ESI

Molecular stacking mode-directed mechanical compliance and room-temperature phosphorescence

achieved by polymorphic 4-cyanobenzamide crystals

Di Wang,[a] Hui-Min Tang,[a] Bo Ding,[a] Xiu-Guang Wang,[a] Haijiao Xie[b] and En-Cui Yang[*, a]

Materials and apparatus. 4-Cyanobenzamide (CN-BZM) and 5-(9H-carbazol-9-yl)isophthalic acid (CzIp) were commercially purchased from Bide Pharmatech Ltd. and Jilin Chinese Academy of Science-Yanshen Technology Co., Ltd., which were further purified by re-crystallization prior to use. Common organic solvents for syntheses were given by Acros Organics and used directly without further purification. Elemental analyses for C, H and N were carried out with a CE–440 (Leeman–Labs) analyzer. Fourier transform (FT) IR spectra (KBr pellets) were taken on an Avatar–370 (Nicolet) spectrometer in the range 4000–400 cm^{-1}. Powder X-ray diffraction (PXRD) patterns were obtained from a Bruker D8 ADVANCE diffractometer at 40 kV and 40 mA for Cu Kα radiation (λ = 1.5406 Å), with a scan speed of 0.1 sec/step and a step size of 0.01° in 2θ. The simulated PXRD pattern was calculated using single-crystal X-ray diffraction data and processed by the free Mercury v1.4 program provided by the Cambridge Crystallographic Data Center. Solid-state ultraviolet−visible (UV−vis) adsorption was collected on a Shimadzu UV-3600 UV−vis−NIR spectrophotometer. Steady-state, time-resolved photoluminescence, and temperature-dependent prompt and delayed emission were obtained through an FLS-1000 spectrophotometer. The organic ultralong phosphorescence was measured using uF900 flash lamp. The percentage distribution of each lifetime component to the total decay curve and photoluminescence quantum yield was recorded using an Edinburgh Instruments FLS-1000.

Synthesis of Form I. CN-BZM (0.1 mmol, 14.0 mg) was dissolved in a binary mixed solvent of methanol and water (6.0 mL, v:v =1:1) with constant stirring. Transparent needle-like crystals were obtained within five days by evaporating the filtrate at room temperature, washed with ethanol, and dried in air. Yield: 67% based on CN-BZM. Anal. Calcd for C$_8$H$_6$N$_2$O: C, 65.75; H, 4.14; N, 19.17%. Found: C, 65.57; H, 4.20; N, 19.16%. FT-IR (KBr pellet,

cm^{-1}): 3382(s), 3309(s), 3251(w), 3207(w), 1670(s), 1619s 1558(s), 1407(s), 1290 (m), 1095 (m), 856 (m), 662(w), 631(w), 543(w).

Synthesis of Form II. CN-BZM (0.1 mmol, 14.0 mg) and CzIp (0.1 mmol, 33.1 mg) were dissolved in a mixed solvent of methanol and water (9.0 mL, v:v = 2:1) with constant stirring at 50℃. Pale yellow thin lamellar-shaped crystals of **Form II** were obtained within one week by evaporating the filtrate at room temperature, washed with methanol, and dried in air. Yield: 50% based on CN-BZM. Anal. Calcd for $C_8H_6N_2O$: C, 65.75; H, 4.14; N, 19.17%. Found: C, 65.59; H, 4.18; N, 18.99%. FT-IR (KBr pellet, cm^{-1}): 3383(s), 3310(s), 3250(w), 3208(w), 1671(s), 1619s 1558(s), 1407(s), 1290 (m), 1095 (m), 856 (m), 662(w), 631(w), 543(w).

X-ray single-crystal data collection and structure determination. Diffraction intensities for the two polymorphs of CN-BZM were collected on a SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer equipped with mirror-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) at 120 K for **Form I** and 293 K for **Form II** by using the φ-ω scan technique. There was no evidence of crystal decay during data collection. SCALE3 ABSPACK scaling algorithm was used for an empirical absorption correction with spherical harmonics.[1] The programs *CrysAlisPro* were used for integration of the diffraction profiles.[2] The structures were solved by direct methods and refined with the full-matrix least-squares technique using the *ShelXT* and *ShelXL* software.[3] The non-H atoms were located by difference Fourier maps and subjected to anisotropic refinement. Hydrogen atoms were added according to theoretical models. All the non-hydrogen atoms of the CN-BZN in **Form II** are disordered between two positions with the occupancies of 0.748 and 0.242. CCDC numbers for **Form I** and **Form II** are assigned to 2288452 and 2288453.

