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Pyromellitic Dithioimides: Thionation Improves Air-Stability and Electron Mobility of N-Type Organic Field-Effect Transistors

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Thionation and fluorination of pyromellitic diimides (PyDIs) increased the electron mobility and on/off ratio of the original diimides by two orders of magnitude and improved the threshold voltage and air-stability of diimide compounds.

Organic field-effect transistors (OFET) have been extensively explored in both academia and industry for their potential applications in large-area and flexible electronics.¹ Under ambient conditions, most of the OFET materials exhibit unipolar transport properties (i.e., they are either P-type or N-type).²⁻⁶ However, complementary circuits with large noise margin and low power dissipation require air-stable OFETs with both P- and N-type transport properties. Remarkable progress has been made on air-stable P-type OFETs such as fused acene, thiophene, and thienoacene derivatives with hole mobilities exceeding that of amorphous silicon FET ($\sim 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).² In contrast, air-stable N-type OFETs have been rarely reported. Although N-type OFET research has accelerated in the past decade, only a few of the proposed devices can be operated under ambient conditions.³⁻⁶ The most attractive candidates for N-type OFETs are perylene diimides (PDIs),³ naphthalene diimides (NDIs),⁴ anthracene diimides (ADIs),⁵ and pyromellitic diimides (PyDIs),⁶ which possess high electron mobilities and deep lowest unoccupied molecular orbital (LUMO) levels. Because of the high susceptibility of radical anions, the electron mobilities of N-alkyl diimide analogues rapidly decay under ambient conditions.^{4a,7} The LUMO levels of diimide compounds can be stabilized by introducing strong electron-withdrawing groups, such as $-\text{CN}$, $-\text{F}$, $-\text{Cl}$, and $-\text{Br}$, into the diimide framework.³⁻⁶ The effectiveness of this strategy in realizing air-stable N-type OFET materials has been already demonstrated. However, the synthesis procedure for the introduction of electron-withdrawing groups (e.g. CN and Br) onto the diimide compounds is lengthy.^{5,6b} Therefore, the investigation of new electron-withdrawing units appropriate to

N-type OFET materials is still sought. Recently, Aso^{8a} and Seferos *et al.*^{8b} sequentially demonstrated that the simple thionation of diimide compounds not only increases the intermolecular interactions but also reduces their LUMO levels compared with those of their parent compounds. Moreover, the electron mobilities of dithioimide compounds are two orders of magnitude higher than those of diimide compounds under a nitrogen atmosphere.

PyDI is one of well-known N-type OFET materials with a small aromatic core which is favorable for tuning its chemical structure and physical property. Furthermore, the starting material of PyDI, pyromellitic dianhydride, is much cheaper and easier prepared than those of NDIs and PDIs which provides an advantage in large scale synthesis. Herein, we report on the syntheses, electron mobilities, and air-stabilities of two pyromellitic dithioimides (PyDTIs) with different N-substituents and their PyDI parent compound (see Fig. 1(a)). The LUMO level (calculated by density functional theory (DFT) at the B3LYP/6-31G** level with GAUSSIAN 09 Program) was 0.71 eV lower in PyDTI-F than in PyDI-F (Fig. 1(b)).⁹ The stabilization of the LUMO level not only decreases the injection barrier of the electrons into the metal electrode but also improves the air-stability of the OFET. Furthermore, the sulfur atoms of PyDTI-F admit a higher population of LUMOs than the oxygen atoms of PyDI-F. This property increases the intermolecular electronic coupling in the solid state, thereby enhancing the charge mobility of the device. The electron mobility of the PyDTI-F-based OFET reached up to 0.6

