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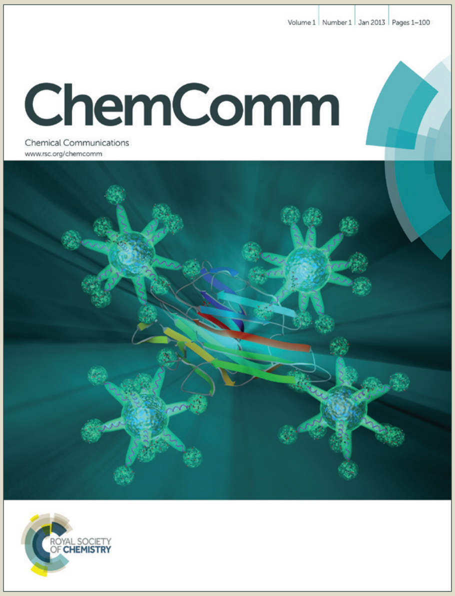

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COMMUNICATION

Unique ultrafast energy transfer in a series of phenylene-bridged subporphyrin-porphyrin hybrids

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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A series of phenylene-bridged subporphyrin-Zn(II) porphyrin (SubP-ZnP) hybrid systems undergo extraordinarily fast excitation energy transfer (EET) processes from the SubP to the ZnP, aided by conjugative electronic elongation of the SubP to the phenylene-bridge.

Recently, as ring-contracted porphyrin analogues, subporphyrins (SubPs) have emerged as a new class of promising functional dyes, displaying intriguing properties such as intense visible fluorescence and bowl-shaped nonplanar aromaticity.[1] While the electronic properties of SubPs have similar features to those of porphyrins, SubPs display characteristically strong electronic interaction between subporphyrin core and *meso*-substituents, which leads to variable absorption and fluorescence features of SubPs.[2] These tunable electronic and optical properties of SubPs can serve advantageously to mediate efficient EET processes in artificial light harvesting molecular systems, but little is explored on the photophysical behaviors of SubP systems, as compared with porphyrin counterparts. In recent years, our group has reported the preparation and characterization of 1,3- and 1,4-phenylene-bridged subporphyrin (SubP)—Zn(II) porphyrin (ZnP) hybrids **3**-**6** (Figure 1), and has revealed intramolecular excitation energy transfer (EET) from the SubP to the ZnP.[3] However, ultrafast features of the EET dynamics have remained unrevealed yet. In this work, we carried out more systematic investigation on the intramolecular EET processes in **3**-**6** including their ultrafast dynamics in femto-second time region. These SubP-ZnP hybrids are ideal molecules to reveal the characteristics of SubPs on the EET processes, because 1) both chromophores possess 14π- and 18π-electronic networks, 2) there is an energy gradient from ^{1}(SubP)* to ^{1}(ZnP)* with well-defined spectral overlap between the fluorescence of SubP and the absorption of ZnP,[2b] 3) the relative spatial arrangements of the two chromophores are well-defined, and 4) the two chromophores are bridged by 1,4-phenylene- or 1,3-phenylene-spacer, which help the evaluation of the importance of conjugative electronic interaction in EET process.

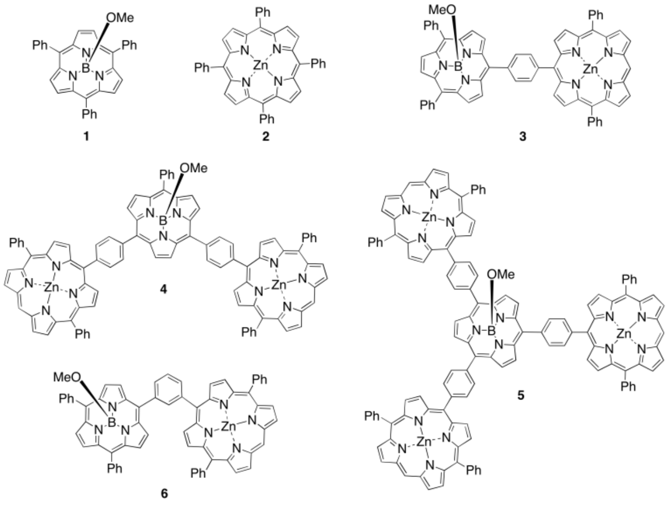

Figure 1. Molecular structures of a series of phenylene-bridged SubP-ZnP hybrids **3**-**6** and their subunits, SubP **1** and ZnP **2**.

