# Effect of Dual Fullerenes on Lifetimes of Charge-Separated States of Subphthalocyanine-Triphenylamine-Fullerene Molecular Systems

Mohamed E. El-Khouly,<sup>\*,†,‡</sup> Sun Hee Shim,<sup>§</sup> Yasuyuki Araki,<sup>\*,†</sup> Osamu Ito,<sup>†</sup> and Kwang-Yol Kay<sup>\*,§</sup>

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira, Sendai, 980-8577 Japan, Department of Chemistry, Faculty of Education, Kafr El-Sheikh University, Egypt, and Department of Molecular Science and Technology, Ajou University, Suwon 443-749, South Korea

Received: November 14, 2007; In Final Form: December 28, 2007

Photoinduced intramolecular electron-transfer events of the newly synthesized subphthalocyanine-triphenylamine-fullerene triad (SubPc-TPA-C<sub>60</sub>) and subphthalocyanine-triphenylamine-bisfullerene tetrad (SubPc-TPA-(C<sub>60</sub>)<sub>2</sub>) were studied. The geometric and electronic structures of the triad were probed by ab initio B3LYP/3-21G method, which predicts SubPc-TPA\*-C<sub>60</sub>\*- as a stable charge-separated state. The photoinduced events via the excited singlet state of SubPc were monitored by time-resolved emission measurements as well as transient absorption techniques. Efficient charge-separations via the excited states of SubPc were observed with the rates of ~10<sup>10</sup> s<sup>-1</sup>. Compared with the SubPc-TPA dyad, a long-lived charge-separated state was observed for the SubPc-TPA-C<sub>60</sub> triad with the lifetime of the radical ion pairs ( $\tau_{RIP}$ ) of 670 ns in benzonitrile. Interestingly, further charge stabilization was achieved in the charge-separated state of SubPc-TPA-(C<sub>60</sub>)<sub>2</sub>, in which the  $\tau_{RIP}$  was found to be 1050 ns in benzonitrile.

#### Introduction

Development of relatively simple donor-acceptor models designed to mimic the events of the photosynthetic reaction center has been an important goal in science and technology. Efficient conversion of light energy into other useful energies requires the effective formation of charge-separated (CS) states that exhibit relatively long lifetimes and high-energy contents.<sup>1</sup> In years past, various conjugated macrocycles such as porphyrins, phthalocyanines, and naphthalocyanines were widely employed as building blocks for the photoactive and electroactive assemblies due to their excellent light-harvesting ability in the wide wavelength region (500–700 nm) and to their rich redox chemistry.<sup>2</sup>

However, only a few studies have been reported for the photophysical behavior of subphthalocyanine (SubPc), a singular lower analogue of phthalocynanine.<sup>3</sup> SubPc has three N-fused diiminoisoindoline units arranged around a central boron atom and  $\pi$ -electron aromatic core associated with their curved structures, which make it different from their higher homologues, phthalocyanines.4-6 Particularly attractive points of SubPc are (1) their optoelectronic features can be finely tuned by varying their axial ligands or by functionalizing the various peripheral positions, (2) they are excellent antenna units that absorb the lights in the visible region (500-700 nm) with excitation energy above 2.0 eV, and (3) they possess a relatively low reorganization energy.7 Moreover, SubPc derivatives are strong fluorophores with high quantum yields, which render them ideal molecules to probe electron transfer and energy transfer via the excited singlet states. Therefore, SubPc derivatives are appealing as new building blocks for the artificial



SubPc-TPA-(C60)2

Figure 1. Molecular structures and expected photoinduced processes of the studied compounds.

photosynthetic systems and as unique materials for nonlinear optical applications.

Because of the versatile chemistry of SubPcs,<sup>8</sup> their assemblies for multicomponent photoactive systems are performed via different routes involving peripheral<sup>9</sup> or axial approaches.<sup>10,11</sup> The advantage of the axial approach is to preserve the electronic characteristics of the macrocycles, since the substitution patterns on the benzene rings remain unaltered. Recently, Torres et al. reported that the exchange of the original axial halogen atom with oxygen nucleophiles, particularly phenol, is a very convenient method for introducing diverse functional groups

<sup>\*</sup> To whom correspondence should be addressed. E-mail: araki@ tagen.tohoku.ac.jp; mohamedelkhouly@yahoo.com; kykay@ajou.ac.kr.

<sup>†</sup> Tohoku University.

<sup>&</sup>lt;sup>‡</sup> Kafr El-Sheikh University.

<sup>§</sup> Ajou University.

SCHEME 1: Syntheses of SubPc-TPA-C<sub>60</sub> and SubPc-TPA-(C<sub>60</sub>)<sub>2<sup>a</sup></sub>



SubPc-TPA-C<sub>60</sub>

SubPc-TPA-(C<sub>60</sub>)<sub>2</sub>

in the axial position of the SubPc ring as well as for increasing the solubility and stability of the SubPc derivatives.<sup>12</sup>

Our strategy is to attach the triphenylamine (TPA) unit and the fullerene ( $C_{60}$ ) units to the SubPc moiety, expecting that the attached units can modulate and modify the electronic properties of SubPcs. As reported earlier, the TPA-based compounds have been used in opto-electronic materials owing to the high electron-donor ability and good film-forming properties.<sup>13</sup> Furthermore, the small reorganization energies for the widely diffused  $\pi$ -electron on the spherical fullerene C<sub>60</sub> radical anion are crucial to accelerate the initial CS process and to decelerate exothermic charge recombination (CR) process.<sup>14,15</sup> Thus, it is expected that the combination of SubPc with C<sub>60</sub> and TPA may represent excellent building blocks for the artificial photosynthetic systems and molecular photovoltaic devices.

Taking these properties into consideration, we present in this article the photosensitizing electron-accepting ability of SubPc combined axially with triphenylamine (TPA) donor unit (SubPc–TPA dyad) and the C<sub>60</sub>-connected triad and tetrad (SubPc–TPA–(C<sub>60</sub>)<sub>n</sub>; n = 1 and 2 in Figure 1). The electronic characteristics of the SubPc–TPA dyad can be compared with those of SubPc–C<sub>60</sub> dyads reported by Torres et al.<sup>16</sup> In the SubPc–TPA–C<sub>60</sub> triad, SubPc would be expected to act as a photosensitizing electron acceptor, TPA as an electron-donor, and C<sub>60</sub> as an additional electron-acceptor. Furthermore, in the SubPc–TPA–(C<sub>60</sub>)<sub>2</sub> tetrad, the dual C<sub>60</sub> moieties would be expected to have synergistic effect for photoinduced CS giving stabilized radical ion pair (RIP).

#### **Results and Discussion**

Synthesis and Characterization. SubPc-TPA- $C_{60}$  and SubPc-TPA- $(C_{60})_2$  have been prepared according to the

procedures depicted in Scheme 1. Every step of the reaction sequence proceeded smoothly and efficiently to give a good or moderate yield of the product (yields are shown in Scheme 1). Details for syntheses of the final products are described in the Experimental Section, which includes synthesis of SubPc-TPA; furthermore, in the Supporting Information, syntheses of the intermediates are included.

**Molecular Orbital Calculations.** For SubPc–TPA, the optimized structure and the molecular orbital (MO) calculated by ab intio B3LYP/3-21G method<sup>17</sup> are shown in Figure 2. The TPA moiety connected with SubPc via short axial linkage makes the TPA moiety lie on just the upper position of SubPc, which has a bent structure with upper curvature.<sup>12</sup> Although the nearest distance between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) is as close as 0.1 Å, the both MOs are distinctly separated, suggesting that the formation of the CS state with the one-electron reduced SubPc and the one-electron oxidized TPA (SubPc<sup>•–</sup>–TPA<sup>•+</sup>) is possible.

