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A dinaphtho[8,1,2-*cde*:2′,1′,8′-*uva*]pentacene derivative and analogues: synthesis, structures, photophysical and electrochemical properties†

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Dinaphtho[8,1,2-*cde*:2′,1′,8′-*uva*]pentacene and analogues as a new type of acene derivatives with scorpion-shaped structures were conveniently synthesized. Their structures, photophysical and electrochemical properties were experimentally and theoretically investigated. It was found that the pentacene derivative has a twisted configuration, but shows marked intermolecular π–π interactions, strong electronic delocalization, and a small HOMO–LUMO bandgap, which are different from those of pentacene and pentatwistacene derivatives with similar structures.

Acenes[1] are highly attractive compounds with good performance as semiconductors and good emission properties, and they have been widely used in organic devices, such as in organic field-effect transistors,[2] organic light-emitting diodes,[3] and organic photovoltaics.[4] However, the relatively poor solubility and easy photodegradation of simple acenes could inhibit their practical applications to some extent. To improve the stability, solubility and control electronic structure and HOMO–LUMO gaps for further applications,[5] one general strategy is to introduce appropriate substituent groups in the acene skeleton. In this regards, the phenyl-substituted[6] and ethynyl-substituted[7,2*d*] acenes were most commonly focused on. The steric resistance and electronic effect of the silyethynyl group not only increases the solubility and stability, but also modifies the molecular packing, which could result in great electronic properties.[1*b*,7*b*,8] In recent years, some new types of acene derivatives, such as the terminal pyrene superimposed acenes[9] and extended terminal benzenoid substituents,[10] have attracted increasing interest because of their specific structures and photoelectric properties. However, such acene derivatives are limited, and most of their synthetic routes are also relatively complicated.

Recently, we have been interested in the synthesis and applications of helicenes and their analogues.[11] Inspired by these results, we herein report a convenient and efficient way to prepare a new type of acene derivatives with scorpion-shaped structures, dinaphtho[8,1,2-*cde*:2′,1′,8′-*uva*]pentacene derivative (**5c**) and its analogues 9,10,19,20-tetrahydrodinaphtho[2,1-*a*:1′,2′-*c*]tetracene derivative (**5a**) and 7,8,17,18-tetrahydrodinaphtho-[8,1,2-*cde*:2′,1′,8′-*uva*]pentacene derivative (**5b**) starting from commercial material. Their structures, photophysical and electrochemical properties were experimentally and theoretically investigated. It was found that **5c** has a twisted configuration, but shows marked intermolecular π–π interactions, strong electronic delocalization, and small HOMO–LUMO bandgap, which are different from those of 6,13-bis(trimethylsilyethynyl)pentacene (**BTMSP**) and 1,2,3,4,6,13-hexaphenyl-7:8,11:12-bisbenzopentacene (**HBP**) with a twisted structure (Fig. 1).

Synthesis of acene derivatives **5a–c** is depicted in Scheme 1. First, compound **2** was prepared in 95% yield by the treatment of 7-methoxy-1-tetralone **1** with NBS in acetonitrile. Treatment of **2** with zinc dust in the presence of TMSCl and HCl gave

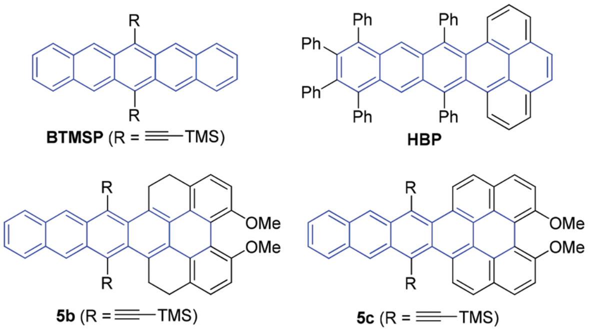

Fig. 1 Chemical structures of **BTMSP**, **HBP**, and **5b–c**.

