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Fullerene- and Pyromellitdiimide-Appended Tripodal Ligands Embedded in Light-Harvesting Porphyrin Macrorings

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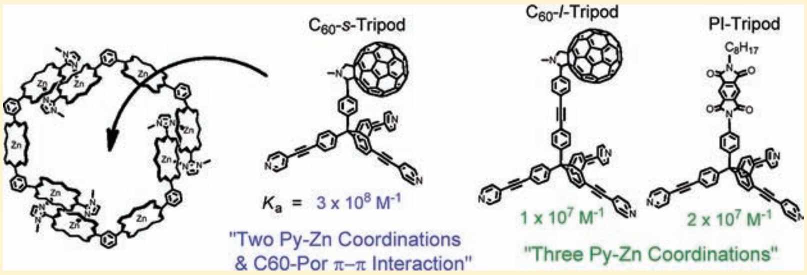
S *Supporting Information*

ABSTRACT:



Three new tripyridyl tripodal ligands appended with either fullerene or pyromellitdiimide moieties, named C_{60}−*s*−Tripod, C_{60}−*l*−Tripod, and PI−Tripod, were synthesized and introduced into a porphyrin macroring N−(**1**−Zn)$_3$ (where **1**−Zn = trisporphyrinatozinc(II)). From UV−vis absorption and fluorescence titration data, the binding constants of C_{60}−*s*−Tripod, C_{60}−*l*−Tripod, and PI−Tripod with N−(**1**−Zn)$_3$ in benzonitrile were estimated to be 3×10^8, 1×10^7, and 2×10^7 M^{-1}, respectively. These large binding constants denote multiple interactions of the ligands to N−(**1**−Zn)$_3$. The binding constants of the longer ligand (C_{60}−*l*−Tripod) and the pyromellitdiimide ligand (PI−Tripod) are almost the same as those without the fullerene or pyromellitdiimide groups, indicating that they interact via three pyridyl groups to the porphyrinatozinc(II) coordination. In contrast, the larger binding constants and the almost complete fluorescence quenching in the case of the shorter ligand (C_{60}−*s*−Tripod) indicate that the interaction with N−(**1**−Zn)$_3$ is via two pyridyl groups to the porphyrinatozinc(II) coordination and a $\pi-\pi$ interaction of the fullerene to the porphyrin(s). The fluorescence of N−(**1**−Zn)$_3$ was quenched by up to 80% by the interaction of C_{60}−*l*−Tripod. The nanosecond transient absorption spectra showed only the excited triplet peak of the fullerene on selective excitation of the macrocyclic porphyrins, indicating that energy transfer from the excited N−(**1**−Zn)$_3$ group to the fullerenyl moiety occurs in the C_{60}−*l*−Tripod/N−(**1**−Zn)$_3$ composite. In the case of PI−Tripod, the fluorescence of N−(**1**−Zn)$_3$ was quenched by 45%. It seems that the fluorescence quenching probably originates from electron transfer from the excited N−(**1**−Zn)$_3$ group to the pyromellitdiimide moiety.

INTRODUCTION

In photosynthesis, sunlight is converted into biochemical energy with a high efficiency. These light reactions begin with the capture of dilute photons from the sun by a network of chromophores, known as light-harvesting (LH) complexes. Photosynthetic purple bacteria have well-defined cyclic bacteriochlorophyll *a*s architectures, such as LH1 and LH2,[1,2] and carry out isotropic energy migration among the LHs in the photosynthetic membrane.[3] The excited energy migrates along the LHs until it finally reaches a special pair of the reaction center (RC) that can produce a stable transmembrane-spanned charge-separated state through a multistep photoinduced electron transfer process.[4] The efficient collection of sunlight and conversion of energy into electrochemical potential enable the photosynthetic living organism to use solar energy for metabolic reactions with a quantum yield of almost 100%. The construction of artificial photosynthetic systems has attracted considerable attention, not only from a pure scientific interest but also from potential applications of photosynthesis in solar energy conversion systems, which could help resolve the energy and environmental problems of the world. Porphyrin is a good chromophore for use in artificial photosynthesis because of its structural and functional similarities to natural chlorophyll. Thus, a number of researchers have studied various types of multiporphyrins and porphyrin−electron acceptor conjugated systems as models for LH and RC systems.[5−7]

We have reported on LH porphyrin macrorings[8] using a supramolecular methodology based on the complementary coordination of spacer-linked bisimidazolylporphyrinatozinc(II),[9] and have developed further the host macroring N−(**1**−Zn)$_3$ having three noncoordinated porphyrinatozinc(II) units as

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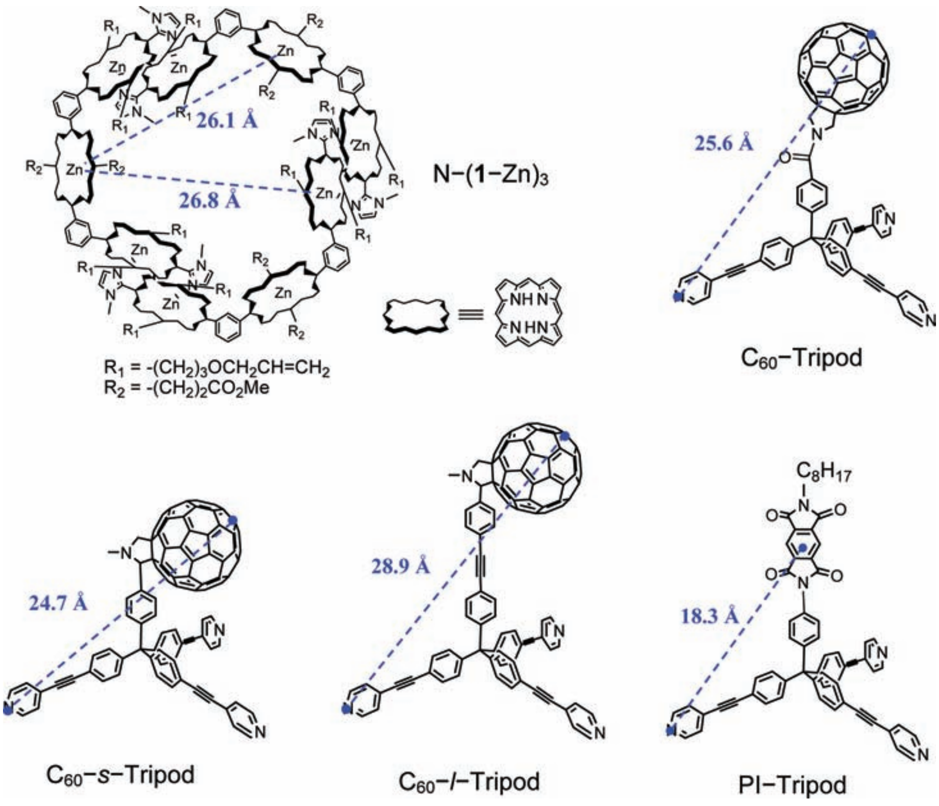


Figure 1. Molecular structures of the macroring N−(**1**−Zn)$_3$ and tripyridyl tripodal ligands. The distances were estimated from molecular models using the Material Studio software package.[13]

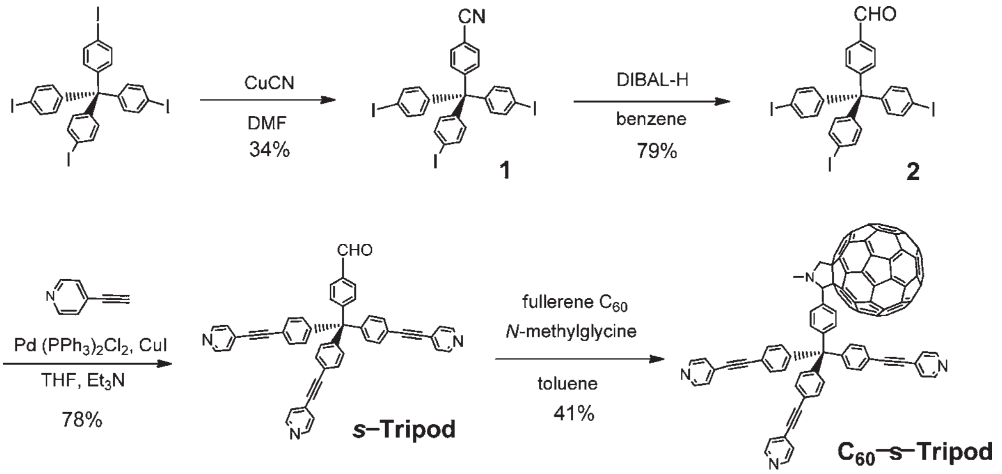
scaffolds that can accommodate the tripyridyl tripodal ligands.[10,11] We employed a tripodal pyridyl ligand with an energy acceptor porphyrin appended to a fullerene (C$_{60}$−ZnP−Tripod) as the specific guest of N−(**1**−Zn)$_3$.[11c] The composite exhibited a smooth singlet−singlet energy transfer process from the excited N−(**1**−Zn)$_3$ group to the acceptor porphyrin, followed by the production of a stable charge-separated state between the acceptor porphyrin and the appended fullerene in C$_{60}$−ZnP−Tripod. We also synthesized a tripodal ligand with a fullerene linked via an amide (C$_{60}$−Tripod), and incorporated it into N−(**1**−Zn)$_3$, aiming to induce the direct electron transfer from the excited N−(**1**−Zn)$_3$ unit to the fullerenyl moiety.[11a] Although C$_{60}$−Tripod was smoothly accommodated into N−(**1**−Zn)$_3$ with a binding constant up to 3×10^8 M^{-1}, even in a polar benzonitrile environment, and the fluorescence of N−(**1**−Zn)$_3$ was almost completely quenched, no peaks from the radical ion were detected in either the nanosecond or the picosecond transient absorption spectral measurements. These results suggest that the fullerenyl moiety of C$_{60}$−Tripod is in direct contact with the porphyrin plane(s) of N−(**1**−Zn)$_3$ through a fullerene−porphyrin $\pi-\pi$ interaction along with coordination with two pyridyl groups, resulting in fast back electron transfer.[12]

