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Energy Transfer Followed by Electron Transfer in a Porphyrin Macrocycle and Central Acceptor Ligand: A Model for a Photosynthetic Composite of the Light-Harvesting Complex and Reaction Center

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Abstract: A system that models a photosynthetic composite of the light-harvesting complex and reaction center is reported in which light energy collected by cyclic antenna porphyrins is transferred to a central energy-acceptor porphyrin, followed by photoinduced electron transfer to a fullerene positioned above the ring plane. Pyridyl tripodal ligands appended with bis(phenylethynyl)porphyrinatozinc(II) (ZnP–Tripod) and additional fulleropyrrolidine moieties (C_{60}–ZnP–Tripod) were synthesized as the reaction center units. The tripodal ligand was strongly accommodated by the light-harvesting porphyrin macrocycle N-(**1**–Zn)$_3$ (**1**–Zn = trisporphyrinatozinc(II)) by using three-point coordination of pyridyl to uncoordinated porphyrinatozinc sites to afford a stable 1:1 composite. The binding constants for ZnP–Tripod and C_{60}–ZnP–Tripod in benzonitrile were estimated from steady-state fluorescence titrations to be 1.4×10^7 and $1.6\times10^7\,\text{M}^{-1}$, respectively. The steady-state fluorescence titration, fluorescence lifetime, and transient absorption studies revealed that in both composites the excitation energy collected by the nine porphyrins of N-(**1**–Zn)$_3$ was efficiently transferred to a ZnP moiety by means of a through-space mechanism with a quantum yield of approximately 90%. Furthermore, in the composite with C_{60}–ZnP–Tripod, the converged energy at the ZnP moiety induced electron transfer to the C_{60} moiety, which afforded the stable charge-separated state ($\Phi_{CS} > 90\%$).

Keywords: fullerenes • photochemistry • photosynthesis • porphyrinoids • self-assembly

Introduction

In photosynthetic organisms, light-harvesting antenna complexes (LH) composed of large numbers of chlorophyll and carotenoid molecules are vital for the effective capture of dilute sunlight energy and delivery of the energy to the reaction center (RC) with minimal loss. LH systems (LH1[1] and LH2[2]) in purple bacteria have been characterized at atomic resolution and are known to have highly ordered cyclic architectures of bacterial chlorophylls. Their cyclic structures are advantageous for forming densely packed, two-dimensional organizations in photosynthetic membranes and are effective in transferring energy from one LH to a neighboring LH in any direction.[3] The photoexcited energy collected by LH2 is transferred to LH1 and finally to the special pair in the RC. Then, electron transfer occurs to produce a stable transmembrane charge-separated state,[4] which leads to adenosine triphosphate (ATP) synthesis by means of the transmembrane protonmotive force.[5]

Mimics of efficient energy-converting systems in photosynthesis are important not only for understanding the natu-

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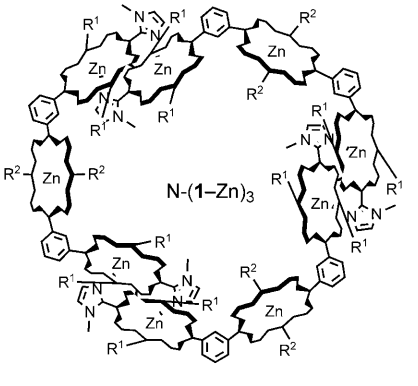
ral systems but also for technological advances in solar energy conversion, which show great potential for the resolution of global energy and environmental problems. A number of researchers have attempted to construct various synthetic models of LH,[6–8] RC,[9,10] and their combined architectures[11] by using porphyrins. Although covalently linked cyclic porphyrin arrays accommodating an energy acceptor by multipoint coordination bonds have been constructed,[11a,c,e] a synthetic model performing energy transfer from the cyclic porphyrin arrays to the reaction center followed by charge separation, to the best of our knowledge, has not been reported so far.

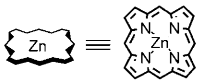
We previously reported a supramolecular system of porphyrin macrocycles N-(**1**–Zn)$_3$ with tetra- and tripodal ligands.[12–14] In this system, the ligand was accommodated in the ring cavity by three-point coordination with binding constants greater than $10^7\,\text{M}^{-1}$. A large binding constant is crucial for supramolecular organization from approximately 1:1 mixtures of composites, even under dilute conditions. It is advantageous to use a tripodal ligand, which is obtained by substituting one of the tetrapodal arms with an appropriate acceptor. In the current report, we describe the synthesis of two new tripyridyl ligands with and without C_{60}: ZnP–Tripod and C_{60}–ZnP–Tripod, respectively. In the former ligand, the bis(phenylethynyl)porphyrinatozinc(II) moiety (ZnP) is connected as an energy acceptor, and in the latter ligand a fulleropyrrolidine moiety (C_{60}) connected as an electron acceptor is additionally linked to ZnP. The latter composite, formed by three-point coordination, can act as an antenna-ring reaction center, in which excited energy is transferred from cyclic antenna porphyrins to energy-acceptor porphyrins, followed by photoinduced electron transfer to produce charge-separated species. Composite formation and photophysical properties were examined by using steady-state and time-resolved fluorescence spectroscopy and nanosecond transient absorption spectra, which demonstrated that excited-energy transfer from N-(**1**–Zn)$_3$ to the ZnP moiety and subsequent electron transfer to the C_{60} moiety occurs.

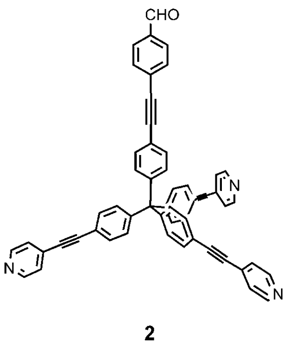
Results and Discussion

Design: 5,15-Bis(phenylethynyl)-10,20-diphenylporphyrinatozinc (ZnP) was selected as an energy acceptor to be introduced to a new tripodal ligand. Comparison of the fluorescence spectrum of N-(**1**–Zn)$_3$ with the absorption spectrum of ZnP ensured sufficient overlap to allow Förster-type energy transfer.[15] Thus, tripodal ligands ZnP–Tripod and C_{60}–ZnP–Tripod were designed, in which the ZnP part was connected to the central quaternary carbon via an ethynylene linker. The half-wave potentials of one-electron oxidation of ZnP and one-electron reduction of pyrrolidino–C_{60} were 0.29 and −1.04 V (versus Fc/Fc$^+$) in benzonitrile, respectively.[15,16] Thus, the energy level of the ion-pair state $\text{ZnP}^{\bullet+}$–$C_{60}^{\bullet-}$ was estimated to be 1.33 eV above the ground



R^1 = -$(CH_2)_3OCH_2CH{=}CH_2$
R^2 = -$(CH_2)_2CO_2Me$





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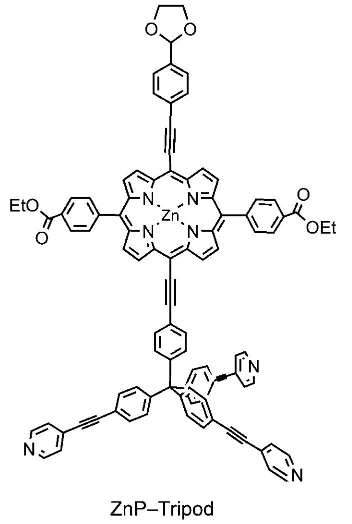
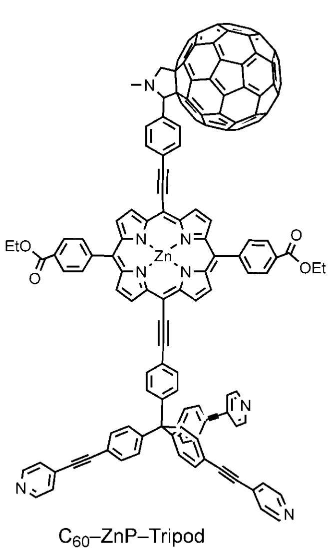


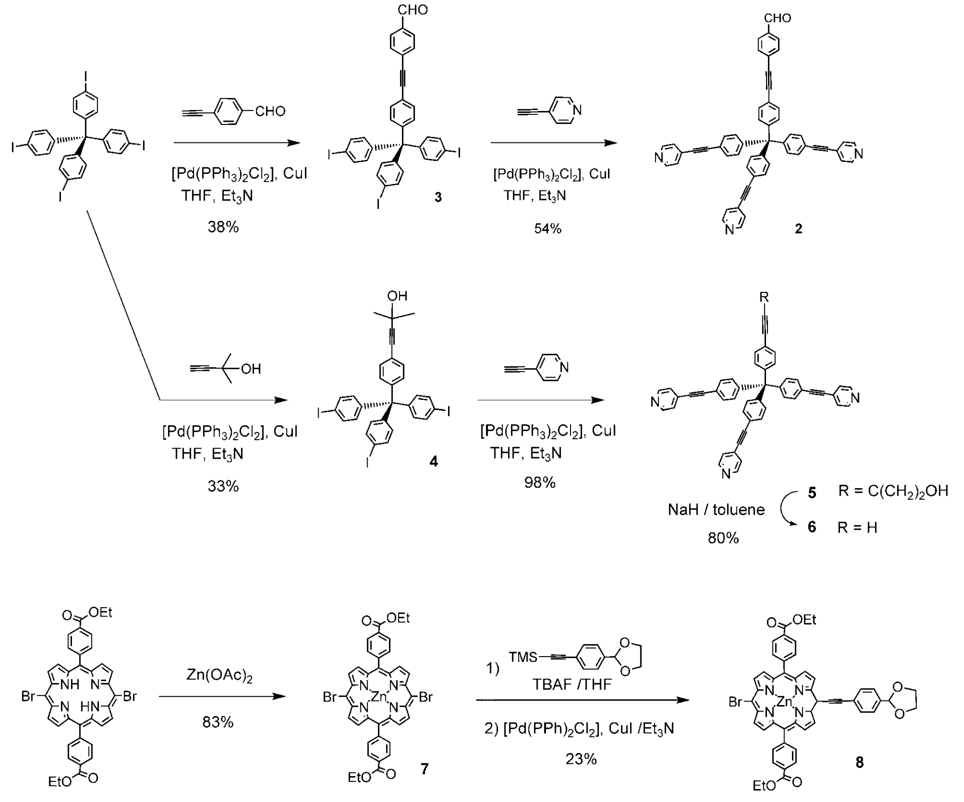
ZnP–Tripod



C_{60}–ZnP–Tripod

state. The energy of the 0–0 transition between the S_1 and S_0 state of the ZnP moiety was estimated to be approximately 1.87 eV. Therefore, the photoinduced electron transfer from C_{60}–^{1}ZnP* to yield ZnP$^{\bullet+}$–$C_{60}^{\bullet-}$ should have sufficient driving force.

