

Switching the light emission of (4-biphenyl)phenyldibenzofulvene by morphological modulation: crystallization-induced emission enhancement

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Materials and Instrumentations

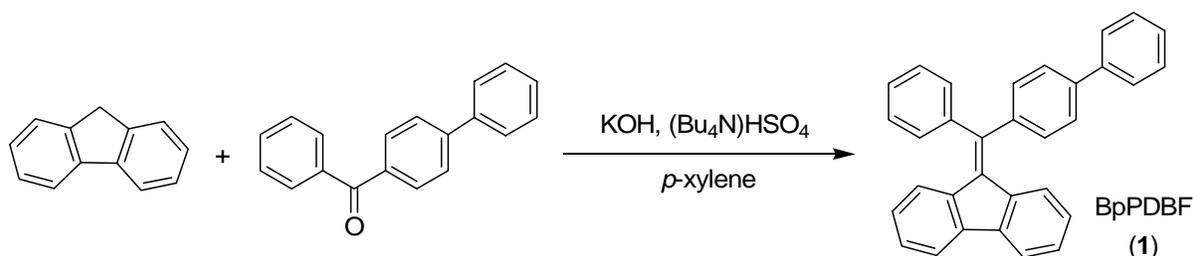
Fluorene, 4-benzoylbiphenyl, potassium hydroxide, and tetra(*n*-butyl)ammonium hydrogen sulfate were purchased from Aldrich and used as received.

¹H and ¹³C NMR spectra were measured on a Varian 300 spectrometer using deuterated chloroform as solvent. Tetramethylsilane was used as internal reference for the NMR analyses. Mass spectra were recorded on a triple quadrupole mass spectrometer (Finnigan TSQ7000). UV-vis absorption spectra were recorded on a Milton Roy Spectronic 3000. X-ray diffraction intensity data were collected at 100 K on a Bruker-Nonius Smart Apex CCD diffractometer with graphite-monochromated Mo K α radiation. Single crystals of **1** were grown from dichloroethane. Processing of the intensity data was carried out using the SAINT and SADABS routines, and the structure solution and refinement were conducted by the SHELXTL suite of X-ray programs (Version 6.10). Thermal transitions were investigated by differential scanning calorimetry (DSC) using a Setaram DSC 92 instrument at a heating rate of 10 °C/min. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer.

The fluorescence quantum yields (Φ_F) of **1** in solutions were measured using the literature procedure.² 9,10-Diphenylanthracene ($\Phi_F = 90\%$ in cyclohexane) was used as reference. The Φ_F values of the crystalline and amorphous films were measured using an integrating sphere with a diameter of 4" (Labsphere Inc.). The films were excited at 325 nm using a He-Cd laser. Transmission electron micrographs (TEM) and electron diffraction (ED) patterns were obtained on a Philips CM-20 TEM instrument. X-ray diffraction patterns were recorded on a PW1830 Powder X-ray diffractometer with a graphite monochromator using 1.5418 Å Cu K α wavelength at room temperature (scanning rate: 0.025°/s; scan range: 2–55°).

Synthesis and Characterization

(4-Biphenyl)phenyldibenzofulvene (BpPDBF; **1**) was prepared according to Scheme S1 following the synthetic procedures given in the literature.¹ Yield 52%. ¹H NMR (300 MHz, CDCl₃): 7.78–7.62 (m, 6H), 7.54–7.32 (m, 10H), 7.32–7.2 (m, 2H), 7.00–6.88 (m, 2H), 6.88–6.80 (d, 1H), 6.68–6.58 (d, 1H). ¹³C NMR (75 MHz, CDCl₃): 145.0, 142.8, 141.7, 140.7, 140.3, 138.6, 138.5, 134.2, 130.3, 129.7, 128.7, 128.2, 127.5, 127.2, 126.9, 126.3, 124.8, 119.2. MS (CI): *m/e* 406.1 (M⁺, calcd 406.2).



Scheme S1. Synthesis of (4-biphenyl)phenyldibenzofulvene (**1**).

References

- 1 J. W. Hill, J. A. Jenson and J. G. Yaritz, *J. Educ. Chem.*, 1986, **63**, 916.
- 2 (a) L. Liao and Y. Pang, *Macromolecules*, 2001, **34**, 7300. (b) J. A. Osaheni and S. A. Jenekhe, *J. Am. Chem. Soc.*, 1995, **117**, 7389. (c) J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991.

