Polymer
Chemistry

RSC Publishing

COMMUNICATION

View Article Online
View Journal | View Issue

Published on 20 November 2012. Downloaded by Jilin University on 07/11/2013 07:10:48.

Supramolecular polymerization of spherical micelles triggered by donor–acceptor interactions†

Cite this: *Polym. Chem.*, 2013, **4**, 268

Received 26th October 2012
Accepted 19th November 2012

DOI: 10.1039/c2py20901b

www.rsc.org/polymers

Zhegang Huang,[a] Yongju Kim,[b] Taehoon Kim[b] and Myongsoo Lee*[b]

We synthesized rigid–flexible amphiphilic molecules consisting of an aromatic block based on a pyrene dimer and a hydrophilic oligoether dendron. The molecules self-assemble into spherical micelles with a diameter of ∼12 nm in an aqueous solution. Notably, these spherical objects could be polymerized through charge transfer interaction by addition of an electron acceptor molecule, 2,4,5,7-tetranitrofluorenone (TNF), to yield linear supramolecular polymers with controlled lengths from several tens to a few micrometers depending on the TNF content.

Supramolecular polymerization requires strong directional interactions such as multiple hydrogen bonding,[1] metal ion complexations,[2] and host–guest complementary interactions.[3] These directional interactions lead molecular modules to interconnect with each other in a one-dimensional fashion to form non-covalent supramolecular polymer chains. The supramolecular polymers exhibit similar macroscopic properties to those of conventional covalent polymers, even though they are based on weak non-covalent forces. The examples include gelation of solvent molecules[4] and thermoelastic properties of bulk samples.[5] In addition, the highlight of the non-covalent systems arises from reversible and switchable characteristics in response to environmental changes. Because of the reversibility in the bonding, the supramolecular polymers are under thermodynamic equilibrium, and their properties can be easily tuned by external stimuli.[6] For example, supramolecular polymers form smart gels through reversible polymerization–depolymerization processes in response to external forces.[7] However, most of the supramolecular polymers reported to date are based on molecular modules that are able to hold together through directional interactions.

Here we report supramolecular polymerization of the spherical micelles consisting of a pyrene aromatic core surrounded by hydrophilic oligoether dendrons in an aqueous solution triggered by electron donor–acceptor interactions (Fig. 1). We have designed the aromatic segment based on a pyrene dimer which shows the unique excimer emission characteristics.[8] The molecules consist of an oligoether dendron and an aromatic segment containing a dimeric pyrene building block. The synthesis of the molecules was started from etherification with an oligoether dendron and an aromatic scaffold, according to the procedures reported previously.[9] Molecule **1** based on an acetylene linkage in the aromatic segment was prepared by Sonogashira coupling of the rigid–flexible

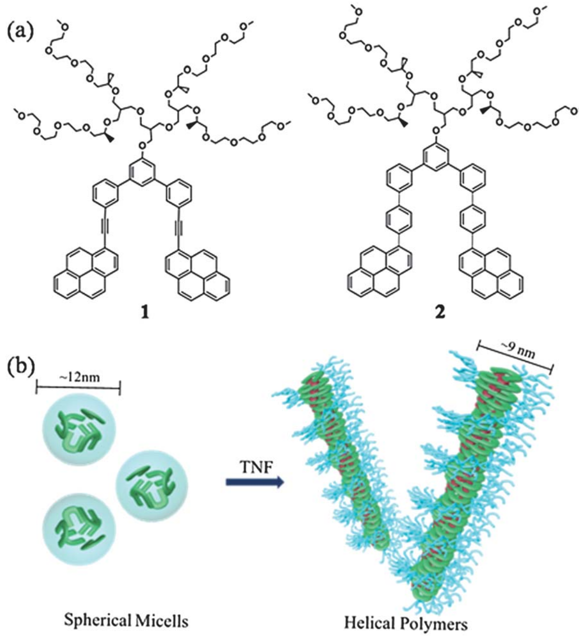

Fig. 1 (a) Chemical structures of aromatic amphiphiles **1** and **2**. (b) Schematic representation of supramolecular polymerization from spherical micelles triggered by electron donor–acceptor interactions.

