Organic single-nanofiber transistors from organogels†

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The self-assembly of molecules in a gel by strong π–π stacking interactions between the thienylvinylene anthracene backbones and van der Waals interactions between the long alkyl chains has generated nanofibers; from the organogels, organic single-nanofiber transistors were successfully embodied.

Recently, low molecular mass organic gelators (LMOGs) have been utilized to prepare three-dimensional supramolecular networks for optoelectronic applications.[1] A gelation process is an attractive method to produce self-assembled nano- or microstructures *via* molecular interactions such as van der Waals, H-bonding, and π–π stacking interactions. The alignment of the gelators through these molecular interactions can provide various types of fibers, strands, tapes, and tubes. There is an increasing number of reports on one-dimensional (1D) structures constructed *via* a gelation process.[2] The supramolecular structures of thiophene-containing compounds formed through H-bonding interactions were used as effective charge transport channels.[3] However, despite the remarkable potential of organogels for organic transistors, to the best of our knowledge, there are no reports in the literature about organic transistors fabricated from organogels. Herein, we report a simple method to form 1D nano- or microfibers of dodecyl-substituted π-conjugated thienyl-vinylene anthracene through a gelation process and the fabrication of organic single-nanofiber transistors from self-assembled organogels. Our single-nanofiber organic transistors fabricated through a gelation process exhibit p-type electrical characteristics with a high field-effect mobility of 0.48 cm^2 V^{-1} s^{-1} and an on/off ratio of 10.[5]

1D nano- or microstructures of organic semiconducting materials[4] are of great interest for their application to solution-processable organic transistors.[5] The 1D self-assembly of π-conjugated molecules can produce single-crystalline structures without any grain boundaries which can be used as an active channel in organic transistors. Recently, several groups worldwide have developed 1D organic semiconductor transistors from π-conjugated molecules: pentacene derivatives,[6] oligoarene,[7] perylene tetracarboxylic diimide derivatives,[8] hexabenzocoronene,[9] and polythiophene polymers[10] *via* solution-phase self-assembly, not through a gelation process. For the solution process, 1D nano- or microstructure formation of the organic semiconductors is accomplished by

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† Electronic supplementary information (ESI) available: Experimental details for the synthesis, gelation test, device fabrication, electrical measurement, and additional supporting data [TGA, UV, CV, XRD, SEM images, device performance data]. See DOI: 10.1039/b816030a

Scheme 1

solvent-exchange, precipitation, slow evaporation of solvent, adding another solvent to the solution, or self-seeding techniques.[6–10]

In this work, in order to produce 1D nano- or microfibers which can be used as charge transport channels in organic field-effect transistors, we pay attention to a gelation process through which LMOGs tend to form fibrous structures *via* gelator-interactions such as π–π stacking interactions.[11] There was a report of an anthracene derivative that was a non-hydrogen bonding gelator.[12] Recently, we reported the synthesis of 2,6-bis(2-thienylvinyl)anthracene (TVAnT) and its organic thin-film transistor (OTFT) device with a field-effect mobility of up to 0.4 cm^2 V^{-1} s^{-1} using a vapor deposition process.[13] We have selected the rigid thienylvinylene anthracene as the backbone for strong π–π stacking interactions, through which 1D nano- or microfiber formation of thienylvinylene anthracene was attained and charge transport occurred in an organic field-effect transistor. From the known fact that an effective gelation requires long alkyl chains,[1d,2a,b] we have designed and synthesized dodecyl-substituted TVAnT (**DOTVAnT**). The molecular structure and synthesis of **DOTVAnT** are given in Scheme 1 (detailed in ESI†).

The gelation behavior of **DOTVAnT** was examined by dissolving it in various solvents. **DOTVAnT** did not dissolve in a majority of solvents at room temperature. Thus, organogels were produced by heating **DOTVAnT** in dimethyl sulfoxide (DMSO) until the solid **DOTVAnT** was completely dissolved (Fig. 1a, left vial) and allowing the resulting solution to cool. About a minute after cooling, solid-like organogels were formed (Fig. 1a, middle vial). The gels well-dispersed in
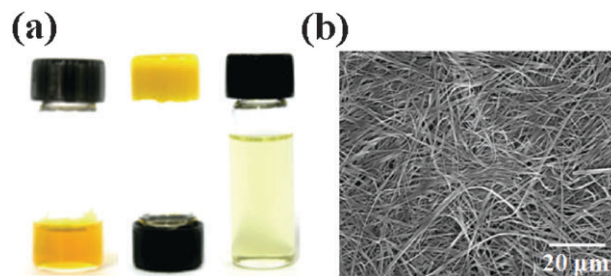

