Excitation energy migration processes in various multi-porphyrin assemblies

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The electronic interactions and excitation energy transfer (EET) processes of a variety of multi-porphyrin arrays with linear, cyclic and box architectures have been explored. Directly \( \text{meso-meso} \) linked linear arrays (\( \text{Z}_N \)) exhibit strong excitonic coupling with an exciton coherence length of approximately 6 porphyrin units, while fused linear arrays (\( \text{T}_N \)) exhibit extensive \( \pi \)-conjugation over the whole array. The excitonic coherence length in directly linked cyclic porphyrin rings (\( \text{CZ}_N \)) was determined to be approximately 2.7 porphyrin units by simultaneous analysis of fluorescence intensities and lifetimes at the single-molecule level. By performing transient absorption (TA) and TA anisotropy decay measurements, the EET rates in \( m \)-phenylene linked cyclic porphyrin wheels \( \text{C}_{12} \text{ZA} \) and \( \text{C}_{24} \text{ZB} \) were determined to be 4 and 36 ps\(^{-1} \), respectively. With increasing the size of \( \text{CNZA} \), the EET efficiencies decrease owing to the structural distortions that produce considerable non-radiative decay pathways. Finally, the EET rates of self-assembled porphyrin boxes consisting of directly linked diporphyrins, \( \text{B}_{1A}, \text{B}_{2A} \) and \( \text{B}_{3A} \), are 48, 98 and 361 ps\(^{-1} \), respectively. The EET rates of porphyrin boxes consisting of alkynylene-bridged diporphyrins, \( \text{B}_{2B} \) and \( \text{B}_{4B} \), depend on the conformation of building blocks (planar or orthogonal) rather than the length of alkynylene linkers.

Keywords: porphyrin; electronic interaction; excitation energy transfer; ultrafast spectroscopy; single-molecule spectroscopy

1. Introduction

Excitation energy transfer (EET) processes are the most important function of natural light-harvesting (LH) antenna complexes. Upon absorption of a photon by the antenna complex, many pigments within the complex convey this photon via EET until it encounters a reaction centre. To duplicate these fundamental features in simplified artificial systems, a variety of porphyrin arrays have been explored, which absorb visible light in a wide spectral range and funnel the resulting excitation energy rapidly and efficiently to a designed site. A key parameter for EET is the electronic interactions among neighbouring porphyrin units. The electronic interaction depends on distance and orientation between the neighbouring pigments, both of which can be controlled elaborately according to the linkage motif connecting them.

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This paper deals with spectroscopic characterizations both at ensemble and single-molecule level of various types of multi-porphyrin arrays, including directly meso–meso linked linear porphyrin arrays (Z_N), meso–meso, β–β, β–β triply linked linear porphyrin arrays (T_N), directly meso–meso linked porphyrin rings (CZ_N), m-phenylene linked cyclic porphyrin wheels (C_NZA and C_NZB) and self-assembled porphyrin boxes (B_NA and B_NB). The order in this paper comes from the dimensionality and linkage motif connecting neighbouring porphyrins. Following this sequence, we first illustrate the electronic interactions of the porphyrin arrays based on the steady-state absorption and emission spectra, and the simultaneous measurements of single-molecule fluorescence intensity and lifetime. Then the EET rates and efficiencies are discussed from the results of time-resolved transient absorption (TA) and transient absorption anisotropy (TAA) measurements and coincidence measurement, respectively.

2. Linear porphyrin arrays

(a) Directly meso–meso linked linear porphyrin arrays (Z_N)

The molecular design of directly meso–meso linked linear porphyrin arrays (Z_N, N = 1, 2, 3, 4, 6, 8, 12, 16, 32, 64 and 128) was envisaged to bring the porphyrin units closer for rapid energy transfer (scheme 1) [1].

The absorption spectra of Z_N exhibit split Soret bands owing to exciton coupling between the adjacent porphyrins, while the Q bands remain nearly at the same positions (figure 1a).

The simple point-dipole exciton coupling theory is useful to interpret the spectral features caused by the interchromophoric interactions [4]. As shown in scheme 2, the transition dipole moments of Soret band, B_x and B_y, which degenerate in a porphyrin monomer, independently interact with those of neighbouring porphyrins.

