Quenching and Recovery of Fluorescence of Azobenzenes by Acid–Base Reactions

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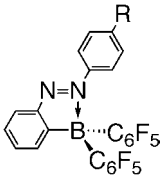
2-[Bis(pentafluorophenyl)boryl]-4′-(dimethylamino)azobenzene was synthesized as a hybrid of the intensely fluorescent 2-borylazobenzene and the pH-responsive 4-(dimethylamino)-azobenzene. Quenching and recovery of fluorescence of this azobenzene were reversibly performed by addition of trifluoroacetic acid and triethylamine, respectively. The reason of fluorescence quenching was investigated by theoretical calculations.

Stimuli-responsive molecules have been widely used for chemosensors. They convert various stimuli into color and/or luminescence changes as output.[1] Azobenzene is one of the most common and frequently used chromophores, and its deep color in the visible region, which can easily be recognized, is suitable for chemosensors as an output signal. One of the most famous examples of the azobenzene based stimuli-responsive molecules are 4-(dimethylamino)azobenzene derivatives, such as methyl yellow, methyl orange, and methyl red, which have been used as pH indicators.[2,3] Their colors can be switched reversibly by protonation and deprotonation. Meanwhile, stimuli-responsive change of fluorescence of azobenzenes have been quite rare,[4–6] because only a few intensely fluorescent azobenzenes themselves have been reported because of the non-emissive nature of azobenzene.[7] We recently reported the synthesis of fluorescent boron-substituted azobenzenes **1a** and **1b** in the continuation of our work on 2-borylazobenzene derivatives (Figure 1).[8–10] Hybridization of the 4-(dimethylamino)azobenzene structure and the fluorescent 2-borylazobenzene structure is expected to achieve switching of both fluorescence and absorption by protonation and deprotonation.[11] Here we report the synthesis and switching of the boron-substituted azobenzenes.

2-[Bis(pentafluorophenyl)boryl]-4′-(dimethylamino)azobenzene (**1c**) was synthesized as purple solid similarly to **1a** and **1b**. The ^{11}B NMR spectrum of **1c** (δ_B −0.9) in $CDCl_3$ suggested that **1c** had a tetracoordinated boron atom with B–N interaction.[12]

Azobenzene **1c** showed strong orange fluorescence in hexane solution at rt upon irradiation with a UV lamp ($\lambda = 254$ nm) in contrast to green fluorescence colors of **1a** and **1b**. In the fluorescence spectrum in hexane at rt, **1c** showed its emission maxima at 566 nm with a moderate fluorescence quantum yield ($\Phi_F = 0.52$), which was comparable to those of **1a** ($\Phi_F = 0.23$) and **1b** ($\Phi_F = 0.76$).



1a: R = H
1b: R = OMe
1c: R = NMe_2

Figure 1. 2-[Bis(pentafluorophenyl)boryl]azobenzenes **1a**–**1c**.

Addition of trifluoroacetic acid to **1c** in hexane caused significant change in both its visible absorption and fluorescence emission. In the UV–vis spectra, decrease in the absorbance at 516 and 543 nm (π–π^* transition) and corresponding increase in the new absorption at about 380 nm were observed (Figure 2). In the fluorescence spectra, decrease in the emission peak of **1c** was observed (Figure 3). When excess trifluoroacetic acid (35 μL, 7.4×10^4 equiv) was added to the hexane solution of **1c** (1.6 μM, 4 mL), in which the concentration of trifluoroacetic acid reached 1.2×10^2 mM, its color and fluorescence could not be recognized by visual observation. At that time, the fluorescence intensity was only 1.5% of the initial intensity. Addition of triethylamine (40 μL, 4.5×10^4 equiv) to the acidified solution of **1c** restored most of the intensity of both the absorption and fluorescence of the original solution of **1c**. In the fluorescence spectra, the intensity was 94% of the initial value. It was found that intensity of the fluorescence of **1c** can be controlled by an acid and a base. A pK_a value of the conjugated acid of **1c** was estimated to be −4.0 from change of the emission spectra during titration of trifluoroacetic acid.

The quenching of the fluorescence is ascribed to the protonation of **1c** by the acid, but there are two nitrogen atoms available for protonation (Scheme 1). Therefore, potential energies of the following two possible protonated products were calculated to determine which nitrogen was protonated: azonium **A** and ammonium **B** (Scheme 1). In the theoretical calculations at B3PW91/6-31G(d) level of theory, azonium **A** was more stable than ammonium **B** by 7.4 kJ/mol in the optimized structures of their cation parts. In addition, azobenzene **1a**, bearing no amino group, also showed fluorescence quenching by addition of trifluoroacetic acid. Both theoretical and experimental results suggested that the protonation at the azo group in **1c** to form

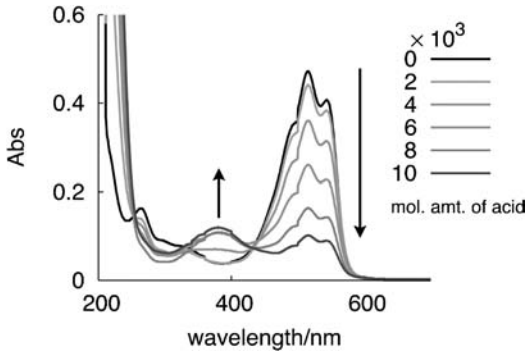


Figure 2. Change of UV–vis spectra of **1c** (8.4 μM) in hexane by addition of trifluoroacetic acid.

