porphyrin terminals, further organization by other imidazolylmetalporphyrins is possible. By this method, manganese(III) porphyrin (**ImMnP**), an acceptor porphyrin, is incorporated into the large antenna–acceptor composite. The process only requires a simple mixing of two components (Figure 1).

This strategy relies on the choice of a good metalloporphyrin having the most appropriate association constant with the terminal free imidazolylzincporphyrins. To estimate this value, imidazolyltriphenylporphyrin was prepared, and Zn and Mn(III) were inserted to give **ImZnP(Ph)<sub>3</sub>** and **ImMnP(Ph)<sub>3</sub>**, respectively. Mixing these two porphyrins yields three different coordination dimers (Figure 2). Their relative amounts are functions of the order of three association

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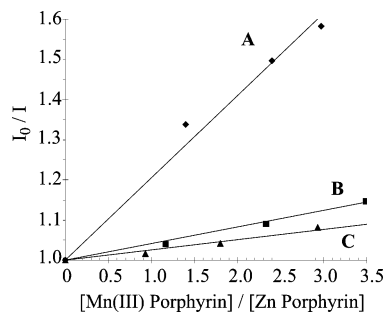


**Figure 2.** Equilibria between **ImZnP** and **ImMnP** to give homodimers  $(\text{ImZnP})_2$  and  $(\text{ImMnP})_2$ , and the heterodimer **ImZnP-ImMnP**.

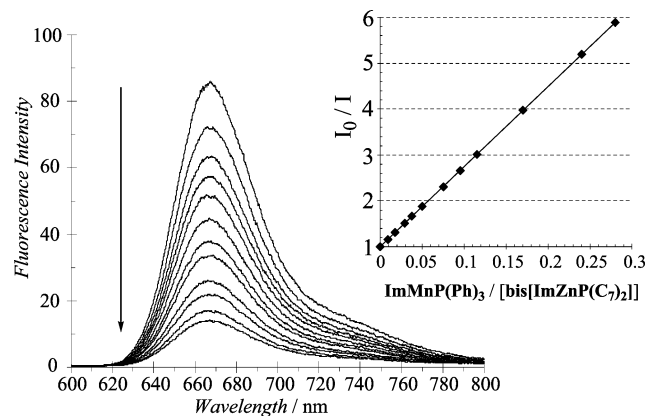
constants:  $K_{\text{ZnZn}}$  (formation of homodimer  $(\text{ImZnP})_2$ ),  $K_{\text{ZnM}}$  (formation of heterodimer **ImZnP-ImMnP**), and  $K_{\text{MM}}$  (formation of homodimer  $(\text{ImMnP})_2$ ). If  $K_{\text{ZnZn}}$  is comparable to or lower than  $K_{\text{ZnM}}$ , the long antenna array of **bis[ImZnP-(C<sub>7</sub>)<sub>2</sub>]** cannot survive upon the addition of **ImMnP**. When  $K_{\text{MM}}$  exceeds  $K_{\text{ZnM}}$ , the heterocomposite becomes only a minor product with predominant formation of the homodimer  $(\text{ImMnP})_2$ . The ideal state, in which a long antenna array of **bis[ImZnP-(C<sub>7</sub>)<sub>2</sub>]** is terminated with **ImMnP**, is obtained when  $K_{\text{ZnZn}} > K_{\text{ZnM}} > K_{\text{MM}}$  is satisfied. The association constant of tetraphenylmanganese(III)porphyrin (**MnTPP**) chloride with *N*-hexylimidazole is  $58 \text{ M}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ,<sup>10</sup> 2 orders of magnitude smaller than that of zinc tetraphenylporphyrin (**ZnTPP**) with *N*-methylimidazole ( $K = 10^4 \text{ M}^{-1}$ ).<sup>11</sup> Thus, the self-association constant of **ImMnP(Ph)<sub>3</sub>** is expected to be much smaller than that of **ImZnP**. In addition, the reduction potential of **MnTPP** ( $-0.28 \text{ V}$  vs. NaSCE in  $\text{CH}_2\text{Cl}_2$ )<sup>12</sup> is low enough to accept an electron from the excited zinc porphyrin. Thus, **ImMnP(Ph)<sub>3</sub>** can be regarded as a suitable candidate for the acceptor in our supramolecular system.