The optimized structure of SubPc-TPA-C<sub>60</sub> is shown in Figure 3. The molecular topology of this molecule shows that the C<sub>60</sub> moiety connected to one of the three phenyl rings of TPA lies closely to the just upper position over SubPc. The center-to-center distances ( $R_{CC}$ ) between SubPc and TPA as well as TPA and C<sub>60</sub> were estimated as 11.0 and 10.0 Å, respectively. It is noticeable that the  $R_{CC}$  value between SubPc and C<sub>60</sub> is also quite short (12.7 Å). The electron distribution of the HOMO was found to be entirely located on the TPA entity, while the electron distribution of the LUMO+3 and LUMO was found to be entirely located over the SubPc moiety and the C<sub>60</sub> spheroids, respectively. The nearest distance between the LUMO of C<sub>60</sub> and the LUMO+3 of SubPc is less than 0.5 Å, which suggests that the through-space electron migration from SubPc<sup>--</sup>





Figure 2. Frontier HOMO and LUMO of SubPc-TPA calculated by ab intio B3LYP/3-21G method.

HOMO

to  $C_{60}$  within SubPc<sup>•-</sup>-TPA<sup>•+</sup>- $C_{60}$  takes place yielding the stable final CS state like as SubPc-TPA<sup>•+</sup>- $C_{60}^{\bullet-}$ .

In the case of SubPc–TPA– $(C_{60})_2$ , the MO calculation predicts several optimized structures with almost the same minimum energies. In the most optimized structure, the second  $C_{60}$  approaches closely to another  $C_{60}$ . Although the HOMO is localized on the TPA moiety, the lower LUMOs are distributed over the  $C_{60}$  units, and the upper LUMO is localized on the SubPc moiety.

Electrochemical Measurements. The CS process from the lowest excited singlet state of SubPc (1SubPc\*) can be supported from the viewpoint of thermodynamics. In differential pulse voltammetry of SubPc-TPA- $(C_{60})_n$  in *o*-dichlorobenzene (*o*-DCB), the first oxidation potential  $(E_{ox})$  of the TPA moiety was located at 0.62 V vs Ag/AgCl, while the first reduction potentials  $(E_{\rm red})$  of the SubPc and C<sub>60</sub> moieties were recorded at -1.20and -0.91 V vs Ag/AgCl. Based on these  $E_{ox}$  and  $E_{red}$  values, the driving forces for the CS processes  $(-\Delta G_{\rm CS})$  via <sup>1</sup>SubPc\* were calculated from the Rehm-Weller equations<sup>18</sup> as listed in Table 1, in addition to  $-\Delta G_{\rm CS}$  values via  ${}^{1}C_{60}^{*}$ . The negative driving forces of the CS processes of the studied compounds (Table 1) suggest exothermic CS processes via <sup>1</sup>SubPc\* and  ${}^{1}C_{60}$ \* in the studied solvents. However, it has been frequently pointed out that  $\Delta G_{CS}$  values in toluene usually contain much estimation errors. The driving forces of CR process  $(-\Delta G_{CR})$ are also listed in Table 2.

**Steady-State Absorption Measurements.** The steady-state absorption spectra of the intense magenta solutions of SubPc– TPA and SubPc–TPA– $(C_{60})_n$  are shown in Figure 4. The absorption spectra of the SubPc moieties consist of a high-energy B-band (between 300–310 nm) and a lower energy Q-band  $(560-580 \text{ nm})^{3-6}$  arisen from the  $\pi-\pi^*$  transitions associated with 14  $\pi$ -electron systems, analogues to those of porphyrins



### HOMO

**Figure 3.** The HOMO and LUMOs of SubPc-TPA- $C_{60}$  calculated by ab intio B3LYP/3-21G method after optimization of structure.

and phthalocyanines. The absorption spectrum of SubPc-TPA in the visible region is almost identical to that of SubPc-OPh reference,12 revealing only weak intramolecular electronic interactions in the ground state between the SubPc and TPA moieties. In benzonitrile (BN), an appreciable red-shift (ca. 5 nm) was observed compared with the peak in toluene (563 nm), which suggests the interaction of the B atom of SubPc with the lone pair of BN. In the UV region, the new band appeared at ca. 350 nm, which may be attributed to the substituted TPA moiety with a triangular pyramidal structure different from substituted TPA showing a band at 300 nm.19 The presence of the fulleropyrrolidine unit was evidenced by the higher absorption between 250 and 350 nm and also by the weak typical band at 432 nm, whereas the expected weak peak near 700 nm may be hidden by the huge absorption of the SubPc unit that dominates in this region. These absorption spectra revealed that intramolecular electronic interactions of the C<sub>60</sub> unit with the SubPc and TPA moieties may be weak in the ground state.

TABLE 1: Free Energy Changes ( $\Delta G_{CS}$ ), Fluorescence Lifetimes of SubPc ( $\tau_t$ ) in the 500–680 nm Region, Rate Constants ( $k_{CS}$ ), and Quantum Yields ( $\Phi_{CS}$ ) of Charge-Separation of SubPc-TPA, SubPc-TPA-C<sub>60</sub> and SubPc-TPA-(C<sub>60</sub>)<sub>2</sub> via <sup>1</sup>SubPc\*

		$-\Delta G_{\rm C}$		$k_{\rm CS}/{\rm s}^{-1c}$	$\Phi_{\mathrm{CS}}{}^{c,d}$	
compounds	solvents	SubPc <sup>·-</sup> -TPA <sup>·+</sup> -C <sub>60</sub>	SubPc-TPA <sup>·+</sup> -C <sub>60</sub> <sup>·-</sup>	$\tau_{\rm f}({\rm fraction})/{\rm ps}$	via	<sup>1</sup> SubPc*
SubPc-TPA	DMF	$(0.66)^{e}$		120 (94%)	$8.1 \times 10^{9}$	0.94
	BN	$(0.55)^{e}$		110 (94%)	$8.4 \times 10^{9}$	0.95
	TN	$(0.13)^{e}$		110 (95%)	$8.9 \times 10^{9}$	0.96
SubPc-TPA-C <sub>60</sub>	DMF	0.69	1.00	40 (94%)	$2.8 \times 10^{10}$	0.98
	BN	0.67	0.97	30 (95%)	$3.4 \times 10^{10}$	0.99
	TN	0.14	0.27	30 (55%)	$3.4 \times 10^{10}$	0.99
$SubPc-TPA-(C_{60})_2$	BN	0.67	0.97	60 (92%)	$1.6  imes 10^{10}$	0.96
	TN	0.14	0.27	50 (92%)	$2.2 \times 10^{10}$	0.98

 ${}^{a}-\Delta G_{CS} = \Delta E_{00} - \{e(E_{ox} - E_{red}) + \Delta G_{S}\}$ , where  $\Delta E_{00}$  is the energy of the 0-0 transition (2.1 eV for <sup>1</sup>SubPc\* and 1.72 eV for <sup>1</sup>C<sub>60</sub>\*).  $\Delta G_{S}$  refers to the static Coulomb energy calculated by  $\Delta G_{S} = -(e^{2}/(4\pi\epsilon_{0}))[(1/(2R_{+}) + 1/(2R_{-}) - (1/R_{CC})/\epsilon_{S} - (1/(2R_{+}) + 1/(2R_{-}))/\epsilon_{R})$ , where  $R_{+}$  and  $R_{-}$  are radii of the radical cation (TPA; 3.7 Å) and radical anion (SubPc (4.8 Å) and C<sub>60</sub> (4.2 Å)).  $R_{CC}$ ; SubPc-TPA (10.0 Å) and TPA-C<sub>60</sub> (11.0 Å). The symbols  $\epsilon_{0}$  and  $\epsilon_{s}$  represents vacuum permittivity and dielectric constant of solvent used for photophysical and electrochemical studies.  ${}^{b}-\Delta G_{CS}$  values for SubPc\*+-TPA-C<sub>60</sub>\*- are in the range of -0.1 - 0.0 eV in DMF and BN using  $E_{ox} = 1.04$  V for SubPc in THF<sup>12b</sup> and  $R_{CC}$ = SubPc- C<sub>60</sub> (12.7 Å).  ${}^{c}$  Include energy transfer.  ${}^{d}\Phi_{CS}$  via <sup>1</sup>SubPc\* calculated by  $\Phi_{CS} = k_{CS}/(1/\tau_{f})$ .  ${}^{e}$  SubPc\*--TPA\*+.