B_z transition dipole moments along the long molecular axis are excitonically coupled to generate an allowed lower energy transition (B_z + B_z), while the mutual Coulombic interactions between B_x and B_y (or B_z) transition dipole moments are negligible owing to their orthogonal orientation. Consequently, the Soret band of Z_N is split into a red-shifted band and an unperturbed one.

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Figure 1. Steady-state absorption spectra of (a) $Z_N$ and (b) $T_N$ taken in CHCl$_3$ at room temperature. In (b), the background absorbance at approximately 6000, 4000 and 3500 cm$^{-1}$ may arise from the overtones of C–H vibration of the solvent. Adapted from Kim et al. [2] and Cho et al. [3]. (Online version in colour.)

The exciton splitting energy ($\Delta E$) for $Z_N$ is given as $\Delta E = \Delta E_0 \cos[\pi/(N + 1)]$, where $\Delta E_0$ represents the exciton splitting energy of the neighbouring porphyrins and $N$ the number of porphyrin units in the array [2]. For the Soret bands of $Z_N$, $\Delta E$ exhibits a good linear correlation against $\cos[\pi/(N + 1)]$ with a slope of $\Delta E_0 = 2150$ cm$^{-1}$, indicating strong exciton coupling between the neighbouring porphyrin units and good arrangement of the porphyrins as a linear form. In a similar manner, the exciton coupling strength in the $S_1$-state of $Z_N$ was determined to be 570 cm$^{-1}$, which is larger than 280 cm$^{-1}$ that assumed only point dipole–dipole coupling between the porphyrin units. The short distance between porphyrin units is believed not only to enhance through-space dipole–dipole coupling but also to increase through-bond interaction.

The coherence length of a strongly coupled molecular array is important in understanding the photoexcited-state dynamics and collective behaviour of the transition dipole moments. A spectroscopic observable directly related to the exciton coherence length is superradiance. The superradiance can be quantified using a superradiance coherence size, which is defined as the ratio of the radiative decay rate of the array to that of the monomer, because the radiative decay rate of the array increases when the constituent chromophores interact with each other and radiate in phase [5,6]. When the superradiance coherence sizes of $Z_N$ were plotted as a function of the number of porphyrin units, a deviation point from the linearity was found to be approximately six porphyrin units, which would be
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Scheme 2. Schematic of the excitonic interaction in directly meso–meso linked diporphyrin.

a reasonable estimation for the exciton coherence length of $Z_N$ [2]. This result is consistent with the calculated exciton coherence length of six porphyrin units that is based on the equation developed by Kakitani et al. [7].

At the single-molecule level, the superradiance effect can be examined based on photobleaching dynamics of single molecules [8]. As seen in the fluorescence intensity trajectories (FITs) in figure 2a, $Z_N$ photobleaches in a stepwise fashion, where the number of steps for each array is compatible with that of porphyrin units.

To estimate the superradiance coherence size of single molecules, fluorescence lifetimes at the first and last emissive levels in the FIT and fluorescence quantum yield from bulk measurement were employed to calculate the radiative decay rates of the array and the monomer. For the molecules shown in figure 2a, the superradiance coherence sizes were calculated to be 1.8, 2.7, 3.6, 4.4 and 5.0 in going from $Z_2$ to $Z_6$. We carried out a statistical analysis by collecting 64 single-molecule datasets for each array. In figure 2b, distributions of the superradiance coherence size show a progressive shift upward to $Z_4$, after which it becomes saturated at a value around 4.5. Thus, at the single-molecule level, approximately four porphyrin units would be the best estimation of the exciton...
coherence length of $Z_N$. Not only the covalent direct linkage with a short centre-to-centre distance but also the orthogonal geometry imposed by a large steric hindrance probably minimize static/dynamic disorders of $Z_N$ and contribute to preserve coherent excitonic interaction in these arrays even in the solid state at room temperature.

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Figure 3. Plots of the energies of the absorption bands B_x and Q_x of T_N as a function of the number of porphyrin units show a good correlation between the experimental data and PPP-SCI calculated values. The electronic character of the B_x band is explained by (a) the splitting energy of the exciton model, whereas that of the Q_x band is well fitted by (b) a particle in a box model. Adapted from Cho et al. [3]. Filled circles, B_x band exp.; open circles, B_x band PPP; filled squares, Q_x band exp.; open squares, Q_x band PPP.

