Tunable Aggregation-Induced Emission of Diphenyldibenzofulvenes

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Materials and Instrumentations

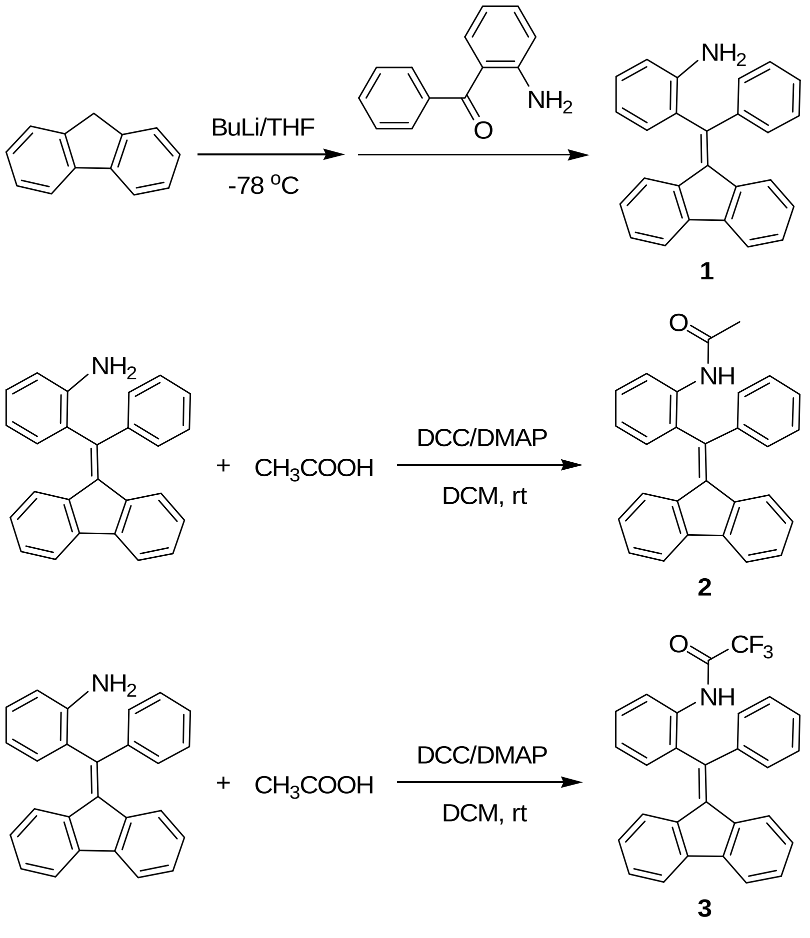
Fluorene, *n*-butyllithium (BuLi, 2.5 M in hexane), 2-aminobenzophenone, 4-dimethylaminopyridine (DMAP), acetic acid, trifluoroacetic acid, and *N,N'*-dicyclohexylcarbodiimide (DCC) were purchased from Aldrich and used as received. Solvents were purified by standard distillation procedures.

^{1}H and ^{13}C NMR spectra were measured on a Bruker ARX 300 or Varian 300 spectrometer using deuterated chloroform as solvent. Tetramethylsilane (TMS) 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 Array spectrophotometer and photoluminescence (PL) spectra were measured on a Perkin-Elmer LS 50B luminescence spectrometer with Xenon discharge lamp excitation. Transmission electron microphotograph (TEM) and electron diffraction (ED) patterns were taken on a JEOL 100CX TEM instrument.

X-ray diffraction intensity data were collected at 295 or 100 K on a Bruker-Nonius Smart Apex CCD diffractometer with graphite-monochromated Mo Kα radiation. Single crystal of **1** was grown from THF. 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).

Synthesis and Characterization

The fulvene derivatives were prepared according to the synthetic routes given in Scheme S1. All the reactions were carried out in an inert atmosphere.



Scheme S1 Synthesis of 9-diphenylmethylene-9*H*-fluorenes **1**–**3**.

