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## Color-tunable and highly solid emissive AIE molecules: synthesis, photophysics, data storage and biological application†

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In this work, several new compounds containing tetraphenylene (TPE) units and dimesitylboron groups were synthesized through Sonogashira coupling reaction. The compounds showed aggregation induced emission (AIE), emitted different colors and gave a relatively high quantum yield of fluorescence in the solid state. Two of the compounds demonstrated potential application in data storage, and one molecule also displayed potential value in biological fluorescence cell imaging.

### Introduction

The luminescent organic molecules have attracted much interest due to their wide range of applications in electronics, optics, storage media, and biological science.<sup>1</sup> For most practical applications, luminescent materials are usually utilized in the solid state but not in solution,<sup>2</sup> thus the development of highly emissive fluorescent materials in the solid state has been an active research topic. It is known that organic luminophores often suffer from partial or even complete quenching of their fluorescence in the solid state because of aggregation. This effect of aggregation caused quenching (ACQ) limited the application of fluorescent materials.<sup>3</sup> In 2001, Tang and co-workers found that the nonemissive silole molecules in solution were induced to emit efficiently by aggregate formation, and proposed the term “aggregation induced emission (AIE)” for this phenomenon.<sup>4</sup> This unique characteristic makes AIE molecules more potent for technological application in the practical solid state. Since then, many molecules with AIE were synthesized and investigated,<sup>5</sup> with the silole derivatives and tetraphenylene (TPE) derivatives as

representatives. These molecules show high potential in the field of organic light-emitting diodes (OLEDs),<sup>6</sup> chemosensors,<sup>7</sup> biological science,<sup>8</sup> *etc.*

The research interests encourage us to exploit more AIE molecules, and enlarge the application of AIE molecules.<sup>9</sup> Most of the AIE luminogens reported so far showed blue or green emission. However, in fluorescence application, the luminogens which show different wavelength emissions are needed. For example, the luminogens with longer-wavelength emission are expected to be used as luminescent materials in order to suffer little interferences from optical self-absorption and autofluorescence from the background.<sup>10</sup> In general, there are two ways to change the emissive color of molecules, one is extending the  $\pi$ -conjugation length of molecules, and the other is the introduction of donating and accepting units into the molecule structure to cause intramolecular charge transfer (ICT) effects. However, the preparation of the AIE molecules with a longer conjugated structure is difficult, while the molecules with the ICT feature usually show weak emission. So, tuning the fluorescent color of AIE molecules is still a challenging task.

TPE is a propeller-like molecule and displays the AIE effect due to the restriction of intramolecular rotation in the solid state, which can serve as a building block to construct AIE molecules.<sup>11</sup> On the other hand, organic boron materials have attracted considerable attention due to their intriguing electronic and photophysical properties owing to the  $p_{\pi}-\pi^*$  conjugation between the vacant p orbital on the boron center with the  $\pi^*$  orbital of the  $\pi$ -conjugated framework.<sup>12</sup> The introduction of the dimesitylboronyl group into the  $\pi$ -conjugated structure can lead to creation of highly emissive solid-state fluorescence, and the steric bulkiness and the electron-accepting character of the group were regarded as important factors for highly emissive luminescence.<sup>12d-f</sup> Both features of the dimesitylboronyl group

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were beneficial for designing and constructing AIE molecules. Our group reported one AIE molecule containing TPE and the dimesitylboryl group, which demonstrated good performance in the OLED experiment.<sup>11a</sup> The results indicated the possibility of constructing new AIE molecules by combination of TPE units and dimesitylboryl groups in more extended  $\pi$ -conjugated structures or by introduction of more dimesitylboryl groups into  $\pi$ -conjugated structure. Introduction of the  $C\equiv C$  unit into these molecules is an effective method to extend their  $\pi$ -conjugation, however, the research on the synthesis and properties of the molecules containing the TPE unit, the dimesitylboryl group, and the  $C\equiv C$  bond is surprisingly limited. Herein, using Sonogashira coupling reaction, a series of AIE molecules containing bulky dimesitylboryl groups and the TPE unit were synthesized, and their photophysics and potential application in the field of data storage and cell imaging were also investigated.

