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Organic Thermometers Based on Aggregation of Difluoroboron β -Diketonate Chromophores

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INTRODUCTION

emission property.

Reversible thermochromism is a perceptible phenomenon that emission color changes as a response to temperature variation over a certain range, and the original color could be restored once this external stimulus is removed.¹⁻⁹ This phenomenon is usually caused by thermal-induced changes in intermolecular interaction,¹⁰ molecular structures,^{11,12} or sample morphologies.¹³ Thermochromic luminescent materials find applications in a variety of fields ranging from decorative showpieces to potentially breakthrough technological applications, e.g., micro-electromechanical systems, marine researches, and aircraft industries.¹⁴⁻²¹ Most of the reported thermochromic luminescent materials were focused on temperature-induced conformational changes of polymer backbones,²² protontransfer-induced property changes of Schiff bases,23 thermal expansion properties regulation of Leuco dyes and liquid crystals,²⁴ or the arrangement and distribution of defects readjusting in a crystalline solid.²⁵ In addition, most of them use the luminescence intensity or lifetime changes of a single emission for temperature sensing. However, the photophysical properties of such single emission can be influenced easily by humidity, oxygen, excitation sources, or detectors.²⁶ Although the ratiometric luminescence thermometry improves the detection accuracy using the ratio change in emissions at two or more wavelengths, they always need some expensive metal ions with biological toxicity that further limits their practical applications.^{6,27-29} Therefore, it is of great significance to develop new thermometers with high sensitivity and accuracy.

for rationally designing high-performance thermometers having a wide

Molecular aggregation of organic chromophores always induce great changes in their physical and chemical properties due to the oriented association of molecules into nano- or microscopic structures through noncovalent interactions such as $\pi - \pi$ interaction, hydrogen bonding, dipole-dipole inter-action, charge transfer interaction, etc.^{2,30-35} Therefore, using temperature-induced aggregation properties of organic chromophores is possible to obtain a new kind of thermochromic luminescent materials with remarkable luminescent color changes. However, many reported organic luminescent materials show obvious aggregation-caused quenching (ACQ) phenomenon that the luminescence is almost quenched after aggregation. Although the materials with aggregation-induced emission (AIE) show strong emission properties after aggregation, their emission in a dilute solution is extremely weak.³⁶⁻³⁸ Thus, these two kinds of materials are not suitable for designing aggregation-induced thermochromic luminescent materials with intensive luminescence both in solution and aggregates.

Difluoroboron β -diketonate (BF2bdk) derivatives exhibit bright emission both in solution and aggregation states. Their emission properties are sensitive to their surroundings. The variation of molecular conformation and intermolecular

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Assembled nanospheres

interactions between BF2bdk molecules usually lead to significant variation in the emission color.^{10,39–53} These characteristics endow BF2bdk derivatives with great potential applications as high-performance thermochromic luminescent materials.

Herein, we report a series of thermometers based on the temperature-induced aggregation of difluoroboron β -diketonate chromophors **JBF1–4**. **JBF1** manifests a wide range of temperature-dependent emission wavelength from 445 to 592 nm in a dilute chloroform solution (as low as 10 μ M; Figures 1



Figure 1. Schematic representation of the temperature-induced aggregation process and the corresponding thermochromic mechanism: the chromophores gradually aggregate as the temperature decrease, which leads to changes in emission properties.

and S1) accompanied by a change in the fluorescence color from blue to red within a wide temperature range from 340 to 77 K. As the temperature decreases to the melting point of chloroform, an abrupt color change from green to orange is observed, and uniform spherical nanoparticles of about 15 nm are formed simultaneously. Experimental spectroscopy measurements and theoretical calculation analysis confirmed that the thermochromic luminescent is a result of reversible changes in noncovalent intermolecular interactions^{54–56} and the abrupt volume shrinkage at the solvent's melting point.

METHODS

Compounds JBF1,¹⁰ JBF2,¹⁰ and JBF4⁴³ were synthesized according to the previously reported literatures. JBF3 and XBF (Scheme 1) were synthesized in the overall yield of above 80%

Scheme 1. Molecular Structures of JBF1, JBF2, JBF3, JBF4, and XBF



by Claisen condensation from the related acetophenone and benzoate, followed by the complexation with borontrifluoride. They were well characterized by ¹H NMR, ¹³C NMR spectroscopy, and high-resolution mass spectroscopy (HRMS) (SI).

