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Modulation of sensitivity to mechanical stimulus in mechanofluorochromic properties by altering substituent positions in solid-state emissive diiodo boron diiminates†

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This manuscript describes modulation of the sensitivity to mechanical forces in diiodo boron diiminates by altering the substituent position of iodine groups. A series of modified complexes were prepared, and their solid-state luminescence properties based on aggregation and crystallization-induced emission mechanisms were observed. By adding mechanical forces to the crystalline samples of each complex, changes in the optical properties were monitored. Interestingly, peak shift degree of the emission bands was varied. From X-ray crystallographic analyses, it was shown that molecular distributions in the crystal packing significantly depended on the positions of the iodine groups in the complex. In particular, it was found that by increasing the dihedral angles between the phenyl substituents and the boron-containing six-membered ring, a larger peak shift width was obtained. Finally, the most planar conformation of the complexes was detected from the complex insensitive to mechanical forces. It was suggested that intramolecular electronic conjugation in the initial crystalline state could be responsible for the degree of peak shift. This is the first example, to the best of our knowledge, to offer regulation of sensitivity to mechanical forces in a series of structural isomers with the same chemical component.

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Introduction

Mechanochromic luminescent dyes are a potential versatile platform for developing advanced optical materials such as writing-type memories, sensors, and bioprobes.[1–13] Therefore, development of new series of mechanochromic luminescent materials and establishment of strategies for regulating luminochromic properties by an external stimulus with solid-emissive materials are a topic of high relevance.[14–32] The class of luminescent molecules that exhibit emission not in a solution but in an aggregation is categorized in an aggregation-induced emission (AIE)-active material.[33–38] Intramolecular motions, which usually consume excitation energy in a solution state, can be suppressed in an aggregation. Therefore, strong emission can be observed only from the solid samples involving films, crystals and aggregates. Moreover, by combining stimuli-responsivity with solid-state emission properties of AIE-active molecules, various types of mechanochromic luminescence behaviors *via* alteration of the morphology and degree of intermolecular interactions, such as stacking, hydrogen bonds, and excimer formation, were accomplished.[39–43]

Boron diketonates are a class of emissive organoboron complexes, and various unique optical properties including mechanochromic luminescence have been reported.[44–56] We reported that boron ketoiminates and diiminates also work as an AIE-inducible "element-block,"[57] which is defined as a functional building block composed of heteroatoms.[58,59] For instance, simply by introducing ketoiminate and diiminate structures into the main-chain conjugation, AIE-active polymers, solid-state emissive materials and film-type chemosensors were readily prepared according to preprogrammed designs.[60–64] It was shown that the intensity of AIE was significantly enhanced by the crystal formation (crystallization-induced emission, CIE).[59] Reversible changes in the emission intensity were accomplished by the phase transitions between crystal and amorphous states. Moreover, it was found that some boron ketoiminate complexes showed mechanochromic luminescence behaviors, and the direction of fluorochromism could be regulated by modulating the size of the end groups.[64] From the structural analyses of the crystalline states, it was suggested that the degree of intermolecular interactions such as π–π stacking could be responsible for emission color. By altering molecular morphology to a random distribution by

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grinding, the degree of molecular interaction could be changed, leading to fluorochromism. To date, emission colors and directions of color changes have been accomplished, as we reported previously.[64] Next, our goal is to modulate degree of peak shift by chemical modification with the single platform molecule. This challenge should be feasible for establishing a strategy for further precise control of mechanical force-induced chromic behaviors.

