Superabsorbers

Deutsche Ausgabe: DOI: 10.1002/ange.201507074
Internationale Ausgabe: DOI: 10.1002/anie.201507074

Wrinkled Graphene Monoliths as Superabsorbing Building Blocks for Superhydrophobic and Superhydrophilic Surfaces

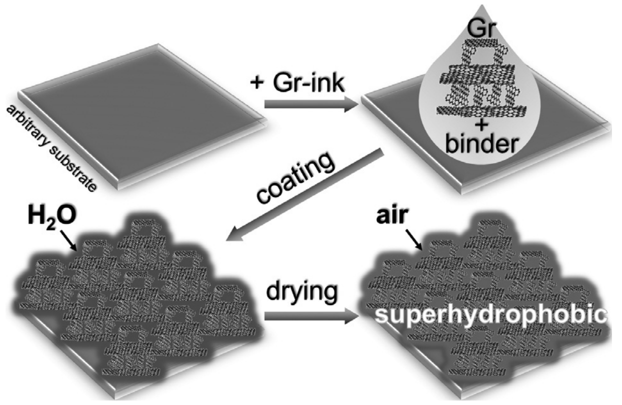
Li-Bing Lv, Tian-Lu Cui, Bing Zhang, Hong-Hui Wang, Xin-Hao Li, and Jie-Sheng Chen**

Abstract: *Superhydrophobic and superhydrophilic surfaces are of great interest because of a large range of applications, for example, as antifogging and self-cleaning coatings, as antibiofouling paints for boats, in metal refining, and for water–oil separation. An aqueous ink based on three-dimensional graphene monoliths (Gr) can be used for constructing both superhydrophobic and superhydrophilic surfaces on arbitrary substrates with different surficial structures from the meso- to the macroscale. The surface wettability of a Gr-coated surface mainly depends on which additional layers (air for a superhydrophobic surface and water for a superhydrophilic surface) are adsorbed on the surface of the graphene sheets. Switching a Gr-coated surface between being superhydrophobic and superhydrophilic can thus be easily achieved by drying and prewetting with ethanol. The Gr-based superhydrophobic membranes or films should have great potential as efficient separators for fast and gravity-driven oil–water separation.*

Superhydrophobic surfaces are characterized by a water contact angle (CA) larger than 150° whereas superhydrophilic surfaces usually have a water CA smaller than 10°.[1–3] Both the intrinsic wettability of a surface and the surface roughness are key factors that generate superhydrophilicity or superhydrophobicity. Much effort has been devoted to constructing superhydrophobic or superhydrophilic surfaces with multiscale roughness by mimicking natural materials.[4–9] Two general approaches for fabricating rough surface have been developed, namely top-down and bottom-up methods. Typical top-down methods are usually applied to construct rough surfaces on flat substrates by template-directed nanocasting, lithographic approaches, and even plasma, laser pulse, or chemical etching methods. For substrates with irregular shapes and surfaces, bottom-up methods, such as chemical deposition, sol–gel approaches, and self-assembly, are preferred as a more homogeneous coating can thus be achieved.

Among the building blocks available for constructing rough surfaces by bottom-up methods, carbon nanomaterials have usually been considered as ideal candidates not only because of their abundance and excellent stability but also owing to the ease of engineering the composition and mesostructure. As a result, carbon nanotubes, nanoparticles, nanowalls, and nanofibers have been casted, deposited, or assembled into rough coatings, followed by coating a hydrophobic (by fluorine treatment) or hydrophilic (by oxidation) layer to further enhance the hydrophilicity or hydrophobicity.[10–12] It is thus difficult to reversibly change the wettability of these surfaces for on-demand applications. Only several examples of carbon materials with surfaces that can be reversibly switched between being superhydrophobic or superhydrophilic by plasma etching or deposition of an additional layer have been reported. The development of sustainable methods for the on-demand construction of superhydrophobic and superhydrophilic surfaces with reversible wettability is thus highly desirable for both fundamental research and practical applications.

Herein, we describe an alternative approach for the on-demand construction of superhydrophobic or superhydrophilic surfaces simply by coating an aqueous ink of graphene monoliths and a commercial binder (Gr-ink) on arbitrary substrates with different surface roughness. An additional Teflon coating or etching were not needed. As depicted in Scheme 1, the high surface area of graphene monoliths makes them superabsorbers for both air and water and thus suitable building blocks for reversibly constructing superhydrophobic (Cassie–Baxter state, water droplets are repelled by the air pocket) and superhydrophilic surfaces (Wenzel state, the liquid follows the roughness of the surface). The superhydrophobic and superhydrophilic membranes, based on Gr-ink and melamine or Ni foam, performed well as filters for fast and gravity-driven oil–water separation.[13,14]



Scheme 1. Construction of superhydrophobic surfaces by coating aqueous ink made from a graphene monolith dispersion and a commercial binder onto an arbitrary substrate and drying in air.