*9-[(o-Aminophenyl)phenylmethylene]-9H-fluorene (**1**).* To a 250 mL two-necked flask were added 4.0 g of fluorene and 100 mL THF under nitrogen. After the solution was cooled down to –78 °C, BuLi in hexane (20 mL, 48 mmol) was injected into the flask and the mixture was stirred at –78 °C for 2 h. 2-

Aminobenzophenone (4.3 g) in 30 mL THF was then added into the flask. The mixture was slowly raised to room temperature and further stirred for 10 h, after which, the mixture was concentrated by a rotary evaporator. The crude product was purified by a silica-gel column using a hexane/chloroform mixture (1:1 by volume) as eluent. The product (**1**) was isolated in 46% yield. Mp: 188–190 °C. IR (KBr), ν (cm^{-1}): 3472, 3381 (ν_{NH}), 1310 (ν_{CN}). ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.70 (d, 2H), 7.49–7.41 (m, 5H), 7.31–7.19 (m, 3H), 7.10 (d, 1H), 7.01 (t, 1H), 6.94 (t, 1H), 6.85–6.73 (m, 4H), 3.82 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 143.7, 142.2, 141.9, 140.8, 140.4, 138.5, 138.1, 135.2, 130.4, 129.5, 129.0, 128.5, 128.2, 128.0, 127.3, 126.6, 125.2, 124.4, 119.4, 119.3, 116.2. MS (FAB), m/e: 345.1 ($[M]^+$ calcd. 345.2).

*9-{[*o*-(Acetylamino)phenyl]phenylmethylene}-9*H*-fluorene (2).* Acetic acid (0.1 g), **1** (0.5 g), and DMAP (0.1 g) were dissolved in 100 mL of dry dichloromethane (DCM) in a 250 mL two-necked flask under nitrogen. The solution was cooled to 0–5°C with an ice-bath, to which 0.48 g DCC in 50 mL of DCM was added under stirring via a dropping funnel with a pressure equalization arm. The mixture was stirred at room temperature overnight and then concentrated by a rotary evaporator. The crude product was purified by a silica gel column using a hexane/chloroform mixture (3:1 by volume) as eluent. The product (**2**) was isolated as white needle crystal in 57% yield. Mp: 248–250°C (decomp). IR (KBr), ν (cm^{-1}): 3323, 3226 (ν_{NH}), 1654 (ν_{CO}). ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.25 (d, 1H), 7.68 (d, 2H), 7.45–7.41 (m, 6H), 7.28–7.15 (m, 5H), 6.94 (t, 2H), 6.80 (d, 1H), 6.51 (d, 1H), 3.73 (s, 1H), 1.80 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 168.6, 141.6, 141.3, 141.0, 140.3, 138.3, 138.1, 137.0, 135.5, 130.8, 130.0, 129.3, 129.0, 128.9, 127.8, 127.2, 125.6, 125.5, 125.0, 122.7, 120.0, 119.9, 31.0. MS (FAB), m/e: 388.2 ($[M + H]^+$, calcd. 388.2).

*9-{[*o*-(Trifluoroacetylamino)phenyl]phenylmethylene}-9*H*-fluorene (3).* Trifluoroacetic acid (0.2 g), **1** (0.5 g), and DMAP (0.2 g) were dissolved in 100 mL of dry DCM in a 250 mL two-necked flask under nitrogen. The solution was cooled to 0–5°C with an ice-bath, to which 0.48 g DCC in 50 mL of DCM was added under stirring via a dropping funnel with a pressure equalization arm. The mixture was stirred at room temperature overnight and then concentrated by a rotary evaporator. The crude product was purified by a silica gel column using a hexane/chloroform mixture (3:1 by volume) as eluent. The product (**3**) was isolated as a pale yellow solid in 52% yield. Mp: 130–132°C. IR (KBr), ν (cm^{-1}): 3387 (ν_{NH}), 1737 (ν_{CO}). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.21 (t, 1H), 7.65 (d, 2H), 7.49–7.36 (m, 7H), 7.30–7.21 (m, 3H), 6.91 (t, 2H), 6.83 (d, 1H), 6.48 (d, 1H), 3.67 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 155.1, 154.6, 141.1, 140.6, 138.4, 137.8, 137.6, 137.5, 132.8, 131.3, 130.0, 129.8, 129.7, 129.4, 129.0, 127.4, 127.2, 127.0, 125.3, 124.5, 122.7, 119.8. MS (FAB), m/e: 442.2 ($[M + H]^+$ calcd. 442.1).

UV and PL Spectra

Stock solutions of **1**–**3** were 1.0×10^{-3} M in acetonitrile. Sample mixtures for measuring the UV and PL spectra were prepared by adding 1 mL of a stock solution to 99 mL of acetonitrile or water under vigorous stirring at room temperature. The mixtures were stirred for half an hour prior to taking their spectra. Crystals of **1** and **2** were grown from THF/methanol mixtures, and their amorphous samples were prepared by rapidly freezing their isotropic melts by liquid nitrogen.