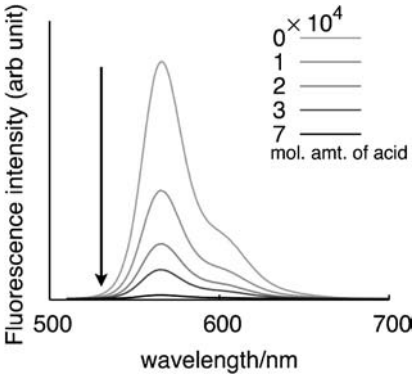
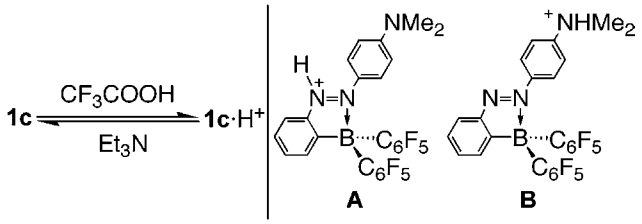


Figure 3. Change of fluorescence spectra of **1c** (1.6 μM) in hexane by addition of trifluoroacetic acid.



Scheme 1. Protonation and depotonation of **1c** and two possible protonated structures, **A** and **B**.

A in Scheme 1, was involved with the fluorescence quenching.

To reveal the reason why protonation of **1c** at the azo group leads to the fluorescence quenching, molecular orbitals and singlet excited states of **1c** and its protonated cation **A** were calculated by DFT and TD-DFT methods at B3PW91/6-31+G(d)//B3PW91/6-31G(d) level of theory. In **1c**, the HOMO (−6.0 eV) and the LUMO (−3.2 eV) are assignable to the π and π^* orbitals of the azobenzene moiety and the HOMO–1 (−6.9 eV) is assignable to the orbitals on the C_6F_5 groups. According to the TD-DFT calculation, excitation from the π orbital to the π^* orbitals of the azobenzene moiety of **1c** gives the lowest singlet excited state S_1. The π–π^* transition character of the transition between S_1 and the ground state makes this transition allowed (calculated oscillator strength $f = 0.6$) and would provide **1c** with relatively high emission efficiency. In the protonated cation **A**, the HOMO (−9.47 eV), LUMO (−7.4 eV), and HOMO–1 (−9.50 eV) are also mainly assignable to the π, π^*, and the orbital on C_6F_5 groups as shown in Figure 4. In **A**, the energy levels of the HOMO and HOMO–1 become almost equal. In this case, after the excitation from the π orbital to the π^* orbitals of the azobenzene moiety of **A** occurred, electron transfer from the C_6F_5 group to the azobenzene moiety can occur due to the closeness in the energy levels between the HOMO and HOMO–1. As a result, the transition from S_1 to the ground state is assigned to the forbidden transition between the HOMO–1 (orbitals of C_6F_5) and LUMO (π^*) (calculated $f = 8 \times 10^{-4}$). This is considered to be the main reason of almost no fluorescence efficiency upon protonation.

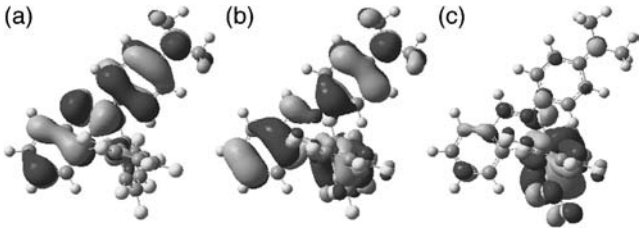


Figure 4. Diagrams of the frontier orbitals of **A**. (a) LUMO, (b) HOMO, and (c) HOMO–1.

In conclusion, new fluorescent 2-borylazobenzene was synthesized and its fluorescence was reversibly controlled by protonation and deprotonation with an acid and a base, respectively. The closeness in the energy levels between the π orbital of the azo group and the orbital on the C_6F_5 group induced by protonation of the azo moiety must be the key to the fluorescence quenching. Hybridization of intensely fluorescent azobenzenes and stimulus-response will produce easily tunable fluorescence chemosensors in the future.

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12 **1c**: purple solids, mp 180.1–184.0 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.11 (s, 6H), 6.60–6.66 (m, 2H), 7.36–7.44 (m, 2H), 7.53–7.57 (m, 1H), 7.91–7.97 (m, 2H), 8.05–8.09 (m, 1H). ^{11}B NMR (128 MHz, $CDCl_3$): δ −0.9 (line width $h_{1/2}$ = 279 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 40.14 (s, CH_3), 111.73 (s, CH), 115.97 (br s, CB), 124.91 (s, CH), 125.71 (s, CH), 127.91 (s, CH), 128.02 (s, CH), 132.82 (s, CH), 134.31 (s, CN), 135.56–138.38 (m, CF), 138.39–141.35 (m, CF), 146.15–149.04 (m, CF), 152.54 (br s, CB), 152.73 (s, CN), 156.25 (s, CN). ^{19}F NMR (376 MHz, $CDCl_3$): δ −162.82 to −162.63 (m, 4F), −156.77 (t, $^3J_{FF}$ = 22 Hz, 2F), −131.66 to −131.44 (m, 4F). MS (EI, 70 eV) m/z 569 (M^+, 100), 331 (32), 312 (49), 134 (21), 120 (22), 105 (16), 91 (10), 77 (19%). HRMS (FAB$^+$) m/z: calcd for $C_{26}H_{14}BF_{10}N_3$ 569.1121, found 569.1111. UV–vis (hexane) λ_{max} (ε) 218 (3.4×10^4), 265 (1.8×10^4), 516 (5.5×10^4), 544 nm (4.8×10^4 M^{-1} cm^{-1}). Anal. Calcd for $C_{26}H_{14}BF_{10}N_3$: C, 54.86; H, 2.48; N, 7.38%. Found: C, 55.10; H, 2.78; N, 7.34%.

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