On the basis of this estimation, we designed the second tripodal ligand C_{60}–ZnP–Tripod, in which the fulleropyrrolidine part was connected to the other end of ZnP in ZnP–Tripod. To estimate the distances among ZnP, C_{60}, and the cyclic porphyrin array, the molecular structure of the C_{60}–ZnP–Tripod/N-(**1**–Zn)$_3$ composite was constructed, and the model was optimized by using molecular mechanics calculations[17] (Figure 1). In this model, the *meso*-to-*meso* ethyne-linked axis of the ZnP moiety constitutes the center axis of the barrel structure of the cyclic porphyrin array. The average center-to-center distance from the nine porphyrins of N-(**1**–Zn)$_3$ to the ZnP moiety was estimated to be 20.2 Å.[18] In C_{60}–ZnP–Tripod, the distance from the center of the ZnP moiety to the edge of the fullerene was estimated to be 12.5 Å.



Scheme 1. Synthetic route to **2**, **6**, and **8** (TBAF = tetrabutylammonium fluoride).

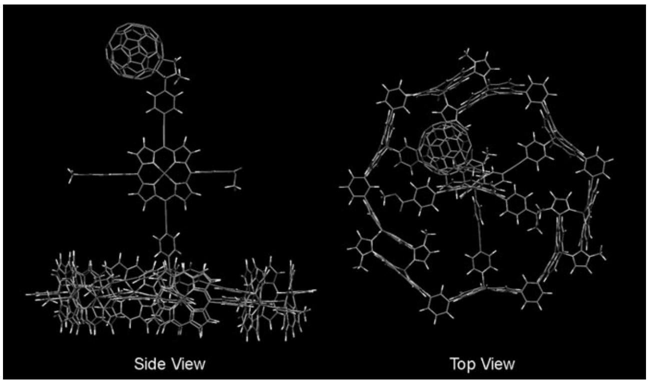
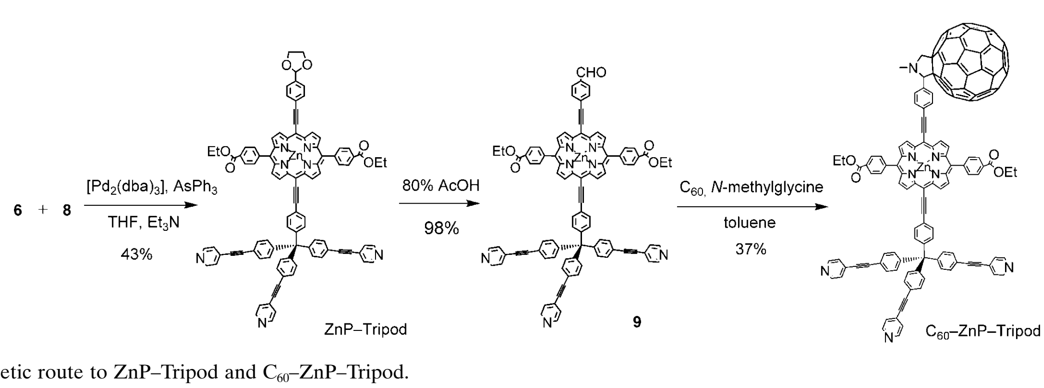


Figure 1. Molecular models of the C_{60}–ZnP–Tripod/N-(**1**–Zn)$_3$ composite optimized by molecular mechanics calculations.[17]

Synthesis: ZnP–Tripod, C_{60}–ZnP–Tripod, and the reference tripodal ligand **2** were synthesized as shown in Schemes 1 and 2. Tetrakis(4-iodophenyl)methane and 5,15-dibromo-10,20-bis(4-ethoxycarbonylphenyl)porphyrin were prepared according to a published procedure.[19,20] A subsequent Sonogashira coupling reaction[21] of tetrakis(4-iodophenyl)methane with 2-methyl-3-butyn-2-ol (1 equiv) and 4-ethynylpyr-



Scheme 2. Synthetic route to ZnP–Tripod and C_{60}–ZnP–Tripod.

idine[22] (5 equiv) afforded **5** in a yield of 32% (two steps). Similarly, a combination of 4-ethynylbenzaldehyde[23] and 4-ethynylpyridine gave **2** in a yield of 21% (two steps). 5,15-Dibromo-10,20-bis(4-ethoxycarbonylphenyl)porphyrin, which was prepared by bromination of 10,20-bis(4-ethoxycarbonylphenyl)porphyrin with *N*-bromosuccinimide (NBS),[20] was treated with zinc acetate to give **7**. Crude **7** included trace amounts of other dibromo isomers that would impair the purification of **8** in the next step. Therefore, recrystallization from $CHCl_3$/MeOH was repeated to obtain pure **7**. 4-Ethynylphenyl-1,3-dioxolane (1.3 equiv) was treated with **7** in the presence of $[PdCl_2(PPh_3)_2]$ and CuI to afford the desired monosubstituted compound **8** (23%), along with unreacted **7** (>23%) and a disubstituted byproduct (21%), which were separated by means of flash silica gel column chromatography.

ZnP–Tripod (Scheme 2) was synthesized by the coupling reaction of **6** and **8** in the presence of the $[Pd_2(dba)_3]$–$AsPh_3$ (dba = dibenzylideneacetone) catalyst in a yield of 43%. Furthermore, C_{60}–ZnP–Tripod was obtained by 1,3-dipolar cycloaddition of deprotected ZnP–Tripod **9**, fullerene C_{60}, and *N*-methylglycine in a yield of 37%. ZnP–Tripod and C_{60}–ZnP–Tripod were characterized by using ^{1}H NMR spectroscopy, MALDI-TOF MS, and UV/Vis and fluorescence spectra (Figure 2). ^{1}H NMR spectra of ZnP–Tripod in $CDCl_3$ ($\approx$10 mM) indicated that a pyridyl part in ZnP–Tripod was coordinated intermolecularly to the ZnP part.[24] Because binding constants of pyridine and zinc–porphyrin are of the order of $10^3\,\text{M}^{-1}$ in nonpolar solvents,[25] the above-mentioned intermolecular coordination is negligible at micromolar concentrations, especially in polar solvents such as benzonitrile.

UV/Vis absorption and fluorescence spectra of ZnP–Tripod and C_{60}–ZnP–Tripod: The UV/Vis absorption spectra of ZnP–Tripod and C_{60}–ZnP–Tripod in benzonitrile are shown in Figure 2A. The spectrum of ZnP–Tripod shows that the Soret band has a maximum at 458.0 nm, and the Q band appears at 663.0 nm. These absorption peaks in benzonitrile were redshifted relative to those measured in $CHCl_3$ (454 and 657 nm, respectively) and were similar to those measured in pyridine (456.5 and 663.0 nm, respectively), which suggests that benzonitrile coordinates to the ZnP moiety.[13a] The spectrum of C_{60}–ZnP–Tripod shows the Soret band has a maximum at 459.0 nm, and the Q band appears at 665.5 nm in benzonitrile. The absorption band at <350 nm is assignable to the fullerene moiety, whereas other characteristic bands of the fullerene moiety at approximately 430 and 700 nm might be hidden by the huge absorptions of ZnP. The spectrum of C_{60}–ZnP–Tripod showed a decrease in the peak absorption at the Soret band and was redshifted relative to that of ZnP–Tripod, which indicates a weak electronic interaction between ZnP and the fullerene moiety.

The steady-state fluorescence spectra of ZnP–Tripod and C_{60}–ZnP–Tripod in benzonitrile measured with excitation at 600 nm are shown in Figure 2B. Although ZnP–Tripod showed intense fluorescence peaks at 667.2 and 728.0 nm (Φ_f = 15%), the fluorescence of C_{60}–ZnP–Tripod was quenched by 99.3%. The significant fluorescence quenching in C_{60}–ZnP–Tripod indicates that photoinduced electron transfer from the excited singlet state of ZnP to C_{60} moieties occurs efficiently.

