

Organoboron Compounds with Morphology-Dependent NIR Emissions and Dual-Channel Fluorescent ON/OFF Switching

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Supporting Information

ABSTRACT: A novel family of organoboron compounds 1–4 with bright near-infrared (NIR) emissions in the crystalline state was synthesized. They show a morphology-dependent emission “ON” and “OFF” feature and volatile acid/base-induced fluorescence saltation which allow the realization of reversible solid-state fluorescence switching in the NIR region by totally different procedures: mechanical grinding/solvent annealing and acid/base vapor fuming.



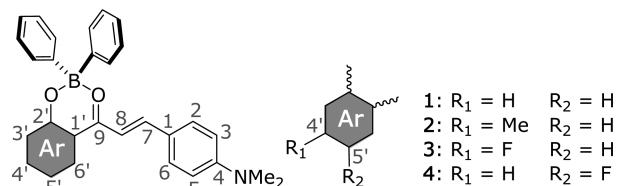
Organic materials with brightly fluorescent solid-state emissions are very important because of their wide applications in optoelectronics including sensors, lasers, and electroluminescent devices.^{1,2} Flat and extended π -conjugated frameworks or strong donor–acceptor skeletons are usually employed in the molecular design strategy to construct red or NIR fluorescent materials.³ Although these structures may be of significance in aggregation-induced emission or some excited species,⁴ they generally result in strong intermolecular π – π stacking or considerable dipole–dipole interactions in the densely aggregated state, thereby indicating aggregation-caused fluorescence quenching (ACQ) as being particularly significant for red/NIR fluorophores which renders the emitters weakly or nonemissive in the solid state.⁵ Due to this serious ACQ effect, only a few examples of organic materials with a solid-state emission peak beyond 700 nm display fluorescence efficiency over 0.3.⁶ Therefore, the construction of NIR emissive materials with high solid-state fluorescence efficiency is in urgent demand.

Four-coordinate organoboron compounds with rigid π -conjugated structures^{7–12} are promising luminescent materials because of their intense luminescence, good thermal stability, and high carrier mobility which enable them to be applied as emitters in optoelectronics such as OLEDs. The structures of the boron-containing materials can be easily modified for desirable properties by functionalizing either the ligands or boron reagents. Among those, organoboron materials with efficient solid-state NIR fluorescence are extremely rare. Recently, Fages and co-workers synthesized a series of boron difluorides (LBF₂) and found that some of them showed solid-state NIR emissions.¹³ We report here a class of boron materials with morphology-dependent “ON/OFF” solid-state NIR emissions as well as volatile acid/base-induced fluorescence saltation. The reversible fluorescence “ON/OFF”

switching has been realized in the NIR region based on these boron compounds by totally different procedures: mechanical grinding/solvent annealing and acid/base vapor fuming.

4-Dimethylamino-2'-hydroxychalcone ligands were chosen to construct the target boron compounds 1–4. Structural modification has been carried out on the Ar group by introducing Me and F on the 4' or 5' position (Scheme 1).

Scheme 1. Molecular Structures of Organoboron Compounds 1–4



The ligands are synthesized through a condensation reaction according to the reported procedure.¹⁴ The targets 1–4 are prepared by refluxing the mixture of ligands and triphenylborane in THF overnight. Recrystallization of the reaction mixture from CH₂Cl₂/MeOH solvent gives rise to tiny dark green or blue crystals as pure products which were characterized by NMR spectra, element analyses, and mass spectra. NMR analyses indicate only *E*-isomers were formed.

The absorption and fluorescence of boron compounds 1–4 in solution were measured in CH₂Cl₂, and the spectra are shown in Figure 1. For 1–3, the lowest-energy transition bands are similar and peaked around 535 nm. The absorption peak of 5'-fluorine-substituted compound 4 is located at 554 nm which

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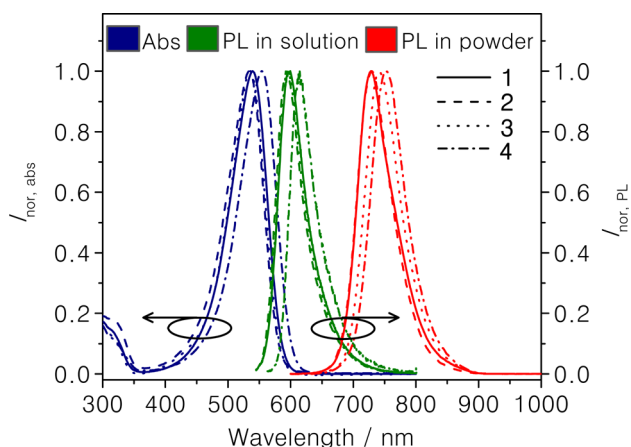


