Enhancing the Photochemical Stability of *N,C*-Chelate Boryl Compounds: C—C Bond Formation versus C=C Bond *cis,trans*-Isomerization

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Abstract: *N,C*-Chelate boron compounds such as B(ppy)Mes$_2$ (ppy = 2-phenylpyridyl, Mes = mesityl) have been recently shown to undergo a facile and reversible C—C/C—B bond rearrangement upon irradiation with UV-light, quenching the emission of the sample and limiting their use in optoelectronic devices. To address this problem, four molecules have been synthesized in which the π-conjugation is extended using either vinyl or acetylene linkers. These compounds, (ph-C≡C-ppy)BMes$_2$ (**B1A**), (ph-CH=CH-ppy)BMes$_2$ (**B1**), [*p*-bis(ppy-CH=CH)benzene](BMes$_2$)$_2$ (**B2**), and [1,3,5-tris(ppy-CH=CH)benzene](BMes$_2$)$_3$ (**B3**) have been fully characterized by NMR and single-crystal X-ray diffraction analyses. All four compounds are light yellow and emit blue or blue-green light upon UV irradiation. The acetylene compound **B1A** has been found to exhibit photochemical instability the same as that of the parent chromophore B(ppy)Mes$_2$. In contrast, all of the olefin-substituted compounds are photochemically stable, instead undergoing *cis*−*trans* isomerization exclusively upon exposure to UV light. Experimental and TD-DFT computational results establish that the presence of the olefinic bond in **B1**−**B3** provides an alternate energy dissipation pathway for the B(ppy)Mes$_2$ chromophore, stabilizing the molecule toward photochromic switching *via cis*−*trans* isomerization. Furthermore, the incorporation of a *cis*−*trans* isomerization pathway may prove to be a useful strategy for the stabilization of photochemically unstable chromophores in other π-systems as well.

Introduction

Conjugated organic materials are a key component of a wide variety of optoelectonic devices. For applications in organic light-emitting diodes (OLEDs),[1] organic photovoltaics (OPVs),[2] and organic thin film transistors (OTFTs),[3] it is necessary to develop conjugated molecules with either electron-transporting or hole-transporting properties. For this reason, conjugated boron-containing compounds have attracted much recent attention, due to their highly emissive nature and excellent electron transport functionality. In the case of conjugated three-coordinate triarylboron compounds, this electron-transporting ability can largely be attributed to the empty p$_\pi$ orbital on the boron center, which stabilizes the formation of radical anions *via* conjugation with the π-orbitals of the attached aryl groups.[4,5] For four-coordinate arylboron compounds, however, the π-conjugated backbone is responsible for electron transport. In this case, boron chelation acts to enhance the π-conjugation of the system, thereby enhancing its electron-accepting ability. This phe-

nomenon has been demonstrated by a number of research groups on several classes of four-coordinate boron chelate chromophores, including *N,O*-,[6a−f] *N,N*-[6g−j] and *N,C*-chelate[6k] π-systems.

Despite their potential usefulness in optoelectronic materials, examples of conjugated *N,C*-chelate boryl compounds remain rare. Previously known *N,C*-chelate ligands used for this purpose are based on either thienylthiazole[6k] or 2-phenylpyridine (ppy),[7] which readily form highly emissive tetrahedral boron compounds with BMes$_2$ (Mes = mesityl). These *N,C*-chelate boron compounds are of particular interest because they are isoelectronic with the well-known fluorene

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Scheme 1

X = H, **A1**; BMes$_2$, **A2**   X = H, **A1'**; BMes$_2$, **A2'**
Scheme 1
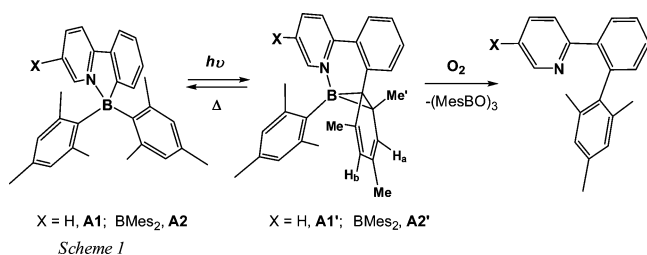
chromophore, which is widely used in organic materials due to its rich photophysical and electronic properties.[8]

However, our group has shown that B(ppy)Mes$_2$ and its derivatives are highly sensitive to light.[7] Exposure to ambient or ultraviolet light under an N$_2$ atmosphere causes these compounds to undergo a rapid structural and color change both in solution and the solid state, with the reversible formation and breaking of carbon—carbon bonds. Although this photochromic behavior is unusual and may find applications in optical switching, the products of this transformation are unstable toward oxygen. On exposure to light under air, the newly formed C—C-bonded species reacts rapidly with O$_2$, eliminating the boron moiety from the chelate site (Scheme 1). Hence, before these highly luminescent materials can be successfully incorporated into devices such as OLEDs, the photostability of the *N,C*-chelate boryl chromophore must be addressed. Furthermore, it is necessary to understand the various factors that influence the photochemical stability and photochromic switching behavior of the *N,C*-chelate boryl system as a point of fundamental research.

As part of our continuing efforts to understand and exploit the unique properties of *N,C*-chelate boryl systems, we have expanded our investigation to conjugated polyboryl systems containing several B(ppy)Mes$_2$ units and olefinic bonds. Using olefinic bonds to build extended π-conjugated systems and influence their optoelectronic properties has been demonstrated extensively.[9] In this case, however, we have found that the olefinic bonds impart remarkable photochemical stability to an otherwise unstable system, preventing these mono- and polyboryl compounds from undergoing photo-

chemical rearrangement under nitrogen or air. Furthermore, we have found that *cis—trans* photoisomerization plays a key role in this stabilization effect. The *cis—trans* isomerization of olefins is essential for many photochemical processes, such as vision (vitamin A)[10a−c] and the absorption of UV radiation in natural and synthetic sunscreens.[10d] It has also been exploited in conjugated organic and organometallic systems as a means for switching and controlling electronic communication, luminescence and molecular motion.[10e−g] Our findings on the stabilization of the photochromic B(ppy)Mes$_2$ chromophore *via* π-conjugated olefinic bonds adds a new dimension to the utility of the olefin *cis—trans* isomerization phenomenon. For comparison, we have also studied the impact of conjugation of the B(ppy)Mes$_2$ chromophore with a phenylacetylene substituent. The details of our investigations are presented herein.

Experimental Section

General Procedure. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk technique unless otherwise noted. THF, diethylether, and DMF were purified using the solvent purification system (Innovation Technology, Inc.). The ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 300, 400, or 500 MHz spectrometers. UV—vis spectra were recorded on an Ocean Optics UV—visible spectrometer. Excitation and emission spectra were recorded on a Photon Technologies International Quanta Master model C-60 spectrometer. High-resolution mass spectra (HRMS) were obtained from a Waters/Micromass GC-TOF EI-MS spectrometer. Elemental analyses were performed at the Canadian Microanalytical Service Ltd. Cyclic voltammetry was performed using a BAS CV-50W analyzer with a scan rate of 200 mV/s and a typical concentration of 5 mg of the compound in 3.0 mL of DMF using 0.10 M NBu$_4$PF$_6$ (TBAP) as the supporting electrolyte and a Ag/AgCl reference electrode. The ferrocenium/ferrocene couple was used as the internal standard (E_o = 0.56 V). 6-Bromo-3-pyridinecarboxaldehyde,[11] 1,4-bis(diethoxyphosphorylmethyl)benzene, 1,3,5-tris(diethoxyphosphoryl methyl)benzene,[12] 2-bromo-5-iodopyridine,[13] and B(ppy)Mes$_2$[7] were prepared by previously published methods in the literature. The synthetic details for the intermediates **1**, **3**, **5**, **6** and **8** are provided in the Supporting Information.

