

## Fluorescence Switch Based on a Porphyrin-perylene Dyad

Xin Guo YANG<sup>1,2</sup>, Jing Zhi SUN<sup>1\*</sup>, Han Ying LI<sup>1</sup>, Jian CAO<sup>1</sup>, Mang WANG<sup>1</sup>

<sup>1</sup>Department of Polymer Science & Engineering and State Key Laboratory for Silicon Materials,  
Zhejiang University, Hangzhou 310027

<sup>2</sup>College of Materials Science and Engineering, Hunan University, Changsha 410082

**Abstract:** Upon excitation of porphyrin or perylene subunit, the porphyrin-perylene dyad exhibits reversible fluorescence emitting and quenching by formation and neutralization of the protonated porphyrin subunit, thereby providing a prototype of molecular fluorescence switch working in an expanded spectral range.

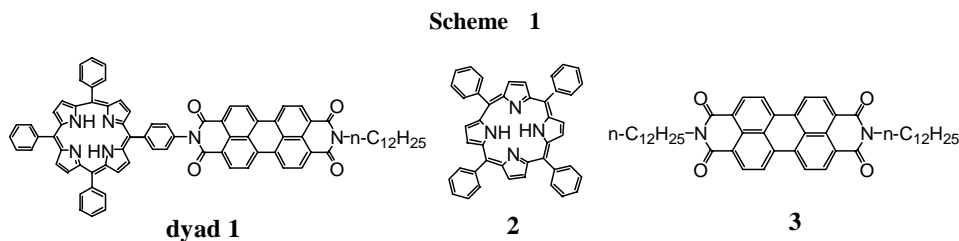
**Keywords:** Molecular arrays, fluorescence switch, protonation.

Porphyrin-perylene molecular arrays have been reported to be promising in the realm of molecular-scale opto-electronics such as molecular wires, gates and switches<sup>1-4</sup>. Photo-excitation of the porphyrin or perylene subunit leads to rapid energy and/or electron transfer processes within the molecular array. Although these processes can be tuned by metalation of porphyrin<sup>5-7</sup>, the ability to turn the photoinduced energy and/or charge transfer on/off in a simple and easily controlled manner would make these molecular arrays even more interesting and potentially useful. Here we report that a free-base-porphyrin-perylene-diimide dyad **1** (**Scheme 1**) was designed to act as a switching component, which displays reversible fluorescence emitting and quenching by protonation and neutralization of the free base porphyrin subunit in the dyad. The synthesis of the dyad **1** will be published elsewhere<sup>8</sup>.

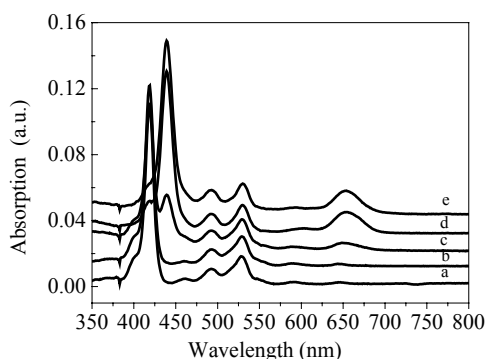
In dilute CHCl<sub>3</sub> solution, the absorption spectrum of **1** featured the Soret band at 419 nm and part of the Q-bands in the 500-650 nm region of free base porphyrin unit as well as the progression of (0, 0), (0, 1), (0, 2), (0, 3) bands of perylene unit (**Figure 1**). When the concentration of CF<sub>3</sub>COOH approached to about 3.26×10<sup>-5</sup> mol/L, the Soret band of the free base porphyrin split into a double-peaked band with a new absorption at 439 nm, which can be assigned to the Soret band of protonated porphyrin subunit<sup>9-11</sup>. With an increasing concentration of CF<sub>3</sub>COOH, the Soret band at 419 nm was gradually declined and replaced by the new absorption at 439 nm. Simultaneously, a new feature developed at 654 nm, which can be assigned to the Q-band of protonated porphyrin subunit<sup>9</sup>. In contrast, the absorption of perylene unit was insensitive to the addition of CF<sub>3</sub>COOH.