Figure 2 shows the absorption and fluorescence spectra of **3**-**6**. The absorption spectra of **3**-**6** display characteristic spectral features of each subunit, where the B, Q(1,0) and Q(0,0) bands of SubP and ZnP are observed nearly at the same positions of the reference subunits.[2,4] Namely, the absorption spectra of **3**-**6** can be well constructed by a linear summation of the absorption spectra of individual subunits. Moreover, the relative absorbance of the B bands of **1** (372 nm) in the absorption spectra of **3**-**5** are 1, 0.46 and 0.31, which is in good accordance with the component ratio of **1** and **2** in the hybrid systems (Table S1). The fluorescence spectra of **3**-**5** are roughly similar to that of **2**. In addition, the fluorescence quantum yields of **3**-**5** are similar, being 0.035-0.038. These features indicate that the electronic coupling between the SubP and the ZnP in **3**-**5** is negligible. On the other hand, while the 1,3-phenylene-bridged dyad **6** shows the absorption spectrum similar to that of **3**, its fluorescence spectrum is slightly different from that of **3**. In addition, the fluorescence quantum yield of **6** was determined to be 0.028. This can be attributable to reduced distance between subunits in 1,3-

phenylene-brided geometry, which induces a slight increase of electronic coupling. However, based on the absorption spectrum, the electronic interaction between subunits is thought to be very weak in **6**.

It should be noted that *meso*-triphenyl subporphyrin **1** exhibits the fluorescence at 516 nm with Φ_F = 0.14,[2a] but such intense fluorescence is not observed in the fluorescence spectra of **3**-**6**. Moreover, the fluorescence spectra taken by 380 nm photoexcitation exhibit very weak fluorescence from the ^{1}(SubP)*, while such fluorescence is not observed by 420 nm excitation. Such fluorescence features are also verified by their excitation spectra measured at 520 and 640 nm (Figure S1). These data indicate the efficient intramolecular EET from the ^{1}(SubP)* to the ZnP.

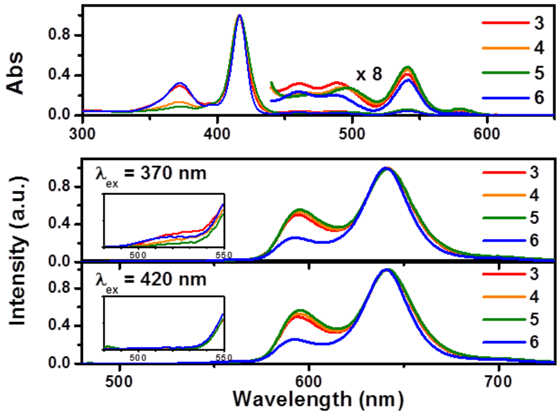

Figure 2. The steady-state absorption and fluorescence spectra of **3**-**6** in toluene.

It is interesting to point out that there are two possible EET pathways in **3**-**6**. One is EET from the Q-state of the SubP to the Q-state of the ZnP and the other is EET from the B-state of the SubP to the B-state of the ZnP followed by internal conversion to the Q-state. The latter route is uncommon but conceivable, since the B-states of SubP have been revealed to undergo relatively slow internal conversion rate[5] and the large spectral overlap was estimated in the B band region. To distinguish the EET route, the fluorescence spectra of **3**-**6** by photoexcitation at 370 and 400 nm were comparatively investigated (Figure S2). The S_2 emission of the ZnP was not observed by 370 nm photoexcitation but was only observed in the range of 420-440 nm by 400 nm photoexcitation. These observations indicate that the EET process predominantly occurs from the Q-state of the SubP to the Q-state of the ZnP.

