Mechanochromic Fluorescence

Deutsche Ausgabe: DOI: 10.1002/ange.201507197
Internationale Ausgabe: DOI: 10.1002/anie.201507197

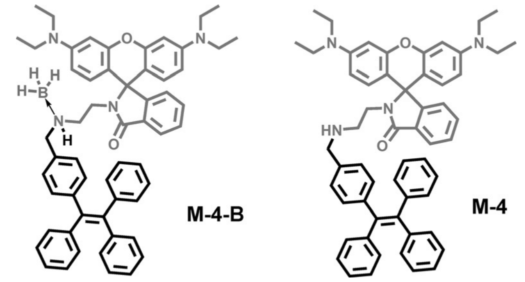
A Mechanochromic Single Crystal: Turning Two Color Changes into a Tricolored Switch

Zhiyong Ma, Zhijian Wang, Xiao Meng, Zhimin Ma, Zejun Xu, Yuguo Ma, and Xinru Jia**

Abstract: *The single crystal of M-4-B was obtained by attaching the boron of BH_3 to the amine linker between a tetraphenylethylene (TPE) unit and rhodamine B. M-4-B showed a novel sequential tricolor switching from dark blue to bluish-green and to a reddish color upon grinding. The boron atom played a key role in developing the single crystal.*

Mechanical stimuli can switch molecular assemblies and induce certain reactions, which is a valuable strategy to create functional materials.[1] Mechanochromic luminescent (MCL) materials alter their photoluminescent colors in response to the action of an external force.[2] Such materials have attracted much attention owing to their promising applications in mechanosensors, fluorescent switches, security papers, and data storage.[3] A number of MCL materials have been documented to date.[4] However, most of the reported examples display a reversible two-color change;[5] multicolor switched materials remain uncommon owing to the lack of universal design principles.[6] The combination of two distinct modulation approaches, by mechanical control of the physical stacking modes and activation of the chemical reactions, is proved as an effective strategy to prepare the multicolored MCL materials.[7] The key points here are to select well-matched luminophores and to regulate the assembled structures of molecules.

Herein, we report a tricolored switchable mechanochromic single crystal M-4-B. It was synthesized simply by combining two different luminophores, a tetraphenyl ethylene (TPE) unit and a rhodamine B (RhB) moiety together (Scheme 1). As reported, some tetraphenyl ethylene (TPE) derivatives exhibited mechanochromic behavior in the solid state because of the transformation from a crystalline to an amorphous phase.[8] Hence, the question in our study is which structure can realize such transition and how to retain the crystalline structure of TPE in the molecule. Surprisingly, we found that a boron atom could function as a trigger to control the crystallization of M-4-B. Boron is known to have strong Lewis acidity, which enables it to bond with nucleophilic species and offers organoboron for addressing specific issues.[5f] In our case, B·N coordination was introduced into the molecular framework to restrict the molecular conformation and to facilitate the crystallization. As expected, a single crystal of M-4-B was developed with the coordination of boron atom with N atom in the spacer. The obtained single crystal switched sequentially from deep-blue to green and to a reddish color. To the best of our knowledge, this is the first example of achieving multicolored switch through controlling the crystallization of an organic compound. Accordingly, we also prepared the compound of M-4 without a boron atom in the structure.[9] M-4 was an amorphous powder and could not be cultured to a single crystal. More importantly, it exhibited only two-color switching from green to reddish upon grinding. It is worth noting that the single crystal was developed by the coordination of a boron atom, which turns the mechanochromic fluorescent emission from two colors to three colors.



Scheme 1. The chemical structures of M-4-B and M-4.

M-4-B was synthesized by a three-step reaction by using RhB and TPE derivative as the reagents. First, the ring-opened form of RhB reacted with ethylenediamine to generate RhB-NH_2 in a spirolactam form; then a nucleophilic addition reaction occurred between the amine group of RhB-NH_2 and aldehyde group of TPE-CHO, to thus give compound **1** (Supporting Information, Scheme S1); then, the C=N double bond was reduced to a C−N bond. M-4-B was initially obtained as a white powder. The single crystal of this molecule was prepared by slowly evaporating a mixed solvent of CH_2Cl_2 and petroleum ether. ^{1}H, ^{13}C, and ^{11}B NMR measurements, X-ray photoelectron spectroscopy (XPS), and HR-ESI mass spectrometry were performed to verify the structure of M-4-B. A characteristic peak of B 1s binding energy (BE) at 188 eV was observed in the XPS spectrum, indicating the existence of boron atom in the structure of M-4-B (Supporting Information, Figure S2). Furthermore, a peak at −14.83 ppm appeared in the ^{11}B NMR spectrum (Support-

