

Supporting information for:

**Response of Strong Fluorescence Carbazole-based Benzoxazole
Derivative to External Force Controlled by Extra Stimuli**

Pengchong Xue,* Boqi Yao, Panpan Wang, Jiabao Sun, Zhenqi Zhang, Ran Lu*

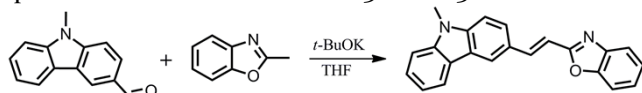
State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin
University, Changchun, P. R. China

Email: xuepengchong@jlu.edu.cn; luran@mail.jlu.edu.cn

Experimental section

General information

All the raw materials were used without further purification. All the solvents as analytical reagent were purchased from Beijing Chemical Works (Beijing, China), and were used without further purification. Water used throughout all experiments was purified with the Millipore system. The UV-vis absorption spectra were obtained using a Mapada UV-1800pc spectrophotometer. Photoluminescence measurements were taken on a Cary Eclipse Fluorescence Spectrophotometer. The fluorescence quantum yields of **C1CVB** in solvents were measured by comparing to a standard (9,10-diphenyl anthracene in benzene, $\Phi_F = 0.85$). The excitation wavelength was 375 nm. The absolute fluorescence quantum yields were measured on an Edinburgh FLS920 steady state fluorimeter using an integrating sphere. Fluorescence decay experiment was measured on an Edinburgh FLS920 steady state fluorimeter equipped with an nF900 nanosecond flash lamp. Mass spectra were obtained with AXIMA CFR MALDI-TOF (Compact) mass spectrometers. C, H, and N elemental analyses were performed with a Perkin-Elmer 240C elemental analyzer. Differential scanning calorimetry (DSC) was measured on a Netzsch DSC204 differential scanning calorimeter. Single crystal was obtained in the mixture of CH_2Cl_2 and n-hexane by slow solvent diffusion method. CCDC 1015257 contains the crystal data. The molecular configuration in crystal was used to obtain electron density and stimulated absorption spectrum of **C1CVB** by density functional theory (DFT) and time-dependent DFT calculations at B3LYP/6-311G level with the Gaussian 09W program package.¹



Scheme S1 Synthesis route of **C1CVB**.

(E)-2-(2-(9-methyl-9H-carbazol-3-yl)vinyl)benzo[d]oxazole (**C1CVB**)

t-BuOK (0.78 g, 6.96 mmol) was added into dry THF (10 mL) and the mixture was stirred for 10 min at 0 °C. 2-methylbenzoxazole (0.38 mL, 3.2 mmol) was dropwise added into above suspension and the mixture was stirred for 10 min at 0 °C. Then, a THF solution of 9-methylcarbazole-3-carbaldehyde (0.67 g, 3.2 mmol) was dropped slowly into the above solution at 0 °C. After stirred for 2 h, the mixture was poured into water (200 mL) and white solid was collected by filtration. The crude product was purified by a silica gel column using CH_2Cl_2 /petroleum ether (V/V = 2/1) as the eluent. Colorless needle-like crystal was obtained in a yield of 85 % (0.88 g). mp: 203–204 °C. FT-IR: 3054, 2963, 2926, 1638, 1626, 1594, 1534, 1499, 1476, 1256, 810, and 743 cm^{-1} . Elemental analysis (%): calculated for $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}$: C, 81.46; H, 4.97; N, 8.64; Found: C, 81.40; H, 5.04; N, 8.68. ^1H NMR (400 MHz, CDCl_3) δ 8.35 (s, 1H), 8.17 (d, $J = 7.7$ Hz, 1H), 8.08 (d, $J = 16.2$ Hz, 1H), 7.80 (dt, $J = 5.4, 2.7$ Hz, 1H), 7.76 (dd, $J = 6.2, 2.8$ Hz, 1H), 7.60 – 7.51 (m, 2H), 7.49 – 7.42 (m, 2H), 7.40 – 7.30 (m, 3H), 7.15 (d, $J = 16.2$ Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 163.60, 150.39, 142.27, 141.93, 141.49, 140.91, 126.31, 125.28, 124.78, 124.38, 123.27, 122.67, 120.48, 120.45, 119.65, 119.53, 110.61, 110.19, 108.94, 108.83, 29.24. MALDI-TOF MS: m/z: calcd: 324.1; found: 324.0 M^+ .

1. Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, M. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.;

Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.;
Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

Table S1. Photophysical data of **C1CVB** in different solvents.

	cyclohexane	toluene	THF	CHCl ₃	CH ₂ Cl ₂	acetone	DMF
λ_{em} (nm)	420	436	445	447	452	456	462
Φ	0.03	0.01	0.02	0.01	0.04	0.03	0.09

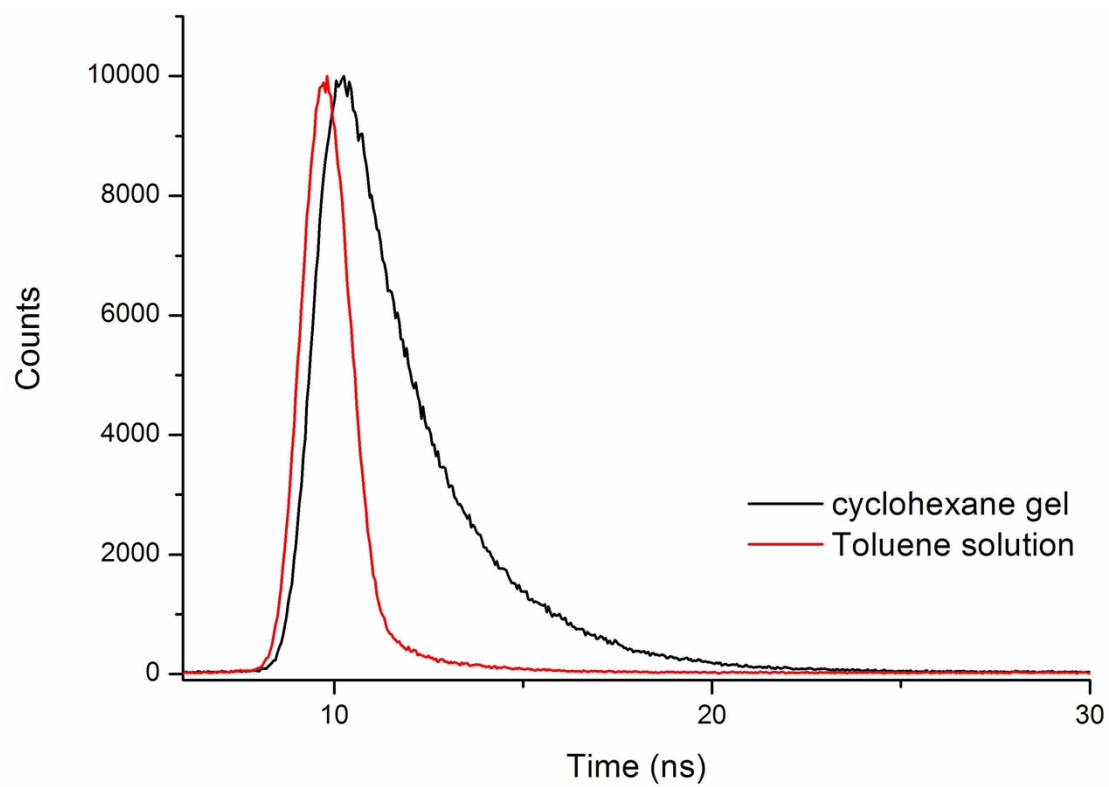


Fig. S1 Time-resolved fluorescence spectra of **C1CVB** in toluene and cyclohexane gel.

