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Supporting Information

Reversible thermo-stimulus solid-state fluorescence-colour/on-off switching and uses as fluorescent thermometers in different temperature ranges

Qiuhua Zhu,[a] Weijie Yang,[a] Sichao Zheng,[a] Herman H.Y. Sung,[b] Ian D. Williams,[b] Shuwen Liu,*[b] and Ben Zhong Tang*[c]*

Contents

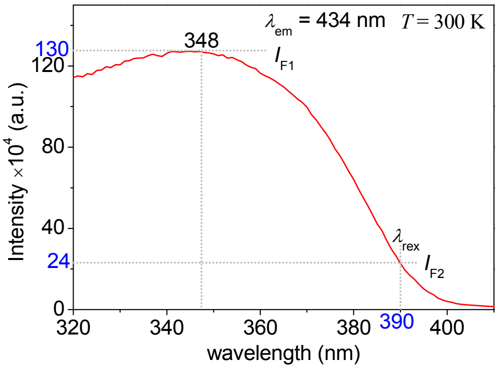
General

THP-1 and its polymorphs (**1b** and **1c**) in different aggregates were prepared as described in our previous work.[1] The 1HNMR spectra, melting points, emission spectra of 1c and 1b are accordance with those reported in previous work.[1] The samples were placed between two pieces of square quartz glass with a cycle hollow in center and measured at different temperatures (Oxford Liquid Nitrogen Cryostat: 77 to 300 K under N_2) by a FLS980 fluorescence spectrophotometer (Step: 1.00 nm, Dwell: 0.200s; Iris: 100; ExBW: 0.40–1.1; EmBW: 0.40–1.1; ExCorr: off; RefCorr: on; EmCorr: on). The excitation and emission spectra 0 to 80 °C (constant temperature water) were recorded on a Shimadzu RF5301PC fluorescence spectrophotometer.

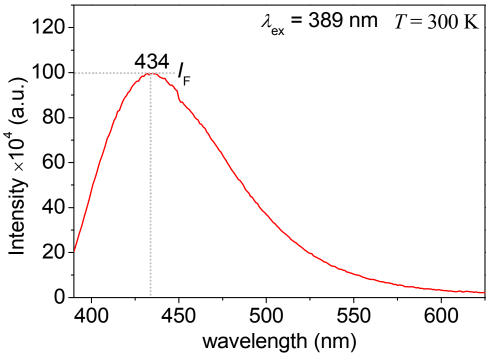
Procedures of using 1b or 1c as a thermometer to detect temperature changes in different temperature ranges

For example, when using **1b** with certain aggregate size as a fluorescent thermometer to detect temperature change in the range of 270 to 300 K, the experimental procedures are:

(a) measuring a excitation spectrum emitted at maximum emission wavelength (434 nm) (ES434) at the highest temperature (300 K) (the excitation spectrum shown below);



(b) increasing the excitation and emission slit widths of fluorescence spectrophotometer and measuring a emission spectrum excited at suitable red-edge excitation wavelength, for example at 390 mm, at which the fluorescence intensity (I_{F2}) in the above excitation spectrum is about 1/5 time of that (I_{F1}) at peak (348 nm) and will turn off when T decreases 30 K, that is, decreases to 270 K (see Figure 4a in the manuscript).



(c) measuring the emission spectra at different temperatures (from 300 to 270 K or from 270 to 300 K) using 390 nm as excitation wavelength under the same conditions in procedure b (see Figure 2b and S1c).

(d) obtaining the linear relationship between T and the ratio of the intensities at 434 nm and 510/550 nm (I_{F434}/I_{F510}) according to the emission spectra obtained in procedure c (see Figure S1c and inset in Figure 2b).

(e) using **1b** with the same aggregate size as a wavelength-ratiometric fluorescent thermometer to indicate temperature change in 270 to 300 K range in researched system by the linear relationship between T and I_{F434}/I_{F510} obtained in procedure d.