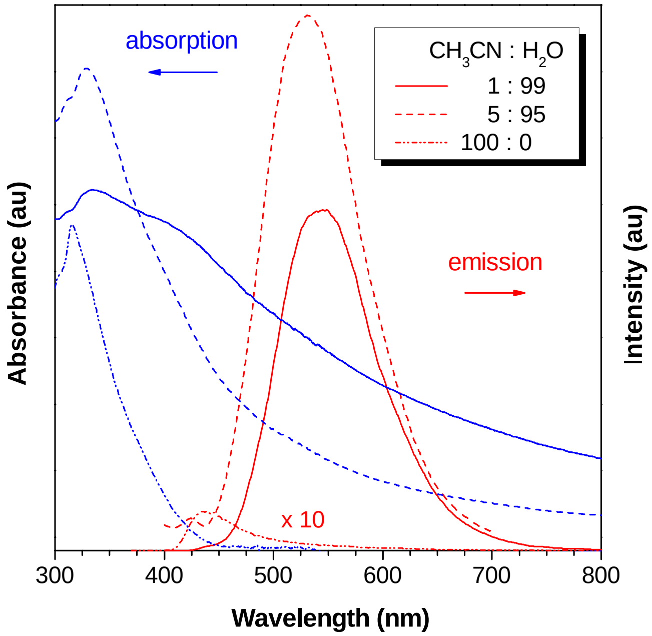


Fig. S1 Absorption and emission spectra of **1** in pure acetonitrile and acetonitrile/water mixtures.

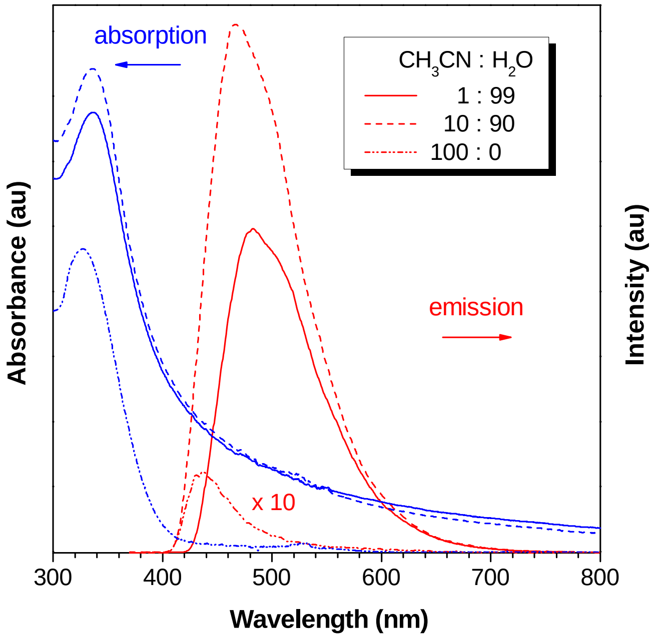


Fig. S2 Absorption and emission spectra of **2** in pure acetonitrile and acetonitrile/water mixtures.

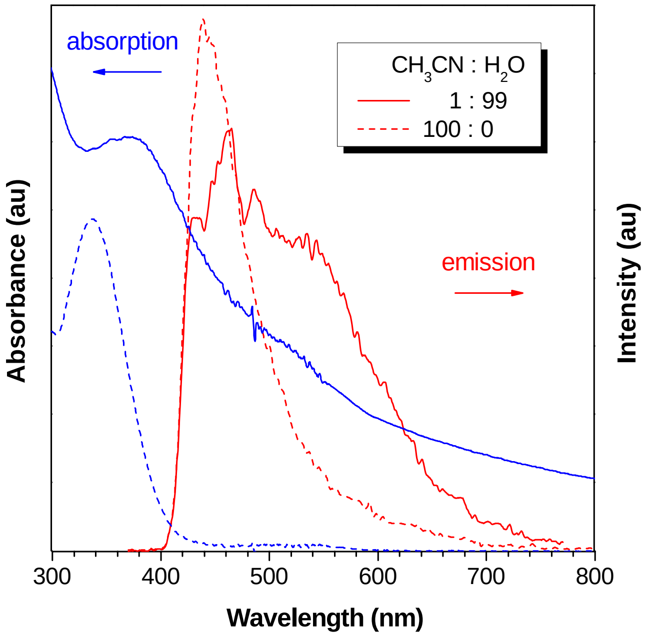


Fig. S3 Absorption and emission spectra of **3** in pure acetonitrile and an acetonitrile/water mixture.