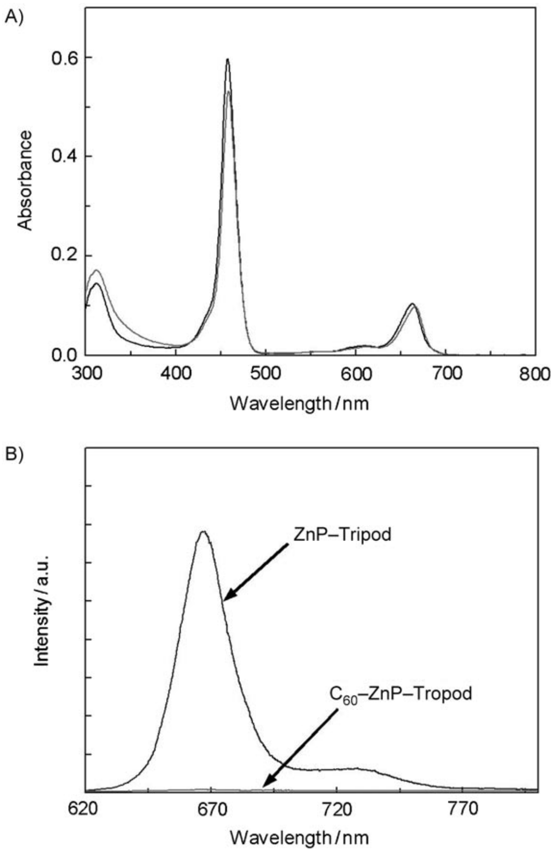


Figure 2. A) UV/Vis absorption and B) fluorescence spectra of ZnP–Tripod (——) and C_{60}–ZnP–Tripod (——) in benzonitrile. The concentrations were kept constant at 1.5 μM (λ_{ex} = 600 nm).

Photodynamic properties of ZnP–Tripod and C_{60}–ZnP–Tripod: The fluorescence lifetimes of ZnP–Tripod and C_{60}–ZnP–Tripod were measured in benzonitrile (Figure S6 in the Supporting Information). The decay profile of ZnP–Tripod at 670 nm was fitted to a monoexponential curve with a lifetime of 1600 ps, whereas that of C_{60}–ZnP–Tripod was fitted to a biexponential curve with time constants of 110 (93%) and 1780 ps (7%). Because the longer lifetime is close to the lifetime of ZnP (1600 ps), this minor component probably arises from a small amount of an impurity that lacks a C_{60} moiety. Therefore, the lifetime of the major component can be attributed to electron transfer from ^{1}ZnP* to C_{60} with a rate constant and quantum yield of $8.5\times10^9\,\text{s}^{-1}$ and 94%, respectively.[26] To obtain direct evidence of the electron transfer, nanosecond transient absorption spectra were measured for C_{60}–ZnP–Tripod in benzonitrile with excitation at 470 nm (Figure S7 in the Supporting Information). In the transient spectrum at 0.1 μs after laser irradiation at 470 nm, a characteristic peak assignable to the anion radical of fulleropyrrolidine[9] was observed at 1020 nm, along with a broad band at approximately 400–900 nm that corresponds to the cation radical of ZnP (Figure S7 in the Supporting Information). From the decay profile at 1020 nm, the rate constant of charge recombination (k_{CR}) was determined to be $3.4\times10^6\,s^{-1}$.[27]

As a control experiment, nanosecond transient absorption spectra of ZnP–Tripod were also measured. A long-lifetime species was observed as two peaks at 500 and 780 nm (Figure S8 in the Supporting Information). Because the decay profile at 500 nm was reduced dramatically by oxygen admission, the species was assigned as a triplet state of ZnP (^{3}ZnP*).

Incorporation of tripodal ligands into macrocycles: Before titrating N-(**1**–Zn)$_3$ with ZnP–Tripod and C_{60}–ZnP–Tripod, we observed the changes in UV/Vis absorption and fluorescence spectra of N-(**1**–Zn)$_3$ upon the addition of the reference **2** in benzonitrile. During the titration with **2**, a small decrease of the Soret band was observed in the UV/Vis spectrum, without a noticeable change in the Q band (Figure S9 in the Supporting Information).[28] The titration plots of the Soret band were well-fitted to the theoretical curves based on a 1:1 complex,[29] and the binding constant was estimated to be $1.1\times10^7\,\text{M}^{-1}$. The fluorescence spectra of N-(**1**–Zn)$_3$ did not change during the titration with **2**, which suggests that the tripyridyl ligand moiety does not perturb the excited energy of N-(**1**–Zn)$_3$.

In contrast to the titration with **2**, titration of N-(**1**–Zn)$_3$ with ZnP–Tripod caused dramatic changes in the fluorescence spectra (Figure 3A). When the N-(**1**–Zn)$_3$ part was excited selectively at 567 nm,[30] the fluorescence from N-(**1**–Zn)$_3$ at 623 nm decreased by the addition of ZnP–Tripod. In contrast, the fluorescence from ZnP at 667 nm increased, which indicates that excited energy transfer occurred from N-(**1**–Zn)$_3$ to the ZnP part. The titration plots of the intensity at 623 nm (Figure 3A, inset) were well-fitted to the theoretical curves based on a 1:1 complex.[31] From the curve-fitting analysis, the binding constant of ZnP–Tripod with N-(**1**–Zn)$_3$ was determined to be $1.4\times10^7\,\text{M}^{-1}$.[32] The energy-transfer efficiency from N-(**1**–Zn)$_3$ to the ZnP part in the 1:1 composite was determined to be 80 % from the titration experiment. This observation is supported by the spectral overlap integral (J) as defined by the Förster theory, which was estimated from the fluorescence of N-(**1**–Zn)$_3$ and the absorption spectra of ZnP–Tripod to be $3.4\times10^{-13}\,\text{cm}^6\,\text{mmol}^{-1}$. This J value is approximately ten times larger than the value $2.6\times10^{-14}\,\text{cm}^6\,\text{mmol}^{-1}$ that was estimated from the spectra of N-(**1**–Zn)$_3$ and 5,10,15,20-tetraphenylporphyrinatozinc in benzonitrile.[33]

Fluorescence spectra for the titration of N-(**1**–Zn)$_3$ with C_{60}-ZnP–Tripod are shown in Figure 3B. Similar to the case of ZnP–Tripod, the addition of C_{60}–ZnP–Tripod induced a decrease in the fluorescence from N-(**1**–Zn)$_3$, but no emission was observed from the ZnP part. From the curve-fitting analysis (Figure 3B, inset), the binding constant of the 1:1 composite and the fluorescence quenching efficiency were determined to be $1.6\times10^7\,\text{M}^{-1}$ and 83 %, respectively.[32] Because the excited-energy-transfer efficiency in the ZnP–Tripod/N-(**1**–Zn)$_3$ composite (80 %) is close to the fluorescence quenching efficiency (83 %), a direct pathway to quench the N-(**1**–Zn)$_3$ moiety by the C_{60} part seems unlikely. Thus, energy transfer from the excited N-(**1**–Zn)$_3$ moiety to ZnP followed by electron transfer from the excited ZnP to the C_{60} part must be a dominant pathway in this system.

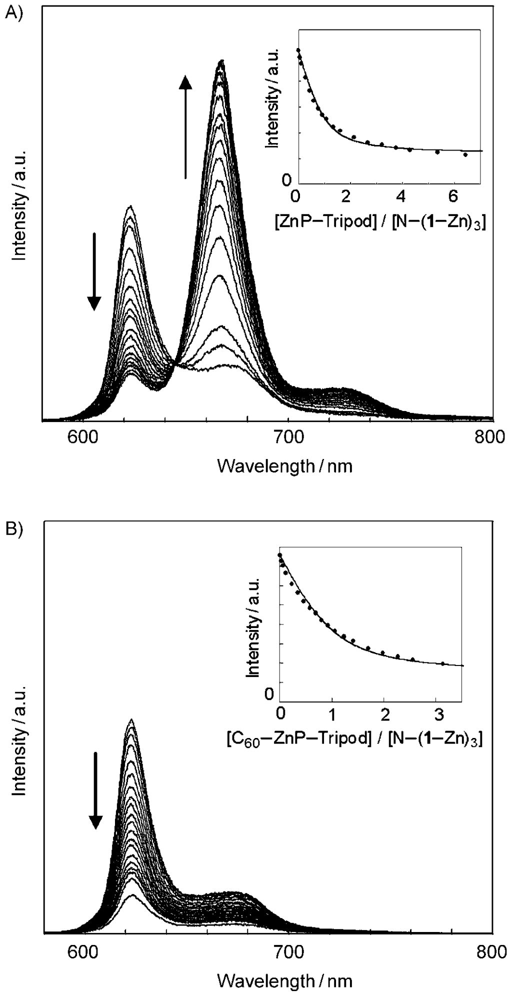


Figure 3. Fluorescence spectral changes for binding of N-(**1**–Zn)$_3$ to A) ZnP–Tripod (0–6.4 equiv) and to B) C_{60}–ZnP–Tripod (0–3.1, 6.4 equiv) in benzonitrile at 25 °C ($\lambda_{ex}=567$ nm; $[\text{N-}(\mathbf{1}\text{–Zn})_3]=3.6\times10^{-7}$ (A), $2.7\times10^{-7}\,\text{M}$ (B)). Insets show plots of the changes in fluorescence intensity at 623 nm and the theoretical curves calculated for $K_a=1.4\times10^7$ ($r^2=0.9916$) (A) and $1.6\times10^7\,\text{M}^{-1}$ ($r^2=0.98916$) (B).

