Supporting Information

The Leverage Effect of the Relative Strength of Molecular Solvophobicity *vs* Solvophilicity on Fine-Tuning Nano-Morphologies of Perylene Diimide Bola-Amphiphiles

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1. Instruments and methods

The UV-visible absorption spectra were measured with a Shimadzu UV-1601PC double-beam spectrophotometer. All spectroscopic measurements were carried out at room temperature. Fluorescence spectra were measured using F-4500 (Hitachi). For the measurements of absorption spectra, we used an ultrathin quartz cell with a typical optical length of 0.2 mm. And the fluorescence spectra were measured using a normal quartz cell with an optical length of 1 cm and a reflection measurement along the 45° direction relative to the excitation light direction was used to eliminate re-absorbing phenomena from high concentrations. The SEM pictures were recorded with a field emission scanning electron microscope (FESEM, Hitachi S-4800), operating at an accelerating voltage of 1.5 kV. The TEM measurements were performed on a Tecnai G2 20 S-TWIN electron microscope, operating at an accelerating voltage of 200 kV. The WXRD measurements were performed by using a X-ray powder diffraction (XRD, BRUKER D8 Focus) with Cu Kα as the radiation source (λ = 1.5418 Å) and operated at 40 kV and 40 mA.

2. Samples preparation

Firstly, a DCM solution with [PDI]=1×10^{-2} M were prepared. Then, it was diluted into a mixture of DCM and EtOH or DCM and MCH by 10 times to form a dilute solution with a final concentration of PDI of 1×10^{-3} M, in which the final R_{EtOH} or R_{MCH} was controlled as 0%, 10%, 20%, 30%, 40%, and 50%, 60%, 70%, 80% and 90%, respectively.

3. Quantum chemical calculations

Computational details are presented as follows:

Density functional theory (DFT) calculations were performed using the Gaussian 03 program[1] with the B3LYP exchange-correlation function.[2] All-electron triple-ξ valence basis sets with polarization functions (6-311G**)[3] are used for all atoms. Geometry optimizations were performed with full relaxation of all atoms. Calculations were performed in gas phase without solvent effects, and the protonation of bay-pyridyloxyl is simulated by adding one proton to each nitrogen atom in the pyridinium moieties. Vibrational frequency calculations were performed to check that the stable structures had no imaginary frequency. Structures with C_i symmetry were found to have small imaginary frequency (less than 10 cm^{-1}) both before and after protonation, so structures with slightly distorted C_i symmetry are used in our calculations. The dihedral angle between the two naphthalene moieties is about 14° and change slightly after protonation, while that between the pyridinium and naphthalene moieties is about 70° and is decreased to about 60° after protonation.

4. Concentration-variable absorption spectra of molecule 2 (a) and 3 (b) in DCM.
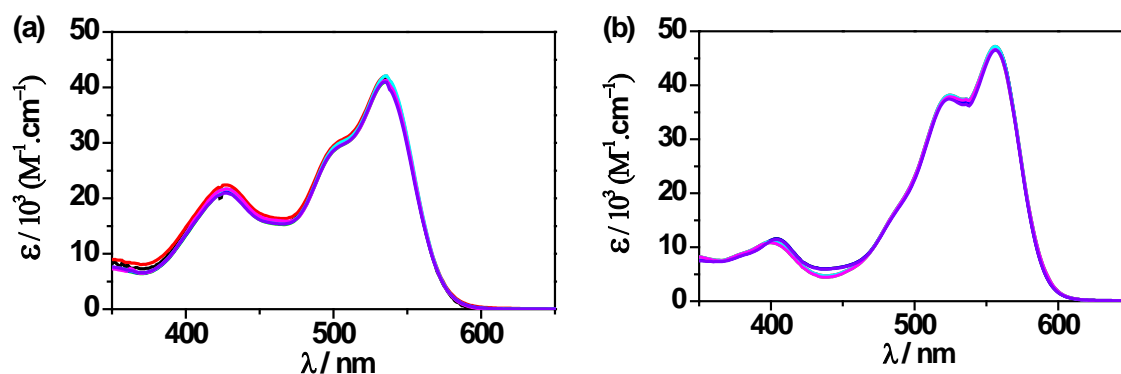
From these absrption spectra with the concentration increasing from 1×10^{-6} M to 1×10^{-3} M, one can see that there are no obvious aggregation appeared in DCM for these two molecules.

References

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