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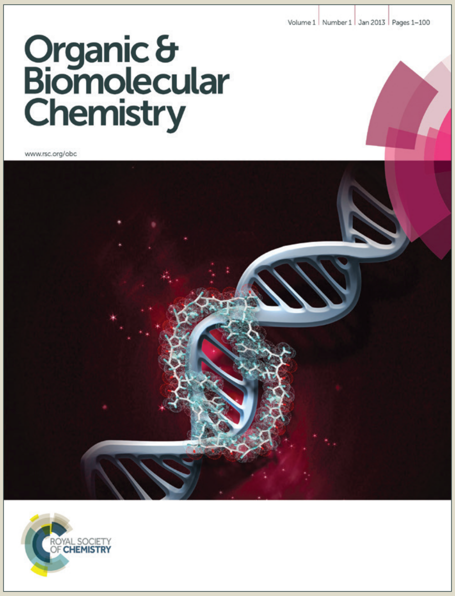

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ARTICLE TYPE

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

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By introducing the electron-deficient guest molecule and the counter anion, the assembly morphology of 1-[11-(2-anthracenylmethoxy)-11-oxoundecyl]pyridinium bromide (2-AP) was transformed to microsheets and nanofibers from microtubes, respectively.

Self-assembly of amphiphiles is an effective way to generate supramolecular materials.[1] Hydrogen bonds, van der Waals forces, π-π stacking, charge-transfer (CT), and electrostatic interactions are the most common noncovalent forces that can contribute to the self-assembly process.[2] Some recent studies demonstrated that the addition of guest molecules can induce significant changes of the final assembly morphologies and spectroscopic properties of host amphiphiles.[3] Specifically, the assembly behaviour of π-conjugated supra-amphiphiles is particularly appealing for their potential applications in sensing and electrochemical devices.[4] For example, Zhang and co-workers reported the morphology transformation from microtubes to vesicles by introducing the electron-deficient ethane-1, 2-diyl bis(3, 5-dinitro benzoate) to the pyrenyl-functionalized amphiphilic system.[5a] Ghosh and co-workers have developed a facile strategy to modulate the reversible assembly transformation between vesicles and micelles through the introduction of pyrenyl group to the naphthalene diimide amphiphile.[5b] Inspired by those works, here we report the responsive assembly behaviour of an pyridinium derivatized 2-anthracene (**2-AP**, Figure 1A) with different guest molecules.