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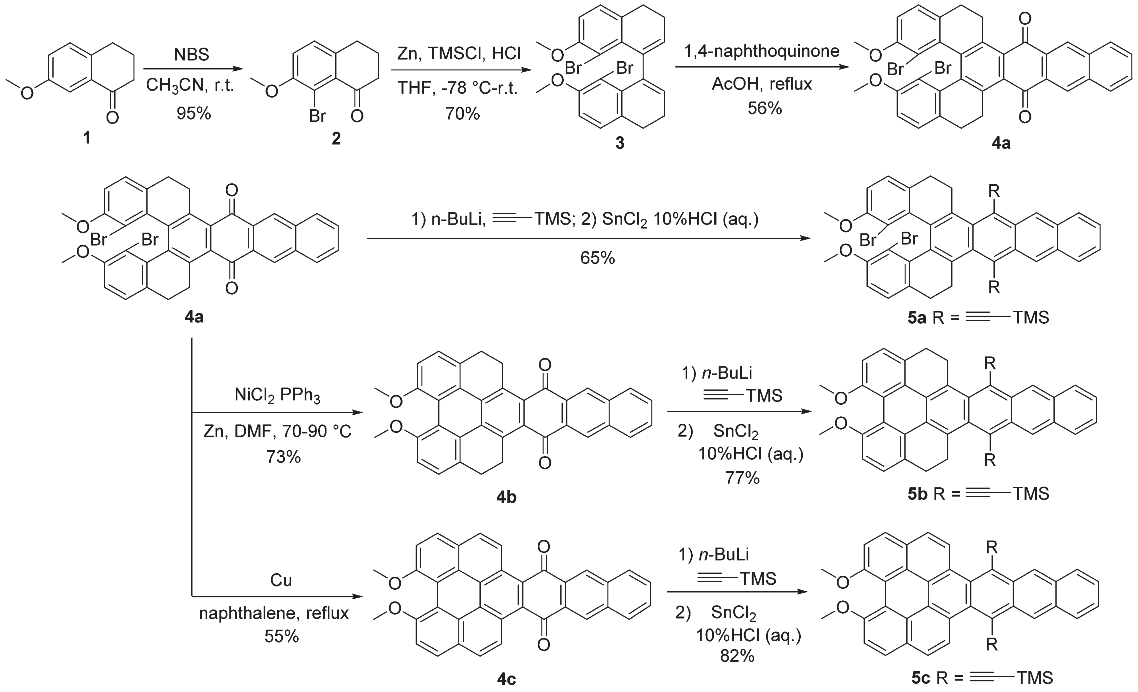
† Electronic supplementary information (ESI) available: Experimental procedures. Copies of ^{1}H and ^{13}C NMR spectra of all new compounds. Cyclic voltammograms of **5a** and **5b**, DFT calculations data and crystal data. CCDC 1058255 (**5a**); 1058256 (**5c**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ob01008j



Scheme 1 Synthesis of acene derivatives **5a–5c**.

diene **3** in 70%, which was followed by a Diels–Alder reaction with 1,4-anthraquinone in refluxing AcOH to yield compound **4a** in 56%. By the treatment of **4a** with $NiCl_2 \cdot 6H_2O$ and Zn powder in the presence of Ph_3P, **4b** could be obtained in 73% yield. While **4c** was prepared in 55% yield by Cu-catalyzed dehydrogen aromatization of **4a** in the presence of naphthalene. Pentacene quinones **4b** and **4c** are useful precursors for further derivatization at the quinone and methoxyl group positions. As a result, the alkynylation of **4c** with trimethylsilylacetylene in the presence of *n*-BuLi, followed by aromatization with $SnCl_2$ in the presence of 10% aqueous HCl gave **5c** in 82% yield. Similarly, **5a** and **5b** were obtained in 65 and 77% yield from **4a** and **4b**, respectively. Compounds **5a–c** have been characterized by the ^{1}H NMR, ^{13}C NMR, HRMS spectra, and X-ray crystal structures. Moreover, it was found that **5a–c** were all stable for weeks in air, and also soluble in various organic solvents including CH_2Cl_2, $CHCl_3$, toluene, acetone, and even cyclohexane.

Single crystals of **5a** and **5c** suitable for X-ray diffraction were obtained by slow evaporation of acetone and water, their crystal structures are shown in Fig. 2. It was found that **5a** keeps the structural characteristics of tetracene and is helicene-like, with a planar core and a helical terminal. **5c** shows a twisted configuration with a torsion angle of 26.70° (Fig. S16†), which is different from **BTMSP** which has a planar structure.[13] However, there exist a couple of significant face to face π–π interactions between two adjacent acene molecules with a distance of 3.37 Å, and another intermolecular π–π stacking between the adjacent perylene subunits with a distance of 3.34 Å, which results in a 2D layer assembled structure (Fig. 2c). This case is different from that of the twistacene **HBP**,[10c,12] in which no effective intermolecular interactions could be found.