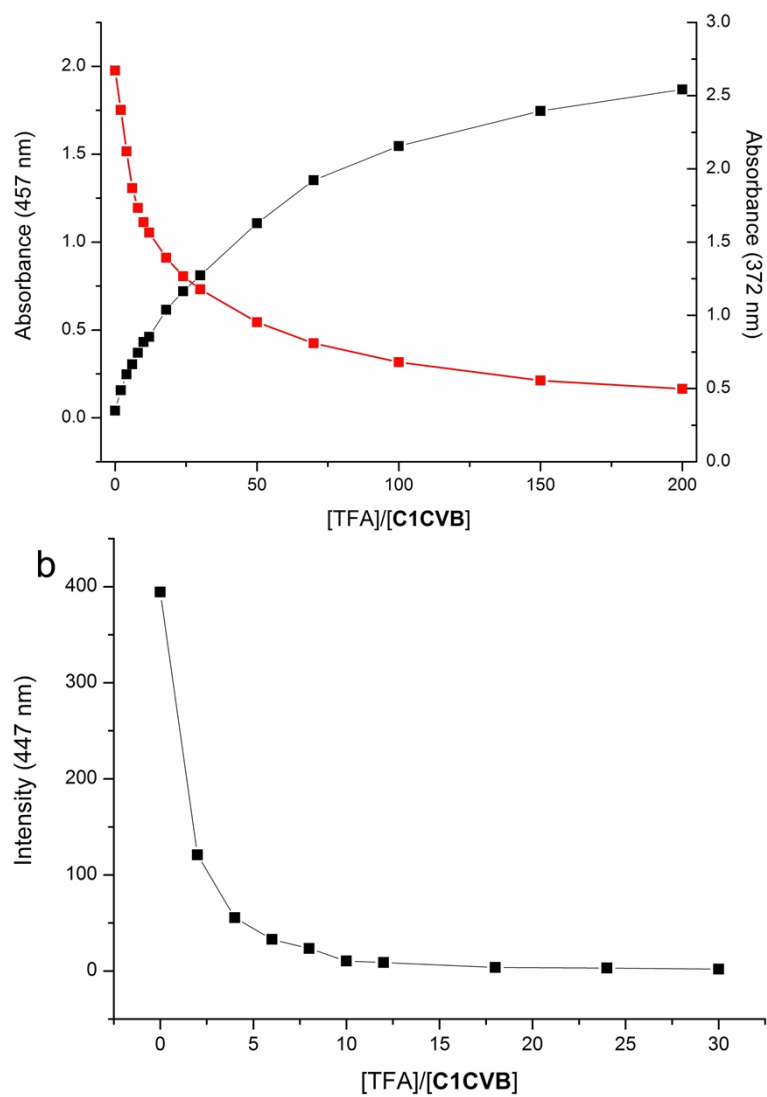


Fig. S2 (a) Absorbance at 457 (black) and 372 (red) nm and (b) fluorescence intensity at 447 nm of **C1CVB** CHCl₃ solution (2×10^{-4} M) vs [TFA]/[**C1CVB**] upon addition of TFA. $\lambda_{\text{ex}} = 370$ nm.

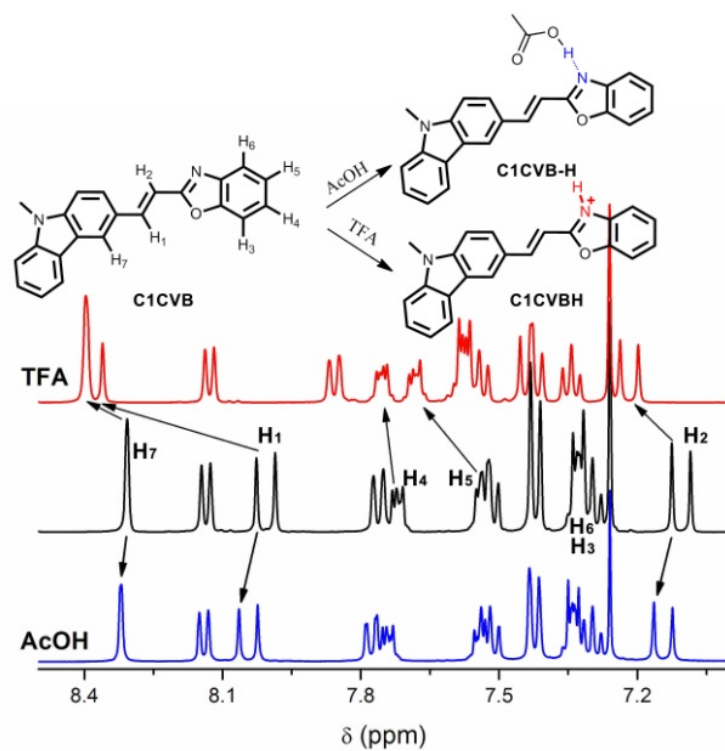


Fig. S3 Partial ¹H NMR spectra of **C1CVB** in CDCl₃ with TFA and HOAc (5 equiv), respectively.