TABLE 2: Rate Constants of Charge-Recombination ( $k_{CR}$ ) and Lifetimes of Radical Ion-Pairs ( $\tau_{RIP}$ ) of SubPc-TPA, SubPc-TPA-C<sub>60</sub>, and SubPc-TPA-(C<sub>60</sub>)<sub>2</sub>

		- $\Delta G_{ m CR}/{ m eV}^{a,b}$			
compounds	solvents	SubPc <sup></sup> -TPA <sup>+</sup> -C <sub>60</sub>	SubPc-TPA <sup>·+</sup> -C <sub>60</sub> <sup>·-</sup>	$k_{\rm CR} / {\rm s}^{-1}$	$ au_{ m RIP}$ /ns
SubPc-TPA	DMF	$(1.44)^{c}$		< 10 <sup>8</sup>	< 10
	BN	$(1.55)^{c}$		$< 10^{8}$	< 10
	TN	$(1.97)^{c}$		$< 10^{8}$	< 10
SubPc-TPA-C <sub>60</sub>	DMF	1.41	1.10	$2.5 \times 10^{6}$	400
	BN	1.43	1.13	$1.5 \times 10^{6}$	670
	TN	1.96	1.83	$1.4 \times 10^{8}$	<7
$SubPc-TPA-(C_{60})_2$	BN	1.43	1.13	$9.5 \times 10^{5}$	1052
	TN	1.96	1.83	$2.1 \times 10^{7}$	47

 $^{a} - \Delta G_{CR} = e (E_{ox} - E_{red}) + \Delta G_{S.} ^{b} - \Delta G_{CR}$  values for SubPc<sup>+</sup>-TPA-C<sub>60</sub><sup>-</sup> are in the range of 2.0–2.1 eV in DMF and BN.  $^{c}$  SubPc<sup>+</sup>-TPA<sup>+</sup>.

Steady-State Fluorescence Measurements. The photophysical behavior was qualitatively investigated by steady-state fluorescence using 520-nm light excitation, which selectively excited the SubPc moiety. As shown in Figure 5a, the fluorescence spectrum of the SubPc-OPh reference shows a maximum at 573 (toluene) and 577 nm (BN) with a fluorescence quantum yield of 0.45. The <sup>1</sup>SubPc\*-energy of SubPc-OPh evaluated as 2.1 eV is substantially higher than those for phthalocyanines (1.7 eV). By the axial linkage of SubPc with TPA, the emission intensity was decreased very much without an appreciable shift of the emission peak in toluene and BN. The fluorescence quantum yields of SubPc-TPA were evaluated to be less than 0.01 in toluene and BN; similar quenching was observed in dimethylformamide (DMF). Since the possibility of the energy transfer process from <sup>1</sup>SubPc\* to TPA is excluded due to energetic considerations, the CS process predominantly takes place via <sup>1</sup>SubPc<sup>\*</sup> generating SubPc<sup>•-</sup>-TPA<sup>•+</sup> in polar and nonpolar solvents.

In SubPc-TPA-C<sub>60</sub>, further efficient fluorescence quenching of the SubPc moiety was observed in all solvents employed



**Figure 4.** Steady-state absorption spectra of SubPc–OPh, SubPc– TPA, and SubPc–TPA– $C_{60}$  in toluene (TN). The concentrations were kept at 2.2  $\mu$ M.

(Figure 5b), suggesting that some intramolecular processes are induced by the  $C_{60}$  moiety, in addition to the vicinal CS process with TPA. Since the weak  $C_{60}$ -fluorescence peak overlaps with the SubPc-fluorescence peak, it is difficult to recognize the rise of  $C_{60}$ -fluorescence, which was usually observed for energy transfer from <sup>1</sup>SubPc\* to  $C_{60}$  in nonpolar solvent. Similar fluorescence spectra were observed for SubPc $-TPA-(C_{60})_2$ . From these findings for SubPc $-TPA-(C_{60})_n$  that the emission intensities of the SubPc moiety are additionally quenched by the  $C_{60}$  moieties, one could speculate the energy-transfer pathway from the <sup>1</sup>SubPc\* moiety to the  $C_{60}$  moieties probably occurring through-space. However, CS pathway generating SubPc\* $-TPA-C_{60}^{--}$  via the <sup>1</sup>SubPc\* moiety may be difficult to occur, because of the high oxidation potential of the SubPc.<sup>12b</sup>

**Fluorescence Lifetime Measurements.** To complement the emission spectral studies, the fluorescence lifetime measurements (Figure 6) were performed, which tracked the above consideration in a more quantitative way. The fluorescence lifetime of <sup>1</sup>SubPc\*-OPh exhibited monoexponential decay with a lifetime ( $\tau_{f0}$ ) of 2080 ps, which is in a good agreement



**Figure 5.** Steady-state fluorescence spectra of (left) SubPc–OPh and SubPc–TPA and (right) SubPc–TPA and SubPc–TPA– $C_{60}$  in toluene (TN) and benzonirtrile (BN). The concentrations were kept at 2.2  $\mu$ M;  $\lambda_{ex} = 520$  nm.



**Figure 6.** Fluorescence decay-profiles of SubPc–OPh, SubPc–TPA, and SubPc–TPA–C<sub>60</sub> in TN and BN in the region of 550–650 nm. The concentrations were kept at 0.05 mM;  $\lambda_{ex} = 400$  nm.



**Figure 7.** Nanosecond transient spectra and time profile of SubPc– TPA in Ar-saturated BN;  $\lambda_{ex} = 532$ -nm laser light.

with the reported value.<sup>12</sup> However, the fluorescence time profiles of <sup>1</sup>SubPc\*-TPA could be fitted satisfactorily with biexponential decay functions, from which the fluorescence lifetimes ( $\tau_f$ ) of the major short-lived components were evaluated as ca. 110 ps in polar and nonpolar solvents as listed in Table 1. The lifetime of the remaining minor slow decay part is almost the same as that of SubPc-OPh. Based on the shortening of the fluorescence lifetimes, the CS rates ( $k_{CS}$ ) of the SubPc-TPA dyad were estimated in the range of (8–9) × 10<sup>9</sup> s<sup>-1</sup>.