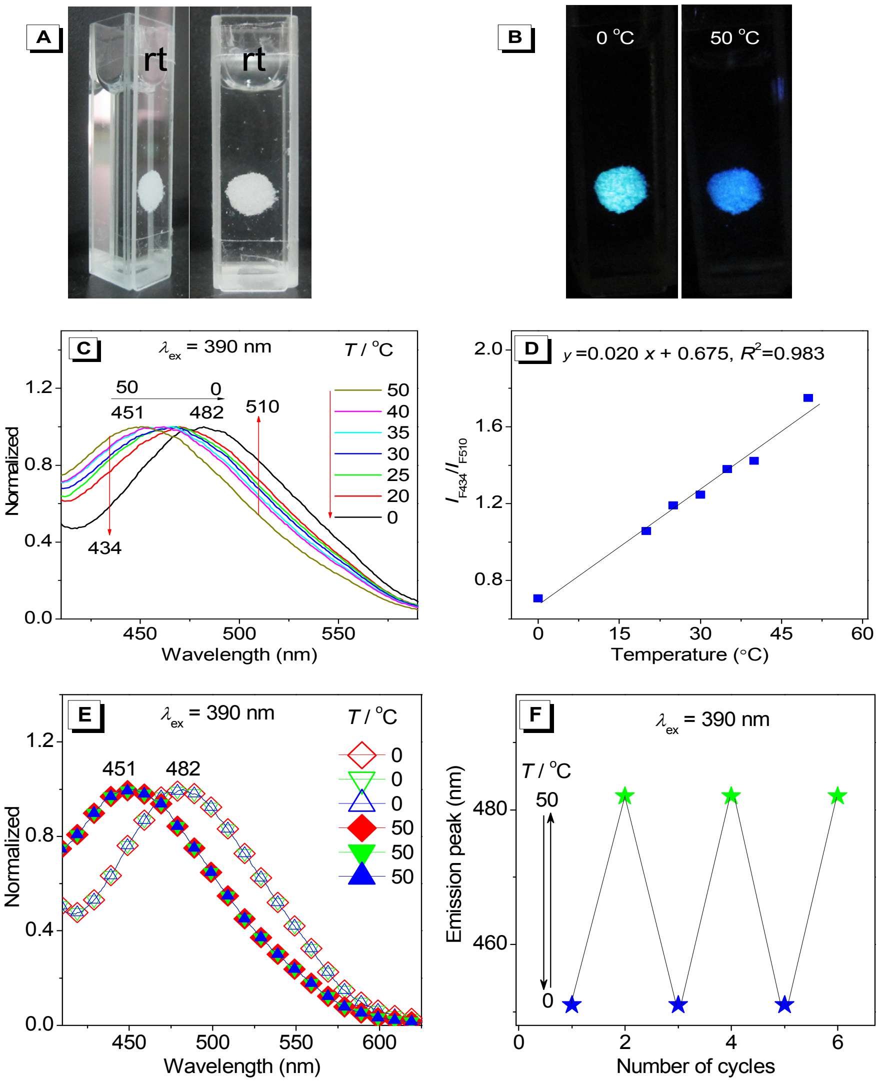


Figure S1 Sensitive and reversible thermo-stimuli solid-state fluorescence-color switching of **1b** in powder **(**sample was sandwiched between a quartz cuvette and a flat piece of quartz glass) in range of 0–50 °C. (A) and (B) photos were taken under daylight and 390 nm of excitation light, respectively. (C) Emission spectra in the range of 0 to 50 °C. (D) Relationship between *T* and the ration of the fluorescence intensities at 434 and 510 nm (I_{F434}/I_{F510}) in C. (E) and (F) emission spectra and emission peaks at 0 and 50 °C in three times of heating and cooling processes, respectively. Spectra were recorded on a Shimadzu RF5301PC fluorescence spectrophotometer (Excitation and emission slit widths: 1.5 and 1.5 nm; excitation wavelength: 390 nm).

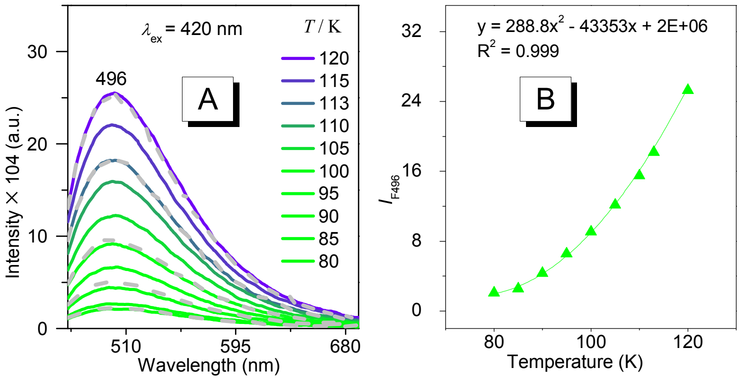


Figure S2 Emission spectra of 1c in crystals in the range of 80–120 K excited at 420 nm. (A) emission spectra. (B) relationship between *T* and fluorescence intensity at peak 496 nm. Spectra were recorded on a FLS980 spectrofluorophotometer. Excitation and emission slit widths: 0.9 and 0.9 nm.

