Supporting Information

for

Dye-Encapsulated Zeolitic Imidazolate Framework (ZIF-71) for Fluorochromic Sensing of Pressure, Temperature, and Volatile Solvents

*Yang Zhang, Mario Gutiérrez, Abhijeet K. Chaudhari and Jin-Chong Tan**

Multifunctional Materials & Composites (MMC) Laboratory,
Department of Engineering Science, University of Oxford,
Parks Road, Oxford OX1 3PJ, United Kingdom.

*Corresponding author:

jin-chong.tan@eng.ox.ac.uk

Characterization Techniques

1. Calculation of the chemical formula of RhB@ZIF-71 and the number of RhB molecules per pore by means of thermogravimetric analysis (TGA) data

To calculate the chemical formula of the RhB@ZIF-71 materials, we firstly estimated the mass percentage of ZIF-71 and RhB corresponding to their mass loss in the TGA curves (Fig. 2b in main manuscript). In the case of RhB_I@ZIF-71, the loss of mass associated to ZIF-71 and RhB was determined to be 93.5% and 7.5%, respectively. For RhB_{II}@ZIF-71 and RhB_{III}@ZIF-71 composites, the mass loss of ZIF-71 was 90.8% and 83.4%, respectively, while for RhB was 9.2% and 16.6%, respectively. From those values, we have calculated the number of moles of RhB per moles of ZIF-71 by applying the following equations:

$$n = \frac{m}{M} \tag{1}$$

where *n* stands for the number of moles, *m* is the mass, and *M* is the molecular weight. From the equation (1) it is possible to estimate the ratio between the moles of ZIF-71 and RhB:

$$\frac{n_{ZIF-71}}{n_{RhB}} = \frac{\frac{m_{ZIF-71}}{M_{ZIF-71}}}{\frac{m_{RhB}}{M_{RhB}}} = \frac{m_{ZIF-71}}{m_{RhB}} \times \frac{M_{RhB}}{M_{ZIF-71}} \tag{2}$$

Knowing that the chemical formula of ZIF-71 is $[Zn_2C_{12}H_4Cl_8N_8]$, the global chemical formula of RhB@ZIF-71 is given by:

(I) RhB_I@ZIF-71:

$$\frac{n_{ZIF-71}}{n_{RhB}} = \frac{93.5}{7.5} \times \frac{479}{674} = \frac{1}{0.098}$$

$$\mathbf{[Zn_2C_{12}H_4Cl_8N_8]\cdot(RhB)_{0.098}}$$

(II) RhB_{II}@ZIF-71:

$$\frac{n_{ZIF-71}}{n_{RhB}} = \frac{90.8}{9.2} \times \frac{479}{674} = \frac{1}{0.143}$$

$$\mathbf{[Zn_2C_{12}H_4Cl_8N_8]\cdot(RhB)_{0.143}}$$

(III) RhB_{III}@ZIF-71:

$$\frac{n_{ZIF-71}}{n_{RhB}} = \frac{83.4}{16.6} \times \frac{479}{674} = \frac{1}{0.280}$$

$$\mathbf{[Zn_2C_{12}H_4C_{l8}N_8]\cdot(RhB)_{0.280}}$$

Once calculated the amount or RhB per two atoms of Zn (i.e. Zn_2), and knowing that a single pore of ZIF-71 contains 24 atoms of Zn, we can estimate the mean number of RhB molecules per pore in each material:

(I) RhB_I@ZIF-71 → 0.098 × 12 = **1.2 RhB molecules per pore**

(II) RhB_{II}@ZIF-71 → 0.143 × 12 = **1.7 RhB molecules per pore**

(III) RhB_{III}@ZIF-71 → 0.280 × 12 = **3.4 RhB molecules per pore**

Because of the spatial constraint of the ZIF-71 pore, only a maximum two RhB guest molecules could occupy a pore volume. On this basis, we reasoned that (I) and (II) are confined inside the pores of ZIF-71, whereas (III) has excess molecules that are adhering to the outer surface of the ZIF-71 crystals.