Compared with <sup>1</sup>SubPc\*-TPA, the fluorescence lifetimes of <sup>1</sup>SubPc\*-TPA-C<sub>60</sub> were further shortened, giving the shortlived components as 30-40 ps in toluene, BN and DMF (Table 1), suggesting that the initial CS process takes place via <sup>1</sup>SubPc\* in SubPc-TPA-C<sub>60</sub> with the  $k_{\rm CS}$  values of ca. 3  $\times$  10<sup>10</sup> s<sup>-1</sup>, which is larger than the  $k_{CS}$  values for the vicinal CS process of SubPc-TPA.<sup>20</sup> In polar solvents, the  $k_{CS}$  values of SubPc-TPA-(C<sub>60</sub>)<sub>2</sub> via <sup>1</sup>SubPc\* were estimated to be as ca.  $2 \times 10^{10}$  $s^{-1}$ . Thus, the  $k_{CS}$  values are in the order of SubPc-TPA-C<sub>60</sub> > SubPc-TPA- $(C_{60})_2$  > SubPc-TPA in BN. Although the acceleration role of the C60 moieties to the CS process is prominent, the dual C<sub>60</sub> effect is less effective; probably the dual attachments of C<sub>60</sub> considerably change the electronic character of SubPc-TPA unit into an adverse tendency. Since the  $k_{\rm CS}$  values are independent from solvent polarities, it is suggested that the CS process is located near the top region of the Marcus parabola.<sup>21</sup>

In Table 1, the CS quantum yields ( $\Phi_{CS}$ ) evaluated from the fluorescence lifetimes of <sup>1</sup>SubPc\* are also listed. The  $\Phi_{CS}$  values of SubPc-TPA-( $C_{60}$ )<sub>n</sub> are larger than the values of the vicinal CS process for SubPc-TPA dyad, supporting that the initial CS process of SubPc-TPA-( $C_{60}$ )<sub>n</sub> accompanies the energy transfer process from the <sup>1</sup>SubPc\* moiety to the  $C_{60}$  moiety.

**Transient Absorption Measurements.** By employing 532nm laser light, which predominately excited the SubPc moiety, the nanosecond transient spectra of SubPc–TPA were observed as shown in Figure 7. A main absorption band appeared at 450 nm together with broad weak bands in the 600–750 nm region



**Figure 8.** Nanosecond transient spectra and time profile of SubPc– TPA–C<sub>60</sub> in Ar-saturated DMF;  $\lambda_{ex} = 532$ -nm laser light.

with a depression in the 500-600 nm region in BN. Since these absorption bands are similar to those of the SubPc-OPh, they are assigned to the <sup>3</sup>SubPc\* unit, which is generated via intersystem crossing from <sup>1</sup>SubPc\*. In the longer time-scale measurements, these absorption bands were decayed within 50  $\mu$ s, which were unchanged with changing the solvent polarity (Supporting Information, Figures S1 and S2). These findings also support the assignment of <sup>3</sup>SubPc\*. Combining with the rapid fluorescence quenching of <sup>1</sup>SubPc\* due to the CS process, the generation of <sup>3</sup>SubPc\*-TPA may be caused by the rapid CR of SubPc<sup>•–</sup>–TPA<sup>•+</sup>, since the energy levels of the SubPc<sup>•–</sup> TPA<sup>•+</sup> (2.0–1.6 eV in Table 2) are located higher than <sup>3</sup>SubPc\* (1.4 eV)<sup>5,12,16</sup> in both polar and nonpolar solvents (Supporting Information, Figure S3). Since SubPc<sup>•-</sup>-TPA<sup>•+</sup> was not observed by our nanosecond laser pulse (6 ns),<sup>22</sup> the CR process is faster than ca.  $2 \times 10^8 \text{ s}^{-1.23}$  This quick CR process seems to be reasonable due to the close distance between the orbital of the LUMO of SubPc and HOMO of TPA in Figure 2. However, since the node at the B atom of the LUMO does not overlap with the O atom of the HOMO in SubPc<sup>•–</sup>–TPA<sup>•+</sup>, the lifetime of the RIP ( $\tau_{RIP}$ ) may not be very short.

The nanosecond transient absorption spectra of SubPc-TPA-C<sub>60</sub> observed in polar solvents show quite different features from those of SubPc-TPA. A typical example is shown in Figure 8 for DMF solvent; the 1000-nm band is undoubtedly attributed to characteristic peak of the C<sub>60</sub>. moiety and the 740nm band to the TPA $^{\bullet+}$  moiety. These observations suggest that the CS state is like as SubPc-TPA $^{\bullet+}$ -C<sub>60</sub> $^{\bullet-}$  in the nanosecond time region in polar solvents.<sup>24</sup> Since the initial CT state via <sup>1</sup>SubPc<sup>\*</sup> is mainly attributed to SubPc<sup>•–</sup>–TPA<sup>•+</sup>–C<sub>60</sub>, the electron migration from SubPc\*- to  $C_{60}$  takes place within 6 ns before the CR between SubPc<sup>•-</sup> and TPA<sup>•+</sup>.<sup>24</sup> As the observed additional fluorescence quenching of <sup>1</sup>SubPc\* by C<sub>60</sub> suggested, the initial energy transfer from  ${}^{1}SubPc^{*}$  to C<sub>60</sub> may be possible forming SubPc-TPA- ${}^{1}C_{60}^{*}$ , from which the CS process takes place from vicinal TPA moiety giving SubPc-TPA $\cdot$ +-C<sub>60</sub> $\cdot$ -. In BN, similar transient absorption spectra were observed (Supporting Information, Figure S4), showing the 1000-nm band of  $C_{60}^{\bullet-}$  and 720-nm band of TPA<sup>•+</sup>. In addition, the 450-nm band of <sup>3</sup>SubPc\* was also found in the same time scale, suggesting that SubPc-TPA $^{\bullet+}$ -C<sub>60</sub> $^{\bullet-}$  coexists with <sup>3</sup>SubPc\*-TPA $-C_{60}$ . On the other hand, the nanosecond transient spectra of SubPc-TPA-C<sub>60</sub> in toluene exhibited the characteristic absorption bands of <sup>3</sup>SubPc\* moiety at 450 nm and 600-700 nm as shown in Supporting Information (Figure S5). Since the energy levels of the CS states in toluene are higher than <sup>3</sup>SubPc\*, the CR process may populate <sup>3</sup>SubPc\* (Supporting Information, Figure S6).



**Figure 9.** Nanosecond transient spectra and time profile of SubPc– TPA– $(C_{60})_2$  in Ar-saturated benzonitrile;  $\lambda_{ex} = 532$ -nm laser light.

The characteristic transient absorption band of the  $C_{60}^{\bullet-}$ moiety was employed to determine the CR rates of SubPc– TPA<sup>•+</sup>- $C_{60}^{\bullet-}$ , since the decays of the  $C_{60}^{\bullet-}$  were well-fitted by a single-exponential function. The  $k_{CR}$  value of SubPc– TPA<sup>•+</sup>- $C_{60}^{\bullet-}$  was found to be 2.5 × 10<sup>6</sup> s<sup>-1</sup> in DMF from inset of Figure 8. Based on the  $k_{CR}$  value, the  $\tau_{RIP}$  value of SubPc–TPA<sup>•+</sup>- $C_{60}^{\bullet-}$  was evaluated as 400 ns in DMF. Such a slow CR process may be explained by the inverted region of the Marcus parabola.<sup>21</sup>

In BN, the  $k_{CR}$  value was evaluated to be  $1.5 \times 10^6 \text{ s}^{-1}$ (Supporting Information, Figure S4), which is slower than that in DMF, giving a longer  $\tau_{RIP}$  value of SubPc–TPA\*+–C<sub>60</sub>\*– as 670 ns in BN. Smaller  $k_{CR}$  value in BN may be related to the coexistence of <sup>3</sup>SubPc\*, which suggests that SubPc– TPA\*+–C<sub>60</sub>\*– gains a triplet spin character prolonging the  $\tau_{RIP}$ value.<sup>25</sup> These  $\tau_{RIP}$  values are significantly longer compared with those of TPA\*+–C<sub>60</sub>\*– dyads,<sup>24</sup> which suggests a role of SubPc in stabilizing SubPc–TPA\*+–C<sub>60</sub>\*–; that is, an electron of C<sub>60</sub>\*– interacts with SubPc in the triad due to their close contact (Figure 3).