(b) Fused linear porphyrin arrays (T_N)

As a straightforward strategy for maximizing \(\pi\)-overlap among the porphyrins, triply meso–meso, \(\beta–\beta\), \(\beta–\beta\) linked linear porphyrin arrays (T_N, \(N = 2, 3, 4, 5, 6, 8\) and 12) were prepared (scheme 1) [9]. These fully conjugated porphyrin arrays have planar tape-shaped structures and display drastically red-shifted absorption spectra that reach into the far-IR region (figure 1b), reflecting extensive \(\pi\)-conjugation [3]. The absorption bands of the fused porphyrin arrays are roughly categorized into three distinct well-separated bands, which are marked as B_y, B_x and Q_x bands in near-UV, visible and IR regions, respectively, on the basis of their transition properties revealed by the PPP-SCI (Pariser–Parr–Pople (PPP) Hamiltonian-based single-configuration interaction (SCI)) calculations. With an increase in the number of porphyrin units, the B_y bands retain nearly the same positions as that of the Zn(II) porphyrin monomer, while the B_x and Q_x bands are continuously red-shifted along with an increase in their band intensities. The band shift of B_x bands as a function of the number of porphyrin units indicates that the B_x bands exhibit a clear saturation behaviour with the effective conjugation length (ECL) number of ca 8. The Q_x bands do not show such saturation behaviour up to T12, i.e. the ECL number of \(N > 12\) in the S_1-state of T_N.

The observed linear plot of the energy difference between B_y and B_x bands as a function of the number of porphyrin units indicates that the absorption spectra are actually influenced by the exciton coupling scheme and the constituent porphyrin units are in regular arrangement as a linear form (figure 3a) [3].

On the contrary, the plot of the Q_x bands deviates strongly from the exciton coupling scheme. Instead, as shown in figure 3b, the plot based on a free electron model (a particle in a box model) gives rise to a well-correlated straight line, indicating that the S_1-state of T_N is characterized by the extensive \(\pi\)-conjugation throughout the entire array.

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Scheme 3. Molecular structures of directly \textit{meso–meso} linked porphyrin rings (CZ$_N$).

3. Cyclic porphyrin arrays

(a) \textit{Directly meso–meso} linked porphyrin rings (CZ$_N$)

Inspired by the efficient EET processes in the circularly arranged chromophoric assemblies in natural LH complexes [10–12], cyclic porphyrin arrays have been prepared as artificial photosynthetic antennae. Directly \textit{meso–meso} linked porphyrin rings (CZ$_N$, $N = 4$, 6 and 8) are attractive in view of not only high molecular symmetry but also large and regular electronic interactions that lead to efficient EET (scheme 3) [13].

The absorption spectra of CZ$_N$ exhibit broad non-split Soret bands at red-shifted Soret band position. These spectral features are explained by that both of the transition dipole moments $B_x$ and $B_y$ are excitonically coupled with those of neighbouring porphyrins to cause an excitonically allowed state of the same energy. In CZ$_N$, in addition to J-type coupling along the circumference of the ring, H-type coupling is also possible because of the bent structures, where the dihedral angles of neighbouring porphyrin planes are deviated from 90$^\circ$.

The exciton coherence length of CZ$_4$ was evaluated at the single-molecule level [14]. In the case of cyclic structures, because the coherence can propagate in both directions owing to the absence of terminal unit, it is necessary to assume that the coherence regions from both directions do not collide. In figure 4, the exciton coherence length of the molecule is calculated to be 2.84 by employing the fluorescence lifetimes at the first and fourth emissive levels in the FIT of 1.65 and 2.28 ns, respectively, and the fluorescence quantum yield of 0.071 of CZ$_4$.

The average exciton coherence length of CZ$_4$ was determined to be 2.74 from 20 single-molecule datasets. This value is shorter than four of the linear array Z$_4$ [8]. The cyclic structure of CZ$_4$ probably cannot cause an exciton to be fully delocalized among all four porphyrins, because the transition dipoles of the porphyrins are arranged nearly orthogonal to one another, which reduces the excitonic interactions among the four porphyrin units. In CZ$_6$ and CZ$_8$, the exciton coherence length could not be examined because their FITs did not show clear stepwise photobleaching behaviours.
(b) **m-Phenylene linked cyclic porphyrin wheels (C$_N$ZA and C$_N$ZB)**

Two types of a series of extremely large yet discrete cyclic porphyrin wheels were also prepared to explore EET processes. The directly meso–meso linked porphyrin dimer $Z_2$ and tetramer $Z_4$ are bridged by $m$-phenylene spacers, respectively, to form cyclic structures C$_N$ZA ($N = 10, 12, 16, 18, 24$ and $32$) and C$_N$ZB ($N = 24$; scheme 4) [15,16].

