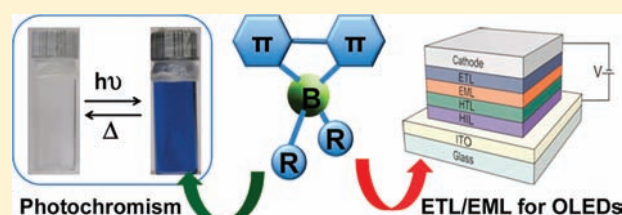


# Four-Coordinate Organoboron Compounds with a $\pi$ -Conjugated Chelate Ligand for Optoelectronic Applications

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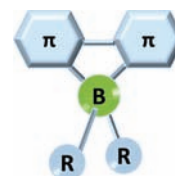
**ABSTRACT:** Four-coordinate organoboron compounds with a  $\pi$ -conjugated chelate backbone have emerged recently as highly attractive materials for a number of applications including use as emitters and electron-transport materials for organic light-emitting diodes (OLEDs) or organic field transistors, photoresponsive materials, and sensory and imaging materials. Many applications of this class of boron compounds stem from the electronic properties of the  $\pi$ -conjugated chelate backbone. Charge-transfer transitions from an aromatic substituent attached to the boron center of the  $\pi$ -conjugated chelate backbone and steric congestion have also been found to play important roles in the luminescent and photochromic properties of the four-coordinate boron compounds. This article provides an update-to-date account on the application aspects of this important class of compounds in materials science with the emphasis on OLED applications and photochromic switching.



## INTRODUCTION

Four-coordinate boron compounds that have a  $\pi$ -conjugated chelate with the general structure shown in Chart 1 have emerged recently as very attractive materials for various optoelectronic applications including emitters, electron-transport materials, and host/hole-blocking materials for organic light-emitting diodes (OLEDs), sensory and biological imaging materials, and photoresponsive materials. Our research interest in four-coordinate boron compounds was driven initially by the need for stable and highly efficient blue emitters for OLEDs.<sup>1</sup> In the past decade, rapid research progress and many important discoveries have been achieved in  $\pi$ -conjugated four-coordinate boron chemistry.<sup>1–4</sup> Although four-coordinate boron compounds with neutral chelate ligands such as 2,2'-bipyridine and interesting properties are known, these cationic boronium compounds have not been investigated for optoelectronic applications.<sup>5</sup> For most materials applications, the chelate ligand is often a monoanion to achieve charge-neutral boron compounds. Thus, the key role of the B atom is to stabilize the anionic chelate ligand by forming covalent bonds with the chelate and dissipating the negative charges on the ligand. As a consequence of chelation to boron, the  $\pi$  conjugation of the chelate is reinforced. The lowest unoccupied molecular orbital (LUMO) of such four-coordinate boron compounds is usually localized on the  $\pi$ -conjugated chelate ligand that achieves a greater stabilization by boron coordination, which enables use of some of the four-coordinate boron compounds as effective electron-transport materials. The highest occupied molecular orbital (HOMO) of the four-coordinate boron compounds is localized either at the chelate ligand or the R group, depending on the nature of the R group.  $\pi \rightarrow \pi^*$  electronic transitions of the chelate or charge-transfer transition from the R group to the chelate are usually responsible for the luminescent properties of this class of molecules. Recent research has also revealed that, with the appropriate choice of the

Chart 1



chelate and R groups, four-coordinate boron compounds are also capable of undergoing facile reversible photothermal isomerization, which opens exciting new opportunities in four-coordinate boron research.

This Forum Article focuses on the applications of  $\pi$ -conjugated neutral four-coordinate boron compounds, especially those that contain a B–C bond, in OLEDs, photochromic materials, and sensors. According to the chelate donor atoms, the four-coordinate boron compounds can be classified as N,O-, N,N-, N,C-, C,C-, C,O-, and O,O-chelate. The well-known boron dipyrromethene (BODIPY), a class of highly fluorescent molecules, with a N,N-chelate ligand and a BF<sub>2</sub> unit has been covered in a recent comprehensive review article<sup>6</sup> and thus will not be discussed here. Four-coordinate boron-functionalized polymers will also not be covered here. Interested readers are referred to the recent comprehensive review articles by Jäkle<sup>7a,b</sup> and Nagai and Chujo.<sup>7c</sup>

## FOUR-COORDINATE BORON COMPOUNDS FOR OLEDs

OLEDs are electroluminescent (EL) devices that convert electricity to light. A typical OLED structure is shown in Figure 1, where the luminescent molecule (emitter) is sandwiched between

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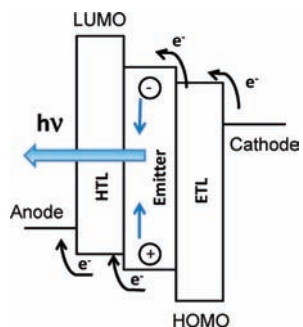


Figure 1. Typical OLED structure.

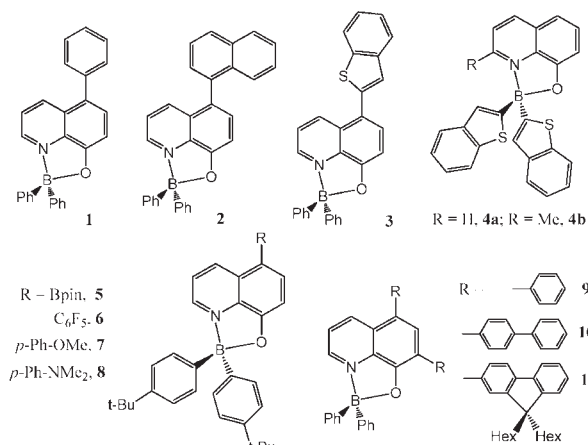
a hole-transport layer (HTL) and an electron-transport layer (ETL) to facilitate charge injection and transport.<sup>8</sup> The anode is usually indium–tin oxide (ITO), while the cathode is usually aluminum. The key applications of OLEDs are information displays and solid-state lighting, which usually require the availability of the three basic color components, namely, blue, green, and red emitters. Because of the poor stability of blue emitters and the low electron mobility of most organic compounds (the electron mobility of organic compounds is usually several orders of magnitude lower than the hole mobility),<sup>9</sup> much of the current research in OLED materials focuses on efficient and stable blue emitters and electron-transport materials. Effective ETL materials require the molecule to have a low LUMO level or a high electron affinity.

The first low-driving-voltage OLED reported by Tang and co-workers in 1987 had a double-layer structure with an organic diamine as a HTL and a N,O-chelate compound Alq<sub>3</sub> (q = 8-hydroxyquinolate) as an emitter and an ETL.<sup>10</sup> Although Alq<sub>3</sub> has an excellent performance in OLEDs, it has a few shortcomings, namely, green emission and a poor long-term stability in the device.<sup>11</sup> Structural modifications of the hydroxyquinoline ligand and the ancillary ligands around the Al<sup>III</sup> ion have been shown to be effective in tuning the color of this class of compounds toward either blue or orange.<sup>12</sup> Nonetheless, their tendency to undergo irreversible degradation in OLEDs has been a major concern. Because aluminum is a member of the group 13 elements, the search for high-performance fluorescent emitters evolved naturally to the development of boron-based materials. The key advantage of boron compounds versus aluminum compounds is the much greater covalency of B–O, B–N, and B–C bonds than the corresponding Al–O, Al–N, and Al–C bonds, which could lead to a greater stability of the boron compounds.

**1. N,O-Chelate Compounds.** Three types of N,O-chelate boron compounds, namely, 8-hydroxyquinolate, 2-pyridylphenolate, and oxazolyphenolate, have been studied for OLEDs.

*8-Hydroxyquinolate.* In 2000, we reported the luminescent properties of a group of 8-hydroxyquinolate boron compounds with the general formula of BR<sub>2</sub>q, where R = ethyl, phenyl, 1-naphthyl, and 2-naphthyl.<sup>13</sup> The luminescences of these compounds were found to originate from  $\pi(\text{Ph}-\text{O}) \rightarrow \pi^*(\text{py})$  transitions, similar to that of Alq<sub>3</sub>,<sup>12</sup> but their emission color ( $\lambda_{\text{em}} = \sim 490\text{--}500\text{ nm}$ ) is blue-green, about 15–20 nm blue-shifted from that of Alq<sub>3</sub>. This was attributed to the greater stabilization of the HOMO level of the chelate ligand by boron. BEt<sub>2</sub>q is a low-melting-point solid (45 °C), while BPh<sub>2</sub>q, B(1-naph)<sub>2</sub>q, and B(2-naph)<sub>2</sub>q have mp > 200 °C. We therefore investigated the performances of BPh<sub>2</sub>q, B(1-naph)<sub>2</sub>q, and

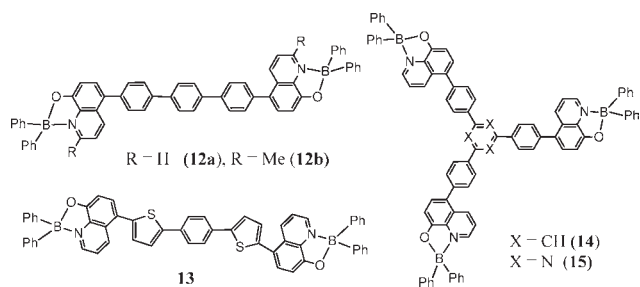
Chart 2



B(2-naph)<sub>2</sub>q in OLEDs. Double- or triple-layer devices with either *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-1,1'-biphenyl-4,4-diamine (NPB) or *N,N'*-bis(3-methylphenyl)-*N,N'*-diphenylbenzidine (TPD) as a HTL and the boron compound as an emitter/ETL were fabricated. The devices were, however, not efficient, with an apparent exciplex emission at the interface of NPB or TPD and the boron compound. At about the same time, Anderson and co-workers reported their study on BPh<sub>2</sub>q and BPh<sub>2</sub>(Me-q) and the methyl substitution effect at various positions.<sup>14</sup> They observed that a methyl at the 4 position induced the largest blue shift of emission ( $\lambda_{\text{em}} = 483\text{ nm}$  in CH<sub>2</sub>Cl<sub>2</sub>), while a methyl at the 5 position induced the largest red shift ( $\lambda_{\text{em}} = 529\text{ nm}$  in CH<sub>2</sub>Cl<sub>2</sub>). This agreed well with the fact that HOMO and LUMO of the boron compounds are localized on the phenoxy and pyridyl rings, respectively, and the general trend observed for Alq<sub>3</sub> and derivatives.<sup>12</sup> To further tune the properties of the boron compounds, we examined a group of 8-hydroxyquinoline chelate compounds functionalized by a 5-aryl group shown in Chart 2.<sup>15a</sup> A phenyl, a naphthyl, and a benzothienyl group at the 5 position (1–3) were found to greatly shift the emission color to red ( $\lambda_{\text{em}} = 530, 534,$  and  $565\text{ nm}$ , respectively, in CH<sub>2</sub>Cl<sub>2</sub>), consistent with Anderson's observation, with significantly diminished quantum efficiencies for 2 and 3, compared to BPh<sub>2</sub>q. The benzothienyl compounds 4a and 4b have an emission color and efficiency similar to those of BPh<sub>2</sub>q. The key feature of these boron compounds is the presence of a low LUMO level ( $\sim -3.0\text{ eV}$ ), which enabled their successful use as bifunctional materials in OLEDs. Indeed, a simple double-layer device using NPB as a HTL and 4a as the emitter and an ETL achieved a brightness of 1050 cd m<sup>-2</sup>.<sup>15a</sup> Some contributions from exciplex emission were once again observed.