To obtain the association constant  $K_{\text{ZnZn}}$ , *N*-methylimidazole was titrated into imidazolylzincporphyrin dimer [**ImZnP(Ph)<sub>3</sub>]<sub>2</sub> ( $2.5 \times 10^{-6} \text{ M}$  in  $\text{CHCl}_3$ ) as a competing ligand. Before the addition, the UV-vis spectrum of [**ImZnP(Ph)<sub>3</sub>]<sub>2</sub> showed characteristic split Soret bands at 415 and 433 nm due to excitonic coupling between two porphyrins.<sup>13</sup> The addition of *N*-methylimidazole induced the convergence of the two bands into a single peak at 429 nm with isosbestic points at 421 and 436 nm resulting from the dissociation of the dimer. The association constant of the dimer,  $K_{\text{ZnZn}}$ , was calculated to be  $3.3 \times 10^{11} \text{ M}^{-1}$  by curve fitting analysis of the titration curve. The UV-vis spectrum of **ImMnP(Ph)<sub>3</sub>** was identical in a wide concentration range ( $10^{-5}$  to  $10^{-7} \text{ M}$ ) without any sign of dimer formation even at  $10^{-5} \text{ M}$ . Thus, the association constant  $K_{\text{MnMn}}$  of the homodimer was estimated to be smaller than  $10^3 \text{ M}^{-1}$ .****

The formation of heterodimer was evaluated by fluorescence titration. **ImMnP(Ph)<sub>3</sub>** was added to [**ImZnP(Ph)<sub>3</sub>]<sub>2</sub> ( $1 \mu\text{M}$  with respect to the monomeric unit in  $\text{CHCl}_3$ ), and the decrease of fluorescence intensity was monitored. As a control experiment, **ZnTPP** was used instead of **ImZnP(Ph)<sub>3</sub>**. Further, the combination of **ZnTPP** and **MnTPP** was tested to compare dynamic quenching. Stern-Volmer plots of three fluorescence titrations are shown in Figure 3. The slope was much steeper in the case of [**ImZnP(Ph)<sub>3</sub>]<sub>2</sub> and **ImMnP(Ph)<sub>3</sub>** (A) than those of **ZnTPP** and **ImMnP(Ph)<sub>3</sub>**,****



**Figure 3.** Stern-Volmer plots of Zn porphyrins ( $1 \mu\text{M}$  in  $\text{CHCl}_3$ ) quenching by Mn(III) porphyrin. (A) [**ImZnP(Ph)<sub>3</sub>]<sub>2</sub> + **ImMnP(Ph)<sub>3</sub>**, (B) **ZnTPP** + **ImMnP(Ph)<sub>3</sub>**, and (C) **ZnTPP** + **MnTPP**.**



**Figure 4.** Fluorescence spectral titration of **ImMnP(Ph)<sub>3</sub>** (0, 0.8, 1.6, 2.6, 3.4, 4.5, 6.8, 8.6, 10.3, 15.3, 21.6,  $25.2 \times 10^{-8} \text{ M}$ ) to **bis[ImZnP(C<sub>7</sub>)<sub>2</sub>]** ( $9 \times 10^{-7} \text{ M}$  as a bisporphyrin unit) in  $\text{CHCl}_3$  at  $25^\circ\text{C}$ . Stern-Volmer plot (inset).

(B), and **ZnTPP** and **MnTPP** (C). Since dynamic quenching should be dominant in the case of C, the difference between A and C corresponds to the formation of the heterodimer. Upon addition of  $3 \mu\text{M}$  Mn(III) porphyrin, fluorescence of the zinc porphyrin decreased to 62% for A and 93% for C. Thus, the contribution of static quenching at this point was estimated to be 67% ( $= 0.62/0.93$ ). Comparison of the slopes of A and B shows that complementary coordination is essential for strong binding. The association constant of heterodimer formation was estimated to be  $1.1 \times 10^8 \text{ M}^{-1}$  by the equation  $K_{\text{ZnMn}} = [\text{ImZnP(Ph)<sub>3</sub>-ImMnP(Ph)<sub>3</sub>] / \{[\text{ImZnP(Ph)<sub>3</sub>][\text{ImMnP(Ph)<sub>3</sub>]\}$ .<sup>14</sup> These considerations satisfied the desired relationship,  $K_{\text{ZnZn}} (10^{11} \text{ M}^{-1}) > K_{\text{ZnMn}} (10^8 \text{ M}^{-1}) > K_{\text{MnMn}} (10^3 \text{ M}^{-1})$ , and the system was applied to the polymeric case.

