

# Synthesis of the most intensely fluorescent azobenzene by utilizing the B–N interaction†

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A boron-substituted azobenzene, (*E*)-[2-(4-methoxyphenylazo)-phenyl]bis(pentafluorophenyl)borane, presented the most intense fluorescence among the azobenzene derivatives.

Azobenzene is one of the most common and frequently-used chromophores.<sup>1</sup> Many azobenzene derivatives have been synthesized and used as dyes. Azobenzenes are also used as photo-responsive molecular switches by taking advantage of their photoisomerization.<sup>2</sup> Their photoisomerization features inhibit another important property of chromophores, fluorescence. Since the photoisomerization process is very efficient in photoexcited azobenzenes, their radiative deactivation processes, which are slower, are not competitive.<sup>3</sup> Hence, azobenzene itself virtually does not emit light.<sup>4</sup> There have been only limited exceptional azobenzene derivatives that show fluorescence, however, most of them fluoresce only in a rigid matrix at low temperature and their fluorescence quantum yields,  $\Phi_F$ , are quite low.<sup>5</sup> *Ortho*-metalated azobenzene complexes<sup>6</sup> and self-assembled aggregates of azobenzene derivatives<sup>7</sup> have also been reported as emissive azobenzene derivatives and most of their fluorescence quantum yields at ambient temperature in the solution state are about  $10^{-3}$ , which are still low compared with organic fluorescent materials. In general, azobenzenes have remained as non-fluorescent chromophores while many other organic dye molecules such as rhodamines and fluoresceins have been developed as highly emissive chromophores and utilized for the labeling of biomolecules such as proteins to make them detectable.<sup>8</sup> Azobenzenes would have promise to be useful as fluorescent materials, with applications in light-emitting devices, fluorescent probes, and molecular detection, if they emitted fluorescence because of the variety of easy methods for synthesizing azobenzenes and for tuning their properties.

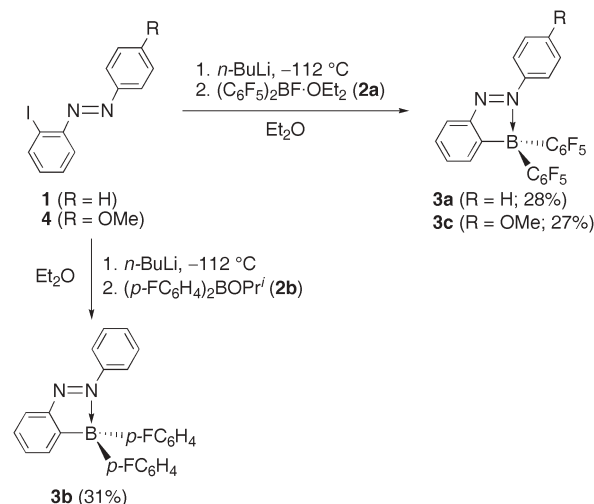
Recently, Yamaguchi *et al.* reported that the fixation of  $\pi$ -conjugate systems of boryl-substituted thienylthiazoles into a planar conformation with the B–N interaction provided them with fluorescence.<sup>9</sup> Meanwhile, during the course of our study on azobenzene derivatives bearing a main-group-element substituent,<sup>10</sup> we have found the most intensely fluorescent azobenzene by utilizing the B–N interaction. We report here the synthesis,

spectroscopic properties, and theoretical calculations of this azobenzene and related compounds.

Successive reaction of (*E*)-2-iodoazobenzene ((*E*)-**1**) with *n*-BuLi and fluoroborane **2a** in Et<sub>2</sub>O at  $-112^\circ\text{C}$  gave a boron-substituted azobenzene (*E*)-**3a** (28%) as a brown solid, which can be handled in the air (Scheme 1). Compounds (*E*)-**3b** (31%) and (*E*)-**3c** (27%) were synthesized similarly from (*E*)-**1** and **2b** and from (*E*)-**4** and **2a**, respectively. Tetracoordination states of the boron atoms of (*E*)-**3a–c** were confirmed by the <sup>11</sup>B NMR spectra in CDCl<sub>3</sub> [(*E*)-**3a**:  $\delta_B$   $-0.8$ , (*E*)-**3b**:  $\delta_B$   $7.0\ddagger$ , (*E*)-**3c**:  $\delta_B$   $-0.6$ ]. The X-ray crystallographic analysis of (*E*)-**3a** revealed that (*E*)-**3a** has a N=N bond length [ $1.2704(18)$  Å]<sup>11</sup> which is almost the same as that of the previously reported (*E*)-azobenzenes (avg.  $1.25$  Å).<sup>12</sup>

