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Color-tunable and highly solid emissive AIE molecules:

Synthesis, photophysics, data storage and biological application

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

Introduction:

The luminescent organic molecules have attracted much interest due to their wide application in electronics, optics, storage media, and biological science.^[1] For most practical application, luminescent materials are usually utilized in solid state but not in solution^[2], thus the development of highly emissive fluorescent material in 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 solid state because of aggregation. This effect of aggregation caused quenching (ACQ) limited the application of fluorescent materials.^[3] In 2001, Tang and co-workers found that the nonemissive silole molecules in solution was induced to emit efficiently by aggregate formation, and proposed the term of “aggregation induced emission (AIE)” for this phenomenon.^[4] This unique characteristic makes AIE molecules have more potential for technological application in practical solid state. Since then, many molecules with AIE were synthesized and investigated,^[5] with the silole derivatives and tetraphenylethylene (TPE) derivatives as representatives. These molecules show high potential in the field of organic light-emitting diodes (OLEDs)^[6], chemosensors^[7] and biological science^[8] etc.

The research interests encourage us to exploit more AIE molecules, and enlarge the application of AIE molecules.^[9] Most of AIE luminogens reported so far showed blue

or green emission. However, in fluorescent application, the luminogens which show different wavelength emission 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.^[10] In general, there have two ways to change the emissive color of molecules, one is extending the π -conjugation length of molecules, and the other is the introduction of donating and accepting units into molecule structure to form intramolecular charge transfer (ICT) effects. However, the preparation of the AIE molecules with longer conjugated structure is synthetic difficult, while the molecules with ICT feature usually show weak emission. So, tuning the fluorescent color of AIE molecules is still a challenging work.

TPE is a propeller-like molecule and displays the AIE effect due to the restriction of intramolecular rotation in solid state, which can serve as a building block to construct AIE molecules.^[11] 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 π^* orbital of the π -conjugated framework.^[12] The introduction of dimesitylboryl group into π -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.^[12d,e,f] Both features of dimesitylboryl group were beneficial for designing and constructing AIE molecules. Our group reported one AIE molecule containing TPE and dimesitylboryl group, and which demonstrated good performance in OLED experiment.^[11a] The result has indicated the possibility to construct new AIE molecules by combination of TPE unit and dimesitylboryl groups in more extending π -conjugated structures or by introduction of more dimesitylboryl groups into π -conjugated structure. Introduction of $C\equiv C$ unit into molecules is an effective way to extend whose π -conjugation, however, the research on synthesis and properties of the molecules containing TPE unit, dimesitylboryl group, and $C\equiv C$ bond are surprisingly limited. Herein, using Sonogashira coupling reaction, a series of AIE molecules containing bulky dimesitylboryl groups and 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

As a kind of unique molecule, TPE could be used as a constructing unit to prepare the molecule which demonstrates 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. TPE unit and boryl groups combining 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. The $^1\text{H NMR}$, $^{13}\text{C NMR}$, High Resolution Mass Spectra (HRMS) were used to characterize the prepared compounds (supporting information).

- Dimesityl(4-((4-(1,2,2-triphenylvinyl)phenyl)ethynyl)phenyl)borane (1),
 1,2-bis(4-((4-(dimesityboryl) phenyl)ethynyl)phenyl)-1,2-diphenylethene (2),
 4-(2-(4-((4-(dimesityboryl) phenyl)ethynyl)phenyl)-1,2-diphenylvinyl)-N,N-diphenylaniline (3)
 4-(2-(4-((7-((4-(dimesityboryl) phenyl)ethynyl)benzo[c][1,2,5]thiadiazol-4-yl)ethynyl)phenyl)-1,2-diphenylvinyl)-N,N-diphenylaniline (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 data are summarized in Table 1. In THF solution, compound **1** exhibits adsorption maximum at 332 nm, introduction of the second dimesityboryl 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 as the derivatives of compound **1**, with R group replaced by dimesityboryl phenylethynyl or diphenylamino group, respectively. Compound **3** contains donor unit of diphenylamine has its absorption at 360nm, which is 14 nm longer than that of compound **2**. This fact suggests that comparing with dimesityboryl phenylethynyl group, the contribution of diphenylamino group to elongating the absorption of compound **1** is more prominent, though the later has shorter conjugated chemical structure. The longest absorption of 427nm was observed in compound **4**, which combines donor-acceptor system and extended π -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.