---

[*] L.-B. Lv, T.-L. Cui, B. Zhang, H.-H. Wang, Prof. X.-H. Li, Prof. J.-S. Chen
School of Chemistry and Chemical Engineering
Shanghai Jiao Tong University
Shanghai 200240 (P. R. China)
E-mail: xinhaoli@sjtu.edu.cn
chemcj@sjtu.edu.cn

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201507074.

As a two-dimensional carbon allotrope with a theoretical surface area of up to 2400 $m^2 g^{-1}$, graphene is a superabsorber for small molecules. The strong interaction between the graphene layers and small molecules affords substrate-supported graphene layers or graphene papers with hydrophilic surfaces.[15,16] A Teflon layer can be coated onto the surface of substrate-supported graphene to obtain graphene-based superhydrophobic surfaces. We mention substrate-supported graphene here because free-standing graphene materials have completely different morphologies, that is, they are highly wrinkled nanosheets. The as-formed wrinkles are ideally suited for obtaining surface roughness. Unfortunately, dispersing wrinkled graphene sheets on various substrates can induce their expansion back into flat sheets. The rational design of building blocks based on wrinkled graphene should be key for their application in the fabrication of superhydrophobic or superhydrophilic films.

We thus turned our attention towards three-dimensional monoliths based on wrinkled graphene sheets. The graphene monoliths used in this work were fabricated through thermal condensation of glucose molecules as described in our previous work.[17–19] Both the graphite degree and the amount of heteroatoms (mainly nitrogen atoms) can be easily tuned by varying the condensation temperature. The wrinkled structures and high surface areas (815–980 $m^2 g^{-1}$; see the Supporting Information, Table S1) of the graphene monoliths were confirmed by electron microscopy (Figure S1) and nitrogen adsorption analysis.

The as-formed graphene monoliths were directly dispersed into deionized water by gentle ultrasonication; then, a small amount of Nafion (Figure S2) was added to the homogeneous dispersion (Figure 1 a) as a binder, resulting in the final Gr-ink, which remained stable for several months without showing signs of aggregation. As depicted in Scheme 1, Gr-ink can be directly drop-casted onto arbitrary substrates to form homogeneous coating layers. For example, a glass slide was coated and dried in air at room temperature for one day; it then exhibited superhydrophobicity (Figure 1 a). The CA of the coated glass slide is 168.2° (Figure 1 c and Figure 2 a). The amount of graphene loaded onto the surface is important for the wettability of the as-formed film, and a minimum loading of 0.24 $mg cm^{-2}$ is necessary to ensure superhydrophobicity. This result is an interesting example of a superhydrophobic surface made from aqueous ink.

The surface roughness of the superhydrophobic coating on the glass slide is demonstrated by a large-area electron microscopy (SEM) image (Figure 1 d). The Gr monoliths were torn into irregular particles with sizes ranging from several to tens of micrometers. A magnified SEM image (Figure 1 e) demonstrates that the wrinkled structure of the graphene nanosheets and the subunits of the Gr monoliths were well preserved after the dispersing, coating, and drying process. Dark-field transmission electron microscopy (TEM; Figure 1 f) revealed the wrinkled structures of the thin graphene sheets. Graphene sheets are known to be soft and flexible and tend to be packed together by the liquid capillary force after solvent removal. High-resolution transmission electron microscopy (HRTEM; Figure 1 g) indicated the Gr monoliths to have a three-dimensional structure. As depicted in Figure 1 g (inset), the interconnected framework thus formed consists of one graphene sheet vertically grown into another graphene sheet. The highly integrated structure is responsible for the mechanical stability of the Gr monoliths,