In the UV–vis spectrum in hexane, (*E*)-**3a** showed an absorption maximum at  $386$  nm ( $\epsilon = 1.9 \times 10^4$ ), assignable to the  $\pi$ – $\pi^*$  transition of the azo group, and no resolved band corresponding to the  $n$ – $\pi^*$  transition (Fig. 1(a)). This large bathochromic shift from the  $\pi$ – $\pi^*$  transition of unsubstituted (*E*)-azobenzene ((*E*)-**5**) ( $\lambda = 315$  nm) suggests a considerable perturbation of the electronic structure of the azobenzene moiety of (*E*)-**3a** by the B–N interaction.

Irradiation ( $\lambda = 360$  nm) of (*E*)-**3a** and (*E*)-**3c** in C<sub>6</sub>D<sub>6</sub> at r.t. with a super-high-pressure mercury lamp (500 W) did not cause their photoisomerization to (*Z*)-**3a** and (*Z*)-**3c**, but caused strong green fluorescence, in contrast to the behavior of most azobenzene derivatives (Fig. 1(b)). In the fluorescence spectra in hexane, (*E*)-**3a** and (*E*)-**3c** showed emission maxima at  $503$  nm (excited at  $386$  nm) and  $524$  nm (excited at  $439$  nm), respectively (Fig. 1(a)). Matching



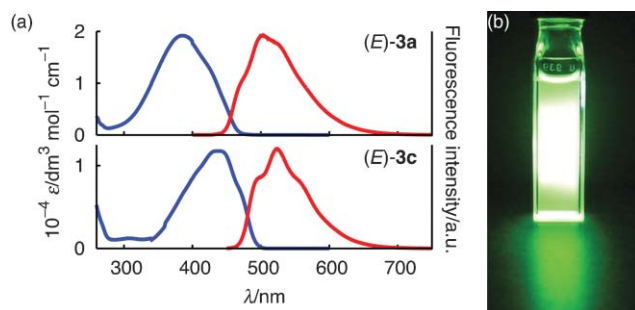
Scheme 1 Synthesis of (*E*)-**3a–c**.

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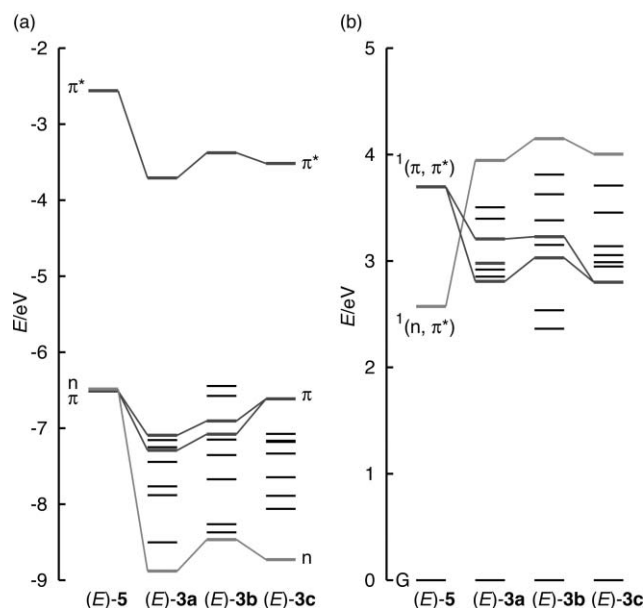
† Electronic supplementary information (ESI) available: Synthesis and characterization of (*E*)-**3a–c**, the X-ray crystallographic analysis for (*E*)-**3a**, Cartesian coordinates and molecular orbital diagrams for (*E*)-**3a–c**. See DOI: 10.1039/b615966d