Figure 1

2.2. AIE phenomenon

When illuminated under UV light, no emission or weak emission seen from their THF solutions but intense fluorescence from solid films were 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 gave sharp promotion 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 was increased by 263 times.

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

For compound **3**, as shown in Fig.4, the PL curve was very similar to compound **1**, even the water fraction (f_w) was as high as 70%, only a weak PL signal was recorded, when $f_w > 80\%$, addition of even a small amount of water gave sharp promotion in the PL intensity at 523 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 was at 500nm, with 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 was enhanced along the further addition of water. This phenomenon indicated the twist intramolecular charge transfer and AIE property coexist in this molecule. In order to support this conjecture, PL of compound **4** in hexane-THF solvent system was examined. It was found the PL intensity of the peak at 500 nm increased with 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 moved down to 538 nm when hexane about 95% was added (Fig S4).

Figure 2

Figure 3

Figure 4

Figure 5

No obvious evidence was revealed that the emission wavelength of the compounds **2** and **3** was affected by different solvents. But compound **4** showed clear solvatochromism, along the polarity of solvent was increased; the fluorescent peak of compound **4** was shifted to longer wavelength (supporting information).

2.3. Photophysics in 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 measured, and their solid state assembly films on anodic aluminium oxide membrane (AAO) were also prepared by dipping the these compounds solution and the PL spectra of these films were measured, the summary of data were also shown in table 1.

Table 1

As shown in Fig. S5, the UV-vis absorption spectra of the compounds **1-4** spin-coated films showed red shift compare with their THF solution, suggesting the formation of aggregates of these compounds in solid state.

The intense solid-state fluorescence was a general characteristic of AIE molecule. These compounds were excited in solid state, they emitted the different color fluorescence in their solid states, and the fluorescence of the spin-coated films was similar to fluorescence of the films on AAO. The C≡C bond was used to extend the π -conjugated length, the introduction of bulky dimesityboryl groups was very effective in suppressing the intramolecular rotation and intermolecular interaction, which was presumably one important factor contributing to the AIE fluorescent phenomena. As shown in Fig.6, compound **1** showed the blue emission, compound **2** emitted blue-green because of extending π -conjugation compare to the compound **1**. The introduction of diphenylamino group and dimesityboryl group in compound **3** make this compound showed green-yellow color, the further introduction of electron-accepting group gave compound **4** red shift emission in solid state, The absolute fluorescence quantum yields were determined by a calibrated integrated sphere system. The data are also summarized in Table 1. The absolute quantum yield of compound **4** is about 15% in solid state, compound **1-3** showed good to excellent quantum yields ($\Phi_F = 0.36-0.90$). The photo picture of the compounds in solid state under 365nm light was demonstrated in Fig.6.

Figure 6

2.4. The morphology of the compounds assembly in porous AAO membrane

The morphology of AIE molecules suspended in 95% and 90% aqueous mixtures usually showed the sphere aggregate.^[11c] In order to elucidate the fluorescent behaviour of different aggregated shape. These samples assembled in porous AAO membrane were investigated. The AAO membranes were dipped with these compounds' THF solution, and dried after solvent evaporation, the AAO film containing the dyes emit strong fluorescence under UV light, further proved the AIE effect of these compounds. The SEM pictures demonstrated the molecules were filled in the pores of 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 AAO membrane dissolved in alkaline solution (Fig. S6). 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 memories. Scanning tunneling microscopy (STM) has proven to be a highly effective tool for ultrahigh density information storage in previous research,^[13] many materials have been used to prepare the thin film as media, and the recording on the nanoscale using STM has been reported. Organic molecules employed as storage media have been attracted increasingly because of the ability to design and tune their electronic and structural properties, the assembly of organic molecules makes it easy that the stable and durable organic films are constructed in an ordered manner for data recording.^[14] The donor-acceptor compounds were usually applied in the information storage by virtue of intramolecular charge transfer. AIE molecules had π -conjugated structure and showed the fluorescent effect, and a few of AIE dyes exhibit multi-functional properties.^[15] The way of tuning the fluorescent color of AIE molecules is the introduction of donating and accepting units into molecule structure to form intramolecular charge transfer effects. These designed AIE molecules with donor-acceptor structure were suggested to use in the STM-based information storage.