Here, we report on the synthesis of three novel tripodal acceptor ligands: C$_{60}$−*l*−Tripod, C$_{60}$−*s*−Tripod, and PI−Tripod (Figure 1). C$_{60}$−*l*−Tripod has a long phenylene−ethynylene−phenylene linker in between a fullerenyl−pyrrolidine and a tris[4-{2-(4-pyridyl)ethynyl}phenyl]methane part. In C$_{60}$−*l*−Tripod, the distance from the pyridyl nitrogen atom to the fullerenyl edge is large enough to prevent the fullerenyl moiety from being enclosed by the N−(**1**−Zn)$_3$ groups, and also to prevent a direct $\pi-\pi$ interaction between the fullerenyl moiety and the porphyrin groups of N−(**1**−Zn)$_3$, which causes a fast back electron transfer. C$_{60}$−*s*−Tripod was the reference compound, as it has a short phenylene linker, where the distance from the pyridyl nitrogen atom to the fullerenyl edge is small enough for the fullerenyl moiety to be enclosed by the N−(**1**−Zn)$_3$ group. PI−Tripod has a pyromellitdiimide as an electron acceptor. In a PI−Tripod/N−(**1**−Zn)$_3$ composite, a three-point coordination from the pyridyl groups to the porphyrinatozinc(II) groups is expected to be an exclusive binding mode, because the $\pi-\pi$ interaction between the pyromellitdiimide and the porphyrin would be weak, and furthermore, a $\pi-\pi$ stacking between PI−Tripod and N−(**1**−Zn)$_3$ is structurally not possible. By comparing the properties of these novel tripodal ligands, we attempted to construct supramolecular composites that would perform an optimal photoinduced electron transfer from LH macrorings to a central acceptor.

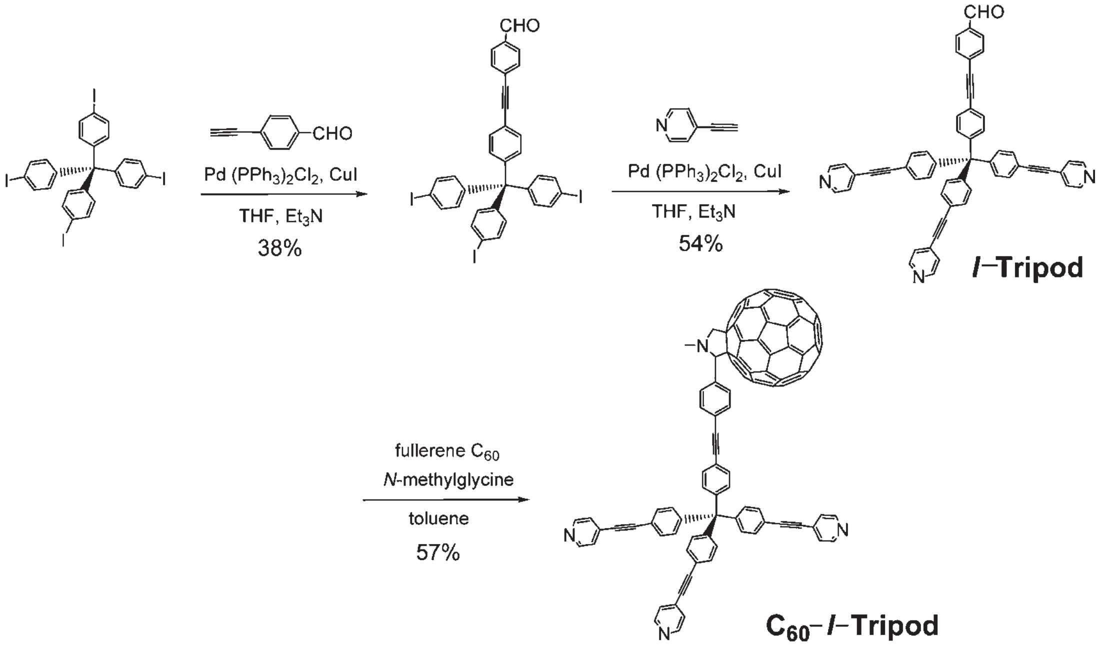
■ RESULTS AND DISCUSSION

Synthesis of C$_{60}$−*s*−Tripod, C$_{60}$−*l*−Tripod, and PI−Tripod. The C$_{60}$−*s*−Tripod, C$_{60}$−*l*−Tripod, and PI−Tripod were prepared according to Schemes 1, 2, and 3, respectively. C$_{60}$−*s*−Tripod was synthesized from tetrakis(4-iodophenyl)methane[14] in four steps. The cyanation of tetrakis(4-iodophenyl)methane was carried using 1 equiv of CuCN in dimethylformamide (DMF) to give a mixture of **1** (35%), unreacted starting material (50%), and a dicyanated byproduct (15%). The crude mixture was purified using a silica gel column to afford **1** in a yield of 34%. Cyanide **1** was reduced by DIBAL-H to the corresponding aldehyde **2** in a yield of 79%. The cross-coupling reaction of **2** with 4-ethynylpyridine[15] was carried out in the presence of a