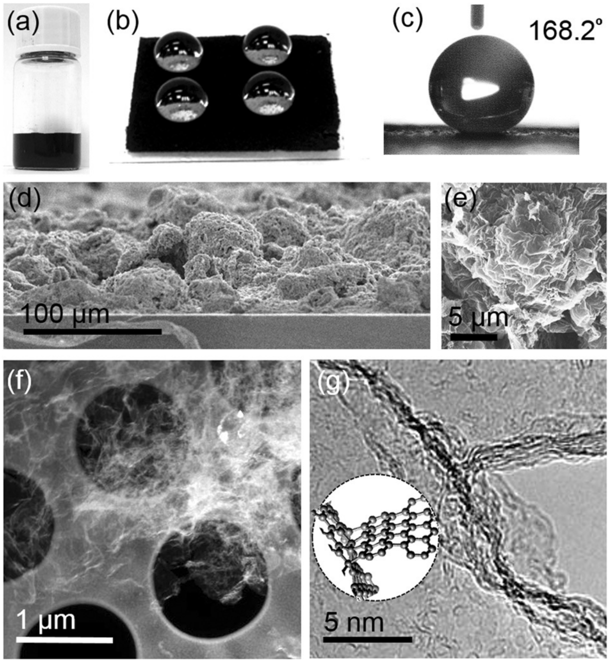


Figure 1. Photographs of Gr-ink (a) and a coated glass slide (b) with a CA of up to 168.2° (c). Side-view SEM image of the coated glass slide (d) and detailed structure of its surface as observed by SEM (e). Dark-field TEM (f) of a typical Gr monolith particle after gentle sonication in water. HRTEM image of the interconnectivity of two graphene nanosheets (g).

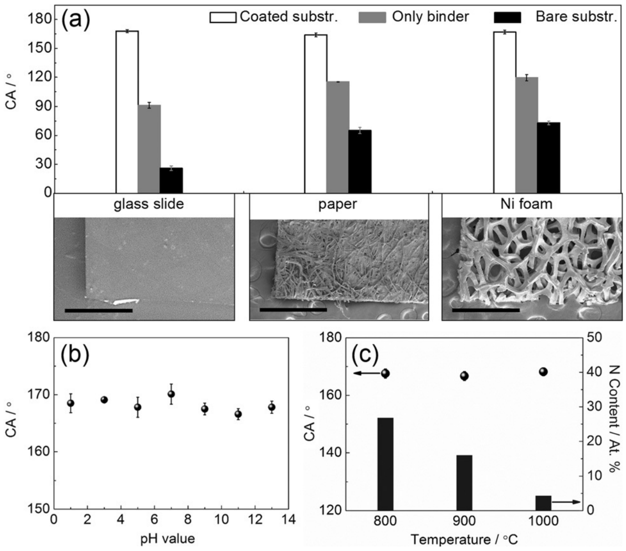


Figure 2. a) The CAs of various substrates (glass slides, paper, and Ni foam) coated with Gr-ink or with the binder (Nafion) only and of the bare substrates. Scale bar: 500 μm. b) Dependence of the CA of the Gr-ink-coated glass slide on the pH value. c) The CAs of glass slides coated with Gr-ink that were prepared at different temperatures and thus differ in their nitrogen content.

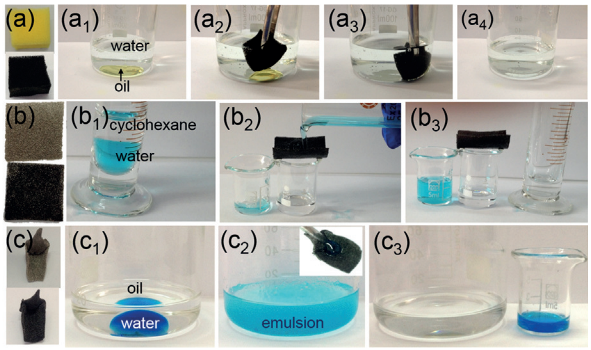


Figure 3. Oil–water separation. a) A melamine sponge was coated with Gr-ink for removing oil (dyed in yellow) from water. The oil was absorbed by the coated melamine sponge (a$_1$–a$_4$). b) Fast separation of water and oil (b$_1$–b$_3$) by using a Gr-ink-coated Ni foam as the filter. Water (dyed in blue) flowed into another beaker (b$_2$, b$_3$) owing to the very small sliding angle (4°) of the coated Ni foam. c) A coated Ni foam was tailored into a shovel-like container for collecting tiny water droplets (dyed in blue) from a water-in-oil emulsion made of water and silicon oil (c$_1$–c$_3$). The dyed blue water was removed from the emulsion, and the oil was left behind.

including the wrinkled structure of the graphene sheets. Indeed, the nanoscale surface roughness of the wrinkled graphene monoliths, as determined by TEM (Figure S3), was well preserved after treatment with the binder. Note that graphene paper that consists of graphene sheets released from Gr monoliths under strong ultrasonication has a flat and hydrophilic surface (Figure S4). Further coating Nafion onto the surface of the graphene paper could not generate a superhydrophobic surface. All of the above-mentioned results suggest that the interconnected structure of the Gr monoliths plays a key role for the formation of hierarchical surface roughness from the nano- to the micrometer scale and thus also for the superhydrophobicity of the surface.