Photodynamic properties of the macrocycle/tripodal ligand composite: To investigate photodynamic processes in the ZnP–Tripod/N-(**1**–Zn)$_3$ composite, time-resolved fluorescence spectra were obtained (Figure 4A). The sample was prepared by mixing N-(**1**–Zn)$_3$ (3.5 μM) and ZnP–Tripod (8.8 μM) in benzonitrile. Under these conditions, 98.7 % of N-(**1**–Zn)$_3$ is expected to exist as the 1:1 composite. The spectra were obtained by laser irradiation at 400 nm so that

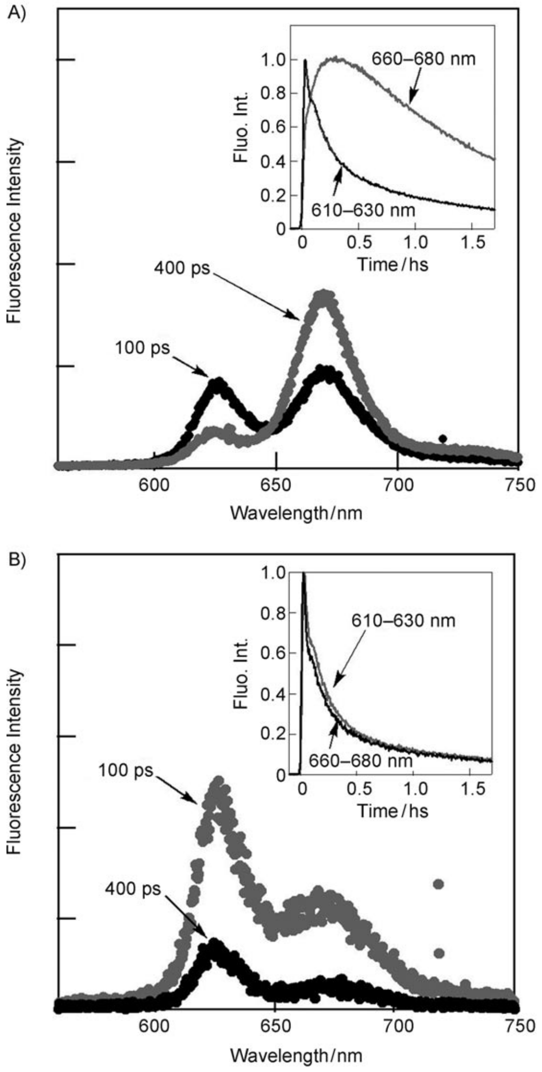


Figure 4. Time-resolved fluorescence spectra of the composite formed by mixing A) ZnP–Tripod (8.8 μM) and N-(**1**–Zn)$_3$ (3.5 μM) and by mixing B) C$_{60}$–ZnP–Tripod (7.5 μM) and N-(**1**–Zn)$_3$ (3.0 μM) in benzonitrile at 100 and 400 ps after the laser irradiation at $\lambda = 400$ nm, which excited predominantly the macrocycle. The absorbance ratios of N-(**1**–Zn)$_3$ to ZnP–Tripod and N-(**1**–Zn)$_3$ to C$_{60}$–ZnP–Tripod at 400 nm were 1:0.07 and 1:0.09, respectively. Insets: time profiles of the fluorescence at 610–630 and 660–680 nm, respectively.

N-(**1**–Zn)$_3$ was excited selectively. From the decay time profile in the region 610–630 nm, two components with lifetimes of 210 and 1490 ps were elucidated (Table 1; Figure 4A, inset). The longer component in the 610–630 nm region had almost the same lifetime as the component in the 660–680 nm region after the rise up to 400 ps, and it was assigned to the decay of ^{1}ZnP*. The shorter-lifetime component corresponds to the energy transfer event from N-(**1**–Zn)$_3$ to ZnP–Tripod, as supported by the increase in ZnP fluorescence. The energy-transfer rate and quantum yield were determined from the fluorescence decay to be 4.3×10^9 s^{-1} and 90 %, respectively. This rate constant was almost the same as the increase in ZnP fluorescence. The rate constant based on through-space energy transfer (k_{TS}) was calculated from the following Förster equation [Eq. (1)]:

$$k_{TS} = \frac{8.8 \times 10^{-25} \kappa^2 \Phi}{n^4 R^6 \tau} J \qquad (1)$$

in which n is the refractive index of the solvent, R is the center-to-center distance between donor and acceptor, τ is the fluorescence lifetime of an energy donor, κ is the orientation factor, Φ is the fluorescence quantum yield, and J is the spectral integral. The energy-transfer rate (k_{TS}) from N-(**1**–Zn)$_3$ to ZnP was calculated to be 3.0×10^9 s^{-1} when using $J = 3.4 \times 10^{-13}$ cm^{6}mmol^{-1}, $\kappa^2 = 0.20$,[34] $\Phi = 0.039$,[13a] $n = 1.53$ (benzonitrile), $R = 20.2$ Å,[35] and $\tau = 2.1$ ns.[13a] The calculated value is consistent with that obtained experimentally, which suggests that the energy transfer occurs by means of a through-space mechanism.

Table 1. Lifetimes of the investigated compounds from time-resolved fluorescence studies at room temperature in benzonitrile.[a]

	Emission lifetime [ps] (fraction %)	
	N-(**1**–Zn)$_3$ (620 nm)	ZnP (670 nm)
N-(**1**–Zn)$_3$	2100 (100)[b]	–
ZnP–Tripod	–	1600 (100)
C$_{60}$–ZnP–Tripod	–	110 (93), 1780 (7)
ZnP–Tripod/N-(**1**–Zn)$_3$	210 (64), 1490 (36)	1470 (100)
C$_{60}$–ZnP–Tripod/N-(**1**–Zn)$_3$	182 (89), 2020 (11)	–

[a] $\lambda_{ex} = 400$ nm. [b] From ref. [13].

Next, the time-resolved fluorescence decay of the C$_{60}$–ZnP–Tripod/N-(**1**–Zn)$_3$ composite was measured. The sample was prepared by mixing N-(**1**–Zn)$_3$ (3.0 μM) and C$_{60}$–ZnP–Tripod (7.5 μM) in benzonitrile. Under these conditions, the composite was expected to be formed from 98.6 % of N-(**1**–Zn)$_3$. The time-resolved fluorescence spectra showed only the decay of ^{1}[N-(**1**–Zn)$_3$]* without a rise in the component of ^{1}ZnP* (Figure 4B). This observation indicates that the electron transfer from ZnP to C$_{60}$ was faster than the energy transfer from N-(**1**–Zn)$_3$ to ZnP. The time profile in the region 610–630 nm features two decay components with lifetimes of 182 and 2020 ps (Table 1; Figure 4B, inset). The longer-lifetime component probably arose from small amounts of impurity or from free N-(**1**–Zn)$_3$. From the time profile of the major component, the quenching rate of the excited singlet state of N-(**1**–Zn)$_3$ was calculated to be 5.0×10^9 s^{-1}, and the quantum yield was 91 %. The rate constant is similar to that for ZnP–Tripod (4.3×10^9 s^{-1}), which indicates that the quenching of ^{1}[N-(**1**–Zn)$_3$]* results predominantly from energy transfer from N-(**1**–Zn)$_3$ to the ZnP moiety. Both the steady-state and time-resolved fluorescence data suggest that direct energy and electron transfers from ^{1}[N-(**1**–Zn)$_3$]* to the C$_{60}$ moiety are negligible.

Nanosecond time-resolved transient absorption spectra were measured to further elucidate the photodynamic processes in the composites. The samples were prepared in the same way as for the fluorescence-decay measurements. The excitation wavelength was 565 nm, at which the contribution of the absorption by N-(**1**–Zn)$_3$ was estimated to be 93 %

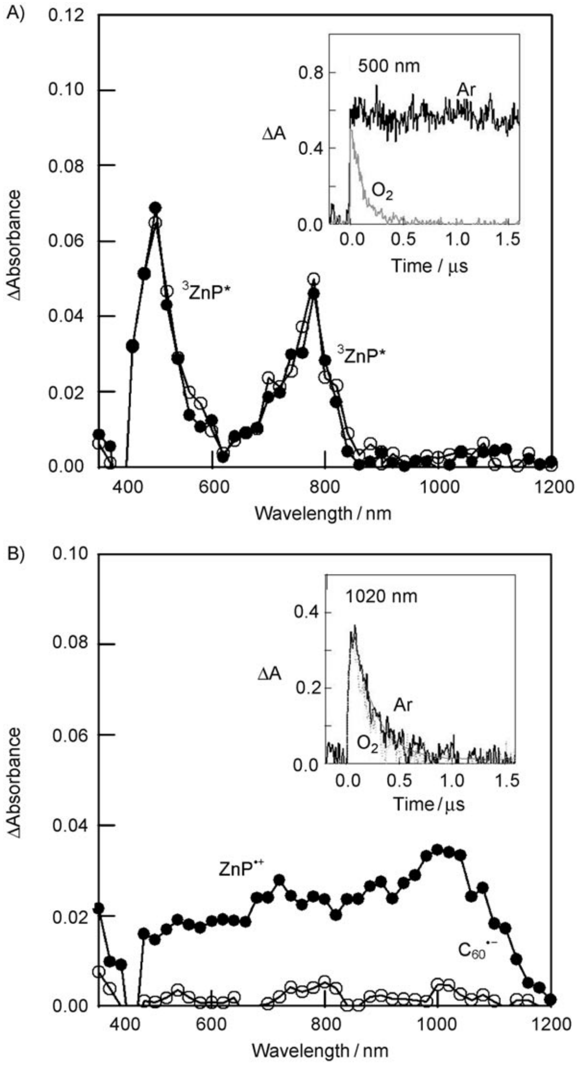


Figure 5. Nanosecond transient absorption spectra of the composite formed by mixing A) ZnP–Tripod (7.5 μM) or B) C_{60}–ZnP–Tripod (7.5 μM) with N-(**1**–Zn)$_3$ (3.0 μM) in Ar/benzonitrile. The spectra were recorded at 0.1 (●) and 1.0 μs (○) after laser irradiation at $\lambda = 565$ nm, which predominantly excited the macrocycle. According to the binding constants, >98 % of N-(**1**–Zn)$_3$ forms the complex. Inset: absorption–time profiles at A) 500 and B) 1020 nm in Ar- and O_2-saturated benzonitrile.