Scheme 1. Synthetic Route of C_{60}−*s*−Tripod

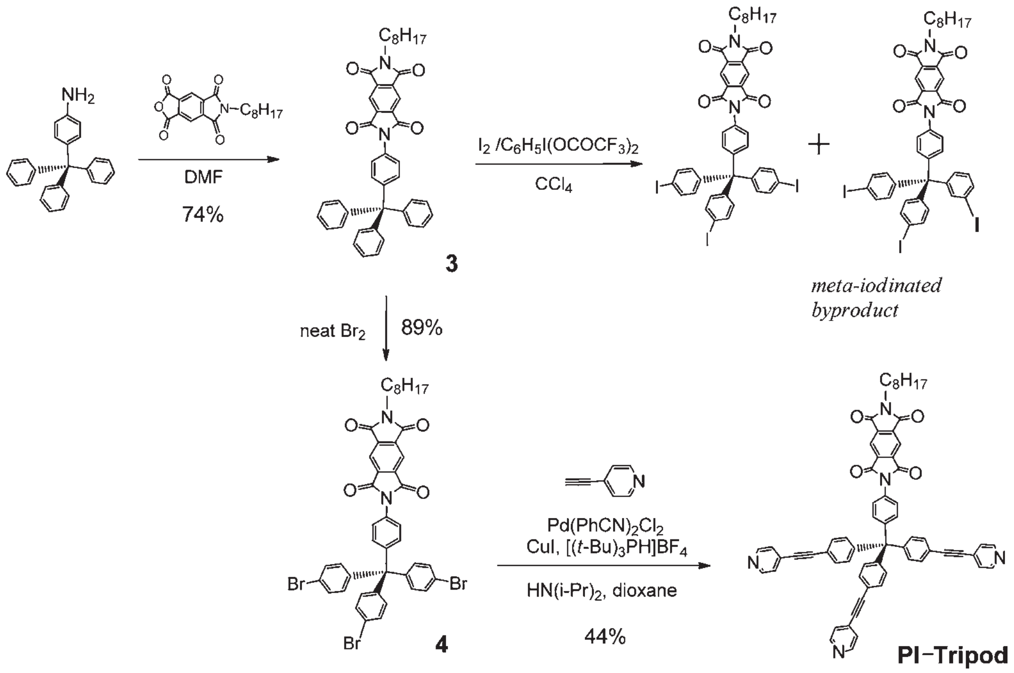


Scheme 2. Synthetic Route of C_{60}−*l*−Tripod



$Pd(PPh_3)_2Cl_2/CuI$ catalyst[16] to afford *s*−Tripod in a yield of 78%. The succeeding 1,3-dipolar cycloaddition with C_{60} and *N*-methylglycine[17] afforded C_{60}−*s*−Tripod in a yield of 41%. C_{60}−*l*−Tripod was synthesized from tetrakis(4-iodophenyl)-methane in three steps. *l*−Tripod was synthesized from tetrakis(4-iodophenyl)methane in a total yield of 21%, as has been described elsewhere.[11c] C_{60}−*l*−Tripod was synthesized using a 1,3-dipolar cycloaddition employing *l*−Tripod, C_{60} and *N*-methylglycine in a yield of 57%. PI−Tripod was synthesized according to Scheme 3. Because the starting material 4-(triphenylmethyl)aniline has an NH_2 group that strongly activates electrophilic substitution at the position *ortho* to the NH_2 group in the aniline moiety, pyromellitic monoanhydride was first introduced at the *para*-positions of the three other phenyl groups before halogenation.[18] The condensation of 4-(triphenylmethyl)aniline[14] and pyromellitic monoanhydride[19] in DMF afforded **3** in a yield of 74%. In the final cross-coupling reaction for PI−Tripod, the reactivity of aryl iodide was expected to be much higher than that of aryl bromide.[20] Thus, we first attempted to synthesize the iodinated precursor for PI−Tripod. Iodination at the *para*-positions of the three phenyl groups of **3** was first attempted using bis(trifluoroacetoxy)iodobenzene (3−5 equiv) and iodine (3−5 equiv) in CCl_4.[14] However, the iodination reaction gave a mixture of *para*- and *meta*-iodinated products (Scheme 3). The *meta* byproduct could not be removed using column chromatography, even after the successful coupling reaction with 4-ethynylpyridine. On the other hand, the bromination reaction only proceeded at the targeted *para*-positions of the three phenyl groups after treatment with neat bromine at room temperature.[21] Purification using a silica gel column gave **4** in a yield of 89%. The

Scheme 3. Synthetic Route of PI—Tripod



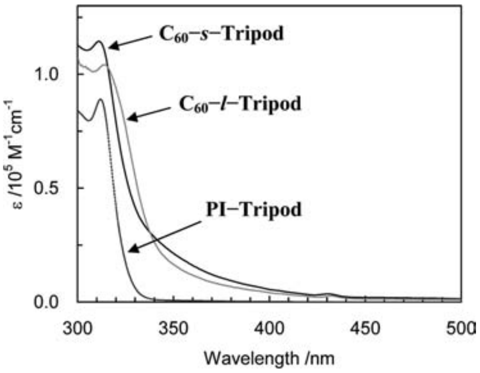


Figure 2. UV—vis absorption spectra of C_{60}—*s*—Tripod ($CHCl_3$), C_{60}—*l*—Tripod (benzonitrile), and PI—Tripod ($CHCl_3$) at 25 °C.

cross-coupling reaction of **4** with 4-ethynylpyridine hardly proceeded when $Pd(PPh_3)_2Cl_2$ and CuI were used as catalysts. To overcome this problem, the bulky and strong electron-donating phosphine ligand ($P(t\text{-}Bu)_3$) was used instead of PPh_3.[20] The coupling reaction proceeded at room temperature in the presence of $Pd(PhCN)_2Cl_2$, ($(t\text{-}Bu)_3PH)BF_4$ and CuI, and afforded PI—Tripod in a yield of 44%. C_{60}—*s*—Tripod, C_{60}—*l*—Tripod, and PI—Tripod were characterized using ^1H and ^{13}C NMR, Matrix-Assisted Laser Desorption/Ionization-Time-of-Flight (MALDI-TOF) mass spectrometry, high-resolution mass spectrometry, and UV—vis absorption spectroscopy.

The UV—vis absorption spectra of C_{60}—*s*—Tripod, C_{60}—*l*—Tripod, and PI—Tripod are shown in Figure 2. The spectra of C_{60}—*s*—Tripod and C_{60}—*l*—Tripod show a strong absorption in the UV region accompanied by a weak absorption that extended continuously to the visible region, which originated from the absorption of the fullerenyl moiety. In the case of PI—Tripod, there was no absorption extending to the visible region (>450 nm).

Binding Modes of C_{60}—*s*—Tripod, C_{60}—*l*—Tripod, and PI—Tripod to N—(1—Zn)$_3$. Incorporation of the acceptor tripodal ligands into the N—(**1**—Zn)$_3$ group was determined using UV—vis absorption and fluorescence titration. The experiments were performed in benzonitrile as a suitable solvent to stabilize the charge-separated species. The binding mode of the tripodal ligands to N—(**1**—Zn)$_3$ was estimated by comparing their binding constants with the corresponding tripodal ligand without their acceptors. If almost the same values were observed between the two tripodal ligands, with and without the acceptor, the binding mode was concluded to maintain the three-point coordination of the pyridyl group to the zinc atom. The changes in the UV—vis absorption spectra are shown in Supporting Information, Figures S15—S17. In all three spectra, a small decrease and a red-shift of the Sorbet band region was observed. No change in the Q-band was observed, because benzonitrile was already coordinated to the uncoordinated porphyrinatozinc(II).[11a] The change in the fluorescence spectra of N—(**1**—Zn)$_3$ on addition of the acceptor ligands is shown in Figure 3. The fluorescence of N—(**1**—Zn)$_3$ (4.0×10^{-7} M) is efficiently quenched by 98% with 2.8 equiv of C_{60}—*s*—Tripod (Figure 3A, inset). The binding constant estimated from the UV—vis absorption and fluorescence titration data was almost same: 3×10^8 and 4×10^8 M^{-1}, respectively.[22] These values are 10 times the value of 2.9×10^7 M^{-1} of the precursor *s*—Tripod, suggesting a switch of the binding mode to a two-point coordination of the pyridyl group to the zinc atom and a π—π interaction between the fullerenyl moiety and the porphyrin(s) in N—(**1**—Zn)$_3$, as was observed previously. [11a] The almost complete fluorescence quenching is similar to the previous case, consistent with this binding mode.

On the titration of C_{60}—*l*—Tripod, the binding constant was estimated from the UV—vis absorption and fluorescence titration

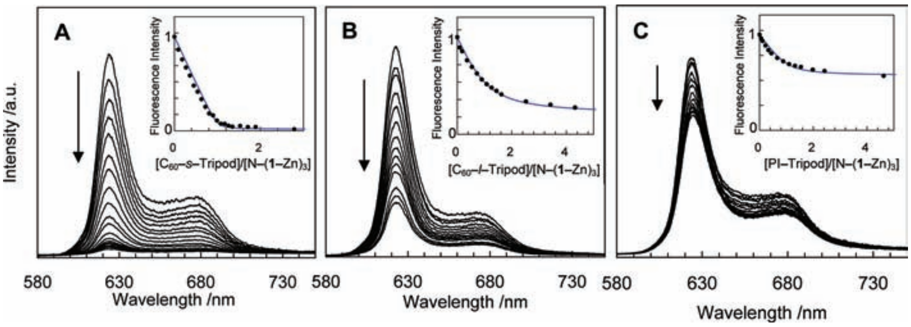


Figure 3. Steady-state fluorescence quenching of N−(**1**−Zn)$_3$ from the addition of: (A) C$_{60}$−*s*−Tripod, (B) C$_{60}$−*l*−Tripod, and (C) PI−Tripod in benzonitrile at 25 °C. When excited at 567 nm: (A) [N−(**1**−Zn)$_3$] = 4.0 × 10^{-7} M, [C$_{60}$−*s*−Tripod] = 0−2.8 equiv, (B) [N−(**1**−Zn)$_3$] = 2.5 × 10^{-7} M, [C$_{60}$−*l*−Tripod] = 0−4.3 equiv, (C) [N−(**1**−Zn)$_3$] = 3.9 × 10^{-7} M and [PI−Tripod] = 0−4.6 equiv. The insets show the change in fluorescence intensity with the signal integration (●) and the theoretical curves (blue lines) for: (A) K_a = 4 × 10^8 M^{-1}, (B) K_a = 1.3 × 10^7 M^{-1}, and (C) K_a = 2.0 × 10^7 M^{-1}.

Table 1. Binding Constants, K_a, and Fluorescence Quenching Efficiencies of N−(1−Zn)$_3$ of Tripodal Ligands in Benzonitrile at 25 °C, and Distances from the Pyridyl Nitrogen Atom and the Fullerene Edge of the Tripodal Ligands

		s−Tripod	C$_{60}$−*s*−Tripod	C$_{60}$−Tripod[a]	*l*−Tripod	C$_{60}$−*l*−Tripod	PI−Tripod
K_a/M^{-1}	fluorescence[b]		4 × 10^{8}[e]	3.4 × 10^8		1.3 × 10^7	2.0 × 10^7
	UV−vis	2.9 × 10^7	3 × 10^{8}[e]	3.1 × 10^8	1.1 × 10^7	1.0 × 10^7	2.3 × 10^7
quenching efficiency[b,c]		*f*	98%	97%	*f*	80%	45%
distance[d]			24.7 Å	25.6 Å		28.9 Å	

[a] Ref 11a. [b] The data were obtained using an excitation wavelength at 567 nm. [c] These values were calculated assuming a complexation rate of 100%. [d] See Figure 1. [e] Ref 22. [f] No fluorescence quenching was observed.

data to be 1.0 × 10^7 and 1.3 × 10^7 M^{-1}, respectively. The fluorescence of N−(**1**−Zn)$_3$ was quenched by 80% (Figure 3B, inset). The binding constant of C$_{60}$−*l*−Tripod was similar to that of the precursor, *l*−Tripod (1.1 × 10^7 M^{-1}), indicating that it maintained the three-point coordination of the pyridyl group to the zinc atom.

