Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting information for

Emission Enhancement of Coplanar π-Conjugated Gelator without Any Auxiliary Substituents

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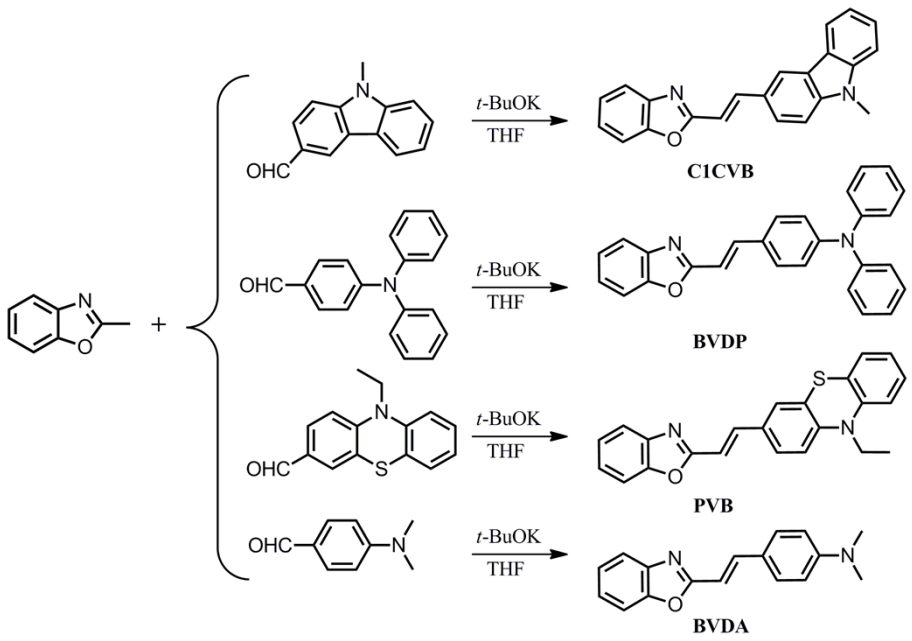
Experimental section

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, Φ_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. Single crystal was obtained in the mixture of CH_2Cl_2 and n-hexane by slow solvent diffusion method. The molecular configuration in crystal was used to obtain dipole moment of **C1CVB** by density functional theory (DFT) calculations at B3LYP/6-31G level with the Gaussian 09W program package.[1]

Single crystal of **C1CVB** was selected for X-ray diffraction analysis on in a Rigaku RAXIS-RAPID diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The crystals were kept at room temperature during data collection. The structures were solved by the direct methods and refined on F2 by full-matrix least-square using the SHELXTL-97 program.[2] The C, N, O and H atoms were easily placed from the subsequent Fourier-difference maps and refined anisotropically. CCDC 1015257, 973275, 978631 and 994905 contain the supplementary crystallographic data for **C1CVB**, **BVDP**, **PVB**, and **BVDA**, respectively.

BVDP, **PVB** and **BVDA** were synthesized based on the reported methods.[3-5]



Scheme S1 Synthesis route of **C1CVB**, **BVDP**, **PVB**, **and BVDA**.

(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 stirred for 10 min at 0 ºC. 2-methylbenzoxazole (0.38 mL, 3.2 mmol) was dropwise added into above suspension and stirred for 10 min at 0 ºC. Then, a THF solution of 9-methyl-carbazole-3-carbaldehyde (0.67 g, 3.2 mmol) was dropped slowly into the above solution at 0 ºC. 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. FT-IR: 3054, 2963, 2926, 1638, 1626, 1594, 1534, 1499, 1476, 1256, 810, and 743 cm^{-1}. Element analysis (%): calculated for $C_{22}H_{16}N_2O$: 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). MALDI-TOF MS: m/z: calcd for $C_{22}H_{16}N_2O$: 324.1; found: 324.0 M^+.