and N-(**1**–Zn)$_3$ was excited selectively. The transient spectra (Figure 5A) of the ZnP–Tripod/N-(**1**–Zn)$_3$ composite showed two sharp peaks at 500 and 780 nm that were similar to those observed for ZnP–Tripod alone (Figure S8 in the Supporting Information). Thus, these absorption bands can be assigned to the excited triplet state of the ZnP moiety that was produced by the energy transfer from N-(**1**–Zn)$_3$ followed by intersystem crossing to the triplet state. In the C_{60}–ZnP–Tripod/N-(**1**–Zn)$_3$ composite, a characteristic peak corresponding to the fullerene radical anion was detected at 1020 nm, along with bands in the region of 400–900 nm that are anticipated to be the cation radical of ZnP (Figure 5B). The observation of the charge-separated state without the triplet excited states of both N-(**1**–Zn)$_3$ and ZnP indicates that the excited energy at N-(**1**–Zn)$_3$ is transferred to the ZnP part followed by photoinduced electron transfer from the excited singlet state of ZnP to the fullerene moiety with high efficiency. The time profile at 1020 nm suggests that after the charge separation occurs within 0.5 ns, the charge recombination takes place within approximately 0.5 μs without an appreciable effect of O_2 in the solution. The rate constant of charge recombination was determined to be 5.0×10^6 s^{-1} from the decay time profile at 1020 nm in Ar-saturated benzonitrile.[36]

All of the energy- and electron-transfer rate constants obtained in this work are listed in Table 2.[37] In the composites ZnP–Tripod and C_{60}–ZnP–Tripod, the energy-transfer efficiency from N-(**1**–Zn)$_3$ to the ZnP moiety was found to be approximately 90 %, which was somewhat greater than the yield of approximately 80 % estimated from the fluorescence titration. Such a difference between steady-state and time-resolved measurements was also observed in the report from Lindsey, Holten et al.[38] The electron-transfer efficiency for C_{60}–ZnP–Tripod was estimated to be 94 % from the time-resolved measurement, whereas a value of 99.3 % was calculated from the steady-state fluorescence quenching. Because the time-resolved measurement extracts the contribution of the energy transfer from several components including the contribution of impurities, the value obtained from the time-resolved measurement is considered to be more reliable. Indeed, the total energy conversion efficiency from the excited cyclic porphyrin array ^{1}[N-(**1**–Zn)$_3$]* to the charge-separation state ZnP$^{•+}$–$C_{60}^{•-}$ was found to reach 85 %.

Table 2. Energy-transfer rate constants (k_{En}) and efficiency (Φ_{En}), charge-separation and charge-recombination rate constants (k_{CS} and k_{CR}), and quantum yields of charge-separation (Φ_{CS}) at room temperature in Ar-saturated benzonitrile.

	N-(**1**–Zn)$_3$→ZnP		ZnP→C_{60}		
	k_{En} [s^{-1}]	Φ_{En}	k_{CS} [s^{-1}]	Φ_{CS}	k_{CR} [s^{-1}]
C_{60}–ZnP–Tripod	–	–	8.5×10^9[a]	0.94[a]	3.4×10^6
ZnP–Tripod/N-(**1**–Zn)$_3$	4.3×10^9[b]	0.90[c]	–	–	–
C_{60}–ZnP–Tripod/N-(**1**–Zn)$_3$	5.0×10^9[b]	0.91[c]	[d]	[d]	5.0×10^6

[a] See ref. [26]. [b] $k_{En} = [1/\tau_{(composite)}] - [1/\tau_{(N-(1-Zn)_3)}]$, in which $\tau_{(N-(1-Zn)_3)} =$ 2100 ps. [c] $\Phi_{En} = [1/\tau_{(composite)} - 1/\tau_{(N-(1-Zn)_3)}]/[1/\tau_{(composite)}]$. [d] Not determined.

Conclusion

The porphyrin macrocycle N-(**1**–Zn)$_3$ nearly quantitatively accommodated the tripyridyl tripodal ligands through the use of three uncoordinated porphyrinatozinc sites. The binding constants of ZnP–Tripod and C_{60}–ZnP–Tripod were found to be of the order of 10^7 M^{-1} in benzonitrile, which enabled us to obtain almost quantitatively the desired composites. The steady-state fluorescence, fluorescence-decay, and transient absorption measurements of the C_{60}–ZnP–Tripod/N-(**1**–Zn)$_3$ composite, along with the experiments on the ZnP–Tripod/N-(**1**–Zn)$_3$ composite, showed that the light energy collected by the nine porphyrins of N-(**1**–Zn)$_3$ was transferred efficiently to the central acceptor porphyrin moiety ZnP, followed by photoinduced electron transfer from ZnP to the C_{60} moiety. The present C_{60}–ZnP–Tripod/N-(**1**–Zn)$_3$ system successfully mimics the combined structure of the light-harvesting complex and the reaction center in natural photosynthesis. The merit of a supramolecular approach was clearly demonstrated by the fact that a series of guest molecules could be tested easily by simple mixing with minimal synthetic effort.

Experimental Section

General procedure: All chemicals and solvents were of commercial reagent quality, and used without further purification unless otherwise stated. Dry tetrahydrofuran (THF) and toluene were prepared by distillation over benzophenone/Na. Dry triethylamine (Et_3N) was prepared by distillation over CaH_2. ^{1}H NMR spectra were recorded on a JEOL ECP-600 spectrometer (600 MHz) and chemical shifts were recorded in parts per million (ppm) relative to tetramethylsilane. Assignments of ^{1}H NMR spectra were based on ^{1}H-^{1}H COSY measurements. UV/Vis absorption spectra were recorded on a Shimadzu UV-3100PC spectrometer. Steady-state fluorescence emission spectra were recorded on a Hitachi F-4500 spectrometer and corrected for the response of the detector system. The fluorescence intensities were normalized at the absorption of their excitation wavelength. UV/Vis $\lambda_{\max}$ ($\log\varepsilon$) values are reported in nm. Fluorescence quantum yields of N-(**1**–Zn)$_3$ and ZnP–Tripod were determined by means of corrected integrated ratios of steady-state fluorescence spectra[39] relative to those of ZnTPP ($\Phi_f = 3.3\%$; tetraphenylporphyrinatozinc)[40] and ZnPc ($\Phi_f = 30\%$; tetra-*tert*-butylphthalocyaninato zinc),[41] respectively. UV/Vis and fluorescence titrations were performed by adding a solution of tripodal ligand to a solution of the macrocycle N-(**1**–Zn)$_3$ in a quartz cuvette (1 cm path length) by using microliter syringes. MALDI-TOF MS spectra were obtained on PerSeptive Biosystems Voyager DE-STR instrument with dithranol (Aldrich) as the matrix. Gel permeation chromatography (GPC) was carried out on a Hewlett Packard HP1100 series equipped with Tosho TSK-GEL G2500H$_{HR}$ (polystyrene gel; exclusion limit: 2×10^4 Da) with pyridine as the eluent. Reactions were monitored on silica gel 60 F_{254} TLC plates (Merck). The silica gel utilized for column chromatography was purchased from Kanto Chemical Co. Inc.: silica gel 60N 60–210 μm (spherical, neutral) and 40–210 μm (flash). The alumina (aluminum oxide 90 active basic) used for column chromatography was purchased from Merck.

Time-resolved emission and transient absorption measurements: The fluorescence lifetimes were measured using an argon-ion pumped Ti:sapphire laser (Tsunami) and a streak scope (Hamamatsu Photonics). The nanosecond transient absorption spectra in the NIR region were measured by means of laser-flash photolysis; light of 565 nm wavelength from an Nd:YAG laser was used as the exciting source, and a Ge-avalanche-photodiode module was used for detecting the monitoring light from a pulsed Xe lamp. The details of the experimental setup are described elsewhere.[42]

4-[2-(4-Formylphenyl)ethynyl]phenyltris(4-iodophenyl)methane (3): A Schlenk flask was charged with tetrakis(4-iodophenyl)methane (200 mg, 2.4×10^{-4} mol),[19] dry Et_3N (2 mL), and dry THF (20 mL) under an Ar atmosphere. The suspension was sonicated and heated to become a homogeneous solution. 4-Ethynylbenzaldehyde (38 mg, 2.9×10^{-4} mol),[23] $[PdCl_2(PPh_3)_2]$ (14 mg, 2.0×10^{-5} mol), and CuI (2 mg, 1.0×10^{-5} mol) were then added and the mixture was degassed by freeze–thaw cycles. The reaction mixture was stirred at room temperature under an Ar atmosphere. After 24 h, extra 4-ethynylbenzaldehyde (17 mg, 1.3×10^{-4} mol) was added because the 4-ethynylbenzaldehyde had already been consumed and tetrakis(4-iodophenyl)methane still remained. The mixture was stirred overnight and then concentrated to dryness. The residue was extracted with $CHCl_3$ and washed with water. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness. Purification with silica gel column chromatography ($CHCl_3$) gave the title compound as a pale yellow solid (75.4 mg, 38%). TLC (silica gel, $CHCl_3$): $R_f = 0.8$; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 10.02$ (s, 1H; CHO), 7.86 (d, J(H,H) = 8.2 Hz, 2H; *Ph*-CHO), 7.65 (d, J(H,H) = 8.2 Hz, 2H; *Ph*-CHO), 7.59 (d, J(H,H) = 8.5 Hz, 6H; Ph), 7.44 (d, J(H,H) = 8.5 Hz, 2H; Ph′), 7.16 (d, J(H,H) = 8.5 Hz, 2H; Ph′), 6.91 ppm (d, J(H,H) = 8.5 Hz, 6H; Ph); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): $\delta = 191.3$, 146.2, 145.1, 137.1, 132.8, 132.6, 132.1, 131.3, 130.7, 129.6, 129.4, 120.8, 92.81, 92.46, 89.05, 64.26 ppm.