Mechanical test. An optical microscope (Stemi 2000-CS, Carl Zeiss Microscopy Gmbh) equipped with plastic plate and digital camera was used for monitoring and recording the mechanical responses of **CN-BZM** crystals using tweezers.

Theoretical calculations. All quantum calculations were carried out with Gaussian 16 software.[4] The functional

PBE0 and basis set 6-31G(d, p) were used for geometry optimization and frequency calculation. The geometries for the CN-BZM monomer and head-to-head dimer were performed by full geometry optimizations. To keep the structural consistency with the SC-XRD data, the geometry optimization for the head-totail dimer is carried out only by fixing the non-hydrogen atoms. The dispersion was considered at the GD3BJ level.[5] The harmonic frequency analyses were performed at the same level of theory to verify that all structures have no imaginary frequency. The spin-orbit coupling matrix elements were calculated by TD-DFT calculation as implemented in ORCA program.[6] The natural transition orbitals (NTOs) were visualized by Vesta program with assisted by Multiwfn program[7, 8]
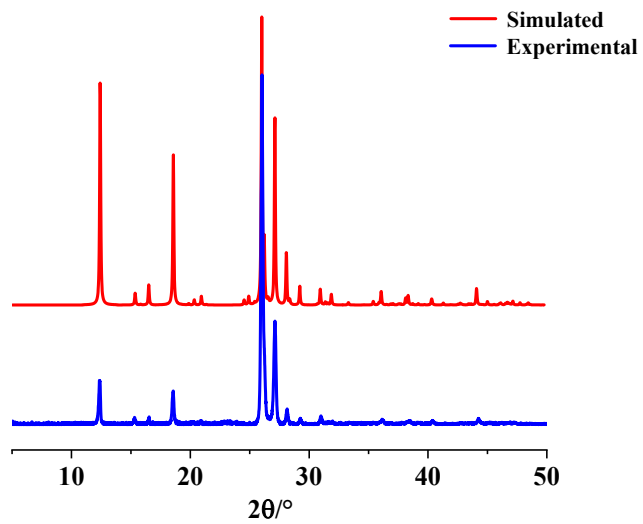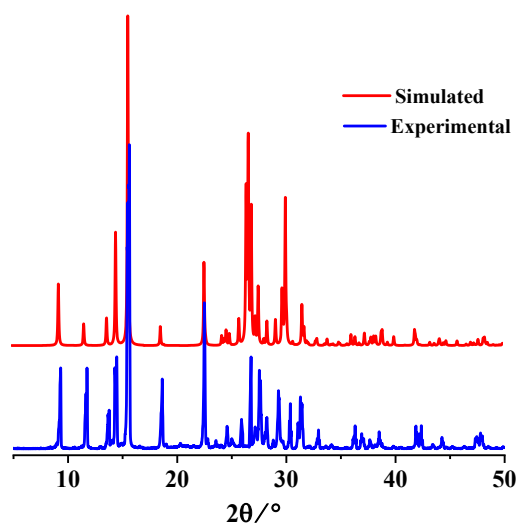
Fig. S1 PXRD patterns for **Form I** (upper) and **Form II** (bottom) of 4-cyanobenzamide crystals.

Table S1 Hydrogen-bonding parameters (Å, deg) for the polymorphic 4-cyanobenzamide crystals

	D – H	H···A	D···A	∠D – H···A
Form I				
N1–H1A···O1[#1]	0.86	2.06	2.9111(2)	172
N1–H1B···N2[#2]	0.86	2.37	3.1800(3)	158
C3–H3···O1[#3]	0.93	2.34	3.2499(3)	167
Form II				
N1–H1A···N2[#1]	0.86	2.25	3.104(4)	174
N1–H1B···O1[#2]	0.86	2.05	2.868(4)	158

[a] Symmetry codes for **Form I**: [#1] $-x$, $-y$, $1-z$; [#2] $3/2-x$, $-1/2+y$, $1/2-z$; [#3] $1/2+x$, $1/2-y$, $-1/2+z$. For **Form II**:

[#1] x, $y-1$, $-z$; [#2] x, $1/2-y$, $1/2+z$.