Drop-casting has been used for preparing the compounds **2** and **3** films, the solution of compound **2** and compound **3** in THF with the 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 with 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 the scratches or running into the surface, the STM tip was set to lift 5-10nm 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 the recording dots could be successfully formed after applying voltage pulses of 2.3V for 5ms. One bright dot corresponds to a recorded mark. In experiment, for compound **3** the recorded marks with the average diameter about 3-4 nm were very stable and no obvious changes could be observed during the continuous scanning process of 5h, but for compound **2** the recorded marks with the average diameter about 2-3nm showed less stable (Fig. S7).

Figure 7

To understand the recording mechanism, local current-voltage (I - V) characteristics of these molecular thin films were measured. Fig. 7 showed 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 pulse onto the films, the tunneling current remained low in their initial state, after a pulse voltage higher than the threshold, 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 was acted as electron-accepting group in molecules though there were no clear evidence of ICT transition.

4. Biological application

Fluorescent molecules have been widely used as biological imaging agents.^[16] AIE organic fluorescent dyes were utilized in biological applications, such as labeling, imaging and biosensing etc.^[17] Based on the fluorescent properties of these compounds, in our experiments, the compound **2** and compound **3** were chosen to use for fluorescent 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.^[18] After the dye-encapsulated silica nanoparticles were prepared (supporting information), the nanoparticle purification was conducted by dialyzing the dispersion against deionized water in a 10kDa cutoff cellulose membrane to remove surfactant and solvent. The dialyzed solution was then filtered through a 0.22 μ m cut off membrane filter. The resulting nanoparticles were stored at 4 $^{\circ}$ C for later experiments. Particle size analysis was determined at room temperature by a ZetaPlus Potential Analyzer (Brookhaven Instruments Corporation, USA).

Cell Culture. HeLa cells were cultured in the MEM containing 10% FBS and antibiotics (100units/mL penicillin and 100g/mL streptomycin) in a humidified incubator with 5% CO₂ at 37 $^{\circ}$ C.

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 hour (by adding 2 μ L of stock solution of nanoparticles to 2 mL of culture medium). The cells were imaged under a FL microscope (BX41 Microscope) using different combination of excitation and emission filters: for TPE derivatives, excitation filter = 330-385 nm, dichroic mirror = 400 nm. The results demonstrated that the compound **2** was active in staining the cells and was well distributed in the cytoplasm, but the fluorescence signal of 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 fluorescent images of HeLa cells incubated with SiNPs encapsulating compound **2** were shown in Fig. 8.

Figure 8

Conclusion

In summary, a series of AIE molecules containing bulky dimesitylboryl groups were synthesized through the Sonogashira coupling. Their solid-state emission show stronger and different color, 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 fluorescent cell imaging. All of this expanded the AIE molecule application, and will trigger new research.

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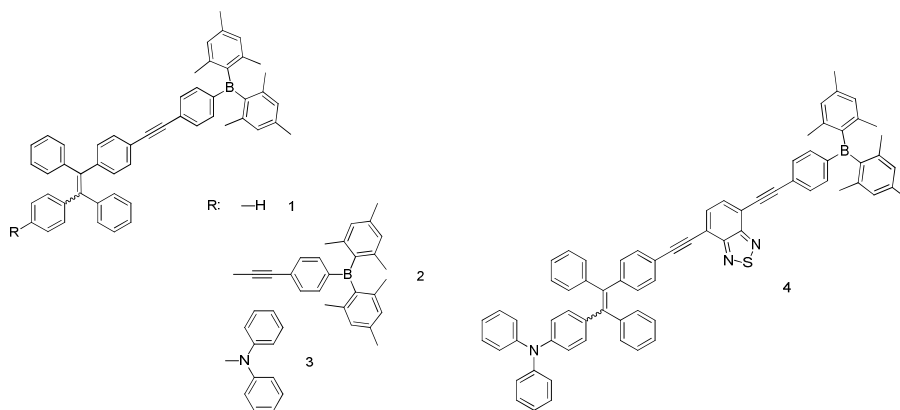
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Figures and figure captions