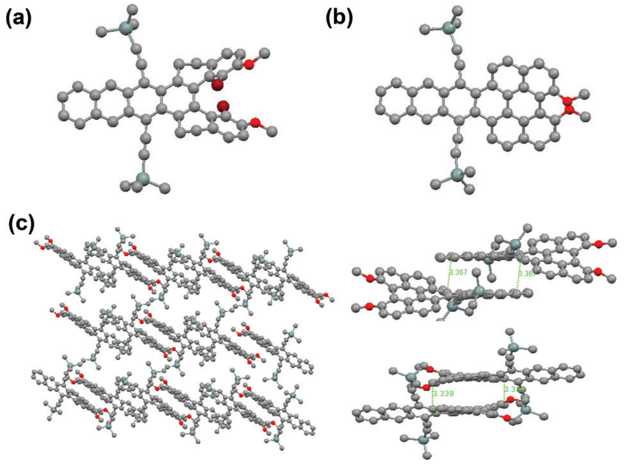


Fig. 2 Crystal structures of (a) **5a**, and (b) **5c**. (c) Packing of **5c**, and the intermolecular interactions.

UV-Vis and fluorescence spectra of **5a–5c** were measured in cyclohexane at room temperature, and the results were summarized in Table 1. As shown in Fig. 3a, the characteristic bands at 500–650 nm for the acene core could be found. Compared with **5a** (586 nm), the maximum absorption of **5b** at 619 nm was obviously red-shifted, which might be mainly due to the extended conjugation along the acene axis leading to a

Table 1 Photophysical and electrochemical properties of **5a–5c**

	Experimental					Calculated[f]		
Compd	$\lambda_{\text{max abs}}$[a] (nm)	λ_{em}[b] (nm)	E_g[c] (eV)	HOMO[d] (eV)	LUMO[e] (eV)	HOMO (eV)	LUMO (eV)	E_g (eV)
5a	586	598	2.05	−4.87	−2.82	−4.66	−2.46	2.20
5b	619	630	1.92	−4.83	−2.91	−4.53	−2.48	2.05
5c	607	637	1.95	−4.76	−2.81	−4.47	−2.39	2.08

[a] All spectra were recorded in cyclohexane ($c = 1.0 \times 10^{-5}$ M) at room temperature. [b] Excited at 360 nm. [c] Band gap estimated from the UV-Vis absorption spectrum. [d] Calculated from the oxidation potentials: $E_{\text{HOMO}} = -(E_{\text{ox}}^{\text{onset}} + 4.4)$ eV,[14] ferrocene/ferrocenium (Fc/Fc$^+$) redox system as an internal standard. [e] Deduced from the HOMO and E_g. [f] DFT calculations were carried out at B3LYP/6-31G(d) level with Gaussian 09 program.

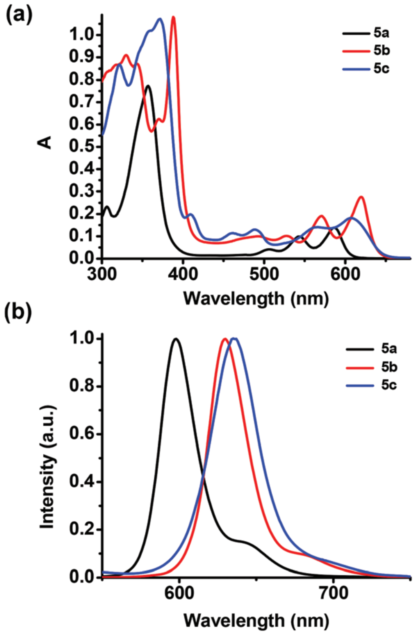


Fig. 3 (a) UV-Vis and (b) fluorescence spectra of **5a–5c** in cyclohexane ($c = 1.0 \times 10^{-5}$ M) at room temperature.

