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Nanofibers generated from nonclassical organogelators based on difluoroboron β-diketone complexes to detect aliphatic primary amine vapors

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New D-A-D type difluoroboron β-diketone complexes with terminal triphenylamines ABA, ABVA and AVBV A were synthesized. It was found that the stable organogels could be gained from ABVA and AVBV A without traditional gelation groups in the mixed solvents containing 1,4-dioxane, and the balanced π-π interactions were the driving forces for the gel formation. Interestingly, the organogels based on ABVA and AVBV A exhibited the emission closing to NIR (near infrared) region. To the best of our knowledge, such narrow band gap low molecular-weight π-gelator has not been reported. In particular, the xerogel-based films generated from ABVA and AVBV A could be used as sensors to detect gaseous aliphatic primary amines with high performance. For example, exposing to saturated n-butylamine and n-propylamine vapors for 30 s, the emission of the films was quenched completely and new strong emission at ca. 560 nm appeared on account of the decomposition of the difluoroboron β-diketone complexes.

Introduction

Detection of volatile organic amines is of great interest in the fields of environmental pollution monitoring and control, food safety, and even medical diagnosis. 1-9 To date, some approaches for detecting organic amines, such as electrochemical devices, 10 gas or liquid chromatography, 11 and various chemical sensors, 12 have been employed. Particularly, fluorescent sensors for detecting amines have received much attention because of high sensitivity, high selectivity, local observation and remote sensing. 13 Recently, some sensory materials based on self-assembled fluorescent fibrous films have been developed for detecting organic amine vapors due to their high sensitivity. For example, Zang and co-workers have reported a sensor based on nanofibers fabricated from n-type organic semiconductor for detecting organic amine vapors. 14,15 Mohr et al. have employed fluorescent dye-based membranes for probing lipophilic primary amines with high sensitivity and selectivity via reversible chemical reactions. 16,17 Fang and co-workers have reported an ultrasensitive fluorescent sensing film based on cholesterol-modified perylene bisimide for detecting organic amines. 18 Our group also developed emitting fibrous-based films fabricated from boron diketone complexes for probing organic amines. 19 We have found that the conjugated molecules with V-shaped π-skeleton preferred to self-assemble into 1D nanofibers in an organogel phase directed by balanced (neither too strong nor too weak) π-π interactions, 20 and the fluorescent organogel nanofibers-based films could become good candidate in sensory materials. 19a Although the organogelation of π-gelators became a facile approach to fabricate functional organic nanostructures, the gelators without traditional gelation groups (such as long carbon chain, cholesterol, hydrogen-bonded units, etc.) were seldom reported. 20 On the one hand, the preparation of nonclassical organogelators without traditional gelation groups would fulfill the atom economy in the synthesis. On the other hand, the obstacles of the information transformation between conjugated systems would be avoided because of the absence of the domain formed from long carbon chains. Previously, we have found that the difluoroboron β-diketone complexes with V-shaped conjugated skeleton exhibited good gelation ability. 20b With this in mind, we synthesized new V-shaped triphenylamine functionalized difluoroboron β-diketone complexes ABA, ABVA and AVBV A (Scheme 1), whose conjugation increased in sequence. We deemed that the increased conjugation would lead to the low-energy region emission. To the best our knowledge, there is no report on the organogel with the emission quite closing to NIR region, which would have potential applications in biological imaging. It was
found that ABVA and AVBVA without traditional gelation groups could form stable organogels in the mixed solvents containing 1,4-dioxane. The fluorescence emission of xerogel-based films generated from ABVA and AVBVA emerged at 710 nm and 745 nm, respectively. Interestingly, the emission of the xerogel-based films of ABVA and AVBVA could be quenched by n-propylamine and n-butylamine vapors, accompanied with the appearance of new strong emission at ca. 560 nm on account of the decomposition of the boron complexes. Other selected organic amines only quenched the emission of films because of the weak interactions between amines and boron complexes. Therefore, the nanofibers generated from nonclassical gelators of some difluoroboron β-diketonate complexes via organogelation could detect gaseous aliphatic primary amines with high performance.

