Role of Sterically Bulky Azobenzenes in the Molecular Assembly of Pyrene Derivatives: Rectangular Sheet-like Structures and Their Emission Characteristics

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Contents

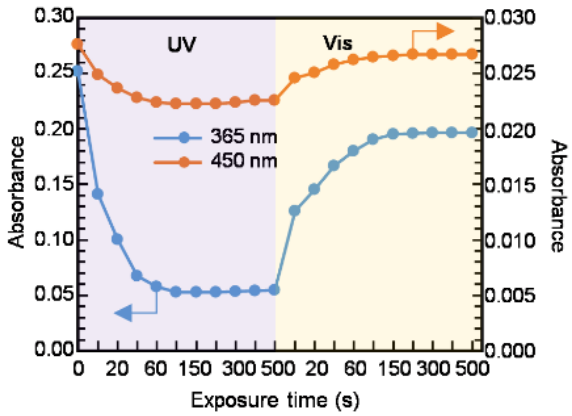

Figure S1. Changes in absorbances at 365 and 450 nm upon alternating irradiation with UV and blue light.

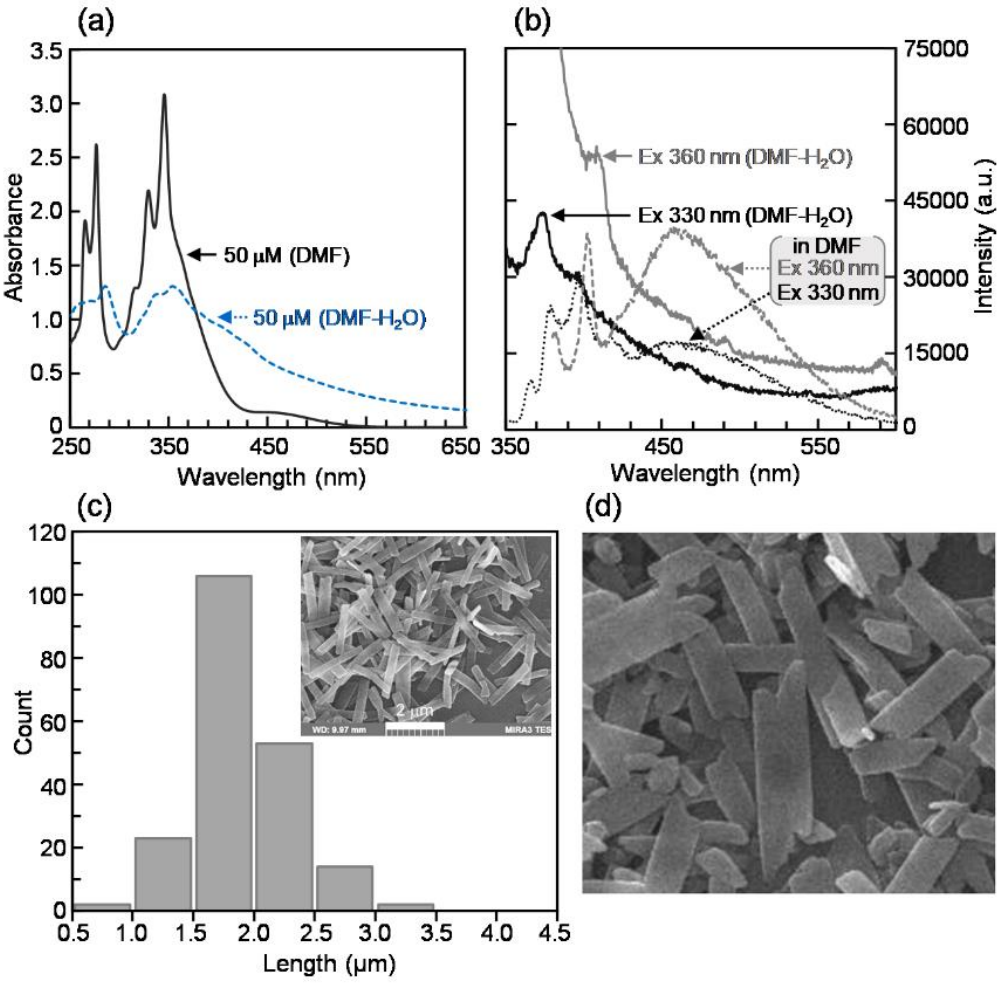

Figure S2. (a) Absorption spectra of **AzPy** in 50 μM DMF and DMF-H_2O (1/1, v/v). (b) Fluorescence spectra in 20 μM DMF and DMF-H_2O (1/3, v/v). (c) Plot of the length