Aggregation-Induced and Crystallization-Enhanced Emissions of 1,2-Diphenyl-3,4-bis(diphenylmethylene)-1-cyclobutene

Yongqiang Dong,[ab] *Jacky W. Y. Lam,*[a] *Anjun Qin,*[a] *Jiaxin Sun,*[a] *Jianzhao Liu,*[a] *Zhen Li,*[a] *Jingzhi Sun,*[b]
Herman H-Y. Sung,[a] *Ian D. Williams,*[a] *Hoi Sing Kwok*[a] *and Ben Zhong Tang**[ab]

[a] Department of Chemistry, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China; E-mail: tangbenz@ust.hk

[b] Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

General Information

^{1}H and ^{13}C NMR spectra were measured on a Varian 300 spectrometer using deuterated chloroform as solvent. Tetramethylsilane was used as internal reference. Mass spectra were recorded on a triple quadrupole mass spectrometer (Finnigan TSQ7000) operating in a chemical ionization (CI) mode with methane as carrier gas. UV-vis absorption spectra were recorded on a Milton Roy Spectronic 3000. PL spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. Quantum yield of fluorescence (Φ_F) was estimated using 9,10-diphenylanthracene (Φ_F = 90% in cyclohexane) as standard.

Single crystals of 1,2-diphenyl-3,4-bis(diphenylmethylene)-1-cyclobutene (HPDMCb) were grown from its THF solution. Processing of the intensity data was carried out using the SAINT and SADABS routines, and the structure solution and refinement were carried out by the SHELXTL suite of X-ray programs (Version 6.10). Particle sizes of the nanoaggregates of HPDMCb in the acetonitrile/water mixtures were measured on a Beckman Coulter Delsa 440SX Zeta potential analyzer. Transmission electron micrographs (TEM) and electron diffraction (ED) patterns were obtained on a Philips CM-20 TEM instrument.

OLED devices were fabricated in the usual manner with sequential vapor depositions of various layers onto indium tin oxide (ITO)-coated glass substrates. The ITO glasses were precleaned in ultrasonic assisted detergent followed by rinsing with deionized water before being dried in an oven at 100 °C. After 25 min of UV-ozone treatment, the substrates were transferred into a vacuum chamber with a base pressure of 2×10^{-4} Pa for device fabrication. EL spectra and current–voltage–luminance curves of the devices were measured on a Spectrascan PR650 photometer and a computer-controlled HP4145B Semiconductor Parameter Analyzer under ambient conditions.

HPDMCb was isolated from a commercial product of rubrene. Characterization data of the dye: ^{1}H NMR (300 MHz, $CDCl_3$): 7.04−6.96 (m, 16H), 6.85−6.67 (m, 10H), 6.56−6.49 (d, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 155.1, 142.1, 141.8, 140.8, 133.4, 132.3, 131.9, 130.4, 128.5, 127.7, 127.6, 127.5, 127.4, 127.3, 126.9. M.p: 245–246 °C. UV (acetonitrile, 10 μM), λ_{max} (nm): 250, 312. MS (CI): *m/e* 534.1 (M^+, calcd. 534.2).

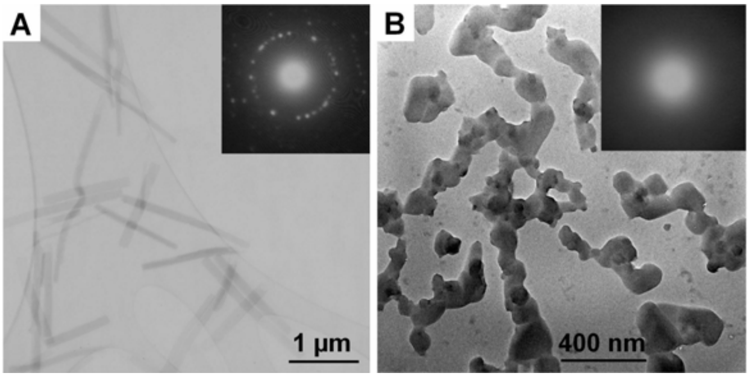

Figure S1. TEM images and ED patterns of (A) crystalline and (B) amorphous aggregates of HPDMCb formed in the acetonitrile/water mixtures with (A) 70% and (B) 90% water contents.

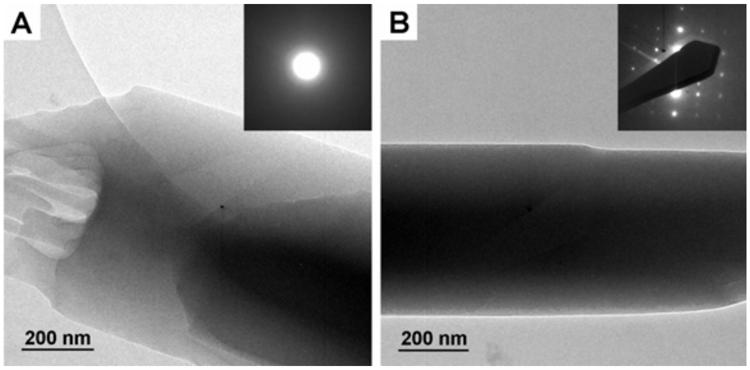

Figure S2. TEM images and ED patterns of HPDMCb films on copper grids (A) before and (B) after annealing at 100 °C for 5 h.