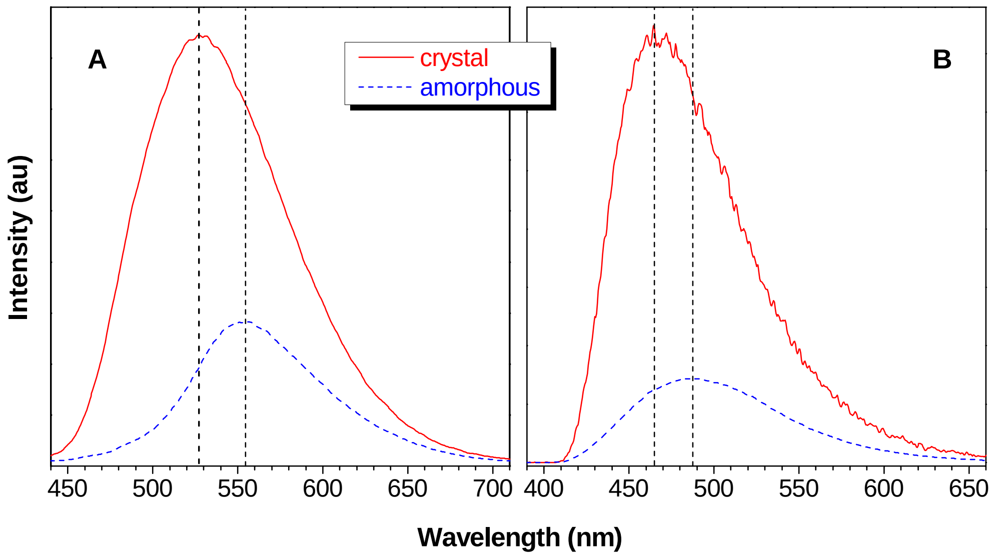


Fig. S4 Emission spectra of (A) **1** and (B) **2** in amorphous and crystalline states.

TEM Images and ED Patterns

One drop of an aggregate suspension in an acetonitrile/water mixture was placed on a copper grid coated with carbon. The deposit was dried in vacuum. The electron microscopy studies were performed using a JEOL 100CX TEM instrument.

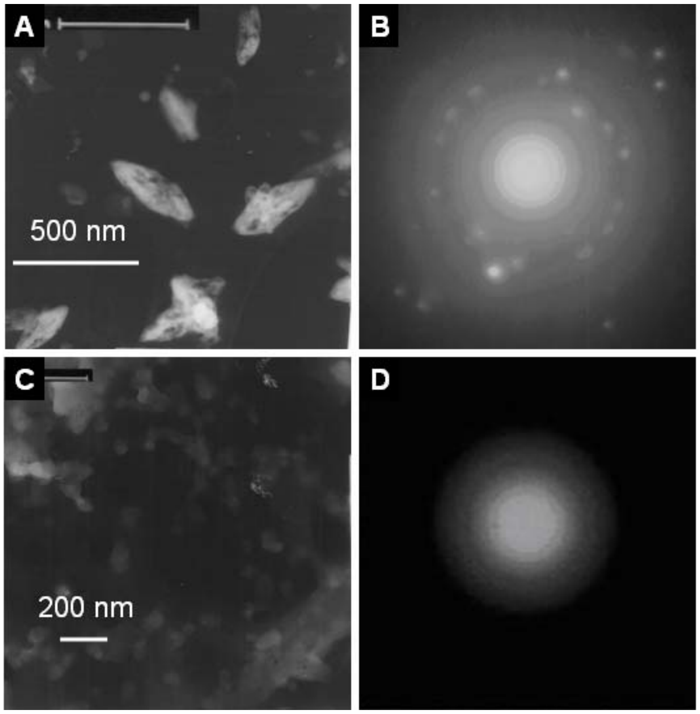


Fig. S5 TEM images (left) and ED patterns (right) of (A and B) crystalline and (C and D) amorphous aggregates of **1** formed in the acetonitrile/water mixtures with water contents of 90 and 99 vol %.

