

Supporting Information for

A Hexagonal Prismatic Porphyrin Array: Synthesis,
STM Detection, and Efficient Energy Hopping in Near
Infrared Region

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Exciton Coupling Energy

The exciton coupling energy $\Delta V_{\text{cal}}(\text{B})$ and $\Delta V_{\text{cal}}(\text{Q})$ can be calculated by analyzing the absorption maximum positions of constituent unit **3** and cyclic wheel **2**. According to the point dipole coupling approximation,¹⁵ the exciton coupling strength, V_{ij} , between the adjacent chromophores with the transition dipoles, $|\vec{\mu}_i|$ and $|\vec{\mu}_j|$ located at a through-space interchromophoric distance R_{TS} can be calculated as:

$$V_{ij} = \frac{5.04 f_{\text{L}}^2 |\vec{\mu}_i| |\vec{\mu}_j| \kappa}{\varepsilon_{\text{r}} R_{\text{TS}}^3} \quad (\text{S1})$$

where ε_{r} is the relative dielectric constant equal to the square-root of refractive index (n) of solvent medium, f_{L} is the Lorentz local field correction factor, $f_{\text{L}} = (\varepsilon_{\text{r}} + 2)/3$, and κ is the orientation factor of the two dipoles, $|\vec{\mu}_i|$ and $|\vec{\mu}_j|$ with the relative in-plane (θ) and out-of-plane (φ) angles to give the relationship of $\kappa^2 = (\cos\varphi - 3\cos\theta_1\cos\theta_2)^2$. In equation (S1), the coupling energy is expressed in cm^{-1} , the transition dipoles in debye and the distance in nm. The transition dipole moments of B- and Q-bands in **3** are calculated by using a relationship between absorption band intensities and oscillator strengths which gives relative transition dipole moments compared with Zn(II)porphyrin monomer.²⁵ The interchromophoric distances R_{TS} and the orientational factors κ can be estimated from the optimized geometry at semi-empirical PM3 level (Figure 4). The calculated exciton coupling strengths V_{ij} with all parameters are summarized in Table S1. With these exciton coupling strengths between two chromophores, a total exciton coupling energy can be obtained by matrix diagonalization which includes all possible interactions between all six transition dipoles for hexameric wheel system. For example, the coupling matrices V_{Q} for Q-bands in **2** are:

$$V_Q = \begin{bmatrix} 0 & V_{12} & V_{13} & V_{14} & V_{13} & V_{12} \\ V_{12} & 0 & V_{12} & V_{13} & V_{14} & V_{13} \\ V_{13} & V_{12} & 0 & V_{12} & V_{13} & V_{14} \\ V_{14} & V_{13} & V_{12} & 0 & V_{12} & V_{13} \\ V_{13} & V_{14} & V_{13} & V_{12} & 0 & V_{12} \\ V_{12} & V_{13} & V_{14} & V_{13} & V_{12} & 0 \end{bmatrix}, \quad V_Q = \begin{bmatrix} 0 & 139 & 35 & 5.6 & 35 & 139 \\ 139 & 0 & 139 & 35 & 5.6 & 35 \\ 35 & 139 & 0 & 139 & 35 & 5.6 \\ 5.6 & 35 & 139 & 0 & 139 & 35 \\ 35 & 5.6 & 35 & 139 & 0 & 139 \\ 139 & 35 & 5.6 & 35 & 139 & 0 \end{bmatrix}$$

Using diagonalization of these coupling matrices with coupling energies V_{ij} , the total exciton coupling energies $\Delta V_{\text{cal}}(\text{B})$ and $\Delta V_{\text{cal}}(\text{Q})$ for B- and Q-bands in **2** are calculated to be 795 and 99 cm^{-1} , respectively.^{2S,3S}

TABLE S1: Calculated Transition Dipole Moments, Exciton Coupling Strengths, Through-space Center-to-center Distances and Orientation Factors between Adjacent Porphyrin Pigments.

sample	transition dipole moment of subunit ^a (debye)	exciton coupling strength ^b (cm ⁻¹)			center-to-center distance ^c (Å)			orientation factor ^d		
		$\mu(\text{B}), \mu(\text{Q})$	$V_{12}(\text{B}), V_{12}(\text{Q})$	$V_{13}(\text{B}), V_{13}(\text{Q})$	$V_{14}(\text{B}), V_{14}(\text{Q})$	R_{12}	R_{13}	R_{14}	κ_{12}	κ_{13}
2	29.2, 10.3	1121, 139	281, 35	45, 5.6	18.5	26.2	44.7	1.75	1.25	1

^aTransition dipole moments of B and Q-states were calculated by integration of each absorption band in the absorption spectra of subunit **3**. Relative strength of transition dipole moments were determined by integration of absorption peak because the absorption cross section is proportional to the square of transition dipole moment. The transition dipole moments for Zn(II)porphyrin arrays were calculated by using the transition dipole moment of 9.5 debye for B-band of Zn(II)porphyrin monomer (see reference 2Sb)

^bExciton coupling strengths V_{ij} between two subunits **3** were calculated by using equation (S1).