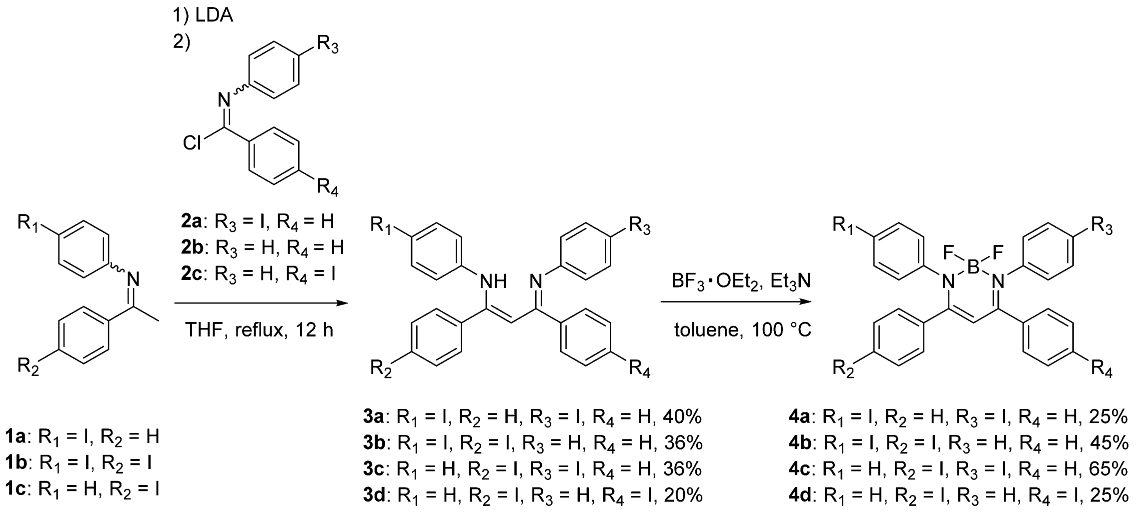
In this report, modulation of the sensitivity in mechanochromic luminescence toward mechanical forces is presented based on diiodo boron diiminates by changing substituent positions. A series of AIE and CIE-active complexes with the same chemical component but variably substituted positions were prepared. Interestingly, although most modified boron diiminates showed mechanochromic luminescence behaviors by the structural transition from crystalline to amorphous, the width of the peak shifts was diverse. In addition, a molecule that was insensitive to the grinding treatment was obtained. To gather information on the mechanism, structural analyses with crystalline samples were executed. From the series of data with diverse crystal packings, the relationships between degree of molecular planarity in the initial crystalline state and the width of peak shifts were proposed. By increasing molecular planarity, the width of peak shifts decreased. The most planar complex in this study showed an insensitive response to mechanical forces. In summary, structural diversity in the crystal packing was generated depending on the positions of the substituents, leading to different emission properties affected by molecular planarity. By adding mechanical forces, structural and subsequently optical diversity were cancelled. Thus, sensitivity changes in fluorochromism should be obtained. This is the first example, to the best of our knowledge, demonstrating regulation of the sensitivity of mechanochromic luminescence properties with the single platform structure having the same chemical component.

Results and discussion

According to the previous report on AIE-active boron ketoiminates with mechanochromic luminescence properties, the introduction of iodine groups to the complex induced drastic changes in solid-state emissive properties.[9] It was suggested that iodine groups should play a significant role in disturbing stacking in the crystalline state because of steric hindrance. Therefore, intrinsic yellow emission was observed. By grinding the crystalline sample, random distribution and free conformation for extending electronic conjugation and forming stacking interaction could be induced. As a result, the red-shifted emission was observed. This result implies that not only optical properties in the crystalline state but also changes in the emission behavior during morphology transition between crystal and amorphous states can be modulated by introducing the bulky substituent into the solid-state emissive molecule. To evaluate the validity of this idea, we designed the series of diiodo boron diiminates **4a–d** and compared their optical properties.

The diiodo ligands **3a–d** with different substituent positions were synthesized *via* coupling reactions with *N*-phenylimines **1a–c** and imidoyl chlorides **2a–c** (Scheme 1).[7] The desired boron complexes **4a–d** were prepared by boron complexation using $BF_3{\cdot}OEt_2$. It was confirmed that the products possessed the designed structure according to the characterization data with ^1H, ^{11}B, ^{13}C and ^{19}F NMR spectroscopies and mass measurements (see ESI†). The synthesized complexes hardly showed degradation under ambient conditions. From the recrystallization, single crystalline samples were obtained. The series of analyses for the determination of the structure and for the optical measurements were performed with these crystalline samples. Thermal properties of the synthesized complexes were investigated by thermogravimetric analysis and differential scanning calorimetry (Fig. S5 and Table S1, ESI†). It was found that boron diiminates showed melting points around 240–262 °C, sufficiently lower than their decomposition temperatures with 5% weight losses (295–316 °C). Therefore, the amorphous states were prepared by rapid cooling with the melted samples.

The basic electronic structure of the complexes was compared with a series of optical measurements. The electronic structures in the ground state were evaluated from the UV-Vis absorption



Scheme 1 Synthetic route of boron diiminates.