Electronic Structure Computations

Geometries of the isolated molecules in the ground state were optimized based on RHF/6-31G* calculations using Gaussian 98 package program.[1] On the basis of the optimized geometries, their electronic absorption spectra and HOMO and LUMO orbitals were calculated by semi-empirical ZINDO/S method in HyperChem 7.5.[2]

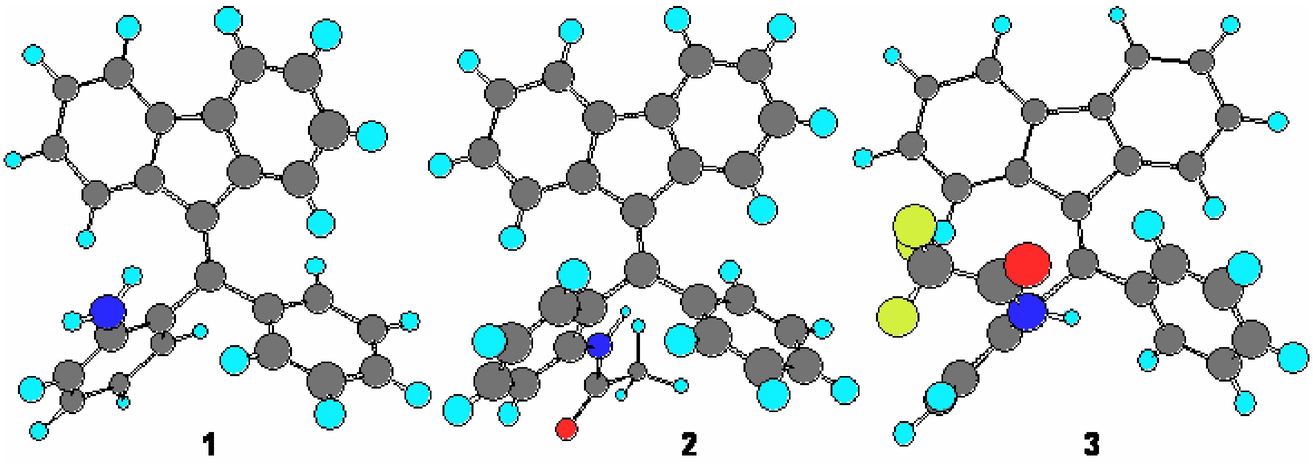


Fig. S6 The optimized structures for **1**, **2** and **3**.

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[1] Gaussian 98, Revision A.7, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.

[2] Hypercheme Release 7.5. Windows Molecular Modeling System, Hypercube, Inc. and Autodesk, Inc. Developed by Hypercube, Inc.

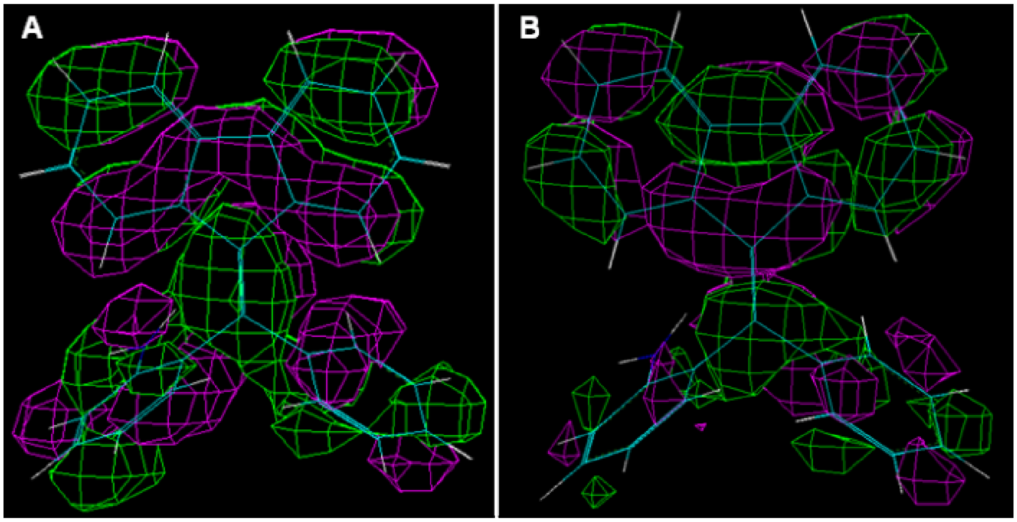

Fig. S7 Molecular orbital amplitude plots of (A) HOMO and (B) LUMO of **1**.

