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that of compound **4b** was 276 °C, so both of them are thermally stable (see Fig. S1 in ESI†).

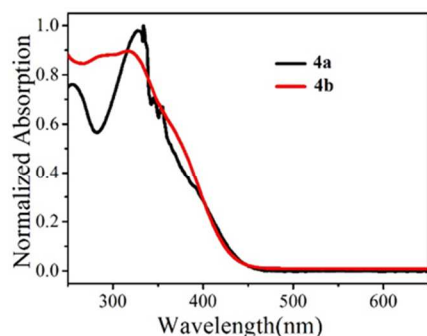
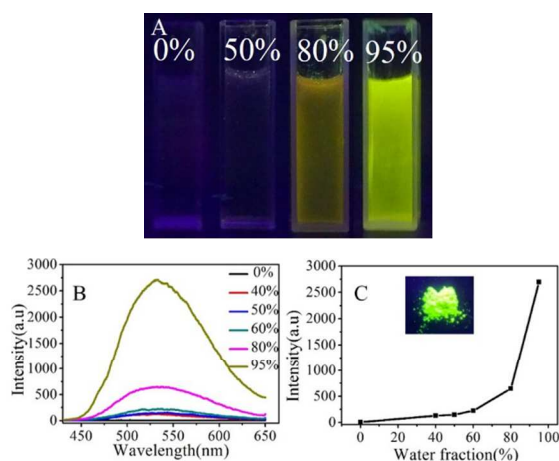


Fig. 1 UV-vis spectra of compounds **4a**, **4b**.

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†), 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** 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 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.

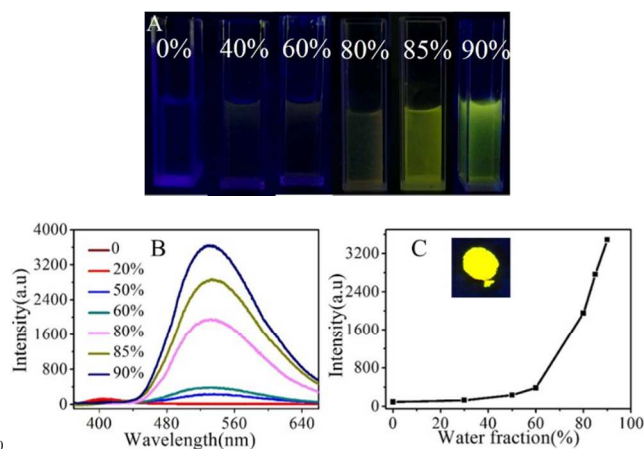


(A) PL pictures of **4a** solutions with different water fractions under UV (365 nm) light. (B) PL spectra of **4a** in different water-THF (v/v) mixtures. (C) The dependence of the PL intensity on the composition of water (inset: luminescent photo of the solid powder under 365 nm). The concentration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

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 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

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 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 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 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.

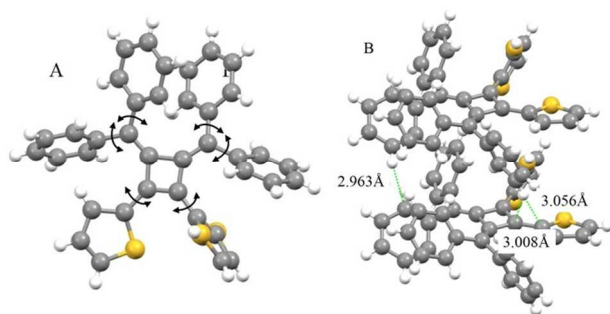


(A) PL pictures of **4b** solutions with different water fractions under UV (365 nm) light. (B) PL spectra of **4b** in different water-THF (v/v) mixtures. (C) The dependence of the PL intensity on the composition of water (inset: luminescent photo of the solid powder under 365 nm). The concentration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

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†. 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  $1.83 \pm 0.11$  ns. The three fold increase of lifetime also corresponds well with the AIE properties.

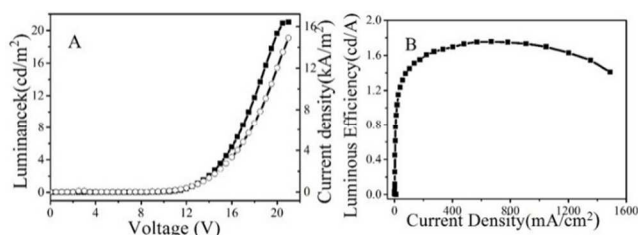
Single crystals of compounds **4a** were obtained from petroleum through evaporation slowly at room temperature (CCDC 973433, Table S2 in ESI†). As shown in Fig. 4, it is obvious that the intramolecular rotation process of those phenyl and thienyl groups in compound **4a** is impeded. The restriction 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

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.



**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)/Alq<sub>3</sub> (20 nm)/LiF (1 nm)/Al (120 nm) was fabricated using vapor deposition processes, in which NPB and Alq<sub>3</sub> served as hole- and electron-transport layers, respectively. The device is turned on at ~14 V and emits a green-yellow 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 HPDMC<sub>b</sub> (13 000 cd m<sup>-2</sup>). The maximum current efficiency attained by the EL 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/HPDMC<sub>b</sub>/Alq<sub>3</sub>/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<sup>-2</sup> relative to phenyl substituted cyclobutene HPDMC<sub>b</sub>. 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 the way in our lab.

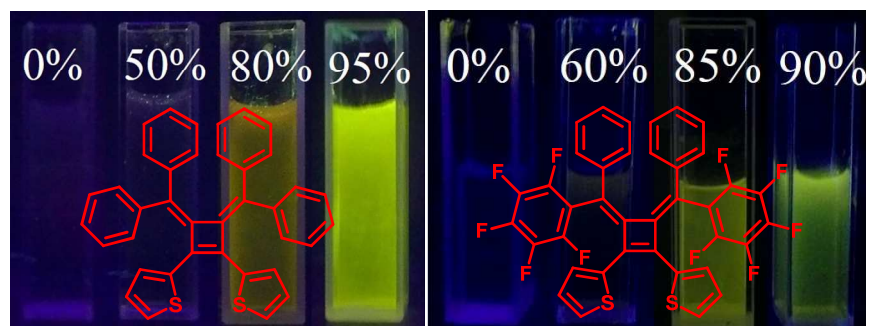
The authors thank for Prof. Hongbing Fu, Dr. Yishi Wu and Mr. Huiying Liu for discussions and measurements of fluorescence lifetime and quantum yields for the cyclobutene derivatives. The authors also acknowledge the financial support from National Natural Science Foundation of China (51303185, 21021091, 51033006, 51222306, 51003107, 61201105, 91027043, 91222203, 91233205), the China-Denmark Co-project, TRR61 (NSFC-DFG Transregio Project), the Ministry of Science and Technology of China (2011CB808400, 2011CB932300, 2013CB933403, 2013CB933500, 2014CB643600) and the Chinese Academy of Sciences.

## Notes and references

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- † Electronic Supplementary Information (ESI) available: Synthesis detail 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 electronic 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”:



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