Dual responsive supramolecular amphiphiles: Guest molecules dictate the architecture of pyridinium-tailored anthracene assemblies

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Content

Experimental Section

2-Anthracenylmethanol, 11-bromoundecanoic acid, thionyl chloride, triethylamine, pyridine, and 4, 4'-bipyridine are purchased from Sigma-Aldrich, and used as received. All organic solvents were dried and distilled before used.

NMR spectra were obtained by using a Varian Mercury 300/400 apparatus; ESI-MS spectra were recorded using a Micromass QTOF apparatus; UV-Vis spectra were measured on Agilent Technologies 95-03 spectrometers; Fluorescence spectra was measured on Varian Cary Eclipse Fluorescence Spectrophotometer; SEM was performed on Variable Pressure Tescan Vega3 SBU. For sample preparation: two drops of the solution were placed on a silicon surface, air-dried, and then was coated by gold before the test. AFM was measured in air on NanoScope IIIA MultiMode AFM (Veeco). For sample preparation: a few drops of the solution were placed on a silicon surface, and then the excess solution was removed by absorption onto filter paper. Finally, the sample was air-dried before test; TEM measurements were carried out on a Hitachi H8000 electron microscope operating at an acceleration voltage of 120 kV. The samples were prepared by drop-casting the aqueous solution on the carbon-coated copper grid and then were negatively stained with a uranyl acetate solution; OM and FM observation were performed on Olympus IX81 fluorescence microscope. The samples were prepared by applying one drop of the test solution onto the glass surface and then covered by a cover slip; The X-ray powder diffraction patterns were recorded using BrukerD8 Discover diffractometer (λ = 0.15406 nm). The Bragg peaks were extracted from the XRPD data and the layer thickness *d* could be obtained according to the Bragg Equation, $d = \lambda/2\sin\theta$. The samples were prepared by placing a few drops of the solution on a silicon surface, and evaporating at room temperature.

1-[11-(2-anthracenylmethoxy)-11-oxoundecyl]pyridinium bromide (2-AP)

The synthesis of **2-AP** was carried out as ref [1]. MS-ESI (+) m/z: 454; HRMS (ESI): m/z calcd for $C_{31}H_{36}NO_2$: 454.2746; found: 454.2748; mp. 145-147 ^oC; ^1H NMR (300 MHz, DMSO, δppm): 9.11 (2H, d, *J* = 6.9 Hz, pyridinium-H), 8.60 (1H, t, *J* = 7.2 Hz, pyridinium-H), 8.57 (1H, s, anthracene-H), 8.56 (1H, s, anthracene-H), 8.15 (2H, dd, J_1 = 7.2 Hz, J_2 = 6.9 Hz, pyridinium-H), 8.07 (4H, m, anthracene-H), 7.50 (3H, m, anthracene -H), 5.28 (2H, s, OCH_2), 4.57 (2H, t, *J* = 7.5 Hz, NCH_2), 2.39 (2H, t, *J* = 7.2 Hz, CH_2CO), 1.84 (2H, m, CH_2), 1.54 (2H, m, CH_2), 1.19 (12H, m, CH_2); ^{13}C NMR (75 MHz, DMSO, δppm): 173.33 (C=O), 145.91, 145.16, 128.92 (5C, pyridinium-C), 133.86, 131.88, 131.81, 131.18,131.07, 128.51, 128.46, 127.06, 126.59, 126.42, 126.19, 126.16, 126.02 (14C, anthracene-C), 65.95, 61.12, 33.95, 31.15, 29.16, 29.11, 29.05, 28.85, 28.76, 25.78, 24.93.

Methyl Viologen (MV)

The synthesis of **MV** was carried out as ref [2]. ^1H NMR (300 MHz, DMSO, δppm): 9.30 (4H, d, *J* = 6.0 Hz, pyridinium-H), 8.79(4H, d, *J* = 6.0 Hz, pyridinium-H), 4.45 (6H, s, methyl); ^{13}C NMR (75 MHz, DMSO, δppm): 148.00, 145.56, 126.01, 48.06.

