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COMMUNICATION

Molecular engineering and solvent dependence of excitation energy hopping in self-assembled porphyrin boxes $\dagger\ddagger$

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It has been demonstrated that the direction and magnitude of transition dipole moments, and hence rates in the excitation energy hopping in the self-assembled porphyrin boxes can be tuned by insertion of ethynyl groups as well as the dielectric constant of solvent.

Recently, supramolecular chemistry utilizing a strategy of non-covalent self-assembly has become a desirable choice to prepare multi-porphyrin arrays as mimicries of light harvesting (LH) antennae complexes.¹ Interesting examples of porphyrin systems so far reported include conjugated porphyrin ladders,² a tetrameric cage that encapsulates a guest porphyrin,³ and linear giant porphyrin arrays assembled by imidazole–zinc(II) porphyrin coordination.⁴ As such, molecular self-assembly can translate the covalent connectivity and molecular shape of the components into tertiary structure.

In this context, the molecular component of a *meso-meso*-linked diporphyrin⁵ is quite attractive because of its perpendicular conformation, which may lead to unique architectures. In addition, two porphyrins in the component are strongly coupled mainly by excitonic interactions but not by π -conjugation.⁶ This feature encouraged us to explore self-assembled porphyrin boxes including **B1** as models for LH antennae.¹ Recently, tetrameric squares formed from 4-pyridine appended zinc(II) chlorophyll or 4-pyridyl-ethynyl-substituted zinc(II) porphyrin were reported to exhibit excitation energy hopping (EEH),⁷ whose rates were accelerated as compared to that of a porphyrin square formed from 4-pyridine-appended zinc(II) porphyrins.⁸ In both cases, larger transition dipole moments are considered to give rise to enhanced EEH

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Chart 1 Molecular structures of D1-D3 and B1-B3.

rates, since the magnitude of the transition dipole moment has a significant role in the Förster-type energy transfer process.⁹

Encouraged by these results, we attempted to engineer the intra-box EEH in **B1** by inserting ethynyl units either along or perpendicular to the long molecular axis to form **B2** or **B3** with intention to increase the transition dipole moments along such directions (Chart 1). As described later, porphyrin boxes **B2** and **B3** were spontaneously self-assembled in non-polar solvents, hence allowing the assessment of the effects of magnitude and direction of transition dipole moment on excitonic interactions and EEH processes.

Full synthetic details of **D2** and **D3** are given in ESI.[‡] The ¹H NMR spectra of **Dn** in CDCl₃ exhibit single sets of signals with distinct up-field shifts for the pyridyl protons (ESI[‡]), indicating the quantitative formation of **Bn**. In contrast, such up-field shifts disappeared in coordinating pyridine- d_5 , indicating the dissociation as **Dn**, which have been taken as a non-assembled reference. The formations of **Bn** were also indicated by their shorter retention times in analytical gel permeation chromatography (Fig. S3, ESI[‡]).

The absorption spectra of **D***n* are characteristic of free *meso-meso*-linked zinc(II) diporphyrin, exhibiting split Soret bands due to the well-established exciton coupling (Fig. 1).^{6,10,11} The insertion of triple bonds gives rise to bathochromic shifts in the Soret bands of **D2** and **D3** as a whole but causes different influences on the spectral shape; an intensified low-energy split band in **D2** and an intensified high-energy band in **D3**, in line with the exciton coupling scheme. In addition, the inserted triple bonds reduce the molecular symmetry, hence increasing

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Fig. 1 Steady-state absorption spectra (left) and fluorescence (right) spectra of Dn (blue) and Bn (orange). The fluorescence spectra were obtained using an excitation wavelength of 430 nm.

the intensity of the Q(0,0) band.^{12,13} The fluorescence spectra of **D2** and **D3** are red-shifted from that of **D1**. As in the case of **D1**, the relatively broad fluorescence spectra of **D2** and **D3** became sharpened in **B2** and **B3**, probably due to the structural rigidification particularly with regard to the dihedral angle of the *meso-meso* linked diporphyrin upon box formation.¹⁴ In line with this interpretation, the Stokes shifts in **B2** and **B3** are much less than those in **D2** and **D3**. These characteristic fluorescence spectra of **B2** and **B3** are rather concentration independent up to 1.0×10^{-8} M, from which the association constants have been estimated to be at least larger than 10^{24} M⁻³.

The steady-state fluorescence excitation anisotropy spectra were comparatively measured. While **D1(B1)** and **D2(B2)** displayed the common anisotropy profiles exhibiting negative anisotropy in the high-energy Soret band and positive anisotropies in the low-energy Soret and Q bands,^{6,10} **D3(B3)** showed a distinctly inverted feature (Fig. 2). From these results, we concluded that the direction of transition dipole moment of the emissive state is along the long axis of diporphyrin (green) in **D1(B1)** and **D2(B2)**, but perpendicular in **D3(B3)** (blue). These features indicate that the insertion of the triple bonds dictates the directions of the transition dipole moments that participate in EEH. This trend is independent of solvent for **B2** and **B3**, while **B1** displays solvent-dependent fluorescence anisotropy, indicating that the predominant direction of the transition dipole moments of emissive states in **B1** changes from the long axis in CH₂Cl₂ to the short axis in toluene.