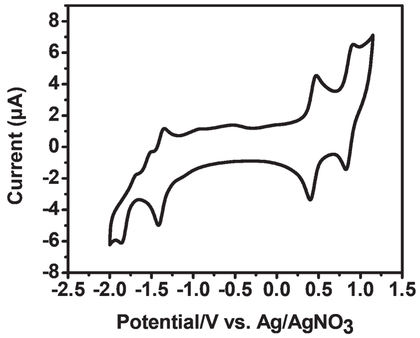


Fig. 4 Cyclic voltammograms of **5c** in 0.1 M n-Bu$_4$NPF$_6$ of CH$_2$Cl$_2$ solution at a scan rate of 100 mV s^{-1}, and with ferrocene/ferrocenium couple as standard.

reduction in the HOMO–LUMO gap. For **5c**, the maximum absorption wavelength appears at 607 nm, which is smaller than that of **BTMSP** (639 nm),[13] but is red-shifted about 130 nm compared with that of **HBP** (475 nm),[9a] which might be attributed to the stronger electronic delocalization of **5c** than that of **HBP**. Moreover, it was also found that the gradual π-extended system of **5a**, **5b** and **5c** made their fluorescence emission peaks show a clear increasing trend in the order of **5a** < **5b** < **5c** (Fig. 3b).

The HOMO and LUMO energy levels are closely related to the redox ionization potentials of polycyclic aromatic hydrocarbons. Thus, to investigate the HOMO and LUMO properties of acenes **5a–5c**, cyclic voltammetry (CV) experiments were performed in 0.1 M n-Bu$_4$NPF$_6$ of CH$_2$Cl$_2$ solution with a Pt electrode and a Ag/Ag$^+$ electrode at room temperature. As shown in Fig. 4, **5c** displayed one reversible reduction peak with a half wave potential ($E_{1/2}$) at −1.38 V, and two oxidation potentials with the lowest one at 0.44 V. For **5a** and **5b**, they each have one reversible reduction and oxidation potential with values of $E_{1/2}$ at −1.30, −1.37 V, and 0.56, 0.49 V, respectively (Fig. S17 and S18†). According to CV, the HOMO levels of **5a–5c** were estimated as −4.87, −4.83, and −4.76 eV, respectively, which suggested that the electrodonation ability was enhanced from **5a** to **5c**. Estimated from the UV-vis absorption spectra, the bandgaps of **5a–5c** were obtained, and the LUMO levels could be also calculated from the energy bandgap and the HOMO levels (Table 1).

To understand the nature of the electrochemical and the HOMO, LUMO properties of acenes **5a–5c**, the DFT calculations at the B3LYP/6-31G (d) level with the Gaussian 09 program were further carried out. The HOMO and LUMO are depicted in Fig. 5. For **5a** and **5b**, the densities in the HOMO and LUMO mainly concentrated in the acene ring. While the molecular orbitals of **5c** showed that the density in LUMO concentrated in the acene ring, but the density in HOMO mainly concentrated on the perylene portion, which is different from those of **5a** and **5b**. Combining the HOMO and LUMO, the gradual delocalization from **5a** to **5c** indicated stronger conjugation order in **5a** < **5b** < **5c**.

As shown in Table 1, the results of DFT calculations for the HOMO energies were consistent with the experimental results, but the LUMO energies from the DFT calculations were consistently smaller than those measured from the electrochemical experiments by as much as 0.26–0.43 eV. This trend was also observed by Miller[15] and Thomas III[16] in their acene

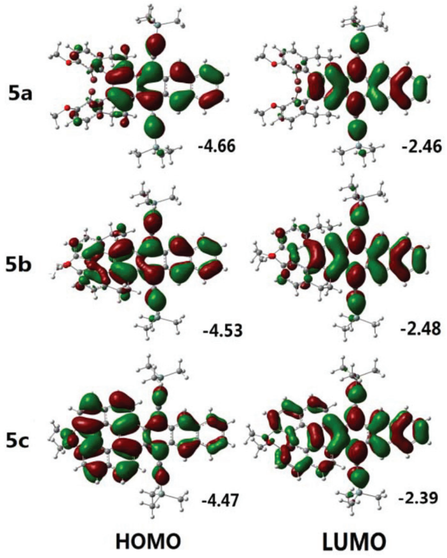


Fig. 5 HOMO and LUMO of **5a–5c** calculated by the B3LYP/6-31G (d) method.

systems. The band gaps of **5a–c** from the DFT calculations were 2.20, 2.05, and 2.08 eV, respectively, which was similar to the results from UV-Vis absorption (2.05, 1.92, and 1.95 eV). Furthermore, both calculation and experimental results showed that the HOMO–LUMO gaps of **5b** and **5c** were higher than that of hexacene (1.84 eV),[1b] but lower than those of pentacene (2.1 eV)[13] and **HBP** (2.67 eV),[9a] which could make **5b** and **5c** have the potential to be narrow bandgap materials.