## Results and discussion

### 1. Synthesis

A kind of unique molecule, TPE, could be used as a constructing unit to prepare the molecule that demonstrates the AIE phenomenon. Dimesitylboryl groups were the steric bulky groups arising from the aryl substituents and electron accepting units, in order to tune the fluorescent color of the prepared molecules. The TPE unit and boryl groups combined with  $C\equiv C$  units were used to develop new AIE molecules and new properties. The following molecules were synthesized further by Sonogashira coupling reactions. <sup>1</sup>H NMR, <sup>13</sup>C NMR, and High Resolution Mass Spectroscopies (HRMS) were used to characterize the prepared compounds (ESI<sup>+</sup>): dimesityl(4-((4-(1,2,2-triphenylvinyl)phenyl)ethynyl)phenyl)borane (1), 1,2-bis(4-((4-(dimesitylboryl)phenyl)ethynyl)phenyl)-1,2-diphenylethene (2), 4-(2-(4-((4-(dimesitylboryl)phenyl)ethynyl)phenyl)-1,2-diphenylvinyl)-*N,N*-diphenylamine (3) and 4-(2-(4-((4-(dimesitylboryl)phenyl)ethynyl)benzo[*c*][1,2,5]thiadiazol-4-yl)ethynyl)phenyl)-1,2-diphenylvinyl)-*N,N*-diphenylamine (4) (Scheme 1).

### 2. Photophysics

**2.1. UV-absorption.** The UV/Vis absorption spectra of compounds 1–4 in THF solution are shown in Fig. 1, and the related

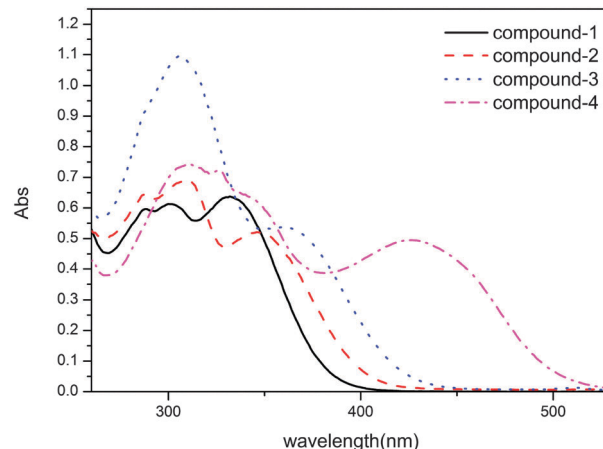


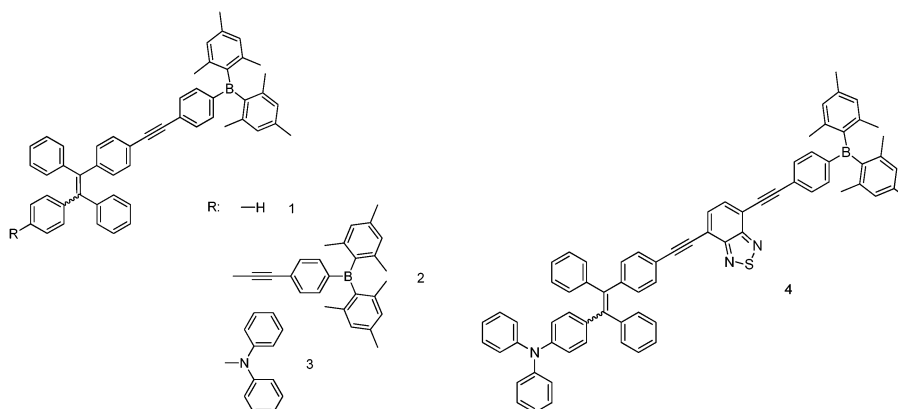
Fig. 1 Absorption spectra of THF solutions.

