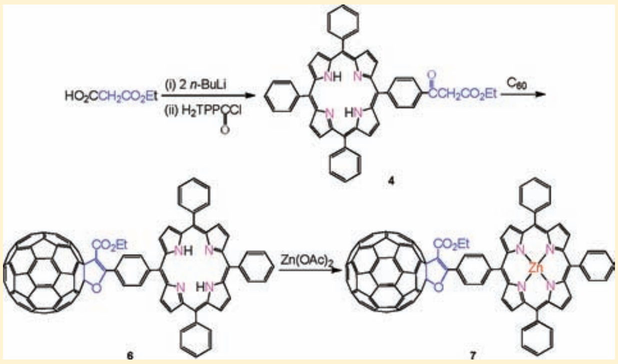
Inorganic Chemistry
ARTICLE
pubs.acs.org/IC

Synthesis and Structural Characterization of Some New Porphyrin-Fullerene Dyads and Their Application in Photoinduced H_2 Evolution

Li-Cheng Song,* Xu-Feng Liu, Zhao-Jun Xie, Fei-Xian Luo, and Hai-Bin Song

Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China

S Supporting Information



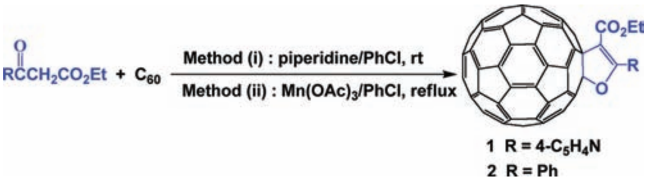
ABSTRACT: The [3 + 2] cycloaddition reaction of C_{60} with ethyl isonicotinoylacetate in the presence of piperidine in PhCl at room temperature or in the presence of $Mn(OAc)_3$ in refluxing PhCl gave the pyridyl-containing dihydrofuran-fused C_{60} derivative (4-$C_5H_4N)C(O){=}C(C_{60})CO_2Et$ (**1**), whereas the phenyl-containing C_{60} derivative $PhC(O){=}C(C_{60})CO_2Et$ (**2**) was similarly prepared by [3 + 2] cycloaddition reaction of C_{60} with ethyl benzoylacetate in the presence of piperidine or $Mn(OAc)_3$. More interestingly, one of the new porphyrin-fullerene dyads, i.e., [4-$C_5H_4NC(O){=}C(C_{60})CO_2Et]\cdot$ZnTPPH (**3**, ZnTPPH = tetraphenylporphyrinozinc), could be prepared by coordination reaction of the pyridyl-containing C_{60} derivative **1** with equimolar ZnTPPH in CS_2/hexane at room temperature. In addition, the β-keto ester-substituted porphyrin derivative $H_2TPPC(O)CH_2CO_2Et$ (**4**) was prepared by a sequential reaction of $HO_2CCH_2CO_2Et$ with *n*-BuLi in 1:2 molar ratio followed by treatment with $H_2TPPC(O)Cl$ in the presence of Et_3N and then hydrolysis with diluted HCl, whereas the porphyrinozinc derivative $ZnTPPC(O)CH_2CO_2Et$ (**5**) could be prepared by coordination reaction of **4** with $Zn(OAc)_2$ in refluxing $CHCl_3$/MeOH. Particularly interesting is that the second new porphyrin-fullerene dyad $H_2TPPC(O){=}C(C_{60})CO_2Et$ (**6**) could be prepared by [3 + 2] cycloaddition reaction of **4** with C_{60} in the presence of piperidine in PhCl at room temperature. In addition, treatment of **6** with $Zn(OAc)_2$ in refluxing $CHCl_3$/MeOH afforded the third new dyad $ZnTPPC(O){=}C(C_{60})CO_2Et$ (**7**). All the new compounds **1**−**7** were characterized by elemental analysis and various spectroscopic methods and particularly for **2**, **3**, and **5** by X-ray crystallography. The five-component system consisting of an electron donor EDTA, dyad **3**, an electron mediator methylviologen (MV^{2+}), the catalyst colloidal Pt, and a proton source HOAc was proved to be effective for photoinduced H_2 evolution. A possible pathway for such a type of H_2 evolution was proposed.

■ INTRODUCTION

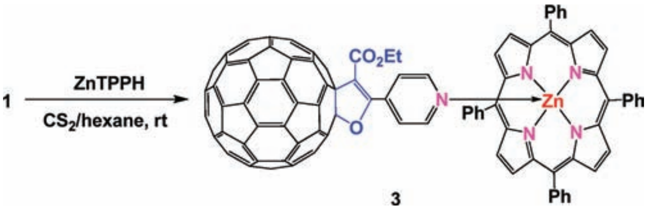
Photoinduced catalytic H_2 evolution has attracted great attention in recent years, largely because of molecular H_2 being considered as a promising energy source to solve the current energy shortage and environmental problems.[1−6] Generally, the photoinduced catalytic system for H_2 evolution consists of five separate components, namely, an electron donor, a photosensitizer, an electron mediator, a catalyst, and a proton source.[7−9]. However, except such a five-component system, some other systems involving less components were also previously reported for H_2 evolution, such as the four-component system in which a dyad assembly replaces the corresponding two components such as photosensitizer and catalyst[4,5] or photosensitizer and electron mediator.[8,10]We are interested in photoinduced H_2 evolution and have recently reported two examples using the three-component system without a mediator but involving two kinds of dyads: one kind of dyad consists of a porphyrin moiety as photosensitizer and a [FeFe]hydrogenase model as catalyst[11] and another kind of dyad includes a fullerene moiety as photosensitizer and a [FeFe]hydrogenase model as catalyst.[12] Particularly interesting is that both catalytic systems have been proved to give molecular H_2, although their H_2-producing efficiency is low.[11,12] To improve the photoinduced H_2-producing efficiency, we continued to study such photoinduced H_2 production using a new type of five-component system, which involves ethylenediamine tetraacetic disodium salt (EDTA) as an electron donor, colloidal Pt as catalyst, methylviologen (MV^{2+}) as an electron mediator, and a new type of dyad in which either a pyridyl-containing dihydrofuran-fused C_{60} derivative is coordinatively linked to Zn atom of the photosensitizer tetraphenylporphyrinozinc (ZnTPPH) or a dihydrofuran-fused C_{60} moiety is covalently linked to a phenyl group of the photosensitizer tetraphenylporphine (H_2TPPH). In principle, such five-component systems may have two advantages compared to our previously reported three-component systems:[11,12] (i) the

Received: August 6, 2011
Published: October 14, 2011

Scheme 1



Scheme 2



catalyst colloidal Pt has been proved to have high catalytic activity for such photoinduced H_2 evolution,[13−15] and (ii) porphyrin-fullerene dyads are well-known donor−acceptor systems for electron transfer and charge separation required for such photoinduced H_2-producing processes.[16−22] It is worth pointing out that, although numerous porphyrin-fullerene dyads are known,[23−30] there is no report regarding their application in the study of photoinduced H_2 production. Herein, we report the synthesis and structural characterization of three new porphyrin-fullerene dyads and their first application in photoinduced H_2 evolution. In addition, the synthesis and characterization of another four new functionalized porphyrin and C_{60} derivatives closely related to the three new porphyrin-fullerene dyads are also described.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of Dihydrofuran-Fused C_{60} Derivatives $RC(O)=C(C_{60})CO_2Et$ (1, R = 4-C_5H_4N; 2, R = Ph) and Coordinatively Bonded Porphyrin-Fullerene Dyad [4-$C_5H_4NC(O)=C(C_{60})CO_2Et]\cdot$ZnTPPH (3). The new pyridyl group-containing dihydrofuran-fused C_{60} derivative **1** was found to be prepared by the base-catalyzed [3 + 2] cycloaddition reaction[31] of ethyl isonicotinoylacetate with C_{60} in the presence of piperidine in chlorobenzene at room temperature in 91% yield or by single-electron oxidant $Mn(OAc)_3$-mediated [3 + 2] cycloaddition reaction[32] of ethyl isonicotinoylacetate with C_{60} in refluxing chlorobenzene in 59% yield (Scheme 1). Similarly, the phenyl-containing C_{60} derivative **2** (a known analogue of **1**)[32] could be prepared by the piperidine-catalyzed cycloaddition reaction of ethyl benzoylacetate with C_{60} in chlorobenzene at room temperature in 70% yield or by the $Mn(OAc)_3$-mediated cycloaddition reaction of ethyl benzoylacetate with C_{60} in chlorobenzene at reflux in 33% yield (Scheme 1). More interestingly, it was further found that the new coordinatively bonded porphyrin-fullerene dyad **3**, similar to the known coordinatively bonded porphyrin-fullerene dyads,[25b,26a] could be prepared by solvent diffusion method and coordination reaction of the pyridyl-containing C_{60} derivative **1** with an equimolar amount of ZnTPPH in CS_2/hexane at room temperature in 97% yield (Scheme 2).

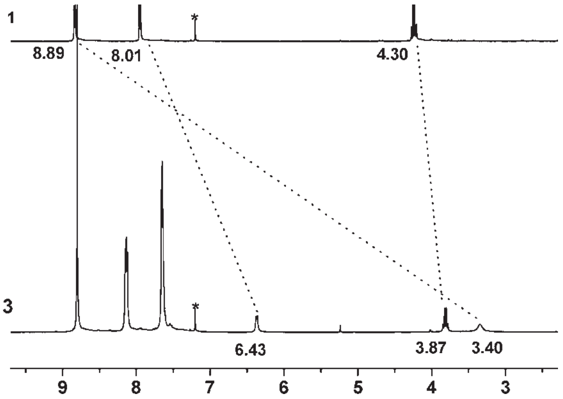


Figure 1. Partial ^1H NMR spectra of **1** and **3** (∗: $CHCl_3$).

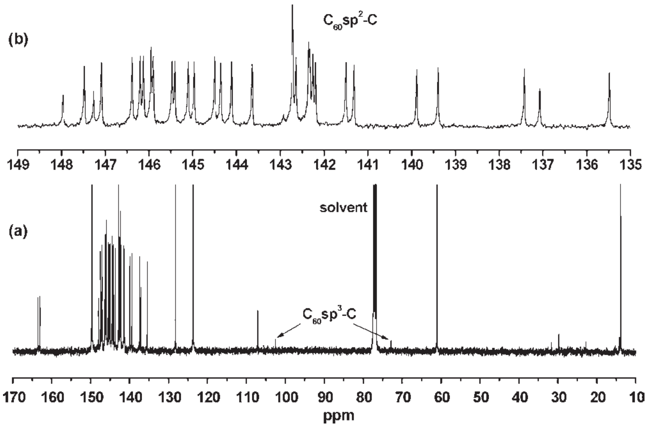


Figure 2. (a) Original ^{13}C NMR spectrum of **1**. (b) Expanded partial ^{13}C NMR spectrum of **1**.

