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# Aggregation-induced and crystallization-enhanced emissions of 1,2-diphenyl-3,4-bis(diphenylmethylene)-1-cyclobutene†

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***Received (in Cambridge, UK) 30th March 2007, Accepted 10th May 2007***
***First published as an Advance Article on the web 30th May 2007***
**DOI: 10.1039/b704794k**

**1,2-Diphenyl-3,4-bis(diphenylmethylene)-1-cyclobutene can be induced to emit efficiently by aggregate formation, with the crystalline aggregates emitting brighter, bluer lights than their amorphous counterparts.**

Scientists are in perpetual quest for luminescent materials that can emit efficiently in the solid state because for most real-world applications the luminophors are used as solid films.[1] Ironically, however, many dyes emit strongly when dissolved in their good solvents but become weak fluorophors when fabricated into solid films or aggregated in their poor solvents.[2] Crystallization can aggravate the situation by further lowering the quantum yields of fluorescence and red-shifting the emission spectra.[3] Researchers have worked hard to fabricate amorphous films in the construction of organic light-emitting diodes (OLEDs), though crystalline films commonly exhibit higher charge carrier mobilities.[4]

Whereas aggregation and crystallization normally quench light emissions, we have recently discovered "abnormal" processes of aggregation-induced emission (AIE)[5] and crystallization-enhanced emission (CEE).[6] We have found that a series of propeller-shaped non-emissive dyes can be induced to emit efficiently by aggregate formation.[5] We have further observed that crystals of many AIE dyes emit bluer lights in higher efficiencies than their amorphous counterparts.[6] Amorphous (4-biphenylyl)phenyldibenzofulvene, for example, emits a faint yellow light of 550 nm, whilst its crystalline films emit a blue light of 450 nm in a 32-fold higher efficiency.[6a]

We are interested in and have worked on further exploration of new AIE and CEE systems. In this work, we identified a new AIE- and CEE-active dye, 1,2-diphenyl-3,4-bis(diphenylmethylene)-1-cyclobutene (HPDMCb), which was isolated from a commercial product of rubrene (Fig. 1). Photoluminescence (PL) of this non-emissive dye was induced by adding poor solvent into its solution and was enhanced by annealing its amorphous film at appropriate temperatures. Its OLEDs emit green lights in a maximum luminance and current efficiency of 13 000 cd m$^{-2}$ and 1.78 cd A$^{-1}$, respectively.

During our search for new AIE fluorophors, we speculated that rubrene might be AIE active. Although it turned out that rubrene was not AIE active, we made a "side" discovery that one of its impurities was AIE active. When we purified rubrene using a silica gel column, we found that one of its impurities behaved like a typical AIE dye: its wet spot on the TLC plate could hardly be visualised but it became brightly emissive under the illumination of a UV lamp after solvent evaporation.[5] In other words, the impurity does not luminesce when molecularly dissolved but does so upon aggregate formation.

We isolated the impurity and characterized it spectroscopically (ESI†). Its pale yellow needle-like single crystal was grown from THF and X-ray analysis confirmed its structure as HPDMCb.‡ The dye is stable: the sample isolated from rubrene in May 2004 shows no change in color and TLC trace after it has been stored in air in a black box for several years. No change is detected either after it has been put on a shelf under normal laboratory lighting for 1 month or exposed to the irradiation of a UV light of 365 nm for 4 h. A literature search reveals that the molecule can be synthesized from the reaction of diphenyl-1,1-dibromoethylene with active metallic nickel.[8] Field effect activity of the dye has been reported[9] but its luminescence behaviour is virtually unknown.[7]

To confirm the AIE nature of HPDMCb, we measured its PL spectra. Its dilute solution in acetonitrile (AN) gives an almost flat line parallel to the abscissa (Fig. 2A), with a fluorescence quantum yield as low as 0.17%. When a large amount of water is added into the solution, its PL peak is intensified (up to 925-fold) at the same dye concentration under identical measurement conditions. Water is a nonsolvent of the dye and its molecules must have aggregated in the solvent mixtures with high water content. Apparently, the emission of HPDMCb is induced by the aggregate formation, thus duly verifying its AIE nature. In the dilute solution, rotations of multiple phenyl peripheries against the Cb core (*cf.*, Fig. 1) may have effectively nonradiatively deactivated its excited state, thus making it non-emissive. Restriction of the intramolecular rotations