Scheme 1. Chemical Structure of the prepared compounds



Scheme 1

Fig. 1 Absorption spectra of THF solutions

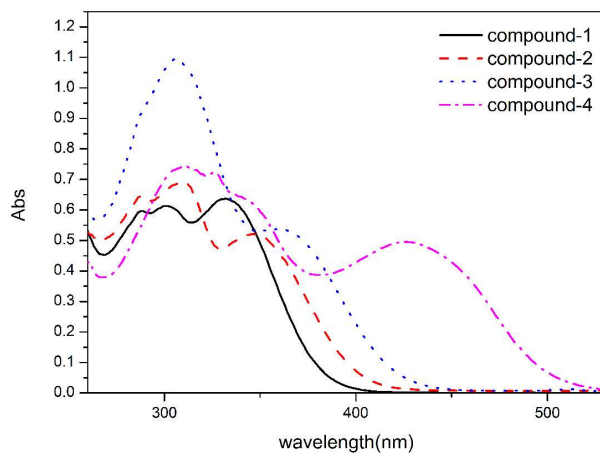


Figure 1

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

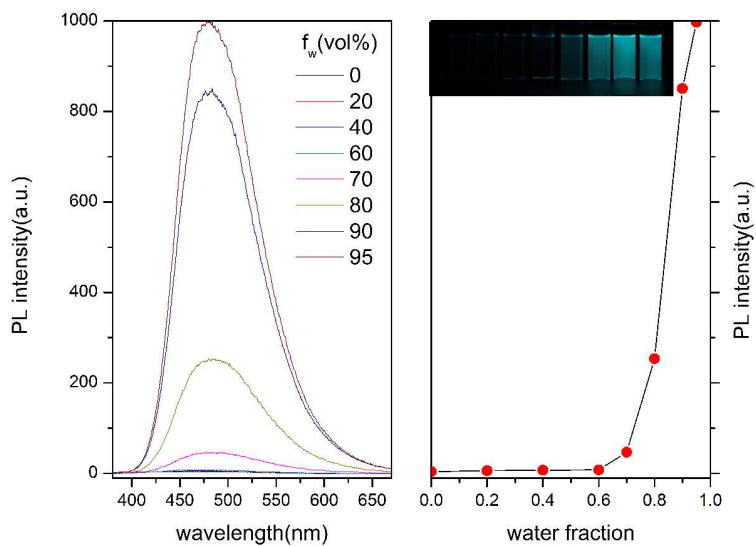


Figure 2

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

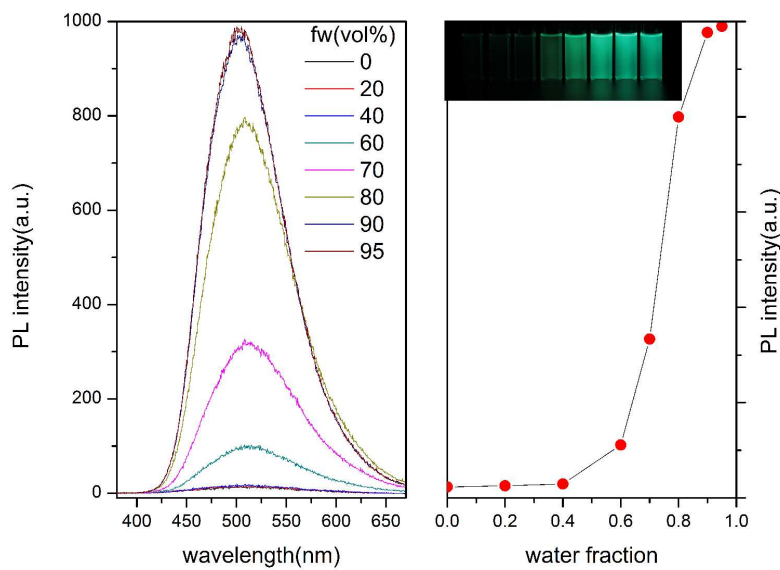


Figure 3

Fig. 4 Fluorescent spectra of the compound **3** in THF/water mixtures (H₂O%); concentration of the sample compound-**3** are about 10⁻⁵ mol/L, $\lambda_{\text{ex.}}$ =345 nm).

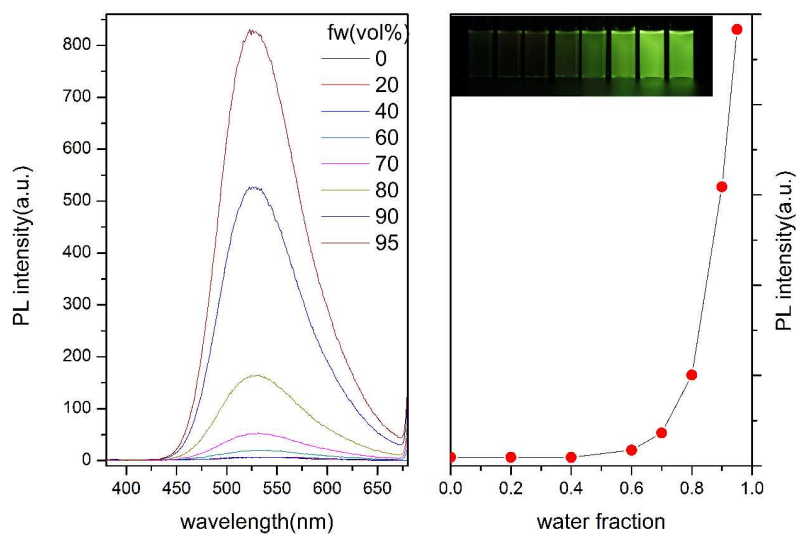


Figure 4