The time-resolved fluorescence and its anisotropy decays of **D***n* and **B***n* were measured in CH₂Cl₂ (Fig. S4, ESI‡). Timeresolved polarization anisotropy measurement is informative in revealing the EEH process, because the energy migration between the same molecular units with different orientations provides a depolarization channel.¹⁵ But in the present case, the fluorescence anisotropy decay time constants τ_{rot} , however, do not reflect the energy migration process within **B***n*, because its time scale (~2.5–4.9 ns) is too slow for the energy transfer time. The fluorescence anisotropy decay time constants τ_{rot} increase in **B***n* compared with those of **D***n*, reflecting an increased molecular volume. Therefore, the τ_{rot} values have been interpreted to originate from the rotational diffusion motions in solution. The initial r_0 value of the fluorescence anisotropy decay became



Fig. 2 Steady-state fluorescence excitation anisotropy spectra (black) and absorption spectra (blue) of **Dn** and **Bn** in CH_2Cl_2 (A) and toluene (B). The spectra were obtained using parallel and perpendicular orientations between excitation and emission polarizations at the fixed emission wavelengths of 630 nm (D1/B1) and 650 nm (D2/B2, D3/B3).

smaller in going from Dn to Bn, indicating the presence of additional depolarization channels in Bn, which are contributed by the EEH processes within Bn.

To investigate the fast EEH processes within **B***n*, pump-power dependent transient absorption (TA) decays were measured in CH₂Cl₂ and toluene (Fig. 3), where the Q band excitations, *i.e.*, $\lambda_{pump} = 570$ nm (**B**1), $\lambda_{pump} = 590$ nm (**B**2/**B**3) were employed to avoid the involvement of S₂–S₁ relaxation.¹⁶ The TA decays of **D***n* were also measured as references. **D***n* revealed pump-power independent slow TA decays in agreement with the S₁-state lifetimes (~1.2–1.6 ns) observed in the fluorescence lifetime measurements. On the other hand, **B***n* showed relatively fast pump-power dependent TA decays in the time region of



Fig. 3 Transient absorption decay profiles of **B***n* that include pumppower dependences. The transient absorption decay profiles of **D***n* are shown as insets in the upper right corner of each panel. In the experiments, the pump wavelengths were 570 nm (**D**1/**B**1), 590 nm (**D**2/**B**2, **D**3/**B**3) and the probe wavelengths were 490 nm (**D**1/**B**1), 510 nm (**D**2/**B**2, **D**3/**B**3) which correspond to the induced absorption bands.

tens of picoseconds in addition to long-lived components corresponding to the S₁-state decays. When the pump power was increased, the relative contributions of the fast τ_1 and τ_2 components were enhanced as compared to the slowest τ_3 one (Table S4, ESI[‡]). The pump-power dependence on the TA decay is indicative of singlet-singlet annihilation processes, because the intense excitation or high density of photons generates two or more excitons in one assembly unit, and then the recombination between the excitons gives rise to fast deactivation processes. In this regard, while the fastest τ_1 components are likely to arise from multiple exciton generation processes, the second fastest τ_2 components from the migration limited exciton-exciton recombination processes between meso-meso-linked zinc(II) diporphyrins rather than zinc(II) porphyrin monomers, because this process does not occur in Dn. The following formula relates the annihilation time (τ_a) to the excitation energy hopping (EEH) time ($\tau_{\rm h}$) for multichromophoric systems where N is the number of hopping sites:¹⁷

$$\tau_{\rm a} = (N^2 - 1)/24\tau_{\rm h} \tag{1}$$

Though **B***n* have eight mutually perpendicular porphyrin monomer units, the number of hopping sites is conceived as N = 4, because there are four major transition dipole moments in Bn as shown in Fig. 2, contributing to the lowest S_1 states from which the EET processes occur. Thus, by using eqn (1), the EEH times $\tau_{\rm h}$ of **B1**, **B2** and **B3** were evaluated to be 28.8, 27.2, and 22.4 ps in CH₂Cl₂ and 17.6, 5.4, and 3.4 ps in toluene, respectively. Therefore, the insertion of triple bonds causes certain enhancement in EEH rate, which is, however, more dependent upon solvent, only modest in CH₂Cl₂ but distinct in toluene. The observed solvent effect may be explained in terms of different dielectric constant; 8.93 for CH₂Cl₂ and 2.38 for toluene. The dielectric constants stand for the storage capacity of electric energy, implying that CH₂Cl₂ can store more electric charge than toluene. As a result, the magnitude of effective transition dipole moments participating in the EEH process should be larger in toluene than in CH₂Cl₂. It should be noted that the decay profiles of B1 in TA measurements do not seem to be affected by the solvent environment. This may be accounted for in terms of the change in the transition dipole moments participating in the EEH from the long to short molecular axes upon the solvent change.

As described above, the decreased r_o values in going from **D***n* to **B***n* indicate the presence of fast depolarization channels contributed by the EEH processes because the change in the orientation of transition dipole moments is accompanied as the EEH process occurs in a multichromophoric system. In this regard, we have measured transient absorption anisotropy (TAA) decays of **D***n* and **B***n* in CH₂Cl₂ and toluene (Fig. S5, ESI‡). The TAA decays of **B***n* exhibit dual exponential decays in which the fast components with $\tau_1 < 0.2$ ps indicate the depolarization processes within the porphyrin monomer and dimer because the similar components were observed in **D***n*.

Thus, the τ_2 components occurring in a few tens of picoseconds seem to be related with the EEH processes in which the exact hopping time can be derived by using a theoretical modeling of the multichromophoric system as a planar 2-dimensional polygon structure (ESI[‡]). In this sense, it is difficult to estimate the EEH times accurately from the TAA decays of **Bn** because of their 3-dimensional structures. Nevertheless, the trends observed in the τ_2 components are in good accordance with the TA decays.

In summary, our attempt to engineer the direction and magnitude of transition dipole moments of **B***n* by inserting ethynyl units along or perpendicular to the long axis of *meso-meso* linked diporphyrin has been verified by our combined photophysical measurements. In addition, we have found that the EEH rates in **B***n* depend on the dielectric constant of solvent.

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