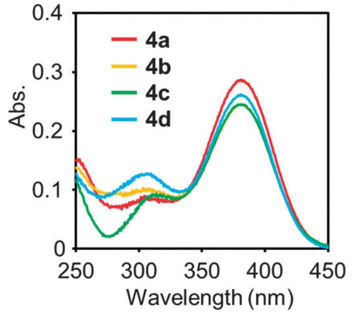


Fig. 1 UV-Vis absorption spectra of **4** in $CHCl_3$ (1.0×10^{-5} M).

spectra (Fig. 1 and Table 1). In the diluted chloroform solutions, all complexes presented similar shapes of absorption bands with peaks around 381 nm attributable to π–π* transitions. This fact means that the substituent positions of dual iodine groups hardly influence the electronic structure of boron diiminate in the ground state. To determine the energy levels of the complexes, electrochemical properties of the complexes were investigated by cyclic voltammetry (CV) (Table S2, Fig. S6 and S7, ESI†). HOMO and LUMO energy levels were estimated from the onset values in the first oxidation and reduction waves by the empirical formula, respectively. It was observed that the HOMO and LUMO energy levels of all complexes were nearly at the same level. From these data including the optical properties, it is revealed that the electronic structures of all complexes in the ground state are independent of the substituent positions of iodine groups. To theoretically support the abovementioned electronic properties of all complexes, density functional theory (DFT) calculations at the B3LYP/6-31G(d) level were performed (Fig. S8, ESI†). Accordingly, the order of the HOMO–LUMO band gaps (E_g) and the energy levels were obtained at the similar level. This theoretical result shows good agreement with the experimental data from the UV-Vis absorption and CV measurements.

To evaluate the electronic properties in the excited state, photoluminescence (PL) spectra of modified boron diiminates were investigated in both the solution and solid states (Fig. 2 and Fig. S9, ESI† Table 1). For investigating the influence of molecular distribution on emission properties, three types of powder samples were prepared. By crushing the crystal powder, the ground sample was obtained. The amorphous sample was obtained after rapid cooling from the melted state. Initially, it was found that in the chloroform solutions, all complexes showed slight luminescence ($\Phi < 0.01$). In contrast, specific emission properties were obtained from all solid samples. In particular, the crystalline samples of all complexes presented larger emission efficiencies than the ground and amorphous samples. This fact clearly indicates that modified boron diiminates have not only AIE but also CIE properties. Emission efficiencies of modified boron diiminates were lower than those of the previous diiminate complexes.[59,61] Similar to pristine boron diiminate, phosphorescence was obtained at 77 K in 2-methyl THF (Fig. S14, ESI†). It is likely that the heavy atom effect of iodine induces intersystem crossing, resulting in the increase of the proportion of non-radiative decay at ambient temperature.

Mechanochromic luminescence properties of all complexes were compared by degree of peak shift after grinding. From the powder X-ray diffraction analyses, it was revealed that ordered structures collapsed on grinding (Fig. S10, ESI†). The emission band of **4a** showed a bathochromic shift by +23 nm after the grinding treatment. **4b** and **4c** also showed bathochromic shifts in the PL spectra by +5 nm and +10 nm, respectively. Interestingly, the emission band of **4d** hardly showed a peak shift (+1 nm). These data clearly mean that the sensitivity of mechanochromic luminescence properties of all complexes to mechanical stress significantly depends on the substituent positions of the iodine groups. In other words, electronic structures in the excited state can be tuned by modulating the position of functional groups despite the chemical components being exactly same. After grinding, all complexes showed emission bands at almost the same positions. On the other hand, the positions of the peak tops of the emission bands were diverse by the substituent positions. In particular, the crystalline sample of **4d** intrinsically presented the emission band at the same position as that from the amorphous sample. These data mean that diversities in the optical property should be cancelled by grinding. It is likely that ordered structures in the crystalline samples would collapse from mechanical forces. Then, similar electronic environments could be realized by the formation of random distribution.