Table S2 The geometric parameters for π-π stackings (Å, deg) of polymorphic 4-cyanobenzamide crystals[a]

	Cg(i)-Cg(j)	$d_{\pi\text{-}\pi}$	α	β	γ	CgI_Perp	CgJ_Perp	Slippage
Form I	Cg(1)-Cg(1)[#1]	3.737(3)	0	21.8	21.8	3.4701	−3.4701	1.389
Form II	Cg(1)-Cg(1)[#1]	3.731(8)	0	17.1	17.1	3.567	3.567	1.095

[a] Symmetry codes for **Form I**: [#1] $-1 + x, y, z$. for **Form II**: [#1] $1 - x, 1 - y, 1 - z$.
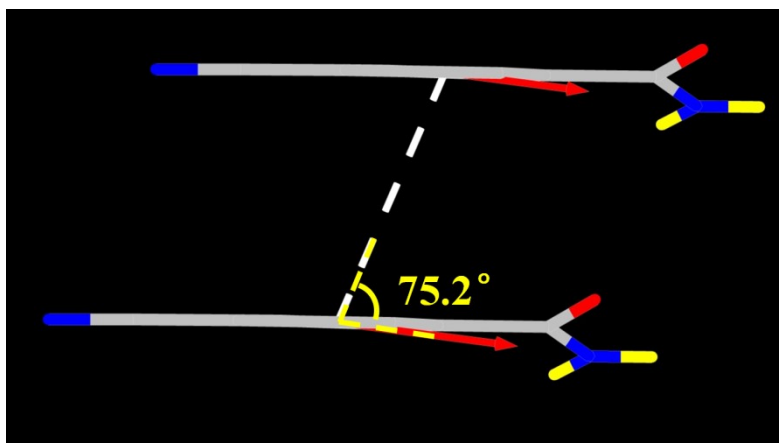
Fig. S2 The co-planar inclined mode of H-aggregation for **Form I**.
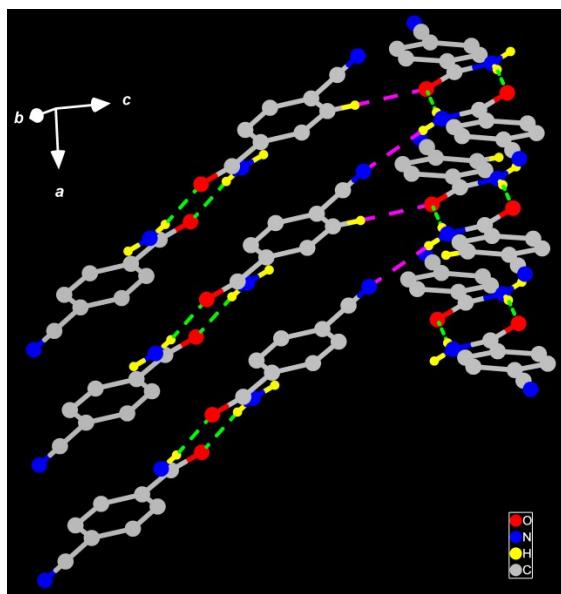
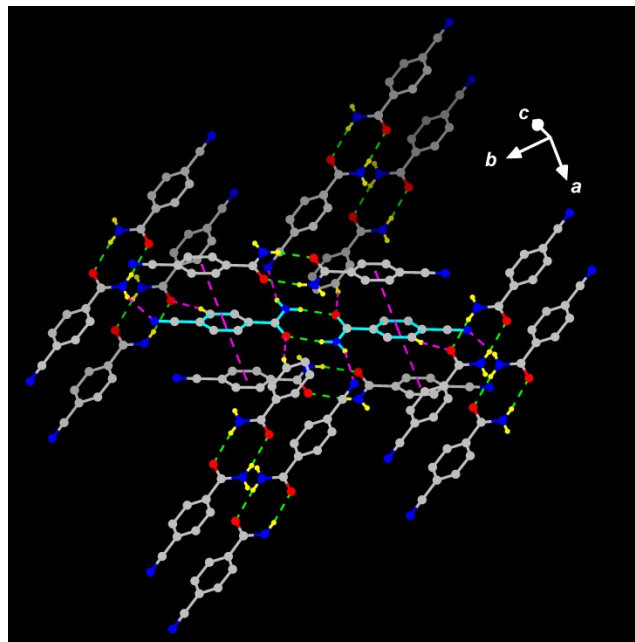**Fig. S3** The interlocked columns in **Form I** by weak −CH···O=C and −NH···N≡C hydrogen-bonding interactions.

