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<th>Journal:</th>
<th>Journal of Materials Chemistry C</th>
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<tr>
<td>Manuscript ID</td>
<td>TC-COM-05-2016-001782.R1</td>
</tr>
<tr>
<td>Article Type:</td>
<td>Communication</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>12-Jun-2016</td>
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<tr>
<td>Complete List of Authors:</td>
<td>Maar, Ryan; The University of Western Ontario, Department of Chemistry Gilroy, Joe; The University of Western Ontario, Department of Chemistry</td>
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Aggregation-Induced Emission Enhancement in Boron Difluoride Complexes of 3-Cyanoformazanates

Ryan R. Maar* and Joe B. Gilroy*

Boron difluoride (BF$_2$) complexes of 3-cyanoformazanates exhibit aggregation-induced emission enhancement in THF-water mixtures due to their severely twisted N-aryl substituents which restrict intramolecular motion and π stacking upon aggregation.

Molecules that exhibit aggregation-induced emission (AIE) or aggregation-induced emission enhancement (AIEE) have garnered significant attention due to their applicability to the fields of organic electronics, chemical sensing, and fluorescence cell imaging. Typically, organic fluorophores experience attenuated emission intensity upon aggregation as a result of aggregation-caused quenching (ACQ). This arises due to the formation of strong intermolecular π-π stacking interactions enabling the formation of excimers/exciplexes, which quench excited states via non-radiative pathways.

The phenomenon of AIE was first described by Tang and co-workers as part of their work on 1-methyl-1,2,3,4,5-pentaphenylsilole 1. Since its discovery, significant efforts have been invested toward the elucidation of the mechanism of AIE. Ultimately, it has been proposed that the restriction of intramolecular motions (RIM), which includes the restriction of intramolecular rotations and restriction of intramolecular vibrations, leads to the AIE phenomenon. Fervent work done by researchers worldwide has led to the development of numerous AIE luminogens (AIEgens), including hydrocarbon-, heteroatom-, and boron-containing systems.

More recently, a variety of substituted tetraphenylethylenes and triphenylamines have been widely studied.

Boron difluoride (BF$_2$) formazanates are an interesting class of molecular materials that possess tunable absorption, emission, and electrochemical properties through structural variation. The parent formazans are commonly used in cell viability assays, and are generally prepared via straightforward aryl diazonium coupling reactions in aqueous media. BF$_2$ formazanates have been incorporated into polymers, explored as electrochemiluminescent materials, used as precursors to B(I) carbenoid intermediates, and employed as fluorescent cell-imaging agents. Herein, we report the first examples of BF$_2$ formazanates that demonstrate AIEE.

BF$_2$ complex 5c was prepared in 96% yield according to a well-established synthetic methodology and the synthesis and characterization of 5a and 5b have been reported elsewhere. We chose these methoxy-substituted compounds for this study due to their superior emission properties, specifically, their relatively higher fluorescence quantum yields (Φ$_F$) relative to other substituted BF$_2$ formazanate derivatives. Complex 5c was fully characterized using multinuclear NMR spectroscopy, UV-vis absorption and emission spectroscopy, IR spectroscopy, cyclic voltammetry, and high-resolution mass spectrometry (Figs. S1–S4).

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†Electronic supplementary information (ESI) available: Synthesis and characterization details. CCDC 1455964. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x
Compounds 5a–c absorb and emit within the visible region of the electromagnetic spectrum with a noticeable blue-shift in the wavelength of maximum absorbance ($\lambda_{\text{abs}}$) when the N-aryl substituents were varied from 4-methoxyphenyl (5a: $\lambda_{\text{abs}} = 556$ nm; $\varepsilon = 33,400$ M$^{-1}$ cm$^{-1}$) to 2-methoxyphenyl (5b: $\lambda_{\text{abs}} = 456$ nm; $\varepsilon = 10,100$ M$^{-1}$ cm$^{-1}$) to 2,6-dimethoxyphenyl (5c: $\lambda_{\text{abs}} = 434$ nm; $\varepsilon = 13,900$ M$^{-1}$ cm$^{-1}$) (Fig. 1 and Table S1). This trend was also evident when examining the wavelength of maximum emission ($\lambda_{\text{em}}$) for 5a ($\lambda_{\text{em}} = 662$ nm), 5b ($\lambda_{\text{em}} = 590$ nm), and 5c ($\lambda_{\text{em}} = 556$ nm). The trends observed for the absorption/emission maxima are consistent with a previous report where the presence of ortho substituents led to twisting of the N-aryl substituents relative to the formazanate backbone and a blue-shift in absorption/emission maxima.$^{22}$ A decrease in the $\Phi_f$ was also observed for the same series of compounds: 5a ($\Phi_f = 0.46$), 5b ($\Phi_f = 0.03$) and 5c ($\Phi_f < 0.01$) (Figs. S5, S6, and Table S1).$^{23}$ The solid-state structures of 5a–c are comprised of carbon-nitrogen and nitrogen-nitrogen bonds with lengths between those of typical single and double bonds of the respective atoms, indicating a delocalized formazanate backbone consistent with previous reports (Tables S2 and S3).$^{22}$ In addition, the dihedral angles between the N-aryl substituents and the formazanate backbone deviate from planarity from 4-methoxyphenyl (5a: 15.3$^\circ$, 21.4$^\circ$, 47.7$^\circ$) to 2-
The electrochemical properties of therefore more electronically conjugated than more difficult due to a less planar π system.