---

[*] Z. Y. Ma, Z. J. Wang, X. Meng, Dr. Z. J. Xu, Prof. Y. G. Ma, Prof. X. R. Jia
Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of the Ministry of Education, College of Chemistry and Molecular Engineering, Peking University
Beijing 100871 (China)
E-mail: xrjia@pku.edu.cn

Z. M. Ma
Department of Materials Science and Engineering, College of Engineering, Peking University
Beijing 100871 (China)

Supporting information for this article (synthesis procedures, the mechanochromic behavior of M-4-B, single-crystal data, AIE test, and characterization of reversibility) is available on the WWW under http://dx.doi.org/10.1002/anie.201507197.

ing Information, Figure S1), which was ascribed to the N$-$BH$_3$ structure according to a previous report.[9b] Scheme 1 depicts the structure of M-4-B. The detailed synthetic procedures and the characterization of M-4-B and M-4 are described in the Supporting Information.

Crystallography verified the chemical structure of M-4-B. The ORTEP drawing is shown in Figure 1 and the associated crystal data are summarized in the Supporting Information, Table S1. The crystal of M-4-B is in a monoclinic crystal system and crystallizes in the space group $P\bar{1}$ (No. 2). The whole molecule is highly twisted, with a boron atom coordinated with N atom of the spacer chain connected near the TPE unit. Each unit cell contains two molecules. The molecules adopts antiparallel coupling and establishes efficient interactions by the adjacent molecules through N$-$B$\cdots\pi$, C$-$C$\cdot\cdot\pi$, and C$-$H$\cdots$O hydrogen bonds (Figure 1 b). Viewing along the *b* axis, M-4-B molecules pack into the molecular layers with the aid of $\pi\cdots\pi$ and weak C$-$H$\cdots\pi$ interactions (Supporting Information, Figure S3). It is worth mentioning that N$-$B$\cdots\pi$ interaction played a key role in the single crystal cultivation. Without N$-$B$\cdots\pi$ interaction, the single crystal of M-4 cannot be obtained despite the different solvents and methods that have been tried in our experiments. The B atom as an accepter coordinated with the N atom of the spacer having an electronic pair as the donor. Such coordination interaction may offer steric hindrance, thereby restricting the molecular conformation and facilitating the crystallization.[10]

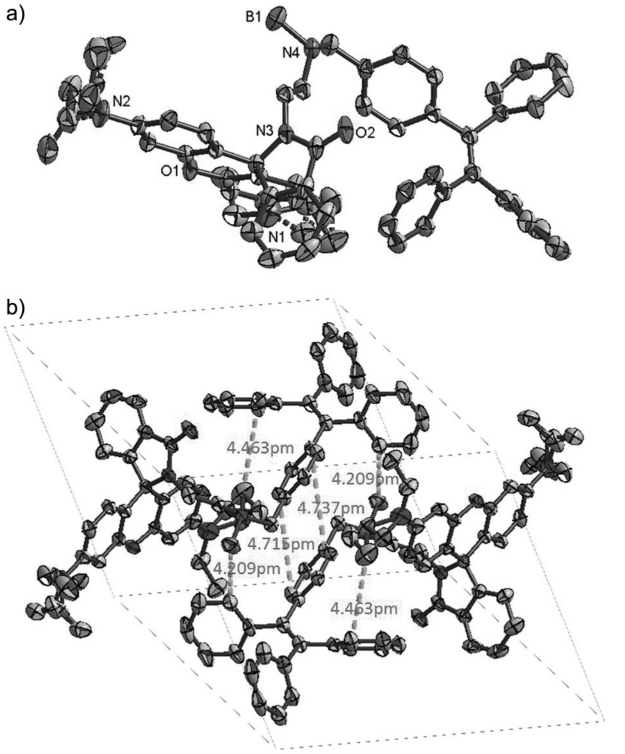


Figure 1. a) ORTEP of M-4-B and b) the stacking mode of the unit cell of M-4-B crystal. Ellipsoids set at 50% probability; hydrogen atoms are omitted for clarity.[13]