In the case of SubPc-TPA- $(C_{60})_2$ , similar transient spectra were observed as shown in Figure 9, in which SubPc-TPA<sup>++</sup>- $(C_{60})_2^{\bullet-}$  was observed in polar solvents. Interestingly, the 1000nm band and 750-nm band are broader than those of SubPc-TPA $^{\bullet+}$ -C<sub>60</sub> $^{\bullet-}$  in BN, suggesting that the C<sub>60</sub> $^{\bullet-}$  moiety interacts with another  $C_{60}$  moiety or with the close SubPc moiety. The  $k_{\rm CR}$  value was found to be 9.5  $\times$  10<sup>5</sup> s<sup>-1</sup> in BN from the inserted time-profile at 1000 nm, which corresponds to the  $\tau_{\rm RIP}$  value as 1052 ns. This  $\tau_{\rm RIP}$  value is longer than that of SubPc-TPA- $C_{60}$  ( $\tau_{RIP} = 670$  ns), suggesting the delocalization of the negative charge over the two  $C_{60}$  units and SubPc unit in SubPc-TPA<sup>•+</sup>- $(C_{60})_2^{\bullet-}$ . A similar prolongation of the  $\tau_{RIP}$  value due to dual  $C_{60}$  moieties attached TPA in TPA<sup>•+</sup>-( $C_{60}$ )<sup>•-</sup> triad was recently found in our previous paper.<sup>24b</sup> In toluene, transient spectra of SubPc-TPA- $(C_{60})_2$  showed predominantly the  ${}^{3}C_{60}*$  moiety at 700-750 nm, to which absorption of the <sup>3</sup>SubPc\* moiety was overlapped (Supporting Information, Figure S7), suggesting much contribution of the  ${}^{3}C_{60}$ \* moiety than the  ${}^{3}SubPc$ \* moiety.

Compared with the initial absorbance at 1000 nm, the final yield of the RIP with  $C_{60}^{\bullet-}$  for SubPc-TPA- $C_{60}$  was higher than that of SubPc-TPA- $(C_{60})_2$ . This tendency was in good agreement with the initial  $\Phi_{CS}$  values via <sup>1</sup>SubPc\* as evaluated by fluorescence quenching experiments, indicating that the final RIP yields are proportional to the observed  $\Phi_{CS}$  values. Thus, the electron-shift process and energy-transfer/charge-transfer process occurring after the initial CS process may be fast enough to generate final RIP competitively with the initial CR of SubPc\*-TPA\*- $(C_{60})_n$ .



**Figure 10.** Energy diagram of SubPc-TPA- $(C_{60})_n$ : CS, charge separation; EN, energy transfer; and CR, charge recombination.

**Energy Diagram Considerations and Conclusive Remarks.** The energy level diagram constructed by utilizing the spectral, electrochemical and photophysical data of SubPc–TPA– $(C_{60})_n$  is schematically illustrates in Figure 10. The initial CS process occurs from TPA to <sup>1</sup>SubPc\*, yielding vicinal radical ion-pairs, SubPc\*–TPA\*+– $(C_{60})_n$ . Subsequently, it is possible to shift an electron on SubPc\*– to  $C_{60}$  as an exothermic process by ca. 300 mV, producing stable SubPc–TPA\*+– $(C_{60})_n^{\bullet-}$ . In addition, the through-space energy transfer process from <sup>1</sup>SubPc\* to  $C_{60}$  is possible to generate the <sup>1</sup>C<sub>60</sub>\* moiety, from which SubPc–TPA\*+– $(C_{60})_n^{\bullet-}$  can be also generated. In polar solvents, the final CS state, SubPc–TPA\*+– $(C_{60})_n^{\bullet-}$ , decays directly to populate the ground state with relatively slow rates. In nonpolar solvent, the radical ion-pairs relaxes to <sup>3</sup>SubPc\* with the quick CR process for SubPc–TPA– $(C_{60})_n$ .

As conclusions, high efficient CS processes of the newly synthesized SubPc-TPA-C<sub>60</sub> and SubPc-TPA-(C<sub>60</sub>)<sub>2</sub> were observed compared with SubPc-TPA by the excitation of the huge absorption of SubPc moiety in the visible region. In polar solvents, the CS processes via <sup>1</sup>SubPc\* generates mainly vicinal RIP (SubPc<sup>•-</sup>-TPA<sup>•+</sup>-(C<sub>60</sub>)<sub>n</sub>) and, subsequently, stable RIP (SubPc-TPA<sup>•+</sup>-(C<sub>60</sub>)<sub>n</sub><sup>•-</sup>). These RIPs have longer lifetimes compared with the corresponding dyads such as SubPc<sup>•-</sup>-TPA<sup>•+</sup>-(C<sub>60</sub>)<sub>n</sub><sup>•-</sup>. Furthermore, the longer lifetime of SubPc-TPA<sup>•+</sup>-(C<sub>60</sub>)<sub>n</sub><sup>•-</sup>. Furthermore, the longer lifetime of SubPc-TPA<sup>•+</sup>-(C<sub>60</sub>)<sub>2</sub><sup>•-</sup> than that of SubPc-TPA<sup>•+</sup>-C<sub>60</sub><sup>•-</sup> was observed revealing the effect of the dual C<sub>60</sub> moieties on the electron-transfer processes. Such photophysical properties afford potentials of SubPc-TPA-(C<sub>60</sub>)<sub>n</sub> for wide applications to artificial photosynthetic systems.

## **Experimental Section**

**Instruments.** Steady-state absorption and fluorescence spectra were measured on a JASCO V-550 spectrometer (UV-vis-NIR) and Shimadzu spectrofluorophotometer equipped with a photomultiplier tube having high sensitivity in the longer wavelength region, respectively.

The redox values were measured using the differential pulse voltammetry (DPV) technique by applying a BAS CV-50W voltammetric analyzer. A platinum disk electrode was used as the working electrode, while a platinum wire served as a counter electrode. An Ag/AgCl electrode was used as a reference electrode. All measurements were carried out in different solvents containing 0.1 M (*n*-Bu)<sub>4</sub>NClO<sub>4</sub> as a supporting electrolyte. The scan rate was 0.1 V s<sup>-1</sup>.

Frontier HOMO and LUMO of SubPc-TPA-C<sub>60</sub> and SubPc-TPA-( $C_{60}$ )<sub>2</sub> were calculated by ab intio B3LYP/3-21G method after optimization of the structure.<sup>17</sup>

The picosecond time-resolved fluorescence spectra were measured by a single-photon counting method using a second harmonic generation (SHG, 400 nm) of a Ti:sapphire laser (Spectra-Physica, Tsunami 3950-L2S, 1.5 ps fwhm) and a streak-scope (Hamamatsu Photonics) equipped with a polychromator as an excitation source and a detector, respectively. Lifetimes were evaluated with software attached to the equipment.

The nanosecond transient absorption measurements in the near-IR region were measured by laser-flash photolysis; 532nm light from a Nd:YAG laser (Spectra-Physics and Quanta-Ray GCR-130, 6 ns fwhm) was used as an excitation source. The monitoring lights from a pulsed Xe-lamp were detected via Ge-avalanche photodiode module. The samples were held in a quartz cell ( $1 \times 1$  cm) and were deaerated by bubbling argon gas through the solution for 20 min.

