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## ARTICLE TYPE

## Synthesis and aggregation-induced emissions of thienyl substituted cyclobutene derivatives

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Thienyl substituted cyclobutenes with aggregation induced emission behaviours were firstly synthesized in good selectivity, opening the possibility of cyclobutenes for 10 application in light emitting diodes.

Aggregation-caused quenching (ACQ), which means organic materials with highly fluorescent in their dilute solutions but become weakly fluorescent along with the increase of solution concentration or aggregation in the solid state, is a notorious

<sup>15</sup> phenomenon in organic luminescent materials.<sup>1,2</sup> Unfortunately, for practical applications, such as organic light emitting diodes (OLEDs), only solid states (powders, films or crystals) are the best candidates for functional layers in electronic devices.<sup>3-5</sup> So luminescent materials with aggregation-induced emission (AIE)
 <sup>20</sup> properties have attracted much interest since the debut of the AIE

concept in 2001.<sup>6-13</sup> The AIE phenomenon is caused by restriction of vibrational

and rotational motion in aggregation states, keeping a distorted conformation for a single molecule and confining the rotation in 25 solid state by dense packing.<sup>14-16</sup> 1,2-diphenyl-3,4bis(diphenylmethylene)-1-cyclobutene(HPDMCb), which was isolated from a commercial product of rubrene, was found to

exhibit AIE property by Tang's group.<sup>17</sup> Regrettably, HPDMCb is the only cyclobutene compound, which exhibit AIE properties <sup>30</sup> and found application in OLEDs. It is interesting and important to investigate substituent dependant AIE properties of cyclobutene derivatives. Meanwhile, scare studies on the synthesis of cyclobutene derivatives, which is often separated from rubrenes in the traditional methods suffered low selectivity and poor yield

<sup>35</sup> for cyclobutenes relative to rubrenes.<sup>18-20</sup>

In this work, we firstly established a modified synthetic method to achieve cyclobutenes in much higher yield and selectivity compared with rubrenes. By changing the halogenating agent into acid anhydride and using N, N-<sup>40</sup> Diisopropylethylamine as the base, we obtained two new derivatives of dimethlene-cyclobutene with excellent AIE properties, both of them emits yellow-green light. Moreover, from the single crystal structure, the aryl groups of cyclobutene shows classical rigid structure with the intramolecular rotation

<sup>45</sup> being impeded, which meet the necessity of AIE property. 1,2-diaryl-3,4-bis (diary methylene)-1-cyclobutene (4a and 4b) were 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 the yield of 75% and 70% <sup>50</sup> respectively. Secondly, the dimerization of the propargyl alcohols afforded the target compound **4a** and **4b** in the yield of 30% and 31% respectively.



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

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

<sup>65</sup> Usually, organic compounds with four-membered ring are thought to be unstable because the tension of the cycle are larger than that of five or six cycles, so first we check the stability of compounds **4a** and **4b** at ambient environment. No change was detected either after it has been put on a shelf under normal <sup>70</sup> laboratory lighting for 18 month 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. 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<sup>†</sup>).



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

- <sup>5</sup> Fig. 1 shows the absorption spectra of compounds **4a** and **4b** in CH<sub>2</sub>Cl<sub>2</sub>. The compounds exhibit similar absorption characteristics. According to the maximum absorption edges, their energy gaps were calculated to be 2.76 eV. According to their cyclic voltammograms curves (see Fig. S2 in ESI<sup>+</sup>), their
- <sup>10</sup> 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 was 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 <sup>15</sup> absorption peaks at around 330 (4a) nm and 325 (4b) nm are initial absorption peaks, which could be used as the excited
- wavelength in order to observe their fluorescence properties.



<sup>20</sup> **Fig. 2** (A) PL pictures of **4a** solutions 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 water (inset: luminescent photo of the solid powder under 365 nm). The concentration was kept at 30 $\mu$ M, excitation wavelength: 332 nm.

- <sup>25</sup> To confirm the AIE properties of these compounds, we measured their PL spectra. The dilute solution in THF gave an almost flat line parallel to the abscissa (Fig. 2 and Fig. 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
- <sup>30</sup> compounds. When a large proportion of water is added into the solution, PL peaks of them should be intensified at the same dye concentration under identical conditions. With the content of water increasing, the emission maximum wavelength of compound 4a exhibits a slightly red shift from about 510 nm to

- <sup>35</sup> 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 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 of them exhibit a red shift of more than 40 nm, this results corresponds well with the fact that HPDMCb emits green light while compounds 4a and 4b emit 45 yellow-green light. Moreover, in the solvent mixture with 90% water content, the fluorescent intensity of both compound 4a and 4b
- **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 fluorescent 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 significantly enhanced fluorescence efficiency of 29% for <sup>55</sup> compound **4a** and 11% for compound **4b** respectively under identical conditions. The introduction of perfluorophenyl groups can enhance the polarity of the compound **4b**, which possibly lead to emission quenching in the solid state.







The decay profiles of fluorescence lifetimes<sup>26, 27</sup> of compound **4a** in solution, powder, and crystal are researched individually. As shown in Fig. S3 in ESI<sup>†</sup>. The lifetime in solution are  $0.63 \pm 0.01$  ns, while that of powder and crystal are  $1.82 \pm 0.06$  ns and  $_{70} 1.83 \pm 0.11$  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<sup>†</sup>). As shown in Fig. 4, it is <sup>75</sup> obvious that the intramolecular rotation process of those phenyl and thienyl groups in compound **4a** is impeded. The restriction of the intramolecular rotations in the aggregates is a classical feature for AIE materials, so compound **4a** is rationalized to be a light emitting material that can be used in photoluminescence and

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electroluminescence devices. Since the molecular structure of compounds **4b** is similar to compound **4a**, and it exhibits good AIE properties with yellow-green light emitting.



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

A multilayer OLED with a device configuration of ITO/NPB (50 nm)/compound **4a** (40 nm)/Alq3 (20 nm)/LiF (1 nm)/Al (120 nm) was fabricated using vapor deposition processes, in which <sup>10</sup> NPB and Alq3 served as hole- and electron-transport layers, respectively. The device is turned on at ~14 V and emits a greenyellow light of 540 nm (Fig. 5). Its luminance reached ~21 000 cd m<sup>-2</sup> at ~22 V, which is much higher than that of HPDMCb (13 000 cd m<sup>-2</sup>). The maximum current efficiency attained by the EL <sup>15</sup> device is 1.76 cd A<sup>-1</sup>.



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

- <sup>20</sup> 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<sup>-2</sup> relative to phenyl substituted cyclobutene
- <sup>25</sup> HPDMCb. Our present work provides a useful guidline for the design of cyclobutene derivatives with AIE properties. Further studies on the cyclobutenes for appliations in photoluminescence and electroluminescence devices is under the way in our lab.
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## **40 Notes and references**

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 † Electronic Supplementary Information (ESI) available: Synthesis detail

- <sup>45</sup> of compounds 4a and 4b, TGA of compounds 4a and 4b, oxidation cyclic voltammogram of 4a and 4b, lifetime of compounds 4a, CCDC reference number 973433. For ESI and crystallographic data in CIF or other electonic format see DOI: 10.1039/b000000x.
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Graphical and textual abstract for "Synthesis and aggregation-induced emissions of thienyl substituted cyclobutene derivatives".

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