Formation of the antenna-acceptor composite was similarly evaluated by fluorescence titration. **ImMnP(Ph)<sub>3</sub>** was titrated to a solution of **bis[ImZnP(C<sub>7</sub>)<sub>2</sub>]** ( $0.9 \mu\text{M}$ ). For the control experiment, titration was performed using **MnTPP**. Fluorescence spectra of titration by **ImMnP(Ph)<sub>3</sub>** are shown in Figure 4. Highly effective quenching was observed in this case, whereas quenching was scarcely observed in the control experiment. Stern-Volmer plots of these fluorescence ti-

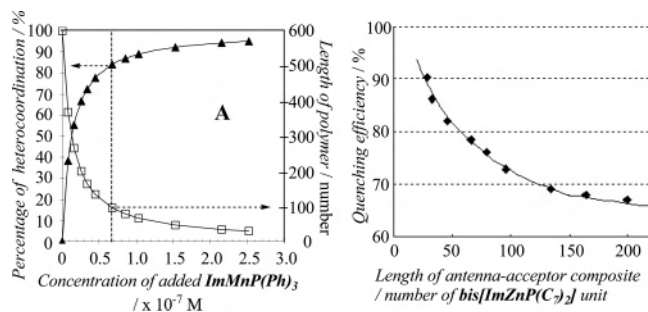
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(14) Since the heterodimer is considered to be nonfluorescent, the concentrations of heterodimer and free **ImMnP(Ph)<sub>3</sub>** at the point of  $3 \mu\text{M}$  Mn(III)porphyrin were calculated as  $3.3 \times 10^{-7} \text{ M}$  and  $2.67 \times 10^{-6} \text{ M}$ , respectively. The concentration of monomeric **ImZnP(Ph)<sub>3</sub>** was calculated as  $1.11 \times 10^{-9} \text{ M}$  on the basis of the association constant  $K_{\text{ZnZn}} (1 \times 10^{11} \text{ M}^{-1})$ .



**Figure 5.** (A) Simulation of heteroassociation of  $\text{bis}[\text{ImZnP}(\text{C}_7)_2]$  ( $0.9 \mu\text{M}$ ) and  $\text{ImMnP}(\text{Ph})_3$  (see text): open square, mean length of polymer as the number of  $\text{bis}[\text{ImZnP}(\text{C}_7)_2]$  unit (right scale); filled triangle, percentage of heterocoordination species (left scale). A broken line indicates the case with added  $6.8 \times 10^{-8} \text{ M}$   $\text{ImMnP}(\text{Ph})_3$ . (B) Quenching efficiency as a function of the length of antenna-acceptor composites obtained by the simulation in Figure 5A.

trations are shown in the inset of Figure 4. The slope of the Stern–Volmer plot in Figure 4 is 85-fold larger than that of A in Figure 3. In the former case, the addition of only 5% of  $\text{ImMnP}(\text{Ph})_3$  quenched approximately 50% of the fluorescence of  $\text{bis}[\text{ImZnP}(\text{C}_7)_2]$ , suggesting that the  $\text{ImMnP}(\text{Ph})_3$  quenched excited porphyrin species in the array, even at long separations.

The initial polymeric structure of  $\text{bis}[\text{ImZnP}(\text{C}_7)_2]$  itself has a molecular length distribution, which presumably changes upon the addition of titrants through the occurrence of competitive Mn–Zn heterocombination cleaving the Zn–Zn pairs to some extent. Thus, the actual species persisting through fluorescence titration should vary depending on the amount of  $\text{ImMnP}(\text{Ph})_3$  added. The average polymeric length and the percentage of the species of heterocomplementary coordination were obtained from the following equations:

$$[\text{Zn}]_t = 2[\text{Zn}_2] + [\text{Zn}] + [\text{ZnMn}]$$

$$[\text{Mn}]_t = [\text{ZnMn}] + [\text{Mn}]$$

$$K_{\text{ZnZn}} = [\text{Zn}_2]/[\text{Zn}]^2$$

$$K_{\text{ZnMn}} = [\text{ZnMn}]/\{[\text{Zn}][\text{Mn}]\}$$

Here,  $[\text{M}]_t$  is total concentration of imidazolylmetalloporphyrin ( $\text{M} = \text{Zn}$  or  $\text{Mn}(\text{III})$ ) unit;  $[\text{M}]$  is concentration of free imidazolylmetalloporphyrins ( $\text{M} = \text{Zn}$  or  $\text{Mn}(\text{III})$ ), where  $\text{Zn}_2$  = zinc homodimer,  $\text{Zn}$  = imidazolylzincporphyrin,  $\text{ZnMn}$  = heterodimer of imidazolylzinc- and manganeseporphyrin, and  $\text{Mn}$  = imidazolylmanganeseporphyrin.  $[\text{Zn}]_t = 1.8 \mu\text{M}$ ,  $K_{\text{ZnZn}} = 10^{11} \text{ M}^{-1}$ , and  $K_{\text{ZnMn}} = 10^8 \text{ M}^{-1}$  were used for this simulation. Concentrations of each species at any titration point of  $\text{ImMnP}(\text{Ph})_3$  were calculated from the above four equations. The results for  $[\text{Zn}_2]$ ,  $[\text{ZnMn}]$ , and  $[\text{Zn}]$  are illustrated in Figure 5A. Before addition of  $\text{ImMnP}(\text{Ph})_3$ , the ratio of free imidazolylzincporphyrin units to zinc homodimer units in  $\text{bis}[\text{ImZnP}(\text{C}_7)_2]$  was calculated to be 1:300 at  $0.9 \mu\text{M}$ . Thus, a 600-mer of the  $\text{bis}[\text{ImZnP}(\text{C}_7)_2]$  unit (FW 780 000 Da) may represent the distribution

maximum. This is compatible with the GPC curve obtained using JAIGEL 4HA column (polystyrene, exclusion limit 500 000). As the  $\text{ImMnP}(\text{Ph})_3$  concentration increases, the polymer length decreases and the percentage of heterocomplementary coordination in the total number of terminals increases sharply. These substantial changes continue until the concentration reaches  $5 \times 10^{-8} \text{ M}$  (5.5 mol %), where the variations become moderate on the basis of molecular length measurements. We see that, at a concentration of  $6.8 \times 10^{-8} \text{ M}$  (broken line in Figure 5A), the mean polymer is composed of 100  $\text{bis}[\text{ImZnP}(\text{C}_7)_2]$  units and 84% of the terminal parts are coordinated by  $\text{ImMnP}(\text{Ph})_3$ .<sup>15</sup>

The relationship between the quenching efficiency and mean length of the antenna-acceptor composites can be calculated (Figure 5B) on the basis of the simulation and the results of fluorescence titration. The quenching efficiency was obtained from the fluorescence titration data by subtracting the fluorescence due to the free antenna component estimated by the simulation. Figure 5B shows the profile of quenching probability for any excited porphyrin in the antenna consisting of less than 200 units. The profile suggests that the excitation energy generated by photoirradiation at any porphyrin in the antenna is transferred to the terminal manganese (III) porphyrin with a probability higher than 67%. The combination of direct *meso*–*meso* linking and slipped co-facial coordination of imidazolylzincporphyrin units provides an effective pathway for long-range energy transfer through the porphyrin array.

In conclusion, a giant light-harvesting antenna-acceptor composite was constructed by heterodimerization of imidazolylmanganese(III)porphyrin to molecular terminals of the zinc porphyrin array. The linear porphyrin array of *meso*–*meso* linked bis(imidazolylzincporphyrin)  $\text{bis}[\text{ImZnP}(\text{C}_7)_2]$  was demonstrated to be an efficient light-harvesting antenna. Since the three association constants satisfy the relationship  $K_{\text{ZnZn}} (10^{11} \text{ M}^{-1}) > K_{\text{ZnMn}} (10^8 \text{ M}^{-1}) > K_{\text{MnMn}} (10^3 \text{ M}^{-1})$ , instantaneous fabrication of the composite is possible by simply mixing two components.

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**Supporting Information Available:** Preparation of porphyrins, UV–vis and fluorescence spectra of Mn(III)porphyrin titration to  $\text{bis}[\text{ImZnP}(\text{C}_7)_2]$ , and gel permeation chromatographic analysis of  $\text{bis}[\text{ImZnP}(\text{C}_7)_2]$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(15) Molecular length estimated in the simulation strongly depends on the binding constants, especially on  $K_{\text{ZnZn}}$ . It is noted that the real  $K_{\text{ZnZn}}$  of  $\text{bis}[\text{ImZnP}(\text{C}_7)_2]$  is difficult to determine. We used a smaller  $K_{\text{ZnZn}}$  parameter,  $1 \times 10^{11} \text{ M}^{-1}$ , than  $3.3 \times 10^{11} \text{ M}^{-1}$  of  $\text{ImZnP}(\text{Ph})_3$  to avoid overestimation.