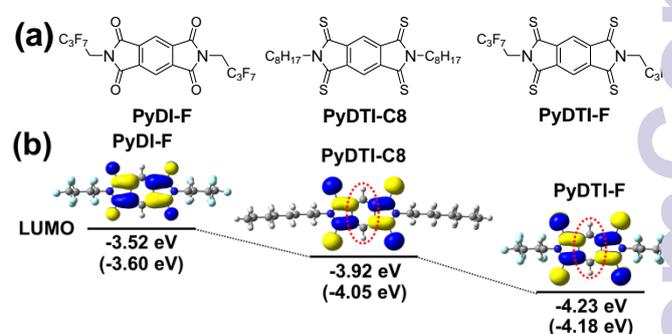


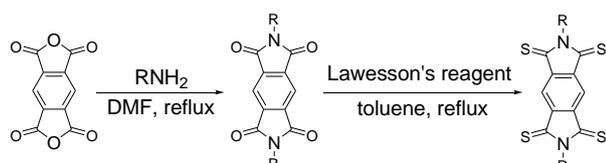
Fig. 1 (a) Chemical structures, (b) calculated LUMO levels of PyDI-F and PyDTIs. Values in parenthesis are obtained from cyclic voltammetry (CV). The red circles indicate the nonbonding characteristics.

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Scheme 1. Synthetic routes, reagents and conditions to PyDTI derivatives.

$\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ under ambient conditions, accompanied by a high on/off ratio (5.5×10^5) and a low threshold voltage ($V_{th} = 16.1$ V).

The PyDTI derivatives were synthesized by the methodology outlined in Scheme 1. First, PyDIs were synthesized by imidization reaction of pyromellitic dianhydride with different amines in the presence of dimethylformamide (DMF). The obtained PyDIs were thionated with Lawesson's reagent in toluene to obtain PyDTI analogues. After purification by flash column chromatography, all compounds were confirmed by NMR and mass spectroscopy. Single crystals of PyDTI-C8 were successfully grown by slow diffusion of hexane into the PyDTI-C8 solution in CHCl_3 . The crystal structure was compared with that of *N,N'*-di(*n*-tetradecyl)pyromellitic diimide (PyDI-C14),¹⁰ which exhibits typical herringbone stacking (Fig. 2(a)). The molecular arrangement of the thionated compound (PyDTI-C8) is face-to-face packing with a very short π - π distance of 3.39 Å owing to the interaction between the electron-rich phenyl ring and electron-poor bisthiosuccinimide (Fig. 2(b)).

To investigate the influence of thionation on OFET performance, thin films of PyDI-F and PyDTIs were fabricated on Si/SiO₂ substrates modified or unmodified with cyclic olefin copolymers (COC) and octadecyltrichlorosilane (ODTS) at variable substrate temperatures (T_s). All PyDTIs devices exhibited typical N-type properties under ambient conditions. The electron mobilities (μ_e) were determined from the saturation regime at a source-drain (V_d) voltage of 80 V. The performances of all OFET devices are summarized in Table 1. Note that none of the PyDI-F-based devices exhibited N-type characteristics under ambient conditions. The OFETs of PyDTI-C8 presented N-type characteristics only when deposited on COC-modified substrate at $T_s = 25$ and 35 °C. (Fig. S1, Supporting Information). The PyDTI-C8 achieved a maximum electron mobility and an on/off ratio of $\sim 5.8 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $\sim 2.54 \times 10^3$, respectively. In comparison, the PyDTI-F-based OFETs exhibited superior performances on all tested substrates. Fig. 3 plots the output and transfer characteristic curves of PyDTI-F-based OFETs fabricated on different substrates at $T_s = 25$ °C. Under ambient conditions, PyDTI-F on ODTS-modified substrate exhibited an electron mobility as high as $0.62 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ along with an on/off ratio of 5.5×10^5 and a low threshold voltage ($V_{th} = 16.1$ V).

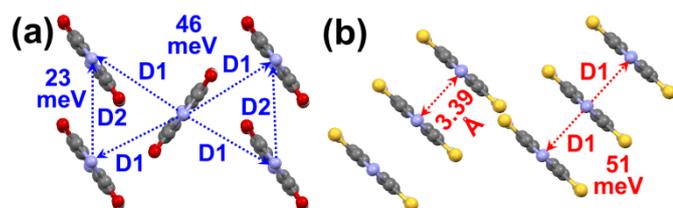


Fig. 2 The electronic couplings and molecular packing of (a) PyDI-C14 and (b) PyDTI-C8 viewed along the molecular axes. For clarity, side chains of molecules are omitted.

