

## Photoinduced Processes of Subphthalocyanine–Diazobenzene–Fullerene Triad as an Efficient Excited Energy Transfer System

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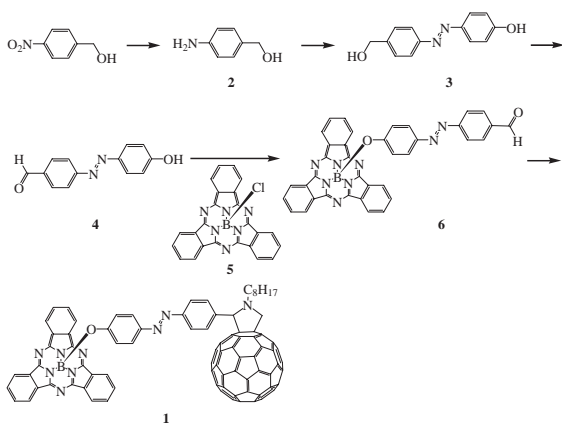
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Photoinduced processes of a newly synthesized subphthalocyanine–diazobenzene–fullerene triad have been studied by the time-resolved spectroscopic techniques. On photo-excitation of subphthalocyanine (SubPc) moiety, the fluorescence quenching of SubPc was observed, suggesting the energy-transfer process from singlet excited energy of the light-harvesting SubPc to C<sub>60</sub> through diazobenzene. This finding is confirmed by the nano-second transient absorption of the triplet excited state of C<sub>60</sub>.

Three-dimensional subphthalocyanines represent an interesting class of chromophores that show a promise as building blocks for the construction of photoactive or electro-active assemblies.<sup>1–6</sup> SubPc is particularly attractive, because their optical and electronic features can be finely tuned by varying their axial ligands or by functionalizing the various peripheral positions. Moreover, the strong absorption and high emission quantum yields of the SubPc in the visible region render them ideal probes for energy- and electron-transfer processes. Here, we report the energy-transfer processes of a newly synthesized triad of SubPc connected to fullerene C<sub>60</sub> through diazobenzene (PhN=NPh) linkage as shown in Scheme 1. In this triad molecule, three-dimensional C<sub>60</sub>, which has been widely used as a building block for the construction of artificial photosynthetic systems, is expected to play as a triplet energy reservoir.<sup>7,8</sup> Role of PhN=NPh might be configuration-changeable bridge by outside stimulus.

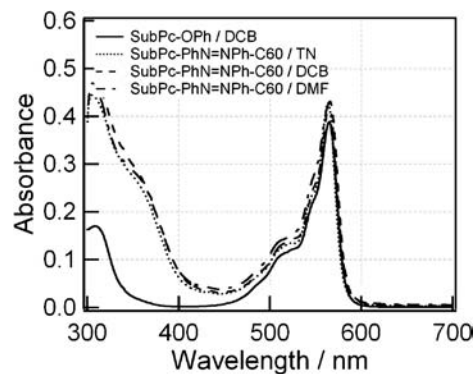
SubPc–PhN=NPh–C<sub>60</sub> (**1**) has been prepared as depicted in Scheme 1. Every step of the reaction sequence proceeded smoothly and efficiently to give a good or moderate yield of the product (see the Supporting Information for the synthetic details).<sup>9</sup>



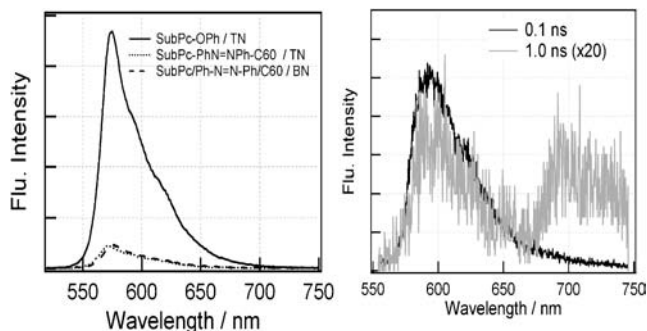
**Scheme 1.** Synthetic route of SubPc–PhN=NPh–C<sub>60</sub> (**1**).