Fig. 1 (a) Photo images of **DOTVAnT** dissolved in dimethyl sulfoxide (left vial), the corresponding organogel at room temperature (middle vial), and well-dispersed **DOTVAnT** xerogel in chloroform (right vial). (b) SEM images of **DOTVAnT** xerogel.

chloroform are also shown (Fig. 1a, right vial). The morphology of the organogels derived from **DOTVAnT** were investigated by analyzing the dried gel (xerogel) with a scanning electron microscope (SEM). As shown in Fig. 1(b), three-dimensional fibrous network structures were formed by the gelation process. The driving forces involved in the gelation process of **DOTVAnT** are strong π–π stacking interactions between the thienylvinylene anthracene backbones and van der Waals interactions between the long alkyl chains. The thin-film X-ray diffraction patterns of the **DOTVAnT** xerogel displayed periodical diffraction peaks. The intense X-ray diffraction peaks obtained at a very low side angle indicated a highly ordered lamellar structure within **DOTVAnT** with a period of 4.75(5) nm (ESI†). Typical dimensions of **DOTVAnT** fibers, determined by SEM and an atomic force microscope (AFM) are as follows: height 30–200 nm, width 0.07–1 μm, and length 30–100 μm. The belt-like microstructures of the **DOTVAnT** gelators were also formed when they were treated with 2-ethoxyethanol solvent (ESI†). 1D nano- or microfibers were formed in polar solvents such as DMSO and 2-ethoxyethanol. However, gelation of **DOTVAnT** did not occur in aromatic solvents such as toluene and xylene, which might be due to the disruption of their aromatic stacking by those solvents. Other morphologically different microstructures were obtained in nonpolar solvents without organogel formation (ESI†).

When a film-type **DOTVAnT** was used as an active channel layer in an OTFT *via* a solution process, the **DOTVAnT** OTFTs exhibited p-type characteristics with an estimated hole mobility of 0.02–0.05 cm² V⁻¹ s⁻¹ in the saturation region (ESI†). We also fabricated a 1D single-nanofiber of **DOTVAnT** organic transistor with bottom-contact geometry. A schematic view of such a single-nanofiber of **DOTVAnT** transistor is given in Fig. 2(a). Fig. 2(b) and 2(c) show a SEM image and an AFM image of the **DOTVAnT** nanofiber transistor, respectively. Fig. 3(a) and 3(b) show the output and transfer characteristics of the single-nanofiber transistor. The field-effect mobility (μ) was extracted from the slope in the saturation regime ($V_{DS} = -30$ V) and W/L was defined as the
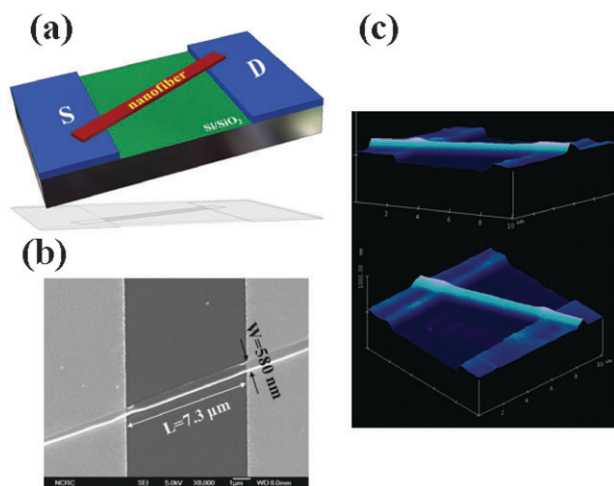
Fig. 2 (a) Schematic view of an individual nanofiber transistor of **DOTVAnT** with bottom-contact geometry. (b) SEM images of the bottom-contact single-nanofiber transistor of **DOTVAnT**. (c) AFM images of the corresponding transistors.
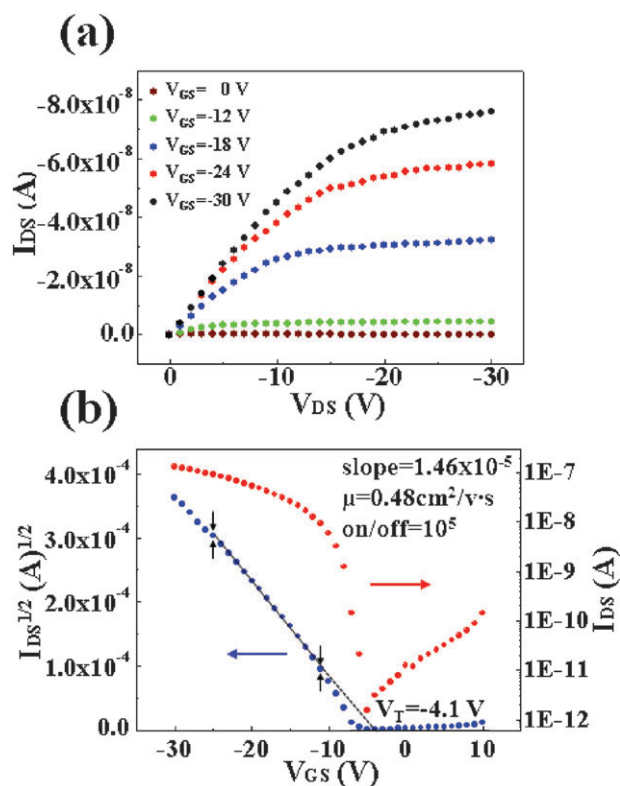
Fig. 3 (a) Output and (b) transfer characteristics of a single-nanofiber transistor of **DOTVAnT**.

