

Short Communication

Surface modification of poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) by confined photo-catalytic oxidation

Ying-Chieh Yen^a, Chih-Chia Cheng^a, Yeh-Sheng Wang^a, Yu-Lin Chu^a, Chu-Hua Lu^a, Wantai Yang^b, Feng-Chih Chang^{a,*}^a Institute of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan^b The State Key Laboratory of Chemical Resource Engineering, College of Materials Science and Engineering, Beijing University of Chemical Technology, P.O. Box 37#, Beijing 100029, China

ARTICLE INFO

Article history:

Received 4 October 2011
Accepted 17 November 2011
Available online 7 December 2011

Keywords:

Confined Photo-catalytic oxidation
MEH-PPV
Water contact angle

ABSTRACT

In this study, the surface of π -conjugated polymer, poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV), was successfully modified with the sulfate anion (SO_4^{4-}) groups by the confined photo-catalytic oxidation (CPO). After the surface modification, the water contact angle of MEH-PPV is changed from 95.5° to 82.1° without influence on its optical properties (based on the UV and PL spectra), and the water droplet can be absorbed on the modified MEH-PPV surface without sliding even at substrate tilt angles of 90° and 180° . The CPO on the MEH-PPV surface is able to further expand the use of MEH-PPV for applications. In addition, the water transport test indicates that the modified MEH-PPV can be a candidate for transporting water droplet.

© 2011 Elsevier Inc. All rights reserved.

1. Introduction

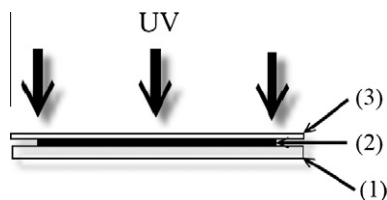
Recently, the development in π -conjugated polymers such as polythiophene (PT) [1], poly(p-phenylenevinylene) (PPV) [2], polyfluorene (PF) [3] and poly(triphenyl amine) [4] derivatives employed for optoelectronic and energy generating devices has spurred more and more attention because of the increased demand for devices with higher performance [5]. Since the Cambridge group discovered the application of PPV in 1990 [2a], it has become one of those popular π -conjugated polymers due to its lower operating voltages, better processability, and easier color tunability in terms of LED application as compared with several π -conjugated polymers and low-molecular-weight organic materials [2,6–8]. Poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) belonging to the PPV derivatives which possesses improved solubility also has attracted much interest from academia and industry. Through appropriate design of the process, it can be successfully incorporated into several advanced optical-electronic devices and play a critical role affecting their performance [6–8].

In order to fit PPV for more applicable use, the modification on it is an important issue in the field. Kang et al. attached PPV to polyhedral oligomeric silsesquioxane (POSS) cage and found that the brightness and efficiency of the related devices were improved. Bakueva et al. introduced iodine into PPV and observed the

influence of the incorporation on the properties of PPV [6b]. Wery et al. [6c] and Li and coworkers [6d] prepared composites comprising carbon nanotubes and PPV, indicating the drastic changes in the properties. Other nanoparticles such as SiO_2 [7a] and TiO_2 [7b–e] were also considered as candidates for the modification of PPV. In addition, the modification of the side chain [8a–d] and end groups [8e] of PPV and the copolymerization of PPV with other polymers have also been studied [8f–h]. Besides these modification strategies mentioned above, the study on the surface modification of the PPV surface is still lacking [9]. Surface modification is a convenient and useful strategy, which can change surface properties of materials without the influence on their bulk properties. In the previous work, Yang et al. has studied the hydrophilic modification method, confined photo-catalytic oxidation (CPO), on the surface of several commercialized polymers and indicated that the sulfate anion (SO_4^-) groups can be quickly attached to their surface [10]. Additionally, further treatment with D.I. water and heat can change the group to hydroxyl group. This surface modification strategy can be carried out easily and the resulting surface can be applied for additional reactions and other advanced use [10]. In the present study, the CPO is performed on the surface of MEH-PPV spin coated on quartz. The XPS and contact angle measurements indicate that the surface can be successfully modified and exhibit relatively higher degree of hydrophilicity. The absorption test shows that the more hydrophilic MEH-PPV surface can absorb water droplet from the pristine surface. This surface modification is able to further expand the use of MEH-PPV for applications.