**Materials.** Reagents and solvents were purchased as reagent grade and used without further purification. All reactions were performed using dry glassware under nitrogen atmosphere. Analytical TLC was carried out on Merck 60 F254 silica gel plate and column chromatography was performed on Merck 60 silica gel (230–400 mesh). Melting points were determined on an Electrothemal IA 9000 series melting point apparatus and are uncorrected. NMR spectra were recorded on a Varian Mercury-400 (400 MHz) spectrometer with the TMS peak used as a reference. IR spectra were recorded on a Nicolet 550 FT infrared spectrometer and measured as KBr pellets. MALDI-TOF MS spectra were recorded with an Applied Biosystems Voyager-DE-STR. Elemental analyses were performed with a Perkin-Elmer 2400 analyzer.

In Scheme 1, commercially available diphenylamine was coupled with 4-iodoanisole under Ullmann condition<sup>26</sup> to give 4-methoxytriphenylamine (1) in 86.0%, and subsequently, Vilsmeier formylation<sup>27</sup> was carried out to produce aldehyde 2 in 93.7% and 3 in 36.7%, respectively. However, direct double formylation of 1 by the Vilsmeier reaction proved to be difficult due to the deactivation effect of the first carbonyl group on TPA and mainly gave monoformylated TPA 2 under normal stoichiometry of POCl<sub>3</sub>/DMF (up to 3.5 equiv). With a large excess of POCl<sub>3</sub>/DMF (~10 equiv), the diformylated TPA 3 was produced with a yield of 36.7%. Subphthalocyanine (SubPc-Cl) 6 was synthesized by condensation reaction of phthalonitrile in the presence of boron trichloride according to the literature procedure,<sup>8,11b</sup> and the axial chlorine atom of SubPc-Cl (6) was then replaced with hydroxytriphenylamine aldehydes 4 and 5, produced from corresponding methoxytriphenyl)amine aldehydes 2 and 3 by demethylation, to give formyl-substituted SubPc-TPA 7 and 8 in 94.4% and 63.6%, respectively. Finally, fulleropyrrolidine formation was achieved by 1,3-dipolar cycloaddition reaction between aldehydes 7 and 8 and  $C_{60}$  in the presence of excess N-octylglycine<sup>28</sup> under the condition described by Prato<sup>29</sup> to give SubPc-TPA-C<sub>60</sub> triad and SubPc-TPA-(C<sub>60</sub>)<sub>2</sub> tetrad in 28.7% and 10.2%, respectively. Although SubPc-TPA- $(C_{60})_2$  tetrad should be obtained as a stereoisomeric mixture due to the formation of two asymmetric centers in 2-fold cycloaddition reaction, high resolution <sup>1</sup>H NMR spectrum (400 MHz) of tetrad showed the presence of only one stereoisomer (see below).

SubPc-TPA- $C_{60}$  and SubPc-TPA- $(C_{60})_2$  are very soluble in aromatic solvents (i.e., toluene, *o*-dichlorobenzene, and benzonitrile) and other common organic solvents (i.e., carbon disulfide, acetone, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and THF). The structure and purity of the new compounds were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and IR spectroscopies; MALDI-TOF mass spectroscopies; and elemental analysis.

<sup>1</sup>H NMR spectra of SubPc-TPA-C<sub>60</sub> and SubPc-TPA- $(C_{60})_2$  in CDCl<sub>3</sub> are consistent with the proposed structures, showing the expected features with the correct integration ratios. The signals of pyrrolidine protons in SubPc-TPA-C<sub>60</sub> and SubPc-TPA-(C<sub>60</sub>)<sub>2</sub> appeared as two doublets (J = 9.5 Hz; germinal protons), and a singlet in the  $\delta = 3.95 - 4.98$  ppm region, which is consistent with spectra obtained for similar derivatives.30 13C NMR spectra contained the signals corresponding to the sp<sup>2</sup> and sp<sup>3</sup> atoms of  $C_{60}$  and the expected signals corresponding to the organic addends. The MALDI-TOF mass spectra provided a direct evidence for the structures of SubPc-TPA-C<sub>60</sub> and SubPc-TPA-(C<sub>60</sub>)<sub>2</sub>. Compound SubPc-TPA- $C_{60}$  showed a singly charged molecular ion peak that matches the calculated value for the molecular weight, and compound SubPc-TPA- $(C_{60})_2$  gave a peak at  $m/z = 962.36 [M-2C_{60}]^+$ . Further confirmation of the hybrid SubPc-fullerene structure was obtained from UV/vis spectra of SubPc-TPA-C<sub>60</sub> and SubPc- $TPA-(C_{60})_2$ , which contain a dihydrofullerene absorption band at around 430 nm together with the expected Soret band (around 300 nm) and Q-band (around 562 nm).

SubPc-TPA-C<sub>60</sub>. Compound 7 (70 mg, 0.10 mmol) and N-octylglycine (20 mg, 0.10 mmol) were added to a solution of fullerene (70 mg, 0.13 mmol) in chlorobenzene (40 mL).<sup>29</sup> The reaction mixture was refluxed for 16 h and then filtered off. The filtrate was evaporated and chromatographed on silica gel with toluene to give compound SubPc-TPA- $C_{60}$  (43 mg, 28.7%) as a black solid. Mp > 410 °C (dec); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.77$  (dd, J = 8.6 Hz, J = 2.8 Hz, 6H), 7.84 (dd, J = 8.6 Hz, J = 2.8 Hz, 6H), 7.15 (m, 3H), 7.10 (t, J = 7.6 Hz, 2H), 6.85 (m, 4H), 6.50 (d, J = 9.5 Hz, 2H), 5.35 (d, J = 9.5 Hz, 2H), 4.94 (d, J = 9.5 Hz, 1H), 4.83 (s, 1H),3.95 (d, J = 9.5 Hz, 1H), 3.24 (t, 2H), 1.25~1.45 (br, 12H), 0.90 (t, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>:CS<sub>2</sub> = 3:1):  $\delta$  = 151.37, 148.03, 146.78, 145.28, 144.62, 143.99, 142.51, 141.28, 139.72, 131.25, 131.06, 130.03, 129.19, 128.98, 126.13, 123.51, 122.53, 119.90, 65.88, 53.79, 32.35, 30.14, 29.80, 23.16, 19.59, 14.60. IR (KBr):  $\nu = 705, 738, 896, 1122, 1265, 1421, 1598, 2306, 2987,$ 3054 cm<sup>-1</sup>. UV/vis (toluene):  $\lambda_{\text{max}}$  ( $\epsilon \times 10^{-5}$  /M<sup>-1</sup> cm<sup>-1</sup>) = 300 (4.723), 431(0.488), 523 (1.241), 562 nm (4.091); MS (MALDI-TOF) for  $C_{112}H_{45}N_8BO$  (M = 1529.45) m/z = 1529.33(M<sup>+</sup>); Anal. Calcd: C, 87.95%; H, 2.96%; N, 7.33%. Found: C, 87.91%; H, 2.95%; N, 7.36%.