Deeper insights into the nature of intramolecular EET process in **3**-**6** can be drawn by femto-second fluorescence upconversion measurements. The fluorescence decay profiles of **3**-**6** were recorded by photoexcitation at 385 nm and monitored at 520 and 640 nm, in which the emission at 520 nm originates from the SubP-like fluorescence and that at 640 nm is dictated by the ZnP-like fluorescence (Figure 3). In the fluorescence decay profiles of **3**, **4**, **5** and **6** at 520 nm, the SubP-like fluorescence is well-described by fast decay time constants, 360 ± 20, 190 ± 15, 150 ± 15 and 680 ± 20 fs, in addition to slow decays on ns time scale, respectively (Figure S3 and Table S1). The corresponding rise components were obtained in the fluorescence temporal profiles of **3**-**6** at 640 nm. These decay and rise fluorescence profiles of **3**-**6** are definitely distinguished from the S_1 and S_2 emission of **1** and **2**, because the S_1 emission rise profile of **1** is observed at 520 nm and the S_2 and S_1 emission profiles of **2** are known to show the decay and rise components with the time constants of 1.2 ps.[4,6] Therefore, the coincidence between the decay and rise components observed in **3**-**6** demonstrates that the obtained time constants in femto-second time scale can be assigned as the intramolecular EET processes from the ^{1}(SubP)* to the ZnP.

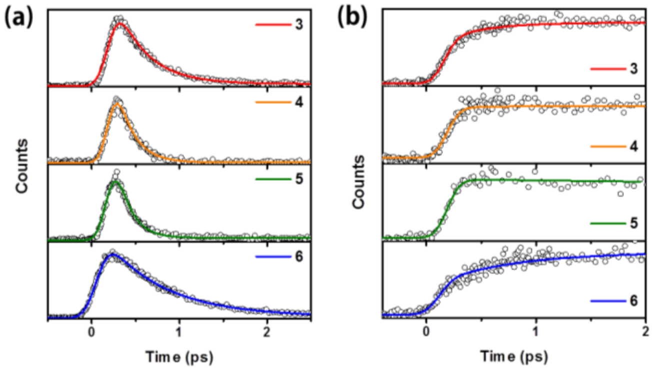

Figure 3. The time-resolved fluorescence decay profiles of **3**-**6** monitored at (a) 520 and (b) 640 nm in toluene by photoexcitation at 385 nm.

Interestingly, these features of **3**-**6** is in sharp contrast with analogous 1,4-phenylene-bridged porphyrin hybrids consisting of meso-meso linked Zn(II) porphyrin arrays as an energy donor and Zn(II) 5,15-di(phenylethynyl)porphyrin as an energy acceptor.[4] While the analogous porphyrin hybrids exhibit EET rates, ~ (3 ps)$^{-1}$, which are well-matched with calculated Förster-type resonance energy transfer (FRET) rates, the remarkably faster EET processes occurs in **3**-**6**. Moreover, the EET rates of **3** and **6** show a significant discrepancy from the FRET rates (Table S2),[7] even though they have similar molecular structure to the analogous porphyrin hybrids and display weak coupling between subunits, as revealed in the absorption spectra.

These unique ultrafast EET processes in **3**-**6** are attributable to the triangular ring-contracted structure of SubP, in which the angles of C_α-C_{meso}-$C_{\alpha'}$ are small, allowing free rotation of *meso*-aryl substitutents.[2] These structural features cause large electronic interactions of *meso*-aryl substituents with subporphyrin π-electronic system.[8] The quantum mechanical calculations of **3** and **6** also demonstrate the effective π-conjugative elongation of the SubP core to the *meso*-phenylene-bridge. In the comparative analysis of MOs, the electron density is negligible on the *meso*-phenylene-bridge in **2**, but the electron density is well distributed onto the *meso*-phenyl substituents of **1** (Figures S4 and S5). These electronic natures can be obviously visualized in terms of electron density difference map (EDDM), representing the change of electron density for a given electronic transition (Figures S6 and S7).[9] The representative EDDMs for two transitions of **3**, where T_2 and T_9 describe electronic transitions to LUMO+1 and LUMO+2, respectively (Figure 4), clearly depict that the π-electron density of electronic excited states of **1** is delocalized onto the *meso*-phenyl substituents as well as the 1,4-phenylene bridge (Tables S3 and S4).