* Corresponding author.

E-mail address: changfc@mail.nctu.edu.tw (F.-C. Chang).



Scheme 1. Schematic diagram of photoirradiation apparatus: (1) quartz, (2) MEH-PPV, and (3) BOPP top layer.

2. Experimental

2.1. Materials

MEH-PPV was purchased from Sigma–Aldrich (USA). Toluene and ammonium persulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ were purchased from Acros Organics (Germany) and used as received. Biaxial oriented polypropylene (BOPP) was from the State Key Laboratory of Chemical Resource Engineering, College of Materials Science and Engineering, Beijing University of Chemical Technology (Prof. Wantai Yang's group). Quartz was purchased from Momentive Performance Materials (USA) with 99.99% purity and it was washed with acetone and dried in an oven before use.

2.2. Sample preparation

Desired amount of MEH-PPV was dissolved in toluene to form a 1 wt% solution. The resulting solution was dropped to quartz and then spin coated at 1500 rpm for 30 s. The sample was dried in vacuum (0.2 torr) for 3 h at 30 °C. The photoirradiation system used was shown schematically in Scheme 1. The BOPP top layer was cleaned with deionized water and acetone. A desired amount of

30 wt% $(\text{NH}_4)_2\text{S}_2\text{O}_8$ aqueous solution (30 μl) was deposited on the MEH-PPV surface coated on quartz through a micro-syringe. The BOPP top layer transparent to UV light covered this solution, and the drop of solution was spread into an even and very thin liquid layer (about 2 μm) under suitable pressure. The assembled unit was then irradiated by UV radiation (UV lamp: 3000 $\mu\text{W}/\text{cm}^2$ at 254 nm measured by spectrometer) from the topside at room temperature for 3, 9, and 15 min. After the irradiation, BOPP top layer was peeled off and the modified MEH-PPV surface was rinsed by deionized water several times to clean the treated surface absolutely, dried in vacuum (0.2 torr) at 30 °C and kept in sealed plastic bag for measurements.

2.3. Characterizations

Ultraviolet–visible (UV–vis) and photoluminescence (PL) spectra were measured using HP 8453 diode-array spectrophotometer and Hitachi F-4500 luminescence spectrometer, respectively. High resolution X-ray Photoelectron Spectrometer (XPS) was measured by PHI Quantera SXM/Auger: AES 650.

3. Results and discussion

Table 1 summarizes the water contact angles of the pristine and modified MEH-PPV surfaces undergone different CPO time. As listed in Table 1, the pristine MEH-PPV is relatively hydrophobic

Table 1
Contact angles of the pristine and modified MEH-PPV.

	Pristine MEH-PPV (°)	UV exposure for 15 min without $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (°)	CPO for 3 min (°)	CPO for 9 min (°)	CPO for 15 min (°)
Contact angle ^a	95.5	93.3	84.3	82.6	82.1

^a The calculation of contact angles is shown in the Supporting information.

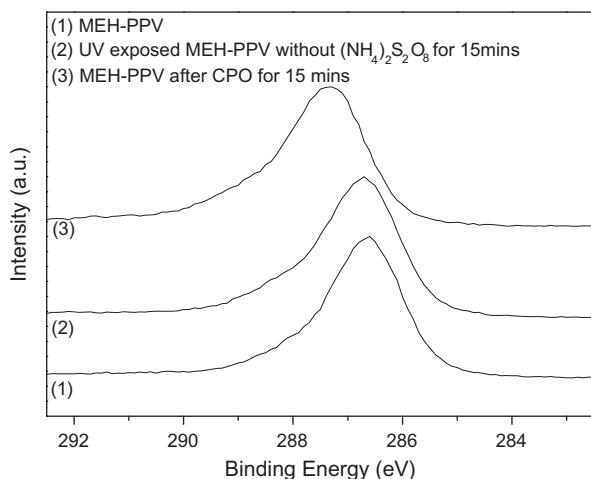


Fig. 1. C1s peaks of XPS measurement from pristine MEH-PPV, MEH-PPV after CPO for 15 min and UV exposed MEH-PPV without $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution.