Detailed spectroscopy measurements were performed to elucidate the AIE (aggregation-induced emission) property of M-4-B. In dilute THF solution, the maximum absorption band of M-4-B appeared at 274 nm. The Mie scattering effect observed in the UV/Vis spectra revealed that the nano-aggregates were formed with high water content (Supporting Information, Figure S5). The luminescent behavior of M-4-B varied with water fraction (fw) in the system. When fw was lower than 70%, the solution of M-4-B had virtually no emission, which is due to the free rotation of C$-$C bond of the spacer. When fw increased above 70%, M-4-B behaved as a strong emitter because the aggregation of M-4-B molecules prohibited the nonradiative relaxation channel and populates radiative excitons, thus resulting in high quantum yield (Supporting Information, Figures S4, S5). These results indicate that M-4-B is AIE active.[11]

M-4-B crystal displayed sequential multicolored switch from deep-blue to bluish-green and to a reddish color triggered by force. The original crystal sample emitted a deep-blue color (Figure 2 a). This color changed to bluish-green after slightly grinding the crystal with a blunt pestle or just simply shearing (Figure 2 b). Sequentially, a reddish color was observed with continuous grinding of the bluish-green sample in situ (Figure 2 c; Supporting Information, Figure S6). The spectroscopy measurements showed that the emission of original sample was centered at 441 nm; it red-shifted 27 nm and peaked at 468 nm after grinding; further force disturbance resulted in the reddish colored powder with a new peak appeared at 576 nm (Figure 2 d).

Reversibility of tricolor switch was observed. The reddish color could be returned to bluish-green with the emission reappearing at around 465 nm by heating the colored powder at 150 °C for ten minutes (Supporting Information, Figure S8). However, the bluish-green powder could not be fully returned to the original deep-blue at 441 nm either by heating or by solvent treatment. Notably, it showed self-recovery behavior. After placing the sample at room temperature for several days, an emission band at 459 nm was observed. Such recovery behavior may be attributed to the original deep-blue sample with highly crystalline nature, which is not easy to fully restore.

Powder X-ray diffraction (XRD) was employed to understand the structure change of M-4-B under force (Figure 2 e). The deep-blue sample showed sharp reflection peaks, which was an indication of well-ordered microcrystalline structure. By contrast, these peaks disappeared after in situ grinding, which clearly indicated the transition of TPE units in M-4-B from the crystalline form to the amorphous state. The ring-opening reaction of RhB occurred by applying further force, which retained the amorphous phase without any diffraction signals in the XRD profile. When the ground powder were treated by heating for several minutes or just being placed at ambient temperature for a longer time, parts of the sharp peaks appeared again although the emission could not be observed at 441 nm (Supporting Information, Figures S7 b, S8 b). This result means that M-4-B can self-recover to the crystalline state. Differential scanning colorimetry (DSC) results confirmed such behavior by measuring the thermal properties of the sample before and after grinding.