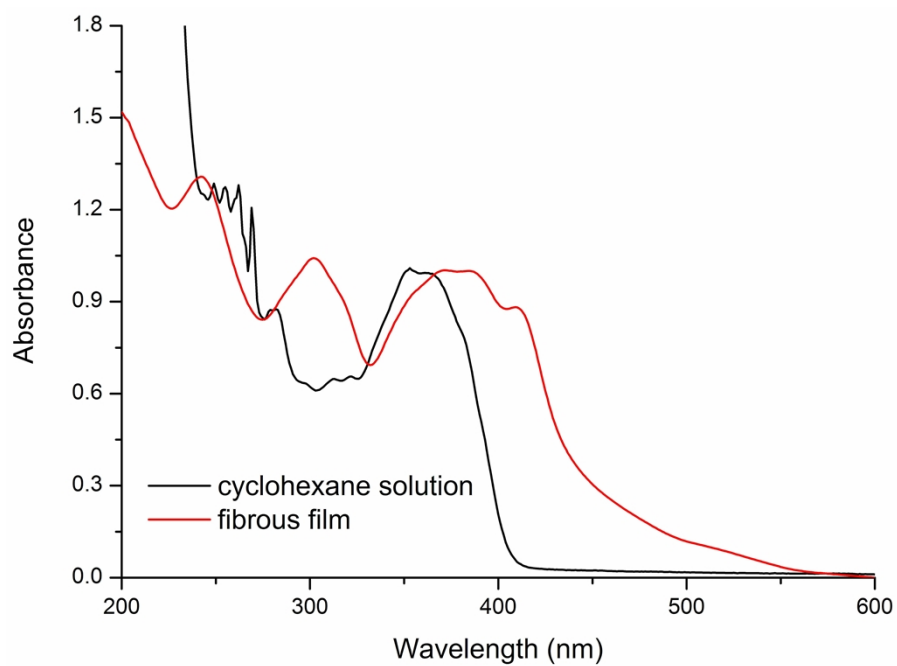


Fig. S4 Absorption spectra of **C1CVB** in cyclohexane solution and fibrous film.

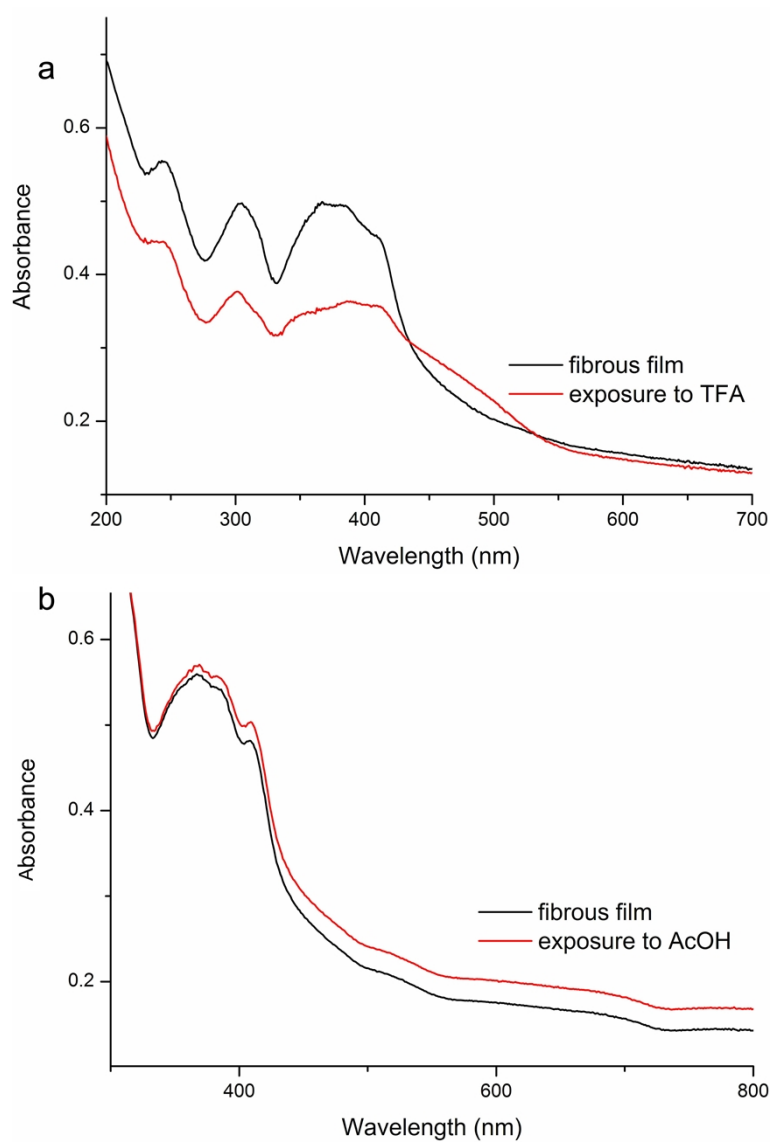


Fig. S5 Absorption spectra of C1CVB fibrous film before and after exposing to (a) TFA (3648 ppm) and (b) HOAc (saturated) vapors.