Compounds **1**−**3** are air−stable solids, which were characterized by elemental analysis and various spectroscopic methods. For example, the IR spectra of **1**−**3** displayed one strong absorption band in the range 1714−1701 cm^{-1} for their ester carbonyls and four absorption bands in the range of 1437−527 cm^{-1} attributed to the C−C stretching frequencies for their C_{60} spheres,[33] whereas dyad **3** showed three additional absorption bands at 1522, 1484, and 1338 cm^{-1} attributed to the skeletal vibrations of pyrrole rings in its porphyrin moiety.[34] The ^1H NMR spectrum of the pyridyl-containing C_{60} derivative **1** as a free ligand displayed two doublets at δ = 8.89 and 8.01 ppm for the two α and two β-protons in its pyridyl group, a quartet at δ = 4.30 ppm for its CH_2 group, and a triplet at δ = 1.22 ppm for its CH_3 group. However, the ^1H NMR spectrum of the pyridyl-containing C_{60} derivative **1** as a coordinated ligand in dyad **3** exhibited a broad singlet for its two α-pyridyl protons that is shifted upfield by 5.49 ppm relative to that of free ligand **1**, a doublet for its two β-pyridyl protons shifted upfield by 1.58 ppm, a quartet for its CH_2 group upfield shifted by 0.43 ppm, and a triplet for its CH_3 group upfield shifted by 0.49 ppm (see Figure 1). Apparently, these upfield shifts should be attributed to the shielding effect caused by the macrocycle of ZnTPPH.[25b,26a,35,36] In addition, the ^{13}C NMR spectrum of free ligand **1** showed two signals at δ = 72.83

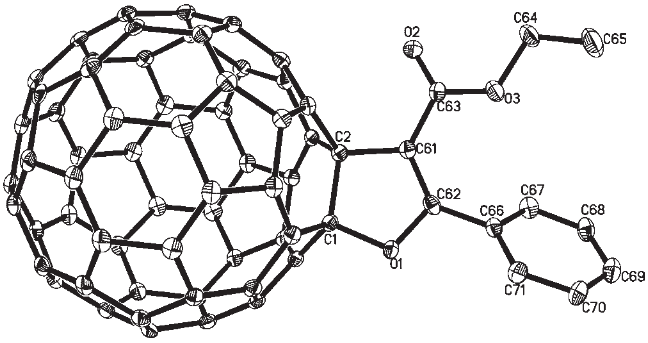


Figure 3. ORTEP view of **2** with 30% thermal ellipsoids.

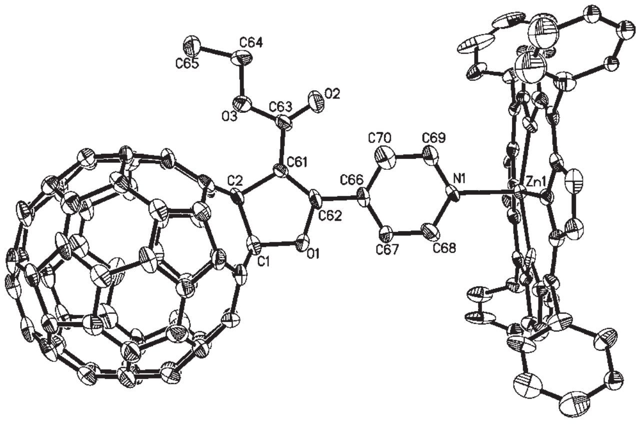


Figure 4. ORTEP view of **3** with 30% thermal ellipsoids.

Table 1. Bond Lengths [Å] and Angles [deg] for 2, 3, and 5

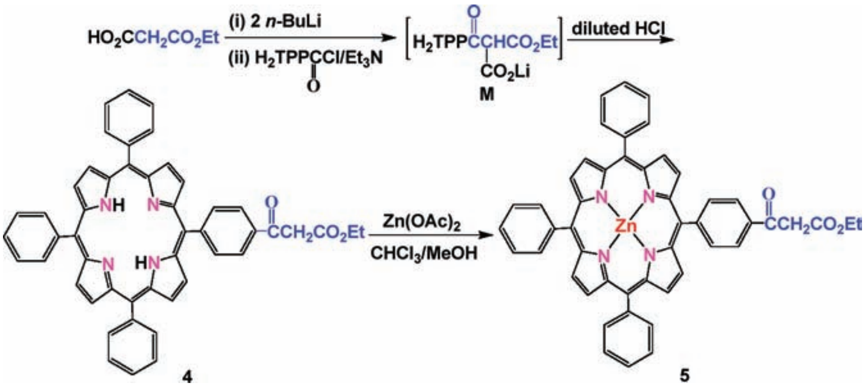
	2		
C(1)−O(1)	1.470(4)	C(1)−C(2)	1.598(4)
C(2)−C(61)	1.527(4)	C(61)−C(62)	1.346(5)
C(62)−O(1)	1.368(4)	C(61)−C(63)	1.467(5)
C(62)−C(66)	1.466(5)	C(63)−O(2)	1.210(4)
O(1)−C(1)−C(2)	105.8(2)	C(61)−C(2)−C(1)	100.3(2)
C(62)−O(1)−C(1)	109.0(2)	C(62)−C(61)−C(2)	110.7(3)
C(61)−C(62)−O(1)	113.9(3)	C(62)−C(61)−C(63)	128.8(3)
C(63)−C(61)−C(2)	120.4(3)	C(61)−C(62)−C(66)	132.6(3)
	3		
Zn(1)−N(1)	2.137(3)	O(1)−C(62)	1.382(9)
O(1)−C(1)	1.459(9)	C(1)−C(2)	1.587(10)
C(61)−C(62)	1.355(11)	C(61)−C(63)	1.464(10)
C(2)−C(61)	1.552(9)	C(62)−C(66)	1.489(8)
O(1)−C(1)−C(2)	105.2(6)	C(61)−C(2)−C(1)	101.2(7)
C(62)−C(61)−C(2)	109.6(6)	C(62)−C(61)−C(63)	126.7(7)
C(63)−C(61)−C(2)	123.8(6)	C(61)−C(62)−O(1)	113.0(6)
C(62)−O(1)−C(1)	110.7(6)	C(61)−C(62)−C(66)	137.2(7)
	5		
Zn(1)−N(1)	2.076(4)	O(3)−C(47)	1.220(6)
Zn(1)−O(1)	2.117(4)	O(4)−C(47)	1.329(7)
N(1)−C(1)	1.377(5)	N(2)−C(12)	1.362(5)
O(2)−C(45)	1.221(6)	N(3)−C(26)	1.378(6)
N(3)−Zn(1)−N(2)	88.89(13)	C(4)−N(1)−Zn(1)	126.1(3)
N(1)−Zn(1)−N(2)	88.37(13)	C(50)−O(1)−Zn(1)	119.7(4)
N(1)−Zn(1)−N(4)	88.03(13)	C(42)−C(45)−C(46)	119.2(5)
C(1)−N(1)−Zn(1)	126.7(3)	O(2)−C(45)−C(42)	120.5(5)

and 102.59 ppm for its two sp^3-C atoms and 30 signals at δ = 135.48−147.96 ppm for its 58 sp^2-C atoms in C_{60} sphere,[37,38] whereas the coordinated ligand **1** in dyad **3** displayed two signals at δ = 72.14 and 101.91 ppm for the corresponding two sp^3-C atoms and 29 signals at δ = 134.82−147.23 ppm for the corresponding 58 sp^2-C atoms.[37,38] It is worth pointing out that, in the ^{13}C NMR spectrum of dyad **3**, the intensity of the signal at δ = 142.72 ppm is much stronger than other signals because it represents two sp^2-C atoms of C_{60} moiety and one γ-pyridyl C atom (see Figure 2).

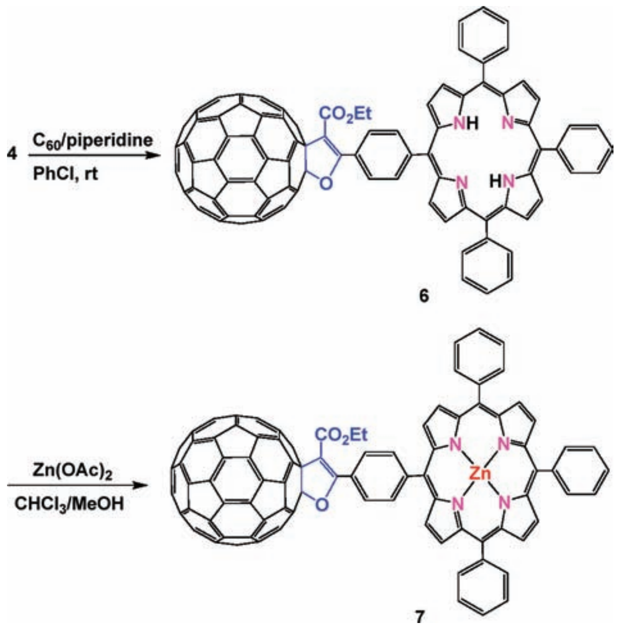
The molecular structures of **2** and **3** have been unequivocally confirmed by X-ray crystal diffraction techniques. Their ORTEP plots are depicted in Figures 3 and 4, and selected bond lengths and angles are given in Table 1. As shown in Figures 3 and 4, both **2** and **3** contain the same ethoxycarbonyl-substituted dihydrofuran-fused C_{60} moiety, in which the five atoms C1, C2, C61, C62, and O1 in the five-membered dihydrofuran ring are nearly coplanar with a mean deviation of 0.003 Å for **2** and 0.018 Å for **3**, respectively. The C1−C2 single bond length is 1.598 Å for **2** and 1.587 Å for **3**, whereas the C61−C62 double bond lengths is 1.346 Å for **2** and 1.355 Å for **3**, respectively. Such single and double bond lengths are very close to those reported in other dihydrofuran-fused C_{60} derivatives.[39,40] In addition, as can be seen in Figures 3 and 4, while **2** contains a benzene ring attached to C62 of the dihydrofuran-fused C_{60} moiety, dyad **3** has a pyridine ring whose N1 atom is axially coordinated to Zn1 atom of the ZnTPPH moiety. The N1−Zn1 bond length is 2.137 Å which compares with those reported for other noncovalently linked porphyrin-fullerene dyads.[25a,b] The distance from porphyrin center to the center of C_{60} is found to be 12.225 Å, whereas the edge-to-edge distance (the closest distance between the porphyrin β-pyrrole carbon atom and the C_{60} carbon atom) is 9.208 Å. The porphyrin ring is slightly ruffled with 0.3033 Å out-of-plane displacement of the central Zn atom due to its axial coordination with N1 atom of the pyridine ring.