The absorption spectra of C$_{12}$ZA and C$_{24}$ZB are similar to those of dimer $Z_2$ and tetramer $Z_4$ subunits, respectively, while the further split Soret bands of C$_{12}$ZA indicate additional dipole–dipole interaction between $Z_2$ subunits via the $m$-phenylene spacer. These data indicate that the electronic interactions are predominated by the exciton coupling within meso–meso linked porphyrin subunits. In the absorption spectra of C$_N$ZA, the peak positions of low-energy Soret bands converge into a single position, which originates from exciton couplings among non-unidirectional transition dipole moments in circular geometries. According to this feature, it can be conceived that three-dimensional orientations between two adjacent $Z_2$ subunits remain relatively the same in all C$_N$ZA [17–19].

To explore the fast EET processes at the ensemble level, femtosecond TA and TAA measurements were conducted on $Z_2, Z_2Z_2$ and C$_{12}$ZA [20,21]. In the TA decays, $Z_2$ and $Z_2Z_2$ reveal no power dependence and show only
Scheme 4. Excitation energy transfer in \( m \)-phenylene linked cyclic porphyrin wheels (\( C_NZA \) and \( C_NZB \)) and one of their reference molecules (\( 2Z2 \)). \( N = 0, 1, 3, 4, 7 \) and 11.

single decay components that are in agreement with the \( S_1 \)-state lifetimes. On the other hand, the TA decay of \( C_{12}ZA \) appears to be very sensitive to the pump power; when the pump power is increased, the contributions of relatively fast components, \( \tau_1 \) and \( \tau_2 \), are enhanced relative to the slowest component, \( \tau_3 \) (figure 5a). The pump power dependence of the TA decays is a strong indication of exciton–exciton annihilation, because the excitation with high density of photons may generate two or more excitons in one cyclic array, followed by recombination between the excitons, which give rise to fast deactivation channels. Figure 5b shows TAA decay profiles of \( Z2 \), \( 2Z2 \) and \( C_{12}ZA \). While \( Z2 \) exhibits the single decay component with a time constant of 0.17 ps, \( 2Z2 \) and \( C_{12}ZA \) exhibit two decay components: 0.18 and 4.70 ps for \( 2Z2 \) and 0.16 and 1.22 ps for \( C_{12}ZA \). Since the time constants of fast components are well matched with that of \( Z2 \), these components are thought to arise from the depolarization within \( Z2 \). On the other hand, we consider that the slow components result from the depolarization owing to the EET between \( Z2 \) subunits via \( m \)-phenylene spacer.

When the Förster-type incoherent energy hopping model is employed by assuming a migration-limited character of exciton–exciton annihilation and a random walk formalism of anisotropy decay [22–25], the analytical exciton–exciton annihilation and depolarization times are connected with EET time by equations (3.1) and (3.2):

\[
\tau_{\text{annihilation}} = \frac{\tau_{\text{hopping}}(N^2 - 1)}{24} \quad (3.1)
\]

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and

\[ \tau_{\text{depolarization}} = \frac{\tau_{\text{hopping}}}{4(1 - \cos^2 \alpha)}, \]  (3.2)

where \( N \) is the number of effective hopping sites, \( \alpha \) the angle between the adjacent transition dipoles, \( \tau_{\text{annihilation}} \) the slowest exciton-exciton annihilation time and \( \tau_{\text{hopping}} \) the inverse of the nearest neighbour energy hopping rate. Equation (3.1) assumes that the exciton-exciton annihilation reflects the migration-limited exciton-exciton recombination along the whole cyclic array and how many hops are required for this recombination to be accomplished. On the other hand, equation (3.2) is understood by considering that the depolarization is complete when the transition dipole migrates through 90° and that how many hops are required for this rotation to be accomplished. As \( \text{C12ZA} \) consists of six \( \text{Z2} \) subunits, the number of hopping sites would be \( N = 6 \). Introducing \( N = 6 \) and \( \alpha = 60° \) in equations (3.1) and (3.2), the EET rates between neighbouring \( \text{Z2} \) subunits are calculated to be 3.66 and 4.25 ps\(^{-1}\), respectively. It is noteworthy

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Table 1. Parameters for calculation of the effective number of hopping sites \((N)\) by using the EET and depolarization times in \(C_NZA\).