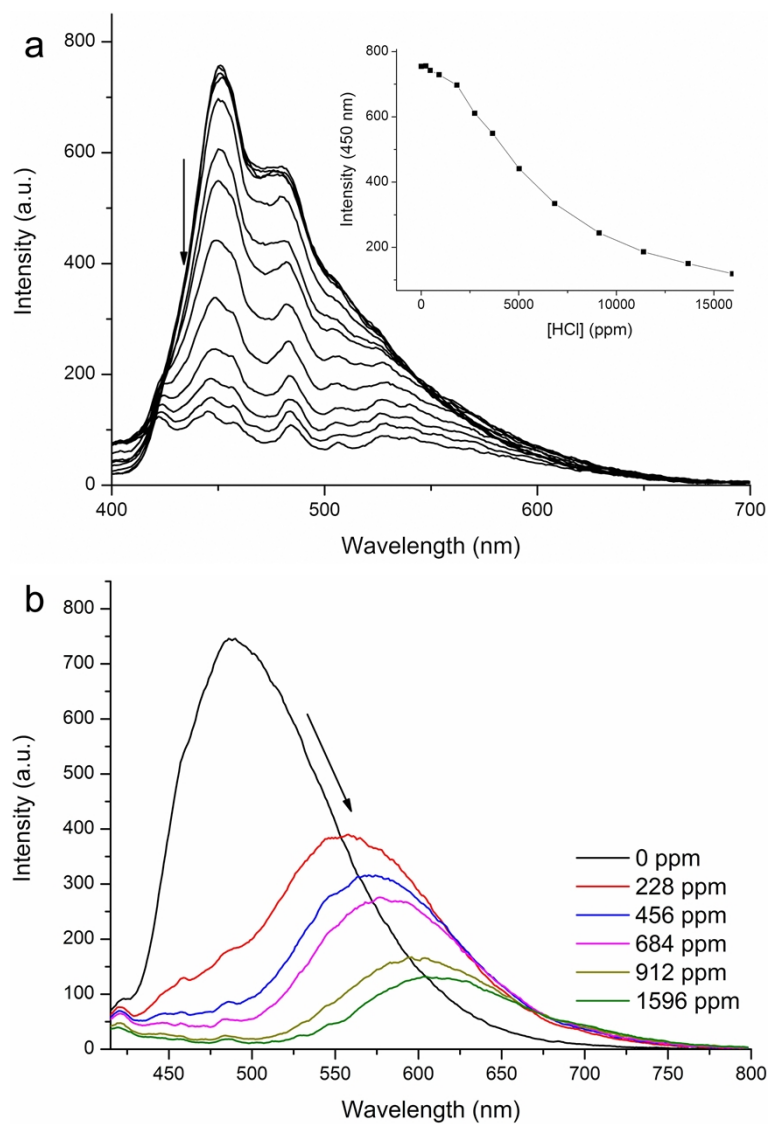


Fig. S6 Fluorescence spectra of (a) fibrous and (b) ground film before and after exposure to HCl vapor.

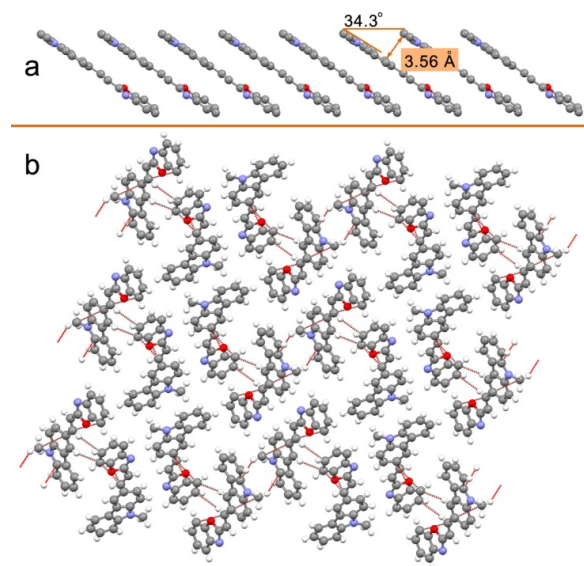


Fig. S7 (a) 1D and (b) 2D packing in crystal. Red lines indicate weak interactions.

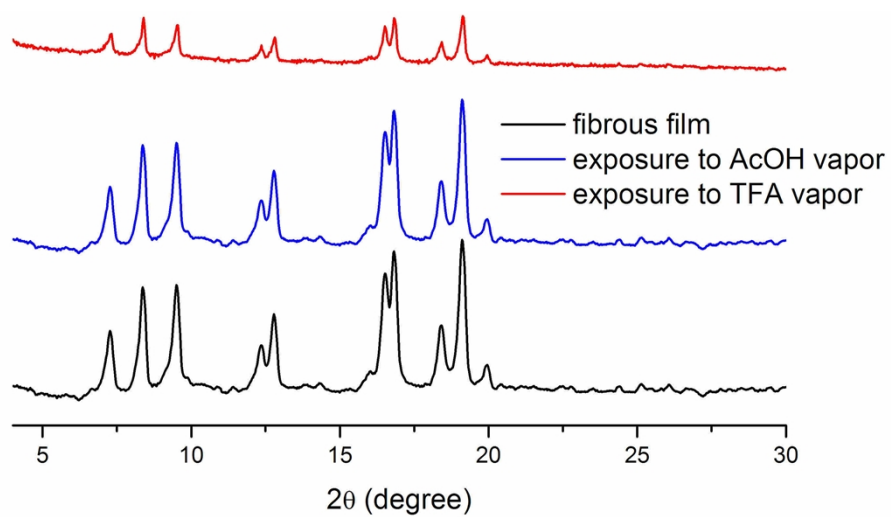


Fig. S8 XRD patterns of **C1CVB** fibrous film upon exposure to HOAc and TFA vapors.