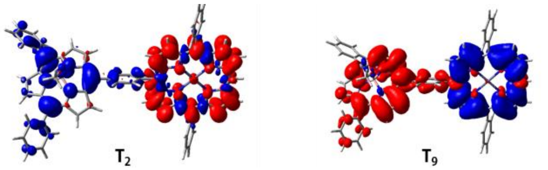

Figure 4. Representative electron density difference maps between the electronic ground and excited states of **3**. Red and blue colors indicate electron rich and deficient charaters in the excited electronic states.

The π-conjugative elongation of the SubP onto the phenylene-bridge in **3**-**6** is a main cause for their fast EET processes. The substantial electronic densities of the (SubP) spreading over the phenylene-bridge invoke that the SubP chromophore is expanded to *meso*-phenyl groups, in which the phenylene-bridged SubP-ZnP hybrids can be considered as directly linked (expanded SubP)-ZnP hybrids. The directly linked structures thus provide a way for effective electron exchange interactions between SubP and ZnP moieties,[10] resulting in the efficient energy transfer by through-bond effect and the remarkable discrepancy between the experimental EET rates and the FRET rates.

Here, the two contrasting propensities in the EET rates of **3**-**6** depending on the linking position of 1,4- and 1,3-phenylene-bridge can be illustrated on the basis of the through-bond effect by the extended conjugation of SubP: the EET rates of **3**-**5** are linearly proportional to the number of ZnP and the EET process in **6** is slower than that in **3** despite its shorter center-to-center distance. In 1,4-phenylene-bridged geometry, the acceleration of EET rates from **3** to **4** and **5** is ascribed to the para-linking position of phenylene-bridge. Since the para position is the most effective in electronic exchange interaction, the efficient EET process occurs through the phenylene-bridge, which induces that the intramolecular EET process acts as the main deactivation pathway of excited population of SubP in **3**-**5**. Therefore, increasing the efficient deactivation channels of SubP according to the number of ZnP from **3** to **4** and **5** bring forth the linear correlation between the EET rate and the number of acceptor. On the other hand, the relatively slow EET rate of **6** compared to **3** can be accounted for in terms of the 1,3-linking position of phenylene-bridge. In phenylene-bridged molecular systems, the *meta*-linked bridges do not act as effective linkers for electronic exchange interaction in contrast to the *para*-linked bridges.[10c] Thus, despite the conjugative elongation, the *meta*-linked geometry of **6** obstructs the electronic communication through phenylene-bridge. As a result of ineffective through-bond effect, **6** shows a smaller discrepancy between experimental EET rate and FRET rate compared to **3**. Consequently, we can conclude that π-conjugation longation of the electronic systems of SubP core onto the phenylene-bridge allows unique ultrafast intramolecular EET processes of **3**-**6** by through-bond effect.

In summary, we have explored the extraordinarily accelerated intramolecular EET process of the phenylene-bridged SubP-ZnP hybrids. The unique ring-contracted structure of SubPs promotes the electronic conjugation interaction between the SubP core and the phenylene-bridge, which efficiently mediates the intramolecular EET processes. We believe that this report has successfully identified the functional properties of SubP in the hybrid systems. Furthermore, our findings presented here can provide useful information on potential applications of SubPs as an efficient EET process element in SubP-based molecular systems for energy gathering or dissipation.

The work at Yonsei was supported by Global Research Laboratory program (2013-8-1472), Mid-carrier Researcher Program (2010-0029668) of National Research Foundation grant funded by MEST of Korea and AFSORD/AOARD grant (No. FA2386-09-4092). The work at Kyoto was supported by Grant-in-Aid from JSPS (No. 25220802 (S)). The quantum calculations were performed using the supercomputing resources of the Korea Institute of Science and Technology Information (KISTI).

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Electronic Supplementary Information (ESI) available. See DOI: 10.1039/c000000x/

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