Figure 1. Absorption and emission spectra of organoboron compounds 1–4 in different states.

is red-shifted by 20 nm compared to its 4'-substituted analog 3, demonstrating that the substitution position plays an important role in tuning the photophysical properties of this type of boron compounds. Compounds 1–3 are all similarly fluorescent with emission bands at 598, 593, and 596 nm, respectively, while 4 displays a largely red-shifted emission band at 613 nm which is consistent with the absorption trend. The fluorescence efficiencies (Φ_f) of 1–4 are 0.02 (1), 0.04 (2), 0.01 (3), and <0.01 (4). Freezing the solution cannot obviously enhance the fluorescence intensity (Figure S1), reflecting that intramolecular rotations and vibrations are not the main factor for the low fluorescence efficiencies of these boron compounds in solution.

As shown in Figure 1, the fluorescence spectra of crystalline solids 1–4 recrystallized from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ are all located in the NIR region with emission bands peaking at 728, 730, 740, and 752 nm, respectively, which are greatly red-shifted compared to those of solutions. The huge red shifts of emission reflect that molecules are densely packed after they aggregated into crystalline solids. Notably, the NIR emissive crystalline powders show very high Φ_f being 0.30, 0.34, 0.26, and 0.21 for 1–4, respectively. This fluorescent behavior matches the description of crystalline-enhanced emission (CEE) proposed by Tang in 2007.¹⁵ There has been only a limited number of reported organic compounds that show CEE.¹⁶ Our case is the first example of crystalline-enhanced NIR emission. The molecular planarization of ligand induced by the crystalline lattice strain and restriction of molecular distortions by intermolecular interactions are considered to be responsible for the observed CEE, although big crystals suited for X-ray crystal analyses have not been obtained. The Φ_f of compound 2 (0.34) is very high for the NIR emissive dye with an emission peak beyond 730 nm. Interestingly, the spin-coated thin films of 1–4 are weakly fluorescent in the NIR region and their Φ_f values are all close to 0. The different emissions of powders and films indicate that the solid-state fluorescence of these boron materials is highly dependent on the morphologies they adopt. The powders show strong and sharp diffraction peaks, whereas the films display no obvious peak (Figure 2), indicating molecules in powders are arranged in an orderly manner while those in thin films are amorphously stacked.

The amorphous and crystalline solids of these boron compounds are fluorescent “OFF” and “ON”, respectively. Thus, reversible switching between the fluorescent dark and

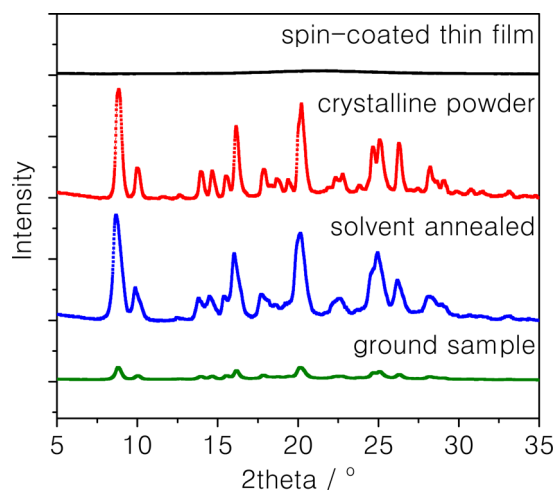


Figure 2. Powder X-ray diffraction (PXRD) patterns of compound 1 in various states.

bright states arouses our interest and further efforts have been concentrated on this issue. Mechanical grinding has proved to be a simple engineering process to convert crystalline powders into amorphous solids.¹⁷ After grinding, the emission intensity of crystalline sample 1 significantly decreases, as shown in Figure 3. The PXRD pattern (Figure 2) of the ground sample