In 2004, Jäkle's group reported several B(*p-i*-PrPh)(thienyl)q compounds with emission at  $\sim 510\text{ nm}$  and a quantum yield of  $\sim 0.15$  in tetrahydrofuran (THF).<sup>16a</sup> Jäkle's group also examined the substitution effect by donor and acceptor groups at the 5 position on the emission properties of B(*p-Ph-t-Bu*)<sub>2</sub>(5-R-q) shown in Chart 2 (5–8).<sup>16b</sup> They observed that electron-withdrawing groups such as Bpin and pentafluorophenyl blue-shift the emission color by  $\sim 7\text{--}20\text{ nm}$  and significantly enhance the emission efficiency, compared to the nonsubstituted one. Substitution by a NO<sub>2</sub> group further shifts the emission energy to the blue region ( $\lambda_{\text{em}} = 456\text{ nm}$  in THF) but with a great loss of quantum yield ( $\Phi = 0.001$ ). Compounds that have an electron-donating

Chart 3

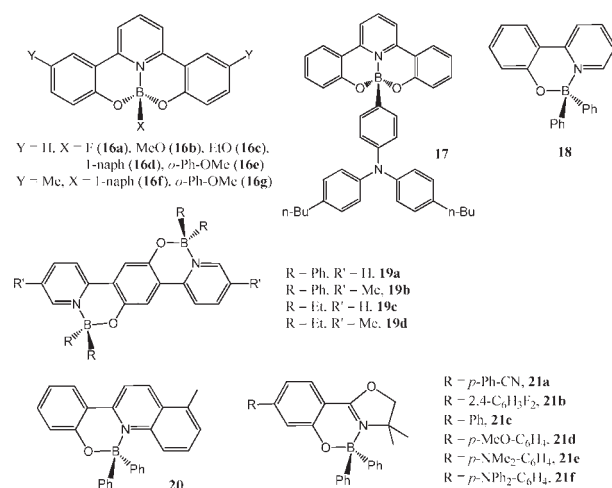


group such as *p*-PhOMe or *p*-PhNMe<sub>2</sub> (7 and 8) have been found to red-shift the emission energy with a much decreased quantum yield, consistent with our earlier observation. In 2006, Slugovc and co-workers reported compounds 9–11, which have substituents at both the 5 and 7 positions.<sup>17</sup> Despite the substantial red-shifted emission energy, relative to the parent molecule, these molecules were found to have good emission efficiencies (0.22–0.30). By insertion of a poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) layer between ITO and TPD, EL devices using 9–11, which have a much lower turn-on voltage and a higher brightness than those we reported, were achieved. Furthermore, no exciplex emission was evident for this group of compounds. This may be attributed to the rise of the HOMO level (–5.5 to –5.6 eV), compared to that of the 5-substituted compounds we investigated. Steric blocking by the aryl group at the 7 position may also play a role in preventing exciplex formation with the HTL.

To examine the impact of extended  $\pi$  conjugation and the mutual influence of multiple boron centers, we synthesized compounds 12–15 as shown in Chart 3.<sup>15b</sup> Because of their highly anisotropic structures, these molecules stack in the solid state. Their emission colors are similar to that of 1 (528–537 nm) with moderate quantum yields. Compound 13 was found to display a concentration-dependent emission. At concentrations below  $5.0 \times 10^{-6}$  M, 13 has  $\lambda_{em}$  at  $\sim 465$  nm, but at higher concentrations, the emission shifts to a longer wavelength. The emission energy of 13 at  $5.0 \times 10^{-5}$  M is at 593 nm, similar to that of the solid-state emission. This was attributed to excimer emission due to strong intermolecular interactions at high concentrations and in the solid state, as confirmed by crystal structural analysis. Compared to the monoboron compound 1, the polyboron compounds showed a much greater thermal stability, with thermal decomposition temperatures being  $\sim 50$ – $100$  °C above that of 1.<sup>15b</sup>

**2-Pyridylphenolate.** The motivation for the study of this class of boron compounds was to achieve efficient and stable blue emitters because pyridylphenolate is much less conjugated than 8-hydroxyquinolate. Wang and his co-workers reported compounds 16a–16c in 2000 and 16d–16g in 2006 (Chart 4).<sup>18a,b</sup> These molecules are blue luminescent with  $\lambda_{em}$  = 445–479 nm. Double-layer EL devices of 16a with TPD as a HTL were fabricated, which were dominated by exciplex emission at 550 nm. Replacing TPD with poly(*N*-vinylcarbazole) eliminated the exciplex emission and a blue EL was achieved, albeit not bright. EL devices with either a double-layer structure (NPB as a HTL) or a triple-layer structure with NPB and Alq<sub>3</sub> as HTL and ETL, respectively, for 16d–16g were also found to be dominated by exciplex emission. Insertion of a hole-blocking layer 4,4'-*N,N'*-dicarbazolebiphenyl between NPB and the boron compound eliminated exciplex emission, but the devices were

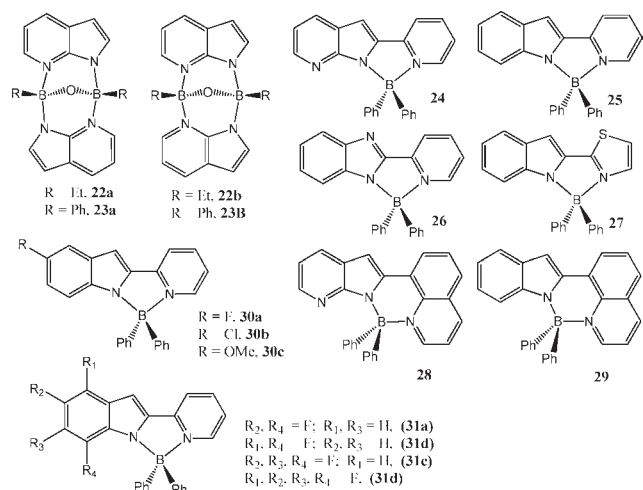
Chart 4



not very efficient. Later, a donor-functionalized molecule 17 was also developed by the same group.<sup>18c</sup> This compound has a HOMO energy similar to that of NPB and a LUMO energy similar to that of Alq<sub>3</sub>. A single-layer EL device using 17 only was therefore fabricated and has a maximum brightness of 1065 cd m<sup>-2</sup> and an efficiency of 12 cd A<sup>-1</sup>, which was very impressive, considering the simplicity of the device. The same group also reported the bidentate chelate compound 18 and the dimers 19a–19d in Chart 4.<sup>18d</sup> Compound 18 emits at 481 nm in THF and at 448 nm in the solid state. The emission color of the dimer 19a is 584 nm in THF and in the solid state, more than 100 nm red-shifted from that of 18, because of a greater  $\pi$  conjugation, but with similar emission efficiency ( $\Phi$  = 0.34 for 18 and 0.29 for 19a). The ethyl analogues 19c and 19d are much less efficient ( $\Phi$  = 0.08). Bright (maximum brightness >8000 cd m<sup>-2</sup>) and efficient (maximum efficiency >2.0 cd A<sup>-1</sup>) OLEDs using NPB as a HTL and the diboron compound as the emitter and an ETL were achieved and were much more superior than those using the monoboron compound 18 with the same device structure, demonstrating the importance of conjugated diboron systems.<sup>18d</sup> Nonetheless, compound 18 was used effectively as a hole-blocking material in phosphorescent OLEDs.<sup>19</sup> We reported compound 20, which has an emission at 497 nm in CH<sub>2</sub>Cl<sub>2</sub> and 520 nm in the solid state.<sup>20</sup> Chujo and co-workers reported a 10-hydroxybenzo[*h*]quinolinat BPh<sub>2</sub> compound recently and its incorporation in polymers.<sup>21</sup> This molecule has an emission at 513 nm and a 0.10 quantum yield.

**Oxazolyphenolate.** This class of boron compounds was reported recently by Kang and co-workers (21 in Chart 4).<sup>22</sup> Because of the much reduced  $\pi$  conjugation, many members of this group of compounds are blue emitters (e.g., compounds 21a–21c;  $\lambda_{em}$  = 422–464 nm). However, their quantum efficiencies are low (0.04–0.15 for 21a–21c). The emission peak of compound 21e was found to be strongly dependent on the solvent polarity, consistent with an intramolecular charge-transfer transition from the amino group to the oxazolyphenolate ring. Because of the relatively high emission efficiency of 21f ( $\lambda_{em}$  = 520 nm and  $\Phi$  = 0.34 in CHCl<sub>3</sub> and 0.19 in the solid state), it was evaluated for its performance in an EL device, but the device was not efficient. Nonetheless, because of the relatively low LUMO level (ca. 2.8 eV) and the large

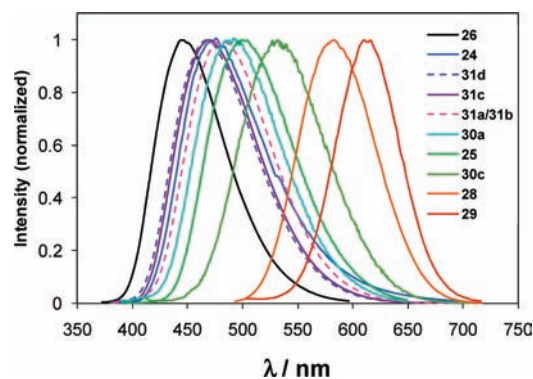
Chart 5



HOMO–LUMO gaps, this group of compounds has the potential to function as electron-transport materials.