(E)-4-(2-(benzo[d]oxazol-2-yl)vinyl)-N,N-diphenylaniline (**BVDP**)

By following the synthetic procedure for **C1CVB**. Yield: 86 %. Element analysis (%): calculated for $C_{27}H_{20}N_2O$: C, 83.48; H, 5.19; N, 7.21; Found: C, 83.40; H, 5.25; N, 7.27. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.78 (d, J = 16.2 Hz, 1H), 7.75 – 7.68 (m, 1H), 7.58 – 7.51 (m, 1H), 7.48 (d, J = 8.7 Hz, 2H), 7.40 – 7.29 (m, 6H), 7.19 (m, 4H), 7.12 (t, J = 7.3 Hz, 2H), 7.07 (d, J = 8.7 Hz, 2H), 6.96 (d, J = 16.2 Hz, 1H). MALDI-TOF MS: m/z: calcd for $C_{27}H_{20}N_2O$: 388.2; found: 389.1 $(M+H)^+$.

(E)-2-(2-(10-ethyl-phenothiazin-3-yl)vinyl)benzoxazole (PVB)

By following the synthetic procedure for **C1CVB**. Yield: 86 %. Element analysis (%): calculated for $C_{23}H_{18}N_2OS$: C, 74.57; H, 4.90; N, 7.56; Found: C, 74.62; H, 4.91; N, 7.53. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 1H), 7.71 (d, J = 16.1Hz), 7.57 – 7.48 (m, 1H), 7.39 (dd, J = 8.5, 1.8 Hz, 1H), 7.37 – 7.31 (m, 3H), 7.17 (td, J = 8.9, 1.2 Hz, 2H), 7.00 – 6.84 (m, 4H), 3.98 (d, J = 6.8 Hz, 1H), 1.47 (t, J = 7.0 Hz, 2H). MALDI-TOF MS: m/z: calcd for $C_{23}H_{18}N_2OS$: 370.1; found: 371.1 $(M+H)^+$.

(E)-4-(2-(benzo[d]oxazol-2-yl)vinyl)-N,N-dimethylaniline (**BVDA**)

By following the synthetic procedure for **C1CVB**. Yield: 81 %. Element analysis (%): calculated for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60; Found: C, 77.20; H, 6.30; N, 10.68. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (t, J = 16.2 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.56 – 7.49 (m, 3H), 7.36 – 7.30 (m, 2H), 6.88 (d, J = 16.2 Hz, 1H), 6.76 (d, J = 8.6 Hz, 2H), 3.06 (s, 6H). MALDI-TOF MS: m/z: calcd for $C_{17}H_{16}N_2O$: 264.1; found: 265.1 $(M+H)^+$.

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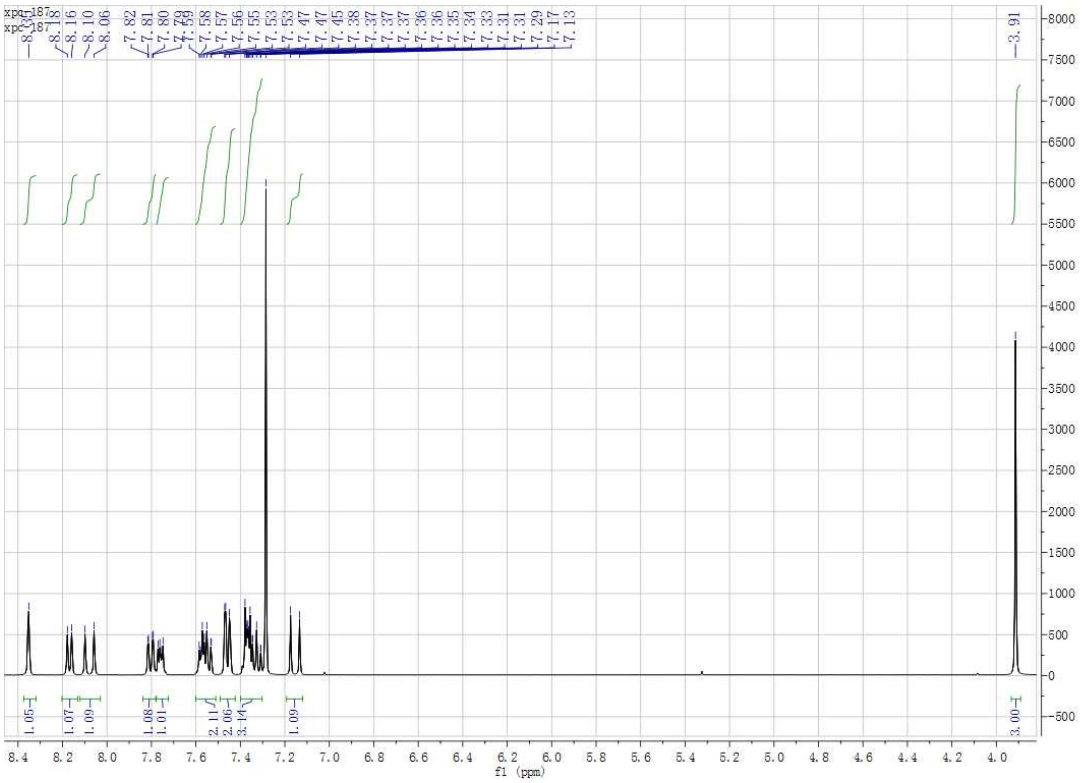