Fig. S4 3D packings of **Form I** with one central {CN-BZM}$_2$ dimer surrounded by ten neighbors through weak intermolecular interactions.
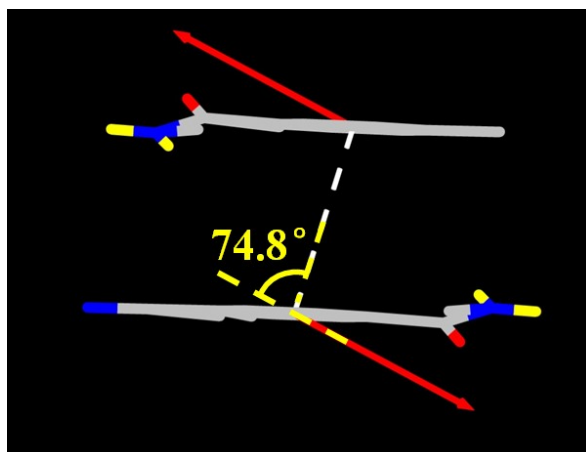
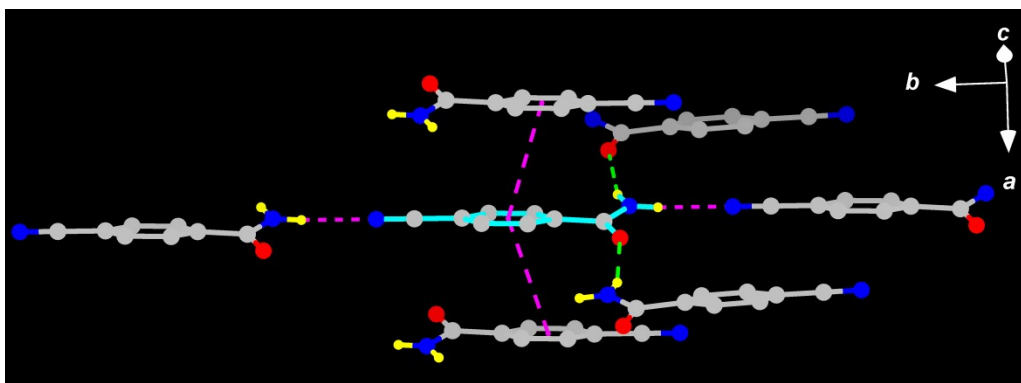**Fig. S5** The co-planar inclined mode of H-aggregation for **Form II**.

Fig. S6 Stacking structure of **Form II** with one central {CN-BZM} monomer surrounded by six neighbors through weak intermolecular interactions.

Fig. S7 Screenshots of reversible elastic bending test of **Form I** crystal under mechanical stress applied through a pair of tweezer under 254 nm UV light.
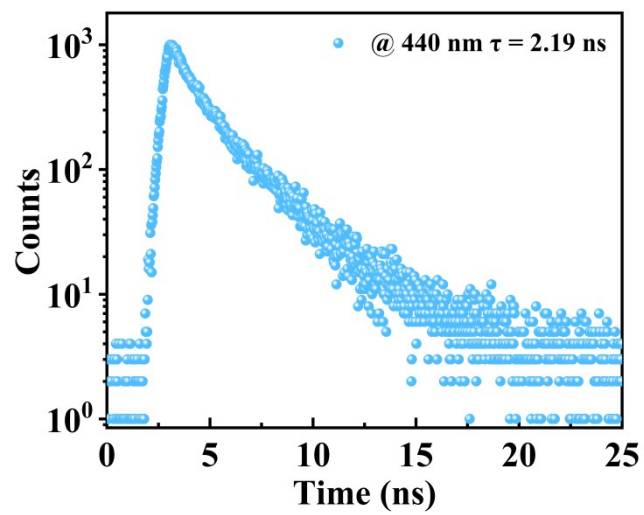
Fig. S8 The lifetime of **Form I** under the emission at 440 nm.