The steady-state absorption spectra of the intense magenta solutions of SubPc–PhN=NPh–C<sub>60</sub> and SubPc–OPh<sup>7</sup> are shown in Figure 1. The absorptions of SubPcs consist of a high-energy B-band (between 300–310 nm) and a lower energy Q-band (560–580 nm), which are analogous to those of porphyrins and phthalocyanines. It is notable that the absorptions of the C<sub>60</sub> and PhN=NPh moieties in the visible region are extremely weak compared to the strong absorption of the SubPc in this region. The presence of the C<sub>60</sub> and PhN=NPh moieties was evidenced by the higher absorptions around 300–350 and 350–420 nm, respectively. Appreciable change was not observed between the triad and sum of their components, suggesting absence of the inter-component interaction in the ground state. The lack of systematic change in absorption maxima with solvent polarity suggests a negligible dipole moment change between the ground state and the excited state.

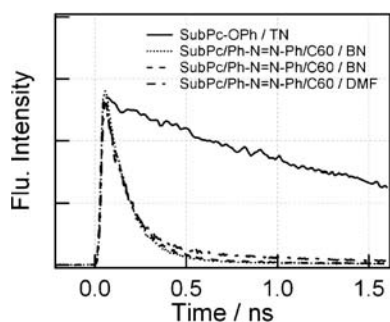
The fundamental photophysical behavior of SubPc–PhN=NPh–C<sub>60</sub> was investigated by using steady-state fluorescence observed with 510 nm excitation, which selectively excited the SubPc moiety. The emission peak maximum of SubPc–OPh is located around 574 nm in toluene as shown in Figure 2, from which the singlet excited energy of the SubPc moiety was evaluated as 2.1 eV. It is important to note that this value is substantially higher than those for phthalocyanines (1.7 eV) and porphyrins (2.0 eV), suggesting high potential of the excited singlet state of the SubPc (<sup>1</sup>SubPc\*) moiety as electron-donor and energy-donor. In SubPc–PhN=NPh–C<sub>60</sub>, the intensity of SubPc emission band was significantly quenched by ca. 90% compared with that of SubPc–OPh. Since the excited singlet state of PhN=NPh is higher than that of SubPc, this



**Figure 1.** Steady-state absorption spectra of SubPc–PhN=NPh–C<sub>60</sub> and SubPc–OPh in toluene (TN), *o*-dichlorobenzene (DCB), and dimethylformamide (DMF); concentrations were kept at  $5 \times 10^{-6}$  M.



**Figure 2.** (Left) Steady-state fluorescence spectra of SubPc-OPh and SubPc-PhN=NPh-C<sub>60</sub> ( $5 \times 10^{-6}$  M);  $\lambda_{\text{ex}} = 510$  nm. (Right) Time-resolved fluorescence spectra of SubPc-PhN=NPh-C<sub>60</sub> in benzonitrile (BN);  $\lambda_{\text{ex}} = 400$  nm.

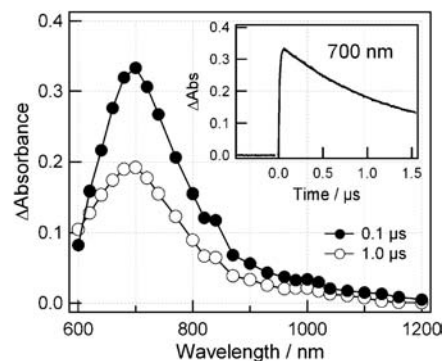


**Figure 3.** Fluorescence decay profiles of SubPc-PhN=NPh-C<sub>60</sub> and SubPc-OPh ( $5 \times 10^{-6}$  M) in 500–650 nm region;  $\lambda_{\text{ex}} = 400$  nm.

observation suggests efficient quenching of the <sup>1</sup>SubPc\* moiety by the appended C<sub>60</sub> moiety.