To gather information on the mechanism of differences of the sensitivity in mechanochromic luminescence properties, X-ray structural analyses were executed with crystalline samples (Fig. 3 and Tables S3–S6, ESI†). A significant feature was revealed from the packing parameters of the crystals (Table 2). Emission properties of boron diiminates were greatly influenced by the electronic structures at the ligand moiety.[58] The molecular planarity of the ligand moiety was higher than those of other complexes according to the dihedral angles (β angle) between the phenyl rings linked to the imine carbons and the boron-containing six-membered ring (42° and 48°). In the crystalline samples of **4a–c**, the distorted conformations represented by larger β angles were

Table 1 Optical properties of **4**

	$\lambda_{abs}{}^{a}$ [nm]	$\lambda_{PL,sol}{}^{a,b}$ [nm]	$\lambda_{PL,cr}{}^{b,c}$ [nm]	$\lambda_{PL,gr}{}^{b,d}$ [nm]	$\lambda_{PL,am}{}^{b,e}$ [nm]	$\Phi_{PL,cr}{}^{c,f}$	$\Phi_{PL,gr}{}^{d,f}$	$\Phi_{PL,am}{}^{e,f}$
4a	381	473	474	497	534	0.04	0.02	0.02
4b	382	480	490	495	533	0.04	0.01	0.01
4c	382	480	489	499	538	0.04	0.01	0.01
4d	381	478	495	496	538	0.04	0.02	0.01

[a] Measured in $CHCl_3$ (1×10^{-5} M). [b] Excited at λ_{abs}. [c] Measured in crystalline states. [d] Measured in grind states. [e] Measured in amorphous states. [f] Determined as an absolute value using the integrated sphere method.

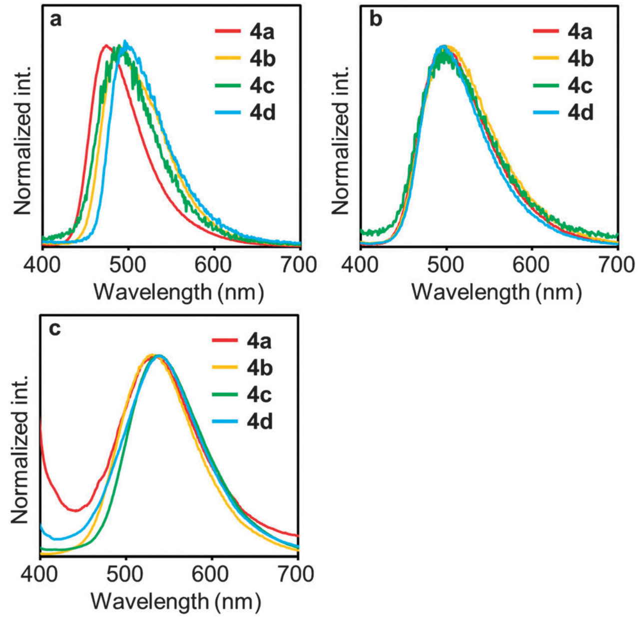


Fig. 2 PL spectra of **4** in (a) crystal, (b) ground and (c) amorphous states.

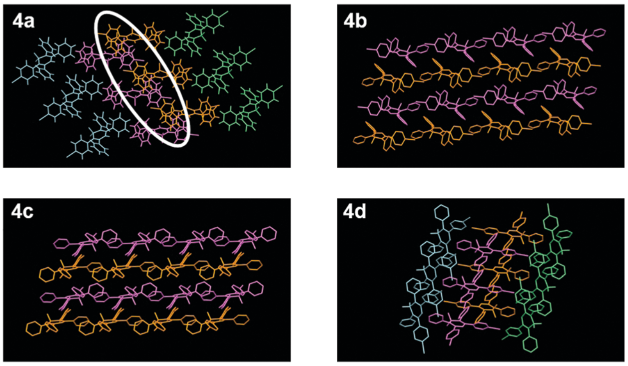
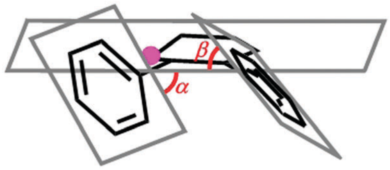


Fig. 3 Packing structures in the crystals of **4**.