Table 1 UV/Vis absorption and fluorescence data

	Absorption <sup>a</sup>		Fluorescence		
	$\lambda_{\text{abs}}^b$ (nm)	$\lambda_{\text{abs}}^c$ (nm)	$\lambda_{\text{em}}^d$ (nm)	$\Phi_F^e$	$\Delta\lambda^f$ (cm <sup>-1</sup> )
Compound 1	332	366	479, 486 <sup>c</sup>	0.36	6450
Compound 2	346	371 <sup>g</sup>	504, 504 <sup>c</sup>	0.90	7120
Compound 3	360	387 <sup>g</sup>	523, 523 <sup>c</sup>	0.42	6720
Compound 4	427	437	607, 609 <sup>c</sup>	0.15	6410

<sup>a</sup> Only the longest absorption maximum wavelengths are given. <sup>b</sup> THF solutions. <sup>c</sup> Spin-coated films were prepared from *ca.* 1.0 mg mL<sup>-1</sup> THF solutions. <sup>d</sup> Excited at the longest absorption maximum. <sup>e</sup> Absolute quantum yield determined using a calibrated integrating sphere system. <sup>f</sup> Stokes shift. <sup>g</sup> Shoulder band.

data are summarized in Table 1. In THF solution, compound 1 exhibits an adsorption maximum at 332 nm, and introduction of the second dimesitylboryl phenylethynyl group red shifts the absorption of compound 2 to 346 nm, about *ca.* 14 nm longer than that of compound 1. Compounds 2 and 3 can be thought of as the derivatives of compound 1, with the R group replaced by the dimesitylboryl phenylethynyl or the diphenylamino group, respectively. Compound 3 containing a donor unit of diphenylamine has its absorption at 360 nm, which is 14 nm longer than that of compound 2. This fact suggests that compared with the



Scheme 1 Chemical structure of the prepared compounds.

dimesitylboryl phenylethynyl group, the contribution of the diphenylamino group to elongation of the absorption of compound **1** is more prominent, though the latter has a shorter conjugated chemical structure. The longest absorption of 427 nm was observed in compound **4**, which combines the donor-acceptor system and the extended  $\pi$ -conjugation framework in one molecule. These compounds showed very weak fluorescence in their THF solution because the TPE unit worked as an emission quencher in the solution state.

**2.2. AIE phenomenon.** When illuminated under UV light, no emission or weak emission was observed from their THF solutions but intense fluorescence from solid films was observed, indicating that aggregation has turned on their light emission. Further photoluminescence (PL) measurement of these compounds in THF–water mixtures verified their AIE-active nature. For compound **1**, as shown in Fig. 2, the PL curve showed a flat line for its pure THF solution, and even when the water fraction ( $f_w$ ) was as high as 70%, only a weak PL signal was recorded because the molecules were still genuinely dissolved in the mixture. However, when  $f_w > 80\%$ , addition of even a small amount of water resulted in a sharp increase in the PL intensity. From the molecular solution in THF to the aggregate suspension in the 95% aqueous mixture, the PL peak intensity of compound **1** at 480 nm increased by 263 times.

For compound **2**, as shown in Fig. 3, the PL curve also showed a flat line for its pure THF solution, even when the water fraction ( $f_w$ ) was about 40%, and when  $f_w > 60\%$ , addition of a small amount of water resulted in a sharp increase in the PL intensity at 504 nm. However, in the 95% aqueous mixture, the PL peak intensity of compound **2** increased slowly because of some of the organic molecules precipitated from the THF–water mixture compared to 90% aqueous solution.

For compound **3**, as shown in Fig. 4, the PL curve was very similar to compound **1**, even when the water fraction ( $f_w$ ) was as high as 70%, only a weak PL signal was recorded, and when  $f_w > 80\%$ , addition of even a small amount of water resulted in a sharp increase in the PL intensity at 523 nm.