Fig. S1 ^{1}H NMR spectrum of **C1CVB** in $CDCl_3$ (400 MHz).

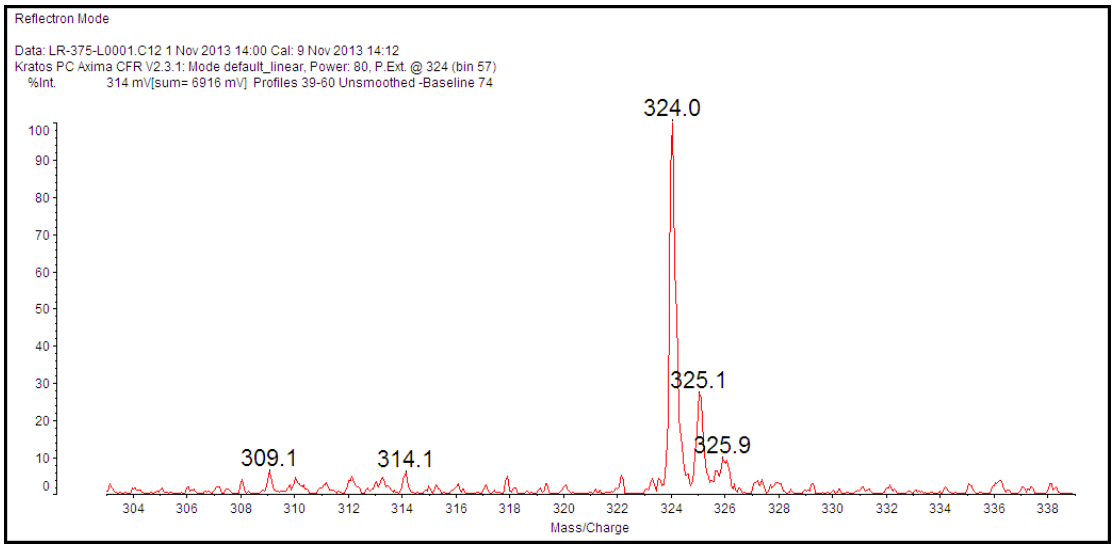

Fig. S2 MALDI-TOF MS of **C1CVB**.