Synthesis of JBF3: acetophenone (1.00 g, 8.3 mmol) was added to 10 mL of anhydrous THF in a high-pressure tube under a N_2 atmosphere, NaH (57–63% oil dispersion, 1.00 g, 24.0 mmol), and Methyl m-Anisate (1.38 g, 8.3 mmol) was added to the mixture. The reaction mixture was allowed to stir

for 24 h at 60 °C under a N2 atmosphere. Upon cooling to room temperature, 100 mL of water was added to quench the reaction, the pH was adjusted to 3 with HCl (aq), and extracted with CH₂Cl₂. The combined organic phase was dried over anhydrous Na₂SO₄, followed by filtration and evaporation of the solvent. The crude product was then dissolved in 20 mL of dry CH₂Cl₂ and Et₃N (840 μ L, 6.0 mmol) and BF₃/Et₂O (3.8 mL, 30.0 mmol) were then added. After stirring at room temperature for 1 h in the dark, 100 mL of water was added, and the organic layer was collected, washed with saturated aqueous NH4Cl, and dried over anhydrous Na2SO4, followed by filtration and evaporation of the solvent. The crude product was then purified by column chromatography using CH₂Cl₂/ petroleum ether (1:2, v/v) as an eluent to afford 2.51 g of JBF3 as an orange solid (yield: 83%). ¹H NMR (400 MHz, chloroform-d) δ 8.15–8.02 (m, 2 H), 7.66 (t, J = 7.4 Hz, 1 H), 7.53 (t, J = 7.8 Hz, 2 H), 7.33 (S, 2 H), 7.08 (S, 1 H), 3.97 (d, J = 10.0 Hz, 9 H). ¹³C NMR (100 MHz, chloroform-d) δ 182.4, 153.4, 145.0, 135.1, 132.1, 129.2, 128.9, 126.6, 106.6, 93.2, 61.3, 56.6. HRMS: calc. for [M + H⁺] 363.1213, found: 363.1211.

Synthesis of **XBF**: To a solution of 1,3-diphenyl-1,3propanedione (1.00 g, 4.5 mmol) in 20 mL of CH₂Cl₂ was added Et₃N (840 μ L, 6.0 mmol) and BF₃/Et₂O (378 μ L, 30.0 mmol). After stirring at room temperature for 1 h in the dark, 100 mL of water was added, and the organic layers were collected, washed with saturated aqueous NH₄Cl, and dried over anhydrous Na₂SO₄, followed by filtration and evaporation of the solvent, purification by column chromatography using CH₂Cl₂/petroleum ether (1:2, v/v) as an eluent to afford 1.11 g of **XBF** as a yellow solid (yield: 92%). ¹H NMR (600 MHz, chloroform-d) δ 8.15 (d, *J* = 8.2 Hz, 4 H), 7.74–7.65 (m, 2 H), 7.56 (t, *J* = 7.9 Hz, 4 H), 7.19 (S, 1 H). ¹³C NMR (150 MHz, chloroform-d) δ 183.4, 135.4, 132.1, 129.3, 129.0, 93.5. HRMS: calc. for [M + Na⁺] 295.0712, found: 295.0712.

RESULTS AND DISCUSSION

The photophysical properties of JBF1 were investigated in different solvents, and the results are shown in Figure 2 and Table S1. The absorption band of JBF1 ranges from 330 to 425 nm, with an absorption peak at 390 nm (molar extinction coefficient: $10^4 \text{ M}^{-1} \text{ cm}^{-1}$), which were slightly affected by the polarity of the solvents (see Figure 2a). In contrast, the emission band of JBF1 red-shifts from 441 to 502 nm upon the increase in the solvent polarity, which indicates that JBF1 is of typical intramolecular charge transfer (ICT) character (see Figure 2b). The corresponding data for JBF2, JBF3, and JBF4 are summarized in Figures S2 and S3 and Table S2.

In addition to the red-shifting phenomena, the most important finding of **JBF1** is its remarkable temperaturedependent emission character in a dilute chloroform solution. As shown in Figure 2c, the fluorescence maximum gradually red-shifts from 445 to 592 nm when the temperature decreases from 340 to 77 K. Meanwhile, one can see an abrupt change in the emission peak from 490 to 575 nm at about 210 K.

To reveal the physical origin of the above novel thermal response behavior of the emission spectra, we measured the concentration-dependent fluorescence spectra of **JBF1** in the chloroform solution at room temperature (Figure 2d). Therein, a new broad emission band appears and gradually increases at 560 nm while the concentration of **JBF1** increases from 1 μ M to 300 mM. The lifetime of this new emission band is measured to be 28.5 ns, which is 17 times longer than that at

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Figure 2. (a) Absorption and (b) fluorescence spectra of JBF1 in different solvents, (c) temperature-dependent fluorescence spectra of JBF1 (100 μ M) in chloroform solution, and (d) concentration-dependent fluorescence spectra of JBF1 in chloroform solution at room temperature.