---

[a] *Department of Chemistry, Harbin Institute of Technology, Harbin, 150001, P.R. China. E-mail: andrew576@hanmail.net*

[b] *Department of Chemistry, Seoul National University, Seoul 151-747, Korea. E-mail: myongslee@snu.ac.kr; Tel: +82-2-880-4340*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c2py20901b

This journal is © The Royal Society of Chemistry 2013

Published on 20 November 2012. Downloaded by Jilin University on 07/11/2013 07:10:48.

precursor with 1-ethynyl pyrene, while molecule **2** based on a phenylene linkage was prepared by the Suzuki coupling reaction of the precursor with pyrene-1-boronic acid.

To investigate the aggregation behavior of **1** and **2**, we examined the emission characteristics of pyrene moieties by means of fluorescence spectroscopy (Fig. 2). In aqueous solutions, the emission of both molecules is dominated by strong signals centered at 510 nm and 480 nm for **1** and **2**, respectively, attributed to excimer emission,[8] indicating that the intramolecular pyrene emitting groups are in close spatial proximity to form a pyrene dimer within the hydrophobic cores of the micellar aggregates.

The evidence for the formation of the discrete micelles was provided by dynamic light scattering (DLS) experiments (Fig. 3a). DLS experiments of the aqueous samples showed monomodal size distributions with a hydrodynamic diameter of ~12 nm, indicative of the formation of small micellar aggregates in an aqueous solution. The micellar structures of **1** and **2** were confirmed by using transmission electron microscopy (TEM). When the samples were cast from the aqueous solution and then negatively stained with uranyl acetate, the images of both molecules showed spherical micelles with a uniform diameter of ~12 nm which is consistent with the DLS result (Fig. 3b). This dimension of diameter is slightly larger than twice the extended molecular length (5.3 nm from CPK modelling), suggesting that the pyrene dimers in the aromatic segments are loosely packed with bilayer arrangements within the hydrophobic aromatic core. No circular dichroism (CD) signals could be detected even though the molecules contain chiral side groups, suggesting that the aromatic segments within the core are packed loosely in a random way. Taken together, the micelles consist of hydrophobic aromatic cores surrounded by hydrophilic dendrons, in which the aromatic segments based on pyrene dimers are loosely packed within the hydrophobic cores (Fig. 1).

The pyrene units are well-known to form electron donor–acceptor complexes with an electron acceptor molecule such as 2,4,5,7-tetranitrofluorenone (TNF) by charge transfer interaction.[10] This additional interaction would force the aromatic segments based on pyrene units to be packed in a more dense, parallel arrangement within the cores. This packing rearrangement could result in anisotropic micelles to interconnect together in a one-dimensional fashion to form linear supramolecular polymers. To substantiate this initial concept, we have investigated the aggregation behavior of the discrete spherical micelles by addition of TNF molecules.

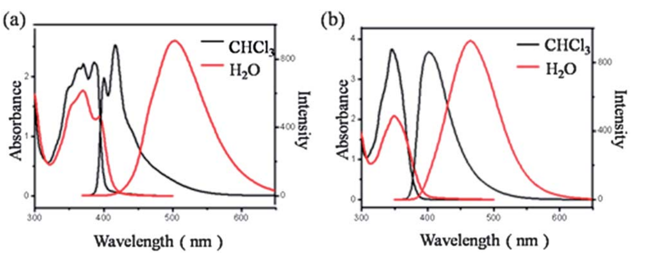

Fig. 2 (a) Absorption and emission spectra of **1** in $CHCl_3$ (56 μM, black line) and in an aqueous solution (56 μM, red line). (b) Absorption and emission spectra of **2** in $CHCl_3$ (53 μM, black line) and in an aqueous solution (53 μM, red line).