Table S1 Gelation ability of **C1CVB**, **BVDP**, **PVB**, and **BVDA**.[a]

solvent	**C1CVB**	**BVDP**	**PVB**	**BVDA**
n-hexane	P	P	P	P
n-octane	P	P	P	P
cyclohexane	G (0.1)[b,d]	S	P	P
$CHCl_3$	G (3.5)[c]	S	S	S
$CHCl_3$/cyclohexane (v/v = 1/3)	G (0.3)[d]	S	P	P
CHCl3/cyclohexane (v/v = 1/4)	G (0.2)[d]	S	P	P
CH_2Cl_2	S	S	S	S
benzene	S	S	S	S
toluene	S	S	S	S
o-dichlorobenzene	S	S	S	S
bromocyclohexane	G (1.1)[d]	S	S	S
chlorocyclopentane	G (1.2)[d]	S	S	S
acetone	G (1.0)[d]	S	S	P
THF	S	S	S	S
DMF	S	S	S	S
DMSO	G (4.0)[d]	S	S	P
ethanol	P	P	P	P
n-butanol	G (1.7)[d]	P	P	P
isobutanol	G (0.9)[c]	P	P	P
cyclopentanol	G (0.9)[c]	P	P	P
n-pentanol	G (2.0)[d]	P	P	P

[a] G : stable gel formed at room temperature; S: soluble; I: insoluble; P: precipitate. [b] Critical gelation concentration (CGC, g/ml%). [c] Gel formation by naturally cooling, [d] by ultrasonic stimulus or rapid cooling in an ice-water bath.

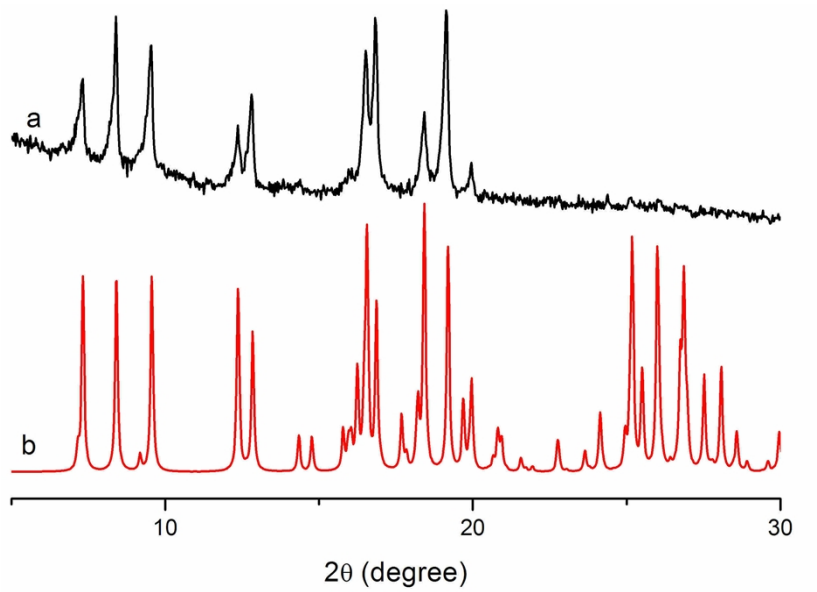

Fig. S3 XRD patterns of cyclohexane xerogel (a) and stimulated one based on the crystal structure.