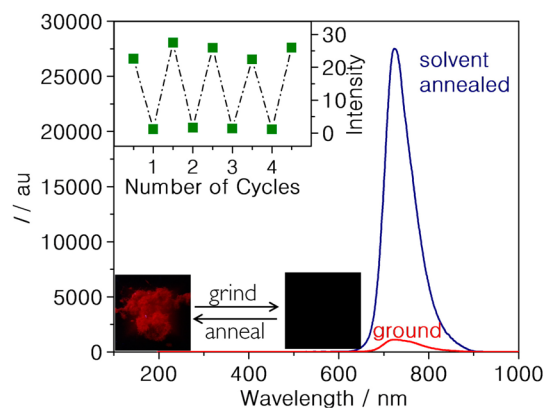


Figure 3. PL spectra comparison of ground/annealed samples (1) and repeated switching between dark and bright states.

shows very weak and sparse diffraction peaks, reflecting that the highly ordered structure has been transformed into a random packed one after grinding. Therefore, the bright NIR emission of crystalline powders always faded away by this simple process. Turning on the extinguished emission of the solids was attempted next. Molecular repacking by solvent/thermal annealing may convert amorphous solids into crystalline powders. Indeed, the weakly emissive ground sample on a glass substrate placed in a small container saturated with CH_2Cl_2 vapor will quickly convert to a brightly fluorescent state and the $I_{\text{fumed}}/I_{\text{ground}}$ is about 22. The annealed sample shows sharp diffraction peaks, similar to the unground powders, indicating that the amorphous ground solid transfers into the crystalline state after solvent annealing (Figure 3). This switching between the fluorescence “OFF” and “ON” state by mechanical grinding and solvent annealing can be repeated many times without an obvious fatigue response. Compounds 2–4 show similar solid-state NIR fluorescence “ON/OFF” switching, reflecting the generality of this elegant luminescent

behavior. The $I_{\text{ground}}/I_{\text{fumed}}$ ratios of emission intensity are 12, 13, and 15 for **2**, **3**, and **4**, respectively. The on–off switching of solid-state luminescence by external stimuli has become of increasing importance in a variety of applications. It is worth noting that solid-state fluorescence “ON/OFF” switching has seldom been realized in the NIR region. Thus, we believe the achievements in the present study might be valuable and have important scientific significance in this research area.

Another notable feature is that all the boron compounds display trifluoroacetic acid (TFA) and triethylamine (TEA) induced fluorescence quenching and lighting. Because of the electron-donating dimethylamino group on the 2'-hydroxychalcone ligand, these boron compounds **1–4** exhibit a prominent polar nature as well as Lewis base character. Following this consideration, an experiment of compound **1** focused on an acid stimulation response has been carried out and the volatile TFA was selected as the stimulus. As shown in Figure 4, The bright NIR emissive crystalline samples can

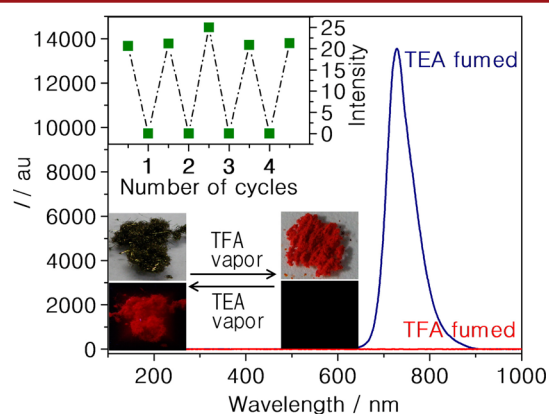


Figure 4. PL spectra comparison of TFA/TEA fumed samples (**1**) and repeated switching between dark and bright states.

gradually convert into completely nonemissive solids which are accompanied by a color change from dark green to red when treated with TFA vapor in a closed container within 10 min. The spectroscopic instrument cannot detect the fluorescence signal of the TFA fumed sample. Thus, this fluorescence “ON/OFF” switching has a very high $I_{\text{ON}}/I_{\text{OFF}}$ value. The fluorescence “ON/OFF” transformation is probably caused by the protonation of the amino group that completely eliminates the intrinsic intramolecular charge-transfer character of the donor–acceptor molecule which is of great benefit to its high fluorescence efficiency in the crystalline state. Protonation induced molecular conformation variation and/or a molecular packing change are other possible reasons for the acid-induced fluorescence quenching. Interestingly, the fluorescent “OFF” sample would immediately recover its highly efficient NIR emission by fuming with TEA vapor, reflecting that the acid–base fuming process could also induce reversible solid-state fluorescent “ON/OFF” switching. Moreover, this process can be repeated many times without any obvious attenuation of the emission intensity. The three other NIR fluorescent boron compounds **2**, **3**, and **4** also show switching properties similar to those of compound **1**. Thus, reversible NIR fluorescent “ON/OFF” switching in the solid state of these four-coordinate boron compounds has been realized by a simple acid–base fuming process which might have great importance in the new strategy of constructing fluorescent molecule switches.