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Synthesis of (Ph-CH=CH-ppy)BMes₂ (B1). 1,4-bis((E)-2-(6-bromopyridin-3-yl)vinyl)benzene (2). A mixture of compound **1** (0.80 g, 3.05 mmol) and diethyl benzylphosphonate (0.70 g, 3.05 mmol) in THF (15 mL) was slowly added to a THF solution of potassium *tert*-butoxide (0.40 g, 3.66 mmol). The solution was stirred overnight, and the THF evaporated *in vacuo*. After the addition of water, the mixture was extracted with diethyl ether. The crude product was then purified by column chromatography (ethyl acetate:hexanes = 1:4) to afford compound **2** in 85% yield (0.87 g). ¹H NMR (δ, ppm CD₂Cl₂): 8.32 (d, J = 2.0 Hz, 1H), 7.97 (dd, J = 8.0 Hz, J = 2.0 Hz, 1H), 7.72 (dd, J = 8.0 Hz, J = 1.2 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.60 (m, 3H), 7.44 (m, 3 H), 7.32 (m, 2H), 7.30 (d, J = 16.4 Hz, 1H), 7.20 (d, J = 16.4 Hz, 1H); ¹³C{¹H} NMR (δ, ppm, CD₂Cl₂): 157.3, 148.5, 141.4, 137.1, 133.7, 132.7, 132.1, 131.9, 131.2, 130.0, 129.1, 128.6, 127.9, 127.1, 124.9, 124.8, 122.0. HRMS calcd for C₁₉H₁₄BrN: *m/z* 335.0310; found: 335.0311.

***trans*-B1.** To a stirred THF solution of compound **2** (0.52 g, 1.54 mmol) was added dropwise an *n*-BuLi solution (1.60 M in hexanes, 1.16 mL, 1.85 mmol) at −78 °C. The resulting solution was left to stir for 1 h at −78 °C, and BMes₂F (0.80 g, 3.06 mmol) in Et₂O was added. The reaction mixture was slowly warmed up to room temperature and stirred overnight. After the addition of water, the solution was then extracted with dichloromethane. The crude product was then purified by column chromatography (CH₂Cl₂/hexanes = 1:3) to afford *trans*-**B1** in 81% yield (0.63 g). ¹H NMR (δ, ppm, CD₂Cl₂): 8.64 (d, J = 1.8 Hz, 1H), 8.25 (dd, J = 8.7 Hz, J = 1.8 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.92 (dd, J = 6.0 Hz, J = 2.1 Hz, 1H), 7.76 (dd, J = 6.3 Hz, J = 2.1 Hz, 1H), 7.55 (d, J = 7.2 Hz, 2H), 7.37 (m, 5H), 7.18 (d, J = 16.2 Hz, 1H), 7.03 (d, J = 16.2 Hz, 1H), 6.67 (s, 4H), 2.19 (s, 6H), 1.83 (s, 12H); ¹³C{¹H} NMR (δ, ppm, CD₂Cl₂): 158.4, 145.0, 140.5, 137.6, 136.8, 135.6, 134.5, 132.7, 132.5, 131.5, 131.4, 130.5, 129.5, 129.4, 127.5, 125.9, 123.7, 122.4, 118.5, 25.4, 21.0. Anal. Calcd for C₃₇H₃₆BN: C 87.91; H 7.18; N 2.77. Found: C 86.92; H 6.81; N 2.64.

***cis*-B1.** The solution of 0.10 g of *trans*-**B1** in benzene (20 mL) was irradiated at 365 nm for 3 h under N₂. The solvent was removed under vacuum. *Cis*-**B1** was isolated as a pale yellow oil in 43% yield by preparative-scale TLC (CH₂Cl₂:hexanes = 1:3). ¹H NMR (δ, ppm, CD₂Cl₂): 8.47 (s, 1H), 7.87 (m, 3H), 7.71 (d, J = 7.0 Hz, 1H), 7.30 (m, 2H), 7.24 (m, 5H), 6.84 (d, J = 12.0 Hz, 1H), 6.61 (s, 4H), 6.48 (d, J = 12 Hz, 1H), 2.16 (s, 6H), 1.70 (s, 12H). ¹³C {¹H} NMR (δ, ppm, CD₂Cl₂): 157.7, 146.4, 141.2, 136.1, 135.2, 134.4, 134.0, 131.9, 131.1, 131.0, 130.1, 129.2, 128.8, 128.3, 125.6, 124.9, 122.0, 117.7, 25.0, 20.8.

Synthesis of (ph-C≡C-ppy)BMes₂ (B1A). 2-(2-Bromophenyl)-5-(phenylethynyl)pyridine (4). A mixture of compound **3** (0.70 g, 2.71 mmol), 2-bromophenyl boronic acid (0.54 g, 2.71 mmol), and Pd(PPh₃)₄ (0.15 g, 0.14 mmol) was added to the solution mixture of degassed THF (40 mL) and degassed aqueous 1 M KOH (20 mL). The mixture was refluxed overnight and the THF evaporated *in vacuo*. After the addition of water, the mixture was extracted with diethyl ether. The crude product was then purified by column chromatography (CH₂Cl₂/hexanes = 1:5) to afford compound **4** in 79% yield (0.72 g). ¹H NMR (δ, ppm, CDCl₃): 8.87 (s, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.59 (m, 3H), 7.44 (m, 4H), 7.28 (m, 1H). ¹³C{¹H} NMR (δ, ppm, CD₂Cl₂): 157.3, 152.2, 140.9, 138.5, 135.4, 133.7, 132.1, 131.8, 130.3, 130.1, 129.2, 128.8, 127.9, 124.4, 122.9, 122.0, 119.5, 93.5, 86.4. HRMS calcd for C₁₉H₁₂BrN: *m/z* 333.0153; found: 333.0160.

B1A. To a stirred THF solution of compound **4** (0.34 g, 1.00 mmol) was added dropwise an *n*-BuLi solution (1.6 M in Hx, 0.69 mL, 1.10 mmol) at −78 °C. The resulting solution was left to stir for 1 h at −78 °C. Then a solution of dimesitylboron fluoride (0.32 g, 1.20 mmol) in Et₂O was added. The solution was slowly warmed to room temperature and stirred overnight. The solvent was evaporated *in vacuo,* and after the addition of water, the mixture was extracted with dichloromethane. The

crude product was then purified by column chromatography (CH₂Cl₂/hexanes = 1:3) to afford compound **B1A** in 46% yield (0.23 g). ¹H NMR (δ, ppm, CD₂Cl₂): 8.70 (s, 1H), 8.14 (d, J = 7.0 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 7.0 Hz, 1H), 7.57 (m, 2H), 7.42 (m, 3H), 7.35 (m, 4H), 6.68 (s, 4H), 2.20 (s, 6H), 1.82 (s, 12H); ¹³C{¹H} NMR (δ, ppm, CD₂Cl₂): 158.4, 148.6, 143.3, 140.2, 134.8, 134.3, 132.0, 131.6, 131.1, 130.2, 129.6, 128.9, 125.8, 122.4, 122.1, 118.6, 117.9, 94.4, 84.6, 25.1, 20.7. Anal. Calcd for C₄₃H₄₈BN: C 87.59; H 8.20; N 2.38. Found: C 86.99; H 7.62; N 2.60.

B1A′. The compound was prepared by following the general procedures for NMR monitoring of the photolysis process. ¹H NMR (δ, ppm, C₆D₆): 9.17 (s, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.0 Hz, 1H), 7.25 (m, 3H), 7.22 (d, J = 8.0 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 7.05 (s, 1H), 6.99 (m, 3H), 6.86 (s, 1H), 6.01 (s, 1H), 5.53 (s, 1H), 2.98 (s, 3H), 2.25 (s, 3H), 2.20 (s, 3H), 2.05 (s, 3H), 1.81 (s, 3H), 0.61 (s, 3H).

Synthesis of [p-bis(ppy-CH=CH)benzene](BMes₂)₂ (B2). Compound 7. To a solution of THF (30 mL) and water (10 mL) was added compound **6** (1.67 g, 3.22 mmol) and trifluoroacetic acid (30 mL). The resulting reaction mixture was refluxed overnight. The reaction was quenched with saturated aqueous Na₂CO₃ and extracted with diethylether. The combined organic layers were then dried (MgSO₄), filtered, and evaporated in vacuo to yield compound **7** as a yellow solid, which was further purified by column chromatography (CH₂Cl₂/hexanes = 1:1) (0.56 g, 40%). ¹H NMR (δ, ppm, CD₂Cl₂): 9.97 (s, 1H), 9.01 (s, 1H), 8.47 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 6.67 (s, 4H), 2.18 (s, 6H), 1.80 (s, 12H). ¹³C{¹H} NMR (δ, ppm, CD₂Cl₂): 188.5, 163.7, 149.6, 140.5, 140.2, 137.1, 134.8, 134.6, 133.1, 131.7, 130.7, 130.6, 126.5, 123.8, 119.1, 112.5, 25.5, 21.1. HRMS calcd for C₃₀H₃₀BNO: *m/z* 431.2420; found: 431.2426.

