Journal of Materials Chemistry C

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](http://www.rsc.org/Publishing/Journals/guidelines/AuthorGuidelines/JournalPolicy/accepted_manuscripts.asp).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](http://www.rsc.org/help/termsconditions.asp) and the Ethical quidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

www.rsc.org/materialsC

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Synthesis and aggregation-induced emissions of thienyl substituted cyclobutene derivatives

Xiaotao Zhang,^a Xiuqiang Lu,^a Yonggang Zhen,*^a Jie Liu,^a Huanli Dong,^a Guangyao Zhao,^aPing He,^a Zongrui Wang,^a Lang Jiang^aand Wenping Hu*^a

⁵*Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX* **DOI: 10.1039/b000000x**

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

 15 phenomenon in organic luminescent materials.^{1,2} 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.³⁻⁵ So luminescent materials with aggregation-induced emission (AIE) 20 properties have attracted much interest since the debut of the AIE

concept in 2001 .⁶⁻¹³

 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.¹⁴⁻¹⁶ 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.¹⁷ Regrettably, HPDMCb

is the only cyclobutene compound, which exhibit AIE properties ³⁰and 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 35 for cyclobutenes relative to rubrenes.¹⁸⁻²⁰

 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-⁴⁰Diisopropylethylamine 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 ⁴⁵being 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% ⁵⁰respectively. 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 $S OCl₂$, MesCl.²¹⁻²⁴ 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. ⁶⁰The relative yield ratio of cyclobutenes **4a** and **4b** to rubrene analogue are 3:1 and 5:1 respectively. Generally, electrondonating aryl group can lead to cyclobutenens in high selectivity. Surprisingly we demonstrated electron-accepting aryl substituents achieved cyclobutenes in much higher yield than rubrenes.²⁵

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 ⁷⁰laboratory 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†).

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

- ⁵Fig. 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 were calculated to be 2.76 eV. According to their cyclic voltammograms curves (see Fig. S2 in ESI†), their
- ¹⁰HOMO 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 ¹⁵absorption 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.

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 30µM, excitation wavelength: 332 nm.

- ²⁵To 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
- 30 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
- ³⁵540 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 ⁴⁰530-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 ⁴⁵yellow-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
- ⁵⁰To 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 $(\leq 0.5\%)$, while the solid state showed significantly enhanced fluorescence efficiency of 29% for ⁵⁵compound **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^{26, 27} 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 ± 0.06 ns and 701.83 ± 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 ⁷⁵obvious 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.

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 ¹⁰NPB and Alq3 served as hole- and electron-transport layers, respectively. The device is turned on at \sim 14 V and emits a greenyellow light of 540 nm (Fig. 5). Its luminance reached ~21 000 cd $m⁻²$ at \sim 22 V, which is much higher than that of HPDMCb (13 000 cd $m²$). The maximum current efficiency attained by the EL 15 device is 1.76 cd A^{-1} .

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.

- 20 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 \sim 21 000 cd m⁻² relative to phenyl substituted cyclobutene
- ²⁵HPDMCb. 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.
- The authors thank for Prof. Hongbing Fu, Dr. Yishi Wu and ³⁰Mr. Huiying Liu for discussions and measurements of fluorescence lifetime and quantum yields for the cylobutene derivatives. The authors also acknowledge the financial support from National Natural Science Foundation of China (51303185, 21021091, 51033006, 51222306, 51003107, 61201105,
- 35 91027043, 91222203, 91233205), the China-Denmark Coproject, TRR61 (NSFC-DFG Transregio Project), the Ministry of Science and Technology of China (2011CB808400, 2011CB932300, 2013CB933403, 2013CB933500, 2014CB643600) and the Chinese Academy of Sciences.

⁴⁰**Notes and references**

^a Beijing National Laboratory for Molecular Sciences, Key Laboratory of *Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China; E-mail: zhenyg@iccas.ac.cn; huwp@iccas.ac.cn* † Electronic Supplementary Information (ESI) available: Synthesis detail