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\* E-mail: mawang@ipsm.zju.edu.cn



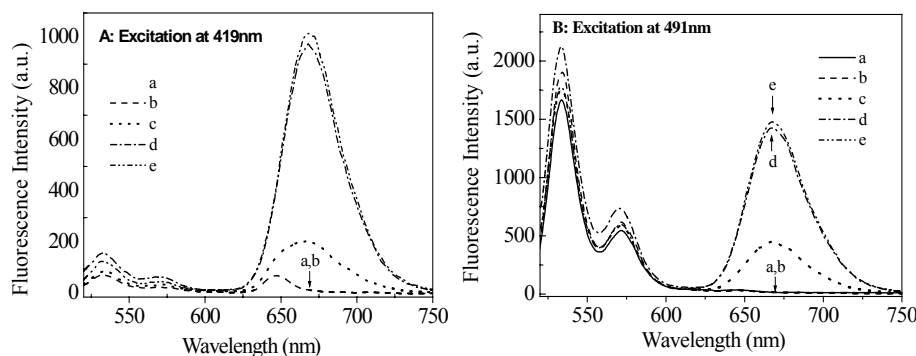
**Figure 1** Absorption spectra of  $1.35 \times 10^{-7}$  mol/L dyad **1** in  $\text{CHCl}_3/\text{CF}_3\text{COOH}$  solution



The lines a-e correspond to the concentrations of  $\text{CF}_3\text{COOH}$  0,  $3.26 \times 10^{-6}$ ,  $3.26 \times 10^{-5}$ ,  $3.26 \times 10^{-4}$ ,  $3.26 \times 10^{-3}$  mol/L, respectively

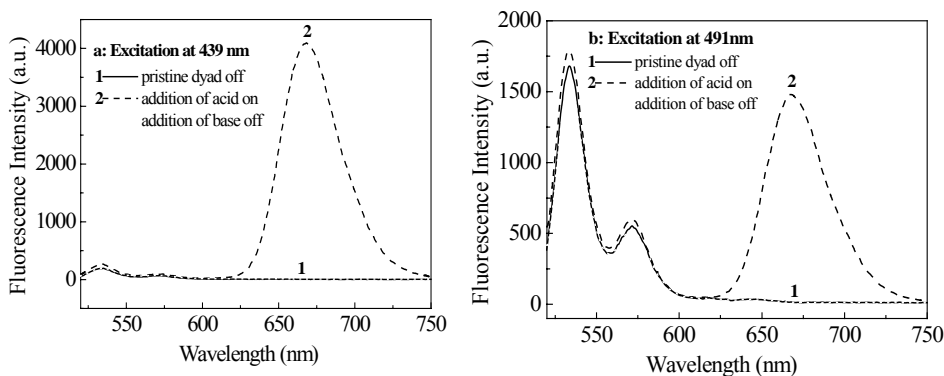
The photoluminescence spectra of dyad **1** in  $\text{CHCl}_3$  and  $\text{CF}_3\text{COOH} / \text{CHCl}_3$  was monitored using excitation at several wavelengths, where either the porphyrin or perylene subunits primarily absorbs. When **1** was excited at 419 nm where the porphyrin absorption was more than 100-fold of the perylene subunit in  $\text{CHCl}_3$ , the fluorescence is dominated by the porphyrin subunit (**Figure 2A**). However, the quantum efficiency of **1** was reduced considerably comparing with the reference compound **2**. Comparison the optically matched solution of dyad **1** with the reference compound **2** in  $\text{CHCl}_3$ , showed that the free base porphyrin emission is diminished by 89-fold and the  $\Phi_f$  changes from  $\sim 0.11$  to 0.0012. It is most likely that the excited states of the free base porphyrin are quenched in dyad **1** relative to the reference compound **2**, which is the result of electron transfer to perylene unit to form the charge-separated states. Within the concentration of  $\text{CF}_3\text{COOH}$  range from 0 to  $2.36 \times 10^{-3}$  mol/L, the emission centered at 668 nm and the intensity increased dramatically; when the concentration of  $\text{CF}_3\text{COOH}$  reached  $3.26 \times 10^{-3}$  mol/L, the fluorescence of protonated porphyrin subunit in **1** approached to saturation and its quantum efficiency was 101-fold of the dyad **1** in  $\text{CHCl}_3$ . Upon illumination at 439 nm, the changes of the derived emission features were similar to those derived from illumination at 419 nm. The phenomena of dramatic increase of the fluorescence yield is explained as follows: in absence of  $\text{CF}_3\text{COOH}$  the predominate decay channel for excited free base porphyrin unit is the electron transfer process from excited free base porphyrin unit to perylene, while the above process was effectively inhibited due to the increase of oxidation potentials by protonation of free base porphyrin subunit after  $\text{CF}_3\text{COOH}$  was introduced.

