

## Supplementary Information

# Unconventional Hydrogen-Bond-Directed Hierarchical Co-Assembly between Perylene Bisimide and Azobenzene-Functionalized Melamine

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## Experimental Section

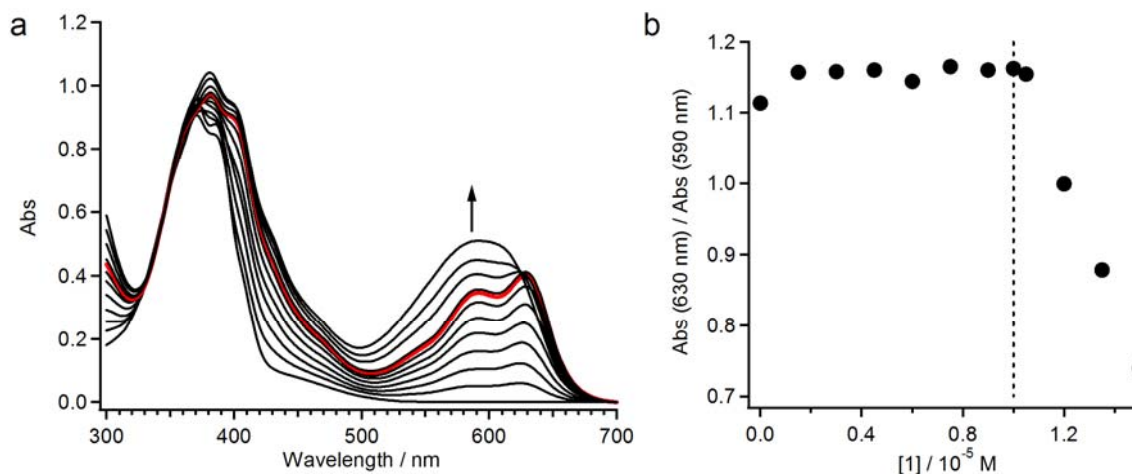
**Materials and methods:** Perylene Bisimide **1**<sup>[5d]</sup> and azobenzene-functionalized melamine **2**<sup>[10a]</sup> were prepared in the previously reported procedures. The solvents for the spectroscopic measurements were all spectral grade and used without further purification. UV/Vis spectra were recorded on a JASCO V660 spectrophotometer with Peltier device temperature-control unit. Molecular modeling calculations were performed on MacroModel version 9.0 (MMFF force field). The solutions of thermodynamically stable assemblies for the UV/Vis titration, DLS (1:2 assemblies) and AFM (1:2 assemblies) studies were prepared as follows. Stock solutions of **1** and **2** (dichloromethane) with appropriate concentrations were mixed in a cuvette with an appropriate ratio and the solvent was vaporized by N<sub>2</sub> flow, and then dried in vacuo. The resulting solid was dissolved in a small amount of methylcyclohexane (MCH) by gentle heating and again dried according to the above method. This procedure was repeated three times in order to remove tiny amount of dichloromethane. Finally, the resulting solid was dissolved in an appropriate amount of MCH, and then heated at to 90 °C for 30 min, giving sample solutions containing thermodynamically stable assemblies. The samples for time-dependent UV/Vis studies and DLS (1:1 assemblies) and AFM (1:1 assemblies) were prepared as follows. Stock solutions of **1** and **2** (dichloromethane) with appropriate concentrations were mixed in a cuvette with a 1:1 molar ratio and the solvent was vaporized by N<sub>2</sub> flow, and then dried in vacuo. The resulting solids were dissolved in a small amount of methylcyclohexane (MCH) without any heating, and the solvent was vaporized by N<sub>2</sub> flow, and then dried in vacuo. This procedure was repeated three times in order to remove tiny amount of dichloromethane. The resulting solids were dissolved in an appropriate amount of MCH and the UV/Vis spectrum was recorded in order to confirm the formation of 1:1 assemblies (blue spectrum in Fig. 2a). This solution was subjected to DLS and AFM measurements.

For time-dependent UV/Vis studies, MCH solution of melamine **2** with an appropriate concentration was prepared. This solution was mixed with the above MCH solution of 1:1 assemblies and time-dependent UV/Vis absorption spectra were recorded at 20 °C.

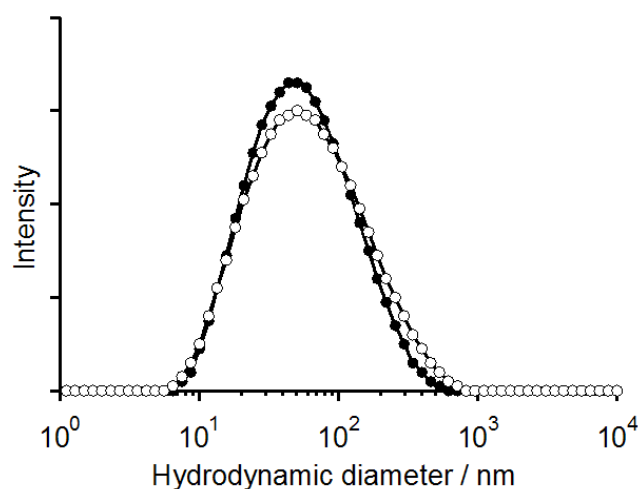
**Dynamic light scattering:** The hot sample solutions were filtered with Millipore membrane filter (pore size = 0.45  $\mu\text{m}$ ) before measurements to remove dust. The filtrates in 1×1 cm quartz cuvettes were analyzed by a Zetasizer Nano (Malvern Instrument) at 20 °C.