In summary, we have synthesized a series of boron-containing compounds that display weak orange to red emission in solutions. The slow aggregation of molecules by a recrystallization approach produces crystalline powders with highly efficient NIR fluorescence whereas the fast accumulation of molecules by a spin-coating method gives rise to amorphous thin films with very weak NIR light. Thus, these boron-containing materials display morphology-dependent solid-state NIR emission and are CEE-active. Interestingly, the NIR fluorescent dark and bright states can be smoothly switched through disrupting ordered molecular packing (mechanical grinding) and molecular repacking processes (solvent annealing). The present study not only reported a series of highly NIR fluorescent boron-containing materials but also demonstrated an interesting morphology-dependent NIR emission phenomenon. In addition, all the boron-containing solids display reversible NIR fluorescent “ON/OFF” responses when treated with volatile acid/base vapors. Thus, an interesting dual-channel “ON/OFF” NIR fluorescent switching process has been first realized by using the present boron materials which might have a significant effect on the design strategy of molecular switching.

■ ASSOCIATED CONTENT

Supporting Information

Details of experimental procedures, NMR and PL spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Recent reviews: (a) Hudson, Z. M.; Wang, S. *Acc. Chem. Res.* **2009**, *42*, 1584. (b) Figueira-Duarte, T. M.; Müllen, K. *Chem. Rev.* **2011**, *111*, 7260. (c) Li, D.; Zhang, H.; Wang, Y. *Chem. Soc. Rev.* **2013**, *42*, 8416. (d) Hong, Y.; Lam, J. W. Y.; Tang, B. Z. *Chem. Soc. Rev.* **2011**, *40*, 5361. (e) Chi, Z.; Zhang, X.; Xu, B.; Zhong, X.; Ma, C.; Zhang, Y.; Liu, S.; Xu, J. *Chem. Soc. Rev.* **2012**, *41*, 3878.
- (2) (a) Kim, Y.; Bouffard, J.; Kooi, S. E.; Swager, T. M. *J. Am. Chem. Soc.* **2005**, *127*, 13726. (b) Wakamiya, A.; Mori, K.; Yamaguchi, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 4273. (c) Jung, B.-J.; Yoon, C.-B.; Shim, H.-K.; Do, L.-M.; Zyung, T. *Adv. Funct. Mater.* **2001**, *11*, 430. (d) Li, D.; Zhang, H.; Wang, C.; Huang, S.; Guo, J.; Wang, Y. *J. Mater. Chem.* **2012**, *22*, 4319. (e) Steffen, A.; Tay, M. G.; Batsanov, A. S.; Howard, J. A. K.; Beeby, A.; Vuong, K. O.; Sun, X.-Z.; George, M. W.; Marder, T. B. *Angew. Chem., Int. Ed.* **2010**, *122*, 2399. (f) Collings, J. C.; Parsons, A. C.; Porres, L.; Beeby, A.; Batsanov, A. S.; Howard, J. A. K.; Lydon, D. P.; Low, P. J.; Fairlamb, I. J. S.; Marder, T. B. *Chem. Commun.* **2005**, 2666. (g) Rourke, J. P.; Batsanov, A. S.; Howard, J. A. K.; Marder, T. B. *Chem. Commun.* **2001**, 2626.
- (3) (a) Yao, Y.-S.; Zhou, Q.-Z.; Wang, X.-S.; Wang, Y.; Zhang, B.-W. *J. Mater. Chem.* **2006**, *16*, 3512. (b) Odom, S. A.; Parkin, S. R.; Anthony, J. E. *Org. Lett.* **2003**, *5*, 4245.