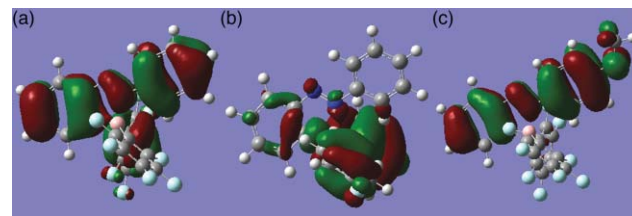
**Fig. 1** (a) Absorption (blue line) and fluorescence (red line) spectra of (*E*)-**3a** and (*E*)-**3c** in hexane at r.t. (b) Photograph of hexane solution (ca. 5  $\mu$ M) of (*E*)-**3c** under irradiation by 360 nm light.

between the peak of the excitation spectra corresponding to the emission at the wavelength of the emission maxima and the absorption maxima due to the  $\pi$ - $\pi^*$  transition for both (*E*)-**3a** and (*E*)-**3c** indicates that these emissions are assignable to the transition from the  $^1(\pi, \pi^*)$  state to the ground state. The fluorescence quantum yields of (*E*)-**3a** and (*E*)-**3c** in hexane at r.t. were determined as  $\Phi_F = 0.23$  and  $0.76$ , respectively,<sup>13</sup> which are extremely high compared with  $2.53 \times 10^{-5}$  for the unsubstituted azobenzene (*E*)-**5**,<sup>14</sup> the latter value is higher than those of any azobenzene derivatives reported previously.<sup>5-7</sup> In contrast, (*E*)-**3b** showed almost no fluorescent emission. The substituents on the boron atom should be responsible for the intensity of the fluorescence, considering the above results.

The electronic states and excitation energies of (*E*)-**3a-c** and unsubstituted azobenzene ((*E*)-**5**) were investigated by theoretical calculations using density-functional theory (DFT) and a time-dependent DFT (TD-DFT) method at the B3PW91/6-31+G(d)//B3PW91/6-31G(d) level of theory.<sup>15</sup> The optimized structure of (*E*)-**3a** matches well with its crystal structure. In (*E*)-**5**, the  $\pi^*$ ,  $n$  and  $\pi$  orbitals are assignable to the LUMO, HOMO, and HOMO-1, respectively. However, the energy levels of the orbitals of (*E*)-**3a-c** that originate from the  $n$  orbital of the azo group ( $-8.9$ ,  $-8.5$ , and  $-8.7$  eV, respectively) are lower than those originating from the  $\pi$  orbital of the azo group ( $-7.1$  to  $-7.3$ ,  $-6.9$  to  $-7.1$ , and  $-6.6$  eV, respectively) (Fig. 2(a)). Lowering of the energy level of the  $n$  orbital would be caused by the B-N bonding interaction. As a reflection of this anomaly, the  $^1(\pi, \pi^*)$  excited states of (*E*)-**3a-c** (2.8 to 3.2, 3.0 to 3.2, and 2.8 eV, respectively) are below the  $^1(n, \pi^*)$  excited states (3.9, 4.1, and 4.0 eV, respectively) (Fig. 2(b)). This order of the energy levels is in contrast to that of (*E*)-**5**. Inversion of the order between the  $^1(n, \pi^*)$  and  $^1(\pi, \pi^*)$  states on the energy scale increases the transition probability from excited states to the ground state based on the orbital symmetries, and this inversion has been considered as one of the causes of fluorescence of protonated azobenzenes and 4-(dialkylamino)azobenzenes.<sup>5a,c-e</sup> In addition, the  $\pi$  orbitals of the azo group of (*E*)-**3a** and (*E*)-**3c** lie on their HOMO (Fig. 3(a) and (c)). As a result, the  $^1(\pi, \pi^*)$  excited state of (*E*)-**3a** and (*E*)-**3c** occupies the lowest singlet excited state  $S_1$ , and the transition between  $S_1$  and ground states is allowed. In contrast, the HOMO of (*E*)-**3b** is not on the azobenzene moiety but localized on the aryl groups attached to the boron atom (Fig. 3(b)). The relatively high energy level of the occupied orbitals of *p*-FC<sub>6</sub>H<sub>4</sub> groups prevents the  $\pi$  orbital of the azo group of (*E*)-**3b** from occupying the HOMO and restricts its fluorescence



**Fig. 2** Calculated (a) energy levels of frontier molecular orbitals and (b) singlet excitation energies of (*E*)-azobenzene ((*E*)-**5**) and (*E*)-**3a-c** at the B3PW91/6-31+G(d)//B3PW91/6-31G(d) level of theory. In (a), the orbitals indicated by gray-black and gray levels originate from the  $\pi$  ( $\pi^*$ ) and  $n$  orbitals of the azo group, respectively. In (b), gray-black and gray excited states have the character of  $^1(\pi, \pi^*)$  and  $^1(n, \pi^*)$  states, respectively.