SubPc-TPA-(C<sub>60</sub>)<sub>2</sub>. Compound 8 (60 mg, 0.084 mmol) and N-octylglycine (47 mg, 0.25 mmol) were added to a solution of fullerene (120 mg, 0.17 mmol) in chlorobenzene (50 mL).<sup>29</sup> The reaction mixture was refluxed for 16 h and then filtered off. The filtrate was evaporated and chromatographed on silica gel with CS<sub>2</sub>/acetone (40:1) to give SubPc-TPA-( $C_{60}$ )<sub>2</sub> (7 mg, 10.2%) as a black solid. Mp > 410 °C (dec); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.76$  (dd, J = 8.6 Hz, J = 2.8 Hz, 6H), 7.83 (dd, J = 8.6 Hz, J = 2.8 Hz, 6H), 7.15 (d, J = 9.5 Hz, 4H), 6.77 (d, J = 9.5 Hz, 4H), 6.42 (d, J = 9.5 Hz, 2H), 5.32 (d, J = 9.5 Hz, 2H), 4.98 (d, J = 9.5 Hz, 2H), 4.87 (s, 2H),4.00 (d, J = 9.5 Hz, 2H), 3.23 (t, 4H), 1.25~1.45 (br, 24H), 0.90 (t, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>:CS<sub>2</sub> = 2:1):  $\delta$  = 156.03, 153.63, 153.16, 152.98, 150.93, 147.38, 146.54, 146.22, 145.97, 145.70, 145.54, 145.38, 145.32, 145.04, 144.94, 144.82, 144.75, 144.50, 144.37, 143.99, 143.81, 143.58, 142.29, 142.03, 141.89, 141.68, 141.54, 141.37, 141.03, 140.78, 139.58, 139.50, 139.23, 138.50, 136.06, 135.23, 130.89, 130.58, 129.61, 128.58, 125.55, 122.19, 68.44, 66.64, 65.40, 53.15, 32.13, 30.67, 29.90, 29.53, 28.60, 27.74, 22.96, 14.42. IR (KBr): v = 705, 738, 896, 1122, 1265, 1421, 1598, 2306, 2987, 3054 cm<sup>-1</sup>; UV/vis (toluene):  $\lambda_{max}$ ( $\epsilon \times 10^{-5}$  /M<sup>-1</sup> cm<sup>-1</sup>) = 301 (6.555), 435 (0.976), 528 (1.332), 565 nm (4.095); MS (MALDI-TOF) for C<sub>182</sub>H<sub>64</sub>N<sub>9</sub>BO (M = 2403.33) *m*/*z* = 962.36 (M-2C<sub>60</sub>)<sup>+</sup>; Anal. Calcd: C, 90.96%; H, 2.64%; N, 5.25%. Found: C, 90.91%; H, 2.62%; N, 5.26%.

SubPc-TPA. To a solution of compound 6 (45 mg, 0.10 mmol) in toluene (7 mL) was added 4-hydroxytriphenylamine (0.11 g, 0.42 mmol, see the Supporting Information), and refluxed for 24 h. The reaction mixture was cooled to room temperature and evaporated. The product was chromatographed on silica gel with dichloromethane/methanol (200:1) to give compound SubPc-TPA (0.042 g, 63.6%) as a red solid. Mp  $153 \sim 154 \text{ °C}$ ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.22$  (dd, J =9.3 Hz, J = 2.7 Hz, 6H), 7.87 (dd, J = 9.3 Hz, J = 2.7 Hz, 6H), 7.08 (t, J = 7.3 Hz, 4H), 6.79–6.86 (m, 6H), 6.49 (d, J =8.6 Hz, 2H), 5.28 (d, J = 8.6 Hz, 2H). IR (KBr):  $\nu = 705$ , 738, 896, 1052, 1133, 1265, 1421, 1596, 2306, 2987, 3054 cm<sup>-1</sup>. UV/vis (toluene):  $\lambda_{\text{max}} (\epsilon \times 10^{-5} / \text{M}^{-1} \text{ cm}^{-1}) = 302 (2.182),$ 385 (1.545), 524 (1.241), 562 nm (4.082); MS (MALDI-TOF); m/z for C<sub>42</sub>H<sub>26</sub>BN<sub>7</sub>O Calcd. 654.71. Found 655.16. Anal. Calcd: C, 76.96%; H, 4.00%; N, 14.96%. Found: C, 76.92%; H, 3.99%; N, 14.98%.

**SubPc−OPh.** To a solution of phenol (0.12 g, 1.28 mmol) in toluene (10 mL) was added compound **6** (0.12 g, 0.28 mmol) and refluxed for 6 h.<sup>12</sup> The reaction mixture was cooled to room temperature and evaporated. The product was chromatographed on silica gel with dichloromethane/methanol (200:1) to give compound SubPc-OPh (0.11 g, 81.2%) as a red solid. Mp 138 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.84 (dd, J = 9.3 Hz, J = 2.7 Hz, 6H), 7.90 (dd, J = 9.3 Hz, J = 2.7 Hz, 6H), 6.73 (m, 2H), 6.60 (m, 1H), 5.37 (d, J = 8.6 Hz, 2H). IR (KBr): ν = 1036, 1052, 1238, 1506, 1585 cm<sup>-1</sup>. UV/vis (toluene); λ<sub>max</sub> (ε× 10<sup>-5</sup>/M<sup>-1</sup> cm<sup>-1</sup>) = 302 (1.545), 524 (1.241), 562 nm (4.093); MS (MALDI-TOF); *m/z* for C<sub>42</sub>H<sub>26</sub>BN<sub>7</sub>O Calcd. 487.51. Found 487.45. Anal. Calcd: C, 73.91%; H, 3.51%; N, 11.49%. Found: C, 73.87%; H, 3.50%; N, 11.45%.

Acknowledgment. K.-Y.K. acknowledges the financial support from Brain Korea 21 Program in 2006.

**Supporting Information Available:** Synthetic procedures, transient absorption spectra, time profiles, and energy diagrams. This material is available free of charge via the Internet at http://pubs.acs.org.

#### **References and Notes**

(1) *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, Germany, 2001; Vols. I–V.

(2) Phthalocyanines: Properties and Applications; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: Weinheim, Germany, 1996; Vol. 4.

(3) (a) del Rey, B.; Keller, U.; Torres, T.; Rojo, G.; Agulló-López, F.; Nonell, S.; Martín, C.; Brasselet, S.; Ledoux, I.; Zyss, J. *J. Am. Chem. Soc.* **1998**, *120*, 12808. (b) Sastre, A.; Torres, T.; Diaz-Garcia, M. A.; Agulló-López, F.; Dhenaut, C.; Brasselet, S.; Ledoux, I.; Zyss, J. *J. Am. Chem. Soc.* **1996**, *118*, 2746.

 (4) (a) de la Torre, G.; Torres, T.; Agulló-López, F. Adv. Mater. 1997,
 9, 265. (b) Kobayashi, N.; Ishizaki, T.; Ishii, K.; Konami, H. J. Am. Chem. Soc. 1999, 121, 9096.

(5) (a) Kang, S. H.; Kang, Y. S.; Zin, W. C.; Olbrechts, G.; Wostyn, K.; Clays, K.; Persoons, A.; Kim, K. *Chem. Commun.* **1999**, 1661. (b) Claessens, C. G.; Torres, T. *Tetrahedron Lett.* **2000**, *41*, 6361. (c) Kobayashi, N. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1. (d) Torres, T. *Angew. Chem. Int. Ed.* **2006**, *45*, 2834.

(6) (a) Hanack, M.; Heckman, H.; Polley, R. In *Methods in Organic Chemistry*; Schauman, E., Ed.; Georg Thieme Verlag: Stuttgart, Germany, 1998; Vol. E 94, p 717. (b) de la Torre, G.; Nicolau, M.; Torres, T. In *Phthalocyanines: Syntheses, Supramolecular Organization and Physical Properties (Supramolecular Photosensitive and Electroactive Materials)*; Nalwa, H. S., Ed.; Academic Press: New York, 2001; pp 1–111.