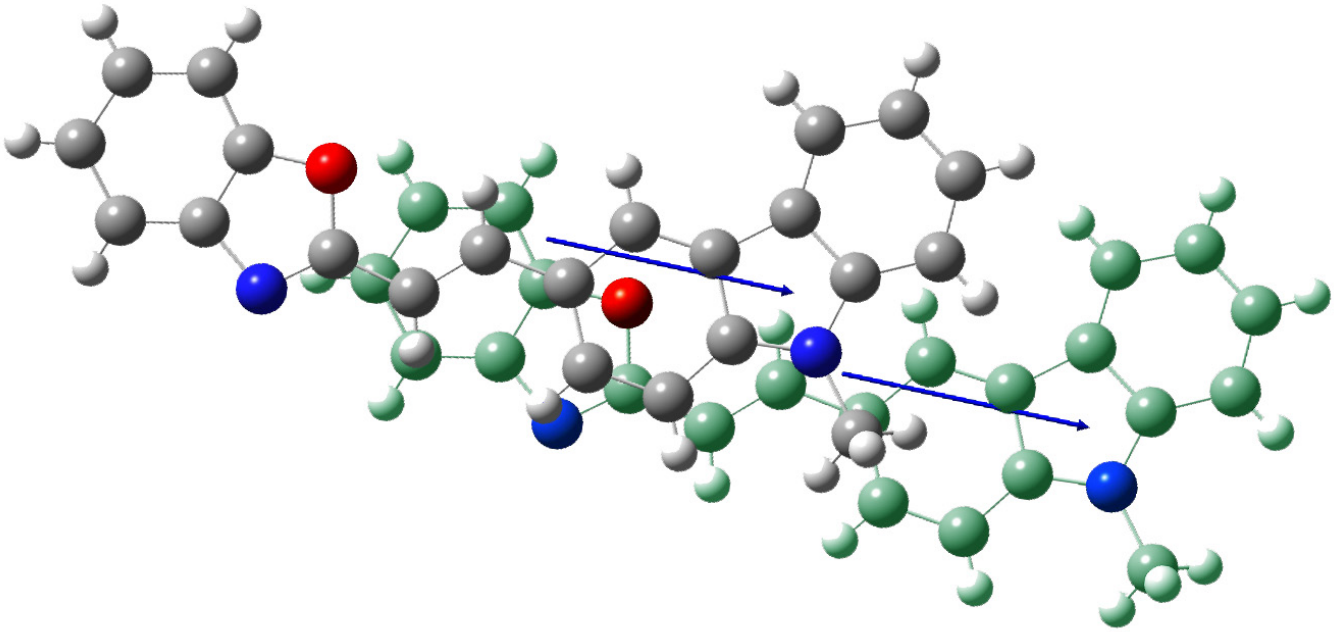

Fig. S4 Molecular packing in a slipped model and the dipole-dipole interaction.