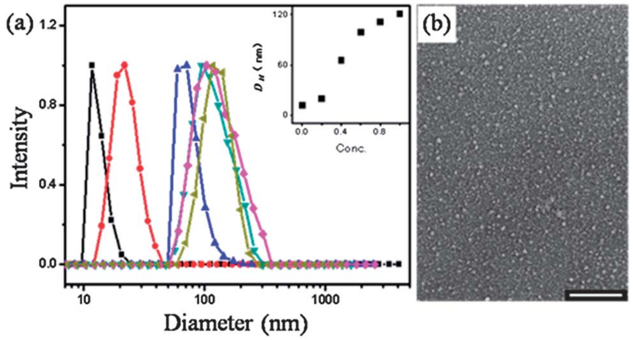

Fig. 3 (a) Size distribution graphs of **1** (112 μM) in the presence of TNF. (b) A TEM image of **1** from a 112 μM aqueous solution (scale bar, 200 nm).

Upon addition of TNF to the aqueous solution of **1**, the excimer emission was abruptly quenched (Fig. 4a), indicating that the acceptor molecules are complexed with the pyrene donor through charge transfer interaction within the aromatic cores of the micelles. Remarkably, addition of TNF to **1** triggers the size of aggregates to remarkably increase in hydrodynamic diameter from 12 nm to ~130 nm, as confirmed by DLS experiments (Fig. 3a). To identify the structural change of the aggregates upon addition of TNF, TEM experiments were performed with the complexed samples (Fig. 4b–d). The TEM image of the complex with 0.4 eq. of TNF revealed short fibers with a reduced diameter of ~9 nm and lengths of several tens of nanometers, in which the trend is consistent with DLS results. When 0.6 eq. of TNF was complexed with **1**, the length of the nanofibers further increased to ~300 nm. The image of the complex containing 1.0 eq. of TNF showed long fibers with lengths of a few micrometers without any noticeable changes in diameter. This result demonstrates that the spherical micelles grow in one direction to form linear supramolecular polymers through charge transfer interaction and the chain length can be controlled as a function of TNF content from a few tens to several hundreds of nanometers.

To investigate the role of TNF in the packing arrangements of the aromatic segments in the hydrophobic cores, UV spectroscopic

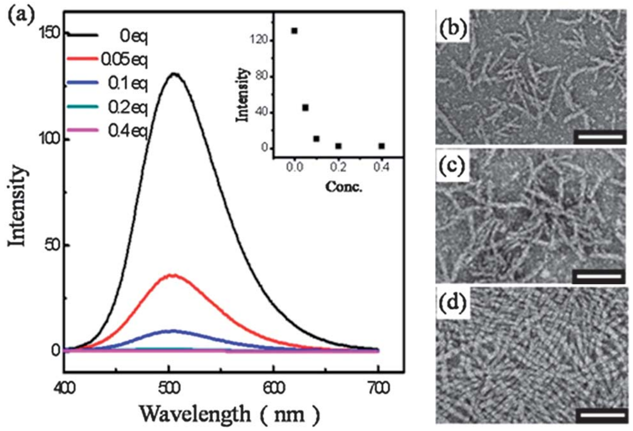

Fig. 4 (a) Fluorescence spectra of **1** (112 μM) in the presence of TNF in an aqueous solution. TEM image of **1** from a 112 μM aqueous solution with (b) 0.4 eq. TNF, (c) 0.6 eq. TNF, and (d) 1.0 eq. TNF (scale bar, 100 nm).

Published on 20 November 2012. Downloaded by Jilin University on 07/11/2013 07:10:48.

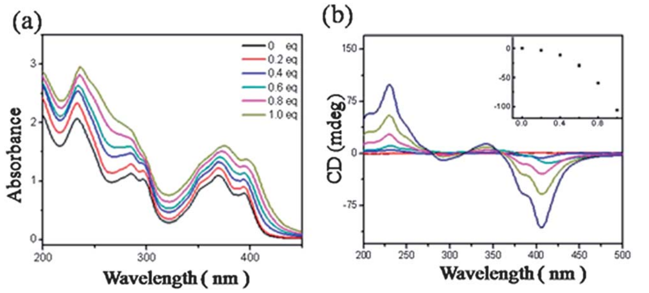

Fig. 5 (a) Absorption spectra of **1** (56 μM) in the presence of TNF in an aqueous solution. (b) CD spectra of **1** (112 μM) in the presence of TNF in an aqueous solution.