Conclusions

In summary, we have conveniently synthesized a new type of acenes, dinaphtho[8,1,2-*cde*:2′,1′,8′-*uva*]pentacene derivative **5c** and its analogues **5a** and **5b** from commercial material. These new acene derivatives showed good stabilities and solubilities in various organic solvents. It was also found that molecule **5c** has a twisted configuration, but showed obvious intermolecular π-stacking interactions in the solid state. The UV-Vis spectra, CV and DFT calculations further showed that **5b** and **5c** have stronger electronic delocalization and smaller bandgap than that of **HBP** with a similar twisted structure. It can be expected that this new type of acenes with specific structures and properties could find potential applications in organic functional materials, and this is currently being investigated.

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Notes and references

1 (*a*) J. E. Anthony, *Angew. Chem., Int. Ed.*, 2008, **47**, 452; (*b*) M. M. Payne, S. R. Parkin and J. E. Anthony, *J. Am. Chem. Soc.*, 2005, **127**, 8028; (*c*) R. Mondal, C. Tönshoff, D. Khon, D. C. Neckers and H. F. Bettinger, *J. Am. Chem. Soc.*, 2009, **131**, 14281; (*d*) D. Chun, Y. Cheng and F. Wudl, *Angew. Chem., Int. Ed.*, 2008, **47**, 8380; (*e*) T. Kushida, Z. G. Zhou, A. Wakamiya and S. Yamaguchi, *Chem. Commun.*, 2012, **48**, 10715.

2 (*a*) W. F. Zhang, Y. Q. Liu and G. Yu, *Adv. Mater.*, 2014, **26**, 6898; (*b*) T. Lei, Y. Zhou, C. Y. Cheng, Y. Cao, Y. Peng, J. Bian and J. Pei, *Org. Lett.*, 2011, **13**, 2642; (*c*) H. Meng, M. Bendikov, G. Mitchell, R. Helgeson, F. Wudl, Z. N. Bao, T. Siegrist, C. Kloc and C. H. Chen, *Adv. Mater.*, 2003, **15**, 1090; (*d*) C. D. Sheraw, T. N. Jackson, D. L. Eaton and J. E. Anthony, *Adv. Mater.*, 2003, **15**, 2009; (*e*) H. L. Dong, C. L. Wang and W. P. Hu, *Chem. Commun.*, 2010, **46**, 5211.

3 (*a*) B.-B. Jang, S. H. Lee and Z. H. Kafafi, *Chem. Mater.*, 2006, **18**, 449; (*b*) J. C. Xiao, S. W. Liu, Y. Liu, L. Ji, X. W. Liu, H. Zhang, X. W. Sun and Q. C. Zhang, *Chem. – Asian J.*, 2012, **7**, 561.

4 (*a*) Y. Shao, S. Sista, C. W. Chu, D. Sievers and Y. Yang, *Appl. Phys. Lett.*, 2007, **90**, 10350; (*b*) D. Fujishima, H. Kanno, T. Kinoshita, E. Maruyama, M. Tanaka, M. Shirakawa and K. Shibata, *Sol. Energy Mater. Sol. Cells*, 2009, **93**, 1029; (*c*) Y. Z. Lin, Y. F. Li and X. W. Zhan, *Chem. Soc. Rev.*, 2012, **41**, 4245.

5 (*a*) K. Ono, H. Totani, T. Hiei, A. Yoshino, K. Saito, K. Eguchi, M. Tomura, J. Nishida and Y. Yamashita, *Tetrahedron*, 2007, **63**, 9699; (*b*) S. S. Palayangoda, R. Mondal, B. K. Shah and D. C. Neckers, *J. Org. Chem.*, 2007, **72**, 6584; (*c*) Y. J. Li, L. Xu, T. F. Liu, Y. W. Yu, H. B. Liu, Y. L. Li and D. B. Zhu, *Org. Lett.*, 2011, **13**, 5692; (*d*) Y. C. Lin, C. H. Lin, C. Y. Chen, S. S. Sun and B. Pal, *Org. Biomol. Chem.*, 2011, **9**, 4507.