Fluorescence titration using PI−Tripod in benzonitrile is shown in Figure 3C. From the UV−vis absorption and the fluorescence titration curves, the binding constants were estimated to be 2.3 × 10^7 and 2.0 × 10^7 M^{-1}, respectively. The fluorescence of N−(**1**−Zn)$_3$ was quenched by 45% (Figure 3C, inset). The binding constant of PI−Tripod was almost the same as that of the tripodal ligands,[10,23] indicating a three-point coordination of the pyridyl group to the zinc atom.

All the binding constants and the fluorescence quenching efficiencies in benzonitrile are summarized in Table 1. Judging from these data, it was estimated that C$_{60}$−*s*−Tripod interacted with the N−(**1**−Zn)$_3$ group as a two-point pyridyl coordination along with a fullerene−porphyrin contact, whereas the other two ligands interacted as a three-point coordination.

According to the molecular model created using the Material Studio software package,[13] the distance in C$_{60}$−*s*−Tripod from the pyridyl nitrogen atom to the fullerenyl edge was estimated to be 24.7 Å, which is smaller than the cavity of N−(**1**−Zn)$_3$ (Figure 1) based on the coordination bond length (approximately 2.1 Å)[24] between the pyridyl nitrogen atom and the porphyrinatozinc atom. Thus, the fullerenyl moiety is incorporated inside the N−(**1**−Zn)$_3$ ring and so gains a high degree of entropy from the release of constricted solvent molecules located inside the cavity.[23] In the case of C$_{60}$−*l*−Tripod, the distance from the pyridyl nitrogen atom to the fullerenyl edge was estimated to be 28.9 Å, which is too large for the fullerenyl moiety to be enclosed by the ring. The pyromellitimide moiety of PI−Tripod cannot be located inside the cavity, because weak $\pi-\pi$ interaction between the pyromellitdiimide and the porphyrin ring cannot replace the three cooperative pyridyl−porphyrinatozinc coordinations. The prospective structures of their composites are shown in Figure 4.

Photodynamic Properties of Macroring/Tripodal Ligand Composites. The results of the binding constant and the fluorescence quenching experiments suggest that the binding mode of C$_{60}$−*s*−Tripod is the same as that of C$_{60}$−Tripod. Thus, a stable charge-separated state is not expected, as observed previously.[11a] On the other hand, the fullerenyl moiety in the C$_{60}$−*l*−Tripod/N−(**1**−Zn)$_3$ composite must locate not inside, but over the cavity. Because the nearest edge-to-edge distance between the porphyrin and the fullerenyl moiety in this composite is estimated to be 13 Å, the formation of a stable charge-separated state is expected if the photoinduced electron transfer from the excited N−(**1**−Zn)$_3$ group to the fullerenyl moiety occurs.[6]

The time-resolved fluorescence decay and nanosecond transient absorption were measured to investigate the photophysical dynamics of the C$_{60}$−*l*−Tripod/N−(**1**−Zn)$_3$ composite. Under these conditions, the binding constants ensured that more than 95% of the macroring existed as a complex with C$_{60}$−*l*−Tripod. The fluorescence time profile of the C$_{60}$−*l*−Tripod/N−(**1**−Zn)$_3$ composite decayed biexponentially with a time constant of 184 ps (70%) and 1220 ps (30%). The minor longer-lived component may arise from impurities or decomposed products. The quenching rate (k_q) and the quantum yield (Φ_q) were evaluated to be 5.0 × 10^9 s^{-1} and 0.9 from the shorter-lifetime component using the lifetime of 2100 ps of free N−(**1**−Zn)$_3$.[11a] The nanosecond transient absorption spectra were measured to elucidate the quenching mechanism of the

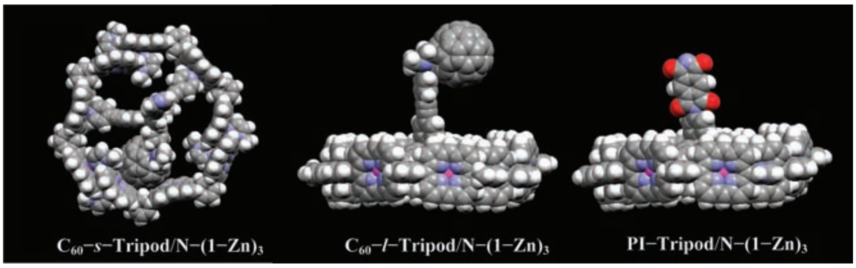


Figure 4. Prospective structures of C_{60}−*s*−Tripod, C_{60}−*l*−Tripod, and PI−Tripod accommodated by N−(**1**−Zn)$_3$. (The left image is depicted from the top. The others are side views).

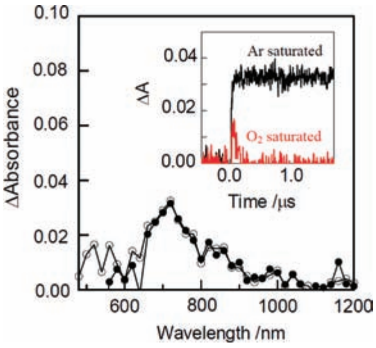


Figure 5. Nanosecond transient absorption spectra of the composite formed by mixing N−(**1**−Zn)$_3$ (1.2×10^{-6} M) and C_{60}−*l*−Tripod (2.6×10^{-6} M) in benzonitrile at 0.1 μs (●) and 1.0 μs (○) after laser irradiation at 532 nm. Inset = absorption-time profiles at 720 nm in Ar- and O_2-saturated benzonitrile.

excited singlet state of N−(**1**−Zn)$_3$. The spectra were obtained using laser irradiation at 532 nm so that the N−(**1**−Zn)$_3$ group was excited selectively. The transient absorption spectra showed a peak occurring at 720 nm without a signal occurring around 1000 nm corresponding to the fullerenyl radical anion (Figure 5), whose spectrum is similar to that observed in only C_{60}−*l*−Tripod (Supporting Information, Figure S18). The decay profile at 720 nm was reduced markedly on exposure to oxygen (Figure 5 inset). These results indicate that the species resulting from photoexcitation of the macroring porphyrins is the excited triplet state of fullerene formed by intersystem crossing (ISC) from $^1C_{60}{}^*$, which is produced after the singlet−singlet energy transfer from N−(**1**−Zn)$_3$ to fullerene. Such energy transfer and ISC processes may occur competitively with the photoinduced electron transfer from $C_{60}/^1$N−(**1**−Zn)$_3{}^*$ and $^1C_{60}{}^*$/N−(**1**−Zn)$_3{}^*$ to yield $C_{60}{}^{\bullet-}$/N− (**1**−Zn)$_3{}^{\bullet+}$, which is thermodynamically possible. Absence of a clear absorption peak from $C_{60}{}^{\bullet-}$ at 1000 nm, even in the spectrum at 0.1 μs in Figure 5, suggests that $C_{60}{}^{\bullet-}$/N− (**1**−Zn)$_3{}^{\bullet+}$ has a considerably shorter lifetime, and mostly returns to the neutral ground state within a period of 0.1 μs, leaving only $^3C_{60}{}^*$.

The energy transfer process is also supported by the result that the fluorescence quenching efficiency of N−(**1**−Zn)$_3$ by the addition of C_{60}−*l*−Tripod in less polar benzene is almost same (83%) as that in benzonitrile (80%). Since fullerene has a weak, but steady absorption band in the visible region (Supporting Information, Figure S19), the through-space singlet−singlet energy transfer rate, k_{TS}, from N−(**1**−Zn)$_3$ to the fullerenyl moiety of C_{60}−*l*−Tripod can be calculated using the following Förster equation:

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

where κ^2, Φ, τ, R, and J are the orientation factor of the donor and acceptor, the fluorescence quantum yield, the fluorescence lifetime of the donor, the distance between the donor and the acceptor, and the spectral integral of the fluorescence of the donor and the absorption of the acceptor, respectively. The orientation factor of $\kappa^2 = 2/3$ was used for randomly orientated dipoles[25] to estimate the energy transfer rate. The fluorescence quantum yield of $\Phi = 0.039$ and the fluorescence lifetime of $\tau = 2.1$ ns were obtained from the experiments.[11a] The distance between the center of the acceptor and the center of the nearest donor, $R = 16$ Å, was estimated from molecular modeling using the Material Studio software package, and the spectral integral was calculated to be $J \approx 5 \times 10^{-15}$ cm^6 mmol^{-1} from the experimental data. The energy transfer rate, k_{TS}, from N−(**1**−Zn)$_3$ to the fullerenyl moiety was calculated to be approximately 6×10^8 s^{-1} using eq 1. The calculated value is comparable to the experimental value (5.0×10^9 s^{-1}). The difference between the two values may come from contributions of Dexter-type through-bond energy transfers or higher-order multipole−multipole interactions, which is neglected in the Förster approximation,[26] otherwise, of electron transfer from $C_{60}/^1$N−(**1**−Zn)$_3{}^*$ to yield $C_{60}{}^{\bullet-}$/N−(**1**−Zn)$_3{}^{\bullet+}$. The three-point coordination from the pyridyl groups to the porphyrins makes fullerenyl moiety of C_{60}−*l*−Tripod to be fixed tightly over the center of the cavity of the N−(**1**−Zn)$_3$. Since the through-bond pathway from the porphyrins to the fullerene moiety is very long, the electron transfer is expected to occur via the through-space pathway. However, the superexchange interaction involving only solvent molecules would be too small for the electron transfer to compete the energy transfer, resulting in the singlet−singlet energy transfer mostly.