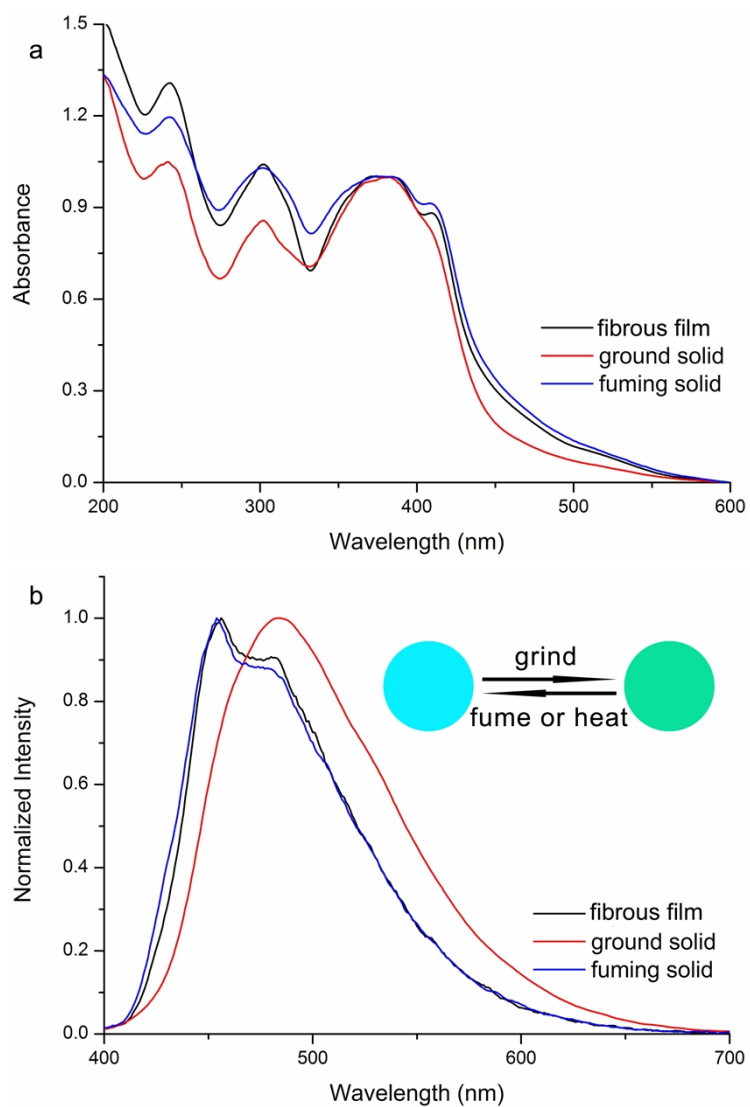


Fig. S9 (a) Absorption and (b) fluorescence spectra of **C1CVB** fibrous film before and after shearing and fuming.

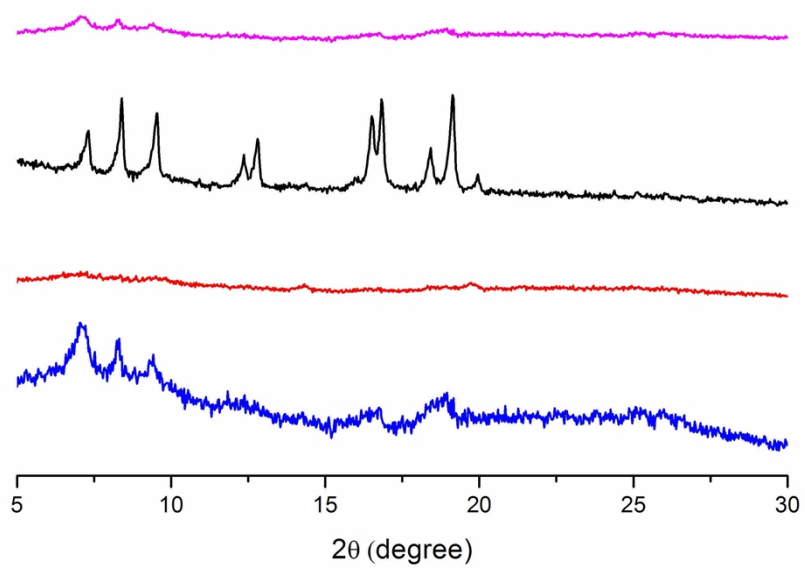


Fig. S10 XRD patterns of **C1CVB** in fibrous (black), ground (red) and fuming (blue by CH_2Cl_2 , magenta by HOAC) films.