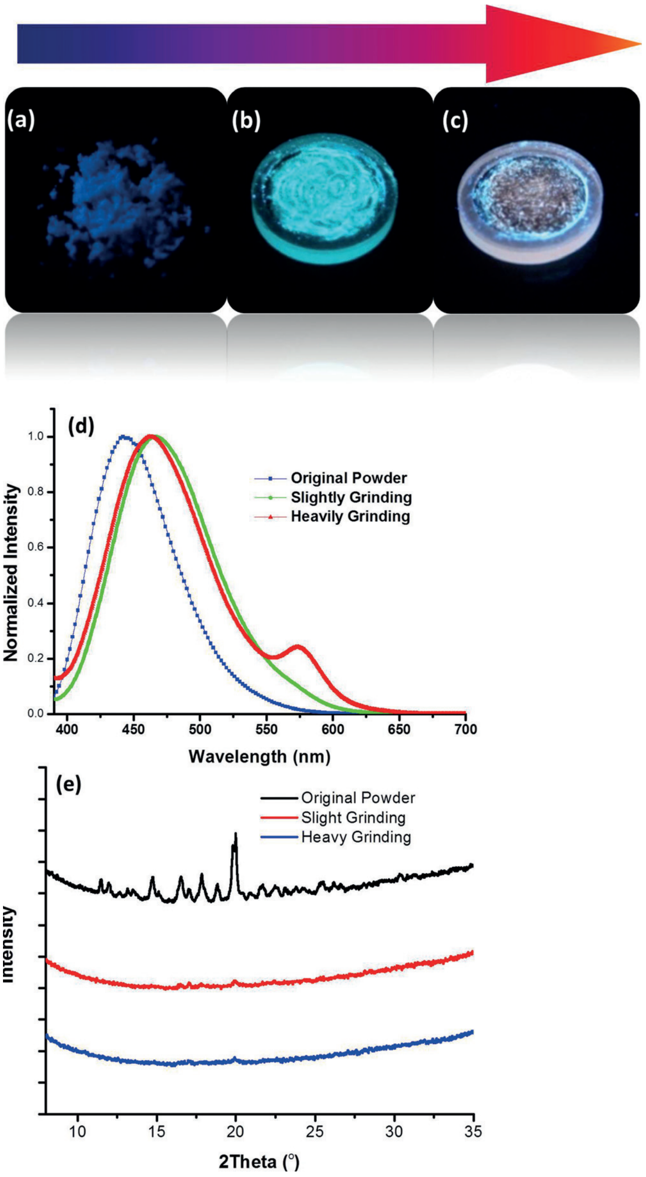


Figure 2. Optical images of a) the original deep-blue powder; b) bluish-green powder after slight grinding; and c) reddish powder after continuous grinding. d) Fluorescent spectra and e) WXRD profiles of original powder (blue line), powder after slightly grinding (green line) and powder after continuous grinding (red line).

An exothermic peak appeared at 152 °C in the DSC thermogram of ground powder, while no such signal presented in the original deep-blue sample (Figure 2; Supporting Information, Figure S10). The exothermic peak is corresponding to the self-recrystallization of M-4-B.

The color switch of M-4-B from deep-blue to bluish-green is associated with the TPE phase change between the crystalline and amorphous state, which is a common phenomenon of some TPE compounds with propeller-like conformations.[8a] As mentioned above, M-4-B in the crystal phase arranged to the molecular layers with the antiparallel coupling by the aid of various interactions, including N−B···π, C−C···π, and C−H···O hydrogen bonds in each layer. The twist stress of TPE molecules in the crystal is enhanced due to the constricted environment. When grinding by a pestle, the crystals transferred to the amorphous powder with the twisted stress released, which causes the red-shift in emission because of the conformational planarization. Interestingly, our result is different from the previously reported example that showed TPE had no response to mechanical grinding owing to the spontaneous crystallization property. This may be attributed to the large twisted molecular conformation of M-4-B, which inhibited the recrystallization of TPE unit.[12] The reddish color is a nature of the ring-opened state of RhB. Further excessive grinding or crushing action provided energy to break the covalent bond between the spiro C atom and the amide N atom in the spirolactam. The molecular conformation transferred from a twisted spirolactam to a planarized zwitterionic structure, which initiates a dramatically absorption change and turns on the fluorescent emission. UV/Vis and fluorescence measurements supported the occurrence of the ring-opening reaction of RhB consisted in M-4-B (Supporting Information, Figure S11).

However, M-4 behaved quite differently. The original powder emitted at 477 nm with a green color (Supporting Information, Figure S13). This color changed to reddish by grinding. XRD measurements evidenced that both of the original solid and the reddish powder of M-4 were amorphous (Supporting Information, Figure S14). It is certain that the boron is critical in the crystallization of M-4-B with original deep-blue color. Here, the B atom is more like a hairpin to fix the molecular conformation and restrain the molecules in the crystalline phase.

Based on the above results and analysis, we may contribute the mechanically induced fluorescence changes of M-4-B to the following reasons (Supporting Information, Figure S15): the initial crystal of M-4-B emits deep-blue luminescence. It changes to bluish-green due to the TPE units transferred to the amorphous phase. Further force action induces the ring-opening reaction of RhB moiety to be a planarized zwitterionic structure, thus leading to the reddish fluorescence. The merits of our present work are the simple connection of two chromophores together without sophisticated and time-consuming synthesis; the control of a single crystal formation by inserting a boron atom to fix the molecular conformation; and the orderly emission switches from deep-blue to bluish-green and to a reddish color as the external force increased. The use of a simple small atom to restrict the molecular conformation and facilitation the crystallization may be a step forward in the preparation of multicolor switched mechanochromic materials. Our study may open a new strategy to provide a broad perspective for the development of mechanochemistry.

Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (21174005) to X.R.J. and partially supported by National Basic Research Program of China (973 program, No. 2011CB933300).

Keywords: boron · mechanochromic fluorescence · multicolored switch · rhodamine B · single crystals

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 519–522
Angew. Chem. **2016**, *128*, 529–532

[1] a) Z. Chi, X. Zhang, B. Xu, X. Zhou, C. Ma, Y. Zhang, S. Liu, J. Xu, *Chem. Soc. Rev.* **2012**, *41*, 3878–3896; b) Z. Ma, Z. Wang, M. Teng, Z. Xu, X. Jia, *ChemPhysChem* **2015**, *16*, 1811–1828; c) X. Zhang, Z. Chi, Y. Zhang, S. Liu, J. Xu, *J. Mater. Chem. C* **2013**, *1*, 3376–3390; d) D. A. Davis, A. Hamilton, J. Yang, L. D. Cremar, D. Van Gough, S. L. Potisek, M. T. Ong, P. V. Braun, T. J. Martinez, S. R. White, J. S. Moore, N. R. Sottos, *Nature* **2009**, *459*, 68–72; e) X. Meng, G. Qi, C. Zhang, K. Wang, B. Zou, Y. Ma, *Chem. Commun.* **2015**, *51*, 9320–9323.

[2] a) Y. Chen, A. J. H. Spiering, S. Karthikeyan, G. W. M. Peters, E. W. Meijer, R. P. Sijbesma, *Nat. Chem.* **2012**, *4*, 559–562; b) Z. Mao, Z. Yang, Y. Mu, Y. Zhang, Y.-F. Wang, Z. Chi, C.-C. Lo, S. Liu, A. Lien, J. Xu, *Angew. Chem. Int. Ed.* **2015**, *54*, 6270–6273; *Angew. Chem.* **2015**, *127*, 6368–6371; c) H. M. Klukovich, T. B. Kouznetsova, Z. S. Kean, J. M. Lenhardt, S. L. Craig, *Nat. Chem.* **2013**, *5*, 110–114; d) S. Xu, T. Liu, Y. Mu, Y.-F. Wang, Z. Chi, C.-C. Lo, S. Liu, Y. Zhang, A. Lien, J. Xu, *Angew. Chem. Int. Ed.* **2015**, *54*, 874–878; *Angew. Chem.* **2015**, *127*, 888–892; e) M. Tanioka, S. Kamino, A. Muranaka, Y. Ooyama, H. Ota, Y. Shirasaki, J. Horigome, M. Ueda, M. Uchiyama, D. Sawada, S. Enomoto, *J. Am. Chem. Soc.* **2015**, *137*, 6436–6439; f) X. Zhang, Z. Chi, H. Li, B. Xu, X. Li, W. Zhou, S. Liu, Y. Zhang, J. Xu, *Chem. Asian J.* **2011**, *6*, 808–811; g) Z. Xie, C. Chen, S. Xu, J. Li, Y. Zhang, S. Liu, J. Xu, Z. Chi, *Angew. Chem. Int. Ed.* **2015**, *54*, 7181–7184; *Angew. Chem.* **2015**, *127*, 7287–7290; h) J. Wang, J. Mei, R. Hu, J. Z. Sun, A. Qin, B. Z. Tang, *J. Am. Chem. Soc.* **2012**, *134*, 9956–9966; i) Y. Matsunaga, J.-S. Yang, *Angew. Chem. Int. Ed.* **2015**, *54*, 7985–7989; *Angew. Chem.* **2015**, *127*, 8096–8100.