***trans,trans*-B2.** A mixture of 1,4-bis(diethoxyphosphorylmethyl)benzene (0.13 g, 0.35 mmol) and compound **7** (0.30 g, 0.70 mmol) in THF (40 mL) was slowly added to a THF solution of potassium *tert*-butoxide (0.10 g, 0.89 mmol). The solution was stirred overnight and the THF was then evaporated *in vacuo*. After addition of water, the residue was extracted with dichloromethane. The crude product was then purified by column chromatography (CH₂Cl₂:hexanes = 1:1) to afford compound **B2** in 73% yield (0.24 g). ¹H NMR (δ, ppm, CD₂Cl₂): 8.66 (d, J = 1.5 Hz, 2H), 8.25 (dd, J = 1.5 Hz, 8.5 Hz, 2H), 8.05 (d, J = 8.5 Hz, 2H), 7.92 (d, J = 7.0 Hz, 2H), 7.62 (d, J = 7 Hz, 2H), 7.56 (s, 4H), 7.34 (m, 4H), 7.17 (d, J = 16.0 Hz, 2H), 7.06 (d, J = 16.0 Hz, 2H), 6.68 (s, 8H), 2.20 (s, 12H), 1.85 (s, 24H); ¹³C {¹H} NMR (δ, ppm, CD₂Cl₂): 158.1, 145.8, 144.9, 138.3, 137.3, 136.8, 135.2, 134.2, 132.2, 131.6, 131.2, 131.1, 130.2, 127.7, 125.7, 124.7, 123.9, 122.1, 118.3, 25.1, 20.8. Anal. Calcd. for C₆₈H₆₆B₂N₂·CH₂Cl₂: C 81.42; H 6.73; N 2.75. Found: C 80.3; H 6.62; N 2.72.

trans, cis-B2. Two mg of all *trans*-**B2** was photolyzed in a NMR tube (C₆D₆, 365 nm) at ambient temperature, which led to the formation of the *trans,cis*-**B2** compound (∼10% conversion). ¹H NMR (δ, ppm, C₆D₆): 8.90 (s, 1H), 8.81 (s, 1H), 8.20 (d, J = 7.5 Hz, 1H), 8.13 (d, J = 7.5 Hz, 1H), 7.69 (d, J = 7.5 Hz, 1H), 7.60 (d, J = 7.5 Hz, 1H), 7.33−7.16 (m, 8H), 7.06 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 6.94 (s, 4H), 6.89 (s, 4H), 6.75 (d, J = 16.0 Hz, 1H), 6.53 (d, J = 16.0 Hz, 1H), 6.39 (d, J = 12.0 Hz, 1H), 5.86 (d, J = 12.0 Hz, 1H), 2.31 (s, 6H), 2.26 (s, 12H), 2.22 (s, 6H), 2.13 (s, 12H). ¹³C was not assigned for this isomer due to the low conversion.

Synthesis of [1,3,5-Tris(Ppy-CH=CH)benzene](BMes₂)₃ (B3). 1,3,5-Tris((E)-2-(6-(2-bromophenyl)pyridin-3-yl)vinyl)benzene (9). A mixture of compound **8** (0.36 g, 0.58 mmol), 2-bromophenyl boronic acid (0.35 g, 1.74 mmol), and Pd(PPh₃)₄ (87 mg, 0.072 mmol) were added to a degassed solution of THF (100 mL) and aqueous 1 M KOH (50 mL). The mixture was refluxed overnight,

and the solvent was then evaporated *in vacuo*. After the addition of water the residue was extracted with dichloromethane. The crude product was purified by column chromatography (CH_2Cl_2: ethyl acetate = 40:1) to afford compound **9** in 38% yield (0.18 g). ^{1}H NMR (δ, ppm, CD_2Cl_2): 8.87 (d, J = 1.5 Hz, 3H), 8.00 (dd, J = 8.0 Hz, 1.5 Hz, 3H), 7.73 (s, 3H), 7.70 (d, J = 8.5 Hz, 3H), 7.67 (d, J = 8.0 Hz, 3H), 7.60 (dd, J = 7.5 Hz, 1.5 Hz, 3H), 7.44 (t, J = 7.5 Hz, 3H), 7.34−7.30 (m, 9H). ^{13}C {^{1}H} NMR (δ, ppm, CD_2Cl_2): 149.0, 143.5, 142.2, 141.1, 137.9, 135.5, 132.5, 130.9, 128.3, 126.6, 125.1, 125.0, 124.8, 123.9, 118.8. HRMS calcd. for $C_{45}H_{30}Br_3N_3$: *m/z* 850.0062; found: 850.0061.

***trans,trans,trans*-B3.** To a stirred THF solution of compound **9** (0.19 g, 0.23 mmol) was added dropwise an *n*-BuLi solution (1.6 M in hexanes, 0.50 mL, 0.80 mmol) at −78 °C. After the mixture was stirred for 1 h at −78 °C, a solution of $BMes_2F$ (0.24 g, 0.88 mmol) in Et_2O was added. The solution was slowly warmed to room temperature and stirred overnight. The solvent was then removed *in vacuo*, and after the addition of water, the mixture was extracted with dichloromethane. The crude product was purified by column chromatography (CH_2Cl_2/hexanes = 1:1) to afford **B3** in 28% yield (0.084 g). ^{1}H NMR (δ, ppm, CD_2Cl_2): 8.64 (d, J = 1.6 Hz, 3H), 8.25 (dd, J = 8.4 Hz, 1.6 Hz, 3H), 8.04 (d, J = 8.4 Hz, 3H), 7.90 (d, J = 6.8 Hz, 3H), 7.74 (d, J = 6.4 Hz, 3H), 7.59 (s, 3H), 7.31 (m, 6H), 7.18 (d, J = 16.4 Hz, 3H), 7.10 (d, J = 16.4 Hz, 3H), 6.66 (s, 12H), 2.21 (s, 18H), 1.86 (s, 36H). ^{13}C{^{1}H} NMR (δ, ppm, CD_2Cl_2): 158.5, 145.8, 145.1, 140.2, 137.7, 137.2, 135.1, 134.2, 131.7, 131.3, 131.1, 131.0, 130.2, 125.7, 125.6, 125.4, 124.7, 122.2, 122.1, 118.3, 25.1, 20.8, 20.7. Anal. Calcd for $C_{99}H_{96}B_3N_3$: C 87.41; H 7.11; N 3.09. Found: C 85.93; H 7.48; N 2.93.

***trans,trans,cis*-B3.** This compound was generated *in situ* by photolysis of the all *trans*-**B3** with ∼50% conversion following the general procedures for NMR monitoring of the photolysis process. ^{1}H NMR (δ, ppm, C_6D_6): 8.94 (s, 2H), 8.71 (s, 1H), 8.19 (d, J = 7.5 Hz, 2H), 8.06 (d, J = 7.5 Hz, 1H), 7.70 (d, J = 7.5 Hz, 2H), 7.58 (d, J = 7.5 Hz, 1H), 7.45 (m, 2H), 7.43 (m, 3H), 7.39−7.17 (m, 6H), 7.11 (s, 2H), 7.02 (s, 2H), 6.92 (s, 8H), 6.77 (d, J = 16.5 Hz, 2H), 6.76 (m, 4H), 6.57 (d, J = 16.5 Hz, 2H), 6.45 (d, J = 12.0 Hz, 1H), 5.96 (d, J = 12.0 Hz, 1H), 2.27 (s, 12H), 2.25 (s, 24H), 2.21 (s, 6H), 2.03 (s, 12H).

Fluorescent Quantum Yield Measurements. The solution photoluminescent quantum yields were measured in dilute toluene solution ($A \approx 0.10$) using the optically dilute method relatively to 9−10-diphenylanthracene at room temperature (Φ_r = 0.90). The quantum yields were calculated using previously reported procedures.[14] Solid-state quantum yields were measured at ambient temperature using a commercial fluorimeter in combination with an integration sphere according to literature procedures.[14b−e]

Photoisomerization Quantum Yield Measurements. The quantum yields of the photoisomerization of **A1** and **B1A** to **A1′** and **B1A′** were determined using ferrioxalate actinometry.[15] An Ocean Optics fiber-optic spectromphotometer connected to a four-way temperature-controlled cuvette holder from Quantum Northwest via 400 μm optical fibers was used to measure the absorbance. The irradiation source was a 200 W Hg/Xe lamp attached to a monochromator (Photon Technology International).