Synthesis

The synthetic routes for ABA, ABVA and AVBVA were shown in Scheme 1. Firstly, compounds 1–5 were prepared according to the reported procedures. The Claisen condensation reaction between compounds 1 and 2 was carried out in anhydrous THF in the presence of sodium hydride to afford the intermediate of β-diketone, which was not further purified and complexed with boron trifluoride-dimethyl etherate directly in anhydrous CH₂Cl₂ to yield complex ABA in a yield of 52%. Similarly, the Claisen condensation reaction between compound 1 and ethyl acetate, followed by complexed with boron trifluoride-diethyl etherate, afforded compound 3 in a yield of 46%. Then, the Knoevenagel condensation reaction between compounds 3 and 4-(diphenylamino)benzaldehyde 4 in the presence of piperidine in anhydrous THF gave ABVA in a yield of 27%. Complex AVBVA was synthesized via the Knoevenagel condensation reaction between compounds 4 and 5 in a yield of 45%. The target complexes were characterized by ¹H NMR, ¹³C NMR, FT-IR and MALDI-TOF mass spectrometries. In ¹H NMR spectrum of AVBVA, the coupling constants of peaks at 7.98 ppm and 6.60 ppm were 16.0 Hz, meaning the trans-form of vinyl group. Similarly, we deduced that the vinyl groups in AVBVA also existed in trans-forms.

Results and discussion

Photophysical properties in solutions

The UV-vis absorption and fluorescence emission spectra of ABA, ABVA and AVBVA in different solvents were shown in Figure 1, and the corresponding photophysical data were summarized in Table S1†. It was clear that the absorption band of ABA appeared at 488 nm in cyclohexane, which red-shifted to ca. 501 nm in toluene, THF and acetone with moderate polarity and to 516 nm in DMSO with high polarity (Figure 1a, Table S1†). It suggested that the maximal absorption band of ABA could be ascribed to charge-transfer (CT) transition. In the cases of ABVA, the structured absorption peaks emerged at 501 nm and 527 nm in cyclohexane, and only one strong absorption band was detected in other solvents. For example, the absorption of ABVA appeared at 539 nm and 560 nm in THF and in DMSO, respectively (Figure 1b). Similar solvent-dependent absorption spectral changes were also observed for AVBVA (Figure 1c). Therefore, the absorption bands for ABVA and AVBVA were also originated from CT transitions. It should be noted that with increasing the molecular conjugated length of difluoroboron β-diketone complexes, the absorption bands red-shifted obviously, for instance, the absorption of ABA, ABVA and AVBVA emerged at 500 nm.
541 nm and 574 nm in toluene. As shown in Figure 1d-f, the emission bands of ABA, ABVA and AVBVA red-shifted obviously with increasing solvent polarities. For example, the emission peak of ABVA was located at 533 nm in cyclohexane and 678 nm in DMSO. Thus, the Stokes shifts increased obviously with increasing solvent polarities, and they were 892 cm\(^{-1}\) and 3108 cm\(^{-1}\) in cyclohexane and DMSO, respectively. Besides, ABVA was highly emissive in toluene with a fluorescence quantum yield (\(\Phi_F\)) of 0.70 using fluorescein in 1 M NaOH (\(\Phi_F = 0.95\)) as the standard, but it was almost non-emissive in DMSO. The red-shift and the broadening of the emission bands, as well as the decrease of \(\Phi_F\) for ABVA with increasing solvent polarities illustrated the occurrence of ICT. Similarly, the emission of ABA and AVBVA was also originated from ICT transitions. Meanwhile, we found that the emission bands of ABVA and AVBVA appeared in low energy region compared with ABA on account of their extended conjugation. For example, the emission of ABA was located at 552 nm and red-shifted to 590 nm and 621 nm for ABVA and AVBVA in toluene. It was noticed that the \(\Phi_F\) values of ABA and AVBVA reached 0.97 and 0.82, respectively, in toluene, meaning high emissive in non-polar solvents of the synthesized difluoroboron \(\beta\)-diketonate complexes.

### Electrochemical properties

The cyclic voltammograms of the synthesized difluoroboron \(\beta\)-diketonate complexes were shown in Figure S1†. The well-defined reversible reduced peaks with half-wave potentials of -0.93 V, -0.73 V and -0.72 V versus ferrocenium/ferrocene were detected for ABA, ABVA and AVBVA, respectively (Table 1). The reductive half-wave potentials reduced in the order of AVBVA > ABVA > ABA because the conjugation increased with increasing the number of vinyl group. The HOMO and LUMO energy levels were calculated using the empirical equations: \(E_{LUMO} = -(E_{red} + 4.8)\) and \(E_{HOMO} = E_{LUMO} - E_g\), in which \(E_g\) was estimated from the onset of the absorption spectrum (\(E_g = 1240/\lambda_{onset}\)). The HOMO energy levels of ABA, ABVA and AVBVA were -5.32 eV, -5.31 eV and -5.18 eV, respectively, and the LUMO energy levels of ABA, ABVA and AVBVA were estimated to be -3.11 eV, -3.31 eV and -3.32 eV, respectively (Table 1). The HOMO-LUMO energy gap of AVBVA was only 1.86 eV, so that we found its absorption as well as emission bands emerged in low energy region.