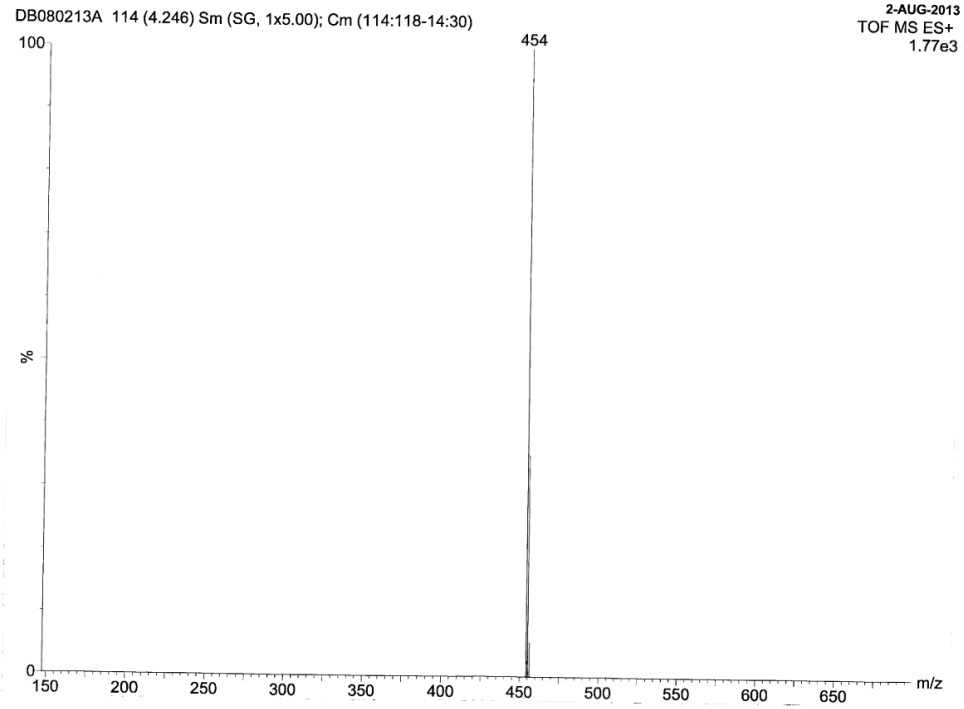

Figure S1. ESI-MS (+) Spectrum of **2-AP**

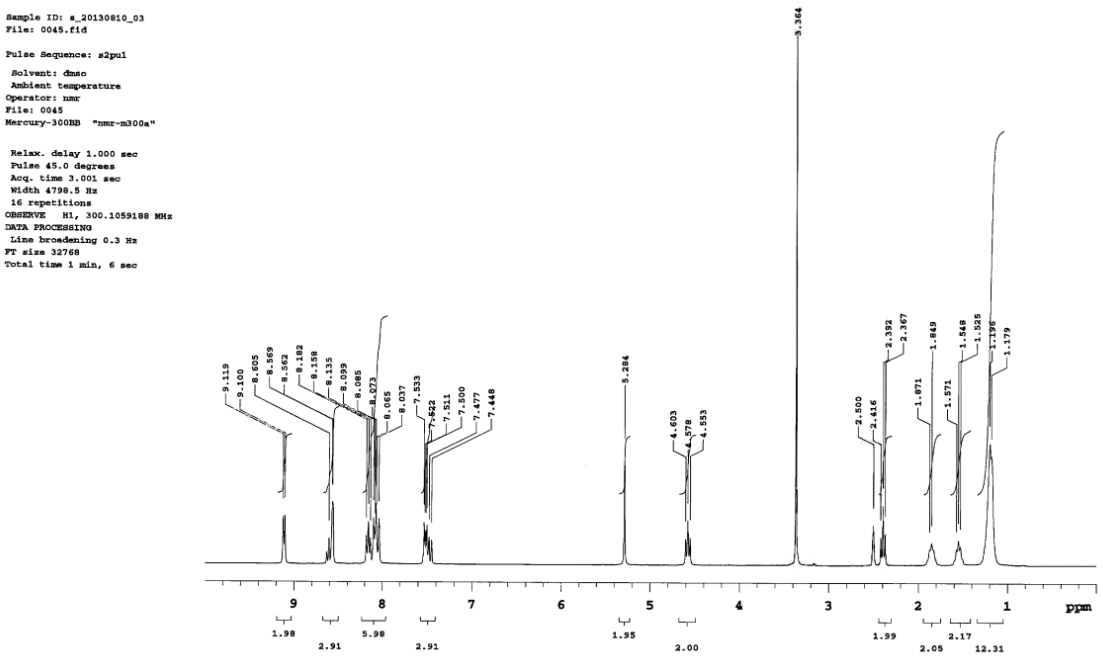

Figure S2. ^{1}H NMR Spectrum (DMSO, 300 MHz) of **2-AP**

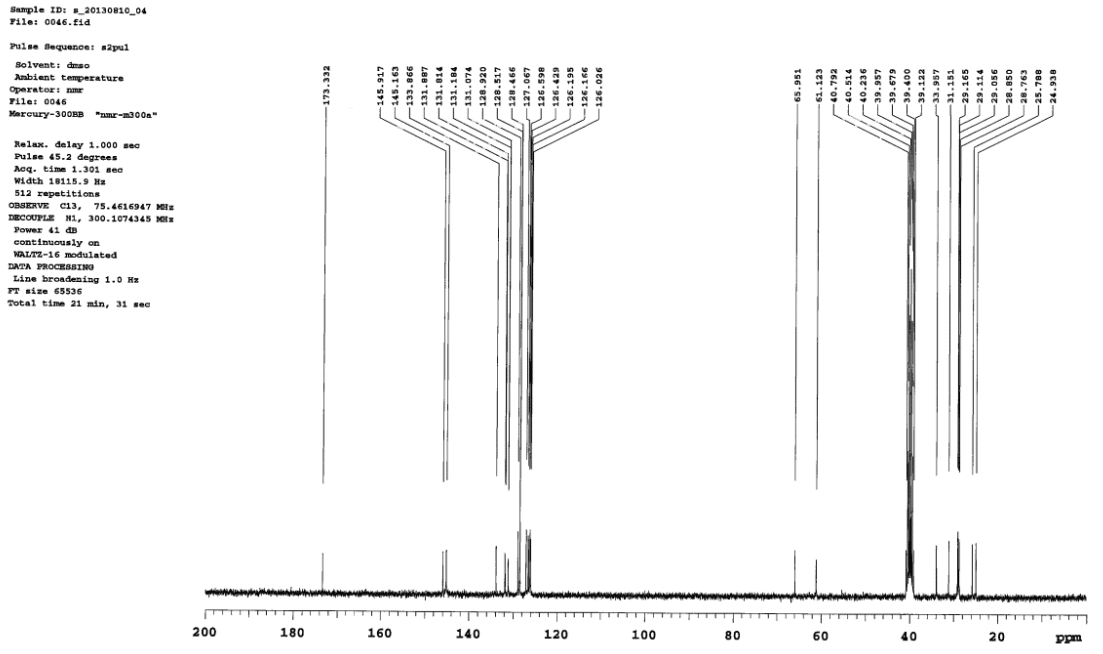