ratio of the width of the nanofiber (580 nm) to its channel length across the source–drain electrodes (7.3 μm) as shown in Fig. 2(b). The single-nanofiber transistors exhibited p-type characteristics with an estimated hole mobility (μ) of 0.48 cm² V⁻¹ s⁻¹ in the saturation region over the range of 0.1–0.48 cm² V⁻¹ s⁻¹ and a current on/off ratio of 10.⁵

We tested more than 24 single-nanofiber transistor devices, their motilities were in the range of 0.1–0.48 cm² V⁻¹ s⁻¹ and their threshold voltages (V_T) varied from −4.1 to −9.8 V. Through the study of film-type and single-nanofiber **DOTVAnT** transistors, we find that a single-nanofiber transitor shows much better performance than a film-type transistor with respect to mobility. The diffraction intensities of higher-order peaks of **DOTVAnT** xerogels were stronger than those of the film-type **DOTVAnT** (ESI†), indicating that the long range order of the **DOTVAnT** xerogels was higher than that of the film-type **DOTVAnT**. This is also in good agreement with the mobilities of the devices made from them. Thus, we can explain these results by the fact that a 1D single-nanofiber of **DOTVAnT** produced through a gelation process has a highly ordered structure and thus provides a well-ordered transport path compared with a film-type transistor for which the conduction method is percolation. In fact, we obtained extremely high mobility (up to 8.7 cm² V⁻¹ s⁻¹) from a single-nanofiber transistor with the width as narrow as 70 nm (ESI†). However, at present, sometimes have difficulties in getting its output characteristic curve of I_{DS} *vs*. V_{DS}. This may be due to contact problems. Further studies on such a single-nanofiber transistor with a width less than tens of nanometers are in progress.

In summary, we have developed a simple method to form 1D nano- or microfiber, or belt-like microstructures of dodecyl-substituted π-conjugated thienylvinylene anthracene through a gelation process. The unique gelation capability of **DOTVAnT** comes from strong π–π stacking interactions between the thienylvinylene anthracene backbones and van der Waals interactions between the long alkyl chains. We demonstrated an example of organic single-nanofiber transistors produced from self-assembled organogels with a field-effect mobility of 0.48 cm^2 V^{-1} s^{-1} and an on/off ratio of 10.[5] We also found that a single-nanofiber transistor exhibited much better mobility than a thin film transistor. The higher mobility of the single-nanofiber transistor than that of a thin film transistor can be attributed to the highly ordered structure of **DOTVAnT** nanofibers, as evidenced by a XRD study. We expect that our results will contribute to the preparation of 1D nano- or mirostructures using a gelation process and further advance high-performance organic single-nanofiber transistors which can be used in low-cost, flexible electronic applications.

Notes and references

1 (a) J. P. Luis, V. Laukhin, A. P. D. Pino, J. V. Gancedo, C. Rovira, E. Laukhina and D. B. Amabilino, *Angew. Chem., Int. Ed.*, 2007, **46**, 238; (b) H. Engelkamp, S. Midderbeek and R. J. M. Nolte, *Science*, 1999, **284**, 785; (c) K. Sugiyasu, N. Shinkai and S. Shinkai, *Angew. Chem., Int. Ed.*, 2004, **43**, 1299; (d) B. K. An, D. S. Lee, J. S. Lee, Y. S. Park, H. S. Song and S. Y. Park, *J. Am. Chem. Soc.*, 2004, **126**, 10232; (e) T. Akutagawa, K. Kakiuchi, T. Hasegawa, S.-I. Noro, T. Nakamura, H. Hasegawa, S. Mashiko and J. Becher, *Angew. Chem., Int. Ed.*, 2005, **44**, 7283; (f) A. D. Guerzo, A. G. L. Olive, J. Reichwagen, H. Hopf and J. P. Desvergne, *J. Am. Chem. Soc.*, 2005, **127**, 17984.