Our previous work has shown that the electron-rich

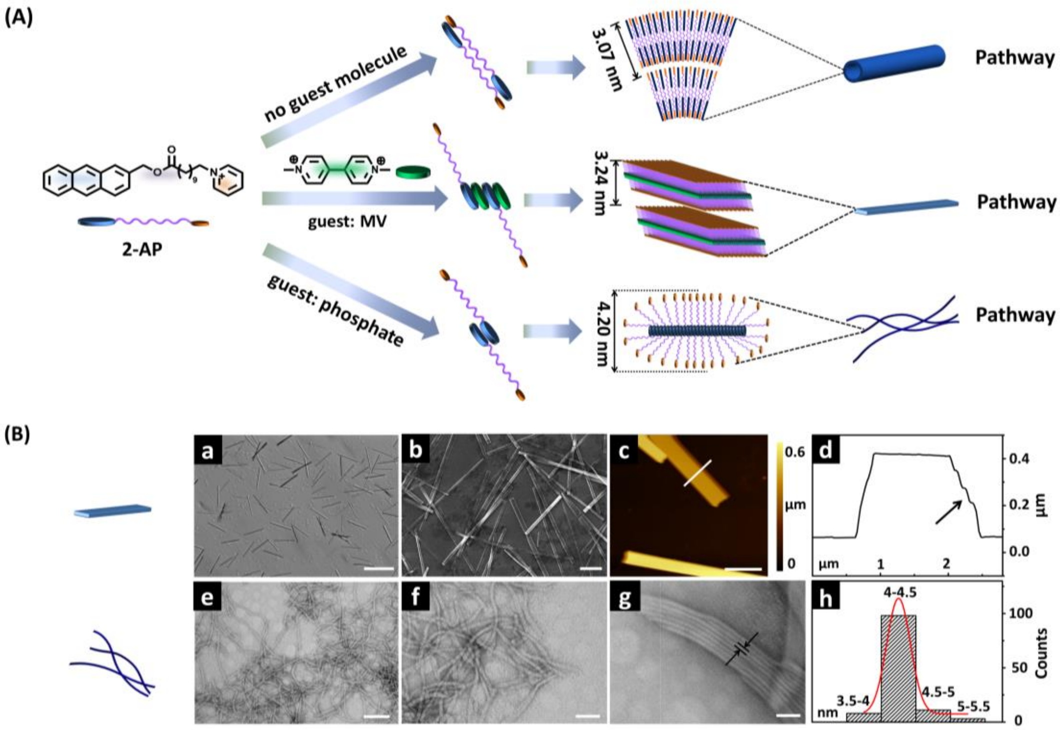

Figure 1 **(A)** Schematic illustration of three pathways of the assembly process of **2-AP** with or without guest molecules. **(B)** Characterization of the final assemblies. (a) OM, (b) SEM, (c) AFM images and (d) AFM height profile of microsheets assembled from **2-AP**/**MV** (1:1, molar ratio, 0.25 mM **2-AP**); (e, f, g) TEM images and (h) statistical analysis of the diameter of nanofibers assembled from **2-AP**/phosphate (pH 7.8, 0.2 mM **2-AP**, 10 mM potassium phosphate). Scale bars are 50 μm for (a), 20 μm for (b), 2 μm for (c), 50 nm for (e), and 20 nm for (f, g).

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anthracene ring and the electron-deficient pyridinium motif of **2-AP** adapt a co-planar structure, which can readily assemble into dimers via the CT interactions and ultimately form microtubes with an average diameter of ~10 μm (Figure 1A, **Pathway a**).[6] The morphology of the final assemblies relies on a fine balance of the CT interactions and hydrophobic feature of anthracene and alkyl linkers. Therefore we hypothesize that the dissociation of the CT pairs by the incorporation of a suitable guest molecule could result in the architectural change of **2-AP** assemblies. To achieve this, the guest molecule needs either to be more electron-deficient than the pyridinium cation (Figure 1A, **Pathway b**), or as a counter anion that can form tight binding with the pyridinium cation with the anthracene ring (Figure 1A, **Pathway c**).

We first tested the addition of methyl viologen (**MV**) into the **2-AP** system. **MV** is more electron deficient than pyridinium cation, and has been used as an electron acceptor to form a CT complex in many studies due to its importance as electronic relays in electron transfer systems.[7] As a general protocol, **MV** was mixed with **2-AP** in aqueous solution (1:1, molar ratio, 0.25 mM) and incubated for 30 min. The final assembly was evaluated with optical microscopy (OM), scanning electron microscopy (SEM), and atomic force microscopy (AFM). As shown in Figure 1B (a-c), microsheets were observed for **2-AP/MV** with an average size of 50, 1.5, and 0.35 μm in length, width, and thickness, respectively. The AFM height profile analysis further confirmed a typical sheet-like structure of **2-AP/MV** (Figure 1B (d); Figure S6).

UV-Vis, fluorescence, and NMR spectra were used to elucidate the driving forces responsible for the assembly. As shown in Figure 2a, the emission of **2-AP** decreased upon the addition of **MV**,[8] and the red shift (12 nm) in UV-Vis spectra suggested the presence of a "J"-type complex.[9] The increase in absorption above 400 nm should be attributed to aggregates light scattering (Figure 2b).[10] In the ^{1}H NMR spectra, the proton resonances of the dipyridinum of **MV** shifted upfield after mixing with **2-AP** (Figure 3a), and shifted back to downfield as the temperature increased, which revealed the formation of **2-AP**/**MV** complex (Figure S7). Furthermore, a 1:1 binding mode of **2-AP** and **MV** was revealed by isothermal titration calorimetry (ITC) measurement, and the fitting data gave a binding constant of 6.3×10^4 M^{-1} using the one site model (Figure S8). Finally, X-ray powder diffraction (XRPD) experiment was performed to study the packing patterns of microsheets. A layered structure was observed with a thickness ~3.24 nm (Figure 3b), which was between 2.80 (the extended length of a single **2-AP** molecule, Figure S9) and 4.87 nm (the length of two **2-AP** molecules with an overlap only on anthracene ring). We conclude that the interactions between the anthracene motif of **2-AP** and the more electron-deficient **MV** molecule promotes a slipped "face-to-face" packing pattern, which consequently results in the final microsheets (Figure 1A, **Pathway b**). However, it is still difficult to predict whether the **MV** molecules were randomly entrapped within the assembly or arranged alternatively with the **2-AP** units.