Figure S3. ^{13}C NMR Spectrum (DMSO, 75 MHz) of **2-AP**

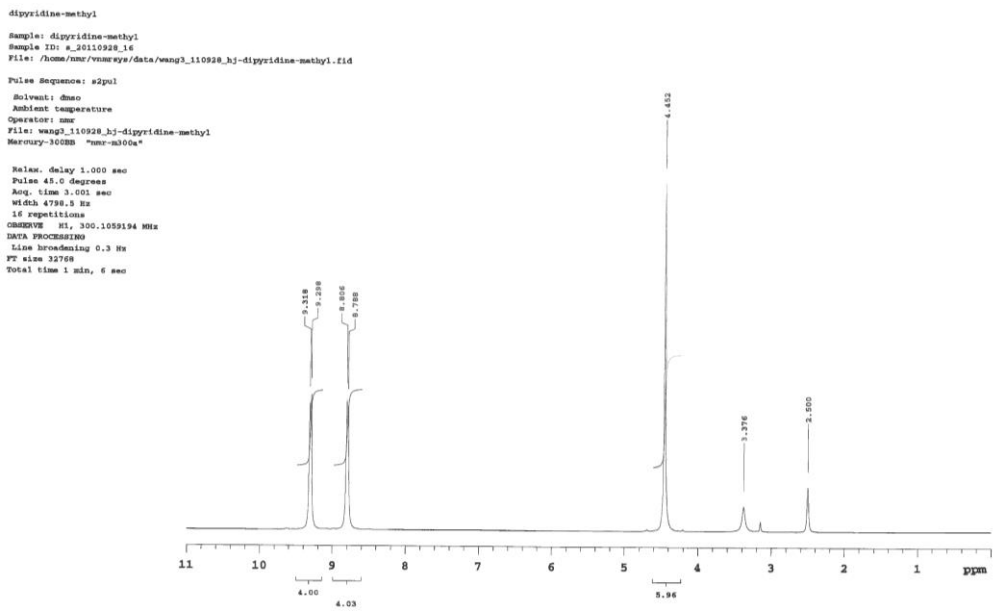

Figure S4. ^{1}H NMR Spectrum (DMSO, 300 MHz) of **MV**

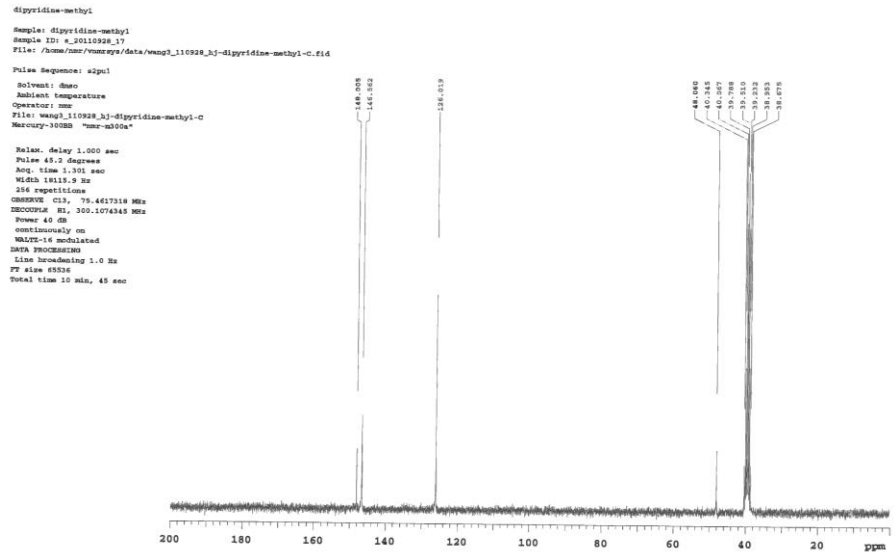

Figure S5. ^{13}C NMR Spectrum (DMSO, 75 MHz) of **MV**