Our Gr-ink can be used to construct superhydrophobic surfaces by simple drop casting onto arbitrary substrates (Figure S5). As shown in Figure 2a, a glass slide, paper, and Ni foam, which differ significantly in their surface roughness, were successfully transformed into superhydrophobic films or membranes, with CAs ranging from 165° to 168° (Figures 1c and S5). Even when the binder was changed from Nafion to an inorganic resin (Figure S2), the coated substrates still maintained their excellent superhydrophobicity (CAs: 168–171°; Figures S6, S7). Neither the bare substrates nor binder-coated substrates without the Gr monoliths were superhydrophobic. We can thus deduce that the superhydrophobicity of these coated substrates is mainly due to the Gr monoliths. This hypothesis was confirmed by the fact that the superhydrophobicity was well maintained over a wide range of pH values (pH 1–13; Figure 2b). Furthermore, the nitrogen content of the Gr monoliths (Figure 2c and Table S1) had a negligible effect on the final CAs of the coated substrates, corroborating the hypothesis that the wrinkled graphene monoliths act as the air superabsorbers in this Cassie-type surface. The air layer adsorbed on the Gr monolith surface remains stable for a very long time (Figure S8). In combination with the stability of the Gr monolith based superhydrophobic surface to acid and alkaline media (Figure 2b),[20,21] the stable superhydrophobicity of Gr coatings could greatly extend their application as anticorrosion coatings for use in harsh environments.

Owing to their high CAs (> 168°) and low sliding angles (< 5°; Figure S9 and Movie S1), Gr-ink-coated melamine sponges or Ni foams could function as excellent collectors or filters for fast oil–water separation (Figure 3). The high porosity and superhydrophobicity of the coated melamine sponge make it a perfect candidate for the quick removal of various oils and organic solvents from water (Figure 3a).

Fast, gravity-driven separation of oil from water could also be achieved with Gr-coated Ni foam as a filter. As shown in Figure 3b and Movie S2, a mixture of water and a light oil (in this case, cyclohexane) was directly poured onto the Gr-coated Ni foam. Whereas the cyclohexane passed through the Ni foam into to the beaker below, the water was repelled and flowed into another beaker. This constitutes a fast and simple process for water–oil separation without the need for a filter or vacuum. It is also suitable for the fast separation of mixtures of water and heavy oils (exemplified with CCl_4 in Figure S10 and Movie S3). It is noteworthy that superhydrophobic filters or membranes usually do not work very well for separating light oil from water as light oils are blocked by the water and cannot pass through the superhydrophobic membrane in a purely gravity-driven process. Similar problems have also occurred when superhydrophilic membranes was used to separate heavy oil from water.

The Ni foam was easily tailored into certain shapes without losing its superhydrophobicity, promising lots of possibilities to separate oil–water mixtures. For example, we shaped the Ni foam into a shovel to collect tiny water droplets from a water-in-oil emulsion without any stabilizer (Figure 3c) and finally achieved complete separation. Oil-in-water emulsions could also be separated with a Gr-coated melamine sponge (Figure S11), again suggesting the convenience of our Gr-ink for the construction of highly efficient separators or absorbers.

Most importantly, the superhydrophobic surface has a high mechanical stability. Gr-coated Ni foam could be subjected to sand abrasion without losing its superhydrophobicity (Figure S12 and Movie S4).