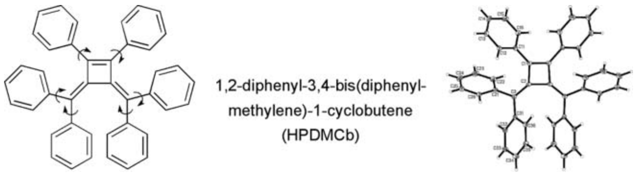

**Fig. 1** Structure of HPDMCb. The ORTEP plot is at 40% probability. The molecule has crystallographically imposed twofold symmetry.

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† Electronic supplementary information (ESI) available: Analysis data of HPDMCb; TEM images and ED patterns of its aggregates formed in aqueous mixtures with 70% and 90% water and its films before and after annealing; top and perspective views of its crystal structure with the multiple C–H$\cdots\pi$ hydrogen bonds marked; EL spectra of its OLEDs with various device configurations at different applied voltages. See DOI: 10.1039/b704794k

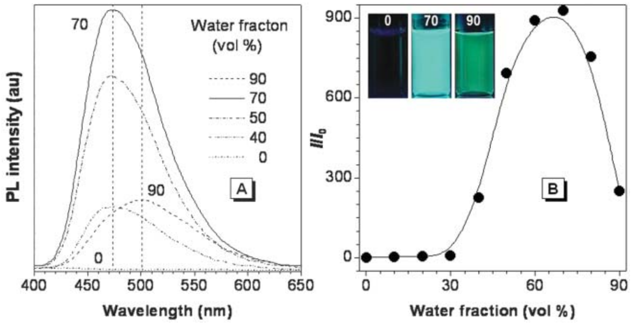

**Fig. 2** (A) PL spectra of HPDMCb in AN–water mixtures. (B) Plot of its PL peak intensity *vs.* water content of the solvent mixture. Inset: photos of HPDMCb in the AN–water mixtures with 0%, 70% and 90% water contents taken under illumination of a UV light. Dye concentration: 10 μM; excitation wavelength: 350 nm.

in the aggregates blocks the channel of nonradiative decay, hence changing the dye to a strong emitter.[6]

Careful inspection of the PL spectra of the dye in the aqueous mixtures reveals a decrease in the intensity ratio ($I/I_0$) and a red-shift in the emission peak when the water fraction is increased from 70% to 90%. This is probably due to the change in the packing mode of the dye molecules in the aggregates. In the mixture with the "low" water content, the dye molecules may steadily assemble in an ordered fashion to form more emissive, bluer crystalline aggregates. In the mixture with the "high" water content, however, the dye molecules may quickly agglomerate in a random way to form less emissive, redder amorphous particles. This proves to be the case from electron microscopy analysis: the aggregates formed in the aqueous mixtures with water contents of 70% and 90% are indeed crystalline and amorphous, respectively (Fig. S1, ESI†).

To further prove our hypothesis, we followed the time course of spectral evolution of HPDMCb dye in the AN–water mixtures with 70% and 90% water contents. When a stock solution of the dye in AN is admixed with appropriate amounts of AN and water to make an aqueous mixture with 70% water content, the PL spectrum of the dye is initially peaked at 500 nm (Fig. 3). With elapse of time, the PL peak shifts progressively from 500 nm to 474 nm (coinciding well with the value obtained from Fig. 2A), with an accompanying increase in the emission intensity. In contrast, almost no changes in the PL spectra of the dye are observed in the aqueous mixture with 90% water content, even after the mixture has been allowed to stand for as long as 50 min (Fig. 3B).