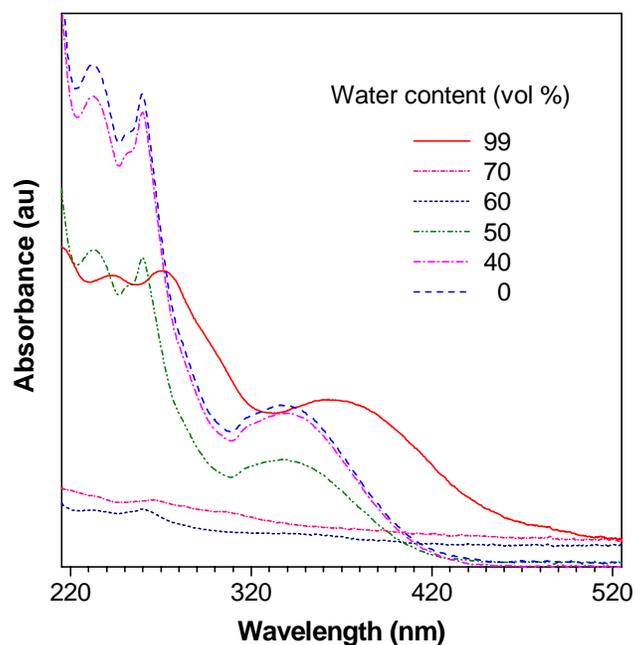


Figure S1. UV spectra of **1** in acetonitrile and acetonitrile/water mixtures.

TEM Images and ED Patterns of Aggregates

A few drops of aggregate suspensions were placed on copper grids coated with carbon. The deposits were dried under vacuum and then examined under an electron microscopy.

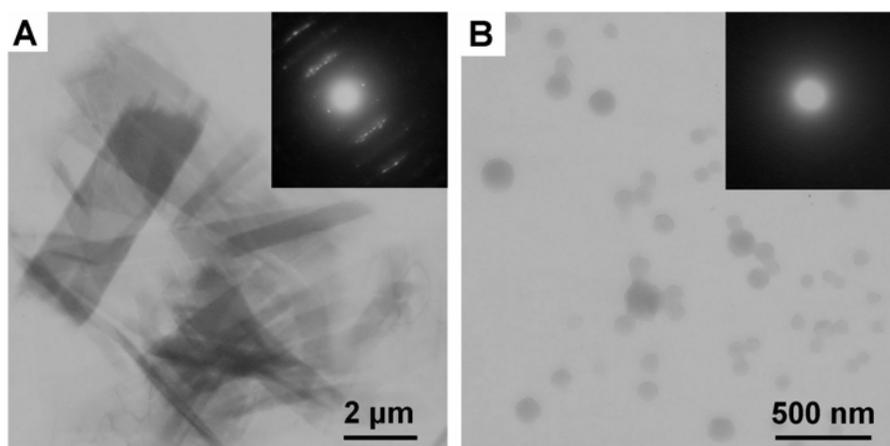


Figure S2. TEM images and ED patterns of (A) crystalline and (B) amorphous aggregates of **1** formed in acetonitrile/water mixtures with water contents of (A) 70 and (B) 99 vol %, respectively.

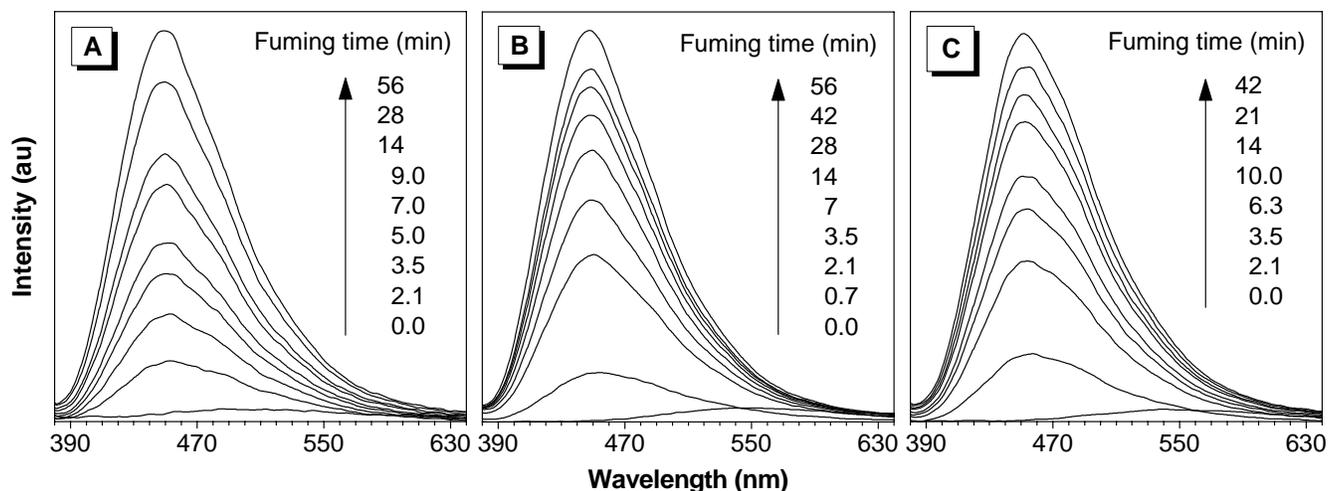


Figure S3. Effects of fuming by the vapors of (A) chloroform, (B) dichloromethane, and (C) toluene on the emission spectra of thin films of **1** coated on the inner walls of quartz cells. Excitation wavelength: 350 nm.