- ⁴⁵of 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.
	- 1. S. A. Jenekhe and J. A. Osaheni, *Science*, 1994, **265**, 765–768.
	- ⁵⁰2. A. J. Heeger, *Solid State Commun*. 1998, **107**, 673–679.
	- 3. Y. N. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev*., 2011, **40**, 5361–5388.
	- 4. C. Wu,Y. Lin,K.Wong, R. Chen and Y. Chien, *Adv. Mater*., 2004, **16**, 61–65.
- ⁵⁵5. A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz and A. B. Holmes, *Chem. Rev*., 2009, **109**, 897–1091.
	- 6. J. D. Luo, Z. L. Xie, J-W. Y. Lam, L. Cheng, H. Y. Chen, C. F. Qiu, H. S. Kwok, X. W. Zhan, Y. Q. Liu, D. B. Zhu and B. Z. Tang, *Chem. Commun*., 2001, 1740–1741.
	- ⁶⁰7. D. Ding, K. Li, B. Liu and B. Z. Tang, *Acc. Chem. Res.*, 2013, **46**, 2441–2453.
	- 8. H. Shi, J. Liu, J. Geng, B. Z. Tang and B. Liu, *J. Am. Chem. Soc.*, 2012, **134**, 9569–9572.
- 9. Y. Kan, L.Wang, Y. Duan, G. Hu, G. Wu and Y. Qiu, *Appl.* ⁶⁵*Phys. Lett.,* 2004, **84**, 1513–1515.
	- 10. A. B. Koren, M.D. Curtis,A.H. Francis and J. W. Kampf, *J. Am. Chem. Soc.*, 2003, **125**, 5040–5050.
	- 11. Q. Q. Li, J. H. Zou, J. W. Chen, Z. J. Liu, J. G. Qin, Z. Li and Y. Cao, *J. Phys. Chem. B*, 2009, **113**, 5816–5822.
- ⁷⁰12. J. Huang, N. Sun, Y. Dong, R. Tang, P. Lu, P. Cai, Q. Li, D. Ma, J. Qin and Z. Li, *Adv. Funct. Mater.*, 2013, **23**, 2329– 2337.
	- 13. S. Xu, Y. Lin, J. Huang, Z. Li, X. Xu and L. Zhang, *J. Mater. Chem. A*, 2013, **1**, 4198–4206.
- ⁷⁵14. J. Liu, Q. Meng, X. T, Zhang, X. Q. Lu, P. He, L. Jiang, H. L. Dong and W. P. Hu, *Chem. Commun*., 2013, **49**, 1199–1201.
	- 15. Y. N. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Commun*., 2009, **29**, 4332–4353.
	- 16. X. Zhang, J. K. Sorensen, X. Fu, Y. Zhen, G. Zhao, L. Jiang, ⁸⁰H. Dong, J. Liu, Z. Shuai, H. Geng, T. Bjornholm and W. Hu, *J. Mater. Chem. C*, 2014, **2**, 884–890.
	- 17. Y. Q. Dong, J.W. Y. Lam, A. Qin, Z. Li, J. Sun, H. H. Y. Sung, I. D. Williams and B. Z. Tang, *Chem. Commun*., 2007, 3255– 3257.
	- ⁸⁵18. C. L. Wang, H. L. Dong, W. P. Hu, Y. Q. Liu and D. B. Zhu, *Chem.Rev*., 2012, **112**, 2208–2267.
	- 19. S. Braverman, E. V. K. Suresh Kumar, M. Cherkinsky,M. Sprechera and I. Goldberg, *Tetrahedron*, 2005, **61**, 3547–3557.
	- 20. V. C. Sundar, J. Zaumseil, V. Podzorov, E. Menard, R. L. ⁹⁰Willett, T. Someya, M. E. Gershenson, J. A. Rogers, *Science* 2004, **303**, 1644–1646.
	- 21. C. Dufraisse, L. Enderlin, *Bull. Soc.Chim.* 1932, **51**, 132.
	- 22. C. Dufraisse, *Bull. Soc. Chim.* 1933, **53**, 789.
	- 23. P. Essenfeld, *Eur. Patent.* 1998, No. 302195.
	- ⁹⁵24. Begley; William J. ; *US.Pate*nt. 2006, No.25642 A1.
	- 25. D. Braga, A. Jaafari, L. Miozzo, M. Moret, S. Rizzato, A. Papagni, and A. Yassar**,** *Eur. J. Org. Chem.* **2011**, 4160–4169.
	- 26. X. Q. Cao, Y. Y. Wu, H. B. Fu and J. N. Yao, J. *Phys. Chem. Lett.* 2011, **2**, 2163–2167.
	- 27. X. Q. Cao, S. M. Bai, Y. Y. Wu, Q. Liao, H. B. Fu and J. N. Yao, *Chem. Commun*., 2012, **48**, 6402–6404.

Journal of Materials Chemistry C Accepted ManuscriptJournal of Materials Chemistry C Accepted Manuscript