4-[2-(4-Formylphenyl)ethynyl]phenyltris{4-[2-(4-pyridyl)ethynyl]phenyl}methane (2): Compound **3** (42 mg, 5.1×10^{-5} mol), $[PdCl_2(PPh_3)_2]$ (4 mg, 5.7×10^{-6} mol), and CuI (0.6 mg, 3.1×10^{-6} mol) were placed in a Schlenk flask and the flask was evacuated and replaced with Ar gas. 4-Ethynylpyridine (21 mg, 2.0×10^{-4} mol),[22] dry Et_3N (0.5 mL), and dry THF (1 mL) were added and the mixture was degassed by freeze–thaw cycles. The reaction mixture was stirred for 4 h at room temperature under an Ar atmosphere. The residue obtained by evaporation of the solvent was extracted with $CHCl_3$ and washed with water. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness. Purification was performed with silica gel column chromatography ($CHCl_3$/MeOH 9:1). The second band showing a bright spot on TLC by UV irradiation was collected and evaporated to dryness. Further purification by reprecipitation with $CHCl_3$/hexane gave the title compound as a pale yellow solid (20.6 mg, 54%). TLC (silica gel, $CHCl_3$/MeOH 9:1): $R_f = 0.7$; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 10.02$ (s, 1H; CHO), 8.61 (d, J(H,H) = 4.8 Hz, 6H; Py), 7.87 (d, J(H,H) = 8.4 Hz, 2H; *Ph*-CHO), 7.67 (d, J(H,H) = 8.4 Hz, 2H; *Ph*-CHO), 7.50 (d, J(H,H) = 8.4 Hz, 6H; Ph), 7.48 (2H; Ph′), 7.38 (d, J(H,H) = 4.8 Hz, 6H; Py), 7.25 (d, J(H,H) = 8.4 Hz, 6H; Ph), 7.24 ppm (2H; Ph′); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): $\delta = 191.3$, 149.8, 146.5, 146.2, 135.5, 132.1, 131.5, 131.4, 131.2, 130.9, 129.6, 129.3, 125.5, 120.8, 120.4, 93.30, 92.76, 89.10, 87.20, 65.04 ppm; MALDI-TOF MS: m/z calcd for $C_{55}H_{34}N_3O$ $[M+H]^+$: 752.9; found: 752.3.

4-(3-Hydroxy-3-methyl-1-butynyl)phenyltris(4-iodophenyl)methane (4): Tetrakis(4-iodophenyl)methane (200 mg, 2.4×10^{-4} mol),[19] $[PdCl_2(PPh_3)_2]$ (17 mg, 2.4×10^{-5} mol), and CuI (4.6 mg, 2.4×10^{-5} mol) were placed in a Schlenk flask and the flask was evacuated and replaced with Ar gas. Dry THF (20 mL) and dry Et_3N (4 mL) were added and the resulting suspension was sonicated and heated to become a homogeneous solution. 2-Methyl-3-butyn-2-ol (31 μL, 3.2×10^{-4} mol) was added and the reaction mixture was degassed by freeze–thaw cycles. The reaction mixture was stirred for 8 h at 40 °C. The residue obtained by evaporation of the solvent was purified with silica gel column chromatography ($CHCl_3$). The second band absorbing UV light was collected and the solvent was evaporated to afford the title compound as a sticky solid (62.6 mg, 33%). TLC (silica gel, $CHCl_3$): $R_f = 0.5$; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.57$ (d, J(H,H) = 9.0 Hz, 6H; Ph), 7.31 (d, J(H,H) = 8.4 Hz, 2H; Ph′), 7.08 (d, J(H,H) = 8.4 Hz, 2H; Ph′), 6.88 (d, J(H,H) = 9.0 Hz, 6H; Ph), 2.06 (s, 1H; OH), 1.60 ppm (s, 6H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): $\delta = 145.3$, 145.2, 137.0, 132.6, 131.2, 130.5, 121.0, 94.38, 92.38, 81.53, 65.57, 64.13, 31.44 ppm.

4-(3-Hydroxy-3-methyl-1-butynyl)phenyltris{4-[2-(4-pyridyl)ethynyl]phenyl}methane (5): Compound **4** (62 mg, 8.0×10^{-5} mol), $[PdCl_2(PPh_3)_2]$ (5.6 mg, 8.0×10^{-6} mol), and CuI (2 mg, 1.0×10^{-5} mol) were placed in a Schlenk flask and the flask was evacuated and replaced with Ar gas. Dry THF (2 mL), dry TEA (1 mL), and 4-ethynylpyridine (41 mg, 4.0×10^{-4} mol) were added, and the mixture was degassed by freeze–thaw cycles. The reaction mixture was stirred for 6 h at room temperature. The resulting crude product obtained by evaporation of the solvents was purified with silica gel column chromatography ($CHCl_3$/MeOH 93:7 to 92:8) to afford the title compound as a pale yellow solid (54.7 mg, 98%). TLC (silica gel, $CHCl_3$/MeOH 9:1): $R_f = 0.4$; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.60$ (br s, 6H; Py), 7.47 (d, J(H,H) = 8.4 Hz, 6H; Ph), 7.37 (d, J(H,H) = 5.4 Hz, 6H; Py), 7.34 (d, J(H,H) = 9.0 Hz, 2H; Ph′), 7.22 (d, J(H,H) = 8.4 Hz, 6H; Ph), 7.15 (d, J(H,H) = 9.0 Hz, 2H; Ph′), 2.13 (s, 1H; OH), 1.62 ppm (s, 6H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 149.3, 146.2, 144.9, 131.0, 130.9, 130.8, 130.5, 130.2, 125.1, 120.8, 119.9, 94.34, 92.97, 86.71, 80.93, 64.96, 64.53, 31.06 ppm; MALDI-TOF MS: m/z calcd for $C_{51}H_{36}N_3O$ $[M+H]^+$: 706.9; found: 706.0.

4-Ethynylphenyl-tris{4-[2-(4-pyridyl)ethynyl]phenyl}methane (6): Compound **5** (20.8 mg, 3.0×10^{-5} mol), NaH (47 mg, 60 % in oil, 1.2×10^{-3} mol), and dry toluene (2 mL) were placed in a test tube with a screw cap and purged with Ar gas. After the test tube was sealed, the reaction mixture was heated in an oil bath. After the reaction mixture had been stirred overnight at 100 °C, the reaction was quenched by the addition of water. The product was extracted with $CHCl_3$ and the organic layer was dried over anhydrous Na_2SO_4. The resulting crude product obtained by evaporation of the solvent was purified with silica gel column chromatography ($CHCl_3$/MeOH 95:5). The first band absorbing UV light was collected and the solvents were evaporated to afford the title compound as a white solid (15.5 mg, 80 %). TLC (silica gel, $CHCl_3$/MeOH 9:1): R_f = 0.5; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.60 (d, J(H,H) = 5.4 Hz, 6H; Py), 7.48 (d, J(H,H) = 8.4 Hz, 6H; Ph), 7.43 (d, J(H,H) = 8.4 Hz, 2H; Ph′), 7.37 (d, J(H,H) = 5.4 Hz, 6H; Py), 7.22 (d, J(H,H) = 8.4 Hz, 6H; Ph), 7.18 (d, J(H,H) = 8.4 Hz, 2H; Ph′), 3.09 ppm (s, 1H; C≡CH); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 149.8, 146.5, 146.0, 131.8, 131.5, 131.2, 130.9, 130.7, 125.5, 120.5, 120.4, 93.34, 87.20, 83.07, 77.79, 65.01 ppm; MALDI-TOF MS: m/z calcd for $C_{48}H_{30}N_3$ $[M+H]^+$: 648.8; found: 648.1.

4-(Bromophenyl)-1,3-dioxolane: *p*-Bromobenzaldehyde (5 g, 2.7×10^{-2} mol), ethylene glycol (3.2 mL, 5.9×10^{-2} mol), *p*-TsOH·H_2O (1.02 g, 5.4×10^{-3} mol), and benzene (100 mL) were placed in a 300 mL flask equipped with a Dean–Stark tube. After the reaction mixture had been stirred for 6 h at reflux under an Ar atmosphere, the reaction was quenched by the addition of ice-cold saturated aqueous $NaHCO_3$. The organic layer was washed with saturated aqueous $NaHCO_3$ and water, and dried over anhydrous Na_2SO_4. The solvent was evaporated to afford the title compound as a pale yellow oil (6 g, 97 %). TLC (silica gel, $CHCl_3$): R_f = 0.6; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.51 (d, J(H,H) = 8.4 Hz, 2H; Ph), 7.35 (d, J(H,H) = 8.4 Hz, 2H; Ph), 5.77 (s, 1H; CH), 4.11 (t, J(H,H) = 6.6 Hz, 2H; CH_2), 4.03 ppm (t, J(H,H) = 6.6 Hz, 2H; CH_2).

4-(Trimethylsilylethynyl)phenyl-1,3-dioxolane: 4-(Bromophenyl)-1,3-dioxolane (1 g, 4.4×10^{-3} mol), $[PdCl_2(PPh_3)_2]$ (61 mg, 8.7×10^{-5} mol), and CuI (17 mg, 8.9×10^{-5} mol) were placed in a test tube with a screw cap. The test tube was evacuated and replaced with Ar gas. Dry THF (5 mL), dry Et_3N (1 mL), and trimethylsilylacethylene (0.9 mL, 6.5 $\times10^{-3}$ mol) were added and the test tube was sealed under an Ar atmosphere. The reaction mixture was heated to 80 °C and stirred for 25 h. The resulting solution was cooled to room temperature and the solvent was evaporated. The residue was passed through a short silica gel column (hexane/EtOAc 2:1) to remove insoluble black materials. The crude brown oil was purified by distillation under reduced pressure. The second fraction afforded the title compound as a pale yellow oil (437 mg, 40 %). B.p. 120 °C/0.045 KPa; TLC (silica gel, $CHCl_3$): R_f = 0.6; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.47 (d, J(H,H) = 8.4 Hz, 2H; Ph), 7.41 (d, J(H,H) = 8.4 Hz, 2H; Ph), 5.79 (s, 1H; CH), 4.11 (t, J(H,H) = 7.2 Hz, 2H; CH_2), 4.03 (t, J(H,H) = 7.2 Hz, 2H; CH_2), 0.25 ppm (s, 9H; CH_3).