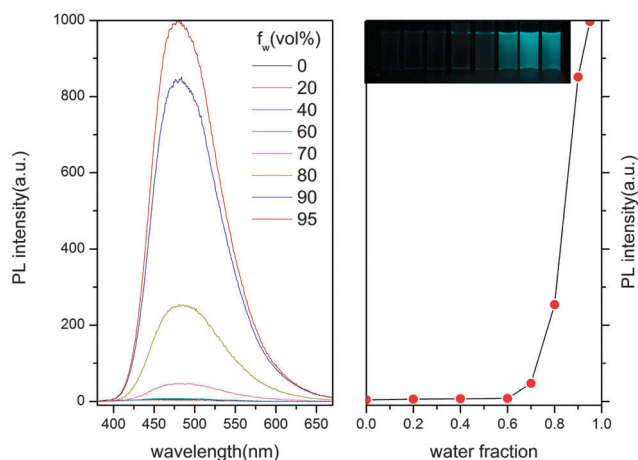


Fig. 2 Fluorescence spectra of compound **1** in THF–water mixtures ( $\text{H}_2\text{O}\%$ ); the concentration of the sample compound **1** was about  $10^{-5} \text{ mol L}^{-1}$ ,  $\lambda_{\text{ex}} = 345 \text{ nm}$ .

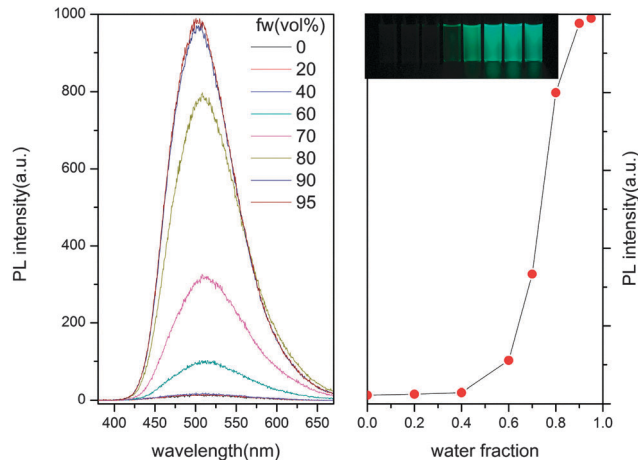


Fig. 3 Fluorescence spectra of compound **2** in THF–water mixtures ( $\text{H}_2\text{O}\%$ ); the concentration of the sample compound **2** was about  $10^{-5} \text{ mol L}^{-1}$ ,  $\lambda_{\text{ex}} = 345 \text{ nm}$ .

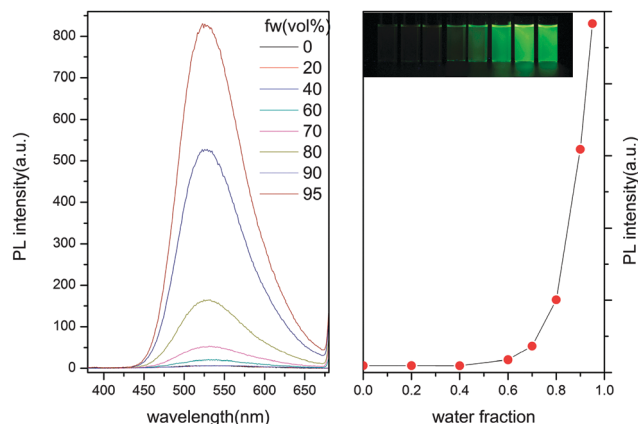


Fig. 4 Fluorescence spectra of compound **3** in THF–water mixtures ( $\text{H}_2\text{O}\%$ ); the concentration of the sample compound **3** was about  $10^{-5} \text{ mol L}^{-1}$ ,  $\lambda_{\text{ex}} = 345 \text{ nm}$ .

However, compound **4** displayed a different change trend of the PL curve, as shown in Fig. 5. The PL peak of compound **4** in THF solution appeared at 500 nm, with the addition of water, the intensity of which decreased and the peak red shifted till the water fraction was as high as 60%. When  $f_w > 80\%$ , the new peak at 607 nm appeared, and its intensity enhanced with the further addition of water. This phenomenon indicated that the twist intramolecular charge transfer and AIE properties coexist in this molecule. In order to support this conjecture, PL of compound **4** in the hexane–THF solvent system was examined. It was found that the PL intensity of the peak at 500 nm increased with the addition of nonpolar solvent, hexane, into THF solution, a new peak at 607 nm appeared when the fraction of hexane reached 40% and gradually shifted to shorter wavelength. The peak shifted down to 538 nm when about 95% of hexane was added (Fig. S4, ESI<sup>†</sup>).