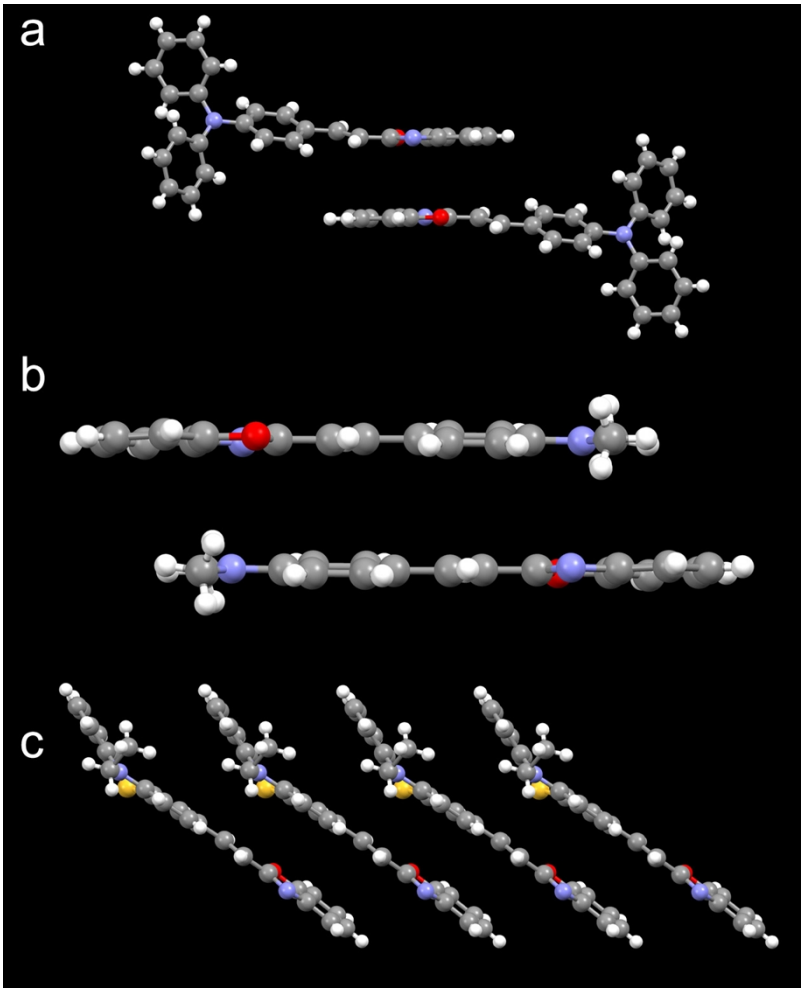

Fig. S5 Molecular packing of **BVDP** (a), **BVDA** (b), and **PVB** (c) in crystals.

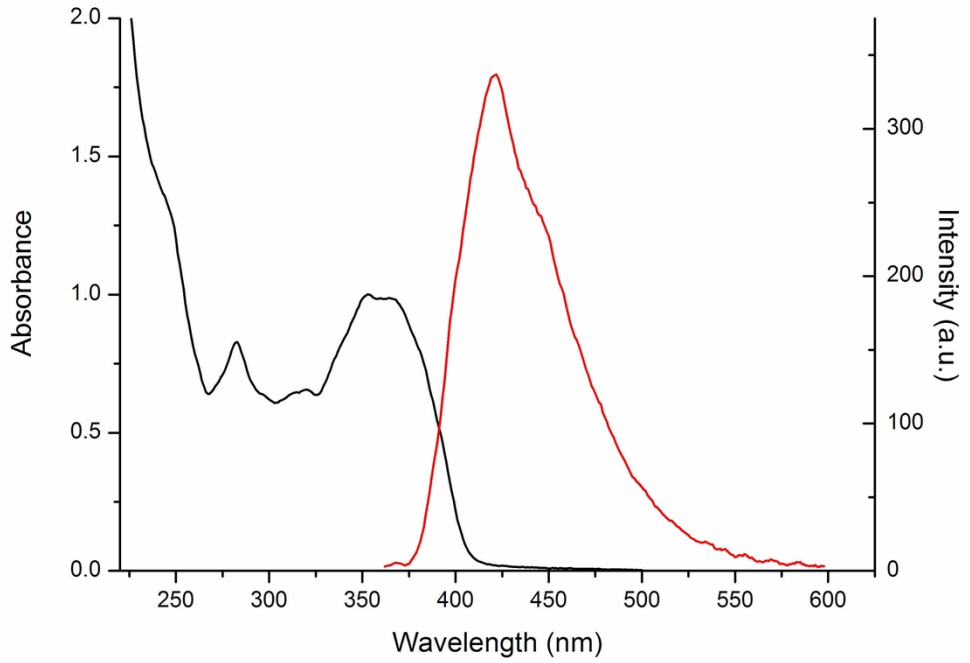

Fig. S6 The absorption (black) and emission (red) spectra of **C1CVB** cyclohexane (2×10^{-5} M).