**2. N,N-Chelate Compounds.** We initiated the investigation of blue-luminescent boron compounds based on a 7-azaindole chromophore more than a decade ago.<sup>1</sup> One advantage of N,N-chelate compounds is that they are less prone to degradation in devices via irreversible oxidation than the hydroxyquinoline compounds are. An ideal blue emitter should have  $\lambda_{em}$  at 430–450 nm, although the actual color depends on the emission bandwidth. During our study of 7-azaindole chemistry, we noted that 7-azaindole, once deprotonated, emits a bright-blue color. The anion can be stabilized by binding to Al<sup>III</sup> or Zn<sup>II</sup>, although the resulting compounds have a poor stability under ambient air.<sup>1,23</sup> The most impressive molecules were found to be the diboron compounds **22** and **23** (Chart 5), where the 7-azaindole anion is stabilized by two boron centers. Compound **22a**, the first purple-blue-luminescent boron molecule that we reported in 1998, is a bright emitter with  $\lambda_{em} = 419$  nm (422 nm in the solid state) and  $\Phi = 0.47$  in toluene.<sup>24a</sup> It has a remarkable stability in the solid state toward air and a high thermal stability (mp  $\sim 290$  °C) and can be easily sublimed. The phenyl analogue **23a** and its isomer **23b** were synthesized soon after.<sup>24b</sup> They were separated, and their structures were determined by X-ray diffraction. The two isomers share similar photophysical properties (bright blue emitters with  $\lambda_{em} = 450$  nm) but very different thermal properties. The zwitterionic isomer **23b** has a much lower thermal stability, decomposing at  $>150$  °C, while **23a** has a mp of 274 °C and can be sublimed readily. A bright-blue EL device using NPB (doped by 1% 9,10-diphenylanthracene) as a HTL, **23a** as the emitter, and Alq<sub>3</sub> as an ETL was achieved.<sup>24a</sup> This device has a turn-on voltage of approximately 7 V and a luminance of 1024 cd mV<sup>-2</sup> at 14 V.

This success led us to investigate the 7-azaindole-based N,N-chelate compound **24** and the indolyl and benzoimidazolyl analogues **25** and **26**.<sup>25</sup> We showed that the location of the N heteroatom in the chelate ligand can have a significant impact on the emission color. For example, **26** emits at 445 nm in solution ( $\Phi = 0.46$ ) and at 451 nm in the solid state, while **24** emits at a much lower energy,  $\sim 475$  nm ( $\Phi = 0.61$ ), in solution and the solid state.<sup>25b</sup> The more electron-rich indolyl analogue **25** emits at even lower energy, 516 nm. Computational studies established that the HOMO level for these molecules is localized on the



**Figure 2.** Diagram showing the solid-state emission spectra of the N,N-chelate compounds in Chart 5.

7-azaindole, benzoimidazolyl, or indolyl ring, while the LUMO level is mostly on the pyridyl ring. The widening of the HOMO–LUMO gap,  $25 < 24 < 26$ , was attributed to the increased stabilization of the HOMO level. The replacement of the pyridyl ring in **25** by a smaller thiazole ring (**27**) was found to blue-shift the emission energy by  $\sim 30$  nm. Extending the  $\pi$  conjugation of the pyridyl ring to a quinolyl ring caused a sharp drop of the LUMO level and an increase of the HOMO level, resulting in orange and red emission colors for compounds **28** and **29**, respectively. Because of the low LUMO levels ( $-2.7$  to  $-3.2$  eV), this class of compounds can also function as a ETL. EL devices using **24**, **25**, and **29** as the emitters or emitters/ETL were fabricated successfully,<sup>25</sup> but further optimization of the devices is necessary to establish their true potential for OLEDs.

We examined the effect of the substituents on the emission color and the quantum yield of compound **25**.<sup>25c</sup> Not surprisingly, electronegative groups such as fluoro and chloro were found to shift the emission maximum to blue by  $\sim 20$  nm (**30a** and **30b**), although substitution by chloro reduced the emission efficiency by about one third. Substitution by multiple fluoro groups on the indolyl ring further shifted the emission to blue (**31a**–**31d**) and doubled the emission efficiency to 0.65 and 0.60 for **31c** and **31d**, respectively. Electron-donating groups such as OMe shifted the emission energy to red by  $\sim 15$  nm with a reduction of the emission efficiency by  $\sim 90\%$ . Thus, color tuning from blue to red was achieved for this class of compounds, as shown by the emission spectra shown in Figure 2.

Chi et al. investigated the pyrrolyl–py chelate boron compounds **32**–**34** shown in Chart 6.<sup>26a</sup> The lowest-energy electronic transition in these compounds was found to be  $\pi(\text{pyrrolyl}) \rightarrow \pi^*(\text{pyridyl})$ , similar to the indolyl–pyridyl chelate compounds that we investigated. The much reduced conjugation of **32**, compared to that of **25**, caused a blue-shift of the emission energy by  $\sim 25$  nm ( $\lambda_{em} = 490$  nm and  $\Phi = 0.52$ ). Extending conjugation of the pyridyl in **32** to the quinolyl in **33** led to a red-shift of the emission energy to 510 nm. The addition of an electronegative N atom to the quinolyl ring further shifted the emission energy to red (572 nm) because of stabilization of the LUMO. A bright-red-orange EL device using NPB as a HTL, **34** as the emitter, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline as the hole-blocking layer, and Alq<sub>3</sub> as an ETL was fabricated successfully. It has the maximum brightness of 5000 cd m<sup>-2</sup> at 15 V. The same team also investigated the pyrazolyl–py chelate compounds **35** and **36**.<sup>26b</sup> In the solid state, these compounds display a single fluorescent peak with  $\lambda_{em}$  in the region of

Chart 6

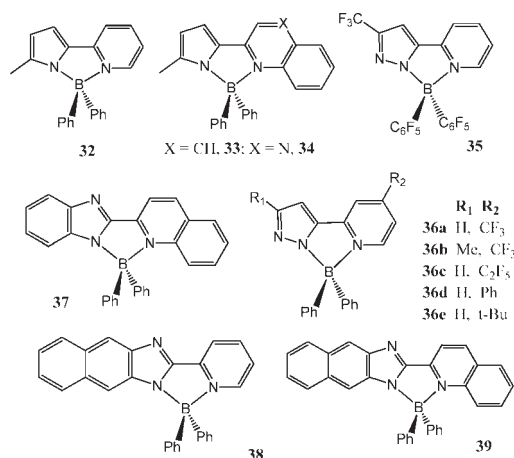
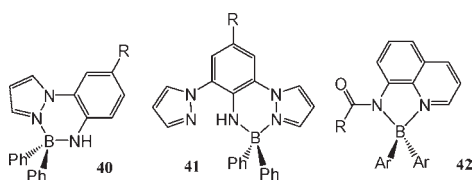


Chart 7

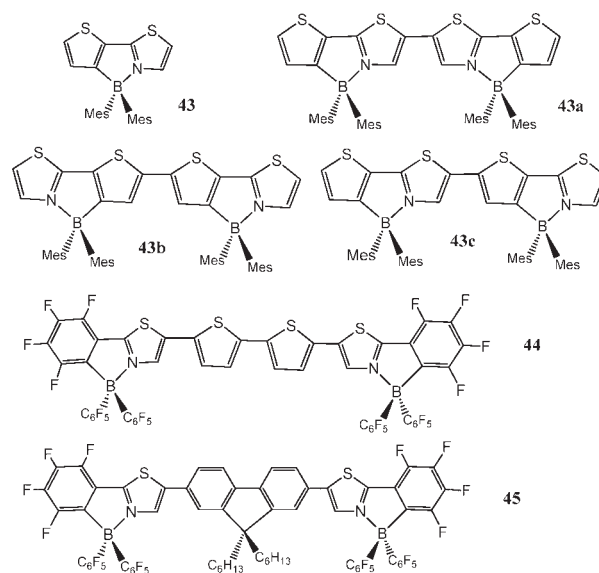


360–510 nm (36d), attributed to a  $\pi \rightarrow \pi^*$  transition localized on the chelate ring, and the general emission energy trend agrees well with that of the N,N-chelate compounds discussed above. However, compounds 36a–36c were found to display intriguing temperature-dependent dual emission in solution with a high-energy emission band that is similar to the solid-state emission band and a low-energy emission band at 505, 488, and 512 nm, respectively. The low-energy emission band was attributed to a photoinduced electron transfer from the phenyl to the  $\pi^*$  orbital of the N,N-chelate. The appearance of this charge-transfer emission band may be caused by the large  $\pi-\pi^*$  gap of the chelate ligands that is close to or greater than the emission energy of the charge-transfer transition.

Chen and co-workers reported compounds 37–39 and their EL devices.<sup>27</sup> However, the origin of emission by this group of compounds appears to be complex and poorly understood. For example, compound 37 was reported to emit at 395 nm at  $1 \times 10^{-8}$  M and at 495 nm at  $1 \times 10^{-4}$  M in N,N-dimethylformamide (DMF) and 610 nm in the solid state. This emission energy dependence on the concentration was attributed to excimer formation at the higher concentration. However, the exceptionally high energy emission of this group of compounds ( $\lambda_{\text{em}} < 400$  nm in DMF) at low concentrations is puzzling and does not agree with the general trend observed for compounds 24–34. For example, the pyridyl analogue 26 with a much smaller chelate than that of 37 emits at 445 nm in CH<sub>2</sub>Cl<sub>2</sub> and at 451 nm in the solid state. The strange behavior of compounds 37–39 could be related to their instability in DMF, especially wet DMF.

Gardinier and co-workers reported 2-(pyrazolyl)aniline-based chelate compounds 40 (Chart 7).<sup>28a</sup> This group of compounds emit bright-blue or green color, depending on the nature of the R group on the aniline with high efficiencies. The HOMO is localized on the aniline ring, while the LUMO is delocalized

Chart 8

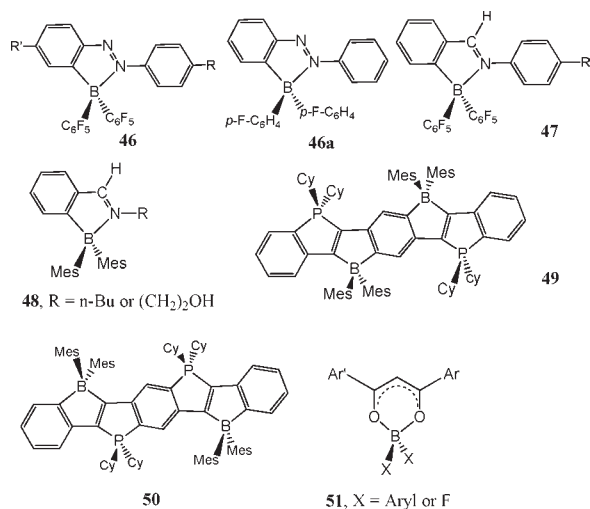


on the entire chelate group. It was found that electron-withdrawing groups shift the emission maximum to blue and increase the stability of the compound toward hydrolysis when exposed to air, while electron-donating groups shift the emission to green and destabilize the compound toward hydrolysis. The solution (CH<sub>3</sub>CN) and solid-state luminescence agree well for this class of compounds. Nonetheless, they were not investigated for OLEDs, perhaps because of their poor stability toward hydrolysis. Compounds 41 were also reported by Gardinier and co-workers and showed a much improved stability and an interesting dynamic exchange by the bound and nonbound pyrazolyl groups.<sup>28b</sup> Chujo and co-workers investigated the green-luminescent 8-aminoquinoline boron compounds 42 (the monomer with R = Me and Ar = Ph was found to have  $\lambda_{\text{em}} = 504$  nm and  $\Phi = 0.24$  in CH<sub>2</sub>Cl<sub>2</sub>) and their incorporation into polymers, but no EL evaluation was performed.<sup>29</sup>