445 nm (1.7 ns) (Figure 4a). These results imply that the emission at 560 nm originates from the aggregates, such as dimers, while the emission at 445 nm is from the monomer.

To examine computationally the above proposal, we performed the density functional theory (DFT) and timedependent DFT (TD-DFT) calculations with the polarizable continuum medium (PCM) model that implicitly considers the solvent effects.^{57–68} Both monomer and dimer models were used to check the effects of the aggregation interaction (see the SI for details). Figure 3 shows the TD-B3LYP-D3/



Figure 3. TD-B3LYP-D3/PCM-calculated vertical emission energies of the monomer and dimer models of JBF1 in the chloroform solution.

PCM-calculated $S_1 \rightarrow S_0$ emission energies of the monomer and dimer models at their S_1 minimum-energy structures, as well as the relevant molecular orbitals. The vertical emission energies of the monomer and dimer models of **JBF1** in the chloroform solution were calculated to be 480 and 621 nm, respectively. Considering that the present theoretical calculations do not consider the temperature effects results, i.e., at 0 *K*, the theoretically calculated values agree well with the available experimental values at low temperatures (490 nm at 200 K and 600 nm at 77 K). This confirms that the emission bands at around 450 and 590 nm originate from the S₁ fluorescence emissions of the monomer and dimer of **JBF1**. A closer electronic structure analysis shows that the S₁ \rightarrow S₀ emission corresponds to de-excition of an electron from the lowest unoccupied molecular orbital (LUMO) to the highest occupied molecular orbital (HOMO) in both the monomer and dimer models. However, the strong intermolecular π - π interaction between the two monomers in the dimer model leads to much-stabilized LUMO and destabilized LUMO. As a result, the HOMO–LUMO energy gap is greatly reduced, 3.09 eV in the monomer vs 2.81 eV in the dimer (see Figure S5). This is the essential reason leading to a very red-shifted emission spectrum in the dimer model.

In terms of the experimental and computational results, we speculate that the thermochromic luminescent character is probably caused by the ordered transition from the monomer to aggregates such as dimers in dilute chloroform solution with the temperature reduction. One should notice that the fluorescence spectra of JBF1 gradually red-shifts with the concentration increase. This could be attributed to the formation of various aggregates (see Figure 2d). We also recorded the temperature-dependent fluorescence spectra of JBF1 (300 mM) in the chloroform solution (Figure 4b). In such a case, only the 560 nm emission band was observed at room temperature. Although the emission peak regularly redshifts from 560 to 595 nm with the decrease in temperature from 300 to 77 K, the abrupt spectral change was not observed. These experimental results further demonstrate that the abrupt spectral change at the melting point of JBF1 in a dilute solution was caused by the formation of temperature-induced aggregates.

According to the concentration- and temperature-dependent ¹H NMR spectra, the chemical shifts of the whole aromatic protons shift to a high magnetic field as the **JBF1** concentration is increased from 1 to 200 mM (Figure 4c).

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Figure 4. (a) Fluorescence decay profiles of the JBF1 monomer (445 nm) and aggregates (560 nm) at room temperature. (b) Temperaturedependent emission spectra of JBF1 (300 mM) in the chloroform solution. (c) Concentration-dependent ¹H NMR spectra of JBF1 in a *d*chloroform solution at room temperature and (d) temperature-dependent ¹H NMR spectra of JBF1 (1 mM) in the *d*-chloroform solution.



Figure 5. Temperature-dependent fluorescence spectra of **JBF1** (80 μ M) in (a) chloroform, (b) methanol solution, and (c) solid powder. (d) The photos of **JBF1** (80 μ M) in (d) chloroform solution at different temperatures and (e) methanol solution and (f) solid powder at 300 and 77 K under irradiation of 365 nm light-emitting diode (LED) lamp. High-resolution cryotransmission electron microscopy images of **JBF1** (80 μ M) in (g) chloroform and (h) methanol solutions. (i) The photos of a gradient fluorescence pattern of 80 μ M chloroform solution of **JBF1** in a quartz tube.

These phenomena are induced by the shielding effects between the aggregates at high concentrations. In contrast, the chemical shifts of JBF1 (1 mM) remain almost constant when the temperature drops from 330 to 220 K in a d-chloroform

solution (still above the melting point of *d*-chloroform; see Figure 4d). These experiments indicate that the aggregation processes were not completed because the system still stays as intermediate states on the way of final oligomers because the temperature remained higher than the melting point of chloroform.