**Atomic force microscopy:** AFM measurements were performed under ambient conditions using a Veeco Multimode Nanoscope IV system operating in tapping mode in air. Silicon cantilevers (OMCL-AC160TS) with a resonance frequency of ~300 kHz were used. The sample solutions were spin-coated (8000 rpm) onto highly ordered pyrolytic graphite (HOPG).

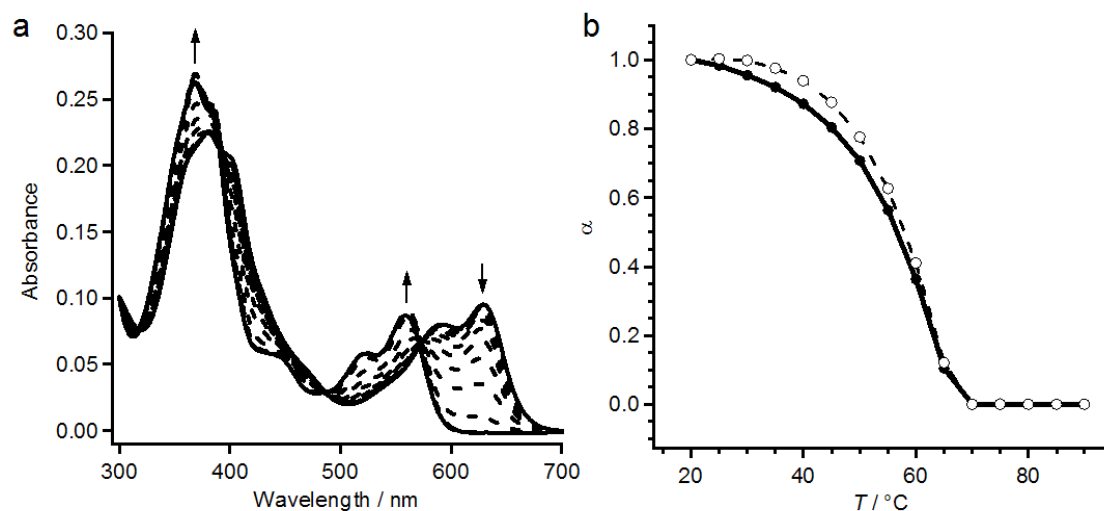
## Supporting figures



**Figure S1.** (a) UV/vis spectra of MCH solutions containing a constant amount of **2** ( $c = 1.5 \times 10^{-5}$  M) and various amounts of **1** (0 to  $1.5 \times 10^{-5}$  M). Each solution was obtained by mixing the two components directly in MCH and the spectra were taken after annealing at 90 °C to obtain thermodynamically stable state. Arrows indicate the increase of **1**. Red spectrum is the spectrum at  $[2]/[1] = 1.5$ . When the concentration of **1** is less than  $1.0 \times 10^{-5}$  M, the addition of **1** resulted in a monotonous increase of the J-aggregated band. Above this concentration, the addition of **1** resulted in an increase of absorption around 590 nm, leading to a structureless absorption band. These results demonstrated that J-type stacking of **1** is 1:1.5. (b) Plot of the ratio of absorbance at 630 and 590 nm versus concentrations of **1**. Dotted line shows the ratio  $[2]/[1] = 1.5$ .



**Figure S2.** Dynamic light scattering of 1:1.5 coassemblies of **1** and **2** in MCH (●,  $[1] = 1.0 \times 10^{-5}$  M; ○,  $[1] = 5.0 \times 10^{-5}$  M) at 20 °C.



**Figure S3.** (a) Temperature-dependent UV/vis spectra of the thermodynamically equilibrated 1:1.5 mixture of **1** and **2** in MCH ( $a$ ,  $[1] = 2.5 \times 10^{-6}$  M). Temperature range: 20–90 °C. Arrows indicate the increase in temperature. (b) Plots of the molar fraction of aggregated chromophores ( $\alpha$ ) versus temperature.  $\alpha$  was calculated from the value of absorbance at 630 nm (● for **1**) and 368 nm (○ for **2**), using equation  $\alpha = (A - A_{90\text{ °C}})/(A_{20\text{ °C}} - A_{90\text{ °C}})$ . Transition temperature ( $\alpha = 50\%$ ) is 56 °C.