**3. N,C-Chelate Compounds.** The other types of chelate boron compounds investigated for potential applications in OLEDs are N,C-chelate compounds. Yamaguchi and co-workers reported the three isomers of diboron compounds 43a–43c based on the building block monomer 43 (Chart 8) in 2006.<sup>30a</sup> These were believed to be the first examples of four-coordinate boron chelate compounds with two bulky mesityl groups. The luminescent quantum yields of this group of compounds are low (<0.10). However, they have a low LUMO energy level and a good electron mobility, with  $\mu = 1.5 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> being observed for 43b. The high electron mobility of this group of compounds was attributed to the extended  $\pi$  conjugation and the boron chelation. Recently, Wakamiya et al. reported compounds 44 and 45, which were also found to display a high electron affinity.<sup>30b</sup>

The other class of luminescent N,C-chelate boron compounds is based on either azobenzene or imine derivatives such as 46 and 47 shown in Chart 9, investigated extensively by Kawashima and co-workers.<sup>31,32</sup> The fluorescences of these molecules were found to originate from a  $\pi \rightarrow \pi^*$  transition localized on the conjugated chelate backbone. For 46a, the replacement of the C<sub>6</sub>F<sub>5</sub> groups by two *p*-fluorophenyl groups rendered the molecule as nonemissive, which was attributed to the change of the

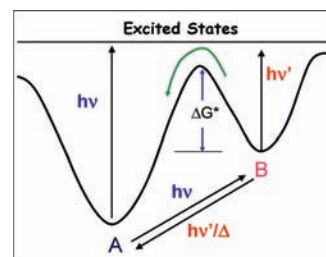
Chart 9



HOMO level from the chelate backbone to the phenyl ring, with the lowest-energy transition being a charge transfer from the phenyl group to the chelate  $\pi^*$  orbital.<sup>31a</sup> The azobenzene compounds **46** emit from 500 to 634 nm in hexanes, depending on the nature of the R and R' groups. The brightest emitters were found to be molecules with R' = H and R = NMe<sub>2</sub> (**46-NMe**<sub>2</sub>,  $\lambda_{em}$  = 566 nm, and  $\Phi$  = 0.52); R' = H and R = OMe (**46-OMe**,  $\lambda_{em}$  = 524 nm, and  $\Phi$  = 0.70), and R' = H and R = OSiMe<sub>2</sub>(*t*-Bu) (**46-OSi**,  $\lambda_{em}$  = 524 nm, and  $\Phi$  = 0.90).<sup>31b</sup> However, it was reported that some members of the azobenzene compounds such as **46-NMe**<sub>2</sub> are not emissive at all in the solid state. The brightest imine compounds are **47-PhNMe**<sub>2</sub> (R = *p*-PhNMe<sub>2</sub>,  $\lambda_{em}$  = 500 and 527 nm, and  $\Phi$  = 0.73) and **47-An** (R = 2-anthryl,  $\lambda_{em}$  = 497 and 531 nm, and  $\Phi$  = 0.39).<sup>32</sup> García-Hernández and Gabbäi reported the sterically congested molecules **48**, which are fluorescent ( $\lambda_{em}$  = 504–512 nm and  $\Phi$  = ~0.09), despite the fact that the lowest-energy transition of **48** was found to be from the mesityl group to the chelate ring.<sup>33</sup> This group of compounds has not been investigated for applications in OLEDs; some of their members, however, have found applications in sensing and imaging.<sup>31b</sup>

**4. Other Chelate Compounds.** Yamaguchi and co-workers reported highly emissive C,C-chelate boron compounds **49** and **50** shown in Chart 9. In these molecules, the positively charged phosphonium chelate units balance the negatively charged borate units (**49** and **50**).<sup>34</sup> These molecules emit in the orange-red region with a high quantum yield (~0.40) in solution. They also possess a low LUMO level, thus very promising for applications in organic devices.

O,O-Chelate boron compounds based on aromatic 1,3-diketone ligands with the general structure of **51** shown in Chart 9 are structural analogues of BODIPY and have attracted much recent research interest.<sup>35–37</sup> The BF<sub>2</sub> and B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> compounds of **51** are, in general, bright fluorescent emitters with highly tunable emission colors, although no OLED data based on this group of compounds are available. The emission of these compounds was found to originate from  $\pi \rightarrow \pi^*$  transitions localized on the diketone backbone. Similar to Kawashima's observation for compounds **46** and **46a**, Chujo et al. reported that the BPh<sub>2</sub> compound of **51** (Ar = Ar' = Ph or *p*-PhOMe) is essentially nonemissive ( $\Phi$  = 0.01–0.06 in CH<sub>2</sub>Cl<sub>2</sub>) because the



**Figure 3.** Diagram showing the pathways of photochromic switching between the two isomers A and B.

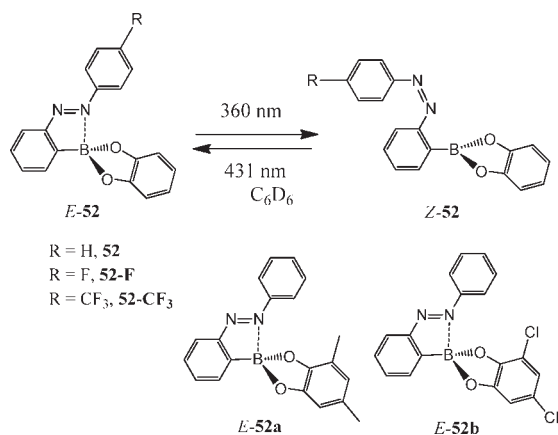
HOMO level is localized on the phenyl group.<sup>35c,d</sup> One frequently observed but not well-understood feature for this class of compounds is their tendency to change emission color from the solution to the solid state.<sup>35–37</sup> Some members of this class of compounds have been found to have an efficient two-photon absorption,<sup>35a</sup> display mechanochromic luminescence,<sup>36a</sup> or influence the photochromic switching of a dithienylethene dye.<sup>34</sup> The introduction of a polymer chain to one of the aryl groups on the diketone of the BF<sub>2</sub> compounds was found to induce unusual and highly oxygen-sensitive solid-state phosphorescence,<sup>36</sup> enabling their use as oxygen sensors/tumor hypoxia imaging reagents.<sup>36c</sup>

## PHOTOCHROMIC FOUR-COORDINATE BORON COMPOUNDS

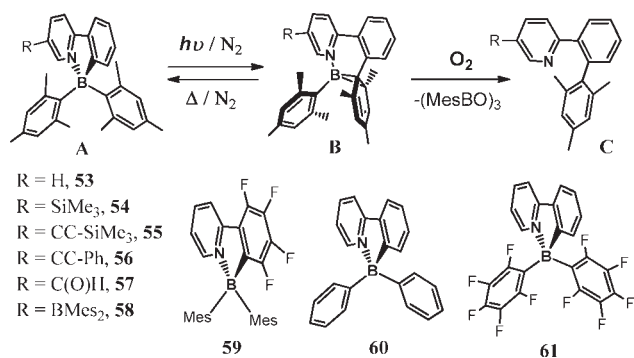
Photochromic compounds are defined as molecules that are capable of undergoing a reversible transformation between two structural forms with a distinct color change when excited at least in one pathway by light,<sup>38</sup> as shown by Figure 3. Because of the rapid and often instant change of the physical and electronic properties such as color, luminescence, conductivity, refractive index, etc., photochromic materials have potential applications in optical memory devices, molecular switches, smart windows, ophthalmic glasses, etc. Many examples of organic photochromic compounds have been extensively investigated including azobenzenes, diarylethenes (DTEs), spiropyrans, spirooxazines, naphthopyrans, etc.<sup>39</sup> With the exception of azobenzenes, the structural transformation for the majority of organic photochromic compounds involves a ring-closure and -opening process. Boron-containing photochromic molecules that involve structural transformation around the boron center upon photoexcitation are rare. Only two classes of molecules, namely, azobenzene N,C-chelate boron compounds reported by Kawashima and N,C-chelate photochromic boron compounds reported by us, are known to display reversible photoisomerization phenomena.

**1. Azobenzene N,C-Chelate Compounds.** Kawashima and co-workers reported that the azobenzene compounds **52** undergo isomerization upon irradiation at 360 nm (Scheme 1).<sup>40a,b</sup> This isomerization process was believed to occur by dissociation of the B–N bond, followed by subsequent *trans* (*E*) to *cis* (*Z*) isomerization of the azobenzene moiety. The *Z* isomer can be reverted back to the *E* isomer by irradiation at 431 nm. Interestingly, similar photoisomerization was not observed in the related molecules **46** and **47** (Chart 9). This difference could be attributed to the exceptionally long B–N “bonds” in (*E*)-**52** to (*E*)-**52-CF**<sub>3</sub> compounds (1.823–1.895 Å), compared to those in **46** [1.625(2)–1.638(3) Å]. The  $\pi$  conjugation of the boron center with the oxygen lone pairs in (*E*)-**52** to (*E*)-**52-CF**<sub>3</sub> is

Scheme 1

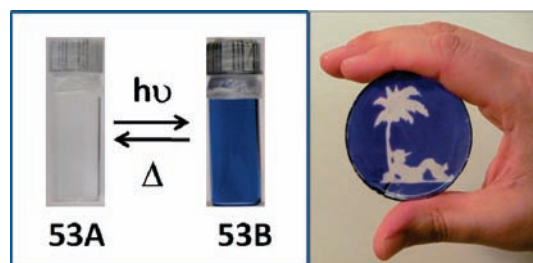


Scheme 2



clearly responsible for the long B–N bonds. The direct impact of the B–N bond strength on photoisomerization was further supported by the behavior of compound (*E*)-**52-OMe** [R = OMe in (*E*)-**52**] and (*E*)-**52b**, both of which possess relatively short B–N bonds (1.773 and 1.721 Å, respectively). The former was attributed to the electron-donating nature of the OMe group that strengthens the B–N bond and the latter to the electron-withdrawing chloro groups that weaken the B–O bonds, thus strengthening the B–N bond. These two molecules were found not to undergo photoisomerization upon irradiation at 360 nm.<sup>40b</sup> When the chloro groups in (*E*)-**52b** were replaced by methyl groups (**52a**), isomerization was once again observed, presumably because of destabilization of the B–N bond. Thus, the photoisomerism displayed by this class of molecules has the same molecular origin as the parent azobenzene molecules. The role of the boron unit is simply to inhibit or partially inhibit isomerization by binding to the azo N atom. The photoisomerization process has been found to be useful for tuning/switching of the Lewis acidity of the boron center in compounds **52**–**52b**.<sup>40a</sup>