General Procedures for NMR Monitoring of the Photolysis Process. The photoisomerization was carried out by preparing a C_6D_6 (dried over NaH) solution (∼0.01 M) in a NMR tube inside an inert atmosphere drybox. The solution was placed under UV (365 nm) at room temperature, and the exposure time was recorded. After each exposure period, the NMR spectrum was recorded.

General Procedure for Uv−Vis Monitoring of the Photolysis Process. A 10^{-5} M solution in freshly distilled toluene was prepared and placed in a screw-cap quartz cuvette. The solution was placed under UV (365 nm) at room temperature and the exposure time was recorded. After each exposure period, the UV−vis spectrum was recorded.

TD-DFT Molecular Orbital Calculations. The geometries of compounds **B1A** and **B1−B3** were optimized using DFT at the B3LYP level of theory[16] with 6-311G* as the basis set,[17] and these results were then used for TD-DFT calculations modeling singlet transitions only.[18] Geometric parameters from crystal structures were used as starting points for the geometry optimizations where possible, and all other starting points were constructed using the *Gaussview* software package. Calculations were carried out using Gaussian 03,[19] and were performed using 16 processors on Sunfire 25000 systems using UltraSPARC-IV+ processors.

X-ray diffraction analysis. Single crystals of the monoboryl and polyboryl compounds were obtained from CH_2Cl_2/hexanes solution. Data were collected on a Bruker AXS Apex II single-crystal X-ray diffractometer with graphite-monochromated Mo Kα radiation, operating at 50 kV and 30 mA at 180 K. Data were processed on a PC with the aid of the Bruker SHELXTL software package (version 5.10)[20] and corrected for absorption effects. All structures were solved by direct methods. The crystal lattice of **B2** contains two CH_2Cl_2 solvent molecules per molecule of **2** which were modeled and refined successfully. The crystal lattice of **B1** contains disordered hexane molecules that could not be fully modeled and were removed with the Platon SQUEEZE program. Compound **B1A** cocrystallizes with 0.5 hexane per molecule, which was successfully modeled and refined. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated, and their contributions in structural factor calculations were included. The crystal data of the compounds are given in Table S1, Supporting Information. Important bond lengths and angles for all compounds are listed in Table S2, Supporting Information. The complete crystal data are provided in the Supporting Information.

Results and Discussion

Syntheses. To compare the impact of an olefinic bond with that of a C≡C bond on the photochemical stability of the B(ppy)Mes$_2$ chromophore, compounds **B1** and **B1A** were synthesized according to Scheme 2. For **B1**, Suzuki−Miyaura coupling of 2-bromopyridyl-5-aldehyde with *o*-bromophenylboronic acid produced **1**, which was coupled to diethyl benzylphosphonate *via* the Horner−Wadsworth−Emmons reaction[21] to produce **2**. Lithiation of **2** and its subsequent reaction with BMes$_2$F produced **B1** in 81% yield. For **B1A**, 2-bromo-5-iodo-pyridine was coupled to phenylacetylene *via*

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Scheme 2
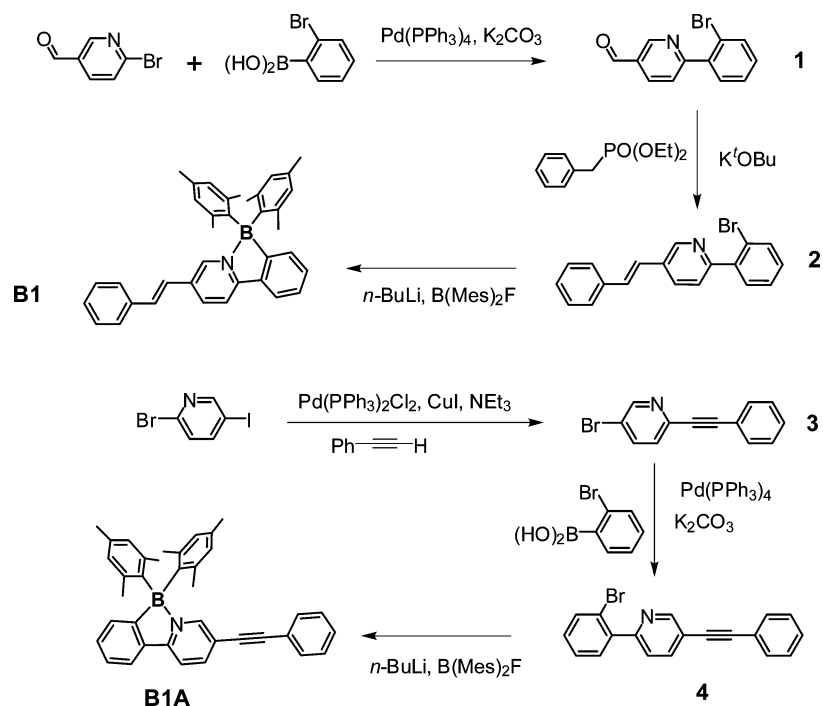
Scheme 3
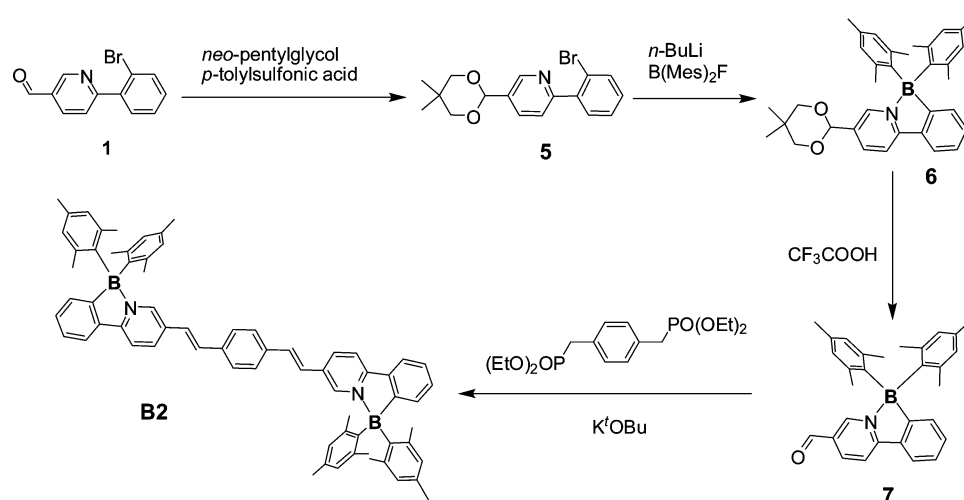
Pd-catalyzed Sonogashira coupling[22] to produce compound **3**, which was then coupled to *o*-bromophenylboronic acid *via* Suzuki−Miyaura coupling[23] to produce compound **4**. Lithiation of **4**, followed by the addition of BMes₂F, produced **B1A** in 46% yield.

To examine the impact of π-conjugated olefinic bonds on the photochemical stability of related polyboryl compounds, a diboryl molecule, **B2**, and a triboryl molecule, **B3**, were synthesized as shown in Schemes 3 and 4, respectively. In the synthesis of **B2**, the starting material **1** was first protected by a *neo*-pentylglycol group and the protected molecule was reacted with *n*-BuLi, followed by the addition of BMes₂F to produce the monoboryl **6**. Deprotection of **6** produced **7**,

which was reacted with a bisphosphonate compound *via* a Horner−Wadsworth−Emmons reaction to produce **B2** in 73% yield. In the synthesis of **B3**, the starting material **8** was obtained first by Horner−Wadsworth−Emmons reaction of **1** with a triphosphonate molecule containing a 1,3,5-trisubstituted benzene core, followed by its coupling to *o*-bromophenylboronic acid by Suzuki−Miyaura coupling to produce **9**. The reaction of **9** with *n*-BuLi, followed by addition of BMes₂F, produced **B3** in 28% yield. All compounds were fully characterized by NMR, HRMS/elemental analyses and single-crystal X-ray diffraction. For **B1**−**B3**, the major product in all cases were found to contain only *trans*-double bonds with only trace amounts of other isomers, which could be readily separated by column chromatography.