Synthesis and Characterization of *β*-Keto Ester-Substituted Porphyrin Derivatives $H_2TPPC(O)CH_2CO_2Et$ (4)/ $ZnTPPC(O)CH_2CO_2Et$ (5) and Covalently Bonded Porphyrin-Fullerene Dyads $H_2TPPC(O){=}C(C_{60})CO_2Et$ (6)/$ZnTPPC(O){=}C(C_{60})CO_2Et$ (7). In order to prepare the covalently linked porphyrin-fullerene dyads **6** and **7**, we first prepared the β-keto ester-substituted porphyrin **4**[41] and its porphyrinozinc derivative **5** via the synthetic route shown in Scheme 3. That is, when monoethyl malonate reacted with *n*-BuLi in 1:2 molar ratio followed by treatment with $H_2TPPCOCl$ in the presence of Et_3N, the corresponding intermediate lithium salt $H_2TPPCOCH(CO_2Li)CO_2Et$ (**M**) was generated. Then, after in situ hydrolysis of lithium salt **M** with diluted hydrochloric acid, the expected β-keto ester-substituted porphyrin **4** was obtained in 81% yield. Further treatment of porphyrin derivative **4** with excess $Zn(OAc)_2$ in refluxing $CHCl_3$/MeOH resulted in formation of the porphyrinozinc derivative **5** in 90% yield. Particularly interesting is that the new covalently bonded porphyrin-fullerene dyad **6** could be prepared by [3 + 2] cycloaddition reaction of C_{60} with porphyrin derivative **4** in the presence of piperidine in chlorobenzene at room temperature in 77% yield, whereas further treatment of **6** with excess $Zn(OAc)_2$ in $CHCl_3$/MeOH

Scheme 3



Scheme 4



at room temperature afforded another new covalently bonded porphyrinozinc-fullerene dyad **7** in 89% yield (Scheme 4).

Compounds **4**−**7** are air−stable solids and were characterized by elemental analysis and various spectroscopic techniques. For example, the IR spectrum of **4** displayed one absorption band at 3316 cm^{-1} assigned to its NH groups, one band at 1742 cm^{-1} for its ketone carbonyl, and one band at 1687 cm^{-1} for its ester carbonyl, whereas **5** exhibited one absorption band at 1740 cm^{-1} for its ketone carbonyl, and one band at 1685 cm^{-1} for its ester carbonyl, respectively. In addition, the IR spectra of **4** and **5** displayed three absorption bands in the range of 1558−1338 cm^{-1} for the skeletal vibrations of pyrrole rings in their porphyrin moieties.[34]

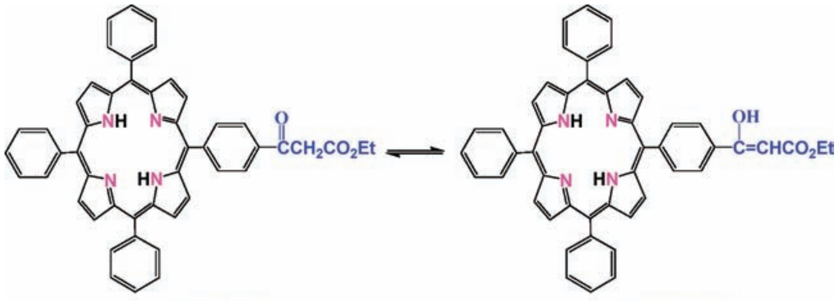
It is interesting to note that the ^{1}H NMR spectrum of **4** displayed three singlets at δ = 4.25, 6.00, and 12.86 ppm. This implies that in solution **4** is a mixture of the keto form with its enol form (Scheme 5). The three singlets could be assigned to the CH_2 group between the two carbonyls in its keto form, and to the both ═CH and OH groups in its enol form, respectively.[42] However, when excess D_2O was added to solution of **4** during ^{1}H NMR determination, the singlet at δ = 12.86 ppm for OH group in its enol form as well as the singlet at δ = −2.75 ppm for NH groups in its keto and enol forms completely disappeared due to D/H exchanges. According to the integrated values of the corresponding ^{1}H NMR signals, the molar ratio between the keto and enol forms was calculated to be 9:1. More interestingly, in contrast to **4**, the ^{1}H NMR spectrum of **5** displayed only one singlet at δ = 4.27 ppm, which implies that **5** existed only in the keto form.

The ^{13}C NMR spectra of **4** and **5** also demonstrated that **4** was a mixture of the keto and enol forms, while **5** was present only in its keto form. This is because the ^{13}C NMR spectrum of **4** displayed three singlets at δ = 46.33, 88.38, and 173.70 ppm, assigned respectively to the carbon atom in CH_2 group between two carbonyls in its keto form and those carbon atoms in ═CH and COH groups in its enol form; in addition, **5** showed only one singlet at δ = 45.94 ppm, assigned to the carbon in CH_2 group between two carbonyls in its keto form without observing any ^{13}C NMR signal for groups ═CH and COH in its enol form.

The IR spectra of dyads **6** and **7** showed one absorption band at ca. 1695 cm^{-1} for their ester carbonyls, three bands in the region of 1558−1368 cm^{-1} for the skeletal vibrations of pyrrole rings in their porphyrin moieties,[34] and three to four bands in the range of 1442−526 cm^{-1} ascribed to the C−C stretching frequencies for their C_{60} spheres.[33] In addition, the ^{1}H NMR spectrum of **6** showed a singlet at δ = −2.82 ppm for its NH groups, which disappeared in **7** since the two H atoms attached to N atoms in **6** were replaced by Zn atom. Particularly noteworthy is that the ^{13}C NMR spectra of **6** and **7** also indicated the presence of both the C_{60} sphere and the porphyrin moiety. For example, the ^{13}C NMR spectrum of **6** showed one signal at δ = 73.96 ppm for its two sp^3-C atoms and 28 signals in the range of 134.97−147.71 ppm for the 58 sp^2-C atoms in its C_{60} sphere.[37,38] In addition, **6** also displayed two signals at δ = 141.93 and 131.32 ppm for α-C and β-C atoms in its pyrrole rings, respectively. The two signals at δ = 118.62 and 120.17 ppm can be attributed to meso-C atoms in the porphyrin macrocycle.

The molecular structure of porphyrin derivative **5** was unambiguously confirmed by X-ray crystallography. The ORTEP drawing of **5** is presented in Figure 5, whereas Table 1 lists its selected bond lengths and angles. It can be seen intuitively from Figure 5 that complex **5** indeed includes a tetraphenylporphyrin macrocycle in which Zn1 atom is coordinated to N1, N2, N3, and

Scheme 5



4 (keto form) **4** (enol form)

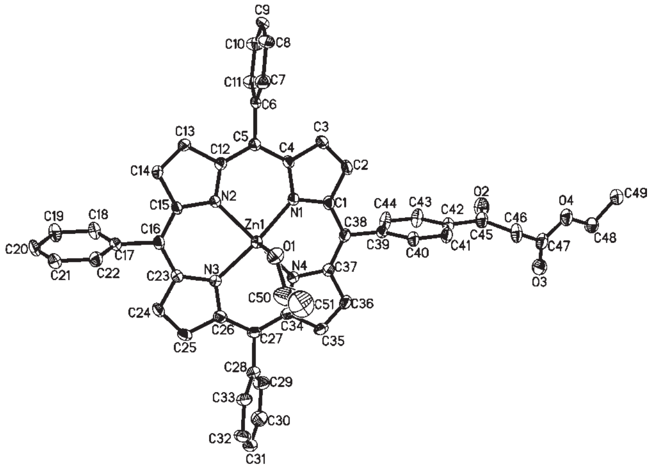


Figure 5. ORTEP view of **5** with 30% thermal ellipsoids.

N4 atoms as well as to O1 atom of the solvent EtOH used in the single-crystal growing process. The four Zn−N bond lengths (2.059−2.093 Å) and Zn1−O1 bond length (2.117 Å) of **5** are very close to those reported for ZnTPPH(MeOH),[43] ZnTPPH-(H_2O),[44] and $[(\mu-SCH_2)_2NFe_2(CO)_6]$ZnTPP(MeOH).[11] In addition, the four benzene rings around the metalloporphyrin moiety are twisted relative to the porphyrin plane with a dihedral angle (84.9°−95.1°) in order to avoid the strong steric repulsions between the proximal H atoms of the benzene and pyrrole rings in the metalloporphyrin macrocycle.

Investigation on Photoinduced H_2 Evolution Under the Action of a Five-Component System Including Dyad 3. In order to study such a photoinduced H_2 evolution process, it was necessary first to study the UV−vis absorption and fluorescence emission spectra of dyad **3** and some related compounds. From such a study, we could select a suitable light wavelength to cause the electron excitation of the photosensitizer porphyrin moiety in dyad **3**; in addition, we would know if the photoexcited electron of the porphyrin moiety can be intramolecularly transferred to the electron acceptor C_{60} moiety (note that such an electron transfer (ET) process is one of the important steps required for proton reduction to H_2). The UV−vis absorption spectra of dyad **3** and ZnTPPH are shown in Figure 6. As can be seen in Figure 6, dyad **3** displayed a Soret band at 418 nm in the near-UV region and two Q bands at 547 and 585 nm in the visible region, which are virtually the same as those displayed by ZnTPPH.[45] In addition, dyad **3** also displayed three bands at 227, 254, and 314 nm in the UV region, which are due to the absorption of C_{60} moiety.[12,46−48]The fluorescence emission spectrum of dyad **3** along with that of a 1:1 mixture of ZnTPPH and **2** are shown in Figure 7. As can be seen in Figure 7, the fluorescence emission spectrum of dyad **3** showed a 71% decrease of the intensity relative to that of the 1:1 mixture of ZnTPPH with **2**. Apparently, such a large decrease can be attributed to the existence of a strong intramolecular electron transfer from the photoexcited ZnTPPH moiety to the axially coordinated C_{60} moiety.[12,25b,26a,49,50]

Interestingly, our experiments indicated that molecular H_2 was indeed produced when a 350 W Xe lamp with a Pyrex−glass filter ($\lambda > 400$ nm) was used to irradiate an aqueous solution of the five-component system consisting of an electron donor EDTA, dyad **3**, an electron mediator methylviologen (MV^{2+}), a catalyst colloidal Pt (stabilized by sodium polyacrylate[51]), and a proton source HOAc in the presence of surfactant Triton X-100. The control experiments showed that all five components were essential for H_2 production. That is, omission of any of the five components afforded unobservable to trace amounts of hydrogen (see entries 2−5 in Table 2). In addition, no H_2 could be detected when the reaction involving the five-component system was carried out in the dark (see entry 6 in Table 2). The highest turnover number of H_2 evolution is 73 under the optimized conditions during 4 h irradiation (see entry 1 in Table 2). Actually, this photoinduced H_2 evolution with 73 turnovers is comparable with those previously reported for photoinduced hydrogen evolution. For example, the system involving chromophore platinum terpyridyl acetylide and colloidal Pt reported by Eisenberg gave 84 turnovers during 10 h irradiation,[52] and that system involving a cobaloxime-based photocatalyst reported by Artero gave 103 turnovers during 15 h irradiation.[5a]

The influences of pH values, the catalyst (colloidal Pt) concentration, and irradiation time are shown in Figures 8, 9, and 10, respectively. As shown in Figures 8−10, the amount of H_2 evolved increases as the pH values decrease, reaching a maximum at pH = 3.99, whereas the evolved H_2 amount is increased with an increase of either the catalyst concentration or the irradiation time. It should be noted that only 0.23 μmol H_2 with 2.3 turnovers were produced after 4 h irradiation when dyad **3** was replaced by photosensitizer ZnTPPH. This shows that the C_{60} moiety plays an important role in the photoinduced hydrogen production process (see entry 7 in Table 2).