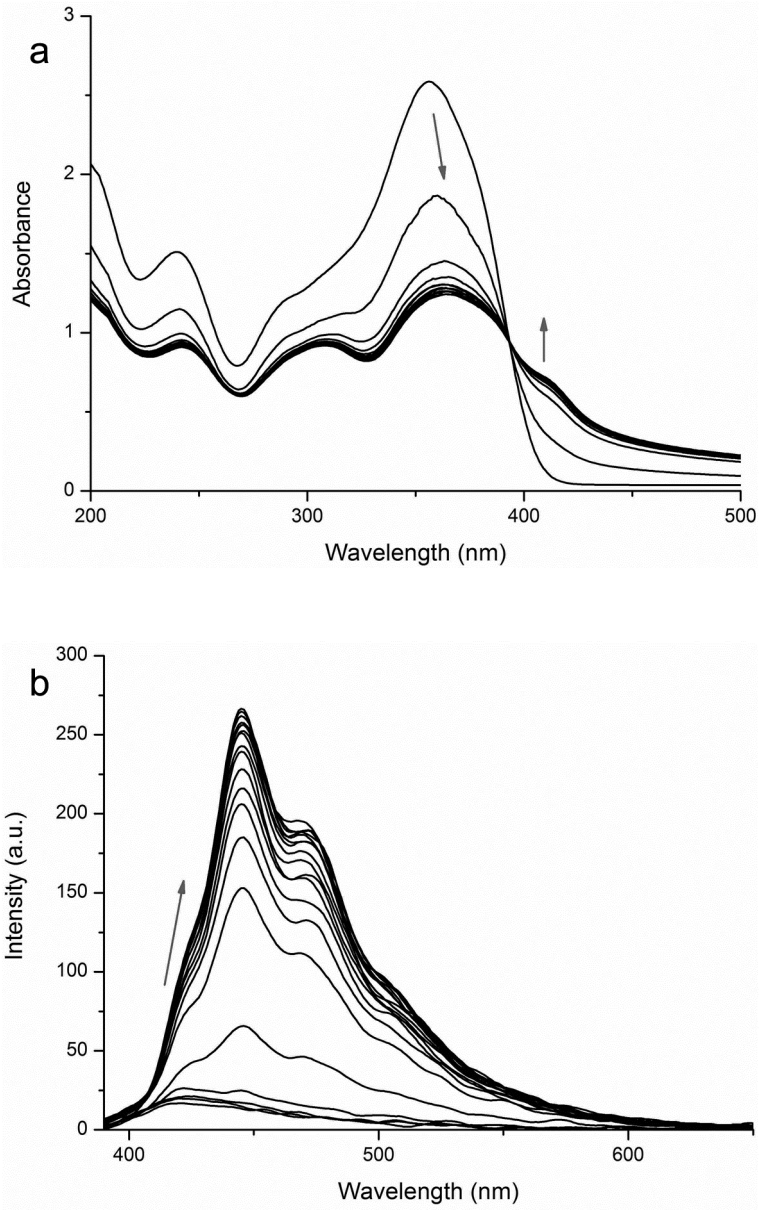

Fig. S7 Absorption (a) and fluorescence (b) spectral changes of **C1CVB** during gelation in cyclohexane (C = 2.3 mM). λ_{ex} = 370 nm.