studies were carried out with the complex solutions of **1** containing different amounts of TNF (Fig. 5a). Upon complexation with TNF, the absorption maximum centered at 365 nm showed to remain nearly unchanged up to 0.2 eq. of TNF and then gradually red-shifted by ~8 nm at 1.0 eq. of TNF, suggesting that the aromatic segments adopt a more planar conformation by addition of a certain amount of TNF. When the complexes were subjected to CD measurements, no apparent CD signals could be detected up to 0.2 eq. of TNF. Notably, a Cotton effect begins to appear at the complex with 0.4 eq. of TNF (Fig. 5b), indicating helical stacking of the aromatic segments with a preferred handedness. Both red-shifted absorption maximum and induction of CD signals at the complex with 0.4 eq. of TNF are consistent with the drastic size increase at the complex with 0.4 eq. of TNF in DLS. These results together with TEM data indicate that donor–acceptor complexation triggers supramolecular polymerization of the spherical micelles based on pyrene dimers above a certain amount of TNF.

The ability of the spherical micelles to grow in a one-dimensional way to form supramolecular polymers can be understood by considering the packing arrangements of the aromatic segments as a function of TNF content. The pure aromatic segments with a pyrene dimer without TNF are loosely packed probably due to a large degree of freedom of the aromatic segments caused by repulsive interactions between the bulky dendritic blocks. The loosened packing of the aromatic segments is reflected in the formation of spherical micelles with a diameter larger than twice the extended molecular length. Complexation with TNF, however, would strengthen hydrophobic and π–π stacking and charge transfer interactions, which triggers the aromatic segments to adopt a more planar conformation due to the restricted rotational freedom of the pyrene units, as reflected in the red-shifted absorption maximum. Eventually, the planar aromatic segments are closely packed to stack on top of one another with mutual rotation in a preferred direction along the stacking axis to form chiral supramolecular polymers (Fig. 1). The close packing arrangements of the aromatic segments are also reflected in the reduction in diameter from 12 nm of the spheres to 9 nm of the polymers. Along the same line, the increase in the length of the supramolecular polymers as a function of TNF content is also attributed to increasing charge transfer interactions.

Molecule **2** based on a phenylene linkage exhibits nearly the same aggregation behavior as that of **1** based on an acetylene linkage as the donor–acceptor complexation with TNF triggers supramolecular polymerization. DLS results showed that the size of aggregates remarkably increases upon addition of 0.4 eq. of TNF. TEM investigations revealed that this size change is accompanied by the structural change from spherical to elongated fibrillar structures, indicating that the discrete micelles are linearly polymerized upon donor–acceptor complexation with TNF. In great contrast to **1**, however, no CD signal in the complexes of **2** could be detected even after supramolecular polymerization by addition of TNF, indicating that the complexes of **2** self-assemble into nanofibers with a lack of supramolecular chirality. This result suggests that the phenyl linkage of the aromatic segment of **2** forces twisted aromatic groups to reduce steric repulsion between the hydrogen atoms of the adjacent phenyl rings. Consequently, π–π stacking of the aromatic segments would be loosened to block the chiral transfer from the side groups, thereby leading to non-chiral supramolecular polymers.

Conclusions

We have demonstrated that pyrene-based rigid–flexible amphiphiles self-assemble into spherical micelles in an aqueous solution. The spherical objects could be polymerized through charge transfer interaction by addition of an electron acceptor molecule, TNF, to form linear supramolecular polymers with controlled lengths from several tens to hundreds of nanometers to a few micrometers depending on the TNF content. This approach to synthesize supramolecular polymers offers new opportunities for the construction of more complex and sophisticated supramolecular materials with switchable functions. Conductive thermoplastic elastomers, healable soft materials, and optoelectronic supramolecular materials are easily envisioned to be explored.

Acknowledgements

This work was supported by the Creative Research Initiative Program of the Ministry of Science and Technology (MEST) (no. 2012-0001240), Korea, and the U.S. Air Force Research Laboratory (FA2386-12-1-4078). M. L. acknowledges the financial support from Harbin Institute of Technology.