- (4) (a) Hinoue, T.; Shigenoi, Y.; Sugino, M.; Mizobe, Y.; Hisaki, I.; Miyata, M.; Tohnai, N. *Chem.—Eur. J.* **2012**, *18*, 4634. (b) Tanaka, M.; Ohta, E.; Sakai, A.; Yoshimoto, Y.; Mizuno, K.; Ikeda, H. *Tetrahedron Lett.* **2013**, *54*, 4380.
- (5) (a) Baumes, J. M.; Gassensmith, J. J.; Giblin, J.; Lee, J.-J.; White, A. G.; Culligan, W. J.; Leevy, W. M.; Kuno, M.; Smith, B. D. *Nat. Chem.* **2010**, *2*, 1025. (b) Koide, Y.; Urano, Y.; Hanaoka, K.; Terai, T.; Nagano, T. *J. Am. Chem. Soc.* **2011**, *133*, 5680. (c) Tang, B.; Yu, F.; Li, P.; Tong, L.; Duan, X.; Xie, T.; Wang, X. *J. Am. Chem. Soc.* **2009**, *131*, 3016. (d) Xie, Y.-S.; Yamaguchi, K.; Toganoh, M.; Uno, H.; Suzuki, M.; Mori, S.; Saito, S.; Osuka, A.; Furuta, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 5496. (e) Yang, Y.; Lowry, M.; Xu, X.; Escobedo, J. O.; Sibrían-Vázquez, M.; Wong, L.; Schowalter, C. M.; Jensen, T. J.; Fronczek, F. R.; Warner, I. M.; Strongin, R. M. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 8829. (f) Umezawa, K.; Nakamura, Y.; Makino, H.; Citterio, D.; Suzuki, K. *J. Am. Chem. Soc.* **2008**, *130*, 1550. (g) Meek, S. T.; Nesterov, E. E.; Swager, T. M. *Org. Lett.* **2008**, *10*, 2991. (h) Sreejith, S.; Divya, K. P.; Ajayaghosh, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 7883. (i) Mayerhöffer, U.; Fimmel, B.; Würthner, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 164.
- (6) Shimizu, M.; Kaki, R.; Takeda, Y.; Hiyama, T.; Nagai, N.; Yamagishi, H.; Furutani, H. *Angew. Chem., Int. Ed.* **2012**, *51*, 4095.
- (7) (a) Lesley, M. J. G.; Woodward, A.; Taylor, N. J.; Marder, T. B.; Cazenobe, I.; Ledoux, I.; Zyss, J.; Thornton, A.; Bruce, D. W.; Kakkar, A. K. *Chem. Mater.* **1998**, *10*, 1355. (b) Entwistle, C. D.; Marder, T. B. *Chem. Mater.* **2004**, *16*, 4574. (c) Entwistle, C. D.; Marder, T. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2927.
- (8) (a) Wang, S. *Coord. Chem. Rev.* **2001**, *215*, 79. (b) Rao, Y.; Amarne, H.; Wang, S. *Coord. Chem. Rev.* **2012**, *256*, 759. (c) Baik, C.; Murphy, S. K.; Wang, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 8224. (d) Rao, Y.-L.; Wang, S. *Inorg. Chem.* **2011**, *50*, 12263. (e) Cui, Y.; Wang, S. *J. Org. Chem.* **2006**, *71*, 6485.
- (9) (a) Iida, A.; Saito, S.; Sasamori, T.; Yamaguchi, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 3760. (b) Nagura, K.; Saito, S.; Fröhlich, R.; Glorius, F.; Yamaguchi, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 7762. (c) Wakamiya, A.; Taniguchi, Y.; Yamaguchi, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 3170. (d) Job, A.; Wakamiya, A.; Kehr, G.; Erker, G.; Yamaguchi, S. *Org. Lett.* **2010**, *12*, 5470. (e) Fukazawa, A.; Yamada, H.; Yamaguchi, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 5582. (f) Fukazawa, A.; Yamada, H.; Sasaki, Y.; Akiyama, S.; Yamaguchi, S. *Chem.—Asian J.* **2010**, *5*, 466. (g) Hudson, Z. M.; Ko, S.-B.; Yamaguchi, S.; Wang, S. *Org. Lett.* **2012**, *14*, 5610.