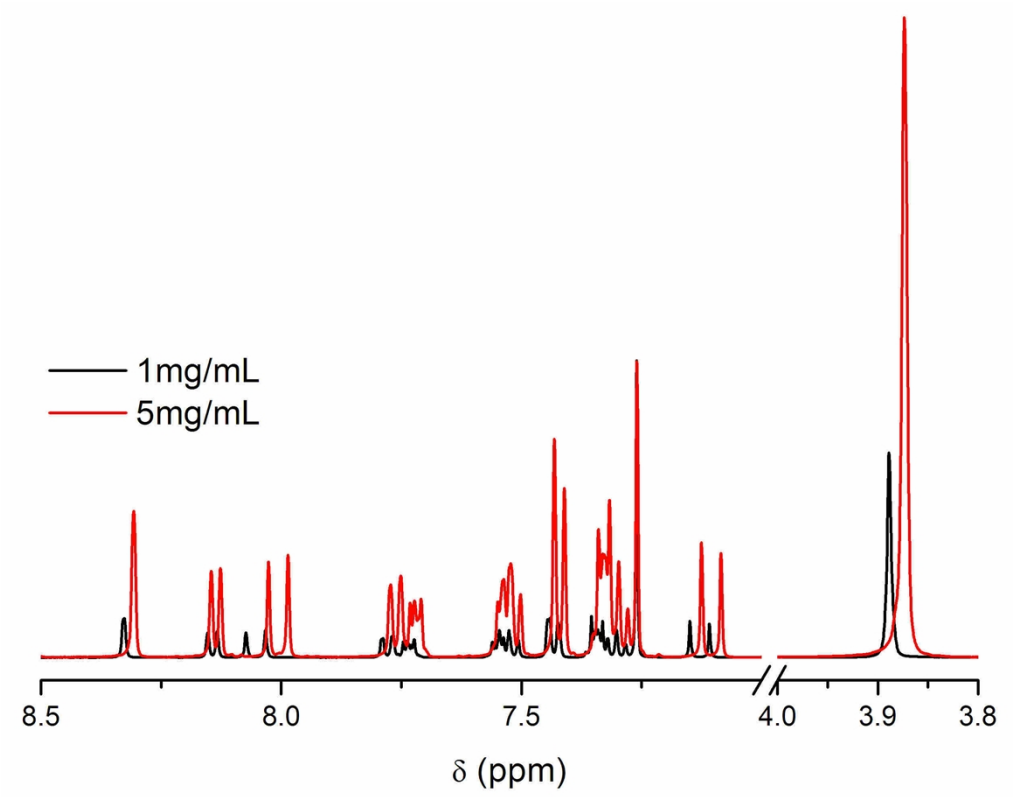

Fig. S8 ^{1}H NMR spectra of **C1CVB** at different concentration in $CDCl_3$.

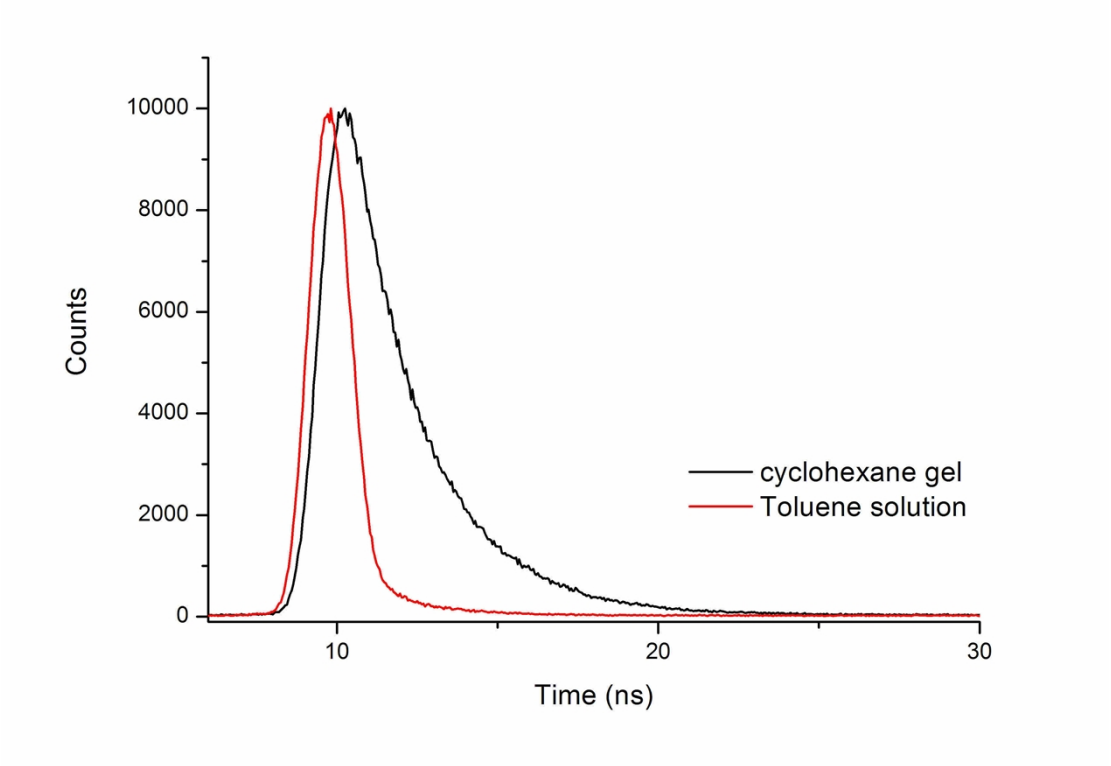

Fig. S9 Time-resolved fluorescence spectra of **C1CVB** in toluene and cyclohexane gel.