Notes and references

1 (*a*) R. P. Sijbesma, F. H. Beijer, L. Brunsveld, B. J. B. Folmer, J. H. K. Ky Hirschberg, R. F. M. Lange, J. K. L. Lowe and E. W. Meijer, *Science*, 1997, **278**, 1601; (*b*) L. Brunsveld, B. J. B. Folmer, E. W. Meijer and R. P. Sijbesma, *Chem. Rev.*, 2001, **101**, 4071.

2 (*a*) J. Benjamin and S. J. Rowan, *J. Am. Chem. Soc.*, 2003, **125**, 13922; (*b*) H.-J. Kim, J.-K. Kim and M. Lee, *Chem. Commun.*, 2010, **46**, 1458; (*c*) H.-J. Kim, E. Lee, H.-s. Park and M. Lee, *J. Am. Chem. Soc.*, 2007, **129**, 10994; (*d*) M. Burnworth, L. Tang, J. R. Kumpfer, A. J. Duncan, F. L. Beyer, G. L. Fiore, S. J. Rowan and C. Weder, *Nature*, 2011, **472**, 334; (*e*) A. Ajayaghosh, P. Chithra and R. Varghese, *Angew. Chem., Int. Ed.*, 2007, **46**, 230; (*f*) A. Ajayaghosh, P. Chithra, R. Varghese and K. P. Divya, *Chem. Commun.*, 2008, 969; (*g*)

Published on 20 November 2012. Downloaded by Jilin University on 07/11/2013 07:10:48.

P. Chithra, R. Varghese, K. P. Divya and A. Ajayaghosh, *Chem.–Asian J.*, 2008, **3**, 1365.

3 (*a*) T. Heino, A. Watanabe, T. Hirao and T. Ikeda, *Angew. Chem., Int. Ed.*, 2012, **51**, 1473; (*b*) M. Zhang, D. Xu, X. Yan, J. Chen, S. Dong, B. Zheng and F. Huang, *Angew. Chem., Int. Ed.*, 2012, **51**, 7011.

4 (*a*) W. Weng, J. Benzamin, A. M. Jamieson and S. J. Rowan, *J. Am. Chem. Soc.*, 2006, **128**, 11663; (*b*) W. Li, I.-S. Park, S.-K. Kang and M. Lee, *Chem. Commun.*, 2012, **48**, 8796; (*c*) S. Toksoz, H. Acar and M. O. Guler, *Soft Matter*, 2010, **6**, 5839.

5 B. J. B. Folmer, R. P. Sijbesma, R. M. Versteegen, J. A. J. Van der Rijt and E. W. Meijer, *Adv. Mater.*, 2000, **12**, 874.

6 (*a*) H. F. J. M. Jonkheijm, E. W. Meijer and A. P. H. J. Schenning, *Chem. Rev.*, 2005, **105**, 1491; (*b*) P. Jonkheijm, P. van der Schoot, A. P. H. J. Schenning and E. W. Meijer, *Science*, 2006, **313**, 80.

7 H.-J. Kim, J.-H. Lee and M. Lee, *Angew. Chem., Int. Ed.*, 2005, **44**, 5801.

8 (*a*) J. B. Birk, *Nature*, 1967, **214**, 1187; (*b*) S. S. Lehrer, *Subcell. Biochem.*, 1995, **24**, 115; (*c*) D. Sahoo, V. Narayanaswami, C. M. Kay and R. O. Ryan, *Biochemistry*, 2000, **39**, 6594.

9 J.-K. Kim, E. Lee, M.-C. Kim, E. Sim and M. Lee, *J. Am. Chem. Soc.*, 2009, **131**, 17768.

10 V. Percec, M. Glodde, T. K. Bera, Y. Miura, I. Shiyanovskaya, K. D. Singer, V. S. K. Balagurusamy, P. A. Heiney, I. Schnell, A. Rappe, H. W. Spiess, H. D. Hudson and H. Duan, *Nature*, 2002, **417**, 384.