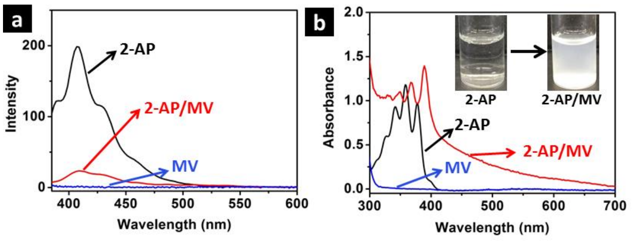

Figure 2 (a) Fluorescence and (b) UV-Vis spectra of **2-AP**, **MV**, and **2-AP/MV** (1:1, molar ratio, 0.25 mM **2-AP**; excitation 376 nm) in water. Insert: photography of **2-AP** and **2-AP/MV**. The transparent solution of **2-AP** became cloudy quickly after the addition of **MV**.

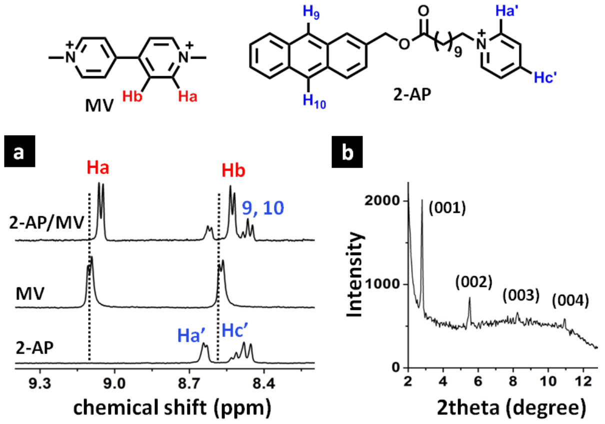

Figure 3 (a) ^{1}H NMR spectra of **2-AP**, **MV**, and **2-AP/MV** (1:1, molar ratio, 0.5 mM **2-AP**) in D_2O-CD_3OD (4:1, v/v). (b) X-ray power diffraction patterns of microsheets assembled from **2-AP/MV**.

On the other hand, potassium phosphate (Kphos), which has been widely applied in controlling the electrostatic interactions,[11] was chosen as the counter anion to interact with the pyridinium motif in order to block the homo-dimer formation of **2-AP**. The assembly behaviour of **2-AP** with Kphos under different pH and concentration was investigated by transmission electron microscopy (TEM). Nanofibers were observed with an average diameter of 4.2 nm, and their lengths reached several micrometers (Figure 1B (e-h); Figure S11). UV-Vis spectra showed a 10 nm red shift of **2-AP** upon the addition of Kphos (Figure 4a), and an excimer peak at 471 nm appeared in the emission spectrum (Figure 4b), which were caused by the "J"-type aggregation from the π-stacking of the anthracene rings.[12] In addition, the phosphate peak shifted upfield and broadened in ^{31}P NMR spectra after mixing with **2-AP** (Figure S10), likely caused by the electrostatic interactions between pyridinium cations and phosphates that decreased the electron density and reduced the relaxation time of phosphate.[13] The pyridinium-phosphate complexes, thus serving as the hydrophilic peripheral layer, encloses the π-stacked anthracene cores and constructs the nanofibrous structures (Figure 1A, **Pathway c**).

It should be pointed out that the nanofibers could be wrapped together to form a hydrogel structure when the concentration of 2-

AP increased to 6 mM (Figure 4d, insert). Its viscoelastic behaviour was characterized by rheological measurements, in which the storage modulus *G′* and the loss modulus *G″* were measured as functions of strain and frequency. As shown in 4c-d, the *G′* was around twenty times greater than *G″*, which indicated the dominant elastic character of the hydrogel exhibiting the clear thixotropic property.[14]