Crystal Structures. The structures of **B1A** and the *trans* isomers of **B1**−**B3** determined by single-crystal X-ray diffraction are shown in Figures 1, 2, and 3, respectively. The structure

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Scheme 4
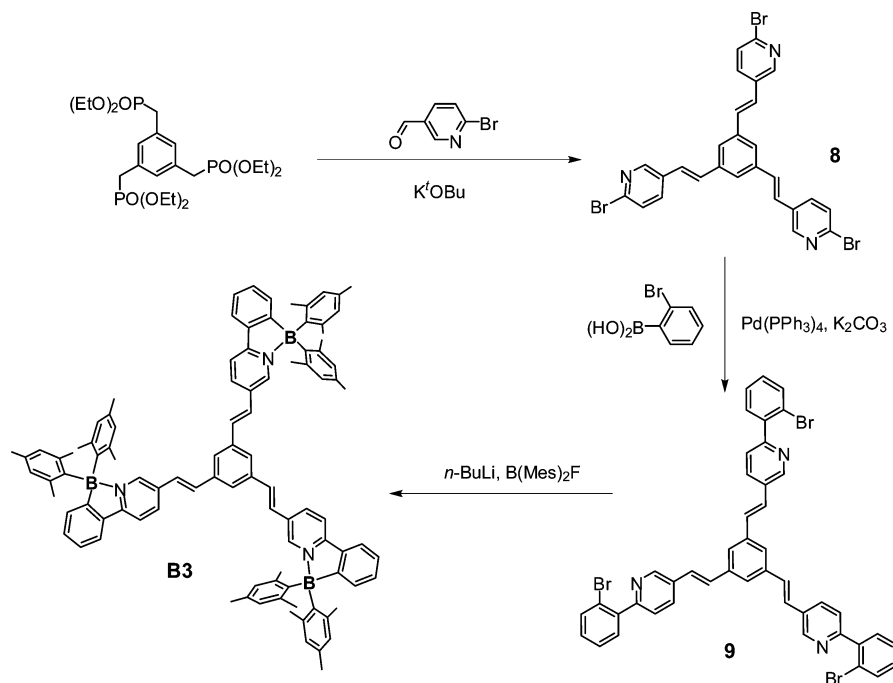
of **B2** possesses a crystallographically imposed inversion center while the structure of **B3** has approximate C_3 symmetry. The average B−C (mesityl) bond length in compounds **B1A**, **B1, B2**, and **B3** is 1.646(5) Å, which agrees well with that of B(ppy)Mes$_2$.[7] The −C≡C− bond length in **B1A** and the −CH=CH− bond lengths in **B1**−**B3** are typical, and the vinylene−phenyl moieties in **B1**−**B3** are approximately planar.

The vinylene−phenyl moiety does show some distortion from planarity with the ppy chelate, however, with dihedral angles of 29.6° (**B1**); 27.8° (**B2**); and 9.4°, 6.1°, and 30.5° (**B3**). The separation distances between the boron centers are 17.78 Å in **B2**, and 14.12, 14.99, 15.75 Å in **B3**, respectively. In the crystal lattices of **B2** and **B3**, all molecules stack along one direction such that the central conjugated cores are approximately parallel.
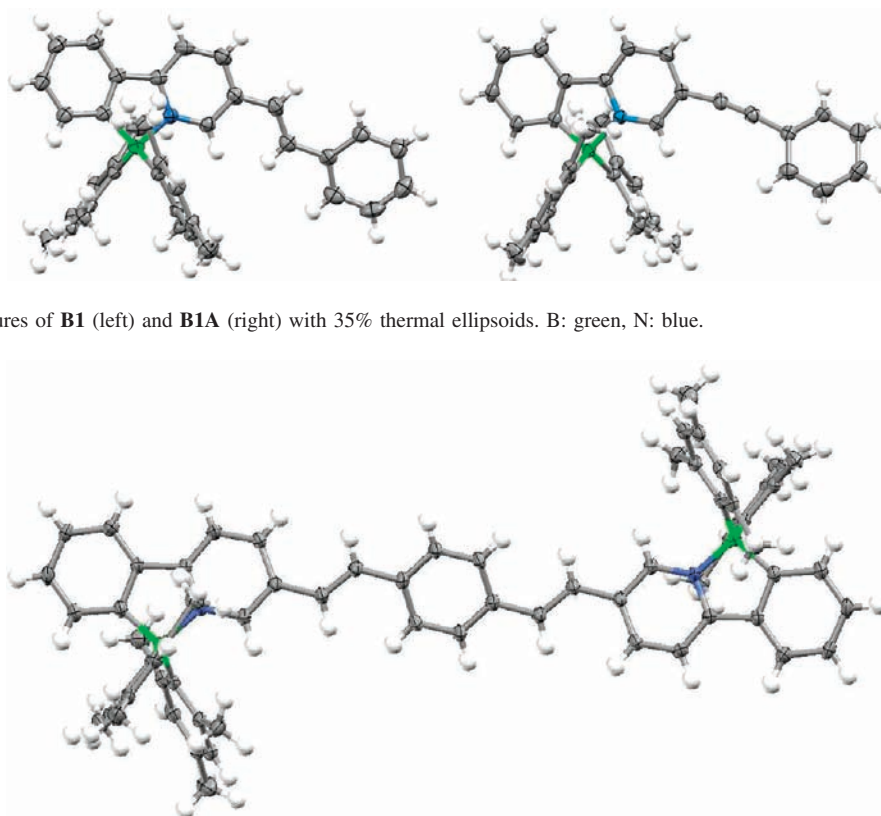
Figure 1. Crystal structures of **B1** (left) and **B1A** (right) with 35% thermal ellipsoids. B: green, N: blue.

Figure 2. Crystal structure of **B2** with 35% thermal ellipsoids. B: green, N: blue.
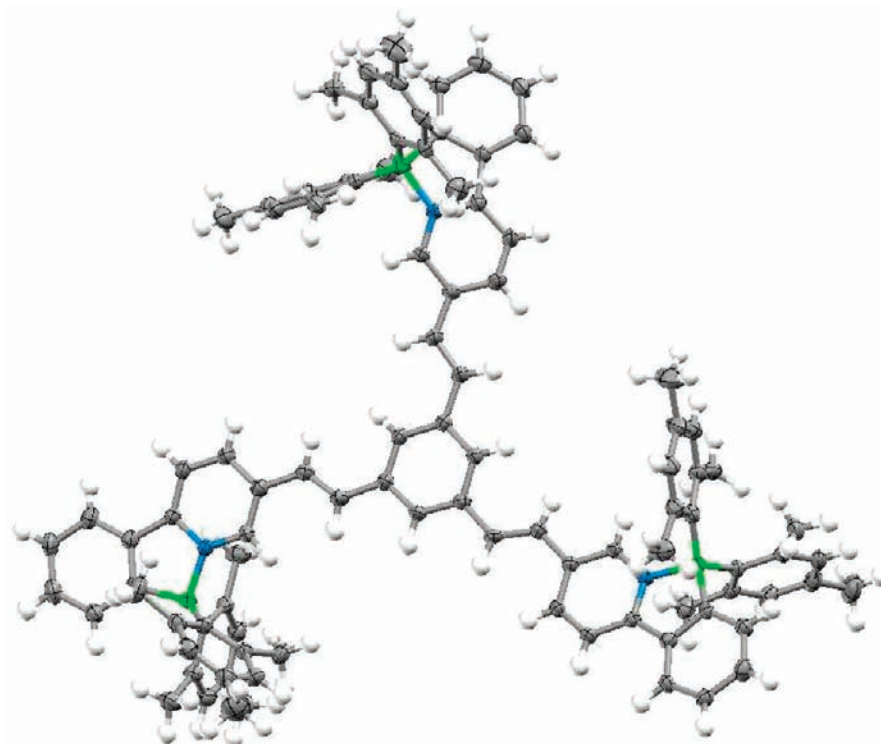
Figure 3. Crystal structure of **B3** with 35% thermal ellipsoids. B: green, N: blue.
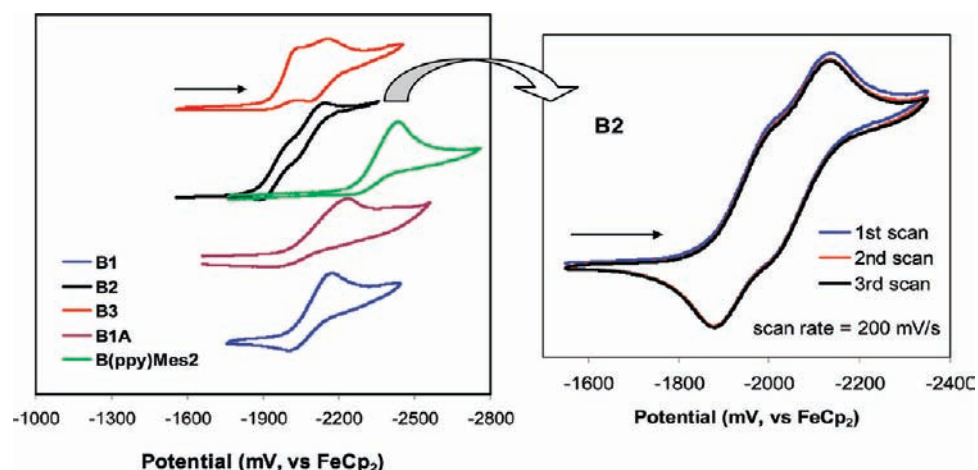

Figure 4. (Left) CV diagrams of the boryl and polyboryl compounds recorded in DMF with scan rates of 100−500 mV/s. (Right) CV diagrams of **B2** showing three continuous scans at 200 mV/s.