Fig.5 Fluorescent spectra of the compound-**4** in THF/water mixtures (H₂O%); concentration of the sample compound-**4** were about 10⁻⁵ mol/L, $\lambda_{\text{ex.}}$ = 430 nm)

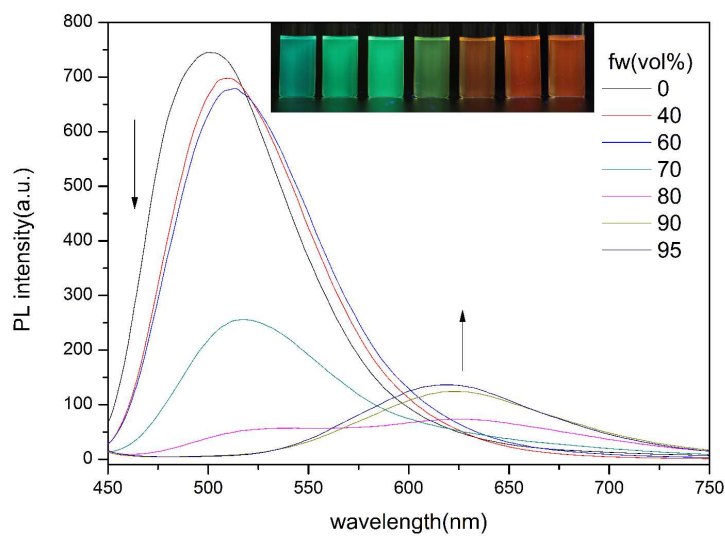


Figure 5

Table 1. UV/Vis absorption and fluorescence data

	Absorption ^[a]		Fluorescence		$\Delta\lambda$ [cm ⁻¹] ^[f]
	λ_{abs} (nm) ^[b] , λ_{abs} (nm) ^[c]	λ_{em} (nm) ^[d] , Φ_{F} ^[e]			
Compound 1	332, 366	479, 486 ^[e] 0.36	6450		
Compound 2	346, 371 ^[g]	504, 504 ^[e] 0.90	7120		
Compound 3	360, 387 ^[g]	523, 523 ^[e] 0.42	6720		
Compound 4	427, 437	607, 609 ^[e] 0.15	6410		

