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Excitonic coupling interactions in the self-assembly of perylene-bridged bis(β -cyclodextrin)s and porphyrin \ddagger

Ke-Rang Wang,^{ab} Dong-Sheng Guo,^a Bang-Ping Jiang^a and Yu Liu^{*a}

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A supramolecular self-assembly has been constructed by perylene-bridged bis(β -cyclodextrin)s with water-soluble porphyrin through hydrophobic interactions, showing strong excitonic coupling interactions between perylene backbones and included porphyrins.

Excitonic interactions between adjacent dye units are one of the key steps in the design of molecular photonic and electronic devices.¹ In Nature, two light-harvesting variants LH1 and LH2 in photosynthetic bacteria are complex assemblies of pigments and protein polymers, which allow for efficient light absorption and unidirectional transfer of energy to the reaction center during photosynthesis because of the excitonic interactions between the bacteriochlorophyll chromophores.² Inspired by these naturally occurring architectures, much attention is currently focused on designing excitonic interaction units, which further exhibit interesting optical and electronic properties.³ Among them, porphyrins have attracted special interest because of their similar structures and photophysical properties to the chlorophyll molecules.⁴

To date, the homo-excitonic interactions between porphyrins have been frequently studied,⁵ and also, there are considerable examples where porphyrins were conjugated to the electron acceptor molecules for evaluating the photoinduced electron transfer.⁶ However, the hetero-excitonic interactions between porphyrins and other chromophoric blocks have received much less attention. Recently, Morisue and Kobuke designed and constructed a discrete heterogeneous stack system of porphyrin and phthalocyanine, which showed unique exciton coupling and charge-transfer properties.⁷ Mathew and Johnston reported novel free-base porphyrin–perylene dyads, which exhibited a moderately excitonic coupling phenomenon in both the ground and excited states.⁸

Herein, we wish to report a novel supramolecular self-assembly constructed by permethyl- β -cyclodextrins (PMCD) modified perylene bisimides (**1**)⁹ and [5,10,15,20-tetrakis-(4-sulfonatophenyl)porphinato]zinc(II) (**2**) (Fig. 1) through

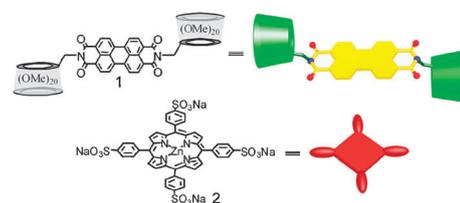


Fig. 1 The molecular structures and corresponding structural illustrations of **1** and **2**.

hydrophobic interactions. In this complex, perylene bisimides acts not only as the bridging spacer, but also as the functional group owing to its excellent optoelectronic properties.¹⁰ Significantly, strong excitonic interactions between perylene backbones and adjacent porphyrins were found in the ground state.

The spectrum of **1** exists in the typical non-aggregated state with the electronic states S_{0-0} , S_{0-1} and S_{0-2} at 526 nm, 490 nm and 458 nm, respectively.¹¹ The absorption spectrum of **2** possesses a metalloporphyrin-derived Soret band at 421 nm, Q-bands at 555 nm and 595 nm. Comparing the typical absorption bands of **1** and **2**, it is obviously seen that there is no obvious overlap with each other (Fig. S1, ESI \ddagger).

The host–guest complexation between **1** and **2** was examined by UV-Vis spectroscopy titrations. The absorption bands of **1** experience obvious changes upon gradual addition of **2** (Fig. S2, ESI \ddagger). The absorption intensity of 0–0 (526 nm) electronic transition decreases, whereas those of 0–1 (490 nm) and 0–2 (458 nm) electronic transitions increase. The 0–1 electronic transition shifts bathochromically from 490 to 503 nm, along with the absorbance enhanced 1.6 times, which indicates that there are significant electronic interactions between host and guest molecules. It is also observed that a new absorption band gradually increases at 553 nm, which is due to the sum of the Q-band of **2** and the excitonic band between perylene and porphyrin.

In order to extract more useful information from the present results rather than complex spectroscopic changes, the following mathematical treatment of the spectra [eqn (1)] was carried out for the observed spectra.

$$\Delta\text{Abs}(\lambda) = \text{Abs}(\lambda)[\mathbf{1}]_{\text{obs}} - \text{Abs}(\lambda)[\mathbf{2} + \text{PMCD}]_{\text{obs}} \quad (1)$$

where $\Delta\text{Abs}(\lambda)$ is the resultant difference absorption; $\text{Abs}(\lambda)[\mathbf{1}]_{\text{obs}}$ is the absorption values for each of a series of solutions of **1** with varying concentrations of **2**; and $\text{Abs}(\lambda)[\mathbf{2} + \text{PMCD}]_{\text{obs}}$ is the

^a Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. China.