Electronic and Photophysical Properties. All four compounds display reversible or quasi-reversible reduction peaks in their CV diagrams as shown in Figure 4, with reduction potentials 0.35−0.40 V more positive than those of B(p-py)Mes$_2$. The diboryl **B2** displays two partially resolved and fully reversible reduction peaks in the CV diagram, indicative of a weak electronic communication that enhances the electron-accepting ability of the molecule by ∼0.15 V. Two partially resolved reduction peaks were also observed for **B3**, but with a poor reversibility, suggesting that the *para*-geometry of **B2** is most effective in stabilizing radical anions and promoting electronic communication *via* π-conjugation, compared to the *meta*-geometry. The similar reduction potentials of **B1A** and **B1** indicate that the C=C and C≡C linkages have a similar impact on the LUMO level of the chromophore.

The UV−vis absorption spectra (Figure 5) show that the optical energy gap follows the order of **B2** < **B3** < **B1** ≈ **B1A** < B(ppy)Mes$_2$, consistent with the extent of π-conjugation in these molecules and further supporting the effectiveness of π-conjugation of the *para*-geometry in **B2**. All compounds emit in the blue-green region, with substantial overlap in their absorption spectra as well. The emission energies of these molecules follow a trend similar to that of the absorption energies (Figure 6), although **B2** has both the highest emission energy ($\lambda_{max} = 456$ nm) and the smallest Stokes' shift. The emission spectrum of **B2** displays the same well-resolved vibronic features as that of the dibromo ligand **11** ($\lambda_{max} = 417$ nm), indicating that the emission in this molecule is primarily a π→π* transition localized on the π-backbone (see ESI). The featureless broad emission bands in all other boron compounds can be attributed to charge transfer transitions (mesityl → π* of the chelate backbone), which often display large Stokes' shifts due
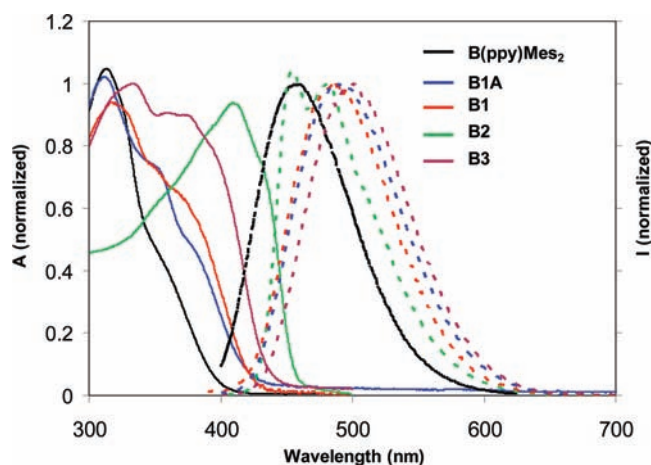
Figure 5. Normalized absorption and fluorescent spectra of the boryl and polyboryl compounds recorded in toluene ($1.0-10^{-5}$ M).

to interactions with solvent molecules.[6] The *cis*-**B1** molecule has absorption and emission spectra similar to those of *trans*-**B1** (see ESI) but with a much lower emission efficiency, which could not be determined accurately due to the oily nature of the *cis* isomer. The solid-state quantum efficiencies of all compounds are similar, as shown in Table 1.

Photoisomerization. Although the monoboryl compounds **B1** and **B1A** have similar absorption spectra with **B1A** having a much greater extinction coefficient, they have distinct responses toward light. Upon prolonged exposure to UV light (365 nm) under nitrogen, no apparent color change was observed for **B1**, while the solution of **B1A** rapidly became dark blue-green in color, quantitatively forming a new species **B1A′** (Figure 6) with a broad absorption band appearing at 600 nm upon irradiation (Figure 7). This is consistent with the behavior of **A1** and **A2** (see Scheme 1). The fluorescent emission intensity of **B1A** diminishes rapidly with irradiation, and the new species **B1A′** is not emissive (see ESI).

The characteristic chemical shifts of the pyridyl and mesityl protons in the ^{1}H NMR spectrum of **B1A′** show excellent agreement with those of **A1′** and **A2′**,[7] confirming that **B1A′** is an analogous compound in which a new C–C bond is formed between the phenyl ring of the phenylpyridine and a

Table 1. Absorption and Luminescent Data

cmpd	A, nm (ε, M^{-1} cm^{-1})	λ_{em}, nm toluene, rt	λ_{em}, nm solid, rt	Φ solution/solid
B(ppy)Mes₂, A1	356 (15,200)	458	n/a	15%/ n.a.
B1	370 (11,400)	487	490	32/23 ± 2%
B2	411 (41,000)	456	491	59/22 ± 2%
B3	374 (53,000)	500	504	30/24 ± 2%
B1A	380 (22,500)	490	496	37/14 ± 2%

The quantum efficiencies in toluene solution were obtained under argon using 9,10-diphenylanthracene as the standard ($\Phi = 0.90$). For the olefinic compounds, the data are for the *trans* or all *trans* isomers.

mesityl group. As observed for **A1′** and **A2′**, the transformation of **B1A** to **B1A′** is fully thermally reversible. The quantum efficiency[15] for the phototransformation of **B1A** to **B1A′** was determined to be 0.33 at $\lambda = 365$ nm, $5.0-10^{-4}$ M, which is much lower than that of the nonsubstituted compound B(ppy)Mes₂ (**A1**) (0.88 at $\lambda = 365$ nm, $5.0-10^{-4}$ M). The rate constants for the conversion of **A1** to **A1′**, and **B1A** to **B1A′** were determined to be $1.08-10^{-3}$ s^{-1} and $5.44-10^{-5}$ s^{-1}, respectively. A ^{1}H NMR competition experiment in which both **B1A** and **A1** were irradiated together at 365 nm in the same NMR tube and at the same concentration further established that **A1** undergoes photoisomerization much faster than **B1A** (see ESI), consistent with the low quantum efficiency of **B1A**. Because **B1A** has a much greater absorbance than **A1** at 365 nm (Table 1), its low photoisomerization quantum efficiency may be attributed to the greater π-conjugation of the ph-py chelate, compared to **A1**, that stabilizes the excited state of the molecule, thus decreasing the photoreactivity. A similar trend was also observed between **A1** and **A2**,[7] **A1** and [*p*-(2-py)-ph-ppy]BMes₂ where a *p*-(2-py)phenyl substituent is attached to the pyridine ring of the ppy chelate.[24]

Surprisingly, however, no analogue of **B1A′** was observed when the olefin-substituted compound **B1** was subjected to the same irradiation conditions. Instead, the *trans*-isomer of **B1** was found to undergo a facile *trans* to *cis*-isomerization at ambient temperature, reaching ∼70% conversion at equilibrium, as shown by the ^{1}H NMR spectra in Figure 8. This isomerization was also monitored by UV–vis and fluorescent spectral measurements. Control experiments on a mixture of **A1** and **B1** show that, upon irradiation, **A1** forms exclusively
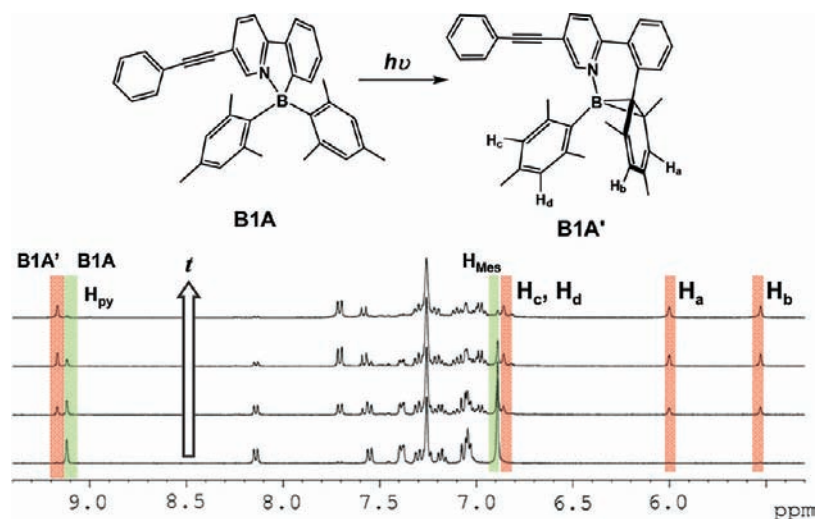