5,15-Dibromo-10,20-bis(4-ethoxycarbonylphenyl)porphyrinatozinc(II) (7): 5,15-Dibromo-10,20-bis(4-ethoxycarbonylphenyl)porphyrin (188 mg, 2.5×10^{-4} mol)[20] was dissolved in $CHCl_3$ (30 mL) and a saturated zinc acetate dihydrate solution in MeOH (2 mL) was added. The mixture was stirred for 3 h at room temperature and then washed with water. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated. The resulting material was recrystallized twice from $CHCl_3$/MeOH to give the title compound as purple crystals (169 mg, 83 %). TLC (silica gel, $CHCl_3$): R_f = 0.2; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.69 (d, J(H,H) = 4.8 Hz, 4H; β-pyrrole), 8.82 (d, J(H,H) = 4.8 Hz, 4H; β-pyrrole), 8.44 (d, J(H,H) = 8.4 Hz, 4H; Ph), 8.26 (d, J(H,H) = 8.4 Hz, 4H; Ph), 4.60 (q, J(H,H) = 7.2 Hz, 4H; CH_2), 1.57 ppm (t, J(H,H) = 7.2 Hz, 6H; CH_3).

5-Bromo-15-[4-(1,3-dioxolanyl)phenylethynyl]-10,20-bis(4-ethoxycarbonylphenyl)porphyrinatozinc(II) (8): Compound **7** (100 mg, 1.2×10^{-4} mol) and 4-(trimethylsilylethynyl)phenyl-1,3-dioxolane (39 mg, 1.6×10^{-4} mol) were placed in a Schlenk flask and the flask was evacuated and replaced with Ar gas. Dry THF (10 mL) and a solution of 1 M TBAF in THF (0.47 mL, 4.7×10^{-4} mol) were sequentially added via a syringe. The mixture was stirred for 30 min at room temperature and then $[PdCl_2(PPh_3)_2]$ (11 mg, 1.6×10^{-5} mol), CuI (4.4 mg, 2.3×10^{-5} mol), and dry Et_3N (3 mL) were added. The solution was degassed by freeze–thaw cycles and replaced with Ar gas and stirred for 24 h at room temperature. The resulting mixture was concentrated to approximately 5 mL and the reaction was quenched by the addition of water (≈5 mL) and the product was extracted with $CHCl_3$ and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified with a flash silica gel column eluting with $CHCl_3$. The second band was collected and evaporated to give a still-impure purple solid, which was further purified by a second flash silica gel column ($CHCl_3$) to give the title compound as a purple solid (25.2 mg, 23 %). TLC (silica gel, $CHCl_3$): R_f = 0.4; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.64 (d, J(H,H) = 4.2 Hz, 2H; β-pyrrole), 9.55 (d, J(H,H) = 4.2 Hz, 2H; β-pyrrole), 8.814 (d, J(H,H) = 4.2 Hz, 2H; β-pyrrole), 8.807 (d, J(H,H) = 4.2 Hz, 2H; β-pyrrole), 8.45 (d, J(H,H) = 7.8 Hz, 4H; Ph), 8.27 (d, J(H,H) = 7.8 Hz, 4H; Ph), 7.48 (d, J(H,H) = 7.2 Hz, 2H; Ph′), 5.30 (d, J(H,H) = 7.2 Hz, 2H; Ph′), 4.56 (q, J(H,H) = 7.2 Hz, 4H; CH_2CH$_3$), 2.04 (s, 1H; CH), 1.65 (br s, 2H; CH_2), 1.57 (t, J(H,H) = 7.2 Hz, 6H; CH$_2$$CH_3$), 1.07 ppm (br s, 2H; CH_2); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 166.8, 152.7, 150.1, 149.4, 149.2, 147.0, 134.5, 133.3, 133.1, 132.6, 132.5, 131.7, 130.8, 129.9, 127.8, 124.9, 124.7, 121.0, 106.0, 101.4, 101.1, 98.84, 93.06, 62.78, 61.35, 14.53 ppm; MALDI-TOF MS: m/z calcd for $C_{49}H_{36}BrN_4O_6Zn$ $[M+H]^+$: 922.1; found: 921.5.

ZnP–Tripod: Compound **8** (12.4 mg, 1.4×10^{-5} mol), **6** (13.6 mg, 2.1×10^{-5} mol), $[Pd_2(dba)_3]$ (4 mg, 3.9×10^{-6} mol), and $AsPh_3$ (10 mg, 3.3×10^{-5} mol) were placed in a Schlenk flask. The flask was evacuated and replaced with Ar gas, and then dry THF (1 mL) and dry Et_3N (0.2 mL) were added and the mixture was degassed by freeze–thaw cycles. After the reaction mixture had been stirred for 48 h at room temperature, $[Pd_2(dba)_3]$ (1.5 mg, 1.5×10^{-6} mol) and $AsPh_3$ (3.4 mg, 1.1×10^{-5} mol) were added. After stirring for 6.5 h at room temperature, the reaction was terminated by evaporating the solvent. The residue was purified with a silica gel column eluting with $CHCl_3$/MeOH 9:1. The third band was collected to afford the title compound as a green solid (8.7 mg, 43 %). TLC (silica gel, $CHCl_3$/MeOH 9:1): R_f = 0.5; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.73 (d, J(H,H) = 4.2 Hz, 2H; β-pyrrole), 9.61 (d, J(H,H) = 4.2 Hz, 2H; β-pyrrole), 8.80 (d, J(H,H) = 4.2 Hz, 2H; β-pyrrole), 8.74 (d, J(H,H) = 4.2 Hz, 2H; β-pyrrole), 8.42 (d, J(H,H) = 7.8 Hz, 4H; Ph), 8.23 (d, J(H,H) = 7.8 Hz, 4H; Ph), 8.04 (d, J(H,H) = 7.8 Hz, 2H; Ph′), 7.83 (d, J(H,H) = 8.4 Hz, 2H; Tripod-*Ph′*), 7.68 (d, J(H,H) = 7.8 Hz, 2H; Ph′), 7.30 (d, J(H,H) = 8.4 Hz, 6H; Tripod-*Ph*), 7.23 (d, J(H,H) = 8.4 Hz, 2H; Tripod-*Ph′*), 7.16 (d, J(H,H) = 8.4 Hz, 6H; Tripod-*Ph*), 6.75 (br s, 6H; Tripod-*Py*), 5.95 (s, 1H; CH), 4.59 (q, J(H,H) = 7.2 Hz, 4H; CH_2CH$_3$), 4.22 (t, J(H,H) = 7.2 Hz, 2H; CH_2), 4.12 (t, J(H,H) = 7.2 Hz, 2H; CH_2), 3.2–3.8 (br s; Tripod-*Py*), 1.56 ppm (t, J(H,H) = 7.2 Hz, 6H; CH$_2$$CH_3$); ^{1}H NMR (600 MHz, $CDCl_3$/2 drops of [D$_5$]pyridine, 25 °C, TMS): δ = 9.72 (d, J(H,H) = 4.2 Hz, 2H; β-pyrrole), 9.70 (d, J(H,H) = 4.2 Hz, 2H; β-pyrrole), 8.81 (d, J(H,H) = 4.2 Hz, 2H; β-pyrrole), 8.80 (d, J(H,H) = 4.2 Hz, 2H; β-pyrrole), 8.58 (d, J(H,H) = 5.4 Hz, 6H; Tripod-*Py*), 8.44 (d, J(H,H) = 7.8 Hz, 4H; Ph), 8.25 (d, J(H,H) = 7.8 Hz, 4H; Ph), 8.03 (d, J(H,H) = 8.4 Hz, 2H; Ph′), 7.95 (d, J(H,H) = 8.4 Hz, 2H; Tripod-*Ph′*), 7.68 (d, J(H,H) = 7.8 Hz, 2H; Ph′), 7.55 (d, J(H,H) = 8.4 Hz, 6H; Tripod-*Ph*), 7.41 (d, J(H,H) = 8.4 Hz, 2H; Tripod-*Ph′*), 7.38 (d, J(H,H) = 5.4 Hz, 6H; Tripod-*Py*), 7.35 (d, J(H,H) = 8.4 Hz, 6H; Tripod-*Ph*), 5.95 (s, 1H; CH), 4.59 (q, J(H,H) = 7.2 Hz, 4H; CH_2CH$_3$), 4.21 (t, J(H,H) = 7.2 Hz, 2H; CH_2), 4.12 (t, J(H,H) = 7.2 Hz, 2H; CH_2), 1.56 ppm (t, J(H,H) = 7.2 Hz, 6H; CH$_2$$CH_3$); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 166.9, 152.2, 151.9, 149.6, 149.4, 147.4, 147.3, 146.6, 145.4, 138.2, 134.5, 132.3, 132.2, 131.6, 131.39, 131.36, 131.2, 131.03, 130.95, 130.9, 130.8, 129.7, 127.7, 126.9, 125.1, 125.0, 122.5, 121.5, 120.1, 103.4, 101.4, 101.0, 96.41, 95.95, 93.86, 93.50, 86.52, 65.43, 65.00, 61.31, 29.70, 14.53 ppm; UV/Vis (pyridine): λ_{max} ($\log\varepsilon$) = 456.5 (5.57), 663.0 nm (4.80); UV/Vis (benzonitrile): $\lambda_{\max}$ ($\log\varepsilon$) = 458.0 (5.60), 663.0 nm (4.84); fluorescence (benzonitrile): λ_{ex} = 600.0 nm, λ_{obs} = 667.2, 728.0 nm; MALDI-TOF MS: *m*/*z* calcd for $C_{97}H_{64}N_7O_6Zn$ $[M+H]^+$: 1489.0; found: 1488.7.