The difference in emission quenching was not observed with changing the solvents from toluene to DMF, suggesting that the intramolecular processes proceed with nearly activationless kinetics processes such as energy transfer.

The time-resolved fluorescence features of SubPc-PhN=NPh-C<sub>60</sub> observed with the picosecond laser light pulse at 400 nm showed the fluorescence of the SubPc moiety predominantly at 100 ps after the laser pulse, whereas after 1 ns a new fluorescence band appeared at 700 nm due to <sup>1</sup>C<sub>60</sub>\* even in BN, supporting the energy transfer. The fluorescence decay of SubPc-OPh obeyed a mono-exponential decay function with a lifetime ( $\tau_f$ ) of 2.1 ns.<sup>7,8</sup> As shown in Figure 3, the fluorescence time profiles of SubPc-PhN=NPh-C<sub>60</sub> exhibited much faster decay, comparing with that of SubPc-OPh reference.<sup>7</sup> They also could be fitted satisfactorily to a mono-exponential decay function, giving the short lifetimes as 120, 140, and 120 ps in toluene, BN, and DMF, respectively. These observations clearly show quenching of the fluorescence of <sup>1</sup>SubPc\* by the attached C<sub>60</sub> moiety. Based on the differences of fluorescence lifetimes between SubPc-PhN=NPh-C<sub>60</sub> and SubPc-OPh, the rates and quantum yields of the quenching process of the <sup>1</sup>SubPc\* moiety were evaluated in the ranges of  $(1.2\text{--}1.3) \times 10^{10} \text{ s}^{-1}$  and 0.96–0.97, respectively. The independency of these quenching quantities from the solvent polarity supports that the energy transfer predominantly takes place from the <sup>1</sup>SubPc\* moiety to the remote C<sub>60</sub> moiety over the PhN=NPh linkage.



**Figure 4.** Transient absorption spectra of SubPc-PhN=NPh-C<sub>60</sub> ( $1 \times 10^{-4}$  M) in DMF;  $\lambda_{\text{ex}} = 532$  nm laser light.

The nanosecond transient spectra of SubPc-PhN=NPh-C<sub>60</sub> observed by excitation with 532 nm laser light exhibit only the characteristic peak of triplet fulleropyrrolidine (<sup>3</sup>C<sub>60</sub>\*) at 700 nm as shown in Figure 4. The spectra show no evidence of forming radical ion pairs like SubPc<sup>•+</sup>-PhN=NPh-C<sub>60</sub><sup>•-</sup>.<sup>7</sup> In nonpolar and less polar solvents, transient spectra were observed with the similar intensity and decay of <sup>3</sup>C<sub>60</sub>\* to those in DMF. These observations for both steady-state emission and time-resolved emission as well as nanosecond transient absorption measurements indicate that the energy-transfer process from the <sup>1</sup>SubPc\* to the C<sub>60</sub> moiety takes place in all the studied solvents generating <sup>1</sup>C<sub>60</sub>\* from which <sup>3</sup>C<sub>60</sub>\* was populated by the intersystem crossing process. Free-energy change of the charge separation in polar solvents is almost iso-energetic to <sup>1</sup>SubPc\*, suggesting slower rates than those of exothermic energy transfer. Since the <sup>3</sup>C<sub>60</sub>\* moiety survives for appreciably longer time than 10 ns (inserted time profile in Figure 4), the <sup>3</sup>C<sub>60</sub>\* moiety remains keeping possibility to utilize the triplet energy to further process to generate the singlet oxygen for the use of photodynamic therapy in the aerobic biological systems. Further study is in progress in these views, in addition to assessment of the effect of the trans-cis isomerization of the PhN=NPh as length- and configuration-tunable molecular bridge.

## References and Notes

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- Supporting Information is also available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.