![Figure 1](image1.png)  
**Figure 1.** Normalized UV-vis absorption spectra of ABA (a), ABVA (b) and AVBVA (c), and fluorescence emission spectra of ABA (d, \(\lambda_{ex} = 515\) nm), ABVA (e, \(\lambda_{ex} = 560\) nm) and AVBVA (f, \(\lambda_{ex} = 598\) nm) in different solvents (2.0 × 10\(^{-3}\) M).

![Figure 2](image2.png)  
**Figure 2.** Energy levels and molecular orbital surfaces in the optimized ground-state structures of ABA, ABVA and AVBVA, in which hexadecyl groups were omitted.
that ICT would take place for the three complexes. That was why ICT would take place for the three complexes. Additionally, quantum chemical calculations were performed on the selected solvents by means of the “stable to unstable” set method. As shown in Figure 2, we could find that the LUMO of ABA, ABVA and AVBVA were mainly distributed in the central difluoroboron β-diketone units. The HOMO of AVBVA mainly distributed at the terminal triphenylamine units, suggesting D-A-D type π-skeleton. The molecular orbital distributions of ABA and ABVA were similar to that of AVBVA. That was why ICT would take place for the three complexes. In addition, the calculated HOMO energy levels of ABA, ABVA and AVBVA were similar to those based on electrochemical results. Although the calculated LUMO energy levels were higher than the data from electrochemical results, they were in the same order of AVBVA < ABVA < ABA.

Gelation properties

The gelation properties of ABA, ABVA and AVBVA were tested in the selected solvents by means of the “stable to unstable” set method. The results were listed in Table 2. The gels could be gained from ABA and ABVA in the mixed solvents containing 1,4-dioxane, such as 1,4-dioxane/cyclohexane (v/v = 1/4), Figure S2†, 1,4-dioxane/n-hexane (v/v = 1/2), 1,4-dioxane/n-heptane (v/v = 1/2), 1,4-dioxane/n-octane (v/v = 1/2), after the hot solutions were first stimulated by ultrasound for few seconds and then were cooled to room temperature. The critical gelation concentrations (CGC) of ABA and AVBVA depended on the solvents and varied in the range of 4.0–7.7 mmol/L and 6.8–33.3 mmol/L, respectively. The obtained gels of AVBVA were stable for several months at room temperature, while the gels of AVBVA disappeared after standing at room temperature for several hours. It indicated that ABVA exhibited better gelation abilities than AVBVA. The formed gels could be transformed into solutions upon heating, which could recover to organogels upon stimulation by ultrasound, followed by cooling. However, complex ABA, in which two triphenylamines were directly linked to difluoroboron β-diketone unit, could not form any gel in the selected solvents due to its good solubility. The introduction of vinyl group between triphenylamine and difluoroboron β-diketone moieties would increase the conjugation degree, so that π–π interaction would play a role in the gel formation of ABA and AVBVA, which will be discussed below. Additionally, we deemed that the reason for better gelation ability of ABVA than AVBVA was that the strong π–π interaction between AVBVA molecules might lead to high crystallization, leading to poor gelation ability. Therefore, the gelation ability of the nonclassical π-gelators could be tuned by theoretical methods.

Theoretical calculation

Table 1 Electrochemical data and HOMO/LUMO energy levels of ABA, ABVA and AVBVA.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{\text{onset}}^{\text{ox}}$ (V)</th>
<th>$E_{\text{HOMO}}$ (eV)</th>
<th>$E_{\text{LUMO}}$ (eV)</th>
<th>$E_1$ (eV)</th>
<th>$E_{\text{HOMO}} - E_{\text{LUMO}}$ (eV)</th>
<th>$E_{\text{LUMO}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABA</td>
<td>-0.93</td>
<td>-5.32</td>
<td>-3.11</td>
<td>2.21</td>
<td>-5.32</td>
<td>-2.48</td>
</tr>
<tr>
<td>ABVA</td>
<td>-0.73</td>
<td>-5.31</td>
<td>-3.31</td>
<td>2.00</td>
<td>-5.23</td>
<td>-2.61</td>
</tr>
<tr>
<td>AVBVA</td>
<td>-0.72</td>
<td>-5.18</td>
<td>-3.32</td>
<td>1.86</td>
<td>-5.17</td>
<td>-2.69</td>
</tr>
</tbody>
</table>