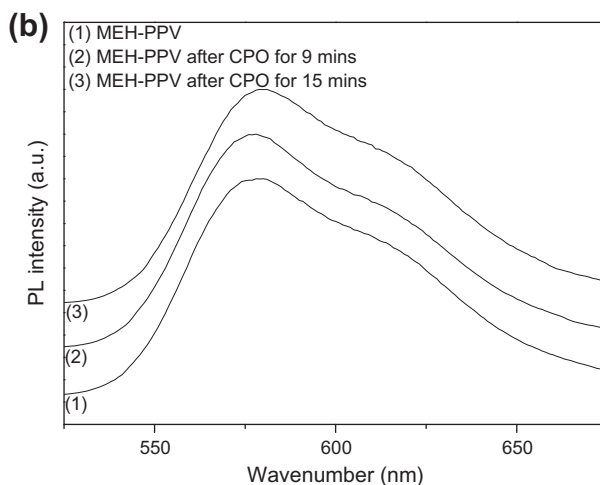
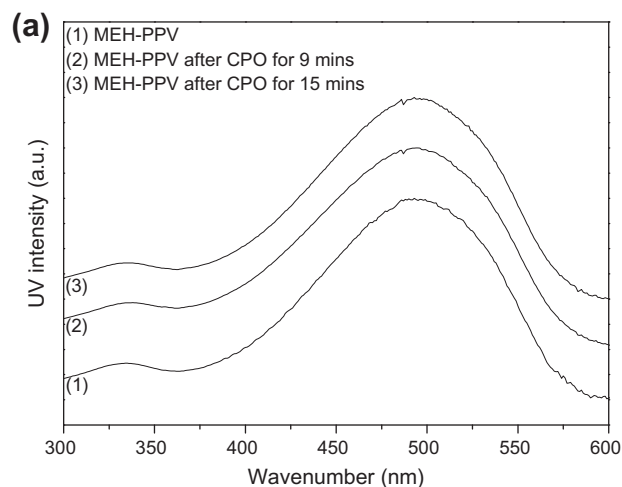


Fig. 2. (a) UV and (b) PL spectra of the pristine and modified MEH-PPV.

and exhibits water contact angle of 95.5° which is attributed to its chemical structure. After the CPO process, the water contact angle is gradually changed to 82.1° , indicating that the modification on the MEH-PPV surface with sulfate anion group indeed leads it being more hydrophilic. On the contrary, the surface of MEH-PPV after UV exposure without the presence of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution still exhibits water contact angle as similar as the pristine MEH-PPV. It can be evidence that the contact angle change is not from MEH-PPV exposed only by UV but is from the CPO.

Fig. 1 displays the C1s peaks from XPS measurement of pristine MEH-PPV, MEH-PPV after CPO for 15 min and UV exposed MEH-PPV without $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution, respectively. As shown in Fig. 1, the binding energy of C1s retains almost unchanged during the UV exposure of MEH-PPV without $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution. However, if there is $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution during UV exposure (CPO), the C1s peak of pristine MEH-PPV is slightly shifted after the surface modification, which implies the change and successful modification of the MEH-PPV surface. In addition, through directly dropping water droplet to the pristine and modified MEH-PPV surfaces, we could observe that the water droplet slid down the pristine MEH-PPV surface very quickly whereas it was absorbed on the modified MEH-PPV surface without further sliding. Although the water contact angle is slightly decreased from 95.5° to 82.1° , the above consequence indicates the substantial change in the MEH-PPV surface behavior.

Fig. 2 shows bulk state UV and PL spectra of the pristine and modified MEH-PPV. In the UV spectra, pristine MEH-PPV exhibits a broad UV absorption at 493 nm, and the UV absorption retains unchanged after CPO, indicating that the CPO process does not affect the UV absorption of MEH-PPV. In addition, the PL spectra also show the same behavior. Both light absorption and emission properties are not affected by the CPO process, revealing that the surface modification can result in appreciable change in the surface properties without the influence on the optical properties of MEH-PPV.