**2. Phenylpyridyl (ppy) Chelate Compounds.** *The Discovery.* In 2008, intrigued by the report of Yamaguchi and co-workers on the congested N,C-chelate four-coordinate boron compounds **43** and **43a**–**43c**,<sup>30a</sup> we decided to investigate the related compound **53** shown in Scheme 2.<sup>41</sup> Despite steric congestion, this molecule was found to retain its structural integrity in solution and in the solid state. Compound **53** does



**Figure 4.** Left: Photographs showing the color change of compound **53** in toluene upon exposure to UV light (365 nm). Right: Photograph showing a polystyrene disk doped by compound **62-S**. The dark area was exposed to UV light (365 nm), while the colorless area was protected from irradiation by a mask.

not react with anions such as fluoride, a common reaction for triarylboranes. However, upon irradiation by light (365 nm), this compound was found to change color rapidly from colorless to dark blue and lose its fluorescence ( $\lambda_{em} = 458$  nm and  $\Phi = 0.15$  in toluene) completely, as shown in Scheme 2 and Figure 4. We observed that this process was fully thermally reversible with an activation barrier of 110 kJ mol<sup>-1</sup> and  $t_{1/2} = \sim 7.7$  h at 323 K. The structure of the dark isomer **53B** was established by NMR and computational studies. NMR studies showed that the transformation of **53A** to **53B** was quantitative, with a C–C bond being formed and dearomatization of a mesityl group. Although the mechanism of this transformation has not been fully understood, it may be considered as a Zimmerman rearrangement,<sup>42</sup> followed by a sigmatropic shift. The electron density of **53B** was found to concentrate on the BC<sub>2</sub> ring, and the HOMO level was destabilized by  $\sim 1$  eV, compared to **53A**, making it highly reactive toward oxygen and generating the C–C-coupled product **C** instantly upon exposure to oxygen. Photoisomerization from **53A** to **53B** was found to be very efficient with a quantum yield of  $\sim 0.85$  ( $\lambda_{ex} = 365$  nm).

This photoisomerization was also found to occur readily in polymer matrixes such as poly(methyl methacrylate), polystyrene, ethylene vinyl alcohol (EVOH), or poly(dimethylsiloxane) (PDMS) doped by compound **53** and related molecules (e.g., **62**). An example of such solid-state switching is illustrated in Figure 4. Polymers such as polystyrene and EVOH shield the molecule from exposure to oxygen such that photochromic switching becomes possible under ambient conditions. In contrast, with PDMS films, which have an excellent permeability toward oxygen, the dark color of **B** can be quenched rapidly by oxygen, thus enabling the use of these molecules as potential solid-state oxygen indicators that can be turned on by light.<sup>43</sup>

In contrast to the N,N- or N,O-chelate compounds, where the lowest-energy electron transition is localized on the chelate ligand, the HOMO and LUMO levels of **53** are located predominantly on one mesityl group and the chelate backbone, respectively. Thus, the lowest excited state of **53** can be described as a charge transfer from a mesityl group to the chelate ring. The emission spectrum of **53**, in fact, experiences a red shift with increasing solvent polarity. Similarly for the dark isomer **53B**, the LUMO level is localized at the ppy unit; thus, the lowest-energy transition can also be ascribed to a charge transfer from the BC<sub>2</sub> unit to the ppy ring. Although C–C coupling between two aryl groups in BAr<sub>4</sub><sup>-</sup> anions under UV (250 nm) irradiation was known previously,<sup>44</sup> it was neither reversible nor selective when two different aryl groups were present in the molecule.

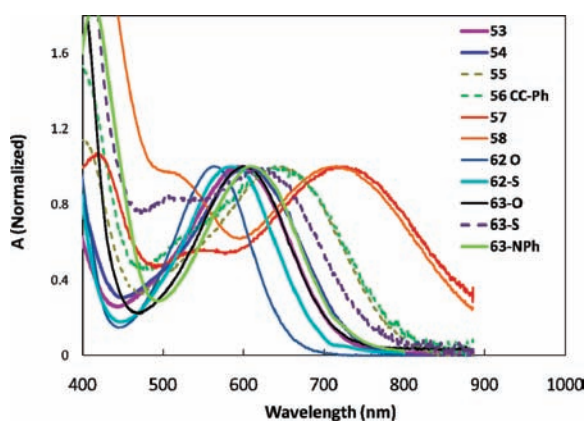


Figure 5. Diagram showing the absorption spectra of selected dark isomers in toluene.

For compound **53**, the C–C coupling occurs exclusively between a mesityl group and the phenyl group of the ppy ligand. The ppy chelate ligand and the low-energy mesityl-to-ppy charge-transfer transition in **53** were believed to play a key role in promoting its highly selective C–C coupling and the reversible structural transformation. To gain further insight on this unusual photoisomerization phenomenon, we investigated a series of substituted ppy chelate boron compounds with selected examples shown in Scheme 2. In addition, we also examined compounds **60** and **61** to establish the role of the mesityl groups.

*Substitution and Steric Effects.*<sup>45</sup> Consistent with the lowest electronic transition being charge transfer from  $\pi_{\text{mesityl}}$  to  $\pi_{\text{ppy}}^*$ , electron-donating groups such as  $\text{SiMe}_3$  were found to blue-shift the emission energy ( $\lambda_{\text{em}} = 418$  nm for **54**), while electron-withdrawing groups such as  $-\text{C}(\text{O})\text{H}$  and  $\text{BMes}_2$  shift the emission maximum to longer wavelengths ( $\lambda_{\text{em}} = 527$  nm for **57** and **58**). Extending  $\pi$  conjugation also red-shifts the emission energy (e.g.,  $\lambda_{\text{em}} = 490$  nm for **56**). In the absorption spectra of compounds **53**–**58**, a low-energy shoulder absorption band that shifts toward longer wavelengths with either substitution by electron-withdrawing groups or increased conjugation was evident. Compounds **54**–**58** all undergo photoisomerization in the same manner as **53** does. For **55**–**58**, isomerization also occurs under ambient light irradiation because of their relatively strong absorption in the 400–470 nm region. Extending  $\pi$  conjugation of the ppy ligand was found to greatly enhance the fluorescence emission efficiency (e.g.,  $\Phi = 0.37$  for **56**), which was believed to be responsible for the reduced photoisomerization efficiency (e.g., 0.33 for **56** at 365 nm).  $\lambda_{\text{max}}$  of the broad low-energy absorption band of the dark isomers **B** follows a trend similar to that of the emission spectra of the isomers **A** (e.g.,  $\lambda_{\text{max}} = \sim 600$  nm for **53B** and **54B** and 640 and 720 nm for **56B** and **58B**, respectively), as shown in Figure 5. Except **57**, the isomerization process was found to be thermally reversible for all compounds and the thermal reversal of the substituted dark isomers to be much faster than the parent molecule **53B**. This was attributed to destabilization of the dark isomer imposed by the substituent due to increased steric congestion.

In contrast to compounds **53**–**58**, the fluoro-containing compounds **59** and **61** were observed to be unstable toward photolysis and no isomerization was observed. Compound **60** was, however, found to be stable toward photolysis, and no photoisomerization was observed at all, even when irradiated at its absorption maximum, 310 nm. Density functional theory

Chart 10

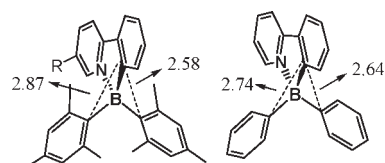
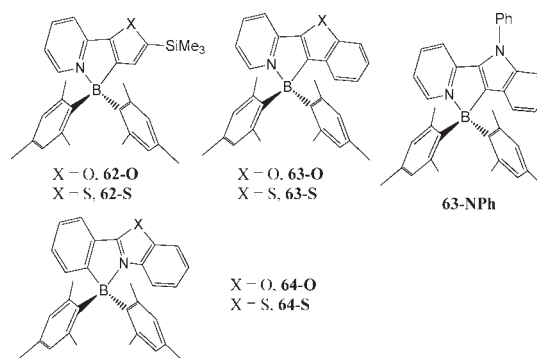


Chart 11



(DFT) computational results showed that the HOMO and LUMO levels of **60** resemble those of **53**; thus, its inertness toward photoisomerization was unlikely caused by electronic effects. We suggested that the key driving force for the photoisomerization process was the steric congestion imposed by the two mesityl groups for compounds **53**–**58**. The average of B–N and B–C<sub>ppy</sub> bond lengths for these molecules are 1.65(1) and 1.63(1) Å, respectively, while the corresponding ones for **60** are 1.62(1) and 1.63(1) Å, respectively. The average B–C<sub>Mes</sub> bond length is 1.65(1) Å for **53**–**58**, much longer than that of B–C<sub>Ph</sub> of **60** [1.61(1) Å]. Furthermore, the arrangement of the two mesityl groups in **53**–**58** is much less symmetric than the two phenyl groups in **60**, with one mesityl group being much closer to the ppy C atom (2.58 Å in average) than the phenyl in **60** (2.64 Å), as shown in Chart 10. This, along with the relatively weak B–C<sub>Mes</sub> bonds of **53**–**58**, was believed to be the most likely key driving force for their facile photoisomerization. Another important observation was that the triarylboron unit in compound **58** remained intact through the photoisomerization process and the C–C-coupled product **58C** was isolated quantitatively when **58** was photolyzed under air.<sup>41</sup> From the coordination chemistry point of view, coordinatively saturated four-coordinate boron compounds are, in general, expected to have a greater thermodynamic stability than their three-coordinate analogues. The unusual and facile photoisomerization phenomenon by compounds **53**–**58** demonstrated that steric congestion in coordinatively saturated boron compounds can be a key driving force in the structural transformation at the excited state.