Figure S6. AFM height image of **2-AP/MV** complex (1:1, molar ratio, 0.25 mM **2-AP**).

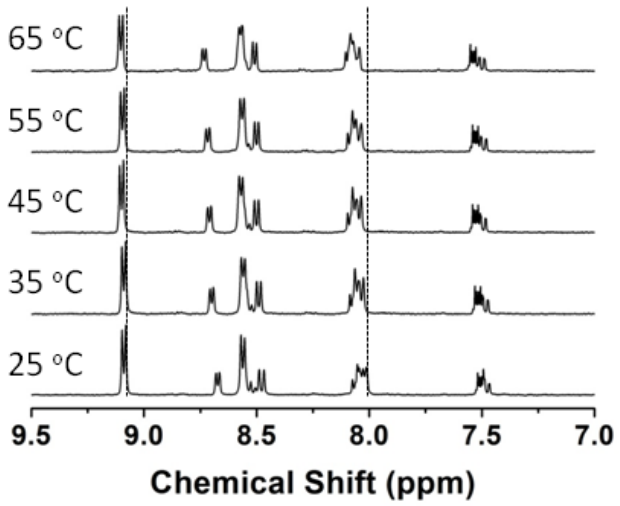

Figure S7. Temperature-dependent ^{1}H NMR of **2-AP**/**MV** (1:1, molar ratio, 0.5 mM **2-AP**) in D_2O-CD_3OD (4:1, volume ratio).