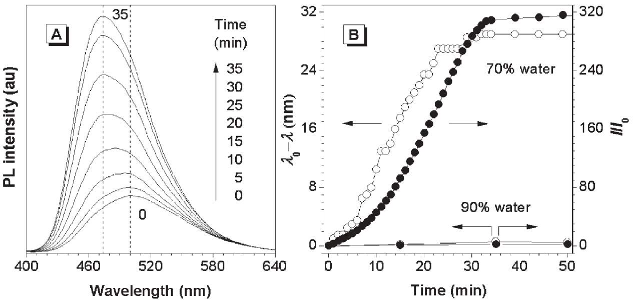

**Fig. 3** Time dependence of (A) the PL spectra of HPDMCb in an AN–water mixture (70 : 30 v/v) and (B) the peak positions and intensities of the dye in the mixtures with 70% and 90% water contents. Dye concentration: 10 μM; excitation wavelength: 367 nm.

In the solvent mixture with 70% water content, initially only a small portion of the dye molecules probably cluster together to form tiny nanoparticles. The larger portion of the dye molecules remaining in the solvent mixture then gradually deposits onto the initially formed nanoparticles in a way similar to recrystallization. This is supported by the fact that the average size of the particles in the dye aggregates is increased from 180 nm to 570 nm in 2 h. On the other hand, in the solvent mixture with 90% water content, all the dye molecules have probably agglomerated immediately and randomly. Little change in the particle size is thus observed (from 230 nm to 250 nm) even after the dye suspension in the aqueous mixture has been allowed to stand for as long as 12 h.

It becomes clear now that HPDMCb is not only AIE-active but also CEE-active. We thus explored the possibility of tuning its PL process by simple thermal perturbation, which has technological implications because materials with thermal manipulability may find applications as rewritable optical media.[10] A thin film of the dye deposited on a quartz plate emits a green light of 508 nm (Fig. 4). After annealing at 100 °C for 5 h, the PL spectrum shifts to the blue region with a peak at 474 nm and with a >3-fold increase in the emission intensity. Full width at half maximum (fwhm) of the PL spectrum changes from 93 nm to 67.5 nm, while the UV absorption peak moves from 363 nm to 354 nm. The blue shift, the emission enhancement and the fwhm narrowing all suggest that the film has crystallized after annealing. Although DSC analysis fails to detect the crystallization temperature of the dye, TEM images and ED patterns affirm that the as-prepared and annealed films of the dye are amorphous and crystalline, respectively (Fig. S2, ESI†).

Crystallization usually weakens and red-shifts light emission. Why are the opposite effects observed in the HPDMCb system? Due to the fast cooling in the vapor deposition process, the dye molecules may have rapidly piled up to form an amorphous film, during which some of its phenyl rings may have experienced π–π stacking interactions.[11] This is supported by a 51 nm red shift in the absorption peak of the amorphous film of the dye from that of its solution. During the long annealing process (5 h), the molecules of the dye may adjust themselves to take more twisted conformations in order to fit into the crystal lattice. Indeed, as can be seen from Fig. 1 and Fig. S3 (ESI†), the molecular conformations of the

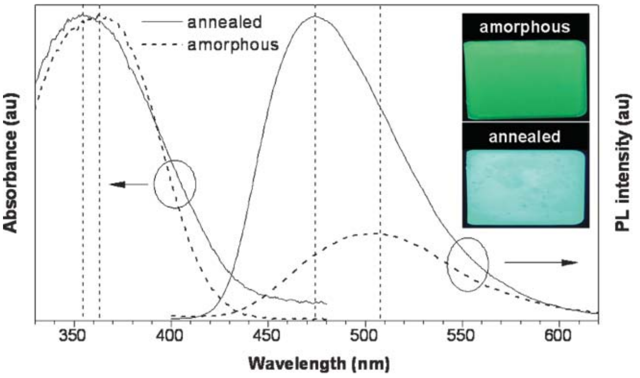

**Fig. 4** UV and PL spectra of amorphous and annealed films of HPDMCb measured at room temperature. Inset: photos of the films of the dye taken under UV illumination.