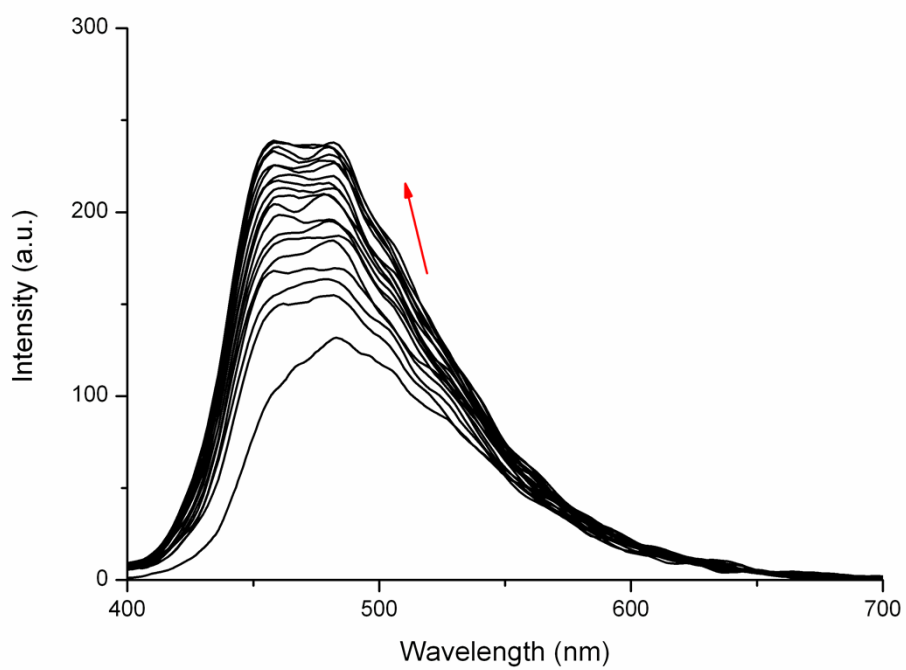


Fig. S11 Fluorescence spectral change of the ground film. Interval time is 1 min.

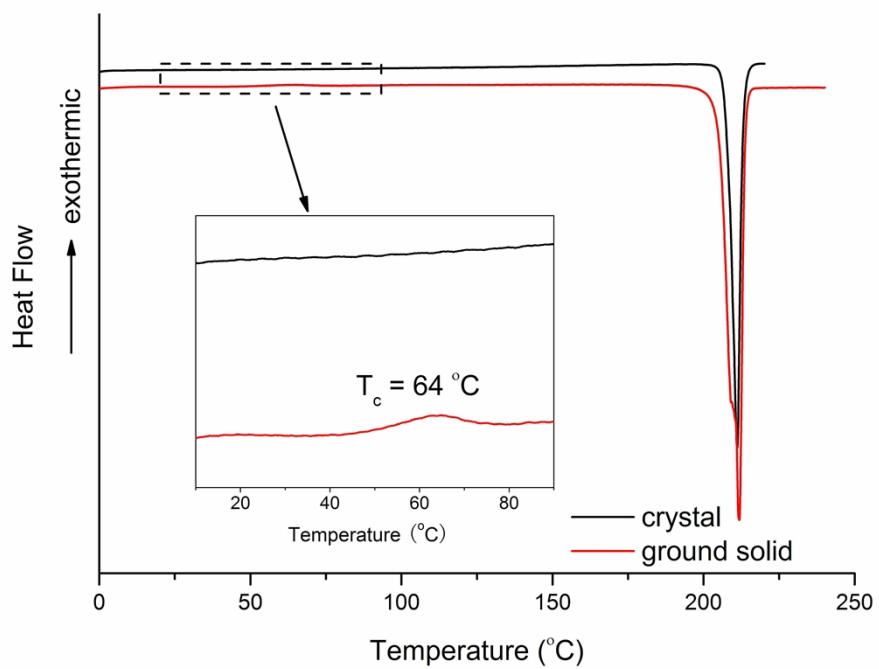


Fig. S12 DSC curves of fibers (black) and ground powder (red).