According to these observations and the previously reported similar cases,[11,12,53] a possible pathway could be proposed for the photoinduced H_2 production catalyzed by colloidal Pt in the presence of dyad **3** (Scheme 6). Upon irradiation, dyad **3**

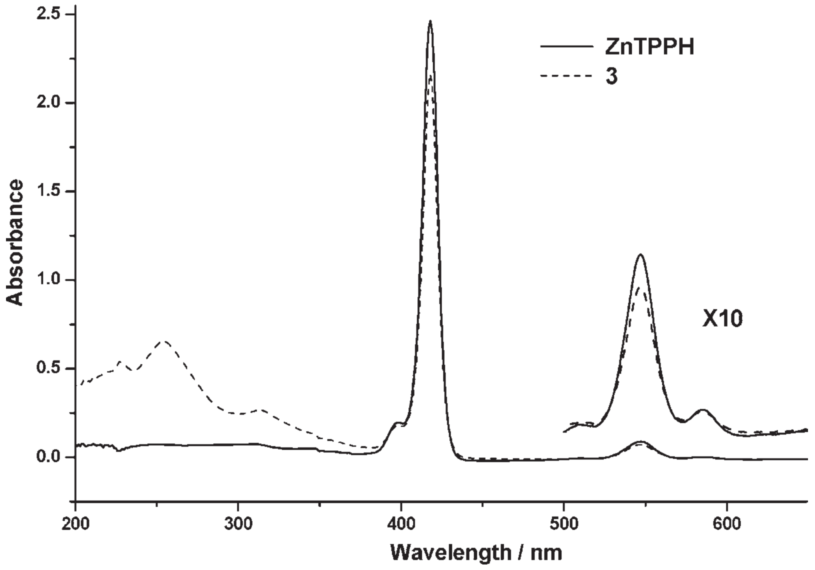


Figure 6. UV−vis spectra of **3** and ZnTPPH in CH_2Cl_2 (5×10^{-6} M). The Soret band absorptions have been normalized, and the spectra have been amplified 10-fold in the Q-band region.

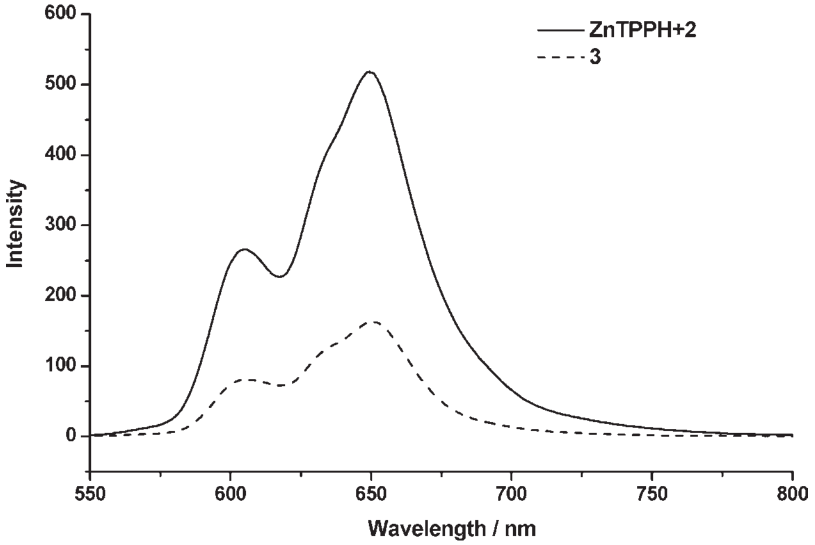


Figure 7. Fluorescence emission spectra (λ_{ex} = 440 nm) of **3** and an equimolar mixture of **2** with ZnTPPH in PhCl (1×10^{-4} M).

Table 2. Photoinduced H_2 Evolution Catalyzed by Colloidal Pt in Aqueous Solutions

entry	photosensitizer	electron donor	electron mediator	proton source	irradiation time	TON[a]
1	dyad **3**	EDTA	MV^{2+}	HOAc	4 h	73
2	dyad **3**	EDTA	MV^{2+}	HOAc	4 h	<1
3	dyad **3**		MV^{2+}	HOAc	4 h	<1
4	dyad **3**	EDTA		HOAc		<1
5		EDTA	MV^{2+}	HOAc	4 h	<1
6	dyad **3**	EDTA	MV^{2+}	HOAc		0
7	ZnTPP	EDTA	MV^{2+}	HOAc	4 h	2.3

[a] TON are calculated on the basis of dyad **3**.

consisting of a photosensitizer ZnTPPH moiety and an electron acceptor C_{60} moiety turns to a charge−separated state $ZnTPPH^{+}\cdots C_{60}^{-}$ via the electron transfer from the excited state of the ZnTPPH* moiety to the electron acceptor C_{60}

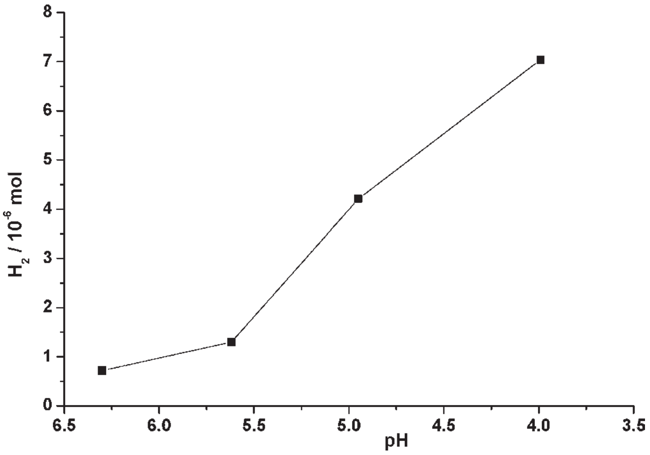


Figure 8. The pH dependence of photoinduced H_2 evolution from an aqueous solution (10 mL) of colloidal Pt (50 μM) containing EDTA (15 mM), **3** (20 μM), MV^{2+} (0.27 mM), and Triton X-100 (0.3 mL) in the presence of HOAc (0.085 M)/NaOAc (0.015 M) at pH = 3.99; HOAc (0.036 M)/NaOAc (0.064 M) at pH = 4.95; HOAc (0.005 M)/NaOAc (0.095 M) at pH = 5.62; $NaH_2PO_4 \cdot 2H_2O$ (0.085 M)/$Na_2HPO_4 \cdot 12H_2O$ (0.058 M) at pH = 6.30 during 4 h irradiation.

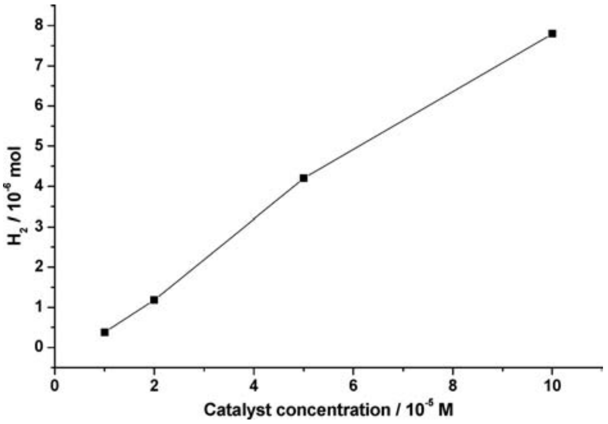


Figure 9. The colloidal Pt concentration dependence of photoinduced H_2 evolution from an aqueous solution (10 mL) of colloidal Pt containing EDTA (15 mM), **3** (20 μM), MV^{2+} (0.27 mM), and Triton X-100 (0.3 mL) in the presence of HOAc (0.036 M)/NaOAc (0.064 M) during 4 h irradiation.

moiety. The electron mediator MV^{2+} is then reduced by the negatively charged C_{60}^- in the charge-separated state $ZnTPPH^+ \cdots C_{60}^-$ to give $MV^{\bullet+}$ and $ZnTPPH^+ \cdots C_{60}$. While reductive quenching of the charge-separated species $ZnTPPH^+ \cdots C_{60}$ by EDTA leads to the ground state of dyad **3**, the electron transfer from $MV^{\bullet+}$ to proton under the action of colloidal Pt gives hydrogen, completing the catalytic cycle.

CONCLUSIONS

We have found that the pyridyl and phenyl-containing dihydrofuran-fused C_{60} derivatives **1** and **2** can be prepared by the base-catalyzed or $Mn(OAc)_3$-mediated [3 + 2] cycloaddition reactions of C_{60} with the corresponding β-keto esters in 70−91% yields, whereas the designed coordinatively bonded porphyrin-fullerene dyad **3** can be prepared in a nearly quantitative yield by coordination reaction of the pyridyl-containing C_{60} derivative **1** with ZnTPPH. Also, we have found that the β-keto ester-functionalized porphyrin derivatives **4** and **5** can be prepared by the sequential reaction involving lithiation of the starting material $HO_2CCH_2CO_2Et$ and subsequent acylation, decarboxylation, and coordination steps, whereas the covalently bonded porphyrin-fullerene dyads **6** and **7** can be prepared by the base-catalyzed cycloaddition reaction of C_{60} with porphyrin derivative **4** and subsequent coordination reaction of **6** with $Zn(OAc)_2$ in 77% and 89% yields, respectively. Particularly interesting is that photoinduced H_2 evolutions using a multicomponent system involving a porphyrin-fullerene dyad. This multicomponent system is a five-component system (consisting of electron donor EDTA, dyad **3**, electron mediator MV^{2+}, catalyst colloidal Pt, and proton source HOAc), which gives H_2 with a high turnover number of 73. On the basis of similar cases and some related studies, a possible pathway for this photoinduced H_2 evolution is suggested. All the prepared compounds **1**−**7** have been characterized by elemental analysis and spectroscopy and particularly for **2**, **3**, and **5** by X-ray crystallography. Further studies on the multicomponent catalytic systems involving dyad **6**, **7**, and other porphyrin-fullerene dyads are in progress in this laboratory.