Exploration of the AIEE behaviour of 

\[ \text{E}^\circ_{\text{red}} = -2.09 \text{ V} \text{ relative to the ferrocene/ferrocenium redox couple}. \]

The results were compared to data obtained for 

\[ \text{E}^\circ_{\text{red}} = -0.90 \text{ V}, \text{ E}^\circ_{\text{red}} = -2.09 \text{ V} \text{ relative to the ferrocene/ferrocenium redox couple} \]

and demonstrated that the introduction of ortho methoxy substituents made electrochemical reduction more difficult due to a less planar π system.16

Exploration of the AIEE behaviour of 

5a−c in THF-water mixtures with different volume fractions of water (\( f_w \)) revealed an interesting trend (Fig. 1 and Table S1). 

5a is a typical organic fluorophore, which undergoes detrimental ACQ accompanied by a red-shift in both the absorbance and emission maxima of 36 nm and 40 nm, respectively (Fig. 1 and Table S1). 

A plausible explanation for the ACQ effect is the presence of intermolecular π-electron interactions that are facilitated by the planar orientation of the N-aryl substituents. This hypothesis is corroborated by the solid-state structure of 5a, which reveals short contacts (2.987−3.286 Å) between the formazanate backbone and the cyano substituent of a neighbouring molecule (Fig. 2a).

The frontier molecular orbitals of 5a−c have been shown previously to include significant intermolecular π−π stacking interactions that are facilitated by the planar orientation of the N-aryl substituents. This hypothesis is corroborated by the solid-state structure of 5a, which reveals short contacts (2.987−3.286 Å) between the formazanate backbone and the cyano substituent of a neighbouring molecule (Fig. 2a).

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5b and 5c act as AIEgens and undergo AIEE likely as a result of RIM (Fig. 1 and Table S1). Initially (\( f_w = 0\% \)), 5c was weakly emissive and its emission intensity was further attenuated and red-shifted upon increasing \( f_w \). The decrease in emission intensity as the solvent mixture became increasingly polar was consistent with previously observed behaviour for similar dyes.16 Upon reaching a critical \( f_w \) (70%), the emission intensity was revitalized and further intensified until it reached a maximum value at \( f_w = 95\% \). Interestingly, \( \lambda_{\text{em}} \) and \( \lambda_{\text{abs}} \) experience a net red-shift of 59 nm and 24 nm at \( f_w = 95\% \) compared to \( f_w = 0\% \) (Fig. 1 and Table S1). Based on the solid-state structure of 5c, it is evident that there are multiple intermolecular interactions present: CH⋯π (2.696 Å and 2.885 Å), CH⋯O (3.113 Å and 3.125 Å), CH⋯N (2.552 Å and 2.725 Å), and CH⋯F (2.611 Å) (Fig. S9). These interactions lock the conformation of the N-aryl substituents and prevent intramolecular motion. Complex 5b also exhibited decreased emission intensity upon the initial addition of water, which was rejuvenated at \( f_w = 80\% \). 5b exhibited red-shifts of 61 nm (\( \lambda_{\text{abs}} \)) and 20 nm (\( \lambda_{\text{em}} \)) from \( f_w = 0\% \) to \( f_w = 95\% \) (Fig. 1 and Table S1) due to intermolecular interactions: CH⋯π (2.655 Å and 2.788 Å), CH⋯O (2.620 Å and 2.794 Å), and CH⋯F (2.398 Å−2.509 Å) (Fig. S10). Red-shifted emission maxima are commonly observed for AIE-active molecules.24 While we are unable to identify the specific interactions leading to the red-shift of the emission maxima observed for 5b and 5c (Figs. 2, S8−S10), we note that the potential π−π interactions observed in the solid-state structures of 5b and 5c have intermolecular distances outside the sum of the Van der Waal radii of the respective atoms (5b: 3.849−3.862 Å; 5c: 3.747−3.758 Å).

In summary, the readily accessible BF3 formazanates 5a−c absorb and emit within the visible region of the electromagnetic spectrum. 5a is a typical organic fluorophore that experienced ACQ whereas 5b and 5c exhibited AIEE. Controlled addition of water into THF solutions of 5b and 5c initially resulted in decreased emission intensity before a critical \( f_w \) (5b: 80%; 5c: 70%) was reached and the emission intensity was invigorated.

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**Fig. 2** Solid-state structures for 5a−c. Intermolecular NC⋯π [3.286 Å] and CH⋯π [2.987 Å and 3.241 Å] interactions for 5a (a).16 Ring-slipped π-stacking motifs for 5b (b),22 and 5c (c). Anisotropic displacement ellipsoids are shown at 50% probability. Hydrogen atoms have been omitted and N-aryl substituents in (a) have been converted to wireframe style for clarity. All distances are quoted in Å.
and enhanced. Complex 5b exhibited a 3-fold increase in emission at $f = 95\%$, while 5e exhibited a 10-fold increase under the same conditions. The degrees of enhancement were significant, but less dramatic than those observed for CF$_3$- and COOMe-substituted boron dipyrromethenes (ca. 40-fold increase in glycerol/methanol), which emit at similar wavelengths. The solid-state structure of 5a indicated the presence of strong intermolecular $\pi$-interactions, which resulted in ACQ, while 5b and 5e exhibited AIEE due to the restriction of intramolecular motion upon aggregation and do not appear to $\pi$ stack in the solid state. This work highlights the potential of BF$_2$ formazanates as AIEGens. Subsequent studies will aim to further explore how substituent variation affects AIEE.

We would like to thank the University of Western Ontario, the Natural Sciences and Engineering Research Council (NSERC) of Canada (J.B.G.: DG, 435675 and R.R.M.: CGS-M Program), the Ontario Ministry of Research and Innovation (J.B.G.: ERA, ER14/10/147), and the Canadian Foundation for Innovation (J.B.G.: JELF, 33977) for funding this work. Finally, we thank Prof. E.R. Gillies and M.S. Workentin for access to instrumentation within their laboratories and Ms. S.M. Barbon for performing X-ray crystallography studies.

**Notes and references**


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