distribution of sheet-like structures obtained from 50 μM DMF-H_2O mixed turbid solution (counting 200 aggregates). (d) SEM image of incomplete thin structures. These aggregates seem to be formed in the early stage of self-assembly.

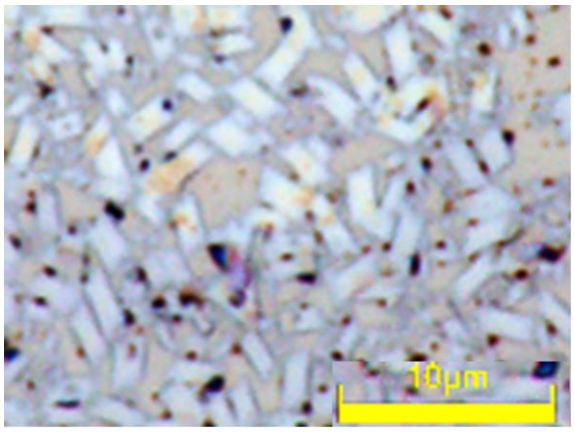

Figure S3. OM image of incomplete rectangular structures obtained from a 20 μM DMF-H_2O mixed suspension.

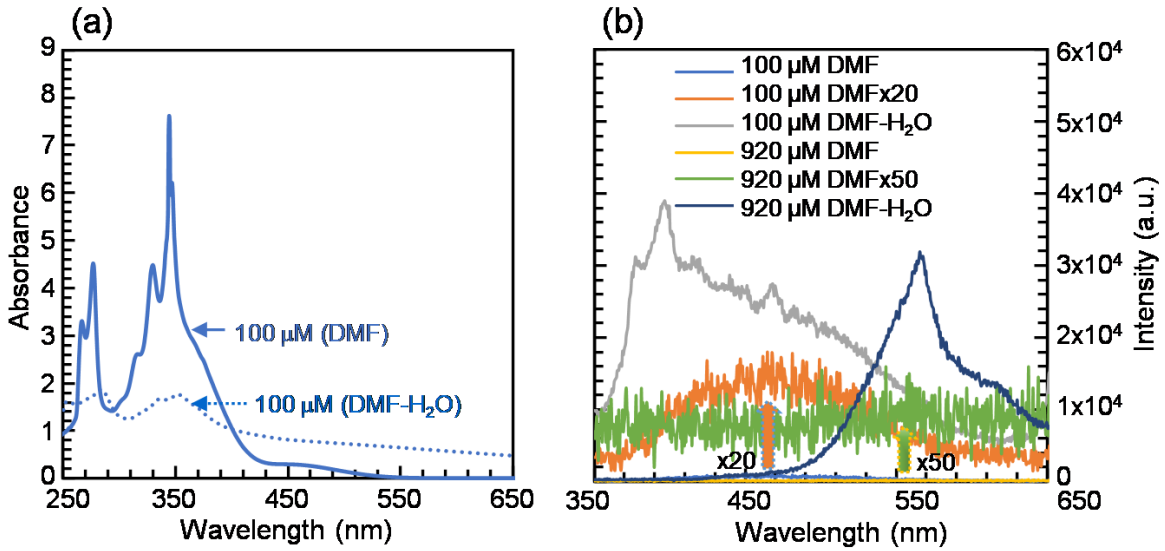

Figure S4. (a) Absorption spectra of **AzPy** in 100 μM DMF and DMF-H_2O (1/1, v/v). (b) Fluorescence spectra of 100 and 920 μM (in DMF and DMF-H_2O).