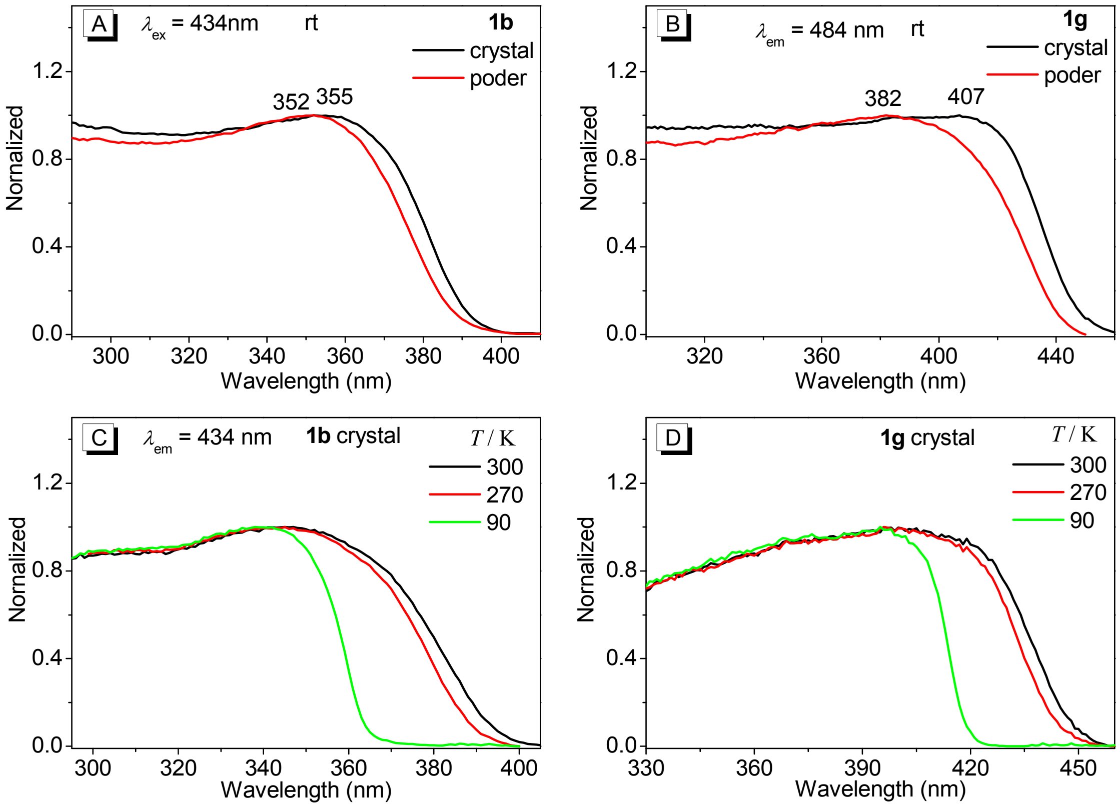


Figure S3 Comparison of the influences of aggregate sizes and temperature on the excitation spectra of 1b and 1c. Excitation spectra of **1b** (A) and **1c** (B) in crystal and powder (ground crystals) at room temperature (rt); Excitation spectra of **1b** (C) and **1c** (D) in crystals at 300, 270 and 90 K. Spectra in A and B were measured under slit widths of 5 and 3 nm by a Shimadzu RF5301PC spectrofluorophotometer, and spectra in C and D were recorded on a FLS980 spectrofluorophotometer (Excitation and emission slit widths: 0.8 and 0.8 nm for spectra in C; 0.4 and 0.4 nm for spectra in D). Crystal and powder samples in Figure 1 were used.