**3. Other Heterocyclic Chelate Compounds.** To establish if the photoisomerization observed for ppy-based boron compounds is a general phenomenon for  $\pi$ -conjugated N,C-chelate  $\text{BMes}_2$  compounds, we synthesized compounds **62** and **63** (Chart 11), where a heterocyclic group such as benzofuryl<sup>43</sup> or *N*-phenylindolyl<sup>46</sup> replaces the phenyl group of ppy in **53**. The average B–N, B–C<sub>heterocycle</sub>, and B–C<sub>Mes</sub> in compounds **63** are 1.67(1), 1.62(1), and 1.64(1) Å, respectively,<sup>43,45,46</sup> comparable



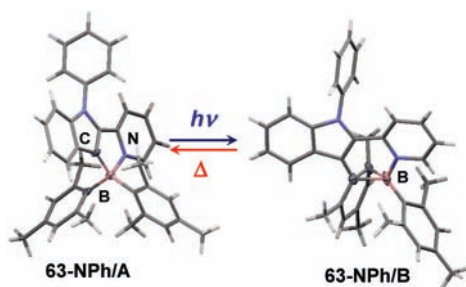
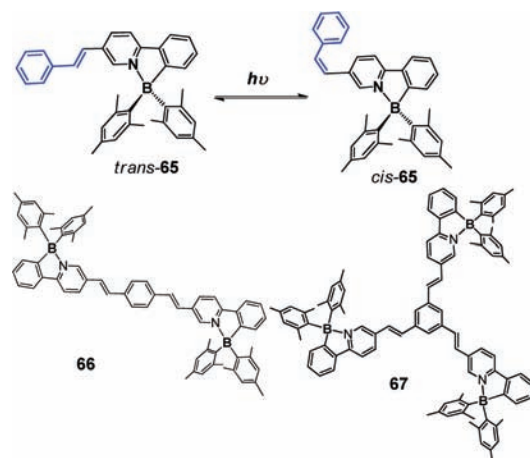


Figure 6. Crystal structures of isomers A and B of 63-NPh.

to those of 53–58 and 62. The two mesityl groups in 62 also have an asymmetric arrangement, with one being much closer to the C atom of the heterocycle (2.57 Å in average) than the other (2.90 Å in average),<sup>43</sup> similar to those of 53–58. For 63, these distances were observed to be 2.60 and 2.86 Å, respectively. Compounds 62-O, 62-S, 63-O, and 63-S are all blue emitters with  $\lambda_{em} \sim 450$  nm and  $\Phi = 0.30$ –0.80, while 63-NPh is a blue-green emitter with  $\lambda_{em} \sim 490$  nm and  $\Phi = 0.32$ . The HOMO level of 62 is very similar to that of 53, dominated by a  $\pi$  orbital of a mesityl group (the one that is close to the heterocycle) with a small contribution from the thienyl or furyl ring, while the LUMO is a  $\pi^*$  orbital dominated by the chelate backbone. Thus, the lowest-energy transitions in these molecules are similar to that of 53–58, namely, a charge transfer from a mesityl group to the chelate backbone. In contrast, for 63, the HOMO level has a very large contribution from the  $\pi$  orbital of the chelate backbone and a modest contribution from the mesityl group, while the LUMO level is a  $\pi^*$  orbital of the chelate backbone.<sup>45,46</sup> Therefore, the lowest-energy transition of 63 has much less charge-transfer character than that of 53 and 62. Upon irradiation by light (365 nm), compounds 62 and 63 all isomerized to a dark isomer (dark blue for 62 and 63-O, dark green for 63-S, and dark blue-green for 63-NPh) in the same manner as that of 53. The photoisomerization quantum efficiencies for compounds 63 were determined to be much lower ( $\sim 0.10$ ) than that of 53. In contrast, compounds 62-O and 62-S were found to have much higher photoisomerization efficiencies (0.35 and 0.75, respectively).<sup>43</sup> The greater  $\pi$  conjugation and steric impediment imposed by the benzo group in 63 were believed to be responsible for the low photoisomerization quantum efficiency. One noteworthy feature that is common for compounds 62 and 63 is the high thermal stability of their dark isomers. The dark isomer of 63-NPh has a thermal reversal half-life of 9.5 h at 50 °C, while no thermal reversal was observed for 62-O, 62-S, 63-O, and 63-S at this temperature for more than 10 h. The high thermal stability of the dark isomer of 63-NPh allowed us to crystallize it and determine its structure by X-ray diffraction analysis,<sup>46</sup> thus unambiguously establishing the structure of the unusual dark isomer (Figure 6). Our study on the heterocyclic chelate compounds established that the photoisomerization phenomenon for N,C-chelate BMe<sub>2</sub> compounds is quite general. To further establish the generality of this phenomenon, we recently synthesized compounds<sup>43</sup> 64-O and 64-S, where a benzothiazolyl or a benzoxazolyl replaces the pyridyl in 53. These compounds undergo photoisomerization and produce dark isomers similar to 53B, based on NMR. However, thermally the dark isomers of this class of compounds appeared to be unstable and undergo further structural transformation. Efforts are being taken in our laboratory to understand the unique and unusual structural

Scheme 3

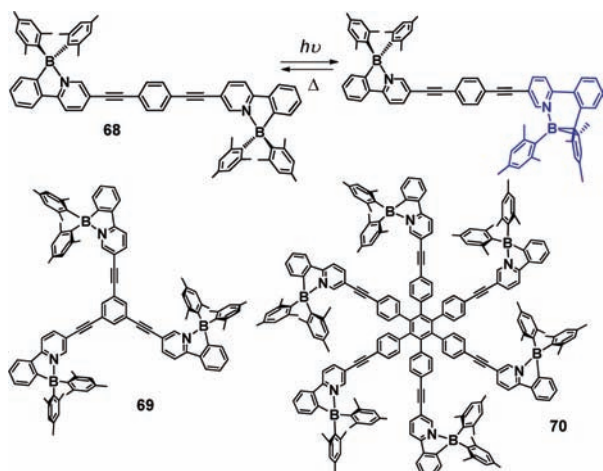


transformation displayed by this class of compounds. The details will be reported in due course.

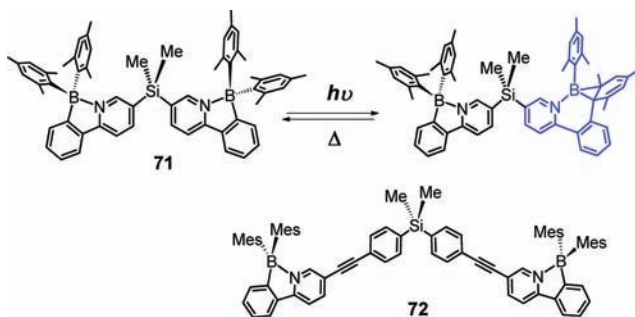
**4. Competitive Isomerization Pathways and Polyboryl Systems.** A vinyl group or an olefinic bond is commonly used in building extended  $\pi$ -conjugated materials.<sup>47</sup> To examine the impact of an olefinic bond on photochromic switching of the N, C-chelate boron compounds, we synthesized compounds 65–67, as shown in Scheme 3.<sup>48</sup> These molecules were all isolated as trans or all-trans isomers. DFT computation indicated that the HOMO and LUMO levels of these molecules resemble those of 53 except that the LUMO spreads over the entire  $\pi$  backbone. These molecules are bright-blue or blue-green emitters with  $\Phi = 0.30$ –0.59 in solution and  $\sim 0.23$  in the solid state. Upon irradiation at 365 nm, no color change was observed for any of the compounds. In the UV spectrum of 65, a distinct blue shift of the main absorption band at 370 nm was observed. NMR studies established that instead of photoisomerization of the boron core, the olefinic bond undergoes a trans–cis isomerization, with the cis isomer being the major isomer at the photo-stationary state for 65, while for the polyboryl compounds 66 and 67, only one olefinic bond was observed to undergo trans–cis isomerization. The olefinic bond isomerization caused a significant loss of the fluorescence intensity in these compounds. Nonetheless, a single olefinic bond isomerization was sufficient to shut off photoisomerization around the boron center, thus stabilizing the boron chromophore toward UV irradiation. The preferential isomerization of the olefinic bond was attributed to the relatively faster kinetics of trans–cis isomerization in the excited state, which effectively quenched the alternative isomerization pathway around the boron core.

To elucidate the impact of multiboryl units on photoisomerization of a conjugated molecule, we synthesized the polyboryl compounds 68–70 shown in Scheme 4, where a phenyl bond and an alkyne bond are used as the linkers.<sup>49a</sup> These compounds are bright-blue-green emitters with  $\lambda_{em} \sim 500$  nm. In contrast to the olefinic compounds, they all underwent photoisomerization upon irradiation at 365 nm in the same manner as the monoboryl compounds 53 and 56 did because of the lack of an alternative photoisomerization pathway. Interestingly, however, only one boron unit in these polyboryl compounds was found to undergo isomerization. This was in contrast to the extensively studied DTE photochromic systems, where simultaneous photoisomerization of multiple chromophores in a single

Scheme 4



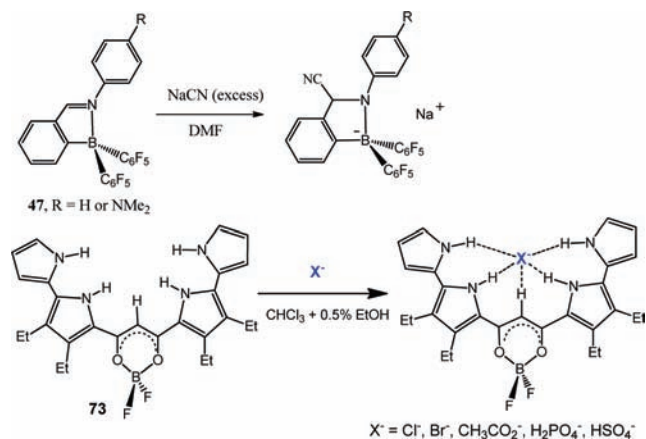
Scheme 5



molecule was frequently observed.<sup>49</sup> We attributed the single-boryl isomerization phenomenon to the much slower kinetics of the B(ppy)Mes<sub>2</sub> photoisomerization, which could not compete with the much faster energy-transfer process that dissipates the excited-state energy to the low-energy absorption of the isomerized boron unit. The presence of multiboryl units did, however, appear to enhance the efficiency of photoisomerization of the single boryl unit through the “antenna” effect. Furthermore, the multiboryl units also accelerated the thermal reversal rate of these compounds, compared to the monoboryl compound **56**, although this phenomenon was not yet well understood. Another interesting phenomenon of the polyboryl compounds was the complete quenching of fluorescence caused by photoisomerization of a single boryl unit. Intramolecular energy transfer was again believed to be responsible for this phenomenon.

To determine if  $\pi$  conjugation was a key factor in the behavior of compounds **68–70**, we synthesized and investigated two nonconjugated molecules **71** and **72**, as shown in Scheme 5.<sup>49b</sup> These two compounds responded to light in the same manner as the conjugated polyboryl compounds **68–70** did, changing color from light yellow to dark green, with only a single boron unit undergoing isomerization. Thus, we suggested that extended  $\pi$  conjugation is not required for the single-boryl isomerization phenomenon. For both **71** and **72**, the photoisomerization quantum efficiencies (0.60 for **71** and 0.58 for **72**) were found to be much higher than those of the corresponding monomers **54** (0.51) and **56** (0.33), further supporting the antenna effect

Scheme 6



observed in molecules **68–70**, with one boryl unit facilitating isomerization of the other boryl unit through fast intramolecular energy transfer. The thermal reversal rate constant of the dark isomer of **72** was found to be similar to that of **56**, while that of **71** was much faster than that of the monomer, which was attributed to a greater steric congestion in **71B**.

We have recently completed our investigation on several new diboryl compounds where the two N,C-chelate boron units are linked together directly<sup>43</sup> with structures resembling those of compounds **43** reported by Yamaguchi et al.<sup>30</sup> A preliminary study indicated that these molecules are inert toward photoisomerization. One significant difference between these new diboryl molecules and the polyboryl compounds **68–72** is domination of the HOMO level by the  $\pi$  orbitals of the chelate backbone. Thus, it appeared that, in addition to steric congestion, the lowest-energy transition being a charge transfer from a mesityl group to the chelate ring may be critical in the photoisomerization process. Further investigation on the new diboryl system is on the way. Efforts are also being taken to understand the excited-state kinetics and the photoisomerization mechanism of the N,C-chelate boron compounds by both experimental and computational studies, and the results will be published in due course.