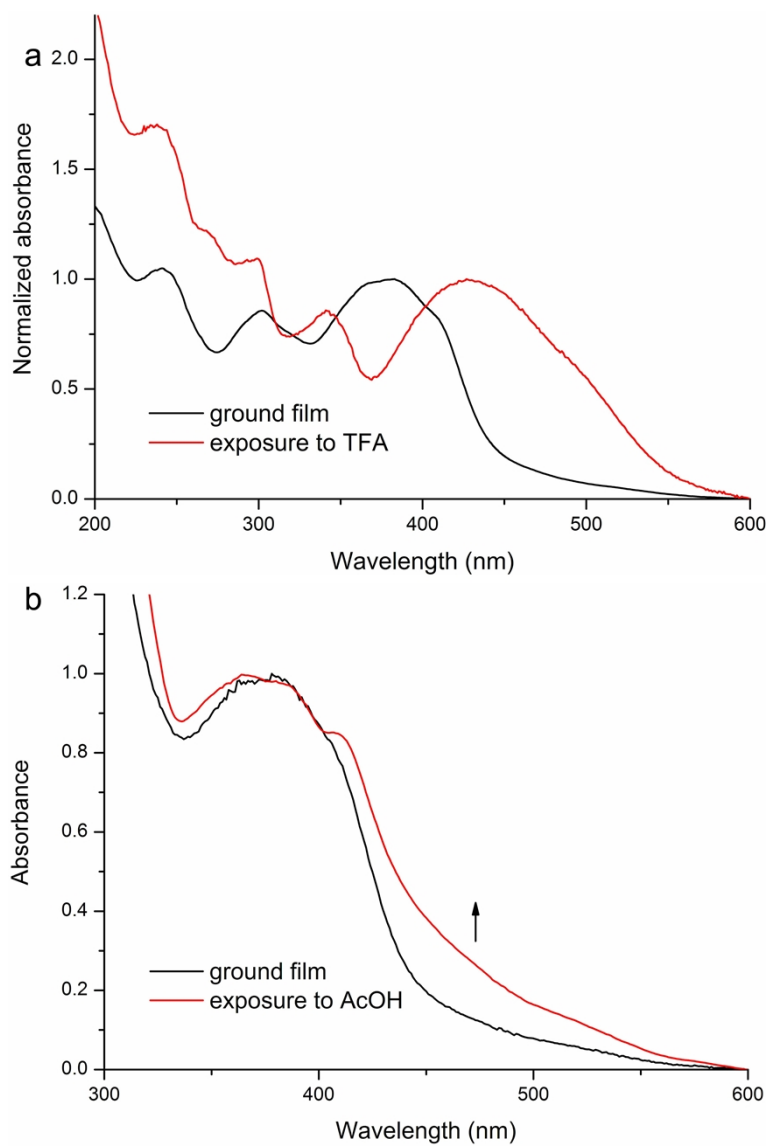


Fig. S13 Absorption spectra of ground films upon exposure to (a) TFA (3648 ppm) and (b) saturated HOAc vapors.

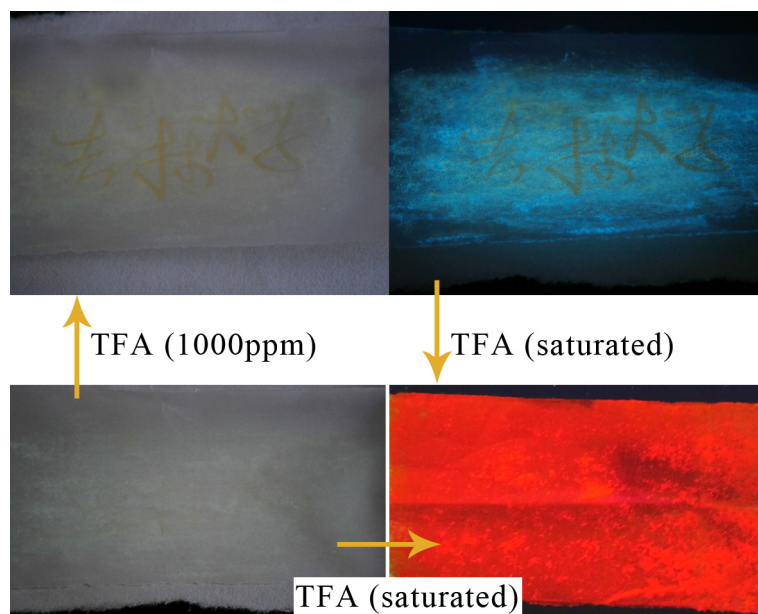


Fig. S14 Photos of patterned fibrous film in response to TFA vapors under daylight (left) and 365 nm light (right).