The water contact angle data and water drop test from the modified MEH-PPV surface promote the further investigation on the

surface property. The water sliding test was performed through dropping water droplet to the modified MEH-PPV surface tilted to 90° and even 180° for observing the change in the water droplet (Supporting information).

The water droplet does not slide from the surface, indicating the good adhesion of the water droplet absorbed on the modified MEH-PPV surface after CPO. The adhesion force of surface was found to depend strongly on its chemical composition [11] and topography [12,13]. For the modified MEH-PPV surface, the change in the surface chemical composition may be the major factor to increase the adhesion force. In addition, the feasibility of materials for transporting water droplet has been studied in our previous study [13]. We also performed the water transport test using the modified MEH-PPV surface. As shown in Fig. 3a, the underside is the pristine MEH-PPV surface while the upper is the modified MEH-PPV surface. Firstly, a water droplet was dropped to the pristine MEH-PPV surface. Then, the underside was shifted gradually to the upper until the water droplet touched the upper surface. Finally, the underside was shifted away from the upper. The change in the water droplet during the whole transport test was observed and the micrographs are shown in Fig. 3b–f. This is the first time that the modified π -conjugated polymer possesses the water transport behavior although the transport is imperfect. The consequence indicates that the hydrophobic MEH-PPV can be a candidate for transporting water droplet after CPO without loss of its optical properties.

4. Conclusions

The surface of the MEH-PPV spin coated on quartz is successfully modified with sulfate anion groups through the CPO. The water contact angle, sliding test, UV, and PL spectra indicate that the surface modification on MEH-PPV can result in appreciable change in the surface behavior without the influence on its optical properties. In addition, the water droplet can be absorbed on the modified MEH-PPV surface without sliding even if at substrate tilt angles of 90° and 180° . The water transport test shows that the modified MEH-PPV surface can absorb water droplet from the pristine MEH-PPV surface. This is the first time that the modified π -conjugated polymer possesses the water transport behavior and the CPO on the MEH-PPV surface is able to further expand the use of MEH-PPV for applications.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jcis.2011.11.040](https://doi.org/10.1016/j.jcis.2011.11.040).

References

- [1] (a) I. McCulloch, M. Heeney, M.L. Chabinyc, D. DeLongchamp, R.J. Kline, M. Coelle, W. Duffy, D. Fischer, D. Gundlach, B. Hamadani, R. Hamilton, L. Richter, A. Salleo, M. Shkunov, D. Sporrowe, S. Tierney, W. Zhong, *Adv. Mater.* 21 (2009) 1091; (b) J. Yu, S. Holdcroft, *Chem. Mater.* 14 (2002) 3705; (c) M.R. Andersson, O. Thomas, W. Mammo, M. Svenson, M. Theander, O. Inganäs, *J. Mater. Chem.* 9 (1999) 1933; (d) J. Ianhua, J. Zou, L. Liu, H. Chen, S.I. Khondaker, R.D. McCullough, Q. Huo, L. Zhai, *Adv. Mater.* 20 (2008) 2055.
- [2] (a) J.H. Bourroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackey, R.H. Friend, P.L. Burns, A.B. Holmes, *Nature* 347 (1990) 539; (b) T.E. Dykstra, E. Hennebicq, D. Beljonne, J. Gierschner, G. Claudio, E.R. Bittner, J. Knoester, G.D. Scholes, *J. Phys. Chem. B* 113 (2009) 656.
- [3] (a) Q. Pei, Y. Yang, *J. Am. Chem. Soc.* 118 (1996) 7416; (b) J.I. Lee, G. Klaerner, R.D. Miller, *Chem. Mater.* 11 (1999) 1083; (c) F.I. Wu, S. Reddy, C.F. Shu, M.S. Liu, A.K.Y. Jen, *Chem. Mater.* 15 (2003) 269; (d) D. Marsitzky, R. Vestberg, P. Blainey, B.T. Tang, C.J. Hawker, K.R. Carter, *J. Am. Chem. Soc.* 123 (2001) 6965; (e) W.L. Yu, J. Pei, Y. Cao, W. Huang, A.J. Heeger, *Chem. Commun.* (1999) 1837; (f) J. Gao, M. Kwak, J. Wildeman, A. Hermann, M.A. Loi, *Carbon* 49 (2011) 333.