E-mail: yuliu@nankai.edu.cn; Fax: +86 22-2350-3625;

Tel: +86 22-2350-3625

^b College of Chemistry and Environmental Science, Hebei University, Baoding 071002, P. R. China

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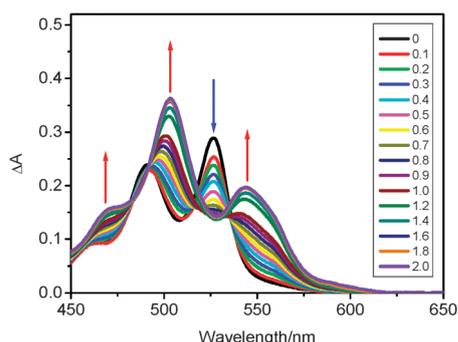


Fig. 2 The resultant UV–Vis spectrum of **1** (5.0×10^{-6} M) upon addition of **2** (0–2 equiv.) in phosphate buffer (pH 7.0, 0.05 M) at 25 °C calculated according to eqn (1).

absorbance values of varying concentrations of **2** with 2 equiv. PMCD. It is well known that the absorption spectra of metalloporphyrins suffer obvious changes when encapsulated by PMCD.¹² As shown in Fig. 2, the resultant difference spectra ($\Delta\text{Abs}(\lambda)$) show very interesting characteristics that the spectra hold a clear new absorption band at 544 nm. This characteristic feature is indicative of strong excitonic interactions between perylene backbones and porphyrins in the ground state.^{8,13} The complex structures were determined by 2D NOESY spectroscopy (Fig. S3, ESI†). Obvious cross-peaks with the protons of the PMCD and the protons of $\delta = 7.7$ ppm (assigned to the porphyrin protons) were observed. It indicates that **2** is deeply included into the cavities of **1**. The intuitionistic insight into the excitonic interactions can be clearly observed from the photographs in Fig. 3a. Under the daylight, **1** is yellow in color, **2** and the complex of **2** with PMCD are colorless at the concentration of 1.0×10^{-5} M. Remarkably, the complex of **1** and **2** exhibits red color, indicating that the absorption band was a bathochromic shift because of the π -orbital overlap and significant excitonic interactions between hosts and guests.

Evidence of the strong level of excitonic interactions was further investigated by circular dichroism spectroscopy. As shown in Fig. 4, **1** exhibits a positive induced Cotton effect, which indicates that the $\pi \rightarrow \pi^*$ transition of perylene bisimides is perpendicular to the axis of the PMCD cavity.¹⁴ **2** and the complex of **2** with PMCD have no induced circular dichroism signal at the Q-band of porphyrin, which is indicative of no electronic perturbation in the region of Q-band. Interestingly, strong induced bisignate Cotton effects were observed in the assembly of **1** and **2**, possessing

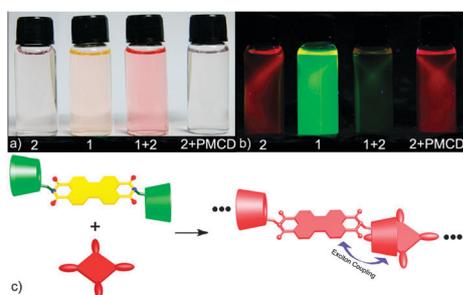


Fig. 3 The photographs of **2**, **1**, **1** with 1 equiv. **2** and **2** with 2 equiv. PMCD (1.0×10^{-5} M) under the daylight (a), and under UV-light irradiation at 365 nm (b). The diagrammatic representation of the excitonic coupling units of **1** with **2** (c).

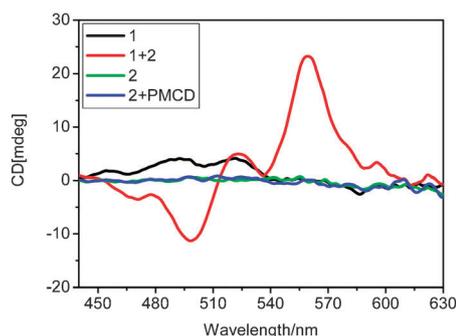


Fig. 4 Circular dichroism spectra of **1** (black, 1.0×10^{-5} M), **1** (red, 1.0×10^{-5} M) with 1 equiv. **2**, **2** (green, 1.0×10^{-5} M), and **2** (blue, 1.0×10^{-5} M) with 2 equiv. PMCD in phosphate buffer (pH 7.0, 0.05 M).

a positive maximum at 559 nm and a negative maximum at 498 nm. Two positive Cotton effects are assigned to the S_{0-0} transition and the new excitonic interactions absorption band combining the Q-band of guest **2**, and two negative Cotton effects to the S_{0-1} and S_{0-2} transitions. These spectral characteristics also prove strong excitonic interactions between the perylene bisimides and porphyrins.¹⁵