Table 1. The average electrical parameters of PyDTI-C8 and PyDTI-F based OFETs. The parameters in parenthesis are the best values achieved from all the devices.

Device	T_s (°C)	Substrate	μ_e ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	V_{th} (V)	On/off
PyDTI-C8	25	COC	3.5×10^{-3} (5.8×10^{-3})	23.2 (21.2)	6.0×10^2 (7.3×10^2)
		COC	3.3×10^{-3} (4.4×10^{-3})	29.2 (26.5)	5.6×10^2 (2.5×10^3)
	Bare	0.26 (0.31)	8.9 (8.5)	9.8×10^3 (4.3×10^4)	
PyDTI-F	25	ODTS	0.46 (0.62)	22.9 (16.1)	1.9×10^5 (5.5×10^5)
		COC	0.52 (0.59)	10.0 (8.3)	9.0×10^3 (1.8×10^4)
	Bare	0.18 (0.22)	3.0 (1.9)	2.1×10^3 (3.9×10^3)	
	50	ODTS	0.32 (0.43)	18.8 (12.2)	1.1×10^5 (3.8×10^5)
		COC	0.56 (0.59)	11.3 (9.7)	7.4×10^5 (2.8×10^6)

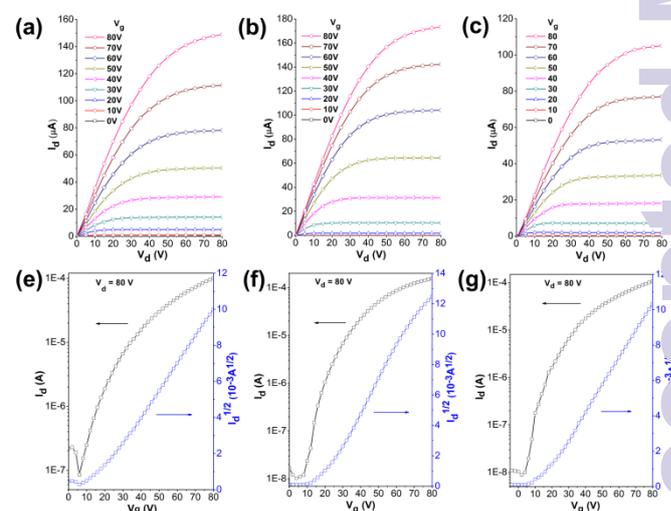


Fig. 3 (a-c) Output and (e-g) transfer characteristics of PyDTI-F OFETs ($T_s = 25$ °C) on (a, e) bare (b, f) ODTS-modified and (c, g) COC-modified substrates.

Surprisingly, thionation and fluorination not only increased the electron mobility and on/off ratio of the original diimide compounds by two orders of magnitude but also improved the threshold voltage and air-stability of these compounds. As given in Fig. S2, the X-ray diffraction (XRD) patterns of both PyDTI-C8 and PyDTI-F films ($T_s = 25$ °C) exhibited sharp (00l) reflections corresponding to *d*-spacings of 14.3 and 17.7 Å, respectively, which are consistent with crystallographic *c*-axis of PyDTI-C8 (14.1 Å) and the molecular length of PyDTI-F (18.6 Å). These results suggest that the PyDTIs molecules have a π -stacking orientation parallel to the substrate to form highly ordered lamellar structures, which are favorable for the charge transport between source and drain electrodes. To investigate the influence of substrate and substrate temperature on the OFET performance, the morphologies of thin films of PyDTI-F were analyzed by atomic force microscopy (AFM). As shown in Fig. 4, they have similar textures of terraced plate, regardless of the substrate and substrate temperature. The terrace sizes increased with substrate temperature on all substrates. At substrate