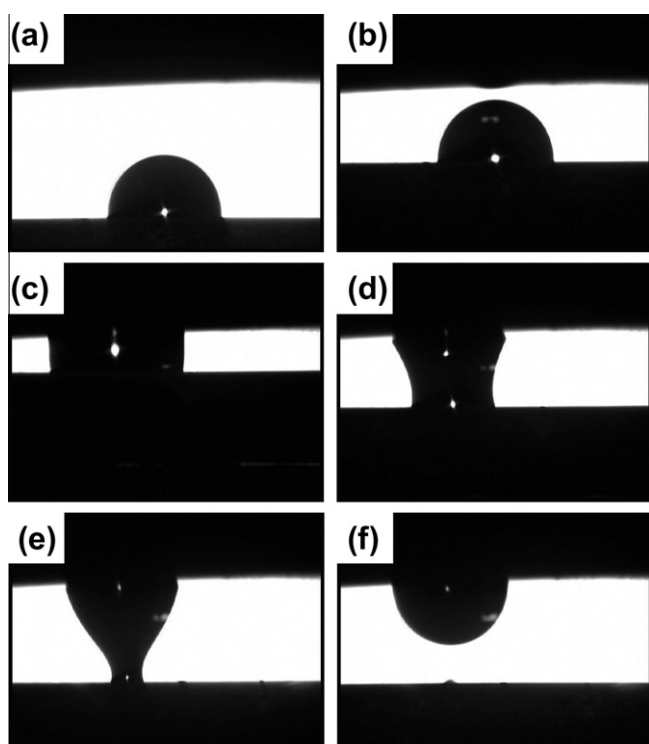


Fig. 3. Graphs illustrate the change during the water droplet transport test.