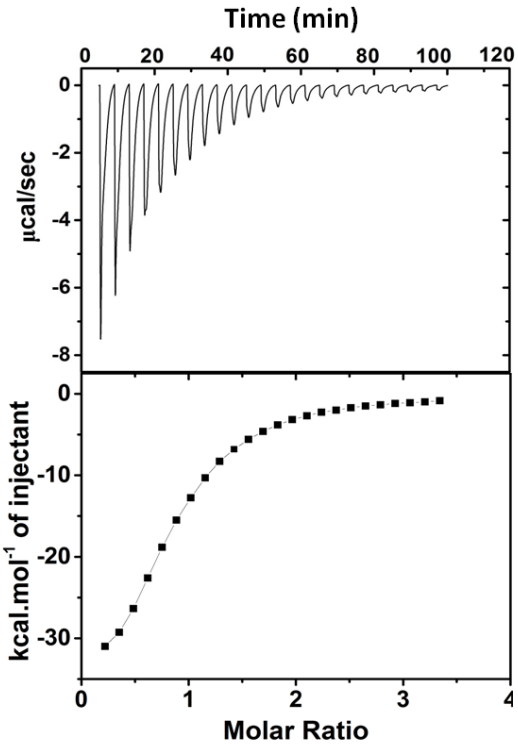

Figure S8. ITC data for the titration of **2-AP** with **MV** at 26°C. Fittting data using the one site mode gave a binding constant of $6.3\pm0.1\times10^{4}$ M^{-1}.

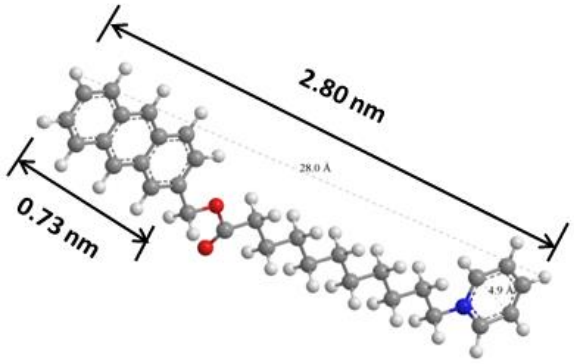

Figure S9. Simulated structure of **2-AP** using Chem 3D. Oxygen atoms are presented in red, nitrogen atoms in blue.

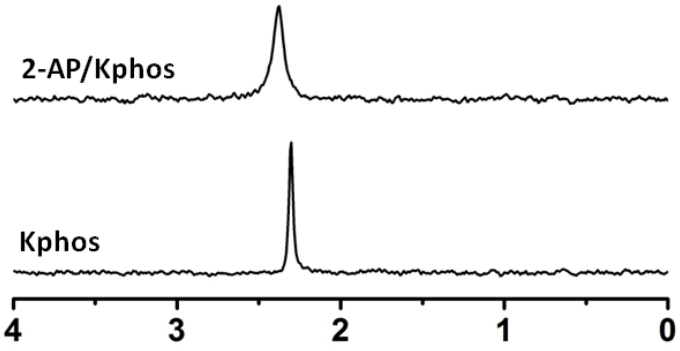

Figure S10. ^{31}P NMR of Kphos and **2-AP**/Kphos (pH 7.8, 0.2 mM **2-AP**, 10 mM Kphos).

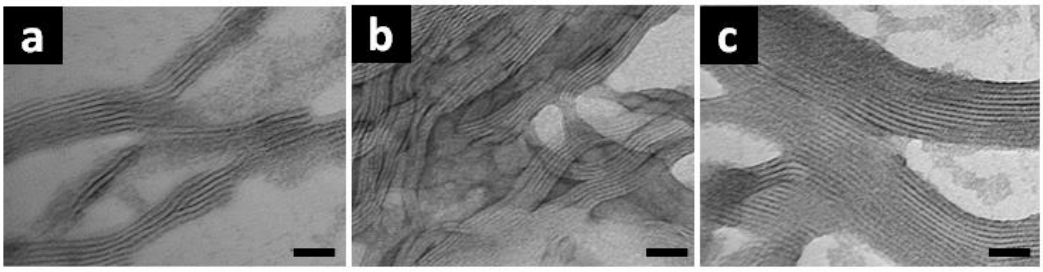

Figure S11. TEM images of **2-AP**/Kphos (0.2 mM **2-AP**) (a) 1 mM Kphos, pH 7.8; (b) 100 mM Kphos, pH 7.8; (c) 10 mM Kphos, pH 5.5. Scale bar are 20 nm for (a, c) and 50 nm for (b).

References

1. J. Hu, P. Wang, Y. Lin, J. Zhang, M. Smith, P. J. Pellechia, S. Yang, B. Song and Q. Wang, *Chem. Eur. J.*, **2014**, DOI: 10.1002/chem. 201402631.
2. C. Wang, Y. Guo, Y. Wang, H. Xu and X. Zhang, *Chem. Commun.*, **2009**, 5380-5380.