Figure 6. ^{1}H NMR spectral change of **B1A** in C_6D_6 under N_2 upon irradiation at 365 nm. The chemical shifts of the 2-pyridyl proton (H_{py}) and the protons from the mesityl groups are highlighted. Orange: **B1A′**, yellow: **B1A**.
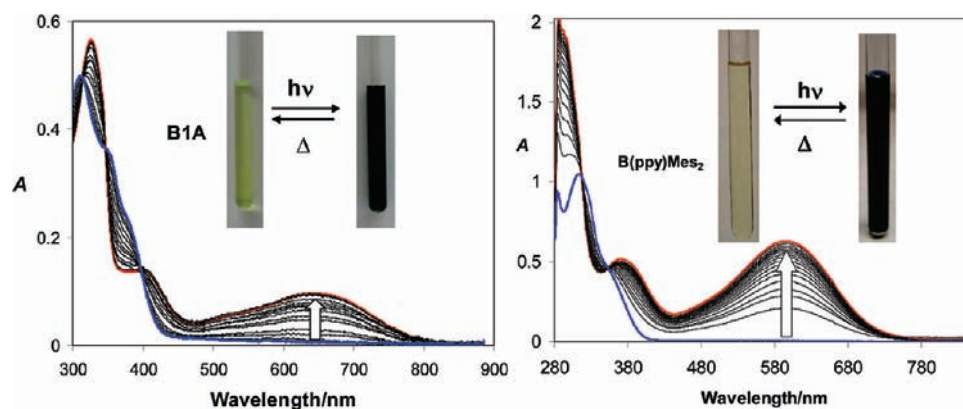
Figure 7. Comparison of the UV–vis spectral change of **B1A** (left, 1s interval, ~1.0–10^{-5} M) with that of **A1** (right, 5s interval, 1.25–10^{-4} M) in toluene upon irradiation under N$_2$ at 365 nm and photographs of **B1A** and **A1** solutions before and after irradiation.
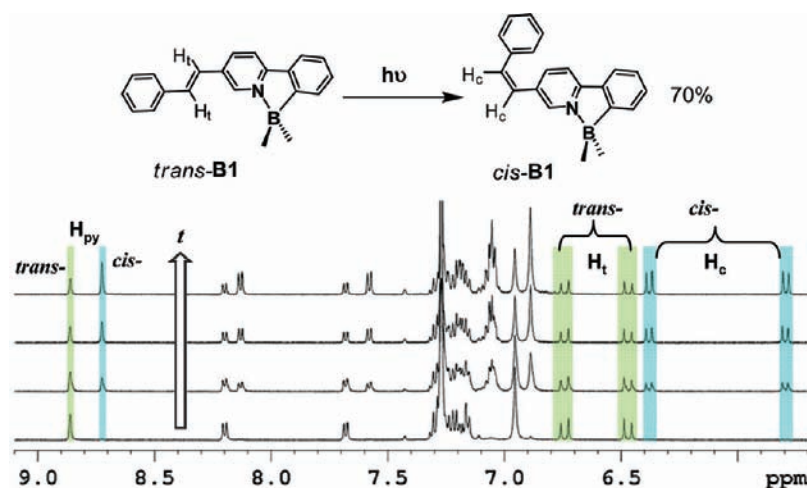

Figure 8. ^{1}H NMR spectral change of **B1** in C$_6$D$_6$ under N$_2$ upon irradiation at 365 nm. The chemical shifts of the 2-pyridyl proton (H$_{py}$) and the olefinic protons are highlighted. Yellow: *trans*-**B1**, blue: *cis*-**B1**.
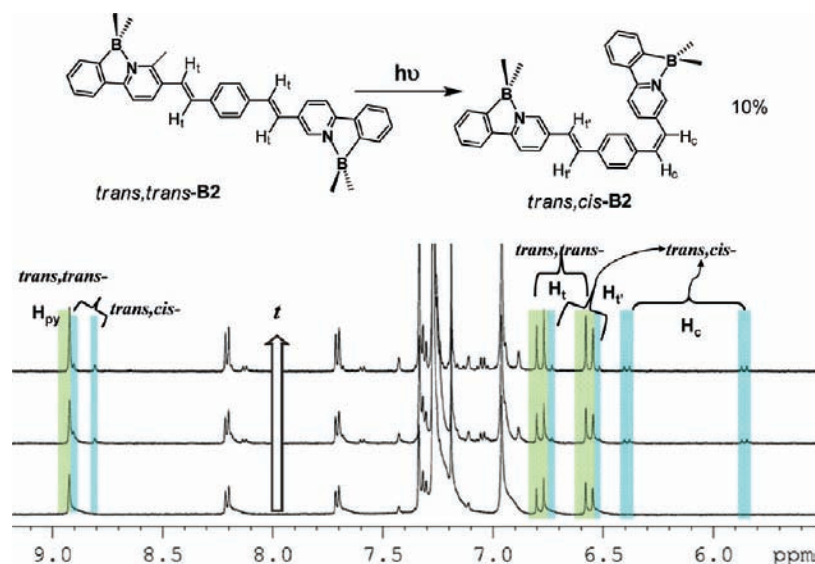

Figure 9. ^{1}H NMR spectral change of **B2** in C$_6$D$_6$ under N$_2$ upon irradiation at 365 nm. The chemical shifts of the 2-pyridyl proton (H$_{py}$) and the olefinic protons are highlighted. Yellow: all *trans*-**B2**, blue: *trans,cis*-**B2**.

A1′, while **B1** simply undergoes isomerization (see ESI). This confirms unequivocally that the olefinic bond is responsible for the stabilization of the boron chelate chromophore toward photolysis.

Similarly, we have found that the tetrahedral boron cores in the diboryl compound **B2** and the triboryl compound **B3**

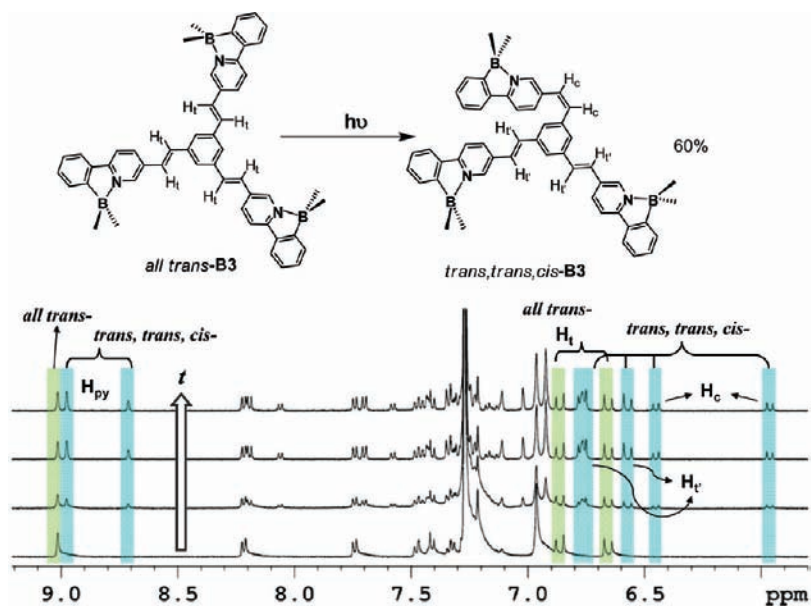(24) Rao, Y. L.; Wang, S. Unpublished results.