Table 2 Molecular structures in the crystalline samples



	α_1 [degree]	α_2 [degree]	β_1 [degree]	β_2 [degree]	$\lambda_{\mathrm{PL,cr}}$ [nm]
4a	61	50	55	49	474
4b	59	45	45	44	490
4c	54	51	52	45	488
4d	58	53	48	42	495

$\alpha_1 > \alpha_2$, $\beta_1 > \beta_2$, $\gamma_1 > \gamma_2$.

obtained (**4a:** 49°, 55°; **4b:** 44°, 45°; **4c:** 45°, 52°). The order of magnitude of distortion corresponded to the width of the peak shifts. These data represent that the degree of electronic conjugation could be enhanced by improving the planarity of molecular conformation. Because higher planar structures are favorable for extending the conjugation system, the emission band in the relatively longer wavelength region can be observed from the crystalline sample particularly with **4d**. From these data including structural parameters and optical properties, a plausible scenario can be proposed. By changing the positions of the substituent groups, a structural diversity is realized in the initial crystalline state. The planarity in each complex in the crystal packing is also varied, leading to the alteration in the peak position of emission bands. By grinding the crystalline samples, random distributions and conformations should be induced, resulting in the cancellation of structural and optical diversities. Finally, a sensitivity difference in mechanochromic luminescence should be obtained in this system. In the crystalline samples of **4b** and **4c**, the complexes were aligned in the plane and partially formed stacking (Fig. 3). The phenyl rings directly connected to the imine carbon formed stacking in **4a** (white circle). It is likely that a structural restriction should exist in these crystals. In contrast, the space group of **4d** was distinctly different from those of other complexes. The perpendicular distribution toward the neighboring molecules was confirmed. Smaller intermolecular interaction including stacking should be formed in **4d**. It is implied that significant alteration in electronic interactions might be hardly induced to **4d** during the grinding treatment. Thus, the insensitive response might be obtained.

Conclusion

Synthesis and optical properties of the series of modified boron diiminates with mechanochromic luminescence properties are presented. In particular, it was clearly demonstrated that sensitivity in luminescence chromism toward mechanical forces depended on substituent positions in the complexes. From the view point of material design, based on the difference between AIE and CIE behaviors, mechanochromic luminescence properties can be realized. In the solid state, strong intermolecular interaction is usually formed, and significant changes in electronic structures can be induced by the morphological transition between crystalline and amorphous phases. In this study, it is proposed that the luminescence chromism can be accomplished *via* the cancellation by the formation of amorphous state to the diversity of optical properties in the initial crystalline state. Finally, it was demonstrated that chromic luminescent materials both sensitive and insensitive toward an external mechanical stimulus can be simultaneously obtained among boron diiminates with the same chemical component molecules. Our strategy should be valid not only for the preparation of mechanochromic luminescence molecules but also for precise modulation of chromism properties to produce advanced functional materials.