2. Fluorescence spectroscopy using the Edinburgh Instruments FS-5 setup

i. Steady-state excitation (solid) in module SC-10: for the measurement of excitation spectra, the emission wavelength was selected at 650 nm. The dwell time was 0.2 s, the step size was 1 nm and 2 scans were performed for each measurement.

ii. Steady state emission (solid) in module SC-10: for the measurement of emission spectra, the excitation wavelength for RhB@ZIF-71 was 515 nm. The dwell time was 0.2 s, the step size was 1 nm and 2 scans were performed for each measurement.

iii. Lifetime TCSPC measurement (solid): A 362.5 nm laser was used for lifetime measurement. The stop condition was set to be at 10,000 counts.

iv. QY measurement (solid) in module SC-30: the starting scan wavelength was selected as 20 nm before the excitation wavelength. QY analysis was done using the 'Fluoracle' software.

v. Steady-state thermochromism measurement (solid) in module SC-28: The luminescent properties of the sample were measured when the set temperature was reached for 10 minutes (the instrumental settings were the same as 1 and 2 above).

vi. Mechanochromism measurement (solid): The RhB@ZIF-71 powder was pressed into pellets using the Specac hydraulic press with pellet Ø1 cm. Then the excitation/emission spectra and lifetime of these pellets were measured (the instrumental settings were the same as 1 and 2 above).

vii. Characterization of solutions in module SC-05 or SC-20: Liquid solutions were performed in quartz cuvettes. For excitation, emission, lifetime and QY measurements, all the instrumental settings were the same as solid-state measurements described above.

viii. Solvatochromism measurement: After the RhB@ZIF-71 powder was combined with a solvent, it was sonicated for 10 minutes to obtain a good dispersion. The luminescent properties of the solution were measured using instrumental settings as in 1 and 2 above.

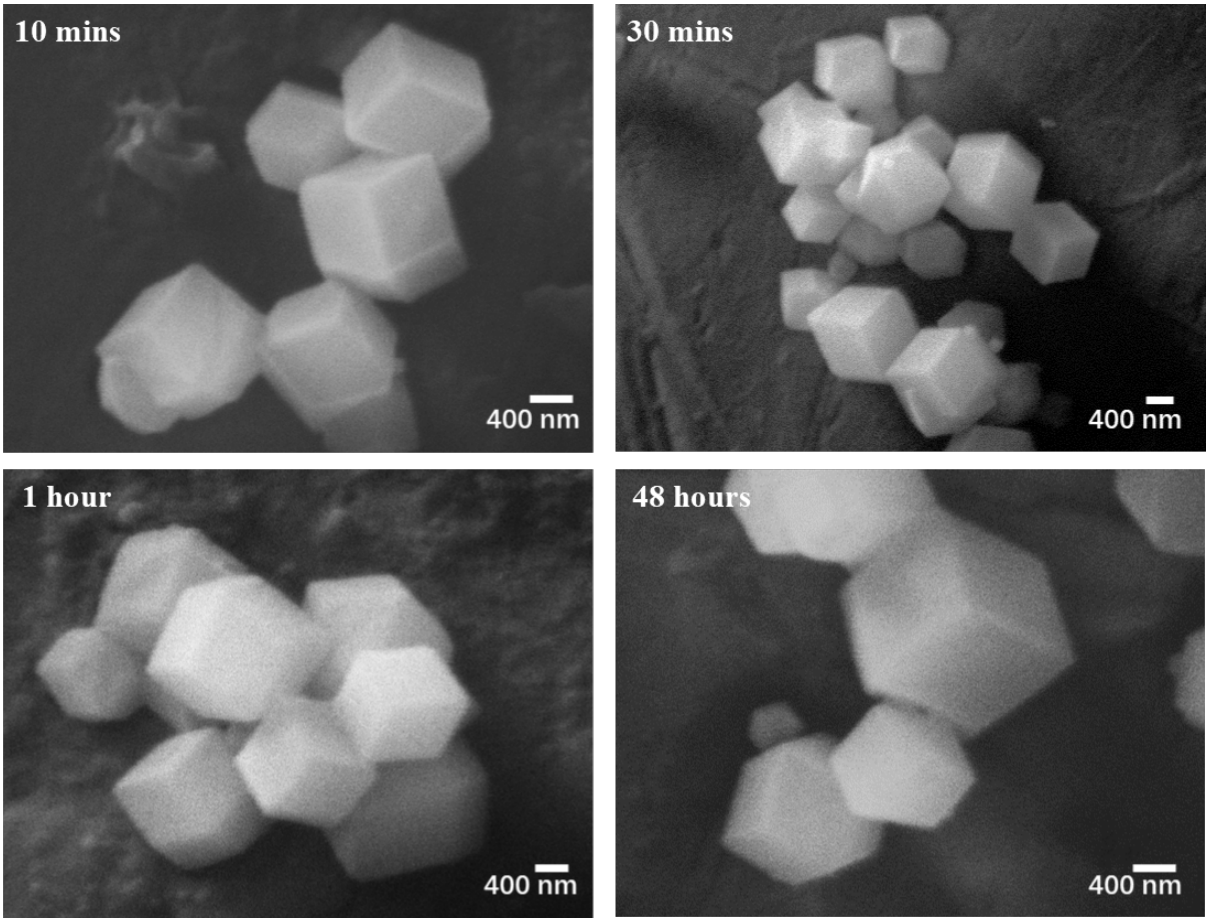

Figure S1. The SEM images of RhB@ZIF-71 prepared using different reaction times, ranging from 10 mins to 48 hours.