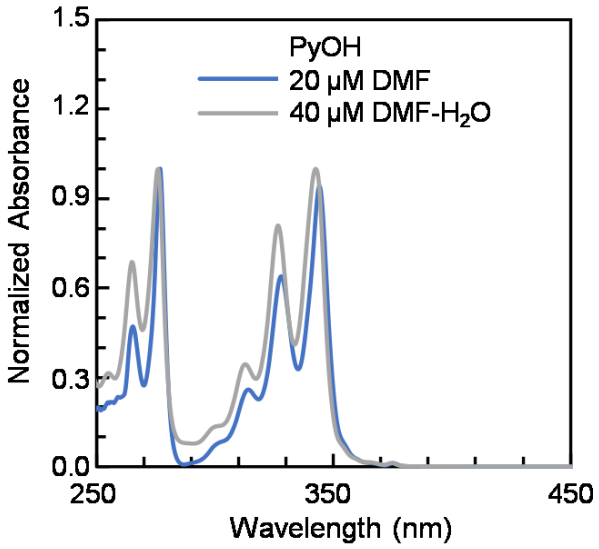

Figure S5. Absorption spectra of **PyOH** in DMF (20 μM) and DMF-H_2O (1/4, v/v, 40 μM).

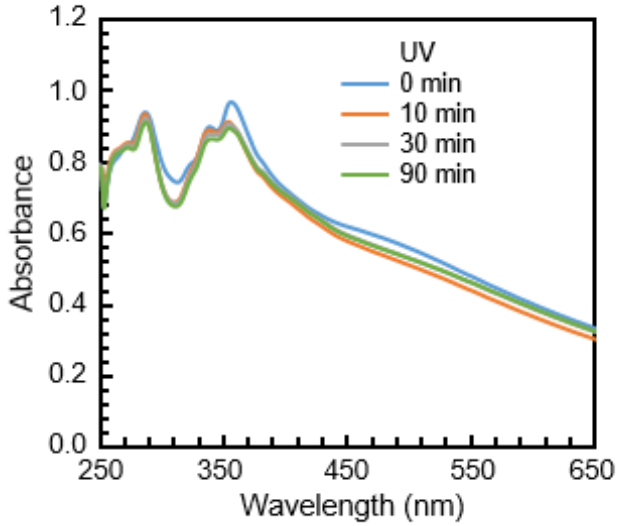

Figure S6. Absorption spectral changes of **AzPy** in DMF-H_2O (1/1, v/v, 50 μM) as a function of exposure time of UV light.