<table>
<thead>
<tr>
<th>molecules</th>
<th>(\tau_{\text{dep}}) (ps)</th>
<th>(4(1 - \cos^2 \alpha_{\text{exp}})^b)</th>
<th>(\alpha_{\text{exp}}) (deg)</th>
<th>(N_{\text{exp}}^d)</th>
<th>(\alpha_{\text{flat}}^e) (deg)</th>
<th>(N_{\text{flat}}^f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C10ZA</td>
<td>1.77</td>
<td>3.08</td>
<td>61.4</td>
<td>5.9</td>
<td>72</td>
<td>5</td>
</tr>
<tr>
<td>C12ZA</td>
<td>1.93</td>
<td>2.83</td>
<td>57.2</td>
<td>6.3</td>
<td>60</td>
<td>6</td>
</tr>
<tr>
<td>C16ZA</td>
<td>2.90</td>
<td>1.88</td>
<td>43.3</td>
<td>8.3</td>
<td>45</td>
<td>8</td>
</tr>
<tr>
<td>C18ZA</td>
<td>3.10</td>
<td>1.76</td>
<td>41.6</td>
<td>8.7</td>
<td>40</td>
<td>9</td>
</tr>
<tr>
<td>C24ZA</td>
<td>3.06</td>
<td>1.78</td>
<td>41.9</td>
<td>8.6</td>
<td>30</td>
<td>12</td>
</tr>
<tr>
<td>C32ZA</td>
<td>3.29</td>
<td>1.65</td>
<td>40.1</td>
<td>9.0</td>
<td>22.5</td>
<td>16</td>
</tr>
</tbody>
</table>

\(^a\)Depolarization times obtained by TAA measurement.

\(^b\)The value of \((\tau_{\text{hop}}/\tau_{\text{dep}})\), where EET time \(\tau_{\text{hop}}\) is fixed to be 5.4 ps taken from \(2Z2\). On the basis of a regular polygon model, the relationship between EET and the depolarization times is given by \(\tau_{\text{dep}} = \tau_{\text{hop}}/[4(1 - \cos^2 \alpha)]\), where \(\alpha = 360/N\).

\(^c\)Experimentally observed angles between adjacent \(Z2\) subunits.

\(^d\)Effective numbers of hopping sites.

\(^e\)Angles between adjacent \(Z2\) subunits.

\(^f\)Effective numbers of hopping sites when the cyclic arrays are regarded as flat regular polygons.

that the two different experimental observables, exciton–exciton annihilation and anisotropy depolarization times, result in a consistent EET rate of 4.0 \(\pm\) 0.4 ps\(^{-1}\) within a small error range.\(^1\)

The EET rate between neighbouring \(Z4\) subunits in \(C24ZB\) was determined similarly by TAA measurements to be 36 ps\(^{-1}\) (scheme 4), which is almost the same as that of the reference molecule \(2Z4\) [15,17]. A large difference between the EET rates of \(C12ZA\) and \(C24ZB\) is explained in terms of a large difference in the centre-to-centre distance of \(meso–meso\) linked porphyrin subunits: the distance of \(C24ZB\) is \(\text{ca} 1.5\)-fold longer than that of \(C12ZA\), which, on the basis of the distance factor of \(R^{-6}\) in the Förster EET equation, explains well the approximately 10 times difference in the observed EET rates.

To calculate the EET rates in \(C_NZA\), an appropriate modelling is important because it is thought that, for all cyclic arrays, numerous conformational isomers could exist in solution [19]. If all cyclic arrays have ideal circular structures (regular polygon model), we can obtain the values of \(\alpha_{\text{flat}}\) and \(N_{\text{flat}}\) from equation (3.2) as shown in table 1. On the other hand, if we assume that the geometrical structure of \(2Z2\) would be similar to those in \(C_NZA\) as supported by the absorption spectra, we can regard the EET time \(\tau_{\text{hopping}}\) in all \(C_NZA\) as that