^cCenter-to-center distances were obtained from optimized geometry at semi-empirical PM3 level. It was assumed that the center of subunit **3** corresponded to the central point of $C_{meso}-C_{meso}$ bond.

^dIn-plane and out-of-plane angles ($\varphi, \theta_1, \theta_2$) were used (60°, 30°, 30°), (120°, 60°, 60°), and (180°, 90°, 90°) to determine the orientation factors κ_{12} , κ_{13} and κ_{14} , respectively. In this paper, the positive values of orientation factors should be considered which leads to positive energies for stabilized excitonic states with respect to uncoupled states. See the reference 2Sa for more details.

Incoherent Energy Hopping Model

The excitation energy relaxation processes of **2** are illustrated in Scheme 1 assuming that EEH processes occur only between the adjacent porphyrin units **3**. When monomeric unit **3** is photoexcited, population of the excitation energy temporally evolves in each chromophore, which is given by the following rate equations:^{4S,5S}

$$\begin{aligned}
 \frac{d[\mathbf{3}(1)]}{dt} &= -(k_F + 2k_{\text{hop}})[\mathbf{3}(1)] + k_{\text{hop}}[\mathbf{3}(2)] + k_{\text{hop}}[\mathbf{3}(6)] \\
 \frac{d[\mathbf{3}(2)]}{dt} &= k_{\text{hop}}[\mathbf{3}(1)] - (k_F + 2k_{\text{hop}})[\mathbf{3}(2)] + k_{\text{hop}}[\mathbf{3}(3)] \\
 \frac{d[\mathbf{3}(3)]}{dt} &= k_{\text{hop}}[\mathbf{3}(2)] - (k_F + 2k_{\text{hop}})[\mathbf{3}(3)] + k_{\text{hop}}[\mathbf{3}(4)] \\
 \frac{d[\mathbf{3}(4)]}{dt} &= k_{\text{hop}}[\mathbf{3}(3)] - (k_F + 2k_{\text{hop}})[\mathbf{3}(4)] + k_{\text{hop}}[\mathbf{3}(5)] \\
 \frac{d[\mathbf{3}(5)]}{dt} &= k_{\text{hop}}[\mathbf{3}(4)] - (k_F + 2k_{\text{hop}})[\mathbf{3}(5)] + k_{\text{hop}}[\mathbf{3}(6)] \\
 \frac{d[\mathbf{3}(6)]}{dt} &= k_{\text{hop}}[\mathbf{3}(1)] + k_{\text{hop}}[\mathbf{3}(5)] - (k_F + 2k_{\text{hop}})[\mathbf{3}(6)]
 \end{aligned} \tag{S2}$$

These differential rate equations can be solved by using master equation:

$$\frac{d\mathbf{P}}{dt} = \mathbf{K}\mathbf{P} \tag{S3}$$

where **K** and **P** are defined as follows:

$$\mathbf{K} = \begin{bmatrix}
 -(k_F + 2k_{\text{hop}}) & k_{\text{hop}} & 0 & 0 & 0 & k_{\text{hop}} \\
 k_{\text{hop}} & -(k_F + 2k_{\text{hop}}) & k_{\text{hop}} & 0 & 0 & 0 \\
 0 & k_{\text{hop}} & -(k_F + 2k_{\text{hop}}) & k_{\text{hop}} & 0 & 0 \\
 0 & 0 & k_{\text{hop}} & -(k_F + 2k_{\text{hop}}) & k_{\text{hop}} & 0 \\
 0 & 0 & 0 & k_{\text{hop}} & -(k_F + 2k_{\text{hop}}) & k_{\text{hop}} \\
 k_{\text{hop}} & 0 & 0 & 0 & k_{\text{hop}} & -(k_F + 2k_{\text{hop}})
 \end{bmatrix}$$

$$\text{and } \mathbf{P} = \begin{bmatrix} \mathbf{3}(1) \\ \mathbf{3}(2) \\ \mathbf{3}(3) \\ \mathbf{3}(4) \\ \mathbf{3}(5) \\ \mathbf{3}(6) \end{bmatrix} \quad (\text{S4})$$

where k_F and k_{hop} represent the fluorescence decay rate of individual units **3** and EEH rate, respectively.