No obvious evidence revealed that the emission wavelength of the compounds **2** and **3** was affected by different solvents. But compound **4** showed clear solvatochromism, when the

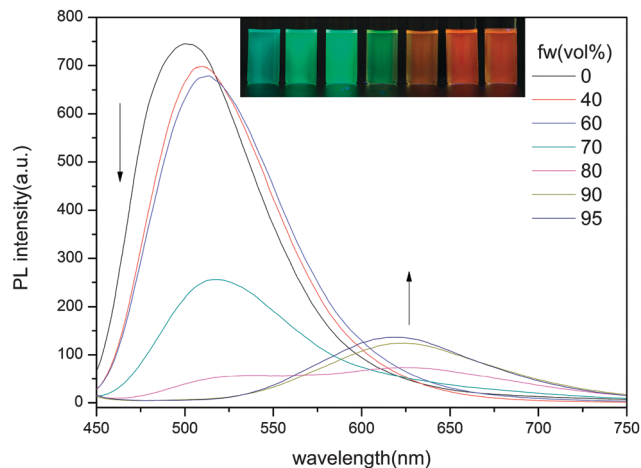


Fig. 5 Fluorescence spectra of compound **4** in THF–water mixtures ((H<sub>2</sub>O%); the concentration of the sample compound **4** was about  $10^{-5}$  mol L<sup>-1</sup>,  $\lambda_{\text{ex}} = 430$  nm).

polarity of solvent was increased; the fluorescence peak of compound **4** was shifted to a longer wavelength (ESI<sup>†</sup>).

**2.3. Photophysics in the solid state.** To examine the solid state emission of the new compounds, spin-coated films of which on quartz were prepared and their UV-Vis/PL spectra were recorded, and their solid state assembly films on an anodic aluminium oxide membrane (AAO) were also prepared by dipping these compounds in solution and the PL spectra of these films were recorded, the summary of data is also shown in Table 1.

As shown in Fig. S5 (ESI<sup>†</sup>), the UV-Vis absorption spectra of the spin-coated films of compounds **1–4** showed red shift compared with their THF solution, suggesting the formation of aggregates of these compounds in the solid state.

The intense solid-state fluorescence was a general characteristic of AIE molecules. These compounds were excited in the solid state, they emitted the different color fluorescence in their solid states, and the fluorescence of the spin-coated films was similar to the fluorescence of the films on AAO. The C $\equiv$ C bond was used to extend the  $\pi$ -conjugation length, and the introduction of bulky dimesitylboryl groups was very effective in suppressing the intramolecular rotation and intermolecular interaction, which was presumably one important factor contributing to the AIE fluorescence phenomena. As shown in Fig. 6, compound **1**

showed the blue emission, compound **2** emitted blue-green because of extended  $\pi$ -conjugation compared to compound **1**. The introduction of the diphenylamino group and the dimesitylboryl group in compound **3** enables this compound to show a green-yellow color, and the further introduction of an electron-accepting group resulted in the red shifted emission of compound **4** in the solid state. The absolute fluorescence quantum yields were determined using a calibrated integrated sphere system. The data are also summarized in Table 1. The absolute quantum yield of compound **4** is about 15% in the solid state, and compounds **1–3** showed good to excellent quantum yields ( $\Phi_{\text{F}} = 0.36\text{--}0.90$ ). The photo of the compounds in the solid state under 365 nm light is demonstrated in Fig. 6.

**2.4. The morphology of the compound assembly in a porous AAO membrane.** The morphology of AIE molecules suspended in 95% and 90% aqueous mixtures usually showed spherical aggregates.<sup>11c</sup> In order to elucidate the fluorescence behaviour of different aggregated shapes, the samples assembled in porous AAO membranes were investigated. The AAO membranes were dipped in the compounds' THF solution, and dried after solvent evaporation; the AAO films containing the dyes emit strong fluorescence under UV light, further proving the AIE effect of these compounds. The SEM pictures demonstrated that the molecules were filled in the pores of the AAO membrane, the organic dyes should be confined by the pores of the template, and the fiber-like organic aggregates were formed inside the pores, many flexible organic fiber-like aggregates were observed after the AAO membrane dissolved in alkaline solution (Fig. S6, ESI<sup>†</sup>). There is almost no difference in emissive wavelength between sphere aggregates in suspension and fiber-like aggregates in solid film. The stable and stronger intensity of emission in AAO film could be ascribed to larger amounts of molecules absorbed in porous film.