[3] a) C. H. Woodall, C. M. Beavers, J. Christensen, L. E. Hatcher, M. Intissar, A. Parlett, S. J. Teat, C. Reber, P. R. Raithby, *Angew. Chem. Int. Ed.* **2013**, *52*, 9691–9694; *Angew. Chem.* **2013**, *125*, 9873–9876; b) Y. Dong, B. Xu, J. Zhang, X. Tan, L. Wang, J. Chen, H. Lv, S. Wen, B. Li, L. Ye, B. Zou, W. Tian, *Angew. Chem. Int. Ed.* **2012**, *51*, 10782–10785; *Angew. Chem.* **2012**, *124*, 10940–10943; c) H.-J. Kim, D. R. Whang, J. Gierschner, C. H. Lee, S. Y. Park, *Angew. Chem. Int. Ed.* **2015**, *54*, 4330–4333; *Angew. Chem.* **2015**, *127*, 4404–4407; d) Y. Sagara, T. Kato, *Angew. Chem. Int. Ed.* **2008**, *47*, 5175–5178; *Angew. Chem.* **2008**, *120*, 5253–5256; e) Y. Sagara, T. Kato, *Angew. Chem. Int. Ed.* **2011**, *50*, 9128–9132; *Angew. Chem.* **2011**, *123*, 9294–9298; f) Q. Benito, X. F. Le Goff, S. Maron, A. Fargues, A. Garcia, C. Martineau, F. Taulelle, S. Kahlal, T. Gacoin, J.-P. Boilot, S. Perruchas, *J. Am. Chem. Soc.* **2014**, *136*, 11311–11320; g) P. Galer, R. C. Korosec, M. Vidmar, B. Šket, *J. Am. Chem. Soc.* **2014**, *136*, 7383–7394; h) M. Krikorian, S. Liu, T. M. Swager, *J. Am. Chem. Soc.* **2014**, *136*, 2952–2955; i) M. B. Larsen, A. J. Boydston, *J. Am. Chem. Soc.* **2013**, *135*, 8189–8192.

[4] a) G. Li, F. Song, D. Wu, J. Lan, X. Liu, J. Wu, S. Yang, D. Xiao, J. You, *Adv. Funct. Mater.* **2014**, *24*, 747–753; b) Y. Sagara, T. Komatsu, T. Ueno, K. Hanaoka, T. Kato, T. Nagano, *Adv. Funct. Mater.* **2013**, *23*, 5277–5284; c) M. S. Kwon, J. Gierschner, S.-J. Yoon, S. Y. Park, *Adv. Mater.* **2012**, *24*, 5401–5401; d) M.-J. Teng, X.-R. Jia, S. Yang, X.-F. Chen, Y. Wei, *Adv. Mater.* **2012**, *24*, 1255–1261; e) W. Z. Yuan, Y. Tan, Y. Gong, P. Lu, J. W. Y. Lam, X. Y. Shen, C. Feng, H. H. Y. Sung, Y. Lu, I. D. Williams, J. Z. Sun, Y. Zhang, B. Z. Tang, *Adv. Mater.* **2013**, *25*, 2837–2843; f) Y. Zhang, T. Han, S. Gu, T. Zhou, C. Zhao, Y. Guo, X. Feng, B. Tong, J. Bing, J. Shi, J. Zhi, Y. Dong, *Chem. Eur. J.* **2014**, *20*, 8856–8861; g) L. Wang, K. Wang, B. Zou, K. Ye, H. Zhang, Y. Wang, *Adv. Mater.* **2015**, *27*, 2918–2922.

[5] a) S.-J. Yoon, J. W. Chung, J. Gierschner, K. S. Kim, M.-G. Choi, D. Kim, S. Y. Park, *J. Am. Chem. Soc.* **2010**, *132*, 13675–13683; b) G.-G. Shan, H.-B. Li, H.-Z. Sun, D.-X. Zhu, H.-T. Cao, Z.-M. Su, *J. Mater. Chem. C* **2013**, *1*, 1440–1449; c) J. Shi, N. Chang, C. Li, J. Mei, C. Deng, X. Luo, Z. Liu, Z. Bo, Y. Q. Dong, B. Z. Tang, *Chem. Commun.* **2012**, *48*, 10675–10677; d) C. Y. Y. Yu, R. T. K. Kwok, J. Mei, Y. Hong, S. Chen, J. W. Y. Lam, B. Z. Tang, *Chem. Commun.* **2014**, *50*, 8134–8136; e) N. Zhao, Z. Yang, J. W. Y. Lam, H. H. Y. Sung, N. Xie, S. Chen, H. Su, M. Gao, I. D. Williams, K. S. Wong, B. Z. Tang, *Chem. Commun.* **2012**, *48*, 8637–8639; f) Z. Zhao, Z. Chang, B. He, B. Chen, C. Deng, P. Lu, H. Qiu, B. Z. Tang, *Chem. Eur. J.* **2013**, *19*, 11512–11517.