2 (a) P. Terech and R. G. Weiss, *Chem. Rev.*, 1997, **97**, 3133; (b) D. J. Abdallah and R. G. Weiss, *Adv. Mater.*, 2000, **12**, 1237; (c) T. Kitahara, M. Shirakawa, S. i. Kawano, U. Beginn, N. Fujita and S. Shinkai, *J. Am. Chem. Soc.*, 2005, **127**, 14980; (d) H. Y. Lee, S. R. Nam and J. I. Hong, *J. Am. Chem. Soc.*, 2007, **129**, 1040.

3 (a) F. S. Schoonbeek, J. H. V. Esch, B. Wegewijs, D. B. A. Rep, M. P. D. Haas, T. M. Klapwijk, R. M. Kellogg and B. L. Feringa, *Angew. Chem., Int. Ed.*, 1999, **38**, 1393; (b) D. B. A. Rep, R. Roelfsema, J. H. V. Esch, F. S. Schooneek, R. M. Kellogg, B. L. Feringa, T. T. M. Palstra and T. M. Klapwijk, *Adv. Mater.*, 2000, **12**, 563; (c) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer and A. P. H. J. Schenning, *Chem. Rev.*, 2005, **105**, 1491.

4 (a) A. L. Briseno, S. C. B. Mannsfeld, S. A. Jenekhe, Z. Bao and Y. Xia, *Mater. Today (Oxford, U. K.)*, 2008, **11**, 38; (b) K. Balakrishnan, A. Datar, R. Oitker, H. Chen, J. Zuo and L. Zang, *J. Am. Chem. Soc.*, 2005, **127**, 10496; (c) Q. Tang, H. Le, Y. Song, Y. Xu, W. Hu, L. Jiang, Y. Liu, X. Wang and D. Zhu, *Adv. Mater.*, 2006, **18**, 3010; (d) Q. Tang, H. Li, Y. Liu and W. Hu, *J. Am. Chem. Soc.*, 2006, **128**, 14634; (e) Q. Tang, H. Li, M. He, W. Hu, C. Liu, K. Chen, C. Wang, Y. Liu and D. Zhu, *Adv. Mater.*, 2006, **18**, 65; (f) Q. Tang, L. Li, Y. Song, Y. Liu, H. Li, W. Xu, Y. Liu, W. Hu and D. Zhu, *Adv. Mater.*, 2007, **19**, 2624; (g) A. P. H. J. Schenning and E. W. Meijer, *Chem. Commun.*, 2005, 3245; (h) Y. Che, A. Datar, K. Balakrishnan and L. Zang, *J. Am. Chem. Soc.*, 2007, **129**, 7234; (i) L. Jiang, Y. Fu, H. Li and W. Hu, *J. Am. Chem. Soc.*, 2008, **130**, 3937.

5 (a) S. Allard, M. Forster, B. Souharce, H. Thiem and U. Scherf, *Angew. Chem., Int. Ed.*, 2008, **47**, 4070; (b) J. E. Anthony, *Chem. Rev.*, 2006, **106**, 5028; (c) S. R. Forrest, *Nature*, 2004, **428**, 911.

6 (a) A. L. Briseno, S. C. B. Mannsfeld, X. Lu, Y. Xiong, S. A. Jenekhe, Z. Bao and Y. Xia, *Nano Lett.*, 2007, **7**, 668; (b) D. H. Kim, D. Y. Lee, H. S. Lee, W. H. Lee, Y. H. Kim, J. I. Han and K. Cho, *Adv. Mater.*, 2007, **19**, 678.

7 Y. Zhou, W. J. Liu, Y. Ma, H. Wang, L. Qi, Y. Cao, J. Wang and J. Pei, *J. Am. Chem. Soc.*, 2007, **129**, 12386.

8 A. L. Briseno, S. C. B. Mannsfeld, C. Reese, J. M. Hancock, Y. Xiong, S. A. Jenekhe, Z. Bao and Y. Xia, *Nano Lett.*, 2007, **7**, 2847.

9 S. Xiao, J. Tang, T. Beetz, X. Guo, N. Tremblay, T. Siegrist, Y. Zhu, M. Steigerwald and C. Nuckolls, *J. Am. Chem. Soc.*, 2006, **128**, 10700.

10 D. H. Kim, J. T. Han, Y. D. Park, Y. Jang, J. H. Cho, M. Hwang and K. Cho, *Adv. Mater.*, 2006, **18**, 719.

11 N. M. Sangeetha and U. Maitra, *Chem. Soc. Rev.*, 2005, **34**, 821.

12 F. Placin, M. Colomes and J.-P. Desvergne, *Tetrahedron Lett.*, 1997, **38**, 2665.

13 M.-C. Um, J. Jang, J. Kang, J.-P. Hong, D. Y. Yoon, S. H. Lee, J.-J. Kim and J.-I. Hong, *J. Mater. Chem.*, 2008, **18**, 2234.