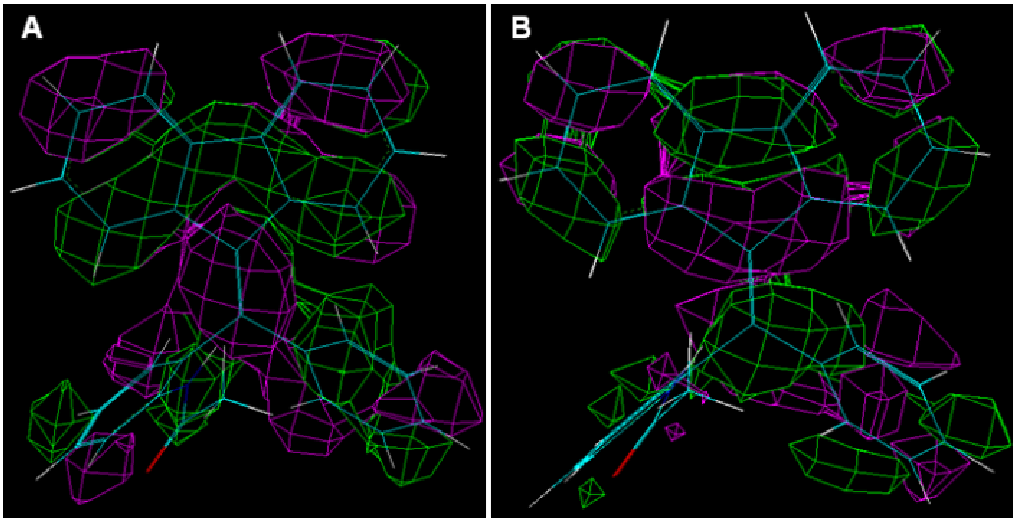

Fig. S8 Molecular orbital amplitude plots of (A) HOMO and (B) LUMO of **2**.

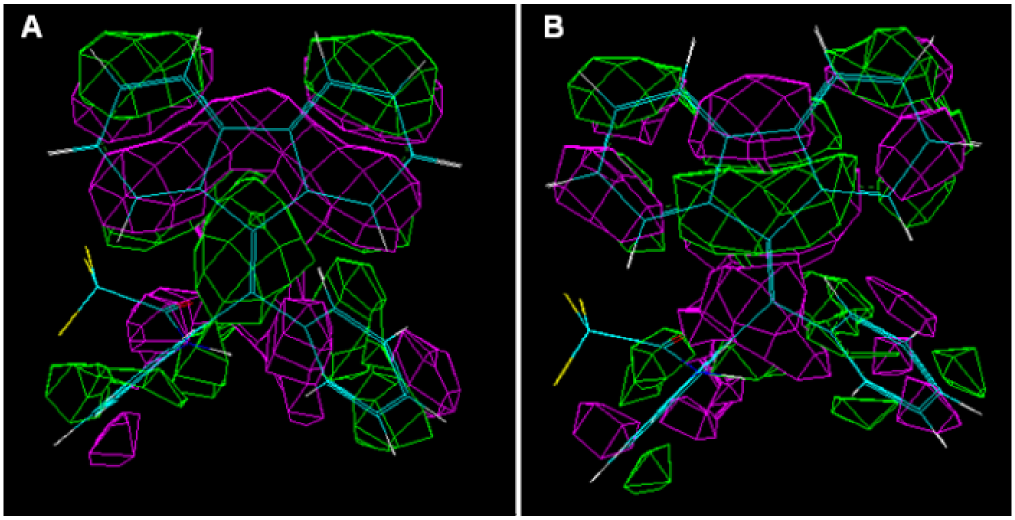

Fig. S9 Molecular orbital amplitude plots of (A) HOMO and (B) LUMO of **3**.

Single Crystal Structures

There are two independent molecules of **1** in an asymmetric unit. The principal differences between the two molecules are the corresponding torsion angles –87.3(4)^{o} for C(13A)–C(14A)–C(15A)–C(16A) and 83.9(4)^{o} for C(13B)–C(14B)–C(15B)–C(16B) that are opposite to each other. They differ by being enantiomeric conformers.