Fig. S9 Fractures of **Form II** crystal upon application of a mechanical stress under UV light.
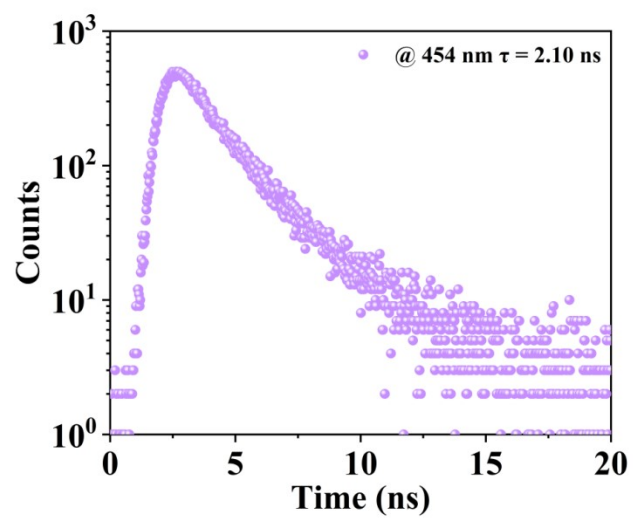
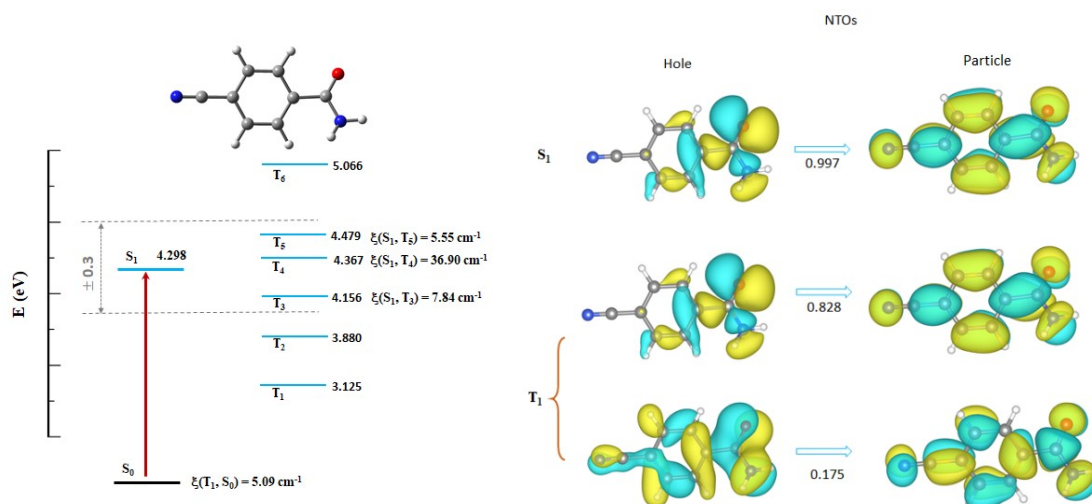**Fig. S10** The lifetime of **Form II** under the emission at 454 nm.

Fig. S11 The calculated energy level diagram, SOC matrix element (ξ), and NTO for the S_1 and T_1 states of the

isolated CN-BZM monomer.

References

1. SCALE3 ABSPACK: *Empirical absorption correction, CrysAlis Software package*. Oxford Diffraction Ltd., Oxford, England, 2006.

2. *CrysAlisPro*, Agilent Technologies, Yarnton, Oxfordshire, England, 2010.

3. (a) G. M. Sheldrick, *SHELXL-97, Program for X-ray Crystal Structure Refinement*. Göttingen University: Göttingen, Germany, 1997. (b) G. M. Sheldrick, *SHELXS-97, Program for X-ray Crystal Structure Solution*. Göttingen University: Göttingen, Germany, 1997.

4. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

5. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, *J. Chem. Phys.*, 2010, **132**, 154104.

6. F. Neese, Software update: the ORCA program system, version 4.0, *Wilres Comput. Mol. Sci.*, 2018, **8**, e1327.

7. K. Momma and F. Izumi, VESTA: a three-dimensional visualization system for electronic and structural analysis, *J. Appl. Crystallogr.*, 2008, **41**, 653-658.

8. T. Lu and F. Chen, Multiwfn: A multifunctional wavefunction analyzer, *J. Comput. Chem.* 2012, **33**, 580-592.