6 (*a*) C. F. H. Allen and A. Bell, *J. Am. Chem. Soc.*, 1942, **64**, 1253; (*b*) Q. Miao, X. Chi, S. Xiao, R. Zeis, M. Lefenfeld, T. Siegrist, M. L. Steigerwald and C. Nuckolls, *J. Am. Chem. Soc.*, 2006, **128**, 1340; (*c*) Y. Zhao, R. Mondal and D. C. Neckers, *J. Org. Chem.*, 2008, **73**, 5506.

7 (*a*) C. A. Landis, S. R. Parkin and J. E. Anthony, *J. Appl. Phys.*, 2005, **44**, 3921; (*b*) J. E. Anthony, D. L. Eaton and S. R. Parkin, *Org. Lett.*, 2002, **4**, 15; (*c*) M. M. Payne, J. H. Delcamp, S. R. Parkin and J. E. Anthony, *Org. Lett.*, 2004, **6**, 1609.

8 (*a*) M. A. Wolak, B.-B. Jang, L. C. Palilis and Z. H. Kafafi, *J. Phys. Chem. B*, 2004, **108**, 5492; (*b*) J. E. Anthony, J. S. Brooks, D. L. Eaton and S. R. Parkin, *J. Am. Chem. Soc.*, 2001, **123**, 9482.

9 (*a*) J. C. Xiao, Y. Divayana, Q. C. Zhang, H. M. Doung, H. Zhang, F. Boey, X. W. Sun and F. Wudl, *J. Mater. Chem.*,

2010, **20**, 8167; (*b*) J. B. Li, Y. B. Zhao, J. Lu, G. Li, J. P. Zhang, Y. Zhao, X. W. Sun and Q. C. Zhang, *J. Org. Chem.*, 2015, **80**, 109.

10 (*a*) R. A. Pascal Jr., *Chem. Rev.*, 2006, **106**, 4809; (*b*) J. Lu, D. M. Ho, N. J. Vogelaar, C. M. Kraml, S. Bernhard, N. Byrne, L. R. Kim and R. A. Pascal Jr., *J. Am. Chem. Soc.*, 2006, **128**, 17043; (*c*) D. Rodríguez-Lojo, D. Pérez, D. Peña and E. Guitián, *Chem. Commun.*, 2013, **49**, 6274.

11 (*a*) Y. Shen and C.-F. Chen, *Chem. Rev.*, 2012, **112**, 1463; (*b*) J. D. Chen, H. Y. Lu and C.-F. Chen, *Chem. – Eur. J.*, 2010, **16**, 11843; (*c*) M. Li, Y. L. Niu, X. Z. Zhu, Q. Peng, H. Y. Lu, A. D. Xia and C.-F. Chen, *Chem. Commun.*, 2014, **50**, 2993.

12 J. C. Xiao, H. M. Duong, Y. Liu, W. X. Shi, L. Ji, D. Li, S. Z. Li, X. W. Liu, J. Ma, F. Wudl and Q. C. Zhang, *Angew. Chem., Int. Ed.*, 2012, **51**, 6094.

13 B. H. Northrop, K. N. Houk and A. Maliakal, *Photochem. Photobiol. Sci.*, 2008, **7**, 1463.

14 (*a*) B. Liang, C. Y. Jiang, Z. Chen, X. J. Zhang, H. H. Shi and Y. Cao, *J. Mater. Chem.*, 2006, **16**, 1281; (*b*) X. K. Gao, W. P. Wu, Y. Q. Liu, S. B. Jiao, W. F. Qiu, G. Yu, L. P. Wang and D. B. Zhu, *J. Mater. Chem.*, 2007, **17**, 736.

15 I. Kaur and G. P. Miller, *New J. Chem.*, 2008, **32**, 459.

16 J. J. Zhang, Z. C. Smith and S. W. Thomas III, *J. Org. Chem.*, 2014, **79**, 10081.