Deprotected ZnP–Tripod (9): ZnP–Tripod (8.7 mg, 5.8×10^{-6} mol) was placed in a test tube and cooled to 0 °C. A cold 80 % acetic acid aqueous solution (5 mL) was added and the mixture was stirred for 9 h at 0 °C. The reaction was quenched by addition of saturated cold $NaHCO_3$ aqueous solution and the resulting product was extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$ aqueous solution and water, and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave the title compound (8.2 mg, 98 %). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS) δ 10.11 (s, 1 H; CHO), 9.71 (d, *J*(H,H) = 4.2 Hz, 2 H; β-pyrrole), 9.62 (d, *J*(H,H) = 4.2 Hz, 2 H; β-pyrrole), 8.82 (d, *J*(H,H) = 4.2 Hz, 2 H; β-pyrrole), 8.75 (d, *J*(H,H) = 4.2 Hz, 2 H; β-pyrrole), 8.44 (d, *J*(H,H) = 7.8 Hz, 4 H; Ph), 8.23 (d, *J*(H,H) = 7.8 Hz, 4 H; Ph), 8.14 (d, *J*(H,H) = 7.8 Hz, 2 H; Ph′), 8.05 (d, *J*(H,H) = 7.8 Hz, 2 H; Ph′), 7.83 (d, *J*(H,H) = 8.4 Hz, 2 H; Tripod-Ph′), 7.30 (d, *J*(H,H) = 8.4 Hz, 6 H; Tripod-Ph), 7.24 (d, *J*(H,H) = 8.4 Hz, 2 H; Tripod-Ph′), 7.16 (d, *J*(H,H) = 8.4 Hz, 6 H; Tripod-Ph), 6.76 (brs, 6 H; Tripod-Py), 4.60 (q, *J*(H,H) = 7.2 Hz, 4 H; *CH₂*CH₃), 3.2–3.8 (brs; Tripod-Py), 1.57 ppm (t, *J*(H,H) = 7.2 Hz, 6 H; CH₂*CH₃*); MALDI-TOF MS: *m*/*z* calcd for $C_{95}H_{60}N_7O_5Zn$ $[M+H]^+$: 1444.9; found: 1443.8.

C_{60}–ZnP–Tripod: Compound **9** (8.2 mg, 5.7×10^{-6} mol), fullerene C_{60} (20 mg, 2.8×10^{-5} mol), *N*-methylglycine (25 mg, 2.8×10^{-4} mol), and dry toluene (3 mL) were placed in a test tube and then the tube was purged with N_2 gas. The reaction mixture was stirred for 42 h at 100 °C. The resulting mixture was passed through an alumina column (toluene to $CHCl_3$/MeOH 9:1) to remove excess fullerene and *N*-methylglycine. The crude product was further purified by preparative GPC (TSK G3000H_{HR} column; eluent: pyridine; flow rate: 3.5 mL min^{-1}) to give the title compound (4.38 mg, 37 %). ^{1}H NMR (600 MHz, $CDCl_3$/[D$_5$]pyridine, 25 °C, TMS): δ = 9.73 (d, *J*(H,H) = 4.2 Hz, 2 H; β-pyrrole), 9.71 (d, *J*(H,H) = 4.2 Hz, 2 H; β-pyrrole), 8.79 (d, *J*(H,H) = 4.2 Hz, 4 H; β-pyrrole), 8.61 (Tripod-*Py*), 8.44 (d, *J*(H,H) = 7.8 Hz, 4 H; Ph), 8.24 (d, *J*(H,H) = 7.8 Hz, 4 H; Ph), 8.09 (brs, 2 H; Ph′), 8.02 (brs, 2 H; Ph′), 7.96 (d, *J*(H,H) = 8.4 Hz, 2 H; Tripod-*Ph′*), 7.55 (d, *J*(H,H) = 8.4 Hz, 6 H; Tripod-*Ph*), 7.42 (d, *J*(H,H) = 8.4 Hz, 2 H; Tripod-*Ph′*), 7.38 (d, *J*(H,H) = 5.4 Hz, 6 H; Tripod-*Py*), 7.36 (d, *J*(H,H) = 8.4 Hz, 6 H; Tripod-*Ph*), 5.06 (s, 1 H; pyrrolidine *CH*), 5.04 (d, *J*(H,H) = 9.6 Hz, 1 H; pyrrolidine *CH₂*), 4.58 (q, *J*(H,H) = 7.2 Hz, 4 H; *CH₂*CH₃), 4.32 (d, *J*(H,H) = 9.6 Hz, 1 H; pyrrolidine *CH₂*), 2.91 (s, 3 H; N-CH₃), 1.55 ppm (t, *J*(H,H) = 7.2 Hz, 6 H; CH₂*CH₃*); UV/Vis (pyridine): $\lambda_{\max}$ ($\log\varepsilon$): 456.5 (5.57), 663.0 nm (4.81); UV/Vis (benzonitrile): $\lambda_{\max}$ ($\log\varepsilon$): 459.0 (5.55), 665.5 nm (4.82); MALDI-TOF MS: *m*/*z* calcd for $C_{157}H_{65}N_8O_4Zn$ $[M+H]^+$: 2192.6; found: 2192.9.

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[27] The transient spectrum at 1 μs after laser irradiation at 470 nm (Figure S7 in the Supporting Information) showed the bands of the triplet excited state of ZnP. Because the energy level of the triplet state of 5,15-bis[bis(octyloxyphenyl)]-10,20-bis(4-butylphenylethynyl)porphyrin is approximately 1.4 eV, the triplet band observed at 1 μs would form by the intersystem crossing from ^{1}ZnP*: M. U. Winters, E. Dahlstedt, H. E. Blades, C. J. Wilson, M. J. Frampton, H. L. Anderson, B. J. Albinsson, *J. Am. Chem. Soc.* **2007**, *129*, 4291.

[28] It is well known that coordination of pyridyl and similar ligands to zinc porphyrins leads to a band shift of the Q band. In this case, the three uncoordinated porphyrinatozinc(II) sites of N-(**1**–Zn)$_3$ are already coordinated by benzonitrile. Thus, the spectral change of the Q band is negligible (see ref. [13a]).

[29] Although there are two topological isomers in N-(**1**–Zn)$_3$, which is noted in ref. [12], no heterogeneity of isomers was observed in the titration due to the flexibility of the carbon core that connects the three pyridyl arms in the tripodal ligand.

[30] The contributions of N-(**1**–Zn)$_3$ and ZnP–Tripod in the absorption spectrum of an equimolar mixture were 97 and 3%, respectively, at 567 nm.

[31] At $\lambda = 623$ nm, the contribution of fluorescence from ZnP is negligible. See Figure S10 in the Supporting Information.

[32] UV/Vis spectral changes during the titration of ZnP–Tripod and C_{60}–ZnP–Tripod are shown in Figures S11 and S12 in the Supporting Information, respectively. Reliable binding constants could not be determined from the UV/Vis spectral changes due to overlap in the absorption of the ZnP and N-(**1**–Zn)$_3$ moieties.

[33] Expansion of the π conjugation and removal of the degeneracy of the LUMO of the porphyrin by the attachment of arylethynyl moieties to the porphyrin *meso* positions leads to redshifted and enhanced Q-band absorption (see ref. [15]), which results in a large overlap with the fluorescence of N-(**1**–Zn)$_3$.

[34] Because the 5,15-bis[(aryl)ethynyl]-10,20-diphenylporphyrin structure possesses an approximately ten times larger transition dipole moment along the axis of (aryl)ethynyl (Q_y) than along the perpendicular axis (Q_x), we assume that only the transition dipole of Q_y in ZnP–Tripod relates to the energy transfer (see ref. [15]).

[35] Preliminary evaluation from a femtosecond transient absorption anisotropy measurement shows the excitation energy hopping time between the slipped-cofacial dimeric and the monomeric porphyrin units of N-(**1**–Zn)$_3$ to be 6.3 ps. Because this time scale is much shorter than that of the energy transfer from N-(**1**–Zn)$_3$ to ZnP, the excitation energy is considered to be delocalized all over the porphyrin pairs (see ref. [13a]). Thus, the average distance (20.2 Å) from the nine porphyrins of N-(**1**–Zn)$_3$ to the ZnP moiety was chosen as R in the Förster equation.

[36] In the transient absorption spectra of the C_{60}–ZnP–Tripod/N-(**1**–Zn)$_3$ composite, the excited triplet state of ZnP was not observed (Figure 5B), whereas the spectra of C_{60}–ZnP–Tripod showed the existence of ^{3}ZnP* (Figure S7 in the Supporting Information). This observation suggests that the accommodation into N-(**1**–Zn)$_3$ made the charge-separation process of C_{60}–ZnP–Tripod more efficient. On the other hand, the charge-recombination rate was decreased by this accommodation. These observations can be explained if the charge-separated state of $ZnP^{\bullet+}$–$C_{60}^{\bullet-}$ is stabilized by N-(**1**–Zn)$_3$.

[37] We experienced difficulty in estimating the electron-transfer rate in the C_{60}–ZnP–Tripod/N-(**1**–Zn)$_3$ composite by direct excitation at the ZnP moiety in the time-resolved fluorescence-decay measurement because of the instability of the laser power at approximately 460 and 660 nm, which are wavelengths that are required for selective excitation at the ZnP moiety.

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