In the PI−Tripod/N−(**1**−Zn)$_3$ composite, the possibility of a through-space singlet−singlet energy transfer from an excited N−(**1**−Zn)$_3$ group to a pyromellitdiimide moiety can be excluded owing to both the zero absorption of PI−Tripod in the visible region where the fluorescence of N−(**1**−Zn)$_3$ occurs (Figure 2) and the higher energy of ^{1}PI*/N−(**1**−Zn)$_3$ (approximately 3.7 eV) than PI/^{1}N−(**1**−Zn)$_3{}^*$ (2.0 eV). The energy level of the ion-pair state, PI$^{\bullet-}$/N−(**1**−Zn)$_3{}^{\bullet+}$, was estimated to be 1.34 eV above the ground state.[28] Therefore, the photoinduced electron transfer from PI/^{1}N−(**1**−Zn)$_3{}^*$ to yield PI$^{\bullet-}$/N−(**1**−Zn)$_3{}^{\bullet+}$ should have sufficient driving force. Table 2 shows the solvent dependency of the binding constant of PI−Tripod and the fluorescence quenching. The fluorescence

Table 2. Solvent Dependency of the Steady-State Fluorescence Quenching Rate of PI-Tripod/N−(**1**−Zn)$_3$ Composite[a]

			N−(**1**−Zn)$_3$			
solvent	ε[b]	binding constant[c]/M^{-1}	Φf[d]	τ_f[e]/ns	quenching efficiency[f]	quenching rate[g]/s^{-1}
toluene	2.38	$>10^8$ ($>4 \times 10^8$)	5.1%	2.2	31%	2.0×10^8
chloroform[h]	4.81	4.5×10^7 (3.0×10^7)	3.4%	2.0	38%	3.1×10^8
benzonitrile	25.2	2.0×10^7 (2.3×10^7)	3.9%	2.1	45%	3.9×10^8

[a] Excited at 567 nm. [b] Dielectric constant. [c] Estimated from fluorescence titration. The values in parentheses were estimated from UV−vis titration data. [d] The fluorescence quantum yield of free N−(**1**−Zn)$_3$ was determined using ZnTPP of = 3.3% as the standard value.[27] [e] Fluorescence lifetime of free N−(**1**−Zn)$_3$. [f] These values were calculated assuming a complexation rate of 100%. [g] The quenching rate constant was calculated using the following equation, $k_q = 1/\tau_f \times \Phi_q/(1 - \Phi_q)$, where τ_f is the fluorescence lifetime of free N−(**1**−Zn)$_3$ and Φ_q is the steady-state fluorescence quenching efficiency. [h] Chloroform containing 0.5% EtOH as a stabilizer.

quenching was more efficient in a polar solvent, such as benzonitrile. This observation suggests that photoinduced electron transfer occurs from N−(**1**−Zn)$_3$ to the pyromellitdiimide moiety. Since the center-to-center distance between the nearest porphyrin ring and the pyromellitdiimide moiety in the composite was estimated to be 16 Å, photoinduced electron transfer in the PI−Tripod/N−(**1**−Zn)$_3$ composite is considered most likely to be the result of a superexchange coupling via the linker moieties of PI−Tripod. The transient absorption spectrum at 0.1 μs after laser irradiation showed neither a definitive charge-separated species nor a triplet excited state of N−(**1**−Zn)$_3$ formed by ISC from ^{1}N−(**1**−Zn)$_3$*. This strongly indicates that a fast charge recombination to the ground state occurred after the initial charge separation.

CONCLUSIONS

We have synthesized three new acceptor tripodal ligands having fullerene or pyromellitdiimide moieties. The tripodal ligands having fullerene through a long linker (C_{60}−*l*−Tripod) and the tripodal ligand containing pyromellitdiimide (PI−Tripod) were accommodated via a three-point coordination from a pyridyl group to a porphyrinatozinc(II) group. In a C_{60}−*l*−Tripod/N−(**1**−Zn)$_3$ composite, the singlet−singlet energy transfer from the excited porphyrin in N−(**1**−Zn)$_3$ to the fullerene occurs in preference to electron transfer, even in polar benzonitrile. In this case, the fullerene works as a good energy acceptor because the fullerenyl moiety of C_{60}−*l*−Tripod is tightly fixed over the center of the cavity of the N−(**1**−Zn)$_3$ group with a lower electronic orbital coupling with the donor N−(**1**−Zn)$_3$ group, and the fullerenyl moiety has an absorption peak in the region where the fluorescence of the N−(**1**−Zn)$_3$ group appears. In the case of the PI−Tripod/N−(**1**−Zn)$_3$ composite, where the pyromellitdiimide moiety has no absorption in the visible region, a solvent dependence of the quenching rate was observed, indicating that electron transfer from the excited N−(**1**−Zn)$_3$ group to the pyromellitdiimide moiety occurred.

EXPERIMENTAL SECTION

General Procedure. All chemicals and solvents were of commercial reagent grade, and used without further purification unless otherwise stated. Dry tetrahydrofuran (THF), 1,4-dioxane, benzene, and toluene were prepared by distillation over benzophenone-Na. Dry dimethylformamide (DMF) and triethylamine (Et_3N) were prepared by distillation over CaH_2. ^{1}H NMR spectra (600 MHz) were recorded on JEOL ECP-600, and chemical shifts were recorded in parts per million (ppm) relative to tetramethylsilane. 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. The fluorescence intensities were normalized at the absorption of their excitation wavelengths. UV−vis λ_{max} (log ε) values are reported in nanometers (nm). Quantum yields were determined by corrected integrated ratios of steady-state fluorescence spectra relative to that of ZnTPP (Φ_f = 3.3% in benzene; tetraphenylporphyrinatozinc(II)).[27] MALDI-TOF mass spectra were obtained on PerSeptive Biosystems Voyager DE-STR with dithranol (Aldrich) as the matrix. 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 (Spherical, Neutral) 60−210 μm and 40−210 μm (Flash). The nanosecond transient absorption spectra in the NIR region were measured by means of laser-flash photolysis; 565 nm light from 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.[29]

4-Cyanophenyl-tris(4-iodophenyl)methane (1). In a 300 mL three necked flask equipped with a dropping funnel, a reflux condenser, and a N_2 balloon were placed tetrakis(4-iodophenyl)methane (1 g, 1.2×10^{-3} mol)[14] and dry DMF (100 mL) under N_2 atmosphere. The mixture was heated at 140 °C to become a homogeneous solution. CuCN (78 mg, 1.2×10^{-3} mol) dissolved in dry DMF (40 mL) was then added dropwise. The reaction mixture was stirred for 24 h at 140 °C. After the solvent was evaporated, toluene (approximately 100 mL) and aqueous ammonia solution (approximately 100 mL) were added and stirred overnight. The organic layer was collected, washed with aqueous ammonia solution and water, and dried over anhydrous Na_2SO_4. The residue obtained by evaporation of the solvent was purified with a short silica gel column chromatography ($CHCl_3$/hexane 1:1 to $CHCl_3$). The fraction eluted with $CHCl_3$ was collected and evaporated to afford 295 mg (34%) of the titled compound: TLC (silica gel, $CHCl_3$/hexane 1:2) R_f = 0.2, (silica gel, $CHCl_3$) R_f = 0.7; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS) δ 7.60 (d, *J* = 8.4 Hz, 6H, *Ph*), 7.56 (d, *J* = 8.4 Hz, 2H, *Ph*-CN), 7.29 (d, *J* = 8.4 Hz, 2H, *Ph*-CN), 6.86 (d, *J* = 8.4 Hz, 6H, *Ph*).