TEM Images and ED patterns of the Films before and after Solvent Fuming

Samples were prepared by dropping solution of **1** on copper grids coated with carbon and then exposed to acetone vapor for 2 h. After vacuum drying, the samples were analyzed using a Philips CM-20 TEM instrument.

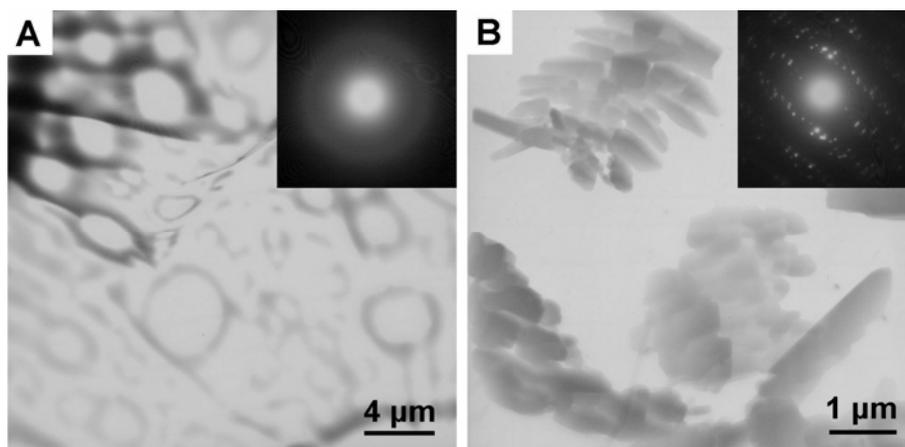


Figure S4. TEM images of films of **1** (A) before and (B) after exposure to acetone vapor for 2 h. The ED patterns are shown in the insets.

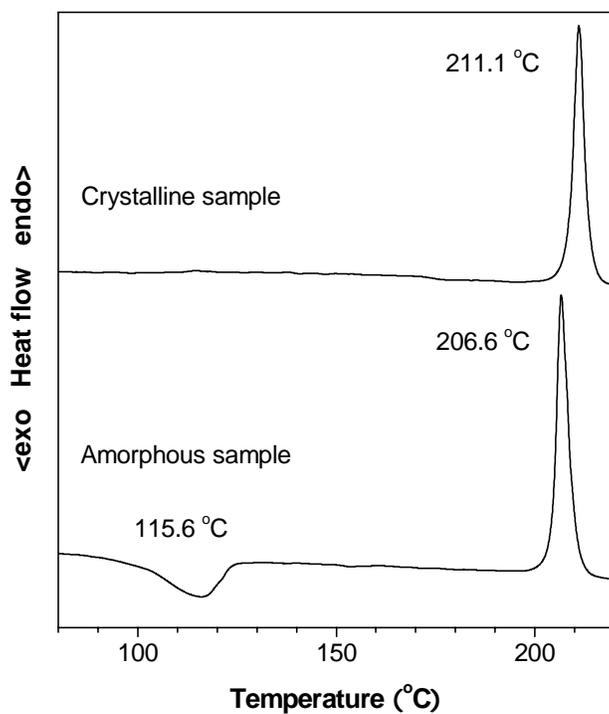


Figure S5. DSC thermograms of crystalline and amorphous samples of **1**.