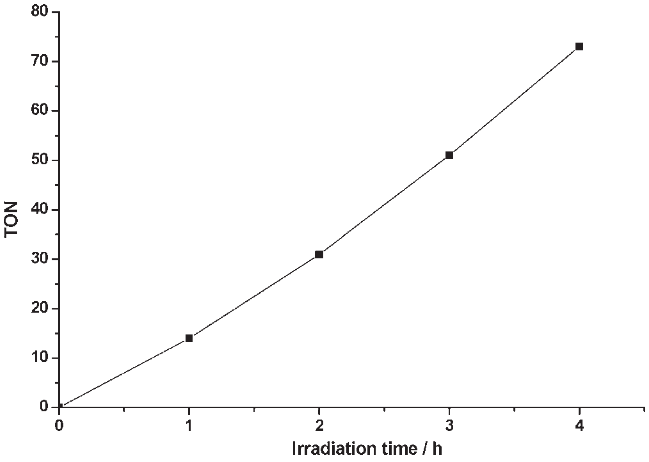
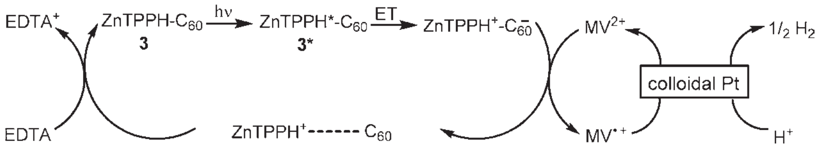


Figure 10. The time dependence of photoinduced H_2 evolution from an aqueous solution (10 mL) of colloidal Pt (0.10 mM) containing EDTA (15 mM), **3** (20 μM), MV^{2+} (0.41 mM), and Triton X-100 (0.3 mL) in the presence of HOAc (0.10 M) during 4 h irradiation.

EXPERIMENTAL SECTION

General Comments. All reactions were carried out under an atmosphere of highly purified nitrogen using standard Schlenk or vacuum-line techniques. Chlorobenzene was distilled from CaH_2; THF was distilled from Na/benzophenone ketyl, and piperidine was redistilled under nitrogen prior to use. Ethyl isonicotinoylacetate,[54] ZnTPPH,[55]monoethyl malonate,[56] H_2TPPCO_2H,[57] $H_2TPPCOCl$,[58] and colloidal Pt[51] were prepared according to literature methods. Ethyl benzoylacetate, C_{60}, $Mn(OAc)_3 \cdot 2H_2O$, ethylenediamine tetraacetic disodium salt (EDTA), *N*,*N*′-dimethyl-4,4′-bipyridium (methylviologen, MV^{2+}), Triton X-100, and other chemicals were of commercial origin and used as received. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 or a Bruker Avance 400 NMR spectrometer. IR spectra were taken on a Bio-Rad FTS 135 spectrophotometer. Elemental analysis was performed on an Elementar Vario EL analyzer. UV−vis spectra and fluorescence emission spectra were carried out, respectively, on a Varian CARY 100 Bio spectrophotometer and on a Varian CARY Eclipe spectrophotometer. Melting points were

Scheme 6



determined on a Yanaco MP-500 melting point apparatus and are uncorrected.

Preparation of (4-C_5H_4N)C(O)=C(C_{60})CO_2Et (1). Method (i): A 100 mL two-necked flask fitted with a magnetic stir-bar, a rubber septum, and a N_2 inlet tube was charged with C_{60} (72 mg, 0.1 mmol), ethyl isonicotinoylacetate (39 mg, 0.2 mmol), piperidine (30 μL, 0.3 mmol), and PhCl (20 mL). The mixture was stirred at room temperature for 36 h to give a red-brown solution. After volatiles were removed at reduced pressure, the residue was subjected to column chromatography (silica gel). Elution with toluene developed a purple band, from which unreacted C_{60} (20 mg) was recovered. Elution with toluene/ethyl acetate (v/v 1:1) developed a brown band, from which **1** (60 mg, 91% yield based on the consumed C_{60}) was obtained as a brown-black solid. Mp: >300 °C. Anal. Calcd. for $C_{70}H_9NO_3$: C, 92.21; H, 0.99; N, 1.54. Found: C, 91.93; H, 1.09; N, 1.57. IR (KBr disk): $\nu_{C=O}$ 1714 (vs), $\nu_{C=C}$ 1636 (m), ν_{C60} 1436 (m), 1180 (m), 575 (w), 527 (s) cm^{-1}. ^{1}H NMR (300 MHz, CS_2:$CDCl_3$ = 1:1): 1.22 (t, *J* = 7.2 Hz, 3H, CH_3), 4.30 (q, *J* = 7.2 Hz, 2H, CH_2), 8.01 (d, *J* = 6 Hz, 2β-H in C_5H_4N), 8.89 (d, *J* = 6 Hz, 2α-H in C_5H_4N) ppm. ^{13}C NMR (100.6 MHz, CS_2:$CDCl_3$ = 1:1): 13.84 (CH_3), 61.05 (CH_2), 107.05 (*C*=C–O), 123.65 (2β-C in C_5H_4N), 149.67 (2α-C in C_5H_4N), 163.05, 163.53 (C=*C*O/CO_2); C_{60} 72.83, 102.59 (2C of sp^3-C), 135.48 (2C), 137.08 (2C), 137.43 (2C), 137.40 (2C), 139.89 (2C), 141.32 (2C), 141.50 (2C), 142.20 (2C), 142.26 (2C), 142.33 (2C), 142.35 (2C), 142.64 (2C), 142.72 (3C, including one γ-C in C_5H_4N), 143.64 (2C), 144.11 (2C), 144.36 (2C), 144.50 (2C), 144.97 (2C), 145.10 (2C), 145.41 (2C), 145.47 (2C), 145.90 (2C), 145.95 (2C), 146.13 (2C), 146.20 (2C), 146.38 (2C), 147.09 (2C), 147.26 (1C), 147.48 (2C), 147.96 (1C) ppm. UV–vis (CH_2Cl_2, 5 × 10^{-6} M): λ_{max} (log ε) = 228 (4.99), 255 (5.11), 314 nm (4.67).

Method (ii): A 100 mL two-necked flask equipped with a magnetic stir-bar, a serum cap, and a reflux condenser topped with a N_2 inlet tube was charged with C_{60} (36 mg, 0.05 mmol), ethyl isonicotinoylacetate (19 mg, 0.10 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (40 mg, 0.15 mmol), and PhCl (10 mL). While stirring, the mixture was heated at reflux for 15 min and then was cooled to room temperature. The same workup as that used in Method (i) afforded unreacted C_{60} (8 mg) and **1** (21 mg, 59% yield based on the consumed C_{60}).

Preparation of PhC(O)=C(C_{60})CO_2Et (2). The same procedures were utilized as described for preparation of **1** except that ethyl benzoylacetate (35 μL, 0.2 mmol) was employed instead of ethyl isonicotinoylacetate. Using Method (i), unreacted C_{60} (30 mg) and **2** (37 mg, 70% yield based on the consumed C_{60}) as a brown-black solid were obtained. Using Method (ii), unreacted C_{60} (12 mg) and **2** (10 mg, 33% yield based on the consumed C_{60}) were obtained. Mp: >300 °C. Anal. Calcd. for $C_{71}H_{10}O_3$: C, 93.62; H, 1.11. Found: C, 93.41; H, 1.19. IR (KBr disk): $\nu_{C=O}$ 1701 (vs), $\nu_{C=C}$ 1618 (m), ν_{C60} 1437 (m), 1182 (m), 576 (w), 527 (s) cm^{-1}. ^{1}H NMR (300 MHz, CS_2:$CDCl_3$ = 1:1): 1.20 (t, *J* = 7.2 Hz, 3H, CH_3), 4.28 (q, *J* = 7.2 Hz, 2H, CH_2), 7.60–7.63 (m, two *m*-H/one *p*-H in C_6H_5), 8.11–8.14 (m, two *o*-H in C_6H_5) ppm. ^{13}C NMR (100.6 MHz, CS_2:$CDCl_3$ = 1:1): 14.39 (CH_3), 60.98 (CH_2), 109.99 (*C*=CO), 128.23, 129.81, 130.35, 131.42 (C_6H_5), 163.31, 163.55 (C=*C*O/CO_2); C_{60}: 72.43, 105.03 (2 sp^3-C), 135.82 (2C), 137.86 (2C), 139.73 (2C), 140.24 (2C), 141.83 (2C), 141.91 (2C), 142.61 (2C), 142.65 (2C), 142.78 (2C), 142.84 (2C), 143.01 (2C), 143.10 (2C), 143.36 (2C), 144.56 (2C), 144.72 (2C), 144.83 (2C), 145.12 (2C), 145.34 (2C), 145.48 (2C), 145.76 (2C), 145.97 (2C), 146.27 (2C), 146.34 (2C), 146.49 (2C), 146.55 (2C), 146.77 (2C), 147.64 (1C), 147.71 (2C), 148.35 (1C), 148.64 (2C) ppm. UV–vis (CH_2Cl_2, 5 × 10^{-6} M): λ_{max} (log ε) = 228 (4.99), 255 (5.11), 315 nm (4.67).