[6] a) X. Luo, W. Zhao, J. Shi, C. Li, Z. Liu, Z. Bo, Y. Q. Dong, B. Z. Tang, *J. Phys. Chem. C* **2012**, *116*, 21967–21972; b) K. Nagura, S. Saito, H. Yusa, H. Yamawaki, H. Fujihisa, H. Sato, Y. Shimoikeda, S. Yamaguchi, *J. Am. Chem. Soc.* **2013**, *135*, 10322–10325; c) C. Li, X. Luo, W. Zhao, C. Li, Z. Liu, Z. Bo, Y. Dong, Y. Q. Dong, B. Z. Tang, *New J. Chem.* **2013**, *37*, 1696–1699; d) C. Li, X. Luo, W. Zhao, Z. Huang, Z. Liu, B. Tong, Y. Dong, *Sci. China Chem.* **2013**, *56*, 1173–1177; e) Y. Zhang, K. Wang, G. Zhuang, Z. Xie, C. Zhang, F. Cao, G. Pan, H. Chen, B. Zou, Y. Ma, *Chem. Eur. J.* **2015**, *21*, 2474–2479; f) S. Yagai, S. Okamura, Y. Nakano, M. Yamauchi, K. Kishikawa, T. Karatsu, A. Kitamura, A. Ueno, D. Kuzuhara, H. Yamada, T. Seki, H. Ito, *Nat. Commun.* **2014**, *5*, 4013.

[7] a) Z. Ma, M. Teng, Z. Wang, S. Yang, X. Jia, *Angew. Chem. Int. Ed.* **2013**, *52*, 12268–12272; *Angew. Chem.* **2013**, *125*, 12494–12498; b) M.-J. Teng, X.-R. Jia, X.-F. Chen, Y. Wei, *Angew. Chem. Int. Ed.* **2012**, *51*, 6398–6401; *Angew. Chem.* **2012**, *124*, 6504–6507; c) Z. Ma, Z. Wang, Z. Xu, X. Jia, Y. Wei, *J. Mater. Chem. C* **2015**, *3*, 3399–3405; d) Z. Ma, M. Teng, Z. Wang, X. Jia, *Tetrahedron Lett.* **2013**, *54*, 6504–6506; e) Z. Ma, F. Yang, Z. Wang, X. Jia, *Tetrahedron Lett.* **2015**, *56*, 393–396.

[8] a) Q. Qi, Y. Liu, X. Fang, Y. Zhang, P. Chen, Y. Wang, B. Yang, B. Xu, W. Tian, S. X.-A. Zhang, *RSC Adv.* **2013**, *3*, 7996–8002; b) Q. Qi, J. Zhang, B. Xu, B. Li, S. X.-A. Zhang, W. Tian, *J. Phys. Chem. C* **2013**, *117*, 24997–25003; c) X. Luo, J. Li, C. Li, L. Heng, Y. Q. Dong, Z. Liu, Z. Bo, B. Z. Tang, *Adv. Mater.* **2011**, *23*, 3261–3265; d) C. Y. K. Chan, J. W. Y. Lam, Z. Zhao, S. Chen, P. Lu, H. H. Y. Sung, H. S. Kwok, Y. Ma, I. D. Williams, B. Z. Tang, *J. Mater. Chem. C* **2014**, *2*, 4320–4327.

[9] a) H. Dong, H. Berke, *J. Organomet. Chem.* **2011**, *696*, 1803–1808; b) C. A. Jaska, K. Temple, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2003**, *125*, 9424–9434.

[10] C. Ma, B. Xu, G. Xie, J. He, X. Zhou, B. Peng, L. Jiang, B. Xu, W. Tian, Z. Chi, S. Liu, Y. Zhang, J. Xu, *Chem. Commun.* **2014**, *50*, 7374–7377.

[11] a) Q. Qi, J. Qian, X. Tan, J. Zhang, L. Wang, B. Xu, B. Zou, W. Tian, *Adv. Funct. Mater.* **2015**, *25*, 4005–4010; b) Q. Qi, J. Qian, S. Ma, B. Xu, S. X.-A. Zhang, W. Tian, *Chem. Eur. J.* **2015**, *21*, 1149–1155; c) Q. Qi, X. Fang, Y. Liu, P. Zhou, Y. Zhang, B. Yang, W. Tian, S. X.-A. Zhang, *RSC Adv.* **2013**, *3*, 16986–16989.

[12] Y. Lin, G. Chen, L. Zhao, W. Z. Yuan, Y. Zhang, B. Z. Tang, *J. Mater. Chem. C* **2015**, *3*, 112–120.

[13] CCDC 1410148 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Received: August 3, 2015