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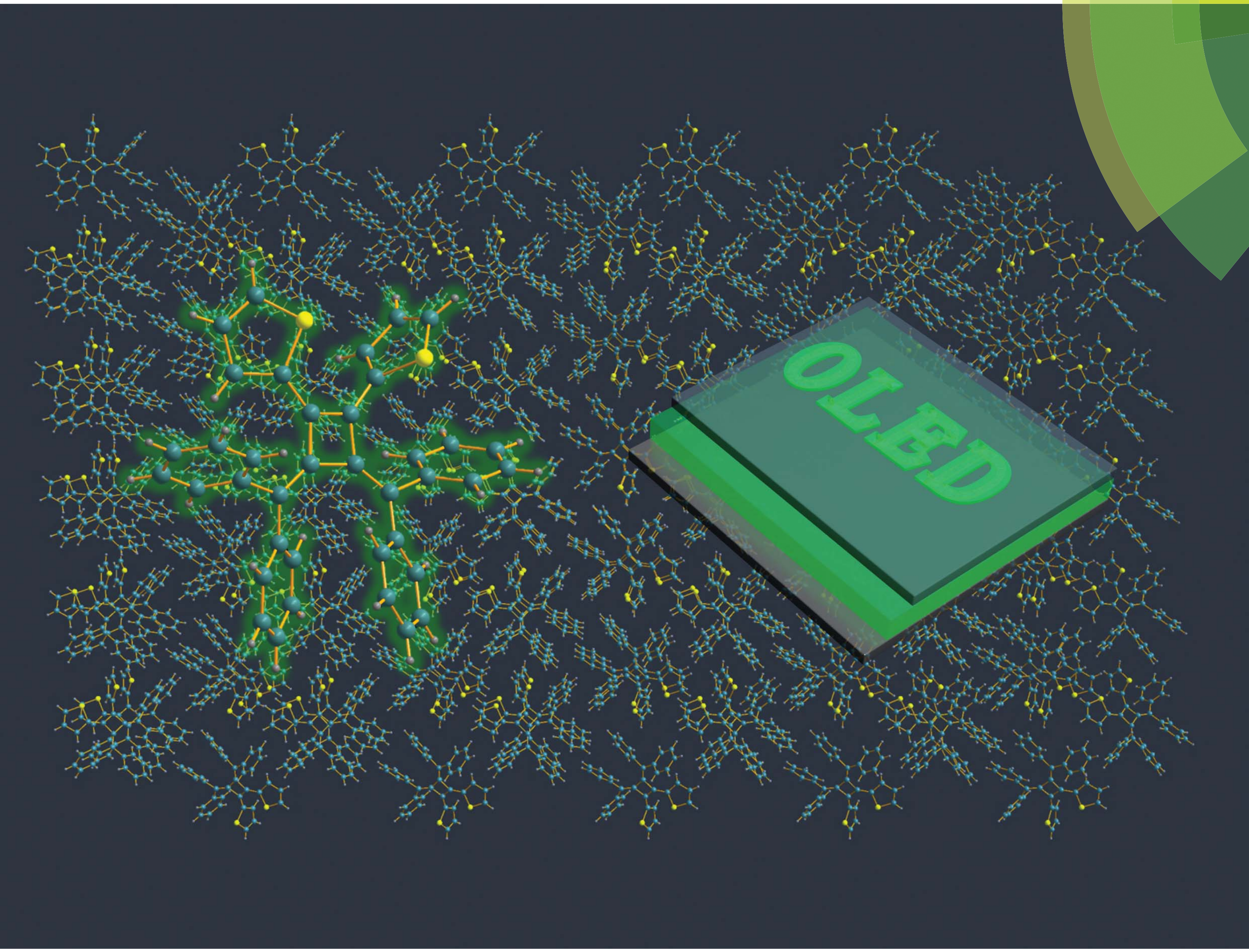

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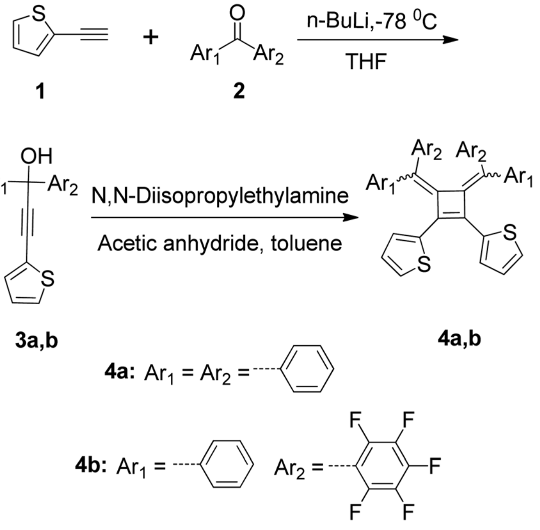
Thienyl substituted cyclobutenes with aggregation induced emission behaviour have been synthesized for the first time in good selectivity, opening the possibility of cyclobutenes for application in light emitting diodes.