- (10) (a) Kubota, Y.; Tanaka, S.; Funabiki, K.; Matsui, M. *Org. Lett.* **2012**, *14*, 4682. (b) Kubota, Y.; Tsuzuki, T.; Funabiki, K.; Ebihara, M.; Matsui, M. *Org. Lett.* **2010**, *12*, 4010. (c) Kubota, Y.; Ozaki, Y.; Funabiki, K.; Matsui, M. *J. Org. Chem.* **2013**, *78*, 7058. (d) Kubota, Y.; Hara, H.; Tanaka, S.; Funabiki, K.; Matsui, M. *Org. Lett.* **2011**, *13*, 6544.
- (11) (a) Zhang, H.; Huo, C.; Zhang, J.; Zhang, P.; Tian, W.; Wang, Y. *Chem. Commun.* **2006**, 281. (b) Zhang, H.; Huo, C.; Ye, K.; Zhang, P.; Tian, W.; Wang, Y. *Inorg. Chem.* **2006**, *45*, 2788. (c) Zhang, Z.; Bi, H.; Zhang, Y.; Yao, D.; Gao, H.; Fan, Y.; Zhang, H.; Wang, Y.; Wang, Y.; Chen, Z.; Ma, D. *Inorg. Chem.* **2009**, *48*, 7230. (d) Li, D.; Zhang, Z.; Zhao, S.; Wang, Y.; Zhang, H. *Dalton Trans.* **2011**, *40*, 1279. (e) Li, D.; Yuan, Y.; Bi, H.; Yao, D. D.; Zhao, X. J.; Tian, W. J.; Wang, Y.; Zhang, H. Y. *Inorg. Chem.* **2011**, *50*, 4825. (f) Li, D.; Wang, K.; Huang, S.; Qu, S. N.; Liu, X.; Zhu, Q.; Zhang, H.; Wang, Y. *J. Mater. Chem.* **2011**, *21*, 15298. (g) Li, D.; Zhang, H.; Wang, C.; Wang, Y. *J. Mater. Chem.* **2012**, *22*, 4319.
- (12) (a) Wu, Y.-Y.; Chen, Y.; Gou, G.-Z.; Mu, W.-H.; Lv, X.-J.; Du, M.-L.; Fu, W.-F. *Org. Lett.* **2012**, *14*, 5226. (b) Ono, K.; Hashizume, J.; Yamaguchi, H.; Tomura, M.; Nishida, J.-I.; Yamashita, Y. *Org. Lett.* **2009**, *11*, 4326. (c) Yoshii, R.; Nagai, A.; Tanaka, K.; Chujo, Y. *Chem.—Eur. J.* **2013**, *19*, 4506. (d) Zhou, Y.; Xiao, Y.; Chi, S.; Qian, X. *Org. Lett.* **2008**, *10*, 633.
- (13) D'Aléo, A.; Gachet, D.; Heresanu, V.; Giorgi, M.; Fages, F. *Chem.—Eur. J.* **2012**, *18*, 12764.
- (14) Cheng, X.; Zhang, H.; Ye, K.; Zhang, H.; Wang, Y. *J. Mater. Chem. C* **2013**, *1*, 7507.
- (15) Dong, Y.; Lam, J. W. Y.; Qin, A.; Li, Z.; Sun, J.; Sung, H. H.-Y.; Williams, I. D.; Tang, B. Z. *Chem. Commun.* **2007**, 40.
- (16) (a) Dong, Y.; Lam, J. W. Y.; Qin, A.; Sun, J.; Liu, J.; Li, Z.; Sun, J.; Sung, H. H. Y.; Williams, I. D.; Kwok, H. S.; Tang, B. Z. *Chem. Commun.* **2007**, 3255. (b) Ueda, Y.; Tanigawa, Y.; Kitamura, C.; Ikeda, H.; Yoshimoto, Y.; Tanaka, M.; Mizuno, K.; Kurata, H.; Kawase, T. *Chem.—Asian J.* **2013**, *8*, 392. (c) Tanaka, D.; Ohshita, J.; Ooyama, Y.; Kobayashi, N.; Higashimura, H.; Nakanishi, T.; Hasegawa, Y. *Organometallics* **2013**, *32*, 4136.
- (17) (a) Bi, H.; Chen, D.; Li, D.; Xia, D.; Zhang, Z.; Zhang, H.; Wang, Y. *Chem. Commun.* **2011**, *47*, 4135. (b) Dou, C.; Han, L.; Zhao, S.; Zhang, H.; Wang, Y. *J. Phys. Chem. Lett.* **2011**, *2*, 666. (c) Liu, D.; Zhang, Z.; Zhang, H.; Wang, Y. *Chem. Commun.* **2013**, *49*, 10001. (d) Wang, K.; Huang, S.; Zhang, Y.; Zhang, H.; Wang, Y. *Chem. Sci.* **2013**, *4*, 3288. (e) Nagura, K.; Saito, S.; Yusa, H.; Yamawaki, H.; Fujihisa, H.; Sato, H.; Shimoikeda, Y.; Yamaguchi, S. *J. Am. Chem. Soc.* **2013**, *135*, 10322.