4-Formylphenyl-tris(4-iodophenyl)methane (2). In a 50 mL flask was placed **1** (295 mg, 4.1×10^{-4} mol), and the flask was evacuated and replaced with Ar gas. Dry benzene (5 mL) was added to it, and the solution was cooled to 0 °C, and then 0.95 M hexane solution of diisobutylaluminum hydride (DIBAL-H, 1.2 mL, 1.1×10^{-3} mol) was added at 0 °C. The reaction mixture was warmed to room temperature and stirred for 1.5 h. The reaction was quenched by addition of 5% H_2SO_4 aqueous solution. The organic layer was collected, and the aqueous layer was extracted with benzene several times (Benzene is a cancer suspect agent and flammable liquid. Toluene should be substituted for benzene.). The combined organic layer was washed with water and dried over anhydrous Na_2SO_4, and then the solvent was evaporated. The residue was purified with a silica gel column chromatography ($CHCl_3$), giving 235 mg (79%) of the titled compound: TLC (silica gel, $CHCl_3$)

R_f = 0.6; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS) δ 9.99 (s, 1H, *CHO*), 7.78 (d, *J* = 7.0 Hz, 2H, *Ph*-CHO), 7.60 (d, *J* = 7.3 Hz, 6H, *Ph*), 7.35 (d, *J* = 7.0 Hz, 2H, *Ph*-CHO), 6.91 (d, *J* = 7.3 Hz, 6H, *Ph*).

4-Formylphenyl-tris[4-{2-(4-pyridyl)ethynyl}phenyl]methane (*s*−Tripod). In a Schlenk flask were placed **2** (116 mg, 1.6×10^{-4} mol), 4-ethynylpyridine (82 mg, 8.0×10^{-4} mol),[15] $Pd(PPh_3)_2Cl_2$ (13 mg, 1.9×10^{-5} mol), and CuI (3.7 mg, 1.9×10^{-5} mol) under Ar atmosphere. Dry Et_3N (0.5 mL) and dry THF (0.5 mL) were added to it, and the mixture was degassed by freeze−thaw cycles. The reaction mixture was stirred at room temperature under Ar atmosphere. After stirring for 1 h, further dry THF (1 mL) was added to the reaction mixture to dissolve the insoluble solid. After stirring for 20 h, the reaction mixture was diluted with chloroform, washed with water and dried over anhydrous Na_2SO_4. The residue obtained by evaporation of the solvent was purified with a silica gel column chromatography ($CHCl_3$/MeOH 9:1). The fractions showing the signals of the target compound on MALDI-TOF mass spectra were concentrated and reprecipitated with hexane to remove a byproduct of 1,4-bis(4-pyridyl)butadiyne. Further purification was performed with a silica gel column chromatography ($CHCl_3$/MeOH 9:1), giving 80.9 mg (78%) of the titled compound: TLC (silica gel, $CHCl_3$/MeOH 9:1) R_f = 0.3; MALDI-TOF MS found *m*/*z* 652.6 (MH^+); HRMS (FAB) calcd for $C_{47}H_{30}N_3O$ (MH^+) 652.2389, found 652.2383; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS) δ 10.02 (s, 1H, *CHO*), 8.60 (d, *J* = 6.0 Hz, 6H, *Py*), 7.83 (d, *J* = 8.2 Hz, 2H, *Ph*-CHO), 7.50 (d, *J* = 8.5 Hz, 6H, *Ph*), 7.43 (d, *J* = 8.2 Hz, 2H, *Ph*-CHO), 7.37 (d, *J* = 6.0 Hz, 6H, *Py*), 7.25 (d. *J* = 8.5 Hz, 6H, *Ph*); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C) δ 191.5, 152.0, 149.8, 146.1, 134.6, 131.6, 131.3, 131.1, 130.8, 129.3, 125.5, 120.6, 93.16, 87.31, 65.36.

C_{60}−*s*−Tripod. In a Schlenk flask were placed *s*−Tripod (15 mg, 2.3×10^{-5} mol), C_{60} (83 mg, 1.2×10^{-4} mol), and *N*-methylglycine (107 mg, 1.2×10^{-3} mol). The flask was evacuated and replaced with Ar gas. Toluene (10 mL) was added to it, and the mixture was heated at 100 °C and stirred for 21 h. The solvent was evaporated to give a crude residue, which was passed through a short silica gel column by using toluene, and then, $CHCl_3$/MeOH 9:1 as eluents to remove excess C_{60}. The fractions eluted with $CHCl_3$/MeOH 9:1 was collected and evaporated. Further purification was performed with a silica gel column chromatography ($CHCl_3$/MeOH 99:1 to 98:2), giving 13 mg (41%) of the titled compound: TLC (silica gel, $CHCl_3$/MeOH 9:1) R_f = 0.6; MALDI-TOF MS found *m*/*z* 1400.6 (MH^+); HRMS (ESI) calcd for $C_{109}H_{35}N_4$ (MH^+) 1399.2862, found 1399.2861; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS) δ 8.60 (*brs*, 6H, *Py*), 7.52−7.77 (*brs*, 2H, *Ph*-pyrrolidine), 7.41 (d, *J* = 8.2 Hz, 6H, *Ph*), 7.34 (*brd*, *J* = 4.8 Hz, 6H, *Py*), 7.25 (*brs*, *Ph*-pyrrolidine), 7.19 (d. *J* = 8.2 Hz, 6H, *Ph*), 4.98 (d, *J* = 9.6 Hz, 1H, pyrrolidine CH_2), 4.96 (s, 1H, pyrrolidine *CH*), 4.28 (d, *J* = 9.6 Hz, 1H, pyrrolidine CH_2), 2.90 (s, 3H, $N-CH_3$); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C) δ 156.19, 153.85, 153.29, 152.96, 149.76, 147.32, 147.28, 146.89, 146.65, 146.43, 146.27, 146.20, 146.11, 146.09, 145.95, 145.88, 145.72, 145.56, 145.52, 145.41, 145.36, 145.29, 145.21, 145.14, 144.98, 144.70, 144.68, 144.40 144.30, 143.16, 143.0,1 142.69, 142.58, 142.44, 142.21, 142.15, 142.07, 142.03, 141.92, 141.72, 141.67, 141.46, 140.21, 140.12, 139.71, 139.06, 136.50, 136.41, 135.97, 135.78, 135.72, 131.42, 131.26, 130.82, 128.79, 125.54, 120.20, 93.54, 87.18, 82.78, 77.37, 70.04, 68.93, 65.11, 40.05; UV−vis ($CHCl_3$) 257 (5.17), 292 (5.08), 311 (5.06), 430 (3.56), 703.5 (2.60).

C_{60}−*l*−Tripod. In a test tube with screw cap were placed *l*−Tripod (4.2 mg, 5.6×10^{-6} mol),[11c] C_{60} (20 mg, 2.8×10^{-5} mol), *N*-methylglycine (25 mg, 2.8×10^{-4} mol), and toluene (1 mL), and the tube was purged with N_2 gas. The reaction mixture was heated to 100 °C and stirred for 32 h. The resulting solution was passed through a short silica gel column (toluene to $CHCl_3$/MeOH 9:1) to remove excess C_{60}. The fraction eluted with $CHCl_3$/MeOH 9:1 was collected and evaporated. Further purification was performed with a silica gel column chromatography ($CHCl_3$/MeOH 99:1 to 98:2), giving 4.8 mg (57%) of the titled compound: TLC (silica gel, $CHCl_3$/MeOH 9:1) R_f = 0.8; MALDI-TOF MS found *m*/*z* 1500.0 (MH^+); HRMS (ESI) calcd for $C_{117}H_{39}N_4$ 1499.3175 (MH^+), found 1499.3170; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS) δ 8.60 (d, *J* = 5.4 Hz, 6H, *Py*), 7.81 (*brs*, 2H, *Ph*-pyrrolidine), 7.59 (d, *J* = 7.8 Hz, 2H, *Ph*-pyrrolidine), 7.47 (d, *J* = 9.0 Hz, 6H, *Ph*), 7.44 (d, *J* = 9.0 Hz, 2H, *Ph′*), 7.36 (d, *J* = 5.4 Hz, 6H, *Py*), 7.23 (d, *J* = 9.0 Hz, 6H, *Ph*), 7.18 (d, *J* = 9.0 Hz, 2H, *Ph′*), 4.99 (d, *J* = 9.6 Hz, 1H, pyrrolidine CH_2), 4.95 (s, 1H, pyrrolidine *CH*), 4.27 (*J* = 9.6 Hz, 1H, pyrrolidine CH_2), 2.81 (s, 3H, $N-CH_3$); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C) δ 156.1, 153.9, 153.1, 153.0, 149.8, 147.33, 147.31, 146.6, 146.4, 146.32, 146.30, 146.23, 146.20, 146.15, 146.01, 145.95, 145.7, 145.6, 145.52, 145.48, 145.42, 145.37, 145.29, 145.27, 145.24, 145.18, 144.7, 144.6, 144.42, 144.36, 143.2, 143.0, 142.7, 142.60, 142.56, 142.25, 142.24, 142.18, 142.14, 142.10, 142.05, 141.99, 141.9, 141.8, 141.7, 141.6, 140.21, 140.19, 139.9, 139.5, 140.22, 140.19, 139.9, 139.5, 137.6, 136.9, 136.4, 135.9, 135.7, 131.9, 131.5, 131.3, 131.2, 130.9, 130.8, 125.5, 123.1, 121.5, 120.4, 93.37, 89.83, 89.45, 87.19, 83.27, 70.00, 69.06, 65.03, 40.00; UV−vis (benzonitrile) 314 (5.02), 432 (3.42).