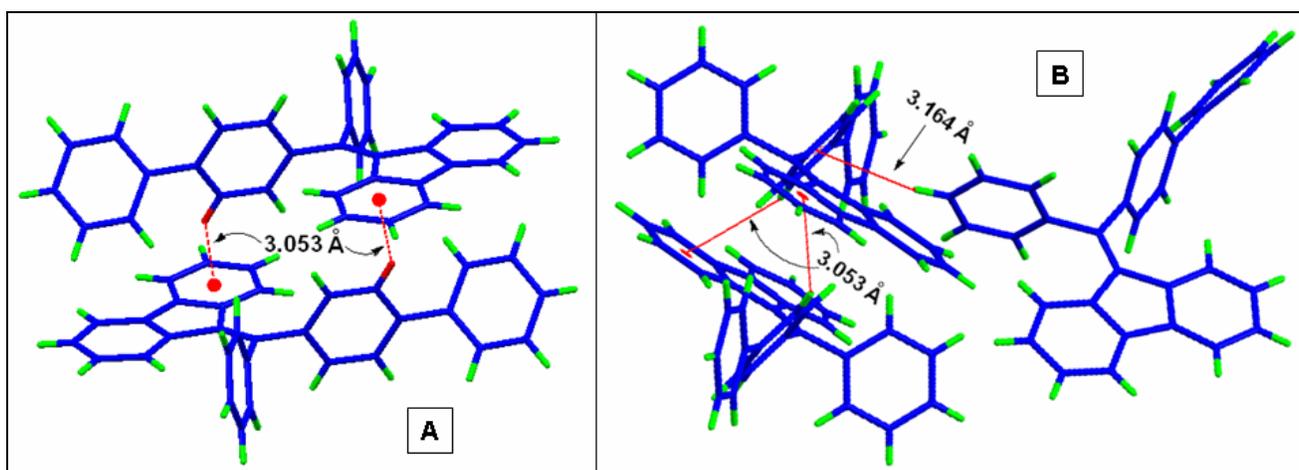


Figure S6. (A) Dimer and (B) trimer structures of **1** with multiple C-H... π hydrogen bonds extracted from its X-ray single crystal analysis data.

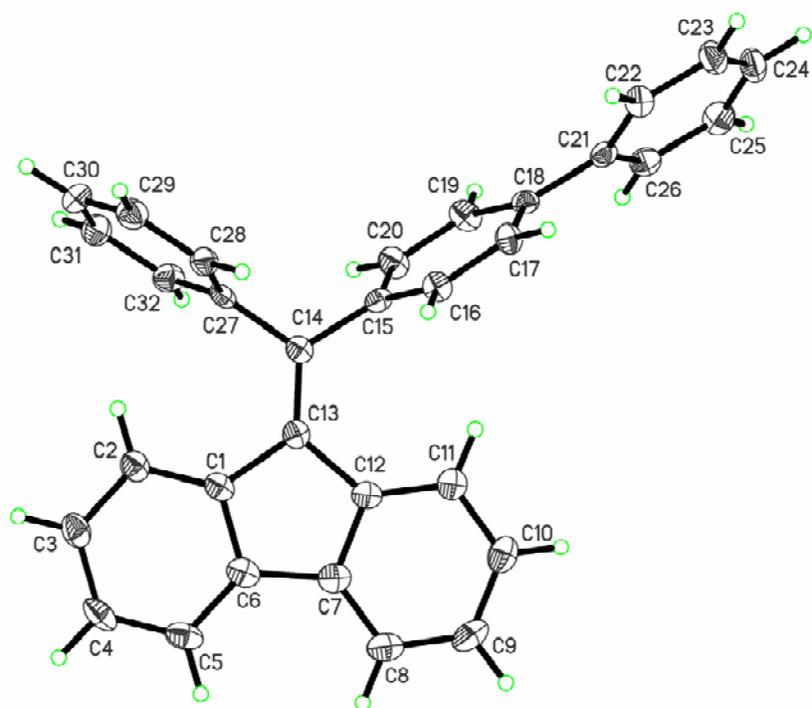


Figure S7. ORTEP drawing of single crystal structure of **1** at the 50% probability.

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	C ₃₄ H ₂₆ Cl ₂	
Formula weight	505.45	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 13.8275(7) Å	α = 90°.
	b = 9.9939(5) Å	β = 108.0360(10)°.
	c = 19.6086(9) Å	γ = 90°.
Volume	2576.6(2) Å ³	
Z	4	
Density (calculated)	1.303 Mg/m ³	
Absorption coefficient	0.274 mm ⁻¹	
F(000)	1056	
Crystal size	0.30 x 0.15 x 0.12 mm ³	
Theta range for data collection	2.31 to 26.00°.	
Index ranges	-17 ≤ h ≤ 17, -12 ≤ k ≤ 9, -24 ≤ l ≤ 24	
Reflections collected	15935	
Independent reflections	4723 [R(int) = 0.0234]	
Completeness to theta = 25.00°	94.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.93	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4723 / 0 / 323	
Goodness-of-fit on F ²	1.036	
Final R indices [I > 2σ(I)]	R1 = 0.0481, wR2 = 0.1093	
R indices (all data)	R1 = 0.0572, wR2 = 0.1136	
Largest diff. peak and hole	0.586 and -0.411 e.Å ⁻³	