Although multiscale surface roughness is essential for the construction of both superhydrophobic and superhydrophilic surfaces, it is still difficult to reversibly switch the wetting properties of a surface with a fixed composition or switch between superhydrophobicity and superhydrophilicity. Several approaches for converting superhydrophobic into superhydrophilic surfaces are irreversible as hydrophilic groups are introduced at the surface by etching or coating additional hydrophilic layers.[22] According to the superior absorption properties of the Gr monoliths, it is possible to replace the air layer with a water layer by prewetting[23] to construct Wenzel-type superhydrophilic surfaces. Indeed, the successful transformation of the superhydrophobic surface into a superhydrophilic one (Figure 4d) was demonstrated by the small water CA (0°). We removed the air layer on the outer surface of a dried Gr film simply by dipping the film into ethanol or methanol for less than five seconds, as directly reflected by

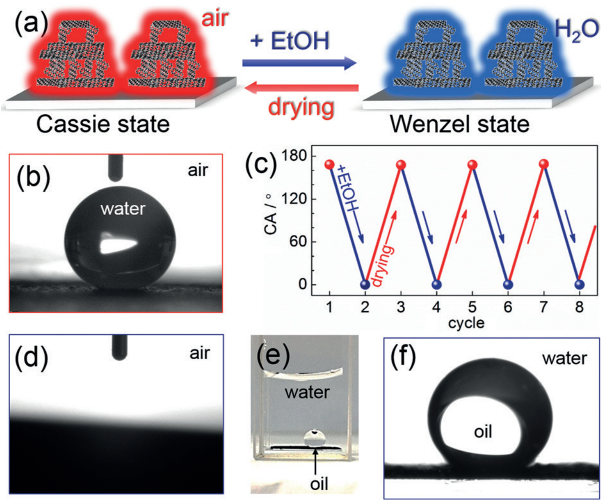


Figure 4. a) Reversible switching between superhydrophilicity (Cassie state, water droplets are repelled by the air pocket) and superhydrophobicity (Wenzel state, the liquid follows the roughness of the surface) by prewetting with ethanol and drying. b) The water CA (168°) of a Gr-ink-coated glass slide after drying under ambient conditions. c) The CAs of a Gr-ink-coated glass slide could be reversibly cycled between 168° and 0°. d) The water CA (0°) a of Gr-ink-coated glass slide after prewetting with ethanol. e) Photograph of an oil droplet in water on top of a prewetted Gr-ink-coated glass slide with an oil CA of 170.2° (f).

the formation of air bubbles on the film surface (Figure S13 and Movie S5). The prewetted surface could easily be covered again with water to become superoleophobic (Figure 4e) with an oil CA of up to 170.2° (Figure 4f). As such, Gr-coated and prewetted Ni foams are efficient materials to separate oil from water (Figure S14).

More importantly, the system could be reversibly switched between superhydrophobicity and superhydrophilicity without disturbing the composition or the need for surface modification. As shown in Figure 4c, the as-formed Gr-coated glass slide could be reversibly switched between superhydrophobicity and superhydrophilicity for many cycles with a negligible change in the wetting behavior. The sustainable transformation of the wetting behavior of Gr-monolith-based films or membranes through the simple prewetting and drying process could obviously extend their practical applications and enable their use as anticorrosion coatings, self-cleaning coatings, or for oil–water separation.

In summary, we have utilized graphene monoliths with a very high surface area and a wrinkled surface as superabsorbing building blocks for constructing superhydrophobic surfaces on arbitrary substrates. The as-formed Gr-ink-based film was superhydrophobic owing to the air layer adsorbed on the surface, resulting in a typical Cassie–Baxter state. Fast and gravity-driven oil–water separation could be achieved with a Gr-ink-coated melamine foam or Ni foam as absorber or filter, respectively. The Gr-coated films and membranes could be reversibly and rapidly switched between the Cassie–Baxter and Wenzel states simply by prewetting with ethanol and drying. These processes can thus be applied for the on-demand construction of superhydrophobic, superhydrophilic, and/or superoleophobic films or membranes on arbitrary substrates for specific applications.

Experimental Section

Fabrication of Gr-ink: Gr monoliths (15 mg) were dispersed in a solution consisting of Nafion (720 μL; or 60 μL of an inorganic resin made from methyltrimethoxysilane and Ludox, methyltrimethoxysilane/Ludox = 0.025, v/v) and 1440 μL of water (or 1440 μL of EtOH). The mixture was sonicated for 30 min to obtain homogenous Gr-ink. The substrate (glass slide, paper, or Ni foam) was cut into a $2 \times 2\,\mathrm{cm}^2$ square and coated with Gr-ink; then, the solvent was evaporated under ambient conditions. The graphene loading of the substrates was minimized to be $0.24\,\mathrm{mg\,cm^{-2}}$ (normalized to the real surface area of the substrate) to ensure the formation of a superhydrophobic surface.

Acknowledgements

This work was financially supported by the National Basic Research Program of China (2013CB934102, 2011CB808703), the National Natural Science Foundation of China (21331004, 21301116), and the Shanghai Eastern Scholar Program.