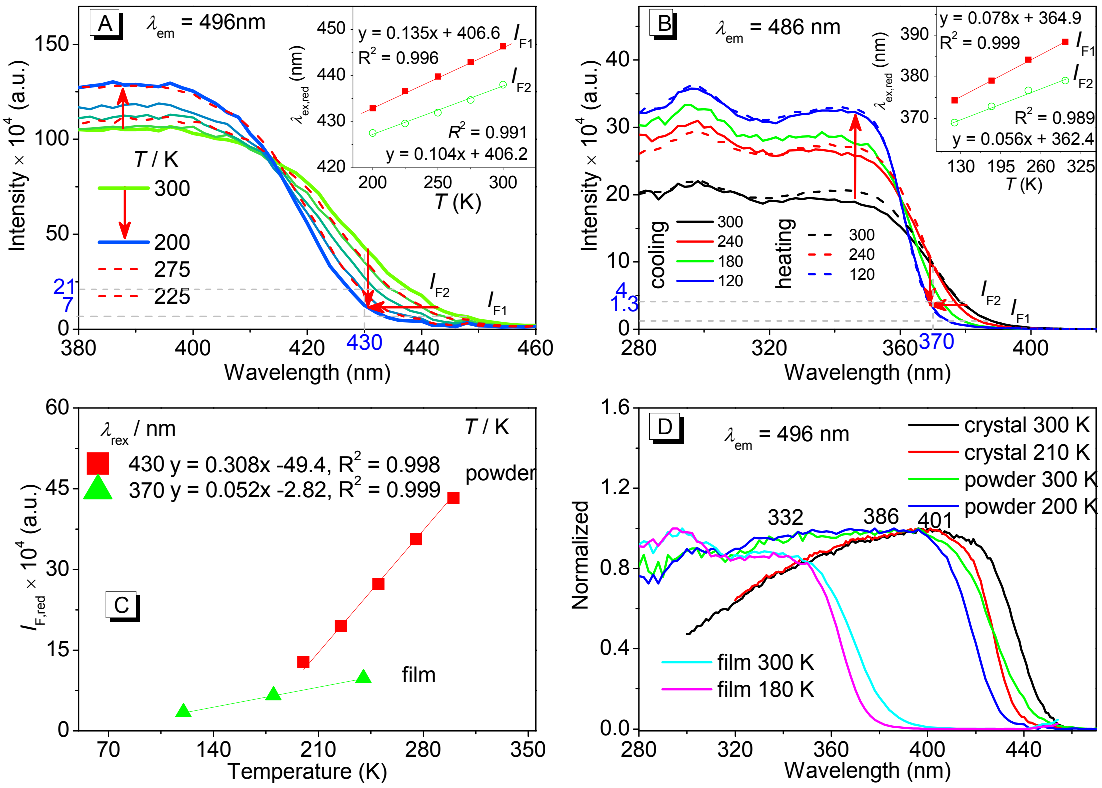


Figure S4 Excitation spectra of 1c in powder and film at different temperatures. (A) excitation spectra of powder emitted at 496 nm, inset in A is the relationship between *T* and red-edge wavelength ($\lambda_{ex,red}$) at fluorescence intensity (I_F) equal to 7 and 21 × 10^4 (about 1/15 and 1/5 times of the I_F at 386 nm, respectively); (B) excitation spectra of film excited at 496 nm, inset in C is the relationship between *T* and $\lambda_{ex,red}$ at I_F equal to 1.3 and 4 × 10^4 (about 1/15 and 1/5 times of the I_F at 332 nm, respectively). (C) relationship between *T* and $I_{F,red}$ at $\lambda_{ex,red}$ equal to 430 and 370 nm of the excitation spectra in A and B, respectively; (D) normalized excitation spectra of crystals, powder and film. Spectra were recorded on a FLS980 spectrofluorophotometer (Excitation and emission slit widths: 0.3 and 0.3 nm for spectra in A; 1.5 and 1.5 nm for spectra in B).