The solution for equation (S3) is as follows:

$$\mathbf{P} = e^{\mathbf{K}t} \mathbf{P}_0 \quad (\text{S5})$$

If the eigenvalues of 6×6 matrix \mathbf{K} are $\lambda_1, \lambda_2, \dots, \lambda_6$ and the set of corresponding eigenvectors is $\mathbf{P} = \{\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_3, \mathbf{v}_4, \mathbf{v}_5, \mathbf{v}_6\}$, equation (S5) can be modified to give following equation.

$$\mathbf{P}(t) = \mathbf{A} \mathbf{E}(t) \mathbf{A}^{-1} \mathbf{P}_0 \quad (\text{S6})$$

where $\mathbf{E}(t)$ is the diagonal matrix as follows:

$$\mathbf{E}(t) = \text{diag}[e^{\lambda_1 t}, \dots, e^{\lambda_6 t}] \quad (\text{S7})$$

Using matrix diagonalization, equation (S6) can be modified to give a series of equations as follows:

$$\begin{aligned} P_1(t) &= \frac{e^{-k_F t} P_1(0)}{6} [1 + 2e^{-k_{\text{hop}} t} + 2e^{-3k_{\text{hop}} t} + e^{-4k_{\text{hop}} t}] \\ P_{2,6}(t) &= \frac{e^{-k_F t} P_{2,6}(0)}{6} [1 + e^{-k_{\text{hop}} t} - e^{-3k_{\text{hop}} t} - e^{-4k_{\text{hop}} t}] \\ P_{3,5}(t) &= \frac{e^{-k_F t} P_{3,5}(0)}{6} [1 - e^{-k_{\text{hop}} t} - e^{-3k_{\text{hop}} t} + e^{-4k_{\text{hop}} t}] \\ P_4(t) &= \frac{e^{-k_F t} P_4(0)}{6} [1 - 2e^{-k_{\text{hop}} t} + 2e^{-3k_{\text{hop}} t} - e^{-4k_{\text{hop}} t}] \end{aligned} \quad (\text{S8})$$

where $P_i(t)$ is the excited-state population of the porphyrin unit i at time t .

The time dependence of the anisotropy is only contributed by excited state population except for fluorescence decay ($e^{-k_F t}$). Hence, time-dependent anisotropy decay can be written as follows.^{5S}

$$r(t) = \sum_{i=1}^6 r_i Q_i(t) \quad (\text{S9})$$

$$\begin{aligned} Q_1(t) &= \frac{Q_1(0)}{6} [1 + 2e^{-k_{\text{hop}}t} + 2e^{-3k_{\text{hop}}t} + e^{-4k_{\text{hop}}t}] \\ Q_{2,6}(t) &= \frac{Q_{2,6}(0)}{6} [1 + e^{-k_{\text{hop}}t} - e^{-3k_{\text{hop}}t} - e^{-4k_{\text{hop}}t}] \\ Q_{3,5}(t) &= \frac{Q_{3,5}(0)}{6} [1 - e^{-k_{\text{hop}}t} - e^{-3k_{\text{hop}}t} + e^{-4k_{\text{hop}}t}] \\ Q_4(t) &= \frac{Q_4(0)}{6} [1 - 2e^{-k_{\text{hop}}t} + 2e^{-3k_{\text{hop}}t} - e^{-4k_{\text{hop}}t}] \end{aligned} \quad (\text{S10})$$

where, r_i is the anisotropy value of the photoinduced absorption of Q_i after photoexcitation of Q_1 ($i=1$) which is the Q-band of triply linked Zn(II)porphyrin dimer **3**.

Because the characteristics of Q-bands of **3** are similar to that of **4**, the transition dipole moment seems to be oriented along the long molecular axis based on the fluorescence excitation anisotropy and theoretical calculation.^{6S} Accordingly, the transition dipole moment of Q-band was regarded as well-ordered linear dipole moment. The fundamental anisotropy for the chromophores with linear transition dipole moments is given by^{7S}

$$r_0 = \frac{2}{5} \left(\frac{3 \cos^2 \beta - 1}{2} \right) \quad (\text{S11})$$

where, β is an angular displacement between two transition dipole moments. According to equation (S11), r_0 should be 0.4, -0.05 and -0.05 if β are 0° , 60° , and 120° , respectively. For **2**, these values are $r_i = 0.4$ (this value corresponds to the experimental initial anisotropy value of monomeric subunit **3**) for $i = 1, 4$ and $r_i = -0.05$ for $i = 2, 3, 5, 6$ according to the relationship between the angular displacement of transition dipole moments β and the anisotropy values r_0 .

The solution of equation (S9) is then:

$$r(t) = 0.1 + 0.3 \exp(-3k_{\text{hop}}t) \quad (\text{S12})$$

According to equation (S12), the relationship between depolarization and EEH can be given as follows:

$$k_{\text{dep}} = 3 k_{\text{hop}} \quad \text{and} \quad 3 \tau_{\text{dep}} = \tau_{\text{hop}} \quad (\text{S13})$$

References for Supporting Information

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