Keywords: graphene · oil–water separation · superabsorbers · superhydrophilicity · superhydrophobicity

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 15165–15169
Angew. Chem. **2015**, *127*, 15380–15384

[1] K. Kota, G. Kwon, W. Choi, J. M. Mabry, A. Tuteja, *Nat. Commun.* **2012**, *3*, 1025.
[2] M. J. Kwak, M. S. Oh, Y. Yoo, J. B. You, J. Kim, S. J. Yu, S. G. Im, *Chem. Mater.* **2015**, *27*, 3441.
[3] Z. Chu, Y. Feng, S. Seeger, *Angew. Chem. Int. Ed.* **2015**, *54*, 2328; *Angew. Chem.* **2015**, *127*, 2358.
[4] X. Zhang, F. Shi, J. Niu, Y. Jiang, Z. Wang, *J. Mater. Chem.* **2008**, *18*, 621.
[5] X.-M. Li, D. Reinhoudt, M. Crego-Calama, *Chem. Soc. Rev.* **2007**, *36*, 1350.
[6] D. Tian, Y. Song, L. Jiang, *Chem. Soc. Rev.* **2013**, *42*, 5184.
[7] K. Liu, X. Yao, L. Jiang, *Chem. Soc. Rev.* **2010**, *39*, 3240.
[8] Y. Li, L. Li, J. Sun, *Angew. Chem. Int. Ed.* **2010**, *49*, 6129; *Angew. Chem.* **2010**, *122*, 6265.
[9] M. Liu, S. Wang, Z. Wei, Y. Song, L. Jiang, *Adv. Mater.* **2009**, *21*, 665.
[10] X. Deng, L. Mammen, H.-J. Butt, D. Vollmer, *Science* **2012**, *335*, 67.
[11] H. Liu, T. Ye, C. Mao, *Angew. Chem. Int. Ed.* **2007**, *46*, 6473; *Angew. Chem.* **2007**, *119*, 6593.
[12] Z.-Y. Wu, C. Li, H.-W. Liang, J.-F. Chen, S.-H. Yu, *Angew. Chem. Int. Ed.* **2013**, *52*, 2925; *Angew. Chem.* **2013**, *125*, 2997.
[13] E. Singh, Z. Chen, F. Houshmand, W. Ren, Y. Peles, H. M. Cheng, N. Koratkar, *Small* **2013**, *9*, 75.
[14] B. G. Choi, H. S. Park, *J. Phys. Chem. C* **2012**, *116*, 3207.
[15] X. J. Feng, L. Jiang, *Adv. Mater.* **2006**, *18*, 3063.
[16] X.-H. Li, J.-S. Chen, X. Wang, M. E. Schuster, R. Schlögl, M. Antonietti, *ChemSusChem* **2012**, *5*, 642.
[17] L.-B. Lv, T.-N. Ye, L.-H. Gong, K.-X. Wang, J. Su, X.-H. Li, J.-S. Chen, *Chem. Mater.* **2015**, *27*, 544.
[18] X. H. Li, M. Antonietti, *Angew. Chem. Int. Ed.* **2013**, *52*, 4572; *Angew. Chem.* **2013**, *125*, 4670.
[19] X. H. Li, S. Kurasch, U. Kaiser, M. Antonietti, *Angew. Chem. Int. Ed.* **2012**, *51*, 9689; *Angew. Chem.* **2012**, *124*, 9827.

[20] L. Feng, Z. Yang, J. Zhai, Y. Song, B. Liu, Y. Ma, Z. Yang, L. Jiang, D. Zhu, *Angew. Chem. Int. Ed.* **2003**, *42*, 4217; *Angew. Chem.* **2003**, *115*, 4349.

[21] C. Ruan, K. Ai, X. Li, L. Lu, *Angew. Chem. Int. Ed.* **2014**, *53*, 5556; *Angew. Chem.* **2014**, *126*, 5662.

[22] Z. Xu, Y. Zhao, H. Wang, X. Wang, T. Lin, *Angew. Chem. Int. Ed.* **2015**, *54*, 4527; *Angew. Chem.* **2015**, *127*, 4610.

[23] X. Liu, C. Leng, L. Yu, K. He, L. J. Brown, Z. Chen, J. Cho, D. Wang, *Angew. Chem. Int. Ed.* **2015**, *54*, 4851; *Angew. Chem.* **2015**, *127*, 4933.

Received: July 30, 2015
Revised: August 27, 2015