***N*-{4-(Triphenylmethyl)phenyl}-*N′*-(*n*-octyl)pyromellitdiimide (3).** In a 20 mL flask were placed *N*-(*n*-octyl)pyromellitic monoanhydride (100 mg, 3.0×10^{-4} mol),[19] 4-(triphenylmethyl)aniline (102 mg, 3.0×10^{-4} mol), and dry DMF (2 mL). The mixture was purged with N_2 gas and then heated at 130 °C for 6 h. A white solid generated during cooling was collected by filtration and washed with hexane, affording 117.6 mg (60%) of the titled compound. The filtrate of the reaction mixture was evaporated and the residue was recrystallized in acetic anhydride. The crystal was collected by filtration and dried in vacuo, giving 26.7 mg (14%) of the titled compound. Total yield was 144.3 mg (74%): TLC (silica gel, $CHCl_3$) R_f = 0.5; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS) δ 8.57 (s, 2H, *Ph-PI*), 7.39 (d, *J* = 9.0 Hz, 2H, *Ph′*), 7.36 (d, *J* = 9.0 Hz, 2H, *Ph′*), 7.20−7.29 (m, 15H, *Ph*), 3.75 (t, *J* = 7.5 Hz, 2H, $C_\alpha H_2$), 1.71 (quintet, *J* = 6.9 Hz, 2H, $C_\beta H_2$), 1.24−1.34 (m, 10H, CH_2), 0.87 (t, *J* = 6.9 Hz, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C) δ 166.2, 165.3, 147.3, 146.3, 137.6, 136.7, 131.9, 131.1, 128.8, 127.6, 126.1, 125.0, 118.7, 64.86, 38.82, 31.72, 29.10, 29.06, 28.41, 26.83, 22.58, 14.04.

***N*-[4-{Tris(4-bromophenyl)methyl}phenyl]-*N′*-(*n*-octyl)pyromellitdiimide (4).** In a 20 mL flask were placed **3** (165 mg, 2.6×10^{-4} mol) and neat bromine (1 mL), and then the reaction mixture was stirred for 30 min at room temperature. The reaction mixture was diluted with $CHCl_3$ (20 mL) and washed successively with an aqueous sodium bisulfite solution and water. The organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated. The residue was purified with silica gel column chromatography ($CHCl_3$/hexane 1:2 to $CHCl_3$/MeOH 9:1) to afford 201 mg (89%) of the titled compound: TLC (silica gel, $CHCl_3$) R_f = 0.8; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS) δ 8.37 (s, 2H, *Ph-PI*), 7.41 (d, *J* = 8.2 Hz, 8H, *Ph* and *Ph′*), 7.32 (d, *J* = 8.5 Hz, 2H, *Ph′*), 7.08 (d, *J* = 8.2 Hz, 6H, *Ph*), 3.75 (t, *J* = 7.1 Hz, 2H, $C_\alpha H_2$), 1.71 (*brquintet*, 2H, $C_\beta H_2$), 1.26−1.34 (m, 10H, CH_2), 0.87 (t, *J* = 6.6 Hz, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C) δ 166.0, 165.1, 145.6, 144.4, 137.7, 136.6, 132.4, 131.4, 131.1, 129.4, 125.4, 120.8, 118.7, 63.80, 38.80, 31.69, 29.06, 29.02, 28.37, 26.78, 22.55, 14.02.

PI−Tripod. $Pd(PhCN)_2Cl_2$ (2.6 mg, 6.8×10^{-6} mol), [(*t*-Bu)$_3$PH]BF_4 (3.9 mg, 1.4×10^{-5} mol), and CuI (1.3 mg, 6.8×10^{-6} mol) were placed in a Schlenk flask and dissolved in dry dioxane (3 mL) and dry (i-Pr)$_2$NH (100 μL, 6.9×10^{-4} mol) under Ar atmosphere. The solution was degassed by freeze−thaw cycles, and then **4** (120 mg, 1.4×10^{-4} mol) and 4-ethynylpyridine (70 mg, 6.8×10^{-4} mol)[15] were added to it. The reaction mixture was stirred for 11 h at room temperature. The solvent was evaporated in vacuo, and the residue was extracted with $CHCl_3$ and washed with water. The solvent was evaporated, and the residue was purified with flash silica gel column chromatography ($CHCl_3$/MeOH 95:5) to give a mixture including the target compound.

Further purification of the mixture by reprecipitation with hexane afforded 56.7 mg (44%) of the titled compound: MALDI-TOF MS found *m*/*z* 951.2 (MH^+); HRMS (FAB) calcd for $C_{64}H_{48}N_5O_4$ 950.3706, found 950.3713; ^1H NMR (600 MHz, $CDCl_3$, 25 °C, TMS) δ 8.64 (*brs*, 6H, *Py*), 8.39 (s, 2H, *Ph-PI*), 7.50 (d, *J* = 8.5 Hz, 6H, *Ph*), 7.45 (d, *J* = 8.8 Hz, 2H, *Ph′*), 7.38−7.40 (m, 8H, *Py* and *Ph′*), 7.28 (d. *J* = 8.2 Hz, 6H, *Ph*), 3.76 (t, *J* = 7.4 Hz, 2H, $C_\alpha H_2$), 1.72 (quintet, *J* = 7.0 Hz, 2H, $C_\beta H_2$), 1.25−1.34 (m, 10H, CH_2), 0.87 (t, *J* = 7.0 Hz, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C) δ 166.0, 165.1, 149.7, 146.5, 145.5, 137.7, 136.6, 131.54, 131.49, 131.2, 130.9, 129.5, 125.5, 120.5, 118.7, 93.32, 87.21, 64.90, 38.82, 31.68, 29.06, 29.02, 28.38, 26.79, 22.55, 14.01; UV−vis. ($CHCl_3$) 292.0 (4.97), 311.8 (4.94).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Listings of ^1H, ^{13}C NMR of **1**−**4**, *s*−Tripod, C_{60}−*s*−Tripod, C_{60}−*l*−Tripod, and PI−Tripod, UV−vis spectral changes of N−(**1**−Zn)$_3$ by bindings of C_{60}−*s*−Tripod, C_{60}−*l*−Tripod, and PI−Tripod, nanosecond transient absorption spectra of C_{60}−*l*−Tripod, spectral overlap of the absorption of C_{60}−*l*−Tripod, and the fluorescence of N−(**1**−Zn)$_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Karrasch, S.; Bullough, P. A.; Ghosh, R. *EMBO J.* **1995**, *14*, 631. (b) Roszak, A. W.; Howard, T. D.; Southall, J.; Gardiner, A. T.; Law, C. L.; Isaacs, N. W.; Cogdell, R. J. *Science* **2003**, *302*, 1969.

(2) (a) McDermott, G.; Prince, S. M.; Freer, A. A.; Hawthornthwaite-Lawless, A. M.; Papiz, M. Z.; Cogdell, R. J.; Isaacs, N. W. *Nature* **1995**, *374*, 517. (b) Koepke, J.; Hu, X.; Muenke, C.; Schulten, K.; Michel, K. *Structure* **1996**, *4*, 581.

(3) (a) Pullerits, T.; Sundström, V. *Acc. Chem. Res.* **1996**, *29*, 381. (b) Ritz, T.; Damjanović, A.; Schulten, K. *ChemPhysChem* **2002**, *3*, 243.

(4) Blankenship, R. E. In *Molecular Mechanisms of Photosynthesis*; Blackwell Science: Oxford, U.K., 2002.

(5) For reviews of multiporphyrin, see: (a) Sanders, J. K. M. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Eds.; Pergamon Press: Oxford, U.K., 1996; Vol. 9, pp 131. (b) Chambron, J.; Heitz, V.; Sauvage, J. P. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000; Vol. 6, pp 1. (c) Burrell, A. K.; Officer, D. L.; Plieger, P. G.; Reid, D. C. W. *Chem. Rev.* **2001**, *101*, 2751. (d) Harvey, P. D. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2003; Vol. 18, pp 63. (e) Choi, M.-S.; Yamazaki, T.; Yamazaki, I.; Aida, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 150. (f) Kobuke, Y. *Eur. J. Inorg. Chem.* **2006**, 2333. (g) Nakamura, Y.; Aratani, N.; Osuka, A. *Chem. Soc. Rev.* **2007**, *36*, 831. (h) Satake, A.; Kobuke, Y. *Org. Biomol. Chem.* **2007**, *5*, 1679. (i) Beletskaya, I.; Tyurin, V. S.; Tsivadze, A. Y.; Guilard, R.; Stern, C. *Chem. Rev.* **2009**, *109*, 1659.