**Fig. 3** Molecular orbital diagrams for the HOMO of (a) (*E*)-**3a**, (b) (*E*)-**3b**, and (c) (*E*)-**3c** (B3PW91/6-31+G(d)//B3PW91/6-31G(d)).

quantum yield to quite low. Therefore, the characteristic emission behavior of (*E*)-**3a** and (*E*)-**3c** should be attributed to the inverted order of the  $^1(n, \pi^*)$  and  $^1(\pi, \pi^*)$  states and the low-lying occupied orbitals of the strong electron-withdrawing C<sub>6</sub>F<sub>5</sub> group.

In addition, the tight B-N coordination caused by fixation of the boron atom and the nitrogen atom at a suitable position to interact can provide more rigidity for the structure around the azo group than protonation of azo groups and substitution with amino groups.<sup>5a,c-e</sup> The enhanced rigidity of the structure of (*E*)-**3a** and (*E*)-**3c** suppresses the conformational change around the azo group like boryl-substituted thienylthiazoles.<sup>9</sup> This suppression locks the photoisomerization process around the N=N double bond, which is the mechanism responsible for the very efficient radiationless deactivation in the unsubstituted azobenzene,<sup>3</sup> and helps provide (*E*)-**3a** and (*E*)-**3c** with the extremely high fluorescence quantum yield.

In conclusion, we have succeeded in synthesizing the most intensely fluorescent azobenzene. Both the intramolecular B-N dative bond and the strong electron-withdrawing C<sub>6</sub>F<sub>5</sub> groups have been revealed to play an important role in providing the azobenzene with extremely high light-emitting ability, which could

not be afforded by protonation, *ortho*-metalation, or self-assembled aggregation. This new design to provide azobenzene with fluorescence will expand the possibilities of utilizing azobenzenes for more versatile fluorescent probes of chemical sensors and light-emitting devices. Tuning of the emission maximum wavelengths and study on excited states and decay processes are underway.

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## Notes and references

‡ The VT-NMR revealed that the equilibrium in the solution between the tricoordinate and tetracoordinate boron state of (*E*)-**3b** is negligible because its chemical shift was almost unchanged in the temperature range from  $-60\text{ }^{\circ}\text{C}$  to  $+60\text{ }^{\circ}\text{C}$ . Our preliminary theoretical calculations on the  $^{11}\text{B}$  NMR chemical shifts of (*E*)-**3a** and (*E*)-**3b** support the proposal that the difference between their observed chemical shifts should be attributed not to the equilibrium but to the difference in the substituents on the boron atom.

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- Crystallographic data for (*E*)-**3a**:  $\text{C}_{24}\text{H}_9\text{BF}_{10}\text{N}_2$ ,  $M = 526.14$ , triclinic,  $a = 9.861(7)$ ,  $b = 10.732(6)$ ,  $c = 10.822(7)$  Å,  $\alpha = 99.976(7)$ ,  $\beta = 113.714(8)$ ,  $\gamma = 91.109(7)^{\circ}$ ,  $U = 1027.7(11)$  Å<sup>3</sup>,  $T = 120$  K, space group  $P\bar{1}$ ,  $Z = 2$ ,  $\mu(\text{Mo-K}\alpha) = 0.164\text{ mm}^{-1}$ , 6375 reflections measured, 3488 unique ( $R_{\text{int}} = 0.0191$ ) which were used in all calculations. The final  $R1$  ( $I > 2\sigma(I)$ ) and  $wR2$  (all data) were 0.0371 and 0.1068, respectively.  $\text{GOF} = 1.089$ . CCDC 607217. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b615966d.
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