### 3. Data storage

The development of the information storage continues to demand innovation of technologies and application of materials for future larger-capacity memory devices. Scanning tunneling microscopy (STM) has proven to be a highly effective tool for ultrahigh density information storage in previous research,<sup>13</sup> many materials have been used to prepare the thin films as media, and the recording on the nanoscale using STM has been reported.

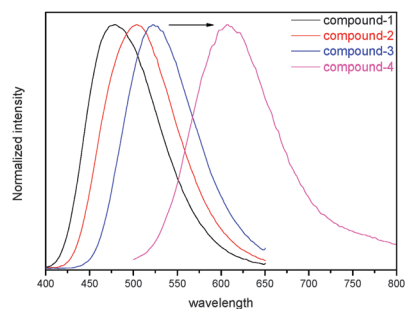


Fig. 6 The PL spectra of the samples (compounds **1–4**) in the solid state and the photograph of the compounds in AAO films under 365 nm light.



Organic molecules employed as storage media have attracted increasing interest because of their ability to design and tune their electronic and structural properties; the assembly of organic molecules makes the construction of stable and durable organic films easy in an ordered manner for data recording.<sup>14</sup> The donor-acceptor compounds were usually applied in the information storage by virtue of intramolecular charge transfer. AIE molecules have  $\pi$ -conjugated structure and showed the fluorescent effect, and a few of the AIE dyes exhibit multifunctional properties.<sup>15</sup> The fluorescent color of AIE molecules is tuned by the introduction of donating and accepting units into the molecule's structure to cause intramolecular charge transfer effects. These designed AIE molecules with donor-acceptor structure were suggested to be used in the STM-based information storage.

Drop-casting has been used for preparing films of compounds 2 and 3, the solutions of compounds 2 and 3 in THF at a concentration of about  $10^{-5}$  M were used, and the thin films were obtained through drop-casting on the HOPG substrates after complete solvent evaporation at room temperature. Recording experiments were performed using a Solver P47 STM in constant-height mode in the selected flat region, using tips made of tungsten wires by electrochemical etching. Pulsed voltages were applied between the STM tip and the HOPG substrate to induce the recording signal. To avoid scratches or running into the surface, the STM tip was set to lift 5–10 nm away from the tunneling position before each pulse voltage was applied. As shown in Fig. 7, the STM images of recording marks on the sample thin films demonstrated that the recording dots could be successfully formed after applying voltage pulses of 2.3 V for 5 ms. One bright dot corresponds to a recorded mark. In experiment, for compound 3 the recorded marks with the average diameter of about 3–4 nm were very stable and no obvious changes could be observed during the continuous scanning process for 5 h, but for compound 2 the recorded marks with the average diameter of about 2–3 nm were less stable (Fig. S7, ESI<sup>†</sup>).

To understand the recording mechanism, local current-voltage ( $I$ - $V$ ) characteristics of these molecular thin films were measured. Fig. 7 shows the typical  $I$ - $V$  curves of the film before and after recording. From the curves it was clear that the electrical resistance of the recorded region was much lower than that of the unrecorded region, which indicated that a conductance transition occurs after application of the voltage

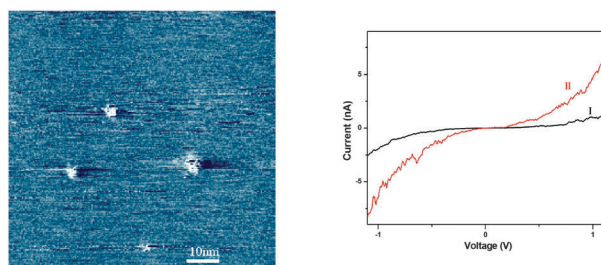


Fig. 7 STM image of typical information dot pattern and the corresponding  $I$ - $V$  curve for the film of compound 3. (Left) Recording dots, voltage pulses: +2.3 V, 5 ms; (Right) typical STM current-voltage ( $I$ - $V$ ) curves in the unrecorded (curve I) and recorded region (curve II).

pulse onto the films, the tunneling current remained low in their initial state, after the pulse voltage was higher than the threshold, and the transition led to the bright dots observed by STM. From previous reports, the recording mechanism was usually benefited from the ICT effect. It was suggested that the dimesitylboryl acted as an electron-accepting group in molecules though there was no clear evidence of ICT transition.