$E_{\text{onset}}^{\text{ox}}$ (V) = onset reduction potential; Fc/Fc was used as external reference. $E_{\text{LUMO}} = -(E_{\text{onset}}^{\text{ox}} + 4.18)$; $E_{\text{HOMO}} = E_{\text{LUMO}} - E_1$. Determined from the onset of the absorption at the lower energy band edge ($E_g = 1240/\lambda_{\text{onset}}$). Calculated data.

Table 2 Gelation abilities of complexes ABA, ABVA and AVBVA in organic solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ABA (CGC/mM)</th>
<th>ABVA (CGC/mM)</th>
<th>AVBVA (CGC/mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane</td>
<td>I</td>
<td>I</td>
<td>I</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>I</td>
<td>I</td>
<td>I</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>I</td>
<td>I</td>
<td>I</td>
</tr>
<tr>
<td>n-Octane</td>
<td>I</td>
<td>I</td>
<td>I</td>
</tr>
<tr>
<td>tert-Amyl alcohol</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Chloroform</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>DMF</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>DMSO</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>THF</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>1,4-Dioxane/n-Hexane (v/v = 1/2)</td>
<td>S</td>
<td>G (7.1)</td>
<td>G (9.1)</td>
</tr>
<tr>
<td>1,4-Dioxane/Cyclohexane (v/v = 1/4)</td>
<td>S</td>
<td>G (4.0)</td>
<td>G (6.8)</td>
</tr>
<tr>
<td>1,4-Dioxane/n-Heptane (v/v = 1/3)</td>
<td>S</td>
<td>G (8.7)</td>
<td>PG</td>
</tr>
<tr>
<td>1,4-Dioxane/n-Heptane (v/v = 1/2)</td>
<td>S</td>
<td>PG</td>
<td>G (16.7)</td>
</tr>
<tr>
<td>1,4-Dioxane/n-Octane (v/v = 1/2)</td>
<td>S</td>
<td>G (7.7)</td>
<td>PG</td>
</tr>
<tr>
<td>1,4-Dioxane/n-Octane (v/v = 1/1)</td>
<td>S</td>
<td>PG</td>
<td>G (33.3)</td>
</tr>
</tbody>
</table>

I: insoluble; P: precipitate; PG: partly gel; S: soluble; G: gel.

Figure 3. SEM images of xerogels ABVA (a) and AVBVA (b) obtained from 1,4-dioxane/cyclohexane (v/v = 1/4).
the strength of π-π interaction, and the balanced π-π interaction would be yielded from moderate conjugation degree and then promoted the gel formation. The morphologies of the xerogels ABVA and AVBVA obtained from 1,4-dioxane/cyclohexane (v/v = 1/4) were observed by SEM investigation (Figure 3). We could find that lots of straight and long fibers in diameters of ca. 200-500 nm were formed in the xerogel ABVA. However, AVBVA self-assembled into short and thick rods with diameters of 0.5-1.0 μm. Thus, the formed 3D networks consisting lots of nanofibers made the gel of ABVA more stable than the gel of AVBVA.

Figure 4c showed the time-dependent fluorescence emission spectra of ABVA upon cooling the hot solution, which was first stimulated by ultrasound, to room temperature. It was clear that ABVA emitted strong red light with an emission at 653 nm in hot solution. During the gelation process, the emission band red-shifted gradually, accompanying with the decrease of the emission intensity. However, the organogel of ABVA still exhibited strong red emission centered at 702 nm (inset in Figure 4c). Similarly, AVBVA gave a strong emission at 606 nm in hot solution, which red-shifted to 730 nm and decreased dramatically in gel state. Such aggregation-caused quenching of the emission further suggested that π-aggregates were formed in organogels.24

Figure 5a showed the XRD pattern of xerogel ABVA deposited on glass slide and (b) Schematic illustration of the layered structure with the period of 1.64 nm in organogel AVBVA.