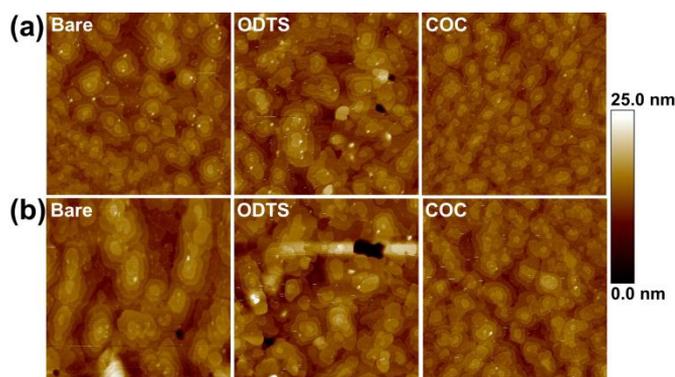


Fig. 4 AFM images ($3 \mu\text{m} \times 3 \mu\text{m}$) of PyDTI-F films based on different substrates (a) $T_s = 25 \text{ }^\circ\text{C}$ and (b) $T_s = 50 \text{ }^\circ\text{C}$.

temperatures exceeding $50 \text{ }^\circ\text{C}$, however, significant cracks appeared in the thin films, which appropriately explain the OFET performances.

At room temperature, charge transfer in organic semiconductors is believed to be governed by thermal hopping between neighboring molecules. This phenomenon is described by Marcus electron-transfer theory,¹¹ which posits that a high charge-transfer rate can be achieved by minimizing the reorganization energy (λ) and maximizing the electronic coupling (t). The electronic couplings (t) between electron transfers in dimers extracted from single crystalline structures were predicted by the Amsterdam density functional (ADF) program at the PW91PW91/TZ2P level with dispersion correction.¹² The t value of PyDTI-C8 along dimer 1 (D1) was 51 meV, higher than those of PyDI-C14 (D1 = 46 meV; D2 = 23 meV; see Fig. 2). Moreover, the reorganization energy of electron transfer ($\lambda = 530 \text{ meV}$) was much higher in PyDI-F than in PyDTI-C8 ($\lambda = 255 \text{ meV}$) and PyDTI-F ($\lambda = 287 \text{ meV}$). The relatively small λ values of the PyDTIs are related to the nonbonding characteristics of the edge-tip carbon atoms of phenyl rings (Fig. 1(b))¹³ and sufficiently explain the high electron mobility of PyDTI-F relative to the PyDI derivatives.⁶ The λ values also decreased in thionated NDI and PDI derivatives (Table S2, Supporting Information).

The electrochemical behaviors of PyDI-F and PyDTIs were explored by cyclic voltammetry (CV) (see Fig. 5). The experimental LUMO levels were estimated from the empirical relation $E_{\text{LUMO}} = -4.8 - (E_{\text{red}}^{1/2} - E_{\text{ox, ferrocene}}) \text{ eV}$. The experimental LUMO level of

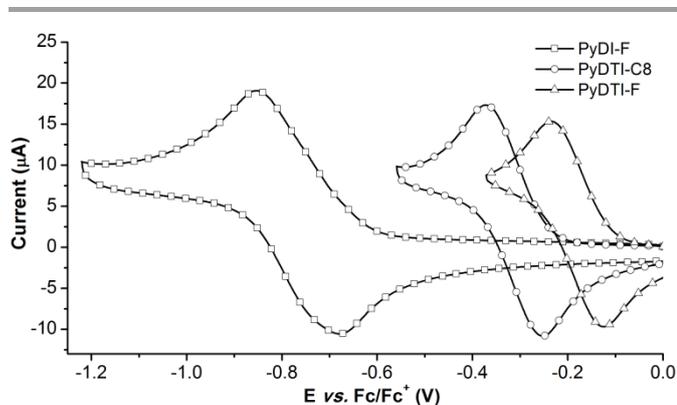


Fig. 5 Cyclic voltammograms of PyDI-F and PyDTIs in CH_2Cl_2 containing $0.1 \text{ M } n\text{-Bu}_4\text{NPF}_6$.