The packing diagram (Figure S10) shows two distinct molecules stacking about the independent screw-axes of 0.5, y, 0.5 and 0, y, 0 respectively. The two separate stacks of conformers are neither related by scres-axis nor inversion. Note that similar packing in $P2_1$ with enantiomeric conformations has been seen for *N*-ethylbenzhydrylamine hydrochloride.[3]

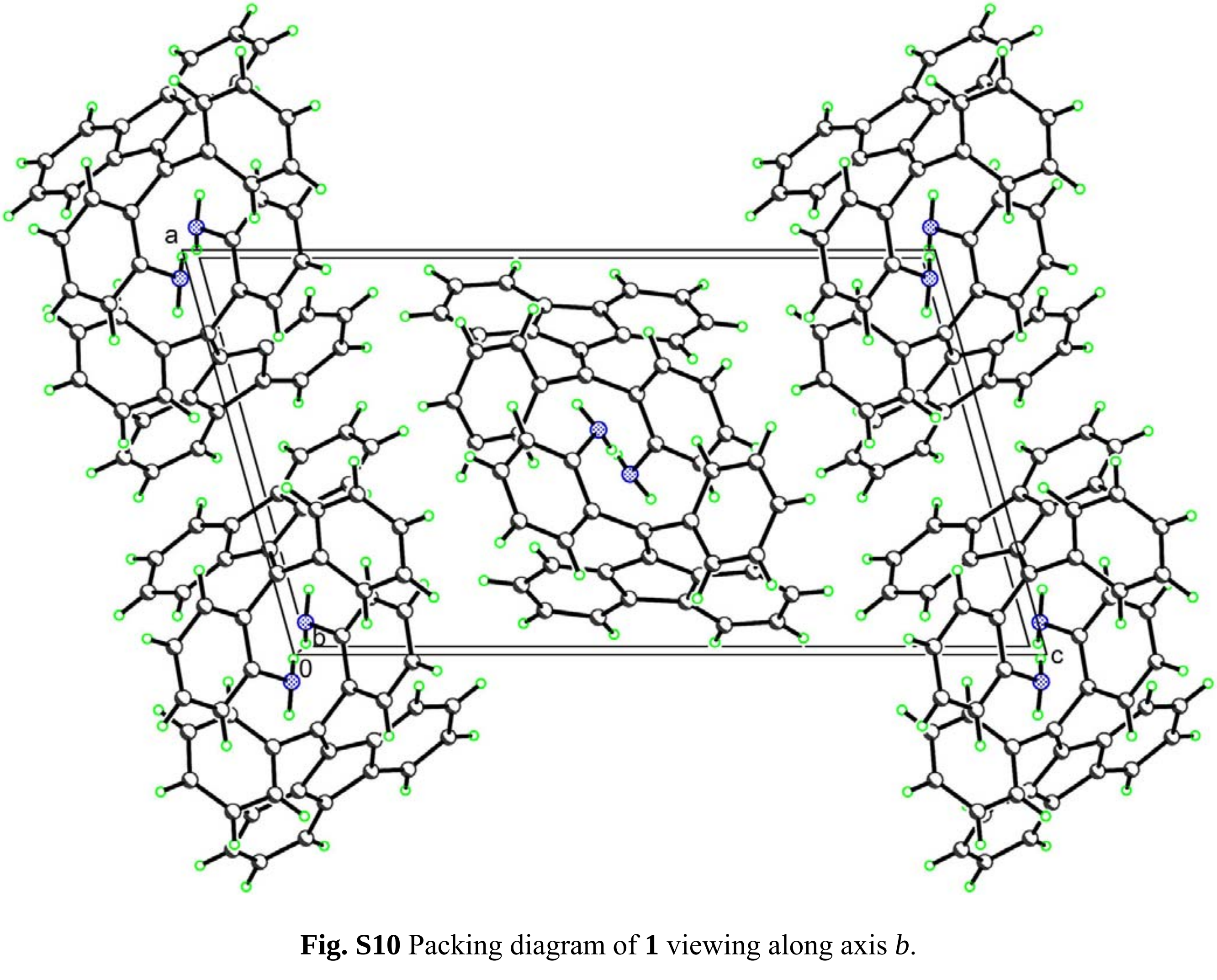

Fig. S10 Packing diagram of **1** viewing along axis *b*.

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[3] Goeta, A. E.; Punte, G.; Rivero, B. E.; Blanch, L. B. *Acta Cryst.* **1997**, *C53*, 1913.

As shown in Figure S11, there exist N(1A)–H···π, N(1B)–H···π, C(8A)–H···π, C(8B)–H···π, C(5B)–H···π, and C(24B)–H···π hydrogen bonds in the crystal structure of **1**. Such intermolecular interactions may stabilize the conformations in crystal structure, resulting in the formation of two independent molecules with different torsion angles in one asymmetric unit.