Aggregation-caused quenching (ACQ), occurring when organic materials are highly fluorescent in their dilute solutions but become weakly fluorescent with the increase of solution concentration or aggregation in the solid state, is a notorious phenomenon in organic luminescent materials.[1,2] Unfortunately, for practical applications, such as organic light emitting diodes (OLEDs), the solid state (powders, films or crystals) provides the best candidates for functional layers in electronic devices.[3–5] So luminescent materials with aggregation-induced emission (AIE) properties have attracted much interest since the debut of the AIE concept in 2001.[6–13]

The AIE phenomenon is caused by a restriction of vibrational and rotational motion in aggregation states, keeping a distorted conformation for a single molecule and confining the rotation in the solid state by dense packing.[14–16] 1,2-Diphenyl-3,4-bis-(diphenylmethylene)-1-cyclobutene (HPDMCb), which was isolated from a commercial product, rubrene, was found to exhibit AIE properties by Tang's group.[17] Regrettably, HPDMCb is the only cyclobutene compound that exhibits AIE properties and has found application in OLEDs. It is interesting and important to investigate substituent dependant AIE properties of cyclobutene derivatives. Meanwhile, there are few studies on the synthesis of cyclobutene derivatives, which are often separated from rubrenes by traditional methods and suffer low selectivity and poor yields for cyclobutenes relative to rubrenes.[18–20]

In this work, we firstly established a modified synthetic method to achieve cyclobutenes in a much higher yield and selectivity compared with rubrenes. By changing the halogenating agent to acid anhydride and using *N*,*N*-diisopropylethylamine as the base, we obtained two new derivatives of dimethylene-cyclobutene with excellent AIE properties, both of which emit yellow-green light. Moreover, from the single crystal structure, the aryl groups of cyclobutene show a classical rigid structure with the intramolecular rotation being impeded, which meet the requirements of AIE properties.

1,2-Diaryl-3,4-bis(diarylmethylene)-1-cyclobutene (**4a** and **4b**) was synthesized in two steps as shown in Scheme 1. Firstly, arylacetylene (**1**) reacted with diaryl ketone **2a** and **2b** to give the intermediate product **3a** and **3b** in yields of 75% and 70% respectively. Secondly, the dimerization of the propargyl alcohols afforded the target compound **4a** and **4b** in yields of 30% and 31% respectively.



Scheme 1 Synthetic route of compounds **4a** and **4b**.

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† Electronic supplementary information (ESI) available: Synthetic details of compounds **4a** and **4b**, TGA of compounds **4a** and **4b**, oxidation cyclic voltammogram of **4a** and **4b**, lifetime of compounds **4a**. CCDC 973433. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4tc00221k

Halogenating agents, such as $SOCl_2$ and MesCl, were used in the dimerization of propargyl alcohols in previous research of rubrene.[21–24] We swapped halogenating agents for acetic anhydride, which is a good leaving group, then obtained compounds **4a** and **4b** in a 2–3 fold higher yield than previously reported. The relative yield ratio of cyclobutenes **4a** and **4b** to the rubrene analogue is 3 : 1 and 5 : 1 respectively. Generally, the electron-donating aryl group can lead to cyclobutenes in high selectivity. Surprisingly we demonstrated that electron-accepting aryl substituents achieved cyclobutenes in much higher yield than rubrenes.[25]

Usually, organic compounds with four-membered rings are thought to be unstable because the tension of the ring is larger than that of five or six-membered rings, so first we check the stability of compounds **4a** and **4b** under ambient conditions. No change was detected after it was put on a shelf under normal laboratory lighting for 18 months or exposed to the irradiation of a UV light of 365 nm for 24 h. Their thermal stability was measured under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. The decomposition temperature of **4a** was 298 °C while that of compound **4b** was 276 °C, so both of them are thermally stable (see Fig. S1 in ESI†).

Fig. 1 shows the absorption spectra of compounds **4a** and **4b** in CH_2Cl_2. The compounds exhibit similar absorption characteristics. According to the maximum absorption edges, their energy gaps are calculated to be 2.76 eV. According to their cyclic voltammogram curves (see Fig. S2 in ESI†), their HOMO levels are calculated to be −5.31 eV for compound **4a** and −5.67 eV for compound **4b** respectively. The LUMO values for **4a** and **4b** are calculated to be −2.55 eV and −2.91 eV, respectively. Therefore, the introduction of perfluorophenyl lowered the HOMO and LUMO levels by 0.36 eV. The absorption peaks at around 330 nm (**4a**) and 325 nm (**4b**) are the initial absorption peaks, which could be used as the excitation wavelength in order to observe their fluorescence properties.