Upon addition of **2**, the emission spectrum of **1** was gradually quenched because of photoinduced electron transfer from porphyrin to excited perylene bisimides, 95% quenched with addition of 2 equiv. **2** (Fig. 5). The intuitionistic insight into the fluorescence quenching is shown in Fig. 3b. The fluorescence of the assembly of **1** with **2** was completely quenched under the UV-light irradiation at 365 nm. The binding stoichiometry of **1** with **2** was determined as 1:1 by a Job's plot method (Fig. S4, ESI†). Two possible morphologies of the 2:2 molecular wedge or $n:n$ aggregation can be postulated. The size distribution of the complexes of **1** and **2** was determined by dynamic light scattering (DLS) at the concentration of 5.0×10^{-6} M (Fig. S5, ESI†). The mean diameter is about 100 nm, which indicated that the $n:n$ aggregation formed. The complexation stability constant can be calculated as $1.3 \times 10^7 \text{ M}^{-1}$ using the nonlinear least-squares curve-fitting method¹⁶ by fitting the emission spectral changes at 535 nm of **1** upon gradual addition of **2** (Fig. 5 inset).

The host–guest complexation between **1** and **2** was also examined at the Soret band of **2**. Upon gradual addition of **1**, the intensity of the Soret band at 421 nm for **2** decreases

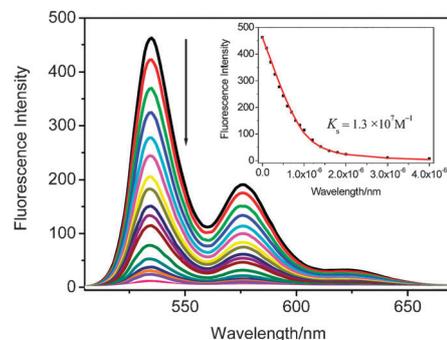


Fig. 5 Fluorescence spectral changes of **1** ($\lambda_{\text{ex}} = 490$ nm, 1.0×10^{-6} M) with addition of **2** (0–4 equiv.) in phosphate buffer (pH = 7.0, 0.05 M) at 25 °C. Inset: the curve of the complexation stability constants fitting at 535 nm.

gradually, and a new absorption band appears at 424 nm with an isosbestic point at 421 nm (Fig. S6a, ESI†). The appreciable bathochromic shift of the Soret band reflects the electronic perturbations arising from solvent effects and from changes in the solvent–solute dipole interactions caused by reduced exposure of the solute to water.¹⁷ The complexation stability constant was obtained as $2.2 \times 10^7 \text{ M}^{-1}$ by fitting the experimental data of the Soret band changes (Fig. S6b, ESI†),¹⁶ which is in the same magnitude of the result obtained by the emission spectral changes at 535 nm.

The fluorescence spectrum of **2** is obviously quenched upon gradual addition of **1**, 86% quenched with 2 equiv. **1** (Fig. S7, ESI†). The fluorescence quenching of porphyrin is because of the photoinduced electron transfer from the electron donor (excited porphyrin) to the acceptor molecule (perylene).¹⁸ The fluorescence spectra at 534 nm and 575 nm are attributed to the emission of **1** with increasing the concentration. The photographs are shown in Fig. 3b.

In addition, circular dichroism spectra studies were performed to further clarify the nature of the excitonic interactions in the Soret band. At the region of 400 nm to 450 nm (Fig. S8, ESI†), **1** has no circular dichroism signal, **2** exhibits a very weak positive Cotton effect,¹⁹ and an induced opposite Cotton effect is observed in the complex of **2** with 2 equiv. PMCD because of the inclusion complexation. It should be noted that a strong induced circular dichroism signal was observed, showing a split Cotton effect centered at 426 nm, with a positive maximum at 421 nm and a negative maximum at 429 nm (Fig. S8, ESI†). The excitonic coupling can be explained that the Soret transition of porphyrin included into the cyclodextrin cavity, and which is electronically perturbed by the perylene backbones in the neighbourhood.²⁰ All the UV-vis, fluorescence and circular dichroism spectra reveal strong excitonic interactions between perylene bisimides and porphyrin in the ground state, but no obvious excitonic interactions in the excited state because of robust photoinduced electron transfer between porphyrin and perylene bisimides. The diagrammatic representation of the excitonic interactions is shown in Fig. 3c.

In conclusion, a supramolecular self-assembly has been constructed by perylene-bridged bis(β -cyclodextrin)s with water-soluble porphyrin through hydrophobic interactions. The photophysical properties of the subunit indicate the presence of strong excitonic interactions between perylene backbones and adjacent porphyrins in the ground state, which have potential applications in fabrication of photovoltaic cells, electrical data storage and optical sensors.

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