(6) For reviews of porphyrin and fullerene conjugate, see: (a) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435. (b) Ward, M. D. *Chem. Soc. Rev.* **1997**, *26*, 365. (c) Gust, D.; Moore, T. A. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000; Vol. 8, pp 153. (d) Fukuzumi, S.; Guldi, D. M. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, Germany, 2000; Vol. 2, p 270. (e) Imahori, H. *Org. Biomol. Chem.* **2004**, *2*, 1425. (f) D'Souza, F.; Ito, O. *Chem. Commun.* **2009**, 4913.

(7) For most recent reports of cyclic porphyrin array and multiporphyin and fullerene conjugate, see: (a) Hoffmann, M.; Wilson, C. J.; Odell, B.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 3122. (b) Kelley, R. F.; Lee, S. J.; Wilson, T. M.; Nakamura, Y.; Tiede, D. M.; Osuka, A.; Hupp, J. T.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2008**, *130*, 4277. (c) Jensen, R. A.; Kelley, R. F.; Lee, S. J.; Wasielewski, M. R. *Chem. Commun.* **2008**, 1886. (d) Flamigni, L.; Ventura, B.; Oliva, A. I.; Ballester, P. *Chem.—Eur. J.* **2008**, *14*, 4214. (e) Aratani, N.; Osuka, A. *Chem. Commun.* **2008**, 4067. (f) Song, J.; Kim, P.; Aratani, N.; Kim, D.; Shinokubo, H.; Osuka, A. *Chem.—Eur. J.* **2010**, *16*, 3009. (g) Maeda, C.; Kim, P.; Cho, S.; Park, J. K.; Lim, J. M.; Kim, D.; Vura-Weis, J.; Wasielewski, M. R.; Shinokubo, H.; Osuka, A. *Chem.—Eur. J.* **2010**, *16*, 5052. (h) Takai, A.; Chkounda, M.; Eggenspiller, A.; Gros, C. P.; Lachkar, M.; Barbe, J.-M.; Fukuzumi, S. *J. Am. Chem. Soc.* **2010**, *132*, 4477. (i) Fukuzumi, S.; Saito, K.; Ohkubo, K.; Khoury, T.; Kashiwagi, Y.; Absalom, M. A.; Gadde, S.; D'Souza, F.; Araki, Y.; Ito, O.; Crossley, M. J. *Chem. Commun.* **2011**, *47*, 7980. (j) Grimm, B.; Schornbaum, J.; Cardona, C. M.; van Paauwe, J. D.; Boyd, P. D. W.; Guldi, D. M. *Chem. Sci.* **2011**, *2*, 1530.

(8) (a) Takahashi, R.; Kobuke, Y. *J. Am. Chem. Soc.* **2003**, *125*, 2372. (b) Shoji, O.; Okada, S.; Satake, A.; Kobuke, Y. *J. Am. Chem. Soc.* **2005**, *127*, 2201. (c) Hajjaj, F.; Yoon, Z. S.; Yoon, M.-C.; Park, J.; Satake, A.; Kim, D.; Kobuke, Y. *J. Am. Chem. Soc.* **2006**, *128*, 4612. (d) Fujisawa, K.; Satake, A.; Hirota, S.; Kobuke, Y. *Chem.—Eur. J.* **2008**, *14*, 10735.

(9) Kobuke, Y.; Miyaji, H. *J. Am. Chem. Soc.* **1994**, *116*, 4111.

(10) The Job plot of the tripyridyl tripodal ligand and N−(**1**−Zn)$_3$ showed a maximum at a mole fraction value of 0.5, supporting a 1:1 stoichiometry of binding, see: Kuramochi, Y.; Satake, A.; Kobuke, Y. *J. Am. Chem. Soc.* **2004**, *126*, 8668.

(11) (a) Kuramochi, Y.; Satake, A.; Itou, M.; Ogawa, K.; Araki, Y.; Ito, O.; Kobuke, Y. *Chem.—Eur. J.* **2008**, *14*, 2827. (b) Nagata, N.; Kuramochi, Y.; Kobuke, Y. *J. Am. Chem. Soc.* **2009**, *131*, 10. (c) Kuramochi, Y.; Sandanayaka, A. S. D.; Satake, A.; Araki, Y.; Ogawa, K.; Ito, O.; Kobuke, Y. *Chem.—Eur. J.* **2009**, *15*, 2317. (d) Satake, A.; Azuma, S.; Kuramochi, Y.; Hirota, S.; Kobuke, Y. *Chem.—Eur. J.* **2011**, *17*, 855.

(12) A lifetime of charge separated state on $\pi-\pi$ stacked fullerene−porphyrin system is 38 ps in benzonitrile, see: Guldi, D. M.; Hirsch, A.; Scheloske, M.; Dietel, E.; Troisi, A.; Zerbetto, F.; Prato, M. *Chem.—Eur. J.* **2003**, *9*, 4968. In the previous report (ref 11a), we also observed a lifetime of 77 ps in the $\pi-\pi$ stacked fullerene−macroring system.

(13) *Material Studio* (version 4.1/ Forcite/ Force Field UNIVERSAL); Accelrys, Inc.: San Diego, CA, 2001.

(14) Su, D.; Menger, F. M. *Tetrahedron Lett.* **1997**, *38*, 1485.

(15) Yu, L.; Lindsey, J. S. *J. Org. Chem.* **2001**, *66*, 7402.

(16) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467.

(17) Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798.

(18) Treatment of 4-(triphenylmethyl)aniline with 3 equiv of bromine in $CHCl_3$ at room temperature quantitatively afforded 2,6-dibromo-4-(triphenylmethyl)aniline, which was selectively brominated at the *ortho*-position of the NH_2 group.

(19) Hayes, R. T.; Walsh, C. J.; Wasielewski, M. R. *J. Phys. Chem. A* **2004**, *108*, 2375.

(20) (a) Hundertmark, T.; Littke, A. F.; Buchwald, S. L.; Fu, G. C. *Org. Lett.* **2000**, *2*, 1729. (b) Netherton, M. R.; Fu, G. C. *Org. Lett.* **2001**, *3*, 4295.

(21) Rathore, R.; Burns, C. L.; Guzei, I. A. *J. Org. Chem.* **2004**, *69*, 1524.

(22) Since the measurements were performed in around six times larger concentration of N−(**1**−Zn)$_3$ (4.0×10^{-7} M) than that (7.2×10^{-8} M) of C_{60}−Tripod, the reliable value was just one-digit number.

(23) Uyar, Z.; Satake, A.; Kobuke, Y.; Hirota, S. *Tetrahedron Lett.* **2008**, *49*, 5484.

(24) (a) Collins, D. M.; Hoard, J. L. *J. Am. Chem. Soc.* **1970**, *92*, 3761. (b) Kojima, T.; Nakanishi, T.; Honda, T.; Harada, R.; Shiro, M.; Fukuzumi, S. *Eur. J. Inorg. Chem.* **2009**, 727.

(25) (a) Armaroli, N.; Barigelletti, F.; Ceroni, P.; Eckert, J.-F.; Nicoud, J.-F.; Nierengarten, J.-F. *Chem. Commun.* **2000**, 599. (b) Beckers, E. H. A.; van Hal, P. A.; Schenning, A. P. H. J.; El-ghayoury, A.; Peeters, E.; Rispens, M. T.; Hummelen, J. C.; Meijer, E. W.; Janssen, R. A. J. *J. Mater. Chem.* **2002**, *12*, 2054. (c) Kesti, T.; Tkachenko, N.; Yamada, H.; Imahori, H.; Fukuzumi, S.; Lemmetyinen, H. *Photochem. Photobiol. Sci.* **2003**, *2*, 251.

(26) Fückel, B.; Köhn, A.; Harding, M. E.; Diezemann, G.; Hinze, G.; Basché, T.; Gauss, J. *J. Chem. Phys.* **2008**, *128*, 074505.

(27) Quimby, D. J.; Longo, F. R. *J. Am. Chem. Soc.* **1975**, *97*, 5111.

(28) The first oxidation potential of N−(**1**−Zn)$_3$ is considered to be similar to that of slipped-cofacial dimeric porphyrin; see ref 11a. The first oxidation potential of slipped-cofacial dimeric porphyrin was measured to be 0.17 V (vs. Fc/Fc$^+$, in benzonitrile). The first reduction potential of a pyromellitdiimide was calculated to be −1.17 V (vs. Fc/Fc$^+$, in DMF) from reported data, see: Gosztola, D.; Niemczyk, M. P.; Svec, W.; Lukas, A. S.; Wasielewski, M. R. *J. Phys. Chem. A* **2000**, *104*, 6545–6551.

(29) Nakamura, T.; Fujitsuka, M.; Araki, Y.; Ito, O.; Ikemoto, J.; Takamiya, K.; Aso, Y.; Otsubo, T. *J. Phys. Chem. B* **2004**, *108*, 10700.