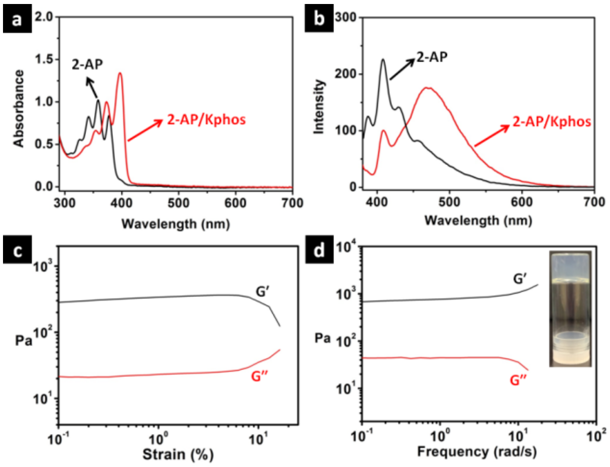

Figure 4 (a) UV-Vis and (b) fluorescence spectra of **2-AP** and **2-AP**/Kphos (pH 7.8, 0.2 mM **2-AP**, 10 mM Kphos; excitation 376 nm). (c, d) Rheological measurement of the **2-AP**/Kphos hydrogel (pH 7.8, 12 mM **2-AP**, 10 mM Kphos) showing the evolution of storage modulus (*G′*) and loss modulus (*G″*) of the hydrogel with (c) strain, and (d) frequency. Insert: photograph of the formation of hydrogel of **2-AP**/Kphos.

In conclusion, we demonstrated that the assembly structure of **2-AP** can be switched from microtubes to microsheets or nanofibers, respectively, through the addition of suitable small molecular modulators. Furthermore, the nanofibers can be wrapped together to form the hydrogel with an increase of the concentration. The present work will stimulate further studies on the anthracene-contained supra-amphiphiles for controlled self-assembly and disassembly.

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Notes and references

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† Electronic Supplementary Information (ESI) available: MS and NMR spectra of **2-AP** and **MV**; AFM height image, temperature-dependent ^{1}H NMR and ITC data of **2-AP/MV**; Simulated structure of **2-AP**; ^{31}P NMR of **2-AP**/Kphos; TEM images of **2-AP/**Kphos with different concentration and pH. See DOI: 10.1039/b000000x/