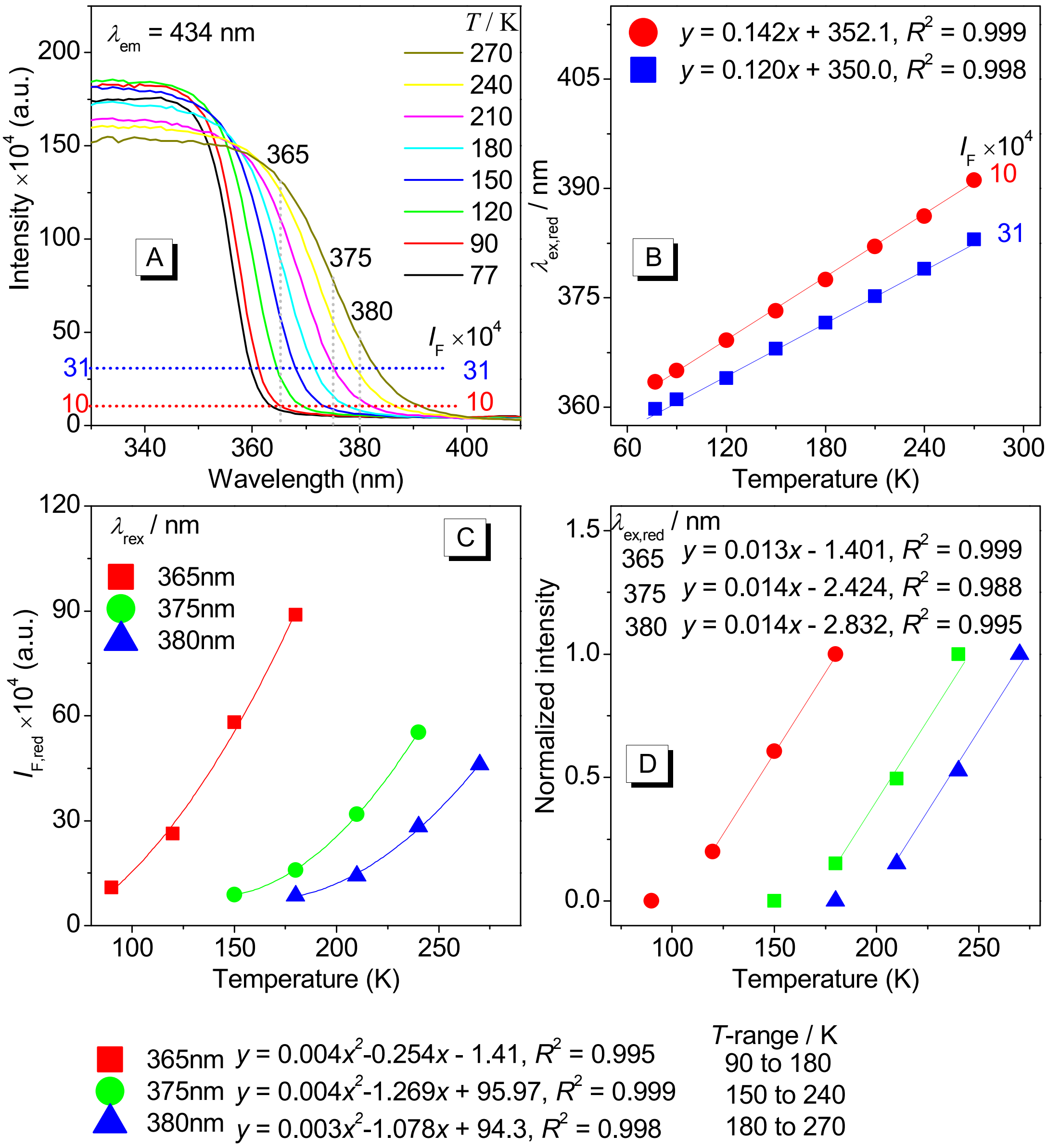


Figure S5 Excitation spectra of 1b in powder at different temperatures. (A) Excitation spectra in the range of 77 to 270 K. (B) Relationship between T and $\lambda_{\mathrm{ex,red}}$ at I_{F} = 10 and 31 $\times 10^4$ (about 1/15 and 1/5 times of the I_{F} at 352 nm, respectively). (C) Relationship between T and $I_{\mathrm{F,red}}$ at $\lambda_{\mathrm{ex,red}}$ = 365, 375 and 380 nm, respectively. (D) Relationship between T and normalized $I_{\mathrm{F,red}}$ at $\lambda_{\mathrm{ex,red}}$ =365, 375 and 380 nm, respectively. Spectra were recorded on a FL-3 spectrofluorophotometer (Excitation and emission slit widths: 1.0 and 1.0 nm). Powder samples in Figure 1 were used.

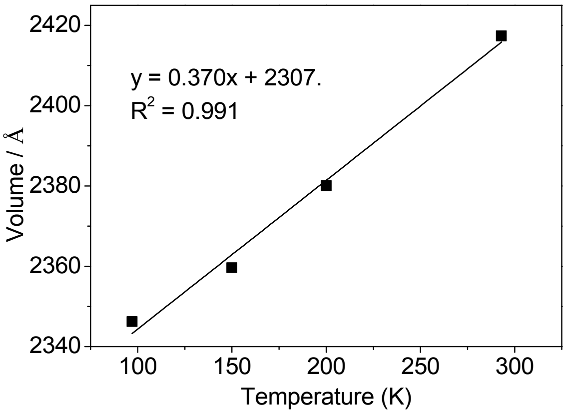


Figure S6 Temperature dependence of the unit cell volume of 1b in a single crystal.