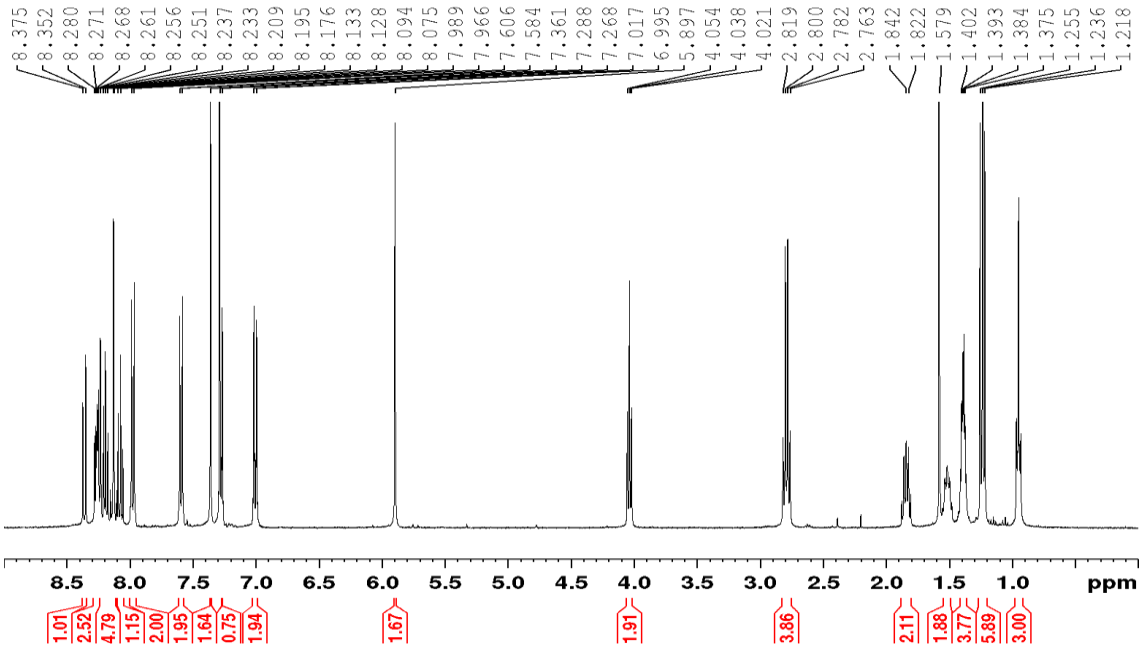

Figure S7. ^{1}H NMR spectrum of **AzPy** (in $CDCl_3$).

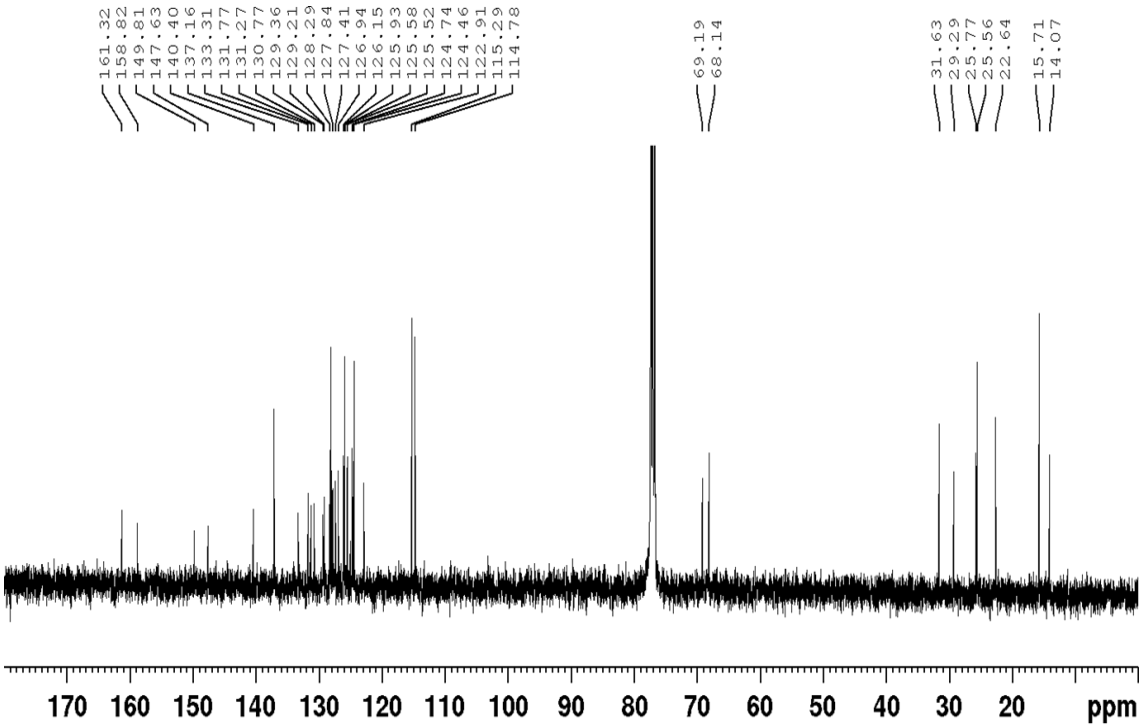

Figure S8. ^{13}C NMR spectrum of **AzPy** (in $CDCl_3$).