- [4] (a) C. Adachi, K. Nagai, N. Tamoto, *Appl. Phys. Lett.* 66 (1995) 2679;
(b) G.K. Paul, J. Mwaura, A.A. Argum, P. Taraneekar, J.R. Reynolds, *Macromolecules* 39 (2006) 7789;
(c) J. Li, C. Ma, J. Tang, C. Lee, S. Lee, *Chem. Mater.* 17 (2005) 615;
(d) Q. Zhang, J. Chen, Y. Chen, L. Wang, D. Ma, X. Jiang, F. Wang, *J. Mater. Chem.* 14 (2004) 895.
- [5] (a) N.K. Guimar, N. Gomez, C.E. Schmidt, *Prog. Polym. Sci.* 32 (2007) 876;
(b) H. Peng, L.J. Zhang, C. Soeller, J. Travas-Sejdic, *Biomaterials* 30 (2009) 2132;
(c) E. Frackowiak, F. Beguin, *Carbon* 39 (2001) 937;
(d) L. Akcelrud, *Prog. Polym. Sci.* 28 (2003) 875;
(e) T.M. Clarke, J.R. Durrant, *Chem. Rev.* 110 (2010) 6736.
- [6] (a) H.K. Shim, J.I. Jin, *Adv. Polym. Sci.* 158 (2002) 193;
(b) L. Bakueva, D. Matheson, S. Musikhin, E.H. Sargent, *Synth. Metal* 126 (2002) 207;
(c) J. Wery, H. Aarab, S. Lefrant, E. Faulques, E. Mulazzi, R. Perego, *Phys. Rev. B* 67 (2003) 115202;
(d) Z.P. Li, H.T. Guan, N. Yu, Q. Xu, I. Imae, J.Y. Wei, *J. Phys. Chem. B* 114 (2010) 10119.
- [7] (a) Q. Zhang, Y.G. Zhai, F.Q. Liu, M. Yang, G. Gao, *Eur. Polym. J.* 44 (2008) 3957;
(b) D.A.R. Barkhouse, H.E. Bishop, B.M. Henry, G.R. Webster, P.L. Burn, H.E. Assender, *Org. Electron.* 11 (2010) 649;
(c) J.C. Liu, W.L. Wang, H.Z. Yu, Z.L. Wu, J.B. Peng, Y. Cao, *Energy Mater. Sol. C* 92 (2008) 1403;
(d) S.N. Hsieh, S.P. Chen, C.Y. Li, T.C. Wen, T.F. Guo, Y.J. Hsu, *Org. Electron.* 10 (2009) 1626;
(e) H.W. Geng, R.X. Peng, S.K. Han, X.H. Gu, M.T. Wang, *J. Electron. Mater.* 39 (2010) 2346.
- [8] (a) J. Davenasa, M. Chouikia, S. Besbesa, A. Ltaiefa, H. ben Ouadab, A. Bouazizib, H. Tradc, M. Majdoubc, *Synth. Metal* 139 (2003) 617;
(b) C. Buchgraber, J. Spanring, W. Kern, A. Pogantsch, *Macromol. Chem. Phys.* 206 (2005) 2362;
(c) T. Tanase, J. Wildeman, P.W.M. Blom, M.E. Mena Benito, D.M. de Leeuw, A.J.J.M. van Breemen, P.T. Herwig, C.H.T. Chlon, J. Sweelssen, H.F.M. Schoo, *J. Appl. Phys.* 97 (2005) 123703;
(d) W.L. Yeh, H.L. Chen, S.A. Chen, *Synth. Metal* 157 (2007) 407;
(e) Y. Huang, Z.Y. Lu, Q. Peng, Q. Jiang, R.G. Xie, S.H. Han, L.G. Dong, J.B. Peng, Y. Cao, M.G. Xie, *Macromol. Chem. Phys.* 93 (2005) 95;
(f) B. Zaidi, S. Ayachi, A. Mabrouk, J.L. Fave, P. Molinie, M. Ghedira, K. Alimi, *J. Appl. Polym. Sci.* 89 (2003) 3091;
(g) F. D'Amore, J. Osmond, S. Destri, M. Pasini, V. Rossi, W. Porzio, *Synth. Metal* 149 (2005) 123;
(h) C.S. Wu, Y. Chen, *Macromolecules* 42 (2009) 3729.
- [9] C.D. Skordoulis, H.J. Brouwer, G. Hadziioannou, *Opt. Laser Technol.* 1 (1999) 259.
- [10] (a) P. Yang, J.Y. Deng, W.T. Yang, *Polymer* 44 (2003) 7157;
(b) J. Liang, Y. Ma, F. Wang, W. Yang, *Chem. Mater.* 22 (2010) 4254;
(c) P. Yang, M. Yang, S. Zou, J. Xie, W. Yang, *J. Am. Chem. Soc.* 129 (2007) 1541;
(d) J. Deng, L. Wang, L. Liu, W. Yang, *Prog. Polym. Sci.* 34 (2009) 156.
- [11] (a) K. Feldman, T. Tervoort, P. Smith, N.D. Spencer, *Langmuir* 14 (1998) 372;
(b) J. Tsibouklis, P. Graham, P.J. Eaton, J.R. Smith, T.G. Nevell, J.D. Smart, R.J. Ewen, *Macromolecules* 33 (2000) 8460;
(c) P. Eaton, J.R. Smith, P. Graham, J.D. Smart, T.G. Nevell, J. Tsibouklis, *Langmuir* 18 (2002) 3387.
- [12] (a) M. Jin, X. Feng, L. Feng, T. Sun, J. Zhai, T. Li, L. Jiang, *Adv. Mater.* 17 (2005) 1977;
(b) L. Feng, Y. Zhang, J. Xi, Y. Zhu, N. Wang, F. Xia, L. Jiang, *Langmuir* 24 (2008) 4114;
(c) S. Boduroglu, M. Cetinkaya, W.J. Dressick, A. Singh, M.C. Demirel, *Langmuir* 23 (2007) 11391.
- [13] (a) C.S. Liao, C.F. Wang, H.C. Lin, H.Y. Chou, F.C. Chang, *J. Phys. Chem. C* 112 (2008) 16189;
(b) X. Hong, X. Gao, L. Jiang, *J. Am. Chem. Soc.* 129 (2007) 1478;
(c) C.S. Liao, C.F. Wang, H.C. Lin, H.Y. Chou, F.C. Chang, *Langmuir* 25 (2009) 3359.