Preparation of (4-C_5H_4N)C(O)=C(C_{60})$CO_2Et \cdot$ZnTPPH (3). A 25 mL Schlenk tube was charged with fullerene derivative **1** (9.1 mg, 0.01 mmol), ZnTPPH (6.8 mg, 0.01 mmol), and CS_2 (1.5 mL). To the top of the resulting CS_2 solution was carefully added hexane (1 mL), and then, the system was allowed to diffuse its hexane into the CS_2 solution. After 2 days of slow diffusion at room temperature, a black precipitate was formed, which was collected by filtration, washed with hexane, and finally dried under vacuum to afford **3** (15.5 mg, 97%) as a black solid. Mp: 290–292 °C. Anal. Calcd. for $C_{114}H_{37}N_5O_3Zn \cdot 3C_6H_5Cl$: C, 82.25; H, 2.72; N, 3.63. Found: C, 82.09; H, 2.74; N, 3.58. IR (KBr disk): $\nu_{C=O}$ 1706 (s), $\nu_{C=C}$ 1598 (s), $\nu_{C=C}$ 1522 (m, pyrrole C=C), $\nu_{C=N}$ 1484 (m, pyrrole C=N), ν_{C-N} 1338 (m, pyrrole C–N), ν_{C60} 1400 (m), 1175 (m), 575 (w), 527 (s) cm^{-1}. ^{1}H NMR (300 MHz, CS_2:$CDCl_3$ = 1:1): 0.73 (t, *J* = 7.2 Hz, 3H, CH_3), 3.40 (br s, 2α-H in C_5H_4N), 3.87 (q, *J* = 7.2 Hz, 2H, CH_2), 6.42 (d, *J* = 6.0 Hz, 2β-H in C_5H_4N), 7.70–7.72 (m, 8*m*-H/4*p*-H in 4C_6H_5), 8.18–8.21 (m, 8*o*-H in 4C_6H_5), 8.86 (s, 8H in 4 pyrrole rings) ppm. ^{13}C NMR (75.4 MHz, CS_2:$CDCl_3$ = 1:1): 13.64 (CH_3), 60.84 (CH_2), 107.25 (*C*=C–O), 120.82 (4meso-C attached to phenyl groups), 122.63 (2β-C in C_5H_4N), 126.45, 127.23 (8*m*-C/4*p*-C in 4C_6H_5), 131.86 (8β-C in pyrrole rings), 134.74 (8*o*-C in 4C_6H_5), 143.47 (4ipso-C in 4C_6H_5), 150.12 (2α-C in C_5H_4N/8α-C in pyrrole rings), 161.44, 162.22 (C=*C*O/CO_2); C_{60}: 72.14, 101.91 (2sp^3-C), 136.46 (2C), 136.98 (2C), 138.81 (2C), 139.06 (2C), 140.31 (2C), 140.94 (2C), 141.41 (4C), 141.55 (2C), 141.69 (2C), 141.83 (2C), 141.89 (2C), 142.09 (2C), 142.52 (2C), 143.23 (2C), 143.60 (2C), 143.94 (3C, including one γ-C in C_5H_4N), 144.22 (2C), 144.39 (2C), 144.50 (2C), 144.72 (2C), 145.16 (2C), 145.25 (4C), 145.42 (2C), 145.52 (2C), 146.46 (2C), 146.48 (2C), 146.57 (1C), 147.23 (1C) ppm. UV–vis (CH_2Cl_2, 5 × 10^{-6} M): λ_{max} (log ε) = 227 (5.03), 254 (5.13), 314 (4.77), 418 (5.68), 547 (4.24), 585 nm (2.93).

Preparation of H_2TPPC(O)CH_2CO_2Et (4). A 100 mL two-necked flask fitted with a magnetic stir-bar, a rubber septum, and a N_2 inlet tube was sequentially charged with THF (20 mL), monoethyl malonate (0.86 mL, 7.3 mmol), and several milligrams of 2,2′-dipyridyl as an indicator. The mixture was cooled to −65 °C, and then, *n*-BuLi (1.6 M in hexane, 9 mL, 14.6 mmol) was slowly added to allow the low temperature to raise to ca. −5 °C. While the pink indicator persisted at −5 °C, the mixture was recooled to −65 °C. To this mixture were added H_2TPPCOCl (494 mg, 0.73 mmol) (prepared from H_2TPPCO_2H and oxalyl chloride), Et_3N (0.4 mL, 2.87 mmol), and THF (15 mL). The new mixture was stirred at this temperature for 20 min and at room temperature for 1 h and then was poured into a mixture of CH_2Cl_2 (100 mL) and 1 N HCl (20 mL). The organic layer was washed with the $NaHCO_3$-saturated aqueous solution of (2 × 30 mL), dried over Na_2SO_4, and evaporated to dryness at reduced pressure. The residue was subjected to column chromatography (silica gel). Elution with CH_2Cl_2/petroleum ether (v/v 3:1) developed a purple band, from which **4** (430 mg, 81%) was obtained as a purple solid. Mp: 84 °C (dec).

Anal. Calcd. for $C_{49}H_{36}N_4O_3$: C, 80.75; H, 4.98; N, 7.69. Found: C, 80.56; H, 4.90; N, 7.67. IR (KBr disk): ν_{N-H} 3316 (m), $\nu_{C=O}$ 1742 (s), $\nu_{OC=O}$ 1687 (s), $\nu_{C=C}$ 1558 (m, pyrrole C=C), $\nu_{C=N}$ 1472 (s, pyrrole C=N), ν_{C-N} 1349 (m, pyrrole C−N) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): −2.75 (s, 2H, 2NH), 1.40 (t, *J* = 7.2 Hz, 3H, CH_3), 4.25, (s, 2H in $COCH_2CO_2$ of keto form), 4.37 (q, *J* = 7.2 Hz, 2H, OCH_2CH_3), 6.00 (s, 1H in C=CH of enol form), 7.78 (s, 6*m*-H/3*p*-H in $3C_6H_5$), 8.24 (s, 8*o*-H in $3C_6H_5/C_6H_4$), 8.35 (s, 2*m*-H in C_6H_4), 8.79−8.90 (m, 8H in 4 pyrrole rings), 12.86 (s, 1H in HOC=C of enol form) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) for keto form: 14.63 (CH_3), 46.33 ($COCH_2CO_2$), 61.95 (OCH_2CH_3), 118.52, 120.97 (4meso-C attached to phenyl groups), 127.12 (8*m*-C in C_6H_5/C_6H_4), 128.19 (3*p*-C in C_6H_5), 131.78 (8*β*-C in pyrrole rings), 134.94 (6*o*-C in C_6H_5), 135.17 (2*o*-C in C_6H_4), 142.38 (4ipso-C in $3C_6H_5/C_6H_4$), 148.16 (8*α*-C in pyrrole rings), 167.90 (CO_2), 192.96 (C=O) ppm; for enol form: 14.55 (CH_3), 60.88 (OCH_2CH_3), 88.38 (CH=COH), 119.25, 121.24 (4meso-C attached to phenyl groups), 124.77 (8*m*-C in $3C_6H_5/C_6H_4$), 128.15 (3*p*-C in $3C_6H_5$), 133.17 (8*β*-C in pyrrole rings), 135.10 (6*o*-C in $3C_6H_5$), 135.46 (2*o*-C in C_6H_4), 145.63 (4ipso-C in $3C_6H_5/C_6H_4$), 152.51 (8*α*-C in pyrrole rings), 171.65 (OC=O), 173.70 (CH=COH) ppm. UV−vis (CH_2Cl_2, 5 × 10^{-6} M): λ_{max} (log *ε*) = 418 (5.62), 514 (4.15), 551 (3.65), 590 (3.38), 645 nm (3.30).

Preparation of ZnTPPC(O)CH_2CO_2Et (5). To the same equipped flask as that described for preparation of **4** were added porphyrin derivative **4** (50 mg, 0.069 mmol) and $CHCl_3$ (10 mL). To the stirred solution was added a MeOH (10 mL) solution of Zn-$(OAc)_2\cdot 2H_2O$ (50 mg, 0.23 mmol), and then, the new mixture was heated at reflux for 1 h. After cooling to room temperature, it was washed with water (3 × 10 mL) and the separated organic layer was dried over Na_2SO_4 and evaporated to dryness at reduced pressure. The residue was subjected to column chromatography (silica gel). Elution with CH_2Cl_2/petroleum ether (v/v 2:1) developed a purple-red band, from which **5** (49 mg, 90%) was obtained as a purple-red solid. Mp: 214 °C (dec). Anal. Calcd. for $C_{49}H_{34}N_4O_3Zn$: C, 74.29; H, 4.33; N, 7.07. Found: C, 74.09; H, 4.50; N, 7.09. IR (KBr disk): $\nu_{C=O}$ 1741(s), $\nu_{OC=O}$ 1685 (s), $\nu_{C=C}$ 1558 (w, pyrrole C=C), $\nu_{C=N}$ 1487 (m, pyrrole C=N), ν_{C-N} 1338 (s, pyrrole C−N) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): 1.38 (t, *J* = 7.2 Hz, 3H, CH_3), 4.27 (s, 2H, $COCH_2CO_2$), 4.35 (q, *J* = 7.2 Hz, 2H, OCH_2CH_3), 7.77 (s, 6*m*-H/3*p*-H in $3C_6H_5$), 8.21−8.23 (m, 6*o*-H in $3C_6H_5$), 8.35 (s, 4H, C_6H_4), 8.87−8.96 (m, 8H in 4 pyrrole rings) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): 14.13 (CH_3) 45.94 ($COCH_2CO_2$), 61.55 (OCH_2CH_3), 119.06, 121.45 (4meso-C attached to phenyl groups), 126.60 (8*m*-C in $3C_6H_5/C_6H_4$), 127.58 (3*p*-C in $3C_6H_5$), 131.38 (one *p*-C in C_6H_4), 132.18, 132.43 (8*β*-C in pyrrole rings), 134.48 (6*o*-C in $3C_6H_5$), 134.82 (2*o*-C in C_6H_4), 142.79 (4ipso-C in $3C_6H_5/C_6H_4$), 148.79, 149.46, 150.27, 150.48 (8*α*-C in pyrrole rings), 167.50 (CO_2), 192.52 (C=O) ppm. UV−vis (CH_2Cl_2, 5 × 10^{-6} M): λ_{max} (log *ε*) = 419 (5.73), 548 (4.37), 587 nm (3.67).