In order to reveal the driving force for the gelation, the UV-vis absorption and fluorescence emission spectra of ABVA and AVBVA in solutions and in gel phases were compared. As shown in Figure 4a, the maximal absorption peaks of ABVA in solution and in gel state were both located at ca. 528 nm, but a new absorption peak at 600 nm emerged in gel state. It indicated that π-π interaction happened in the gel of ABVA.23 Unlike ABVA, the maximal absorption peaks of AVBVA was little red-shifted in gel state compared with in solution and a new strong absorption band at 650 nm emerged in gel state. We speculated that the new strong absorption bands were originated from strong π-π interaction due to the larger conjugation degree of AVBVA. It also indicated that π-π interaction played a key role in gel formation of AVBVA.23 Moreover, it suggested that the balanced π-π interaction could lead to the gel formation of nonclassical π-gelators without alkyl chain and H-bonding units.

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propylamine vapor (Figure 6). When the concentration of n-propylamine vapor increased to $1.3 \times 10^4$ ppm, a new emission peak at 591 nm emerged. With further increasing the quantity of n-propylamine vapor, the new emission peak blue-shifted gradually. When the film was exposed to saturated n-propylamine vapor ($3.3 \times 10^5$ ppm) for 30 s, the emission peak at 710 nm disappeared completely and the new emission peak blue-shifted to 564 nm. At the same time, the emitting color of film changed from dark red to bright yellow (the insets of Figure 6), so the film based on nanofibers of ABVA could sense n-propylamine vapor by naked eyes.

In order to understand the fluorescence sensory mechanism of ABVA in the nanofibers-based film towards gaseous n-propylamine, the UV-vis absorption and fluorescence emission spectral titration experiments were performed. As shown in Figure 7a, the emission peak at 592 nm for ABVA in toluene reduced gradually with the increasing amount of n-propylamine. A new emission at 415 nm emerged when the equiv. of n-propylamine reached $1.5 \times 10^5$ versus fluorescent probe, and its intensity increased gradually upon adding more n-propylamine. When $9.0 \times 10^5$ equiv. of n-propylamine was added, we could only find one emission band at 410 nm. It was clear that the fluorescence spectral changes for ABVA induced by n-propylamine in toluene and in xerogel-based film were similar, so was the sensing mechanism. Figure 7a showed that the maximal absorption peak at 541 nm for ABVA decreased gradually with the increasing amount of n-propylamine, accompanying with the appearance of new absorption at 372 nm. When the equiv. of n-propylamine increased to $9.0 \times 10^5$ versus ABVA, the absorption at 541 nm disappeared completely. The isobestic point at 404 nm was observed, suggesting new species was yielded from ABVA induced by n-propylamine. In addition, we also found similar UV-vis absorption spectral changes for the xerogel-based film of ABVA upon exposure to n-propylamine (Figure S4†), further suggesting similar sensory mechanisms in solution as well as in xerogel-based film. To verify this speculation, 1H NMR spectra of ABVA in CDCl$_3$ before and after adding n-propylamine were compared. As shown in Figure S5, two new signals at 5.60 ppm and 11.37 ppm were found when excess of n-propylamine was added. The new signal at 11.37 ppm was probably assigned to the hydrogen in hydroxyl group of the enol form for β-diketone and another one at 5.60 ppm may be ascribed to the hydrogen in methylene in β-diketone. Moreover, when a drop of D$_2$O was added to the above system containing ABVA and n-propylamine in CDCl$_3$, the signal at 11.37 ppm disappeared. It further illustrated that it was originated from active hydrogen. Therefore, we suggested that n-propylamine could attract electron-deficient boron unit in the complex to lead to the decomposition of difluoroboron β-diketoneate, and β-diketone might probably one of the main deposited product. Additionally, the UV-Vis absorption and fluorescence spectral changes of ABVA in xerogel-based film were similar to those of ABVA upon exposure to n-propylamine vapor (Figure S6†). It meant that the sensory mechanism of ABVA in response to n-propylamine was same as that of ABVA.

Moreover, we also studied the fluorescence response behaviors of ABVA in xerogel-based film upon exposure to other amines and pyridine. As shown in Figure S7†, the

**Figure 6.** Fluorescence emission spectra of the xerogel-based film of ABVA upon exposure to n-propylamine in different concentrations (ppm) for 30 s ($\lambda_{ex} = 360$ nm). Insets: the xerogel films before and after exposed to saturated n-propylamine vapor under UV irradiation.