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References

1 A. Pucci and G. Ruggeri, *J. Mater. Chem.*, 2011, **21**, 8282.
2 T. M. Figueira-Duarte and K. Müllen, *Chem. Rev.*, 2011, **111**, 7260.
3 Y. Sagara and T. Kato, *Nat. Chem.*, 2009, **1**, 605.
4 M. Tanioka, S. Kamino, A. Muranaka, Y. Ooyama, H. Ota, Y. Shirasaki, J. Horigome, M. Ueda, M. Uchiyama, D. Sawada and S. Enomoto, *J. Am. Chem. Soc.*, 2015, **137**, 6436.
5 Y. Matsunaga and J.-S. Yang, *Angew. Chem., Int. Ed.*, 2015, **54**, 7985.
6 K. Nagura, S. Saito, H. Yusa, H. Yamawaki, H. Fujihisa, H. Sato, Y. Shimoikeda and S. Yamaguchi, *J. Am. Chem. Soc.*, 2013, **135**, 10322.
7 S.-J. Yoon, J. W. Chung, J. Gierschner, K. S. Kim, M.-G. Choi, D. Kim and S. Y. Park, *J. Am. Chem. Soc.*, 2010, **132**, 13675.
8 R. Wei, P. Song and A. Tong, *J. Phys. Chem. C*, 2013, **117**, 3467.
9 M. D. Molin, Q. Verolet, A. Colom, R. Letrun, E. Derivery, M. Gonzalez-Gaitan, E. Vauthey, A. Roux, N. Sakai and S. Matile, *J. Am. Chem. Soc.*, 2015, **137**, 568.
10 M. D. Molin, Q. Verolet, S. Soleimanpour and S. Matile, *Chem. – Eur. J.*, 2015, **21**, 6012.
11 Z. Ma, Z. Wang, Z. Xu, X. Jia and Y. Wei, *J. Mater. Chem. C*, 2015, **3**, 3399.
12 X.-P. Zhang, J.-F. Mei, J.-C. Lai, C.-H. Li and X.-Z. You, *J. Mater. Chem. C*, 2015, **3**, 2350.
13 C. Reus and T. Baumgartner, *Dalton Trans.*, 2016, **45**, 1850.
14 X. Zhang, Z. Chi, Y. Zhang, S. Liu and J. Xu, *J. Mater. Chem. C*, 2013, **1**, 3376.
15 T. Seki, K. Sakurada, M. Muramoto, S. Seki and H. Ito, *Chem. – Eur. J.*, 2016, **22**, 1968.
16 S. Yagai, T. Seki, H. Aonuma, K. Kawaguchi, T. Karatsu, T. Okura, A. Sakon, H. Uekusa and H. Ito, *Chem. Mater.*, 2016, **28**, 234.
17 T. Seki and H. Ito, *Chem. – Eur. J.*, 2016, **22**, 4322.
18 Z. Ma, F. Yang, Z. Wang and X. Jia, *Tetrahedron Lett.*, 2015, **56**, 393.
19 M. Kondo, S. Miura, K. Okumoto, M. Hashimoto and N. Kawatsuki, *Chem. – Asian J.*, 2014, **9**, 3188.
20 S. Perruchas, X. F. Le Goff, S. Maron, I. Maurin, F. Guillen, A. Garcia, T. Gacoin and J.-P. Boilot, *J. Am. Chem. Soc.*, 2010, **132**, 10967.
21 X. Y. Shen, Y. J. Wang, E. Zhao, Z. W. Yuan, Y. Liu, P. Lu, A. Qin, Y. Ma, J. Z. Sun and B. Z. Tang, *J. Phys. Chem. C*, 2013, **117**, 7334.
22 M. Krikorian, S. Liu and T. M. Swager, *J. Am. Chem. Soc.*, 2014, **136**, 2952.
23 G. Zhang, J. P. Singer, S. E. Kooi, R. E. Evans, E. L. Thomas and C. L. Fraser, *J. Mater. Chem.*, 2011, **21**, 8295.
24 Y. Sagara and T. Kato, *Angew. Chem., Int. Ed.*, 2008, **47**, 5175.
25 J. Ni, X. Zhang, N. Qiu, Y.-H. Wu, L.-Y. Zhang, J. Zhang and Z.-N. Chen, *Inorg. Chem.*, 2011, **50**, 9090.
26 T. Seki, T. Ozaki, T. Okura, K. Asakura, A. Sakon, H. Uekusa and H. Ito, *Chem. Sci.*, 2015, **6**, 2187.
27 B. Xu, Y. Mu, Z. Mao, Z. Xie, H. Wu, Y. Zhang, C. Jin, Z. Chi, S. Liu, J. Xu, Y.-C. Wu, P.-Y. Lu, A. Lien and M. R. Bryce, *Chem. Sci.*, 2016, **7**, 2201.
28 K. Ohno, S. Yamaguchi, A. Nagasawa and T. Fujihara, *Dalton Trans.*, 2016, **45**, 5492.
29 T. Abe, T. Itakura, N. Ikeda and K. Shinozaki, *Dalton Trans.*, 2009, 711.
30 T. Tanaka, R. Nouchi, Y. Nakao, Y. Arikawa and K. Umakoshi, *RSC Adv.*, 2014, **4**, 62186.
31 N. Mizoshita, T. Tani and S. Inagaki, *Adv. Mater.*, 2012, **24**, 3350.
32 S. Yamaguchi, I. Yoshikawa, T. Mutai and K. Araki, *J. Mater. Chem.*, 2012, **22**, 20065.
33 Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2011, **40**, 5361.
34 Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Commun.*, 2009, 4332.
35 R. Hu, N. L. C. Leung and B. Z. Tang, *Chem. Soc. Rev.*, 2014, **43**, 4494.
36 D. Ding, K. Li, B. Liu and B. Z. Tang, *Acc. Chem. Res.*, 2013, **46**, 2441.
37 A. Qin, J. W. Y. Lam and B. Z. Tang, *Prog. Polym. Sci.*, 2012, **37**, 182.
38 R. T. K. Kwok, C. W. T. Leung, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2015, **44**, 4228.
39 Y. Q. Dong, J. W. Y. Lam and B. Z. Tang, *J. Phys. Chem. Lett.*, 2015, **6**, 3429.
40 J. Wang, J. Mei, R. Hu, J. Z. Sun, A. Qin and B. Z. Tang, *J. Am. Chem. Soc.*, 2012, **134**, 9956.
41 Q. Qi, J. Zhang, B. Xu, B. Li, S. X.-A. Zhang and W. Tian, *J. Phys. Chem. C*, 2013, **117**, 24997.
42 X. Zhang, Z. Chi, J. Zhang, H. Li, B. Xu, X. Li, S. Liu, Y. Zhang and J. Xu, *J. Phys. Chem. B*, 2011, **115**, 7606.
43 T. Hu, B. Yao, X. Chen, W. Li, Z. Song, A. Qin, J. Z. Sun and B. Z. Tang, *Chem. Commun.*, 2015, **51**, 8849.
44 K. Tanaka and Y. Chujo, *NPG Asia Mater.*, 2015, **7**, e223.
45 T. Butler, W. A. Morris, J. Samonina-Kosicka and C. L. Fraser, *ACS Appl. Mater. Interfaces*, 2016, **8**, 1242.
46 L. Wang, K. Wang, B. Zou, K. Ye, H. Zhang and Y. Wang, *Adv. Mater.*, 2015, **27**, 2918.
47 F. Ito and T. Sagawa, *RSC Adv.*, 2013, **3**, 19785.
48 G. Zhang, J. Lu, M. Sabat and C. L. Fraser, *J. Am. Chem. Soc.*, 2010, **132**, 2160.
49 P. Galer, R. C. Korošec, M. Vidmar and B. Šket, *J. Am. Chem. Soc.*, 2014, **136**, 7383.
50 M. Koch, K. Perumal, O. Blacque, J. A. Garg, R. Saiganesh, S. Kabilan, K. K. Balasubramanian and K. Venkatesan, *Angew. Chem., Int. Ed.*, 2014, **53**, 6378.
51 K. Perumal, J. A. Garg, O. Blacque, R. Saiganesh, S. Kabilan, K. K. Balasubramanian and K. Venkatesan, *Chem. – Asian J.*, 2012, **7**, 2670.
52 Z. Zhang, Z. Wu, J. Sun, B. Yao, G. Zhang, P. Xue and R. Lu, *J. Mater. Chem. C*, 2015, **3**, 4921.