\(^1\)Based on the Förster EET equation, we have calculated the EET rate between neighbouring \(Z2\) subunits in \(2Z2\) to be 251 ps\(^{-1}\). The details of the calculation are presented in Yoon et al. [19]. The large discrepancy between the experimental and the calculated EET rates might be interpreted in two ways: (i) significant participation of through-bond energy transfer processes in the overall energy transfer processes and (ii) failure of the point-dipole approximation of Förster’s resonance energy transfer model in the case of a relatively short distance between donor and acceptor. Since Förster’s model overestimates the EET rate in the latter case, the observed fast hopping rate of \(2Z2\) is more likely elucidated by the contribution of the through-bond energy transfer processes.
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Figure 6. (a) Schematic of the singlet–singlet annihilation in C12ZA. (b) Interphoton arrival time distribution of C12ZA. (c) Histograms for the $N_C/N_L$ values of C24ZB, C12ZA, C10ZA and C16ZA from top to bottom. Adapted from [17,18]. (Online version in colour.)

of 2Z2 (5.4 ps). Hence, equation (3.2) substituted by the observed depolarization time $\tau_{\text{depolarization}}$ and the fixed EET time $\tau_{\text{hopping}}$ provides the calculated values of $\alpha_{\text{exp}}$ and $N_{\text{exp}}$ for C$_{N}$ZA (table 1). Although a different approach is applied, $N_{\text{exp}}$ values of C12ZA, C16ZA and C18ZA are in good accordance with the ideal $N_{\text{flat}}$ values, indicating that these arrays exist as circular polygon structures. In a sharp contrast, C10ZA, C24ZA and C32ZA show a large discrepancy not only between $N_{\text{exp}}$ and $N_{\text{flat}}$ values but also between $\alpha_{\text{exp}}$ and $\alpha_{\text{flat}}$ values. These features reveal that the constituent motif of $m$-phenylene linked 2Z2 is not ideal to form cyclic porphyrin arrays without structural distortions in C10ZA, C24ZA and C32ZA mainly due to the interchromophoric angle of 120° between the neighbouring subunits.

At the single-molecule level, the EET efficiencies of individual cyclic porphyrin arrays were examined by carrying out coincidence measurement [17,18]. This measurement allows for the observation of singlet–singlet annihilation processes occurring in a single molecule (figure 6a) [26,27].

Note that efficient EET mediates the collision of two or more excitons that are generated by single intense laser pulse to bring one exciton to a higher excited state, followed by relaxation of this exciton in the form of fluorescent emission of a photon. In such a case, a time interval between two consecutive detected photons conforms to a multiple of the laser repetition rate ($N_L$ in figure 6b). On the other hand, if photon pairs induced by the same laser pulse are emitted simultaneously
owing to the absence of this process, the interphoton time would be zero \( (N_C \text{ in figure } 6b) \). Thus, a \( N_C / N_L \) value obtained from interphoton arrival time distribution of a single molecule can directly be related to the EET efficiency. In figure 6b, the \( N_C / N_L \) value of \( \text{C12ZA} \) is calculated to be 0.15, which implies that singlet–singlet annihilation readily occurs owing to the efficient EET within the array. For a statistical analysis, histograms of the \( N_C / N_L \) values were constructed. The distribution of \( N_C / N_L \) values of \( \text{C24ZB} \) is slightly shifted to higher values relative to that of \( \text{C12ZA} \) (figure 6c), which reveals less efficient EET in the larger array. Similarly, in the histograms of \( N_C / N_L \) values of \( \text{C10ZA} \), \( \text{C12ZA} \) and \( \text{C16ZA} \), the distributions are shifted to higher values in the order of \( \text{C12ZA} \) (0.24), \( \text{C10ZA} \) (0.34) and \( \text{C16ZA} \) (0.38) (figure 6c). The smallest \( N_C / N_L \) value found for \( \text{C12ZA} \) among the investigated arrays reveals that the overall structure of \( \text{C12ZA} \) is rigid enough without any significant distortion in the solid state.

4. Self-assembled porphyrin boxes

(a) Porphyrin boxes consisting of directly meso–meso linked diporphyrins (\( B_N A \))

Three-dimensional Zn(II) porphyrin boxes \( B_N A \) \( (N = 1, 2 \text{ and } 3) \) were constructed by self-assembly of meso–meso pyridine-appended Zn(II) diporphyrins \( D_N A \) (scheme 5), where the size of \( B_N A \) is controlled by inserting one or two phenyl groups between the porphyrin and pyridyl substituents [28].