Once the temperature drops below the melting point of chloroform, the fluorescence peak continues to red-shift to 592 nm. This phenomenon was also seen in our previously published work,¹⁰ which demonstrated that the thermochromism of **JBF1** crystals is caused by the temperature-induced changes of intermolecular distance and molecular conformation. Thus, further temperature decrease enhances the intermolecular interaction, therefore leading to a continuous red-shift of the emission wavelengths. To further confirm the thermal-induced aggregation behaviors, high-resolution cryotransmission electron microscopy was also implemented in the chloroform solution of **JBF1** (80 μ M). A uniform spherical nanoparticle of about 15 nm was observed at 77 K (Figure 5g).

Interestingly, as we recorded the temperature-dependent fluorescence spectra of JBF1 in methanol solution (Figure 5b,e), the fluorescence maxima remained almost constant throughout the whole temperature range. The regular selfassembled nanoparticles cannot be observed in methanol solution (Figure 5h). In consideration of the worse solubility of JBF1 in methanol than that in chloroform, it should be much easier to precipitate in methanol than in chloroform at low temperatures. Thus, we believe that the high polarity of methanol may have destroyed the intermolecular interactions and the temperature decrease was not enough to set off the intermolecular aggregation.

Pyrene is a kind of organic molecule that has a high tendency to aggregate in poor solution due to strong intermolecular $\pi - \pi$ interactions.^{69–71} In comparison to that of JBF1, the temperature-dependent fluorescence spectra of pyrene (100 μ M) in the chloroform solution was recorded. However, no obvious temperature-induced aggregation was observed. The aggregation was only observed when the concentration increased to 1 mM (Figure S6). The emission spectra also showed a ratiometric change from monomer (380 nm) to excimer (475 nm), which differs from that of JBF1. We also synthesized luminogen XBF with a similar structure to JBF1 but without any substituents in the phenyl group. The absorption and emission spectra of XBF are slightly influenced by the polarity of the solvent, which indicates weak charge transfer properties in XBF. No thermochromic luminescent properties are observed in its chloroform solution (Figure S7). The above results suggest that the introduction of alkyl or carbazole groups makes the distance and arrangement of molecules sensitive to external stimulation, further leading to the sensitive thermochromic luminescent properties.

A simple thermometer was prepared by adding the dilute chloroform solution of **JBF1** in a quartz tube (Figure 5i). We put the bottom of the quartz tube into liquid nitrogen and leave the top in ambient surroundings. The temperature-induced color gradient from blue via green to orange was observed as the temperature decreased from the top (300 K) to the bottom (77 K). Meanwhile, a good linear relationship between the fluorescence maxima and temperature in these two continuous thermochromic stages was obtained, which can be fitted to the equations of $T = 1269.6-2.17 \lambda$ and $T = 3561.2-5.88 \lambda$ (correlation coefficients: 0.9976 and 0.9924; Figure S8), where T is the temperature and λ is the

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fluorescence maxima. The discontinuous thermochromic stage at the melting point of chloroform can be responded to the temperature variation from 215 to 205 K with a distinct color change from green to orange. To evaluate the luminescence stability of these complexes, the chloroform solutions of JBF1-4 are irradiated at ambient surroundings for 10 h by a 5 W LED lamp. The emission intensity of all samples has no obvious change in the whole irradiating duration, indicating the high luminescence stability (Figure S9). The reversibility of JBF1 in chloroform solution is also conducted by measuring 10 cycles of the thermochromic procedures, and the emission spectrum of each cycle is basically unchanged (see Figure S10). Thus, the good photoluminescence quantum yield (PLQY) (Table S1), clear color change, wonderful stability, and reversibility contributed to JBF1 being a good candidate for a high-performance thermometer.

CONCLUSIONS

In summary, we reported a series of highly sensitive thermometers based on the temperature-induced aggregation of difluoroboron β -diketonate chromophores. The luminescence properties of **JBF1** in a dilute solution was distinct with aggregates, which leads to a wide range of temperaturedependent emission wavelength from 445 to 592 nm accompanied by a fluorescence variation from blue to red in chloroform. Both spectroscopy measurements and theoretical calculations demonstrate that the thermochromic luminescence property should be ascribed to the reversible changes of intermolecular interactions and the abrupt volume shrinkage of the solvent at the melting point. The thermochromic luminescent materials based on the aggregation of organic chromophores provide a new strategy for the design of thermometers with high sensitivity.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.0c08649.

Experimental methods, synthesis and characterization, computational details, and supplementary figures and tables are included (PDF)

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Notes

The authors declare no competing financial interest.

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