#### 4. Biological application

Fluorescent molecules have been widely used as biological imaging agents.<sup>16</sup> AIE organic fluorescent dyes were utilized in biological applications, such as labeling, imaging, biosensing, *etc.*<sup>17</sup> Based on the fluorescence properties of these compounds, in our experiments, compounds 2 and 3 were chosen for use in fluorescence imaging, because these two compounds showed relatively high quantum yield and the fluorescence of compound 3 is green-yellow which is suitable for cell imaging. But these organic dyes were not successful in directly being applied in cell imaging, since water solubilization is necessary. Thus, the silica coating-dye nanoparticles were prepared to stain the cells. In general, the synthesis of dye-encapsulated amine terminated silica nanoparticles (SiNPs) was according to the literature report with a little modification.<sup>18</sup> After the dye-encapsulated silica nanoparticles were prepared (ESI<sup>†</sup>), the nanoparticle purification was conducted by dialyzing the dispersion against deionized water in a 10 kDa cutoff cellulose membrane to remove surfactants and solvents. The dialyzed solution was then filtered through a 0.22  $\mu$ m cutoff membrane filter. The resulting nanoparticles were stored at 4  $^{\circ}$ C for later experiments. Particle size analysis was performed at room temperature using a ZetaPlus Potential Analyzer (Brookhaven Instruments Corporation, USA).

**4.1. Cell culture.** HeLa cells were cultured in the MEM containing 10% FBS and antibiotics (100 units per mL penicillin and 100 g per mL streptomycin) in a humidified incubator with 5% CO<sub>2</sub> at 37  $^{\circ}$ C.

**4.2. Cell imaging.** HeLa cells were grown overnight on a 35 mm petri dish with a cover slip. The live cells were stained with nanoparticles for 6 hours (by adding 2  $\mu$ L of stock solution of nanoparticles to 2 mL of culture medium). The cells were imaged under a FL microscope (BX41 Microscope) using different combinations of excitation and emission filters: for TPE derivatives, excitation filter = 330–385 nm, dichroic mirror = 400 nm. The results demonstrated that compound 2 was active in staining the cells and was well distributed in the cytoplasm, but the fluorescence signal of

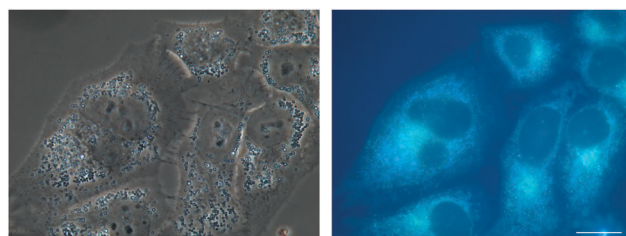


Fig. 8 Images of HeLa cells stained with compound 2 encapsulated SiNPs (5  $\mu$ M) for 6 h. Left, overlap image; right, fluorescence image. Scale bar 15  $\mu$ m.

compound **3** was not detected in the cells which indicate that compound **3** could not be used as a cell imaging agent. The nanoparticle size distribution and fluorescence images of HeLa cells incubated with SiNPs encapsulating compound **2** are shown in Fig. 8.

## Conclusion

In summary, a series of AIE molecules containing bulky dimesitylboryl groups were synthesized through the Sonogashira coupling. Their solid-state emission shows stronger and different colors, demonstrating aggregation-induced emission. Ultra-density data storage has been demonstrated with the formation of nanometer-sized dots on the thin films by applying pulsed voltage between a STM tip and the films. The AIE molecules were used for fluorescence cell imaging. All of this expanded the AIE molecule's application, and will trigger new research.

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