Figure 10. ^{1}H NMR spectral change of **B3** in C_6D_6 under N_2 upon irradiation at 365 nm. The chemical shifts of the 2-pyridyl proton (H_{py}) and the olefinic protons are highlighted. Yellow: all *trans*-**B3**, blue: *trans,trans,cis*-**B3**.
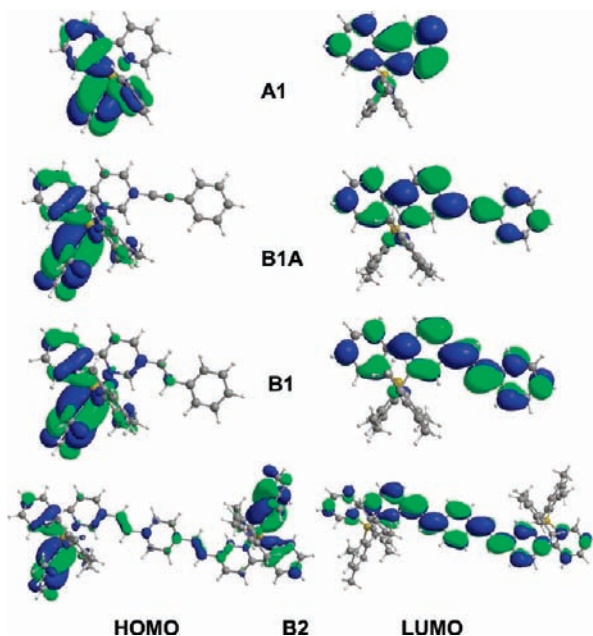

Figure 11. HOMO and LUMO orbitals of **A1**, **B1A**, *trans*-**B1**, and **B2** with an isocontour value of 0.02 for all surfaces.

are also stable toward UV irradiation, and no C—C bond formation products were observed after prolonged UV exposure in toluene or C_6D_6. Instead, both **B2** and **B3** were found to undergo *trans* to *cis* isomerization upon irradiation that causes the diminishing of the lowest absorption band and the emission peak in a similar manner as observed for **B1**.

In both cases, ^{1}H NMR data indicate that irradiation will produce only one *cis* double bond at any given time, giving *trans,cis*-**B2** or *trans,trans,cis*-**B3** (Figures 9 and 10). Since both systems are fully conjugated and *cis* double bonds are

(25) Smith, M.; March, J. *Advanced Organic Chemistry, Reactions, Mechanisms and Structure*, 5th ed.; John Wiley & Sons: New York, 2001.

inherently less stable than their *trans* counterparts, further irradiation preferentially reverts the existing *cis* double bond to the *trans* form rather than forming a second *cis* double bond. In the photostationary state, the conversion of *trans,trans*-**B2** to the (*trans,cis*) isomer is approximately 10%, while the conversion of **B3** reaches approximately 50% at the 365 nm excitation wavelength. Changing the excitation wavelength to 420 nm did not appreciably change the (*trans,trans*) to (*trans,cis*) ratio for a solution of **B2**.

TD-DFT calculations. TD-DFT calculations were performed for **B1A** and the all *trans*- and mono-*cis* isomers of **B1**−**B3** (see ESI). As a result of the steric congestion readily apparent from the optimized structures, these calculations indicate that the *cis* isomers of compounds **B1**−**B3** are 3.9, 4.1, and 3.9 kcal/mol higher in energy than the respective *trans* compounds, consistent with previously reported values for *cis/trans* isomers.[25]

The HOMO and LUMO orbitals of **A1**, **B1A**, and the *trans* isomers of **B1** and **B2** are shown in Figure 11, with an isocontour value of 0.02 for all surfaces. The HOMO and LUMO diagrams for **B3** can be found in the ESI. The HOMO orbitals in all cases are dominated by both mesityl π-character and the phenylpyridine C—B σ-bond. However, while the LUMO of **A1** is almost entirely composed of phenylpyridine π* character, the vinyl or acetylene π* orbitals make large contributions to the LUMOs of **B1A**, and both isomers of **B1**−**B3**. In the vinyl- and acetylene-substituted molecules, therefore, electron density is more delocalized in the excited state. TD-DFT calculation results for **A1**, **B1A**, *trans*-**B1**, and all *trans*-**B2** indicate that the lowest energy transition is almost entirely HOMO → LUMO in nature, with reasonable oscillator strengths (>0.01); these transitions are thus likely responsible for the observed fluorescence of these compounds (see ESI).

Several key conclusions can be drawn from the TD-DFT data. The HOMO in all cases contains significant electron density from the phenylpyridine C—B σ-bond, consistent with a weakening of this bond on irradiation that leads to the bond cleavage observed for **A1** and **B1A**. Also, the LUMO orbitals

Scheme 5
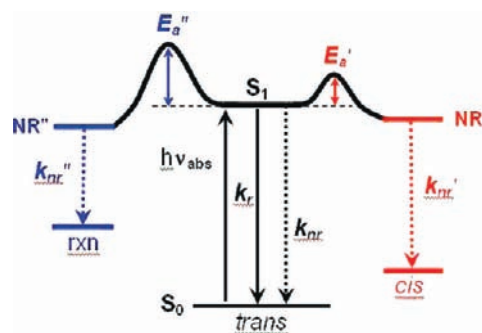
for **B1A** and **B1**−**B3** all contain substantial π-character from their pendant π-bonds, which would lead to a reduction in bond order in the excited state. In the case of **B1**−**B3**, this creates an excited-state single bond that facilitates *trans* to *cis* isomerization, providing an alternative pathway for energy dissipation not available to the parent chromophore, B(p-py)Mes$_2$. However, this same phenomenon is not observed for the acetylene-containing **B1A**, in which bond rotation would still be restricted after a single π-bond is weakened by photoexcitation.

A rationalization of these processes is proposed in Scheme 5. On irradiation, the singlet excited-state *trans* isomer may simply fluorescence, with a radiative rate constant k_r, or may relax *via* one of several nonradiative pathways, k_{nr}. Of these, it may: (1) undergo typical vibrational deactivation to the *trans* ground state (k_{nr});[26] (2) undergo isomerization to the *cis* compound (k_{nr}') or (3) undergo a photochemical rearrangement reaction as depicted in Scheme 1 (k_{nr}''). (The singlet to triplet intersystem crossing is also a possibility,[26] although the role of the triplet state in our system has not been established.) For **B1**−**B3**, *cis*−*trans* isomerization provides a more kinetically accessible relaxation pathway than the C−C coupling reaction, deactivating the rearrangement at ambient temperatures and preserving the integrity of the chromophore. However, with no isomerization pathway available to B(ppy)Mes$_2$ or **B1A**, these molecules undergo

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(26) (a) Lakowicz, J. R. *Principles of Fluorescent Spectroscopy*, 2nd ed.; Kluwer Academic/Plenum Publishers: New York, 1999. (b) Saltiel, J.; D'Agostino, J.; Megarity, E. D.; Metts, L.; Neuberger, K. R.; Wrighton, M.; Zafiriou, O. C. *Org. Photochem.* **1973**, *3*, 1.

photochemical rearrangement with an accompanying loss of emission intensity. *Cis*−*trans* isomerization thus provides a competing nonradiative relaxation pathway for **B1**−**B3**, and may prove to be a useful strategy for the stabilization of a wider variety of otherwise photochemically unstable chromophores as well.

Conclusions

This work demonstrates that highly emissive and photo-active π-conjugated systems can be achieved by incorporating olefinic bonds into the π-backbone of *N,C*-chelate boryl systems. While molecules containing the B(ppy)Mes$_2$ chromophore typically undergo photochemical rearrangement on exposure to UV light, the isomerization of a single olefinic bond in compounds **B1**−**B3** completely inhibits this photoswitching process, thereby stabilizing the chromophore toward light. The results of comparative studies on the monoboryl compounds **A1**, **B1**, and **B1A** establish unequivocally that a single olefinic bond in the conjugated molecule is sufficient to protect the B(ppy)Mes$_2$ chromophore from photodegradation. Furthermore, we have shown that extending the π-conjugation of the phenylpyridine chelate with an acetylene linker does not impart this same stability to the B(ppy)Mes$_2$ chromophore, but does significantly reduce the photoisomerization quantum efficiency.

Supporting Information Available: Complete crystal structural data (CIF files), synthetic and characterization details of intermediates not included in the Experimental Section, details of TD-DFT calculation results, reduction potentials, complete diagrams showing the UV−vis and fluorescent spectral change of **B1A**, **B1**, **B2**, and **B3** upon irradiation at 365 nm, the NMR spectral data of the control photolysis experiment of **B1** in the presence of **A1**, the NMR competition photolysis experiment of **A1** with **B1A**, and complete ref 19. This material is available free of charge via the Internet at http://pubs.acs.org.

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