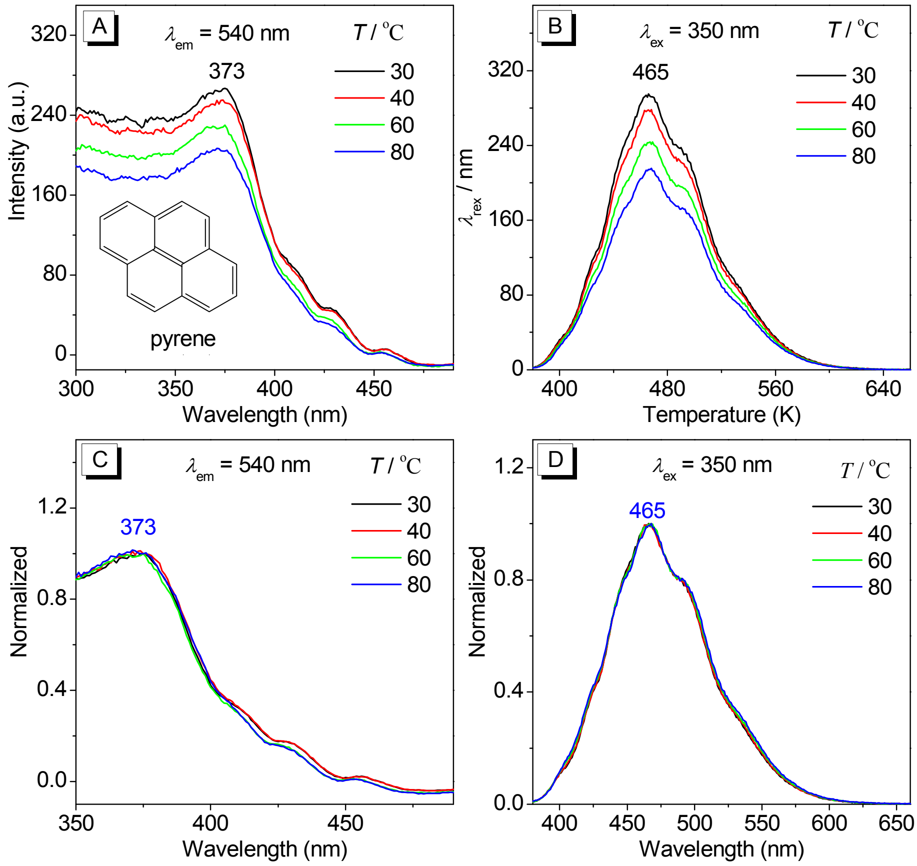


Figure S7 Excitation and emission spectra of pyrene in solid in the temperature range of 30–80 ºC. (A) excitation spectra emitted at 540 nm; (B) emission spectra excited at 350 nm; (C) normalized excitation spectra in (A); (D) normalized emission spectra temperature in (B). Spectra in (A) were measured under 5 and 5 nm of slit widths, and in (B) under 3 and 5 nm of slit widths. Spectra were recorded on a Shimadzu RF5301PC spectrofluorophotometer.

Table S1 Crystallographic data for **1b** at different temperature

T^a [K]	97	150	200	293
crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	$P2(1)/n$	$P2(1)/n$	$P2(1)/n$	$P2(1)/n$
a [Å]	9.6401(3)	9.65524(16)	9.6807(2)	9.7263(19)
b [Å]	26.2037(8)	26.2814(3)	26.3829(6)	26.576(5)
c [Å]	9.8735(4)	9.90428(18)	9.9379(3)	9.993(2)
α [Å]	90	90	90	90
β [deg]	109.829(4)	110.134(2)	110.330(3)	110.62(3)
γ [deg]	90	90	90	90
V [Å^3]	2346.23(14)	2359.66(7)	2380.08(10)	2417.4(9)
Z	4	4	4	4
D_{calcu} [mg/m^3]	1.292	1.285	1.274	1.254
R	0.0456	0.0420	0.0423	0.0507
wR_2	0.1217	0.1040	0.1093	0.1662

Reference

1. Zhu Q, Huang L, Chen Z, Zheng S, Lv L, Zhu Z, *et al.* A New Series of C-6 Unsubstituted Tetrahydropyrimidines: Convenient One-Pot Chemoselective Synthesis, Aggregation-Induced and Size-Independent Emission Characteristics. *Chem Eur J* 2013, **19**(4): 1268–1280.