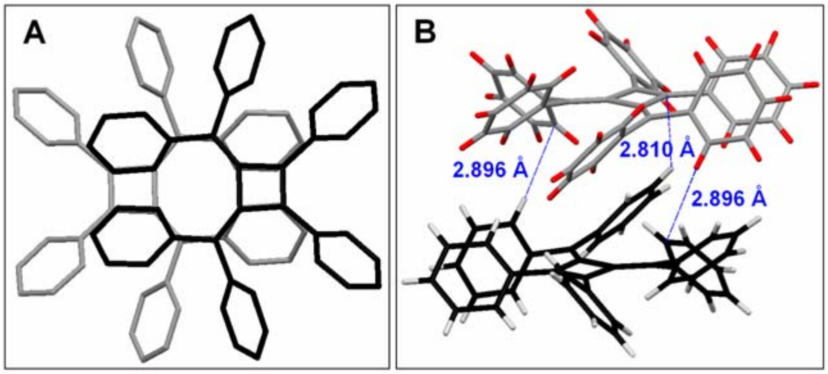

Figure S3. (A) Top and (B) perspective views of the packing arrangement in the crystals of HPDMCb. The aromatic C–H···π hydrogen bonds are marked with dotted lines.

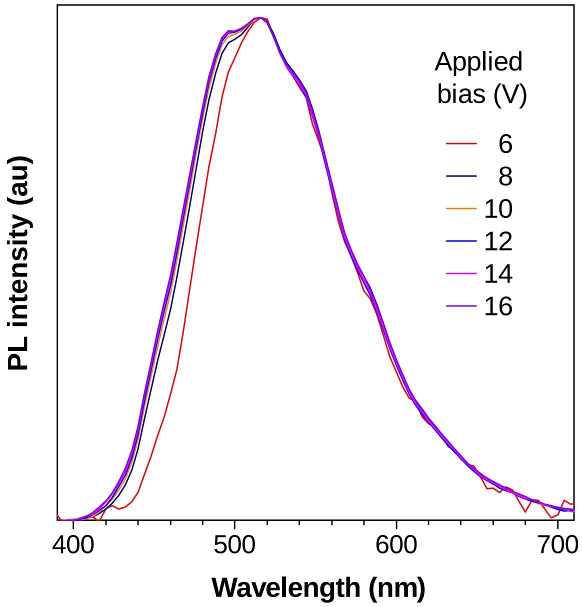

Figure S4. EL spectra of device ITO/NPB/HPDMCb/Alq_3/LiF/Al at different applied voltages.

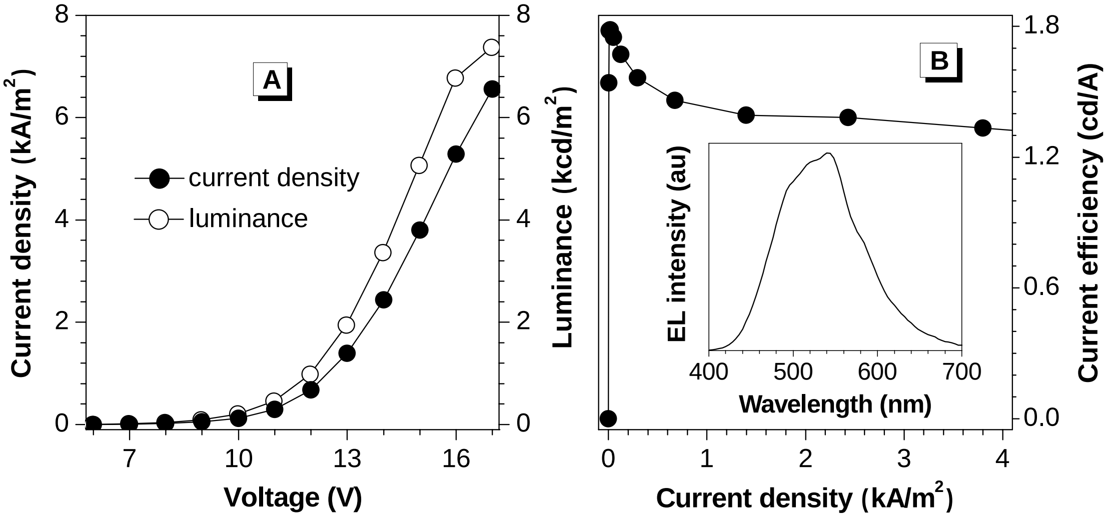

Figure S5. (A) Changes in current density and luminance with applied biases. (B) Current efficiency vs. current density in a multilayer OLED with a device configuration of ITO/NPB (50 nm)/HPDMCb (40 nm)/BCP (20 nm)/LiF (1 nm)/Al (120 nm). Inset: EL spectrum.