## ■ FOUR-COORDINATE BORON COMPOUNDS IN SENSING APPLICATIONS

Unlike triarylboryl compounds, which can act as Lewis acids and are thus very effective in the selective sensing of anions, four-coordinate boron compounds have not been extensively studied for sensing applications mostly because of the coordination saturation around the boron center. There are, however, a few examples of potentially useful sensing systems based on four-coordinate boron compounds. The first system is based on the azobenzene boron compounds **52** in Scheme 1. These compounds and their boronic acid analogues have been shown to be able to reversibly bind pyridine,<sup>40a</sup> hydroxides, or glucose<sup>51</sup> via the reversible opening and closing of the B–N bond. Compound **46-NMe<sub>2</sub>**, which has a much stronger B–N bond than **52**, was found to undergo fluorescence quenching upon the addition of an acid, and fluorescence may be restored by the addition of an amine.<sup>31c</sup> It was suggested that the noncoordinated azo N atom was the proton-binding site. The green fluorescence of several

imine compounds of **47** has been reported to undergo complete quenching upon the addition of excess cyanide ions because of the disruption of  $\pi$  conjugation in the backbone,<sup>32</sup> as shown in Scheme 6. Taking advantage of the chelate backbone for anion sensing was further demonstrated by Maeda and co-workers using 1,3-diketone boron compound **73** and related compounds (Scheme 6).<sup>37</sup> Compound **73** is a bright emitter ( $\lambda_{em} = 599$  nm and  $\Phi = 0.42$  in  $\text{CH}_2\text{Cl}_2$ ). It can bind to a variety of anions through hydrogen bonds in the diketone backbone with a strong binding constant ( $10^5$ – $10^6$   $\text{M}^{-1}$ ) and a distinct change of the absorption spectrum, although it did not have a very good selectivity to differentiate different anions.

## CONCLUDING REMARKS

The examples presented in this article illustrate the rich chemistry and the versatile applications of four-coordinate organoboron compounds that possess a chelate  $\pi$ -conjugated backbone. The B atom in this class of compounds plays dual roles in most instances, namely, stabilizing the anionic chelate ligand and enhancing  $\pi$  conjugation, thus influencing the electronic properties of the  $\pi$  system. This is highly beneficial for the use of this class of compounds in OLEDs as emitters and electron-transport materials. Because of the recent impressive progress on high-efficiency phosphorescent OLEDs (PhOLEDs),<sup>52</sup> phosphorescent emitters are dominating the current research efforts in OLEDs. This, however, does not diminish the importance of main-group-based materials such as four-coordinate boron compounds for the simple reason that fluorescent OLEDs are much simpler and cheaper to fabricate than PhOLEDs and thus can still find their own niche applications. Furthermore, highly effective host materials that possess a large HOMO–LUMO gap and deep HOMO and LUMO levels for the triplet emitters in PhOLEDs are still in high demand. Electron-transport materials with a high electron mobility are still rare. Boron-containing  $\pi$ -conjugated systems are excellent candidates for these applications. Future research efforts on boron-based materials for OLEDs should therefore be directed to this area.

Photochromic N,C-chelate organoboron compounds discovered by our group open a new avenue and a new opportunity in the research and development of photochromic materials and their applications. The highly tunable colors of the dark state, the luminescence of the light-colored state, and the high photoisomerization quantum efficiencies for many members of the new boron compounds make them very attractive for potential applications in photochromic devices. The sensitivity of the dark isomers of the new boron compounds will certainly limit the scope of their practical applications. The fact that photoisomerization of the boron compounds occurs readily in many different polymer matrixes indicates that the oxygen sensitivity may be addressed by the appropriate choice of the matrix material.

Lastly, the recent research efforts on the materials aspects of organoboron compounds have focused on both triarylboron and four-coordinate boron compounds. These two classes of compounds share some common features, i.e., bright luminescence and high electron affinity. Nonetheless, triarylboron compounds possess a unique Lewis acidity that enabled their effective use as highly selective sensors for anions.<sup>53</sup> Incorporating these two functionalities in the same molecule should provide interesting properties to the molecule. Such molecules are, however, still rare. The photochromic compound **58** is one example of such compounds. We are currently investigating a number of hybrid

diboron molecules that are related to compound **58**. The results will be published in due course.

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## REFERENCES

- (1) Wang, S. *Coord. Chem. Rev.* **2001**, *215*, 79.
- (2) (a) Entwistle, C. D.; Marder, T. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2927. (b) Entwistle, C. D.; Marder, T. B. *Chem. Mater.* **2004**, *16*, 4574.
- (3) Fukazawa, A.; Yamaguchi, S. *Chem.—Asian J.* **2009**, *4*, 1386.
- (4) (a) Helber, M. J.; Vargas, J. R. U.S. Patent 7,074,503, 2006. (b) Vargas, J. R.; Kondakov, D. Y. U.S. Patent 7,329,466, 2008.
- (5) Piers, W. E.; Bourke, S. C.; Conroy, K. D. *Angew. Chem., Int. Ed.* **2005**, *44*, 5016 and references cited therein.
- (6) Loudet, A.; Burgess, K. *Chem. Rev.* **2007**, *107*, 4891.
- (7) (a) Jäkle, F. *Chem. Rev.* **2010**, *110*, 3985. (b) Jäkle, F. *Coord. Chem. Rev.* **2006**, *250*, 1107. (c) Nagai, A.; Chujo, Y. *Chem. Lett.* **2010**, *39*, 430.
- (8) *Organic Electroluminescence*; Kafafi, Z. H., Ed.; Taylor and Francis: Boca Raton, FL, 2005.
- (9) (a) Shirota, Y.; Kageyama, H. *Chem. Rev.* **2007**, *107*, 953. (b) Xiao, L. X.; Chen, Z. J.; Qu, B.; Luo, J.; Kong, S.; Gong, Q.; Kido, J. *Adv. Mater.* **2011**, *23*, 926 and references cited therein.
- (10) Tang, C. W.; Van Slyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.
- (11) (a) Aziz, H.; Popovic, Z. D.; Hu, N. X.; Hor, A. M.; Xu, G. *Science* **1999**, *283*, 1900. (b) Papadimitrakopoulos, F.; Zhang, X.-M.; Thomsen, D. L., III; Higginson, K. A. *Chem. Mater.* **1996**, *8*, 1363. (c) Higginson, K. A.; Zhang, X. M.; Papadimitrakopoulos, F. *Chem. Mater.* **1998**, *10*, 1017. (d) Knox, J. E.; Halls, M. D.; Hrachian, H. P.; Schlegel, H. B. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1371.
- (12) (a) Lin, B. C.; Cheng, C. P.; You, Z. Q.; Hsu, C. P. *J. Am. Chem. Soc.* **2005**, *127*, 66. (b) Chen, C. H.; Shi, J. *Coord. Chem. Rev.* **1998**, *171*, 161. (c) Pohl, R.; Anzenbacher, P., Jr. *Org. Lett.* **2003**, *5*, 2769. (d) Montes, V. A.; Li, G.; Pohl, R.; Shinar, J.; Anzenbacher, P., Jr. *Adv. Mater.* **2004**, *16*, 2001. (e) Pohl, R.; Montes, V. A.; Shinar, J.; Anzenbacher, P., Jr. *J. Org. Chem.* **2004**, *69*, 1723. (f) Montes, V. A.; Pohl, R.; Shinar, J.; Anzenbacher, P., Jr. *Chem.—Eur. J.* **2006**, *12*, 4523.
- (13) (a) Wu, Q.; Esteghamatian, M.; Hu, N.-X.; Popovic, Z.; Enright, G.; Tao, Y.; D'Iorio, M.; Wang, S. *Chem. Mater.* **2000**, *12*, 79. (b) Wu, Q. Ph.D. Thesis, Queen's University, Kingston, Ontario, Canada, 2000.
- (14) Anderson, S.; Seaver, M. S.; Hudson, A. J. *Synth. Met.* **2000**, *111–112*, 459.
- (15) (a) Cui, Y.; Liu, Q. D.; Bai, D. R.; Jia, W. L.; Tao, Y.; Wang, S. *Inorg. Chem.* **2005**, *44*, 601. (b) Cui, Y.; Wang, S. *J. Org. Chem.* **2006**, *71*, 6485.
- (16) (a) Qin, Y.; Pagba, C.; Piotrowiak, P.; Jäkle, F. *J. Am. Chem. Soc.* **2004**, *126*, 7015. (b) Qin, Y.; Kiburu, I.; Shah, S.; Jäkle, F. *Org. Lett.* **2006**, *8*, 5227.
- (17) Kappaun, S.; Rentenberger, S.; Pogantsch, A.; Zojer, E.; Mereiter, K.; Trimmel, G.; Saf, R.; Möller, K. C.; Stelzer, F.; Slugovc, C. *Chem. Mater.* **2006**, *18*, 3539.
- (18) (a) Li, Y.; Liu, Y.; Bu, W.; Guo, J.; Wang, Y. *Chem. Commun.* **2000**, 1551. (b) Zhang, H.; Huo, C.; Ye, K.; Zhang, P.; Tian, W.; Wang, Y. *Inorg. Chem.* **2006**, *45*, 2788. (c) Zhang, H.; Huo, C.; Zhang, J.; Zhang,