Synthesis of 1-Bromomethylpyrene **(PyBr)** [1]

Phosphorus tribromide (0.87 g, 3.23 mmol) was added to a suspension of commercial 1-pyrenemethanol (0.50 g, 2.15 mmol) in 5 mL of dry THF and stirred at room temperature for 2 h. The resulting mixture was washed with Et_2O and dried. The yellow solid (0.26 g, yield: 41 %) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, 1H, Py*H*), 8.15 (m, 3H, Py*H*), 7.98 (m, 5H, Py*H*), 5.18 (s, 2H, PyC*H*$_2$).

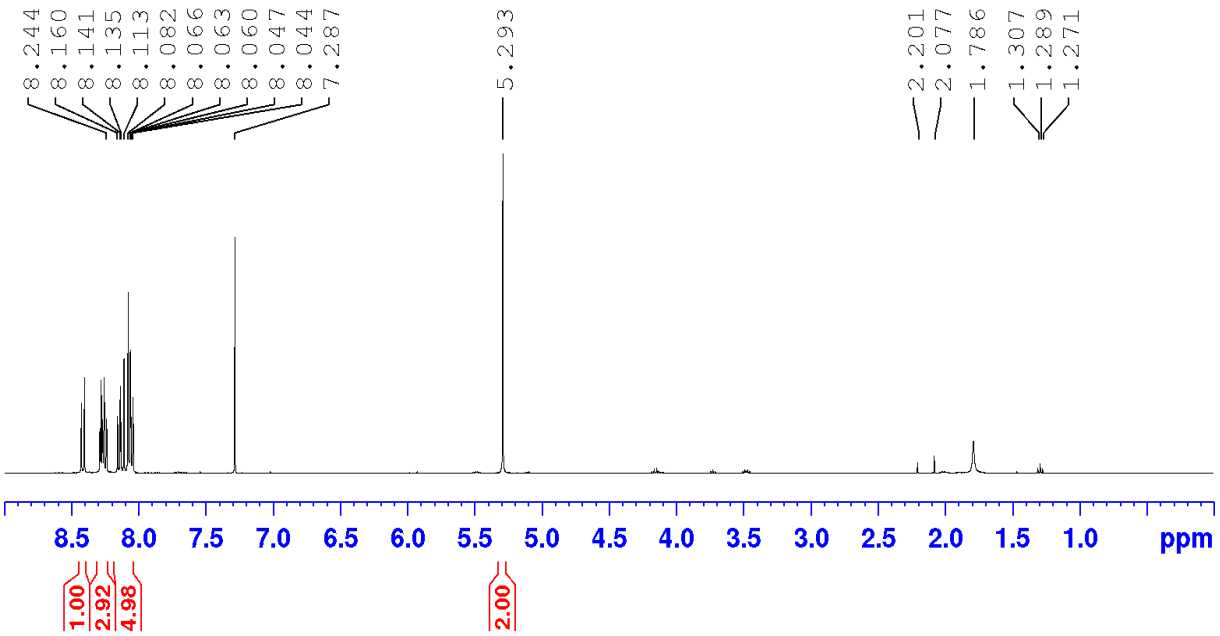

Figure S9. ^{1}H NMR spectrum of **PyBr** (in $CDCl_3$).

Reference

1. Park, S.Y.; Yoon, J.H.; Hong, C.S.; Souane, R.; Kim, J.S.; Matthews, S.E.; Vicens, J. A Pyrenyl-Appended Triazole-Based Calix [4] Arene as a Fluorescent Sensor for Cd^{2+} and Zn^{2+}. *J. Org. Chem.* **2008**, *73*, 8212-8218.