**Figure 7.** UV-vis absorption (a) and fluorescence emission (b, $\lambda_{ex} = 360$ nm) spectra of ABVA in toluene ($2.0 \times 10^{-4}$ M) upon adding different amount of n-propylamine.
fluorescence spectral changes of ABVA in xerogel-based films induced by n-butylamine were similar to n-propylamine, so we deemed that n-butylamine could also decompose ABVA. However, the other selected amines (such as triethylamine, tributylamine, aniline and cyclohexylamine) and pyridine could only quench the emission of ABVA in the film to various extents, and no new emission peak emerged, due to the weak interactions between amine and the boron complex unit in ABVA. Therefore, the nanofibers-based film fabricated via the organogelation of nonclassical organogelators ABVA and AVBVA could be used as fluorescence sensory materials to detect aliphatic primary amine vapors selectively by naked eyes.

Conclusions
Three new D-A-D type triphenylamine functionalized difluoroboron β-diketone complexes ABA, ABVA and AVBVA were synthesized. It was found that ABVA and AVBVA, in which one triphenylamine unit or two triphenylamine units were linked to difluoroboron β-diketone by vinyl spacer, exhibited gelation ability in some mixed solvents containing 1,4-dioxane. They were nonclassical organogelators without long alkyl chains and hydrogen-bonded units. The UV-vis absorption and fluorescence emission spectra of ABVA and AVBVA in solutions and in gel phases revealed that π-π interaction played an important role in gel formation. Moreover, the emission of ABVA and AVBVA in xerogels appeared closing to NIR region. Interestingly, the vapors of n-propylamine and n-butylamine could quench the emission of ABVA and AVBVA in xerogel-based films, accompanied with the appearance of new strong emission at ca. 560 nm. Therefore, the emitting colors of the films changed from dark red to bright yellow. The UV-vis absorption titration experiment and 1H NMR spectral change for ABVA upon adding n-propylamine illustrated that the aliphatic primary amines could lead to the deposition of difluoroboron β-diketone complexes. Therefore, this kind of fluorescent organogels could be used as probes to detect aliphatic primary amines selectively.

Experimental section
Measurement and characterizations
1H NMR and 13C NMR spectra were recorded with a Mercury Plus instrument at 400 MHz and 100 MHz in CDCl3 in all cases. FT-IR spectra were recorded with a Nicolet-360 FT-IR spectrometer by incorporation of samples into KBr disks. UV-vis absorption spectra were obtained on a Shimadzu UV-3100 spectrophotometer. Fluorescent emission spectra were obtained on a Cary Eclipse fluorescence spectrophotometer. Cyclic voltammetry spectra were measured on a CHI 604C voltammetric analyzer with a scan rate at 50 mV/s. A three electrode configuration was used for the measurement: a platinum button as the working electrode, a platinum wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The solution of (C4H9)3NBF4 in CH2Cl2 (0.1 M) was used as the supporting electrolyte. Mass spectra were obtained with Agilent 1100 MS series and AXIMA CFR MALDI-TOF (Compact) mass spectrometers. XRD patterns were obtained on an Empyrean X-ray diffraction instrument. Scanning electron microscopy (SEM) was performed on JEOL JSM-6700F (operating at 5 kV). The samples were prepared by casting the organogels on silicon wafers and dried at room temperature, followed by coating with gold.

Preparation of the organogels and xerogel-based films
A clear solution of ABVA or AVBVA in 1,4-dioxane/cyclohexane (v/v = 1/4) was obtained by heating. After the hot solution was suffered a sonification for 10 s, followed by aging for 10 min at room temperature, the gel was formed. After diluting the gel of ABVA or AVBVA into a “poor” solvent of n-hexane, well-dispersed nanofibers were produced. The mesh-like films were fabricated after casting the nanofibers in n-hexane onto the substrates, followed by the natural evaporation of the solvent.

Investigation on the fluorescence sensory properties
The sensory investigations for the xerogel-based films of ABVA and AVBVA were carried out at 25 °C. Firstly, the organic amine vapors and other analytes at a certain concentration were obtained by diluting the saturated vapors with nitrogen, and then injecting them into a quartz cell (10 mm in width) containing the film. The changes in the emission intensity and wavelength were recorded after injection of the organic amine or other interference vapors for 30 s.

Materials
CH2Cl2 was dried over calcium hydride. THF was dried over sodium and diphenyl ketone. The other reagents were used as received without further purification.