1. a) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer and A. P. H. J. Schenning, *Chem. Rev.*, **2005**, *105*, 1491-1546; b) P. M. Beaujuge and J. M. J. Fréchet, *J. Am. Chem. Soc.*, **2011**, *133*, 20009-20029; c) A. Mishra, C.-Q. Ma and P. Bäuerle, *Chem. Rev.*, **2009**, *109*, 1141-1276; d) L. C. Palmer and S. I. Stupp, *Acc. Chem. Res.*, **2008**, *41*, 1674-1684; e) T. F. A. De Greef, M. M. J. Smulders, M. Wolffs, A. P. H. J. Schenning, R. P. Sijbesma and E. W. Meijer, *Chem. Rev.*, **2009**, *109*, 5687-5754; f) D. Görl, X. Zhang and F. Würthner, *Angew. Chem. Int. Ed.*, **2012**, *51*, 6328-6348; g) J. B. Matson and S. I. Stupp, *Chem. Commun.*, **2012**, *48*, 26-33; h) M. J. M. Munoz and G. Fernandez, *Chem. Sci.*, **2012**, *3*, 1395-1398; i) H.-J. Kim, T. Kim and M. Lee, *Acc. Chem. Res.*, **2011**, *44*, 72-82; j) J.-H. Ryu, D.-J. Hong and M. Lee, *Chem. Commun.*, **2008**, 1043-1054.
2. a) M. L. Saha, S. De, S. Pramanik and M. Schmittel, *Chem. Soc. Rev.*, **2013**, *42*, 6860-6909; b) C. Wang, Y. Guo, Y. Wang, H. Xu, R. Wang and X. Zhang, *Angew. Chem. Int. Ed.*, **2009**, *48*, 8962-8965; c) A. Ajayaghosh and V. K. Praveen, *Acc. Chem. Res.*, **2007**, *40*, 644-656; d) A. Jain, K. V. Rao, C. Kulkarni, A. George and S. J. George, *Chem. Commun.*, **2012**, *48*, 1467-1469; e) J. Puigmarti-Luis, A. Perez del Pino, V. Laukhin, L. N. Feldborg, C. Rovira, E. Laukhina and D. B. Amabilino, *J. Mater. Chem.*, **2010**, *20*, 466-474; f) G. Yu, X. Zhou, Z. Zhang, C. Han, Z. Mao, C. Gao and F. Huang, *J. Am. Chem. Soc.*, **2012**, *134*, 19489-19497.
3. a) K. V. Rao, S. J. George, *Chem. Eur. J.*, **2012**, *18*, 14286-14291; b) K. Liu, Y. Yao, C. Wang, Y. Liu, Z. Li and X. Zhang, *Chem. Eur. J.*, **2012**, *18*, 8622-8628; c) M. T. Fenske, W. Meryer-Zaika, H, Korth, H. Vieker, A. Turchanin, and C. Schmuck, *J. Am. Chem. Soc.*, **2013**, *135*, 8342-8349; d) D. Jiao, J. Geng, X. J. Loh, D. Das, T. Lee and O. A. Scherman, *Angew. Chem. Int. Ed.*, **2012**, *51*, 9633-9637; e) H. Kara, S. Ghosh, *Chem. Commun.*, **2007**, *50*, 1064-1066.
4. a) S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hagele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel and M. Tosoni, *Angew. Chem. Int. Ed.*, **2007**, *46*, 4832-4887; b) D. J. Vinyard, S. Su and M. M. Richter, *J. Phys. Chem. A*, **2008**, *112*, 8529-8533; c) J. H. Olivier, F. Camerel, J. Barbera, P. Retailleau and R. Ziessel, *Chem. Eur. J.*, **2009**, *15*, 8163-8174; d) D. Adam, P. Schuhmacher, J. Simmerer, L. Haussling, K. Siemensmeyer, K. H. Etzbachi, H. Ringsdorf and D. Haarer, *Nature*, **1994**, *371*, 141-143. e) J. E. Anthony, *Chem. Rev.*, **2006**, *106*, 5028-5048.
5. a) C. Wang, S. Yin, S. Chen, H. Xu, Z. Wang and X. Zhang, *Angew. Chem. Int. Ed.*, **2008**, *47*, 9049-9052; b) A. Das and S. Ghosh, *Angew. Chem. Int. Ed.*, **2014**, *53*, 1092-1097.
6. 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.
7. a) P. M. S. Monk and N. M. Hodgkinson, *Electrochim. Acta*, **1998**, *43*, 245-255; b) M. E. Ghica and C. M. A. Brett, *Anal. Chim. Acta*, **2005**, *532*, 145-151; c) K. V. Rao, K. Jayaramulu, T. K. Maji and S. J. George, *Angew. Chem. Int. Ed.*, **2010**, *122*, 4314-4318.
8. a) R. Foster, *Organic Charge-Transfer Complexes*. London, New York, Academic Press, **1969**; b) D. Tanaka, S. Horike, S. Kitagawa, M. Ohba, M. Hasegawa, Y. Ozawa and K. Toriumi, *Chem. Commun.*, **2007**, 3142-3144.
9. a) E. E. Jelley, *Nature*, **1936**, *138*, 1009-1010; b) Z. Chen, C. Zhong, Z. Zhang, Z. Li, L. Niu, Y. Bin and F. Zhang, *J. Phys. Chem. B*, **2008**, *112*, 7387-7394; c) F. Würthner, T. E. Kaiser and C. R. Saha-Möller, *Angew. Chem. Int. Ed.*, **2011**, *50*, 3376-3410.
10. C. E. Barnett, *J. Phys. Chem.*, **1942**, *46*, 69-75.
11. a) J. M. Mason, U. B. Hagemann and K. M. Arndt, *Biochemistry*, **2009**, *48*, 10380-10388; b) H. Hiramatsu and F. E. Osterloh, *Langmuir*, **2003**, *19*, 7003-7011; c) O. Martinez-Avila, S. Wu, S. J. Kim, Y. Cheng, F. Khan, R. Samudrala, A. Sali, J. A. Horst and S. Habelitz, *Biomacromolecules*, **2012**, *13*, 3494-3502.
12. a) C. Janiak, *J. Chem. Soc., Dalton Trans.*, **2000**, 3885-3896; b) C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, **1990**, *112*, 5525-5534.
13. a) P. Acharya, O. Plashkevych, C. Morita, S. Yamada and J. Chattopadhyaya, *J. Org. Chem.*, **2003**, *68*, 1529-1538; b) M. Szafran,

Z. Dega-Szafran, A. Katrusiak, G. Buczak, T. Głowiak, J. Sitkowski and L. Stefaniak, *J. Org. Chem.*, **1998**, *63*, 2898-2908.

14. a) X. Cai, K. Liu, J. Yan, H. Zhang, X. Hou, Z. Liu and Y. Fang, *Soft Matter*, **2012**, *8*, 3756-3761; b) P. K. Sukul and S. Malik, *Soft Matter*, **2011**, *7*, 4234-4241.