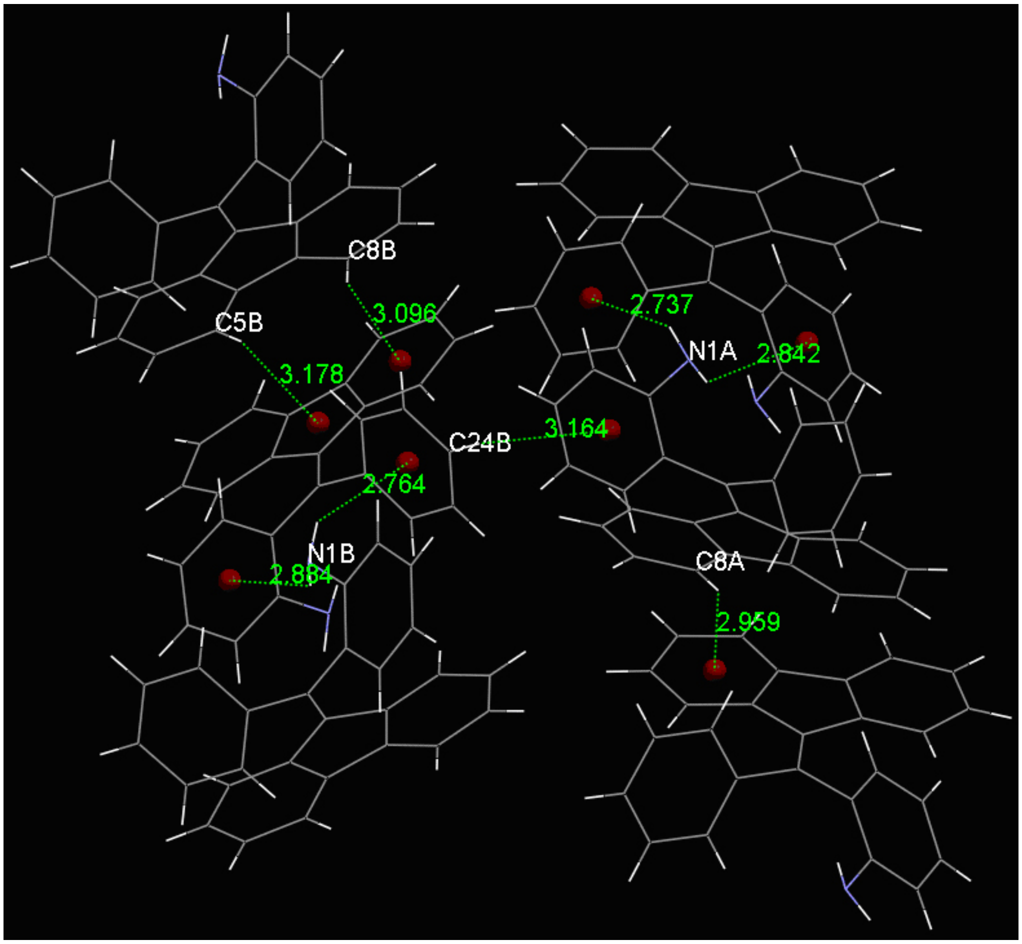

Fig. S11 Perspective view of crystal packing of molecules of **1**.

Table S2. Crystal data and structure refinement for **1**

Identification code	**1**	
Empirical formula	C26 H19 N	
Formula weight	345.42	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 10.6320(18) Å	α= 90°.
	b = 9.2506(15) Å	β= 105.409(3)°.
	c = 18.993(3) Å	γ = 90°.
Volume	1800.8(5) Å^3	
Z	4	
Density (calculated)	1.274 Mg/m^3	
Absorption coefficient	0.073 mm^{-1}	
F(000)	728	
Crystal size	0.40 x 0.35 x 0.25 mm^3	
Theta range for data collection	1.99 to 28.29°.	
Index ranges	–13<=h<=13, –6<=k<=12, –23<=l<=24	
Reflections collected	10729	
Independent reflections	4273 [R(int) = 0.0394]	
Completeness to theta = 25.00°	93.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.85	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4273 / 1 / 487	
Goodness-of-fit on F^2	1.010	
Final R indices [I>2sigma(I)]	R1 = 0.0543, wR2 = 0.1303	
R indices (all data)	R1 = 0.0768, wR2 = 0.1450	
Absolute structure parameter	2(6)	
Largest diff. peak and hole	0.334 and –0.219 e.Å^{-3}	