To confirm the AIE properties of these compounds we measured their photoluminescence (PL) spectra. The dilute solution in THF gave an almost flat line parallel to the abscissa (Fig. 2 and 3). In order to induce aggregation of the dye, a nonsolvent of the dye is necessary. Water was chosen to induce the aggregation of these compounds. When a large proportion of water is added into the solution, the intensity of the PL peaks increased at the same dye concentration under identical conditions. With the increasing water content, the emission maximum wavelength of compound **4a** exhibits a slight red shift from about 510 nm to 540 nm, while that of compound **4b** became significantly red shifted by 145 nm from 405 nm to 550 nm, which is probably due to the increased solvent effects by the introduction of fluorinated phenyl groups and the electronic interactions between the phenyl and fluorinated phenyl rings. Their PL peak intensity was up to 530-fold for **4a** and 39-fold for **4b**, which was measured at the same dye concentration under identical measurement conditions. Compared to HPDMCb, both exhibit a red shift of more than 40 nm, which corresponds well with the fact that HPDMCb emits green light while

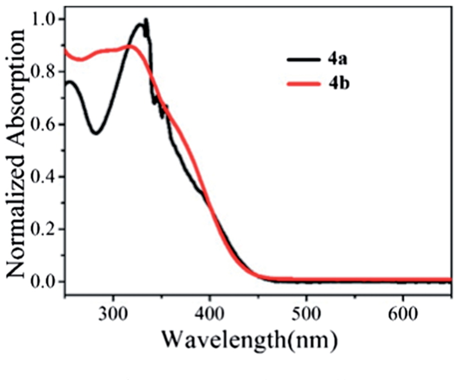

Fig. 1 UV-vis spectra of compounds **4a** and **4b**.

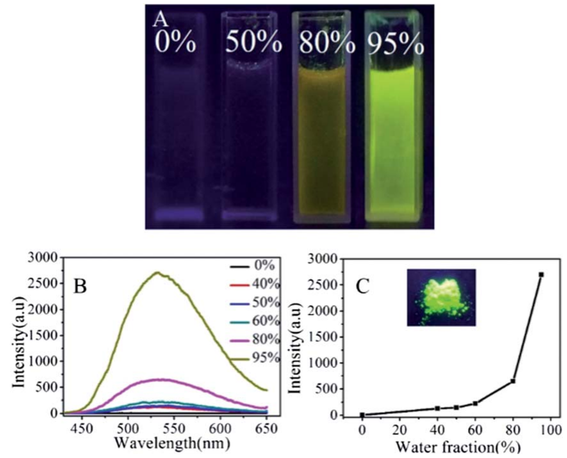

Fig. 2 (A) PL image of solutions of **4a** with different water fractions under UV (365 nm) light. (B) PL spectra of **4a** in different water–THF (v/v) mixtures. (C) The dependence of the PL intensity on the composition of the solution (inset: photo of the luminescent solid powder under 365 nm). The concentration was kept at 30 μM, excitation wavelength: 332 nm.

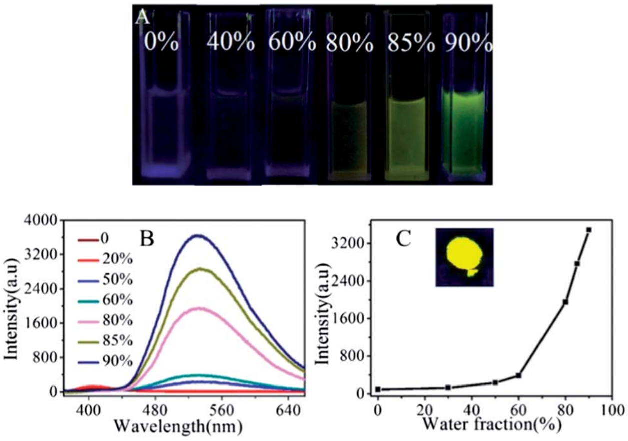

Fig. 3 (A) PL image of solutions of **4b** solutions with different water fractions under UV (365 nm) light. (B) PL spectra of **4b** in different water–THF (v/v) mixtures. (C) The dependence of the PL intensity on the composition of the solution (inset: photo of the luminescent solid powder under 365 nm). The concentration was kept at 30 μM, excitation wavelength: 340 nm.

compounds **4a** and **4b** emit yellow-green light. Moreover, in the solvent mixture with 90% water content, the fluorescent intensity of both compound **4a** and **4b** increased significantly whereas that of HPDMCb reduced sharply, indicating that thienyl substituted cyclobutenes have excellent AIE properties.