(7) Kipp, R. A.; Simon, J. A.; Beggs, M.; Ensley, H. E.; Schmehl, R. H. J. Phys. Chem. A **1998**, 102, 5659.

(8) Claessens, C. G.; González-Rodríguez, D.; Torres, T. Chem. Rev. 2002, 102, 835.

(9) del Rey, B.; Torres, T. *Tetrahedron Lett.* **1997**, *38*, 5351. (b) Claessens, C. G.; Torres, T. J. Am. Chem. Soc. **2002**, *124*, 14522.

(10) (a) Kietaibl, H. *Monatsh. Chem.* **1974**, *105*, 405. (b) Rauschnabel,

J.; Hanack, M. *Tetrahedron Lett.* **1995**, *36*, 1629. (c) Kasuga, K.; Idehara, T.; Handa, M.; Ueda, Y.; Fujiwara, T.; Isa, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2559. (d) Potz, R.; Göldner, M.; Hückstädt, H.; Cornelissen, U.; Tuta, A.; Homborg, H. Z. Anorg. Allg. Chem. **2000**, *626*, 588.

(11) (a) Geyer, M.; Plenzig, F.; Rauschnabel, J.; Hanack, M.; del Rey, B.; Sastre, A.; Torres, T. *Synthesis* **1996**, 1139. (b) Claessens, C. G.; González-Rodríguez, D.; del Rey, B.; Torres, T.; Mark, G.; Schuchmann, H. P.; von Sonntag, C.; MacDonald, J. G.; Nohr, R. S. *Eur. J. Org. Chem.* **2003**, 2547.

(12) (a) González-Rodríguez, D.; Torres, T.; Guldi, D. M.; Rivera, J.; Echegoyen, L. *Org. Lett.* **2002**, *4*, 335. (b) González-Rodríguez, D.; Torres, T.; Olmstead, M. M.; Rivera, J.; Herranz. M. Á.; Echegoyen, L.; Atienza Castellanos, C.; Guldi, D. M. *J. Am. Chem. Soc.* **2006**, *128*, 10680.

(13) Bell, T. D. M.; Stefan, A.; Masuo, S.; Vosch, T.; Lor, M.; Cotlet, M.; Hofkens, J.; Bernhardt, S.; Mullen, K.; van der Auweraer, M.; Verhoeven, J. W.; De Schryver, F. C. *Chem. Phys. Chem.* **2005**, *6*, 942.

(14) (a) Imahori, H.; Hagiwara, K.; Akiyama, T.; Akoi, M.; Taniguchi, S.; Okada, S.; Shirakawa, M.; Sakata, Y. *Chem. Phys. Lett.* **1996**, *263*, 545.
(b) Guldi, D. M.; Asmus, K. D. *J. Am. Chem. Soc.* **1997**, *119*, 5744. (c) Imahori, H.; El-Khouly, M. E.; Fujitsuka, M.; Ito, O.; Sakata, Y.; Fukuzumi, S. *J. Phys. Chem. A* **2001**, *105*, 325.

(15) (a) Gust, D.; Moore, T. A.; Moore, A. L. Acc. Chem. Res. 2001, 34, 40. (b) Guldi, D. M. Chem. Soc. Rev. 2002, 31, 22. (c) Martín, N.; Sanchez, L.; Illescas, B.; Perez, I. Chem. Rev. 1998, 98, 2527. (d) Electron Transfer in Functionalized Fullerenes. In Fullerenes: From Synthesis to Optoelectronic Properties; Guldi, D. M., Martin, N., Eds.; Kluwer Academic Publishers: Norwell, MA, 2002; pp 163–212. (e) Fujutsuka, M.; Ito, O. Photochemistry of Fullerenes. In Handbook of Photochemistry and Photobiology; Nalwa, H. S., Ed.; American Scientific Publishers: Stevenson Ranch, CA, 2003; Vol. 2 Organic Photochemistry, pp 111–145. (f) El-Khouly, M. E.; Ito, O.; Smith, P. M.; D'Souza, F. J. Photochem. Photobiol. C 2004, 5, 79.

(16) González-Rodríguez, D.; Torres, T.; Guldi, D. M.; Rivera, J.; Herranz, M. Á.; Echegoyen, L. J. Am. Chem. Soc. **2004**, *126*, 6301.

(17) Gaussian 03; Gaussian, Inc.: Pittsburgh, PA, 2003.

(18) Rehm, D.; Weller, A. Isr. J. Chem. 1970, 7, 259.

(19) SubPc-TPA dyad shows different absorption characters compared with the reported subphthalocyanine functionalized with TPA, which shows absorption maxima at 618 and 450 nm.<sup>12c</sup> This observation reflects the change of the linkage style between the SubPc and TPA, shifting the B-and Q-bands.

(20) Considerably higher fraction of long fluorescence-lifetime component of SubPc-TPA- $C_{60}$  in toluene suggests that attachment of the  $C_{60}$ moiety considerably changes the electronic character of SubPc-TPA unit in this non-polar solvent.

(21) Marcus, R. A. J. Chem. Phys. **1965**, 43, 679. (b) Marcus, R. A.; Sutin, N. Biochim. Biophys. Acta. **1985**, 811, 265. (c) Marcus, R. A. Angew. Chem., Int. Ed. Eng. **1993**, 32, 111.

(22) In Figure 7, weak absorption peak seems to appear in the 600–650 nm region after recovery of depletion in the 500-650 nm region, due to the decay of the SubPc fluorescence, but not due to appearance of SubPc<sup>-</sup> at 640 nm.<sup>12b</sup>

(23) Compared with the reported SubPc–ferrocene dyad with its extremely long-lived charge-separated state up to 231  $\mu$ s,<sup>12b</sup> the charge-recombination of SubPe<sup>+</sup>–TPA<sup>+</sup> in our present study occurs rapidly (<6 ns), further producing <sup>3</sup>SubPc<sup>\*</sup>. This difference may be attributed to the shorter distance between SubPc and TPA, in addition to the position of TPA right overhead of SubPc as shown in Figure 2, which are quite different from SubPc-ferrocene dyad with longer linkage and side position of the ferrocene donor.

(24) (a) Zeng, H. P.; Wang, T.; Sandanayaka, A. S. D.; Araki, Y.; Ito,
O. J. Phys. Chem. A 2005, 109, 4713. (b) El-Khouly, M. E.; Kim, J. H.;
Kwak, M.; Choi, C. S.; Ito, O.; Kay, K. Y. Bull. Chem. Soc. Jpn. 2007, 80, 2465.

(25) Verhoeven, J. W. J. Photochem. Photobiol. C 2007, 7, 40.

(26) (a) Ullmann, F.; Bierlecki, J. Ber. Dtsch. Chem. Ges. **1901**, 34, 2174. (b) Gauthier, S.; Frechet, J. M. J. Syntesis. **1987**, 383.

(27) (a) Vilsmeier, A.; Haack, A. Ber. Dtsch. Chem. Ges. **1927**, 60, 119. (b) Li, X. C.; Liu, Y.; Liu, M. S.; Jen, A. K. Y. Chem. Mater. **1999**, 11, 1568.

(28) Dever, C. M.; Adawadkar, P. D. Biopolymers 1979, 18, 2375.

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

(30) Prato, M.; Maggini, M.; Giacometti, C.; Scorrano, G.; Sandona, G.; Farnia, G. *Tetrahedron* **1996**, *52*, 5221.