Preparation of H_2TPPC(O)=C(C_{60})CO_2Et (6). To the same equipped flask as that used for preparation of **4** were added porphyrin derivative **4** (109 mg, 0.15 mmol), C_{60} (72 mg, 0.1 mmol), and chlorobenzene (20 mL). To the stirred solution was added piperidine (30 *μ*L, 0.3 mmol), and then, the new mixture continued to be stirred at room temperature for 36 h under the dark. After volatiles were removed at reduced pressure, the residue was subjected to column chromatography (silica gel). Elution with toluene/petroleum ether (v/v 1:1) developed a purple band, from which unreacted C_{60} (28 mg) was recovered. Elution with toluene developed a brown band, from which **6** (68 mg, 77% based on the consumed C_{60}) was obtained as a brown-black solid. Mp: >300 °C (dec). Anal. Calcd. for $C_{109}H_{34}N_4O_3$: C, 90.45; H, 2.37; N, 3.87. Found: C, 90.57; H, 2.32; N, 3.62. IR (KBr disk): ν_{N-H} 3315 (m), $\nu_{OC=O}$ 1700 (s), $\nu_{OC=C}$ 1601 (w), $\nu_{C=C}$ 1558 (m, pyrrole C=C), $\nu_{C=N}$ 1460 (s, pyrrole C=N), ν_{C-N} 1372 (m, pyrrole C−N); ν_{C60} 1442 (m), 1180 (s), 576 (w), 527 (s) cm^{-1}. ^{1}H NMR (400 MHz, CS_2:$CDCl_3$ = 2:1): −2.82 (s, 2H, 2NH), 1.38 (t, *J* = 7.2 Hz, 3H, CH_3), 4.43 (q, *J* = 7.2 Hz, 2H, CH_2), 7.79 (s, 6*m*-H/3*p*-H in $3C_6H_5$), 8.22 (d, *J* = 4.8 Hz, 6*o*-H in $3C_6H_5$), 8.51, 8.53, 8.58, 8.60 (ABq, *J* = 8.0 Hz, 4H, C_6H_4), 8.83, 8.91, 8.96 (3s, 8H in 4 pyrrole rings) ppm. ^{13}C NMR (100.6 MHz, CS_2:$CDCl_3$ = 1:1): 14.15 (CH_3), 60.79 (CH_2), 104.89 (*C*=CO), 118.62, 120.17 (4meso-C attached to phenyl), 131.32 (8*β*-C in pyrrole rings), 126.62, 127.58, 128.42, 134.04, 134.44 (C_6H_5/C_6H_4), 141.93 (8*α*-C in pyrrole rings), 163.57, 166.03 (C=CO/CO_2); C_{60}: 73.96 (2 sp^3-C), 134.97 (2C), 136.74 (2C), 138.91 (2C), 139.06 (2C), 140.52 (2C), 141.17 (2C), 141.51 (2C), 141.57 (2C), 141.83 (2C), 142.02 (2C), 142.05 (2C), 142.31 (2C), 143.43 (2C), 143.55 (2C), 143.85 (2C), 143.94 (2C), 144.48 (2C), 144.68 (2C), 144.83 (4C), 145.27 (4C), 145.41 (2C), 145.54 (2C), 145.60 (2C), 145.70 (2C), 146.86 (1C), 146.96 (2C), 147.54 (1C), 147.71 (2C) ppm. UV−vis (CH_2Cl_2, 5 × 10^{-6} M): λ_{max} (log *ε*) = 254 (5.04), 314 (4.66), 418 (5.58), 514 (4.09), 551 (3.70), 590 (3.36), 645 nm (3.24).

Preparation of ZnTPPC(O)=C(C_{60})CO_2Et (7). To the same equipped flask as that used for preparation of **4** were added dyad **6** (17.6 mg, 0.012 mmol) and $CHCl_3$ (10 mL). While stirring, to the resulting solution was added a MeOH (10 mL) solution of $Zn(OAc)_2\cdot 2H_2O$ (10 mg, 0.046 mmol), and then, the new mixture continued to be stirred at room temperature for 0.5 h. The reaction mixture was washed with water (3 × 10 mL) and dried over Na_2SO_4. After removal of solvents under vacuum, **7** (15.6 mg, 89%) was obtained as a brown-black solid. Mp: >300 °C (dec). Anal. Calcd. for $C_{109}H_{32}N_4O_3Zn$: C, 86.65; H, 2.13; N, 3.71. Found: C, 86.79; H, 2.19; N, 3.69. IR (KBr disk): $\nu_{OC=O}$ 1693 (m); $\nu_{OC=C}$ 1632 (m), $\nu_{C=C}$ 1550 (w, pyrrole C=C), $\nu_{C=N}$ 1439 (w, pyrrole C=N), ν_{C-N} 1368 (w, pyrrole C−N); ν_{C60} 1439 (w), 563 (w), 526 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 1.37 (t, *J* = 7.2 Hz, 3H, CH_3), 4.45 (q, *J* = 7.2 Hz, 2H, CH_2), 8.40 (s, 6*m*-H/3*p*-H in $3C_6H_5$), 8.43 (s, 6*o*-H in $3C_6H_5$), 8.45−8.60 (m, 4H, C_6H_4), 8.95−9.08 (m, 8H in pyrrole rings) ppm. ^{13}C NMR (100.6 MHz, CS_2:$CDCl_3$ = 1:1): 13.24 (CH_3), 59.95 (CH_2), 103.91 (*C*=CO), 118.81, 120.32 (4meso-C attached to phenyl), 125.51, 125.60, 126.51, 127.43, 130.78, 131.11, 131.17, 131.35, 133.02, 133.41, 141.72, 141.78 (C_6H_5/C_6H_4), 162.90, 165.35 (C=CO/CO_2); C_{60}: 72.02, 100.85 (2sp^3-C), 134.05 (2C), 134.57 (2C), 135.85 (2C), 138.00 (2C), 138.05 (2C), 139.40 (2C), 140.27 (2C), 140.50 (2C), 140.58 (2C), 140.88 (2C), 141.11 (4C), 141.40 (2C), 142.45 (2C), 142.69 (2C), 142.98 (2C), 143.04 (2C), 143.55 (2C), 143.75 (2C), 143.95 (2C), 144.31 (2C), 144.49 (2C), 144.62 (2C), 144.69 (2C), 144.79 (2C), 145.14 (2C), 145.93 (1C), 146.06 (2C), 146.66 (1C), 146.88 (2C) ppm. UV−vis (CH_2Cl_2, 5 × 10^{-6} M): λ_{max} (log *ε*) = 228 (5.27), 257 (5.33), 314 (4.94), 419 (5.79), 548 (4.46), 587 nm (3.87).

X-ray Structure Determinations of 2 and 3 and 5. The single crystals of **2** suitable for X-ray diffraction analysis were grown by slow evaporation of its CS_2/hexane solution at rt, those of **3** obtained by slow evaporation of its CS_2/PhCl solution at rt, and those of **5** obtained by slow evaporation of its CH_2Cl_2/EtOH solution at rt. A single crystal of **2**, **3**, or **5** was mounted on a Rigaku MM-007 (rotating anode) diffractometer equipped with Saturn 70CCD. Data were collected at 113 K using a confocal monochromator with Mo K*α* radiation (0.71070 Å) in the *ω*−*ϕ* scanning mode. Data collection and reduction and absorption correction were performed by CRYSTALCLEAR program.[59] All the structures were solved by direct methods using the SHELXS-97 program[60] and refined by full-matrix least-squares techniques (SHELXL-97)[61] on F^2. Hydrogen atoms were located using the geometric method. Crystal data and structural refinement details for **2**, **3**, and **5** are summarized in Table 3 (see Supporting Information).

Photoinduced H_2 Evolution. A 30 mL Schlenk flask fitted with a N_2 inlet tube, a rubber septum, a magnetic stir-bar, and a water-cooling jacket was charged with EDTA (55.83 mg, 0.15 mmol), dyad **3** (0.32 mg, 2 × 10^{-4} mmol), colloidal Pt (10 mL of 0.1 mM, 1 × 10^{-3} mmol), MV^{2+} (1.76 mg, 4 × 10^{-3} mmol), HOAc (57 *μ*L, 1 mmol), and Triton X-100

(0.3 mL). While stirring, the resulting solution was thoroughly deoxygenated by bubbling with nitrogen and then was irradiated through a Pyrex-glass filter ($\lambda > 400$ nm) using a 350 W Xe lamp at about 25 °C (controlled by the cooling jacket). During the photoinduced catalysis, the evolved H_2 was withdrawn periodically using a gastight syringe, which was analyzed by gas chromatography on a Shimadzu GC-9A instrument with a thermal conductivity detector and a carbon molecular sieve column (3 mm × 2.0 m) and N_2 as the carrier gas.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Full tables of crystal data, atomic coordinates, thermal parameters, and bond lengths and angles for **2**, **3**, and **5** as CIF files and Table 3 summarizing the crystal data and structural refinment details for **2**, **3**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: lcsong@nankai.edu.cn.

■ ACKNOWLEDGMENT

We are grateful to 973 (2011CB935902), the National Natural Science Foundation of China (20772059, 20972073), and the Tianjin Natural Science Foundation (09JCZDJC27900) for financial support.

■ REFERENCES

(1) Sakai, K.; Ozawa, H. *Coord. Chem. Rev.* **2007**, *251*, 2753.

(2) Dempsey, J. L.; Brunschwig, B. S.; Winkler, J. R.; Gray, H. B. *Acc. Chem. Res.* **2009**, *42*, 1995.

(3) Magnuson, A.; Anderlund, M.; Johansson, O.; Lindblad, P.; Lomoth, R.; Polivka, T.; Ott, S.; StensJö, K.; Styring, S.; Sundström, V.; Hammarström, L. *Acc. Chem. Res.* **2009**, *42*, 1899.

(4) Ozawa, H.; Haga, M.; Sakai, K. *J. Am. Chem. Soc.* **2006**, *128*, 4926.

(5) (a) Fihri, A.; Artero, V.; Razavet, M.; Baffert, C.; Leibl, W.; Fontecave, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 564. (b) Wang, F.; Wang, W.-G.; Wang, X.-J.; Wang, H.-Y.; Tung, C.-H.; Wu, L.-Z. *Angew. Chem., Int. Ed.* **2011**, *50*, 3193.

(6) Cammack, R.; Frey, M.; Robson, R. *Hydrogen as a fuel: Learning from nature*; Taylor & Francis: London, 2001.

(7) Okura, I. *Coord. Chem. Rev.* **1985**, *68*, 53.

(8) Amao, Y.; Okura, I. *J. Mol. Catal. B: Enzym.* **2002**, *17*, 9.

(9) Rau, S.; Walther, D.; Vos, J. G. *Dalton Trans.* **2007**, 915.

(10) Amao, Y.; Kamachi, T.; Okura, I. *J. Porphyrins Phthalocyanines* **1998**, *2*, 201.

(11) Song, L.-C.; Wang, L.-X.; Tang, M.-Y.; Li, C.-G.; Song, H.-B.; Hu, Q.-M. *Organometallics* **2009**, *28*, 3834.

(12) Song, L.-C.; Liu, X.-F.; Ming, J.-B.; Ge, J.-H.; Xie, Z.-J.; Hu, Q.-M. *Organometallics* **2010**, *29*, 610.

(13) McLendon, G.; Miller, D. S. *J. Chem. Soc., Chem. Commun.* **1980**, 533.

(14) Aono, S.; Kaji, N.; Okura, I. *J. Chem. Soc., Chem. Commun.* **1986**, 170.

(15) Esswein, A. J.; Nocera, D. G. *Chem. Rev.* **2007**, *107*, 4022.

(16) Schuster, D. I.; Cheng, P.; Jarowski, P. D.; Guldi, D. M.; Luo, C.; Echegoyen, L.; Pyo, S.; Holzwarth, A. R.; Braslavsky, S. E.; Williams, R. M.; Klihm, G. *J. Am. Chem. Soc.* **2004**, *126*, 7257.

(17) D'Souza, F.; Deviprasad, G. R.; Zandler, M. E.; Hoang, V. T.; Klykov, A.; VanStipdonk, M.; Perera, A.; El-Khouly, M. E.; Fujitsuka, M.; Ito, O. *J. Phys. Chem. A* **2002**, *106*, 3243.

(18) Imahori, H.; Hagiwara, K.; Aoki, M.; Akiyama, T.; Taniguchi, S.; Okada, T.; Shirakawa, M.; Sakata, Y. *J. Am. Chem. Soc.* **1996**, *118*, 11771.