53 Z. Zhang, P. Xue, P. Gong, G. Zhang, J. Peng and R. Lu, *J. Mater. Chem. C*, 2014, **2**, 9543.

54 A. Sakai, E. Ohta, Y. Yoshimoto, M. Tanaka, Y. Matsui, K. Mizuno and H. Ikeda, *Chem. – Eur. J.*, 2015, **20**, 18128.

55 M. Tanaka, E. Ohta, A. Sakai, Y. Yoshimoto, K. Mizuno and H. Ikeda, *Tetrahedron Lett.*, 2013, **54**, 4380.

56 Y. Chujo and K. Tanaka, *Bull. Chem. Soc. Jpn.*, 2015, **88**, 633.

57 R. Yoshii, A. Nagai, K. Tanaka and Y. Chujo, *Chem. – Eur. J.*, 2013, **19**, 4506.

58 R. Yoshii, A. Hirose, K. Tanaka and Y. Chujo, *Chem. – Eur. J.*, 2014, **20**, 8320.

59 R. Yoshii, K. Tanaka and Y. Chujo, *Macromolecules*, 2014, **47**, 2268.

60 R. Yoshii, A. Hirose, K. Tanaka and Y. Chujo, *J. Am. Chem. Soc.*, 2014, **136**, 18131.

61 A. Hirose, K. Tanaka, R. Yoshii and Y. Chujo, *Polym. Chem.*, 2015, **6**, 5590.

62 R. Yoshii, A. Nagai, K. Tanaka and Y. Chujo, *Macromol. Rapid Commun.*, 2014, **35**, 1315.

63 K. Tanaka, T. Yanagida, H. Yamane, A. Hirose, R. Yoshii and Y. Chujo, *Bioorg. Med. Chem. Lett.*, 2015, **25**, 5331.

64 R. Yoshii, K. Suenaga, K. Tanaka and Y. Chujo, *Chem. – Eur. J.*, 2015, **21**, 7231.