- P.; Tian, W.; Wang, Y. *Chem. Commun.* **2006**, 281. (d) 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.
- (19) Kim, N. G.; Shin, C. H.; Lee, M. H.; Do, Y. *J. Organomet. Chem.* **2009**, *694*, 1922.
- (20) Liu, S.-F.; Seward, C.; Aziz, H.; Hu, N.-X.; Popovic, Z.; Wang, S. *Organometallics* **2000**, *19*, 5709.
- (21) Tokoro, Y.; Nagai, A.; Chujo, Y. *Macromolecules* **2010**, *43*, 6229.
- (22) Son, H.-J.; Han, W.-S.; Wee, K.-R.; Chun, J.-Y.; Choi, K.-B.; Han, S. J.; Kwon, S.-N.; Ko, J.; Lee, C.; Kang, S. O. *Eur. J. Inorg. Chem.* **2009**, 1503.
- (23) (a) Ashenhurst, J.; Brancaleon, L.; Hassan, A.; Liu, W.; Schmider, H.; Wang, S.; Wu, Q. *Organometallics* **1998**, *17*, 3186. (b) Ashenhurst, J.; Wu, G.; Wang, S. *J. Am. Chem. Soc.* **2000**, *122*, 2541. (c) Wu, Q.; Lavigne, J. A.; Tao, Y.; D'Orto, M.; Wang, S. *Inorg. Chem.* **2000**, *39*, 5248.
- (24) (a) Hassan, A.; Wang, S. *Chem. Commun.* **1998**, 339. (b) Wu, Q.; Esteghamatian, M.; Hu, N.-X.; Popovic, Z.; Enright, G.; Breeze, S. R.; Wang, S. *Angew. Chem., Int. Ed.* **1999**, *38*, 985.
- (25) (a) Liu, S. F.; Wu, Q.; Schmider, H. L.; Aziz, H.; Hu, N.-X.; Popović, Z.; Wang, S. *J. Am. Chem. Soc.* **2000**, *122*, 3671. (b) Liu, Q.-D.; Mudadu, M. S.; Schmider, H.; Thummel, R.; Tao, Y.; Wang, S. *Organometallics* **2002**, *21*, 4743. (c) Liu, Q.-D.; Mudadu, M. S.; Thummel, R.; Tao, Y.; Wang, S. *Adv. Funct. Mater.* **2005**, *15*, 143.
- (26) (a) Chen, H.-Y.; Chi, Y.; Liu, C.-S.; Yu, J.-K.; Cheng, Y.-M.; Chen, K.-S.; Chou, P.-T.; Peng, S.-M.; Lee, G.-H.; Carty, A. J.; Yeh, S.-J.; Chen, C.-T. *Adv. Funct. Mater.* **2005**, *15*, 567. (b) Cheng, C.-C.; Yu, W.-S.; Chou, P.-T.; Peng, S.-M.; Lee, G.-H.; Wu, P.-C.; Song, Y.-H.; Chi, Y. *Chem. Commun.* **2003**, 2628.
- (27) (a) Chen, T. R.; Chien, R.-H.; Jan, M.-S.; Yeh, A.; Chen, J.-D. *J. Organomet. Chem.* **2006**, *691*, 799. (b) Chen, T. R.; Chien, R.-H.; Yeh, A.; Chen, J.-D. *J. Organomet. Chem.* **2006**, *691*, 1998.
- (28) (a) Liddle, B. J.; Silva, R. M.; Morin, T. J.; Macedo, F. P.; Shukla, R.; Lindeman, S. V.; Gardinier, J. R. *J. Org. Chem.* **2007**, *72*, 5637. (b) Morin, T. J.; Linderman, S. V.; Gardinier, J. R. *Eur. J. Inorg. Chem.* **2009**, 104.
- (29) Nagata, Y.; Chujo, Y. *Macromolecules* **2008**, *41*, 3488.
- (30) (a) Wakamiya, A.; Taniguchi, T.; Yamaguchi, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 3170. (b) Job, A.; Wakamiya, A.; Kehr, G.; Erker, G.; Yamaguchi, S. *Org. Lett.* **2010**, *12*, 5470.
- (31) (a) Yoshino, J.; Kano, N.; Kawashima, T. *Chem. Commun.* **2007**, 559. (b) Yoshino, J.; Furuta, A.; Kambe, T.; Itoi, H.; Kano, N.; Kawashima, T.; Ito, Y.; Asashima, M. *Chem.—Eur. J.* **2010**, *16*, 5026. (c) Yoshino, J.; Kano, N.; Kawashima, T. *Chem. Lett.* **2008**, *37*, 960.
- (32) Yoshino, J.; Kano, N.; Kawashima, T. *J. Org. Chem.* **2009**, *74*, 7496.
- (33) García-Hernández, Z.; Gabbäi, F. P. *Z. Naturforsch.* **2009**, *64b*, 1381.
- (34) Fukazawa, A.; Yamada, H.; Yamaguchi, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 5582.
- (35) (a) Cogné-Laage, E.; Allemand, J.-F.; Ruel, O.; Baudin, J.-B.; Croquette, V.; Blanchard-Desce, M.; Jullien, L. *Chem.—Eur. J.* **2004**, *10*, 1445. (b) Ono, K.; Yoshikawa, K.; Tsuji, Y.; Yamaguchi, H.; Uozumi, R.; Tomura, M.; Tagaa, K.; Saito, K. *Tetrahedron* **2007**, *63*, 9354. (c) Nagai, A.; Kokado, K.; Nagata, Y.; Arita, M.; Chujo, Y. *J. Org. Chem.* **2008**, *73*, 8605. (d) Nagai, A.; Kokado, K.; Nagata, Y.; Chujo, Y. *Macromolecules* **2008**, *41*, 8295. (e) Poon, C. T.; Lam, W. H.; Wong, H. L.; Yam, V. W. W. *J. Am. Chem. Soc.* **2010**, *132*, 13992.
- (36) (a) Zhang, G.; Lu, J.; Sabat, M.; Fraser, C. L. *J. Am. Chem. Soc.* **2010**, *132*, 2160. (b) Zhang, G.; Evans, R. E.; Campbell, K. A.; Fraser, C. L. *Macromolecules* **2009**, *42*, 8627. (c) Zhang, G.; Palmer, G. M.; Dewhirst, M. W.; Fraser, C. L. *Nat. Mater.* **2009**, *8*, 747. (d) Zhang, G.; Lu, J.; Fraser, C. L. *Inorg. Chem.* **2010**, *49*, 10747.
- (37) (a) Maeda, H.; Mihashi, Y.; Haketa, Y. *Org. Lett.* **2008**, *10*, 3179. (b) Maeda, H.; Haketa, Y. *Pure Appl. Chem.* **2011**, *83*, 189.
- (38) (a) Tamai, N.; Miyasaka, H. *Chem. Rev.* **2000**, *100*, 1875. (b) Irie, M. *Chem. Rev.* **2000**, *100*, 1685.
- (39) (a) Berkovic, G.; Krongauz, V.; Weiss, V. *Chem. Rev.* **2000**, *100*, 1741. (b) Kobatake, S.; Irie, M. *Annu. Rep. Prog. Chem., Sect. C* **2003**, *99*, 277. (c) Crano, J. C.; Guglielmetti, R. J. *Organic Photochromic and Thermochromic Compounds*; Plenum Press: New York, 1999. (d) Ko, C.-C.; Yam, V. W. W. *J. Mater. Chem.* **2010**, *20*, 2063 and references cited therein. (e) Corns, S. N.; Partington, S. M.; Towns, A. D. *Color. Technol.* **2009**, *125*, 249. (f) Feringa, B. L. *Molecular Switches*; Wiley-VCH: Weinheim, Germany, 2001.
- (40) (a) Kano, N.; Yoshino, J.; Kawashima, T. *Org. Lett.* **2005**, *7*, 3909. (b) Yoshino, J.; Kano, N.; Kawashima, T. *Tetrahedron* **2008**, *64*, 7774.
- (41) Rao, Y. L.; Amarne, H.; Zhao, S. B.; McCormick, T. M.; Martić, S.; Sun, Y.; Wang, R. Y.; Wang, S. *J. Am. Chem. Soc.* **2008**, *130*, 12898.
- (42) Zimmerman, H. E.; Armesto, D. *Chem. Rev.* **1996**, *96*, 3065.
- (43) Rao, Y. L.; Amarne, H.; Wang, S., unpublished work.
- (44) (a) Wilkey, J. D.; Schuster, G. B. *J. Org. Chem.* **1987**, *52*, 2117. (b) Wilkey, J. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 7569.
- (45) Amarne, H.; Baik, C.; Murphy, S. K.; Wang, S. *Chem.—Eur. J.* **2010**, *16*, 4750.
- (46) Amarne, H.; Baik, C.; Wang, R.; Wang, S. *Organometallics* **2011**, *30*, 665.
- (47) For example, see: (a) Yamaguchi, S.; Xu, C. H.; Okamoto, T. *Pure Appl. Chem.* **2006**, *78*, 721. (b) Zhao, C. H.; Wakamiya, A.; Inukai, Y.; Yamaguchi, S. *J. Am. Chem. Soc.* **2006**, *128*, 15934. (c) Collings, J. C.; Poon, S. Y.; Le Droumaguet, C.; Charlot, M.; Katan, C.; Pålsson, L. O.; Beeby, A.; Msely, J. A.; Kaiser, H. M.; Kaufmann, D.; Wong, W. Y.; Blanchard-Desce, M.; Marder, T. B. *Chem.—Eur. J.* **2009**, *15*, 198. (d) Yuan, Z.; Collings, J. C.; Taylor, N. J.; Marder, T. B.; Jardin, C.; Halet, J.-F. *J. Solid State Chem.* **2000**, *154*, 5. (e) Chen, J.; Xie, Z.; Lam, J. W. Y.; Law, C. C. W.; Tang, B. Z. *Macromolecules* **2003**, *36*, 1108. (f) Matsumi, N.; Chujo, Y. *Polym. J.* **2008**, *40*, 77.
- (48) Baik, C.; Hudson, Z. M.; Amarne, H.; Wang, S. *J. Am. Chem. Soc.* **2009**, *131*, 14549.
- (49) (a) Baik, C.; Murphy, S. K.; Wang, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 8224. (b) Murphy, S. K.; Baik, C.; Lu, J. S.; Wang, S. *Org. Lett.* **2010**, *12*, 5266.
- (50) (a) Aubert, V.; Guerchais, V.; Ishow, E.; Hoang-Thi, K.; Ledoux, I.; Nakatani, K.; Le Bozec, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 577. (b) Areephong, J.; Logtenberg, H.; Browne, W. R.; Feringa, B. L. *Org. Lett.* **2010**, *12*, 2132. (c) Areephong, J.; Hurenkamp, J. H.; Milder, M. T. W.; Meetsma, A.; Herek, J. L.; Browne, W. R.; Feringa, B. L. *Org. Lett.* **2009**, *11*, 721. (d) Areephong, J.; Browne, W. R.; Feringa, B. L. *Org. Biomol. Chem.* **2007**, *5*, 1170.
- (51) Egawa, Y.; Gotoh, R.; Seki, T.; Anzai, J.-I. *Mater. Sci. Eng. C* **2009**, *29*, 115.
- (52) (a) Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Lee, H.-E.; Adachi, C.; Burrows, P. E.; Forrest, S. R.; Thompson, M. E. *J. Am. Chem. Soc.* **2001**, *123*, 4304. (b) Thompson, M. E. *MRS Bull.* **2007**, *32*, 694 and references cited therein. (c) Chen, K.; Yang, C. H.; Chi, Y.; Liu, C. S.; Chang, C. H.; Chen, C. C.; Wu, C. C.; Chung, M. W.; Cheng, Y. M.; Lee, G. H.; Chou, P. T. *Chem.—Eur. J.* **2010**, *16*, 4315. (d) You, Y.; Park, S. Y. *Dalton Trans.* **2009**, 1267 and references cited therein.
- (53) (a) Wade, C. R.; Broomsgrove, A. E. J.; Aldridge, S.; Gabbäi, F. P. *Chem. Rev.* **2010**, *110*, 3958 and references cited therein. (b) Hudnall, T. W.; Chiu, C. W.; Gabbäi, F. P. *Acc. Chem. Res.* **2009**, *42*, 388.