Owing to the different meso–aryl substituents, \( D1A–D3A \) are all chiral. Accordingly, the spontaneous box formation is achieved through homochiral self-sorting association of the respective \( (R) \) and \( (S) \) isomers of \( D1A–D3A \). The absorption spectra of \( B_N A \) show much smaller split Soret bands than those of \( D_N A \). In addition, the extent of split also exhibits a systematic change depending on the size of box [28]; while the high-energy Soret band remains at the same position, the low-energy Soret band shifts to blue in the order of \( B3A < B2A < B1A \). The complicated Soret band splitting observed in \( B_N A \) arises from various dipole–dipole excitonic interactions among eight mutually
perpendicular porphyrin units. The low-energy Soret state indicates excitonic dipole–dipole interactions among eight parallel transition dipole moments along the \( x \)-axis, whereas the high-energy Soret state implies excitonic dipole–dipole interaction among four parallel transition dipole moments along the \( y \)- or \( z \)-axis (scheme 5).

The EET processes in \( B_N A \) were examined by performing TAA measurements [28]. While \( D_N A \) reveal only slow TA decays without any anisotropy decays in the time region of tens of picoseconds, \( B_N A \) show a relatively fast TAA rise (12, 25 and 89 ps for \( B_1 A – B_3 A \)). The EET rates were calculated to be 48, 100 and 356 ps\(^{-1} \) for \( B_1 A – B_3 A \) by introducing \( \alpha = 90^\circ \) in equation (3.2). On the other hand, the slowest exciton–exciton annihilation times of 30, 60 and 228 ps were observed for \( B_1 A – B_3 A \) from the TA measurements. Using equation (3.1) with \( N = 4 \) gives rise to the EET rates of 48, 96 and 365 ps\(^{-1} \) for \( B_1 A – B_3 A \). The number of hopping sites of four seems to be reasonable because, in \( B_N A \), directly \textit{meso–meso} linked diporphyrin is likely to act as a single hopping site. The obtained exciton hopping rates from the two separate measurements are consistent with each other.

\( b \) Porphyrin boxes consisting of conjugated diporphyrins (\( B_N B \))

Another type of three-dimensional Zn(II) porphyrin boxes, \( B_2 B \) and \( B_4 B \), were also prepared by self-assembly of alkynylene-bridged diporphyrins, \( D_2 B \) and \( D_4 B \) [29]. Because of the rotational conformational heterogeneities of \( D_N B \) along the alkynylene linkers, two kinds of self-assembled porphyrin boxes are constructed by planar or orthogonal conformers, respectively (scheme 6).

Using the alkynylene-bridged diporphyrins as building blocks is advantageous in that the alkynylene linkers provide extended \( \pi \)-conjugation between porphyrin units, resulting in new, low energy and strong electronic transitions of
Q-bands. These features ensure enhanced solar spectral absorption and efficient EET processes.

To reveal fast EET processes in B2B and B4B, TA measurements were performed [29]. The planar and orthogonal conformers were selectively excited to explore the effect of the dihedral angle between porphyrin units in alkynylene-bridged diporphyrins on the EET processes in B_NB. In the case of porphyrin boxes comprising planar conformers, introducing $N = 4$ and the observed time component of 1.1 ps in equation (3.1) reveals the EET rate of approx. 1.2 ps$^{-1}$ (scheme 6). Because the time component related to this process does not become slower as the distance between two porphyrin units within a dimer changes, we can directly assign this annihilation component as the exciton hopping time among the four building blocks. In a similar manner, the time component of 0.7 ps of porphyrin boxes that are constructed by orthogonal conformers also can be related to the EET rate of approx. 1 ps$^{-1}$ among the four constituents. For these porphyrin boxes, additional slow time component of 10 ps was observed and this component gives rise to the EET rate of 12 ps$^{-1}$ by assuming $N = 4$ (scheme 6). On the basis of the analysis of the calculated Förster energy transfer rates, it is suggested that the dihedral angle of 90$^\circ$ causes additional EET processes among exciton states localized on porphyrin monomers within the orthogonal dimer.

5. Conclusions

The EET processes of various forms of porphyrin arrays have been explored for the purpose of applications in molecular photonics and electronics. It has been proved that the mechanisms and rates of EET processes are modulated by the electronic interactions of porphyrin arrays, which range from excitonic dipole–dipole interaction to extensive $\pi$-conjugation and a proper combination of these two as well. The fundamental information on the EET processes presented here will serve as a platform in designing novel porphyrin arrays with tuned electronic couplings to elicit desired photophysical properties.

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