PyDTI-F was -4.18 eV , which is 0.58 eV deeper than that of PyDI-F and consistent with the calculation. The experimental LUMO levels of PyDTIs were much lower than those of PyDI-F, indicating a stronger electron withdrawing ability of the thioimide group than that of the imide group. Although oxygen is more electronegative than sulfur, oxygen atoms are comparatively small and consequently their electronic orbitals are very tight. The interelectronic repulsion induced by an additional electron is higher in oxygen than in sulfur. Thus, the electron withdrawing ability of the imide group is lower than expected. The low lying LUMO level of PyDTI-F improves the air-stability and reduces the threshold voltage of the N-type OFET.

In conclusion, the LUMO levels of diimide compounds can be simply stabilized by thionation. Moreover, thionation simultaneously increases the electronic couplings and reduces the reorganization energies of diimide compounds. Therefore, N-type devices based on PyDTI-F display superior performance and air-stability under ambient conditions. The present work conducted a comprehensive experimental and theoretical examinations of the effects of thionation in OFET materials. The insights gained will benefit not only applications of OFETs but also the development of organic photovoltaic devices and light-emitting diodes.

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References

- (a) C. D. Dimitrakopoulos and P. R. Malenfant, *Adv. Mater.*, 2002, **14**, 99-117; (b) C. R. Newman, C. D. Frisbie, D. A. da Silva Filho, J. Brédas, P. C. Ewbank and K. R. Mann, *Chem. Mater.*, 2004, **16**, 4430-4451; (c) J. E. Anthony, *Chem. Rev.*, 2006, **106**, 5028-5048; (d) V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey and J. Brédas, *Chem. Rev.*, 2007, **107**, 926-952; (e) Y. Shirota and H. Kageyama, *Chem. Rev.*, 2007, **107**, 953-1010; (f) A. R. Murphy and M. J. Fréchet, *Chem. Rev.*, 2007, **107**, 1066-1096; (g) M. Mas-Torres and C. Rovira, *Chem. Soc. Rev.*, 2008, **37**, 827-838; (h) J. Zhang, Y. Zha, Z. Wei, Y. Sun, Y. He, C. Di, W. Xu, W. Hu, Y. Liu and D. Zhu, *Adv. Funct. Mater.*, 2011, **21**, 786-791.
- (a) K. Takimiya, H. Ebata, K. Sakamoto, T. Izawa, T. Otsubo and Kunugi, *J. Am. Chem. Soc.*, 2006, **128**, 12604-12605; (b) M. L. Tang, D. Reichardt, T. Siegrist, S. C. B. Mannsfeld and Z. Bao, *Chem. Mater.*, 2008, **20**, 4669-4676; (c) T. Yamamoto and K. Takimiya, *J. Am. Chem. Soc.*, 2007, **129**, 2224-2225; (d) H. Ebata, T. Izawa, E. Miyazaki, K. Takimiya, M. Ikeda, H. Kuwabara and T. Yui, *J. Am. Chem. Soc.*, 2007, **129**, 15732-15733; (e) M. M. Payne, S. R. Parkin, J. E. Anthony, C. Kuo and T. N. Jackson, *J. Am. Chem. Soc.*, 2005, **127**, 4986-4987.
- (a) M. Gsänger, J. H. Oh, M. Könemann, H. W. Höffken, A. -M. Kraus, Z. Bao and F. Würthner, *Angew. Chem. Int. Ed.*, 2010, **49**, 740-743; (b) R. Schmidt, J. H. Oh, Y. S. Sun, M. Deppisch, A. M. Krause, K. Radtke, H. Braunschweig, M. Könemann, P. Erk, Z. Bao and F. Würthner, *J. Am. Chem. Soc.*, 2009, **131**, 6215-6228; (c) M. M. Ling, P. Erk, M. Gomez, M. Koenemann, J. Locklin and Z. Bao, *Adv. Mater.*, 2007, **19**, 1121-1127; (d) B. A. Jones, M. J. Ahrens, M. H. Yoon, A. Facchetti, T. Marks and M. R. Wasielewski, *Angew. Chem. Int. Ed.*, 2004, **43**, 636-6366; (e) H. Z. Chen, M. M. Ling, X. Mo, M. M. Shi, M. Wang and Z. Bao, *Chem. Mater.*, 2007, **19**, 816-824; (f) R. Schmidt, M. M. Ling, J. H. Oh, M. Winkler, M. Könemann, Z. Bao and F. Würthner, *Adv. Mater.*, 2007, **19**, 3692-3695; (g) B. A. Jones, A. Facchetti, M. R. Wasielewski and T. J. Marks, *J. Am. Chem. Soc.*, 2007, **129**, 15259-15278.