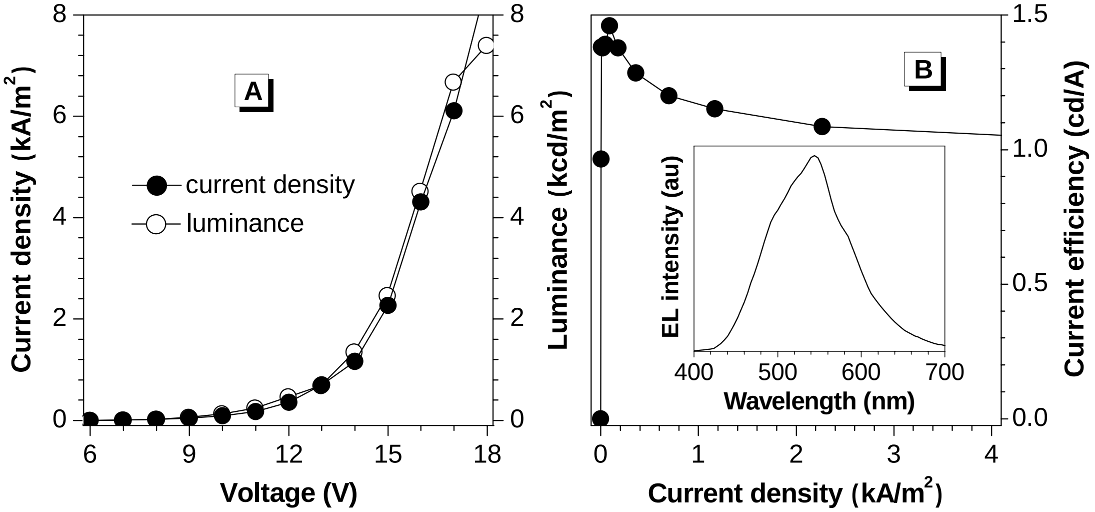

Figure S6. (A) Changes in current density and luminance with applied biases. (B) Current efficiency vs. current density in a multilayer OLED with a device configuration of ITO/NPB (50 nm)/HPDMCb (40 nm)/BCP (10 nm)/Alq_3 (20 nm)/LiF (1 nm)/Al (120 nm). Inset: EL spectrum.

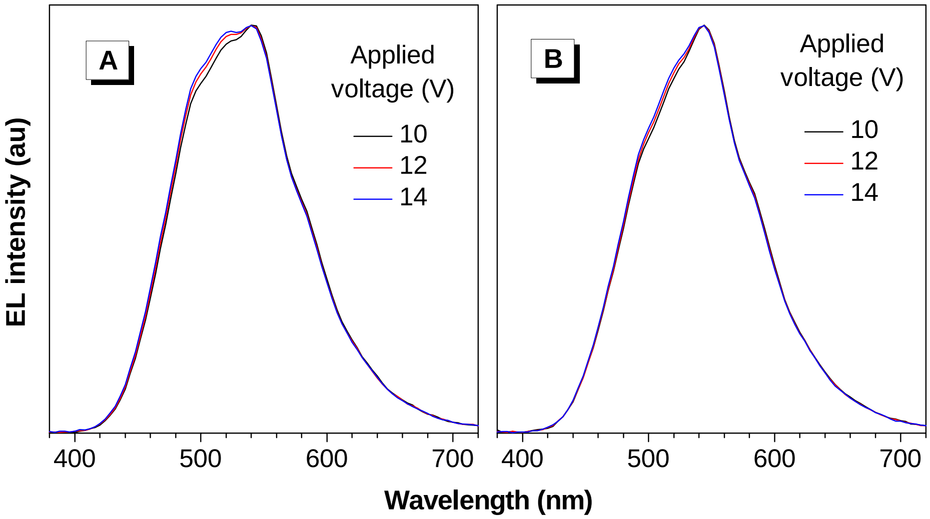

Figure S7. EL spectra of devices (A) ITO/NPB/HPDMCb/BCP/LiF/Al and (B) ITO/NPB/HPDMCb/BCP/Alq_3/LiF/Al at different applied voltages.

Table S1. Crystal Data and Structure Refinement for HPDMCb.

Empirical formula	$C_{46}H_{38}O$	
Formula weight	606.76	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 19.641(10) Å	α= 90°.
	b = 16.858(9) Å	β= 92.159(11)°.
	c = 9.925(5) Å	γ = 90°.
Volume	3284(3) $Å^3$	
Z	4	
Density (calculated)	1.227 Mg/m^3	
Absorption coefficient	0.071 mm^{-1}	
F(000)	1288	
Crystal size	0.40 x 0.15 x 0.15 mm^3	
Theta range for data collection	2.57 to 25.50°.	
Index ranges	-23<=h<=20, -20<=k<=8, -11<=l<=12	
Reflections collected	6834	
Independent reflections	2943 [R(int) = 0.0358]	
Completeness to theta = 25.50°	96.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.82	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	2943 / 5 / 210	
Goodness-of-fit on F2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0560, wR2 = 0.1302	
R indices (all data)	R1 = 0.0750, wR2 = 0.1393	
Largest diff. peak and hole	0.407 and -0.264 e.$Å^{-3}$	