To acquire more convincing results, the absolute fluorescence quantum yield was tested in a calibrated integrating sphere. The fluorescence quantum yield of compounds **4a** and **4b** in solution was below the detection limit (<0.5%), while the solid state showed a significantly enhanced fluorescence efficiency of 29% for compound **4a** and 11% for compound **4b** respectively under identical conditions. The introduction of perfluorophenyl groups can enhance the polarity of compound **4b**, which possibly leads to emission quenching in the solid state.

The decay profiles of the fluorescence lifetime[26,27] of compound **4a** in solution, powder and crystal forms were recorded individually (as shown in Fig. S3, ESI†) The lifetime in solution is 0.63 ± 0.01 ns, while lifetimes in powder and crystal forms are 1.82 ± 0.06 ns and 1.83 ± 0.11 ns. The three fold increase of lifetime also corresponds well with the AIE properties.

Single crystals of compounds **4a** were obtained from petroleum through evaporation slowly at room temperature (CCDC 973433, Table S2 in ESI†). As shown in Fig. 4, it is obvious that the intramolecular rotation process of the phenyl and thienyl groups in compound **4a** is impeded. The restriction of the intramolecular rotation in the aggregates is a classic feature of AIE materials, so compound **4a** is rationalized to be a light emitting material that can be used in photoluminescence and electroluminescence devices. Since the molecular structure of compound **4b** is similar to compound **4a**, and it exhibits good AIE properties with yellow-green light emission.

A multilayer OLED with a device configuration of ITO (Indium Tin Oxides)/NPB (*N*,*N*'-Bis-(1-naphthalenyl)-*N*,*N*'-bis-phenyl-(1,1'-biphenyl)-4,4'-diamine) (50 nm)/compound **4a** (40 nm)/Alq3 (8-Hydroxyquinoline aluminum salt) (20 nm)/LiF (1 nm)/Al (120 nm) was fabricated using a vapor deposition processes, in which NPB and Alq3 served as hole- and electron-transport layers, respectively. The device is turned on at ~14 V and emits a green-yellow light at 540 nm (Fig. 5). Its luminance reached ~21 000 cd m^{-2} at ~22 V, which is much higher than that of HPDMCb (13 000 cd m^{-2}). The maximum current efficiency attained by the EL device is 1.76 cd A^{-1}.

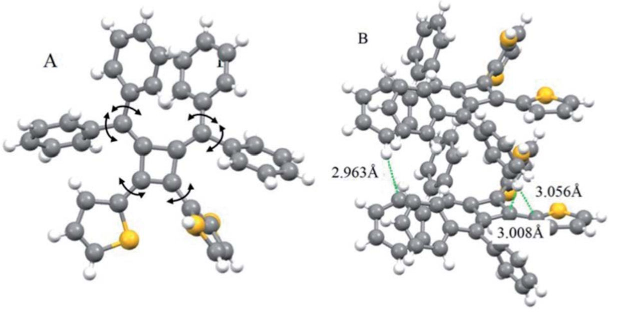

Fig. 4 ORTEP drawing packing motif of compound **4a** (50% probability for thermal ellipsoids).

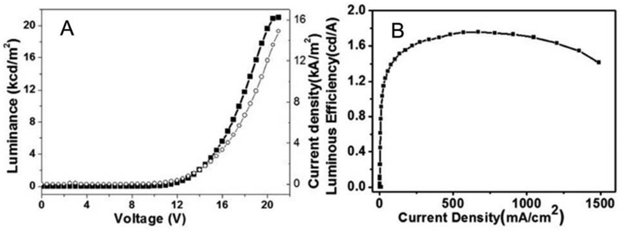

Fig. 5 (A) Changes in current density and luminance with applied biases. (B) Current efficiency *vs.* current density in a multilayer EL device with the configuration ITO/NPB/HPDMCb/Alq3/LiF/Al.

In summary, we developed an efficient and selective synthetic method towards thienyl substituted cyclobutenes **4a** and **4b**, which exhibit red-shifted AIE spectra in the region of 450–550 nm and better electroluminescence performance with luminance up to ~21 000 cd m^{-2} relative to phenyl substituted cyclobutene, HPDMCb. Our present work provides a useful guideline for the design of cyclobutene derivatives with AIE properties. Further studies on the cyclobutenes for applications in photoluminescence and electroluminescence devices is under way in our lab.

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