- 4 (a) H. E. Katz, A. J. Lovinger, J. Johnson, C. Kloc, T. Siegrist, W. Li, Y. Y. Lin and A. Dodabalapur, *Nature*, 2000, **404**, 478-481; (b) K. C. See, C. Landis, A. Sarjeant and H. E. Katz, *Chem. Mater.*, 2008, **20**, 3609-3616; (c) B. J. Jung, J. Sun, T. Lee, A. Sarjeant and H. E. Katz, *Chem. Mater.*, 2009, **21**, 94-101; (d) J. H. Oh, S. -L. Suraru, W. -Y. Lee, M. Könemann, H. W. Höffken, C. Röger, R. Schmidt, Y. Chung, W. -C. Chen, F. Würthner and Z. Bao, *Adv. Funct. Mater.*, 2010, **20**, 2148-2156.
- 5 Z. Wang, C. Kim, A. Facchetti and T. J. Marks, *J. Am. Chem. Soc.*, 2007, **129**, 13362-13363.
- 6 (a) Q. Zheng, J. Huang, A. Sarjeant and H. E. Katz, *J. Am. Chem. Soc.*, 2008, **130**, 14410-14411; (b) M. -L. Yeh, S. -Y. Wang, J. F. M. Hardigree, V. Podzorov and H. E. Katz, *J. Mater. Chem. C*, 2015, **3**, 3029-3037.
- 7 J. R. Chesterfield, J. C. Mckeen, C. R. Newman, P. C. Ewbank, D. A. da Silva Filho, J. L. Brédas, L. L. Miller, K. R. Mann and C. D. Frisbie, *J. Phys. Chem. B*, 2004, **108**, 192821-19292.
- 8 (a) Y. Ie, S. Jinnai, M. Nitania and Y. Aso, *J. Mater. Chem. C*, 2013, **1**, 5373-5380; (b) A. J. Tilley, C. Guo, M. B. Miltenburg, T. B. Schön, H. Yan, Y. Li and D. S. Seferos, *Adv. Funct. Mater.*, 2015, **25**, 3321-3329.
- 9 Gaussian 09, A.1 Revision, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- 10 D. E. Lynch and D. G. Hamilton, *Acta Crystallogr. E*, 2004, **60**, o597-o598.
- 11 R. A. Marcus, *Rev. Mod. Phys.*, 1993, **65**, 599-610.
- 12 G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders and T. Ziegler, *J. Comput. Chem.*, 2001, **22**, 931-967.
- 13 (a) M. Y. Kuo, H. Y. Chen and I. Chao, *Chem. Eur. J.*, 2007, **13**, 4750-4758; (b) W. S. Liu, C. C. Liu and M. Y. Kuo, *Chem. Eur. J.*, 2009, **15**, 5896-5900; (c) M. Y. Kuo and C. C. Liu, *J. Phys. Chem. C*, 2009, **113**, 16303-16306; (d) W. C. Chen and I. Chao, *J. Phys. Chem. C*, 2014, **118**, 20176-20183; (e) Y. C. Chang and I. Chao, *J. Phys. Chem. Lett.*, 2010, **1**, 116-121.