(19) Imahori, H.; Sakata, Y. *Adv. Mater.* **1997**, *9*, 537.

(20) Guldi, D. M. *Chem. Commun.* **2000**, 321.

(21) D'Souza, F.; Deviprasad, G. R.; El-Khouly, M. E.; Fujitsuka, M.; Ito, O. *J. Am. Chem. Soc.* **2001**, *123*, 5277.

(22) Liddell, P. A.; Sumida, J. P.; Macpherson, A. N.; Noss, L.; Seely, G. R.; Clark, K. N.; Moore, A. L.; Moore, T. A.; Gust, D. *Photochem. Photobiol.* **1994**, *60*, 537.

(23) (a) Guldi, D. M. *Chem. Soc. Rev.* **2002**, *31*, 22. (b) D'Souza, F.; Ito, O. *Coord. Chem. Rev.* **2005**, *249*, 1410.

(24) (a) Da Ros, T.; Prato, M.; Guldi, D.; Alessio, E.; Ruzzi, M.; Pasimeni, L. *Chem. Commun.* **1999**, 635. (b) Da Ros, T.; Prato, M.; Guldi, D. M.; Ruzzi, M.; Pasimeni, L. *Chem.—Eur. J.* **2001**, *7*, 816. (c) Sánchez, L.; Martín, N.; Guldi, D. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 5374.

(25) (a) D'Souza, F.; Rath, N. P.; Deviprasad, G. R.; Zandler, M. E. *Chem. Commun.* **2001**, 267. (b) Tat, F. T.; Zhou, Z.; MacMahon, S.; Song, F.; Rheingold, A. L.; Echegoyen, L.; Schuster, D. I.; Wilson, S. R. *J. Org. Chem.* **2004**, *69*, 4602. (c) Hauke, F.; Swartz, A.; Guldi, D. M.; Hirsch, A. *J. Mater. Chem.* **2002**, *12*, 2088. (d) Guldi, D. M.; Luo, C.; Da Ros, T.; Prato, M.; Dietel, E.; Hirsch, A. *Chem. Commun.* **2000**, 375.

(26) (a) Wilson, S. R.; MacMahon, S.; Tat, F. T.; Jarowski, P. D.; Schuster, D. I. *Chem. Commun.* **2003**, 226. (b) D'Souza, F.; Chitta, R.; Gadde, S.; Zandler, M. E.; Sandanayaka, A. S. D.; Araki, Y.; Ito, O. *Chem. Commun.* **2005**, 1279. (c) D'Souza, F.; EI-Khouly, M. E.; Gadde, S.; McCarty, A. L.; Karr, P. A.; Zandler, M. E.; Araki, Y.; Ito, O. *J. Phys. Chem. B* **2005**, *109*, 10107.

(27) (a) Baran, P. S.; Monaco, R. R.; Khan, A. U.; Schuster, D. I.; Wilson, S. R. *J. Am. Chem. Soc.* **1997**, *119*, 8363. (b) Sun, Y.; Drovetskaya, T.; Bolskar, R. D.; Bau, R.; Boyd, P. D. W.; Reed, C. A. *J. Org. Chem.* **1997**, *62*, 3642. (c) MacMahon, S.; Fong, R.; Baran, P. S.; Safonov, I.; Wilson, S. R.; Schuster, D. I. *J. Org. Chem.* **2001**, *66*, 5449. (d) Drovetskaya, T.; Reed, C. A.; Boyd, P. *Tetrahedron Lett.* **1995**, *36*, 7971.

(28) (a) Rieder, A.; Kräutler, B. *J. Am. Chem. Soc.* **2000**, *122*, 9050. (b) Armaroli, N.; Marconi, G.; Echegoyen, L.; Bourgeois, J.-P.; Diederich, F. *Chem.—Eur. J.* **2000**, *6*, 1629. (c) D'Souza, F.; Gadde, S.; Zandler, M. E.; Arkady, K.; EI-Khouly, M. E.; Fujitsuka, M.; Ito, O. *J. Phys. Chem. A* **2002**, *106*, 12393. (d) Ikemoto, J.; Takimiya, K.; Aso, V.; Otsubo, T.; Fujitsuka, M.; Ito, O. *Org. Lett.* **2002**, *4*, 309.

(29) (a) Tkachenko, N. Y.; Lemmetyinen, H.; Sonoda, J.; Ohkubo, K.; Sato, T.; Imahori, H.; Fukuzumi, S. *J. Phys. Chem. A* **2003**, *107*, 8834. (b) Kodis, G.; Liddell, P. A.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Phys. Org. Chem.* **2004**, *17*, 724. (c) Lembo, A.; Tagliatesta, P.; Guldi, D. M. *J. Phys. Chem. A* **2006**, *110*, 11424.

(30) (a) Katterle, M.; Holzwarth, A. R.; Jesorka, A. *Eur. J. Org. Chem.* **2006**, 414. (b) Vail, S. A.; Schuster, D. I.; Guldi, D. M.; Isosomppi, M.; Tkachenko, N.; Lemmetyinen, H.; Palkar, A.; Echegoyen, L.; Chen, X.; Zhang, J. Z. H. *J. Phys. Chem. B* **2006**, *110*, 14155. (c) Schuster, D. I.; Li, K.; Guldi, D. M.; Palkar, A.; Echegoyen, L.; Stanisky, C.; Cross, R. J.; Niemi, M.; Tkachenko, N. V.; Lemmetyinen, H. *J. Am. Chem. Soc.* **2007**, *129*, 15973.

(31) Ohno, M.; Yashiro, A.; Eguchi, S. *Chem. Commun.* **1996**, 291.

(32) (a) Li, C.; Zhang, D.; Zhang, X.; Wu, S.; Gao, X. *Org. Biomol. Chem.* **2004**, *2*, 3464. (b) Wang, G.-W.; Li, F.-B. *Org. Biomol. Chem.* **2005**, *3*, 794.

(33) (a) Hare, J. P.; Dennis, T. J.; Kroto, H. W.; Taylor, R.; Allaf, A. W.; Balm, S.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1991**, 412. (b) Song, L.-C.; Yu, G.-A.; Su, F.-H.; Hu, Q.-M. *Organometallics* **2004**, *23*, 4192.

(34) Thomas, D. W.; Martell, A. E. *J. Am. Chem. Soc.* **1959**, *81*, 5111.

(35) Kruper, W. J.; Chamberlin, T. A.; Kochanny, M. *J. Org. Chem.* **1989**, *54*, 2753.

(36) Bookser, B. C.; Bruice, T. C. *J. Am. Chem. Soc.* **1991**, *113*, 4208.

(37) Balch, A. L.; Olmstead, M. M. *Chem. Rev.* **1998**, *98*, 2123.

(38) Hirsch, A.; Brettreich, M. *Fullerenes: chemistry and reactions*; WILEY-VCH Verlag GmbH & Co. KGaA: Weinheim, 2005.

(39) Miller, G. P.; Briggs, J.; Mack, J.; Lord, P. A.; Olmstead, M. M.; Balch, A. L. *Org. Lett.* **2003**, *5*, 4199.

(40) Chuang, S.-C.; Sander, M.; Jarrosson, T.; James, S.; Rozumov, E.; Khan, S. I.; Rubin, Y. *J. Org. Chem.* **2007**, *72*, 2716.

(41) Wierenga, W.; Skulnick, H. I. *J. Org. Chem.* **1979**, *44*, 310.

(42) Clay, R. J.; Collom, T. A.; Karrick, G. L.; Wemple, J. *Synthesis* **1993**, 290.

(43) Nakazawa, J.; Mizuki, M.; Hagiwara, J.; Shimazaki, Y.; Tani, F.; Naruta, Y. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1431.

(44) (a) Glick, M. D.; Cohen, G. H.; Hoard, J. L. *J. Am. Chem. Soc.* **1967**, *89*, 1996. (b) Diskin-Posner, Y.; Kumar, R. K.; Goldberg, I. *New J. Chem.* **1999**, *23*, 885.

(45) Dave, P. C.; Sriniras, D. *J. Porphyrins Phthalocyanines* **1998**, *2*, 243.

(46) Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1423.

(47) Song, L.-C.; Wang, G.-F.; Liu, P.-C; Hu, Q.-M. *Organometallics* **2003**, *22*, 4593.

(48) An, Y.-Z.; Rubin, Y.; Schaller, C.; McElvany, S. W. *J. Org. Chem.* **1994**, *59*, 2927.

(49) Dudié, M.; Lhoták, P.; Král, V.; Lang, K.; Stibor, I. *Tetrahedron Lett.* **1999**, *40*, 5949.

(50) Baskaran, D.; Mays, J. W.; Zhang, X. P.; Bratcher, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 6916.

(51) Ahmadi, T. S.; Wang, Z. L.; Green, T. C.; Henglein, A.; El-Sayed, M. A. *Science* **1996**, *272*, 1924.

(52) Du, P.; Schneider, J.; Jarosz, P.; Eisenberg, R. *J. Am. Chem. Soc.* **2006**, *128*, 7726.

(53) (a) Amao, Y.; Okura, I. *J. Mol. Catal. A: Chem.* **1996**, *105*, 125. (b) Amao, Y.; Hiraishi, T.; Okura, I. *J. Mol. Catal. A: Chem.* **1997**, *126*, 21. (c) Hiraishi, T.; Kamachi, T.; Okura, I. *J. Mol. Catal. A: Chem.* **1999**, *138*, 107.

(54) Gilman, H.; Broadbent, H. S. *J. Am. Chem. Soc.* **1948**, *70*, 2755.

(55) Rothemund, P.; Menotti, A. R. *J. Am. Chem. Soc.* **1948**, *70*, 1808.

(56) Mandai, T.; Imaji, M.; Takada, H.; Kawata, M.; Nokami, J.; Tsuji, J. *J. Org. Chem.* **1989**, *54*, 5395.

(57) Matile, S.; Berova, N.; Nakanishi, K.; Fleischhauer, J.; Woody, R. W. *J. Am. Chem. Soc.* **1996**, *118*, 5198.

(58) Paolesse, R.; Monti, D.; Monica, L. L.; Venanzi, M.; Froiio, A.; Nardis, S.; Natale, C. D.; Martinelli, E.; D'Amico, A. *Chem.—Eur. J.* **2002**, *8*, 2476.

(59) CRYSTALCLEAR 1.3.6. Rigaku and Rigaku/MSC: The Woodlands, TX, 2005.

(60) Sheldrick, G. M. *SHELXS-97, A Program for Crystal Structure Solution*; University of Göttingen: Germany, 1997.

(61) Sheldrick, G. M. *SHELXL-97, A Program for Crystal Structure Refinement*; University of Göttingen: Germany, 1997.