Synthesis
4,6-bis(4-(diphenylamino)phenyl)-2,2-difluoro-2H-1,3,2-dioxaborin-1-ium-2-uide (ABA)
1-(4-(Diphenylamino)phenyl)ethanone 1 (0.5 g, 1.74 mmol) and methyl 4-(diphenylamino)benzoate 2 (0.53 g, 1.74 mmol) were dissolved in dry THF (20 mL) under an atmosphere of nitrogen. Then, NaH (0.1 g, 4.17 mmol) was added. After the mixture was stirred at 60 °C for 24 h, followed by poured into ice water (200 mL), HCl (6 M, 5 mL) was added to neutralize excess NaH. The mixture was extracted with CH2Cl2 (3 × 50 mL), and the organic phase was combined and dried over anhydrous magnesium sulfate. After removal of solvent, the residue was used directly in the next step without purification. The solution of the β-diketone of 1,3-bis(4-(diphenylamino)phenyl)-3-hydroxyprop-2-en-1-one in dry dichloromethane (50 mL) was heated to reflux under an atmosphere of nitrogen, excess BF3·Et2O (0.5 mL) was added. The mixture was refluxed for 2 h. After the solvent was removed, the residue was purified by column chromatography (silica) using petroleum ether/CH2Cl2 (v/v = 1/1) as eluent, followed by recrystallization from the mixed solvent of CH2Cl2.
and light petroleum to afford ABA as dark red solid in a yield of 48\%. m.p.:134.0-136.0 °C; 1H NMR (400 MHz, CDCl3), δ (ppm): 7.95 (d, J = 8 Hz, 4H), 7.39 (t, J = 2 J = 8 Hz, 8H), 7.25-7.21 (m, 12H), 7.01 (d, J = 4Hz, 4H), 6.90 (s, 1H), (Figure S8†); 13C NMR (100 MHz, CDCl3), δ (ppm): 178.87, 153.62, 145.73, 130.36, 129.85, 126.50, 125.58, 123.41, 118.91, 91.01, (Figure S9); MALDI-TOF MS: m/z: calculated: 606.2; found: 588.4 [M- F + H]+ (Figure S10†); FT-IR (KBr, cm-1): 3442, 1542, 1481, 1387, 1296, 1000, 756, 698.

![Image](image-url)

Figure S4: 3442, 1542, 1481.

4.6-bis((E)-4-(di phenylamino)styryl) -2,2-difluoro-2H,1.3,2-
dioxaborin-1-ium-2-uide (ABVA)

The synthetic method for ABVA was similar to that for ABVA except using compounds 4 (2.5 g, 9.15 mmol) and 2,2-
difluoro-4,6-dimethyl-2H,1,3,2-dioxaborin-1-ium-2-uide (5) (0.54 g, 3.65 mmol) as reactants. The crude product was purified by column chromatography (silica) using petroleum ether/CH2Cl2 (v/v = 1/10) as eluent, followed by recrystallization from the mixed solvent of CH2Cl2 and light petroleum to afford ABVA as black solid in a yield of 43\%. m.p.:148.0-150.0 °C; 1H NMR (400 MHz, CDCl3), δ (ppm): 7.95 (d, J = 16 Hz, 2H), 7.43 (d, J = 8 Hz, 4H), 7.35-7.31 (m, 8H), 7.15 (t, J = 8 Hz, J = 8 Hz, 12H), 6.98 (d, J = 8 Hz, 4H), 6.52 (d, J = 16 Hz, 2H), 5.96 (s, 1H) (Figure S17†); 13C NMR (100 MHz, CDCl3), δ (ppm): 151.29, 146.29, 130.70, 129.68, 126.79, 126.02, 124.85, 120.54, 117.38, 101.75 (Figure S18†); MALDI-TOF MS: m/z: calculated: 658.0; found: 659.0 [M+H]+ (Figure S19†).

Notes and references

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- Electronic Supplementary Information (ESI) available: 1H NMR, 13C NMR, MALDI/TOF MS and CV spectra; Photophysical data for target molecules; Fluorescent sensory properties. See DOI: 10.1039/x0xx00000x


Graphic Abstract For:

Nanofibers generated from nonclassical organogelators based on difluoroboron β-diketonate complexes to detect aliphatic primary amine vapors

Narrow band gap nonclassical π-organogelators self-assembled into nanofibers for detecting primary amine vapors via the decomposition of difluoroboron β-diketonate complexes.