**Figure 2** Fluorescence spectra for  $1.35 \times 10^{-7}$  mol/L dyad **1** in  $\text{CF}_3\text{COOH}/\text{CHCl}_3$  solutions upon excitation at 419 nm(**A**) and 491 nm(**B**)



The lines a, b, c, d, e correspond to the concentrations of  $\text{CF}_3\text{COOH}$  0,  $3.26 \times 10^{-6}$ ,  $3.26 \times 10^{-5}$ ,  $3.26 \times 10^{-4}$ ,  $3.26 \times 10^{-3}$  mol/L, respectively

**Figure 3** Representative acid-base controlled fluorescent switch based on molecular array ( $3.3 \times 10^{-7}$  mol/L) in  $\text{CHCl}_3$  solution



At 491 nm, where the perylene diimide absorption is over 100-fold than that of free base porphyrin, the emission spectrum is dominated by fluorescence of perylene and only weak porphyrin's fluorescence is observed (**Figure 2B**). A quantitative comparison of optically matched solutions of molecule **3** with dyad **1** (at 491 nm) indicated that the perylene unit emission diminished by about 1742-fold in dyad **1**. We associated these results with the primary charge (hole) transfer from perylene to porphyrin subunit. As  $\text{CF}_3\text{COOH}$  was added into the solution of **1**, the changes of the emission from porphyrin subunit is similar to the above results and the  $\Phi_f$  of **1** in  $3.26 \times 10^{-3}$  mol/L  $\text{CF}_3\text{COOH}$  is > 100-fold bigger than that without  $\text{CF}_3\text{COOH}$ . The electrochemistry measurements and spectroscopic data suggested that the hole transfer processes, which occurred from.

Upon excitation at 439 nm (**a**) and 491 nm (**b**), the fluorescence of porphyrin subunit is switched off/on before/after addition of  $3.26 \times 10^{-3}$  mol/L  $\text{CF}_3\text{COOH}$  and off again by neutralization with triethylamine excited perylene unit to free base porphyrin (a predominate decay channel in absence of  $\text{CF}_3\text{COOH}$ ), were not affected by the

protonation of porphyrin subunit. However, a very small fraction of excited states of perylene, decayed by energy transfer to porphyrins unit, leads to form excited states of the free base porphyrin. The emission of the latter was varied greatly with the concentration of CF<sub>3</sub>COOH. The fluorescence of porphyrin subunit increased with the increase of the concentration of CF<sub>3</sub>COOH, even when the primary photo-excitation was on the perylene subunit.

Addition of base to the CF<sub>3</sub>COOH/CHCl<sub>3</sub> solution of **1** resulted in fluorescence quenching due to the deprotonation of porphyrin subunit. As shown in **Figure 3a** and **3b**, when stoichiometric amount of triethylamine was added into the mentioned solution, the pristine strong emission centered at 668 nm vanished whether the solution was illuminated at 419 or 491 nm. These results demonstrated the reversibility of the fluorescence quenching and recovery processes. It lays the working principle for a molecular switch with regard to the protonated and neutralized forms as “on” and “off”. In view of the fact that perylene unit absorbs strongly in the trough between porphyrin’s Soret and Q-bands, a molecular switch based on the dyad **1** can work in an expanded spectral range.

In summary, we have demonstrated a reversible and spectral-range-expanded fluorescence switching process upon the porphyrin-perylene dyad, which works as a fluorescence switch simply controlled by acids and bases. This process is promising to be applied to recognize and detect organic acids/bases, available in environment and biochemistry.

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