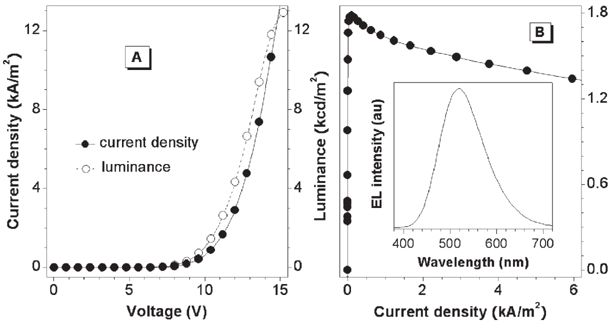

**Fig. 5** (A) Changes in current density and luminance with applied biases. (B) Current efficiency *vs.* current density in a multilayer EL device with a configuration ITO/NPB/HPDMCb/$Alq_3$/LiF/Al. Inset: EL spectrum.

dye are severely twisted in the crystalline state. This may account for the crystallization-induced blue shift in its PL spectrum. As shown in Fig. S3B (ESI†), there exist multiple C–H$\cdots\pi$ hydrogen bonds between the dye molecules, which lock their conformations in the crystal lattice. This structural rigidification effect thus makes the dye a stronger emitter in the crystalline state.[12]

The AIE-active nature of HPDMCb prompted us to use it to construct electroluminescence (EL) devices. A multilayer OLED with a device configuration of ITO/NPB (50 nm)/HPDMCb (40 nm)/$Alq_3$ (20 nm)/LiF (1 nm)/Al (120 nm) was fabricated using vapor deposition processes,[13] in which NPB and $Alq_3$ serve as hole- and electron-transport layers, respectively.[14] The device is turned on at $\sim$6 V and emits a green light of 520 nm (Fig. 5). Its luminance reaches $\sim$13 000 cd m$^{-2}$ at $\sim$15 V. The maximum current efficiency attained by the EL device is 1.78 cd A$^{-1}$, equivalent to a power efficiency of 0.67 lm W$^{-1}$.

We fabricated OLEDs of HPDMCb with other configurations. The devices with structures of ITO/NPB (50 nm)/HPDMCb (40 nm)/BCP (20 nm)/LiF (1 nm)/Al (120 nm) and ITO/NPB (50 nm)/HPDMCb (40 nm)/BCP (10 nm)/$Alq_3$ (20 nm)/LiF (1 nm)/Al (120 nm)[14] give EL spectra with peaks at 540 nm and 544 nm, respectively (Fig. S5 and S6), with the applied voltage exerting almost no effect on the EL spectra (Fig. S7, ESI†). The red shifts in the EL spectra, in comparison to the PL spectra, are probably due to the microcavity effect or the formation of exci- or electroplexes between HPDMCb and charge-transport layers.[15]

In summary, we isolated from rubrene a new dye, HPDMCb, whose light emission is induced by aggregation and enhanced by crystallization. Its AIE and CEE activities are proposed to stem from the restriction of intramolecular rotations and the hydrogen bond-endowed structural rigidification, respectively. Utilizing the novel properties of the dye, we successfully modulated its PL by the simple thermal process of annealing and demonstrated its utility in the fabrication of efficient OLED devices.

This project was partially supported by the Research Grants Council of Hong Kong (602706, HKU2/05C, 603505 and 603304), the Ministry of Science & Technology (2002CB613401) and the National Science Foundation of China (50603021). B. Z. T. thanks the Cao Guangbiao Foundation of Zhejiang University.

## Notes and references

‡ Crystal data for HPDMCb: $(C_{42}H_{30})(C_4H_8O)$, $M = 606.76$, monoclinic, $C2/c$, $a = 19.641(10)$, $b = 16.859(9)$, $c = 9.925(5)$ Å, $\beta = 92.159(11)^\circ$, $V = 3284(3)$ Å$^3$, $Z = 4$, $D_c = 1.227$ Mg m$^{-3}$, $\mu = 0.071$ mm$^{-1}$, $F(000) = 1288$, $T = 100(2)$ K, $2\theta_{max} = 51.00^\circ$, 6834 measured reflections, 2943 independent reflections ($R_{int} = 0.0358$), $R1 = 0.0560$, $wR2 = 0.1393$ (all data), $\Delta e$ 0.407 and $-0.264$ e Å$^{-3}$. CCDC 642388. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b704794k

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14 ITO = indium tin oxide; NPB = *N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenylbenzidine; $Alq_3$ = tris(8-hydroxyquinolinato)aluminium; BCP = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (or bathocuproine).

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