[a] Only the longest absorption maximum wavelengths are given. [b] THF solutions [c] Spin-coated films were prepared from ca. 1.0 mgmL⁻¹ THF solutions. [d] Excited at the longest absorption maximum. [e] Absolute quantum yield determined by a calibrated integrating sphere system. [f] Stokes shift. [g] Shoulder band.

Fig. 6 The PL spectra of the sample (compound 1-4) in solid state and the photography of the compounds in AAO films under 365nm light

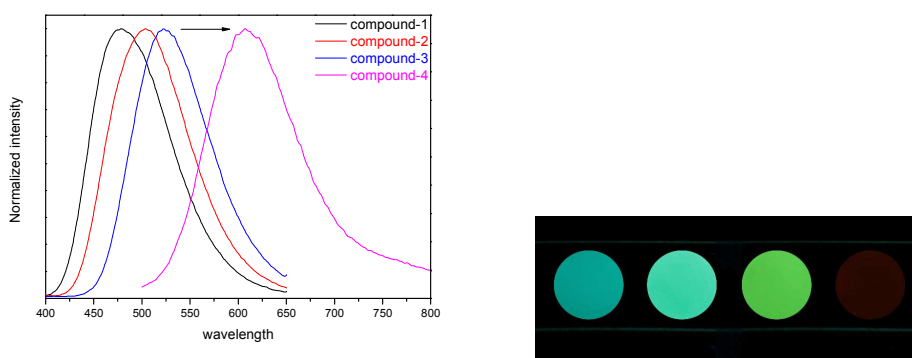


Figure 6

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

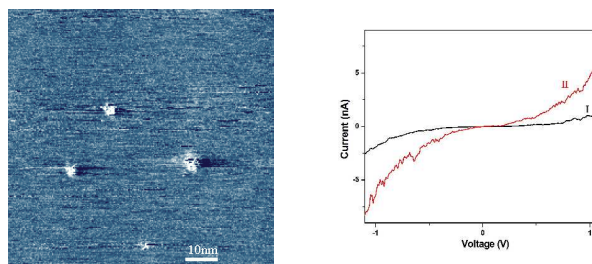


Figure 7

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

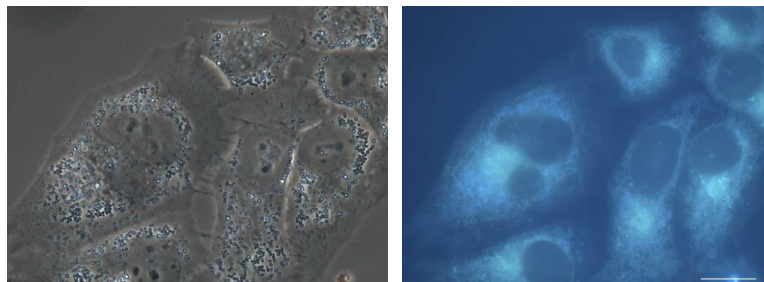
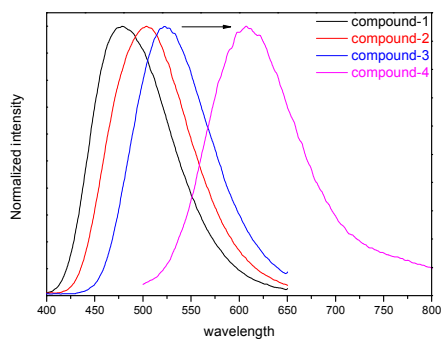


Figure 8

Graphic Abstract



The different color and highly emissive AIE molecules were constructed by tetraphenylene and dimesitylboron groups through $C\equiv C$ bonds, demonstrating the potential prospective in data storage and fluorescent cell imaging.