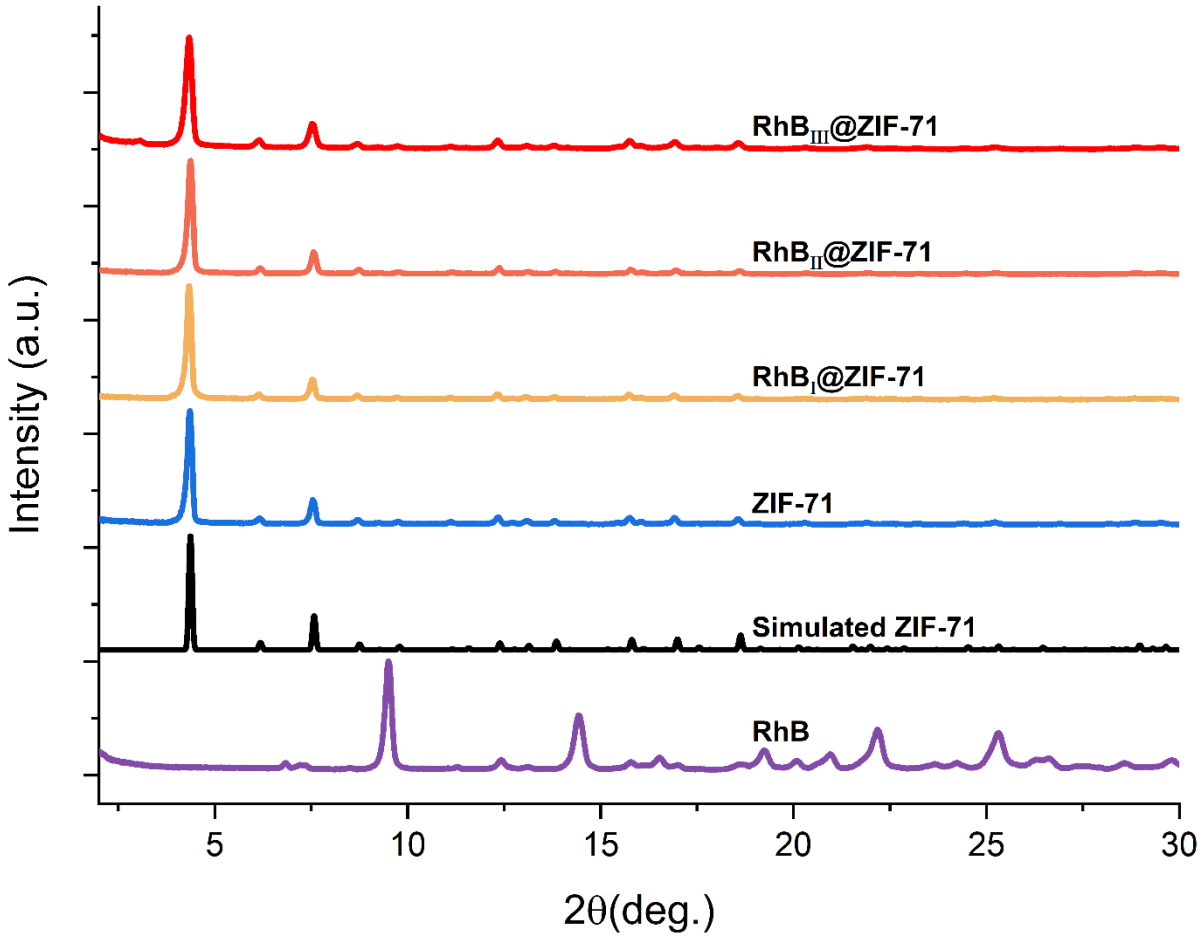

Figure S2. XRD patterns of pure RhB, pristine ZIF-71 crystals, and RhB@ZIF-71 guest-host composites prepared using three different concentrations of RhB guests. The subscripts I, II, and III correspond to the three concentrations of RhB used in the synthesis: 0.01, 0.05, and 0.5 mmol, respectively. The simulated pattern of ZIF-71 was generated from the crystallographic information file (CIF) obtained from the Cambridge Structural Database (CCDC code: GITVIP).

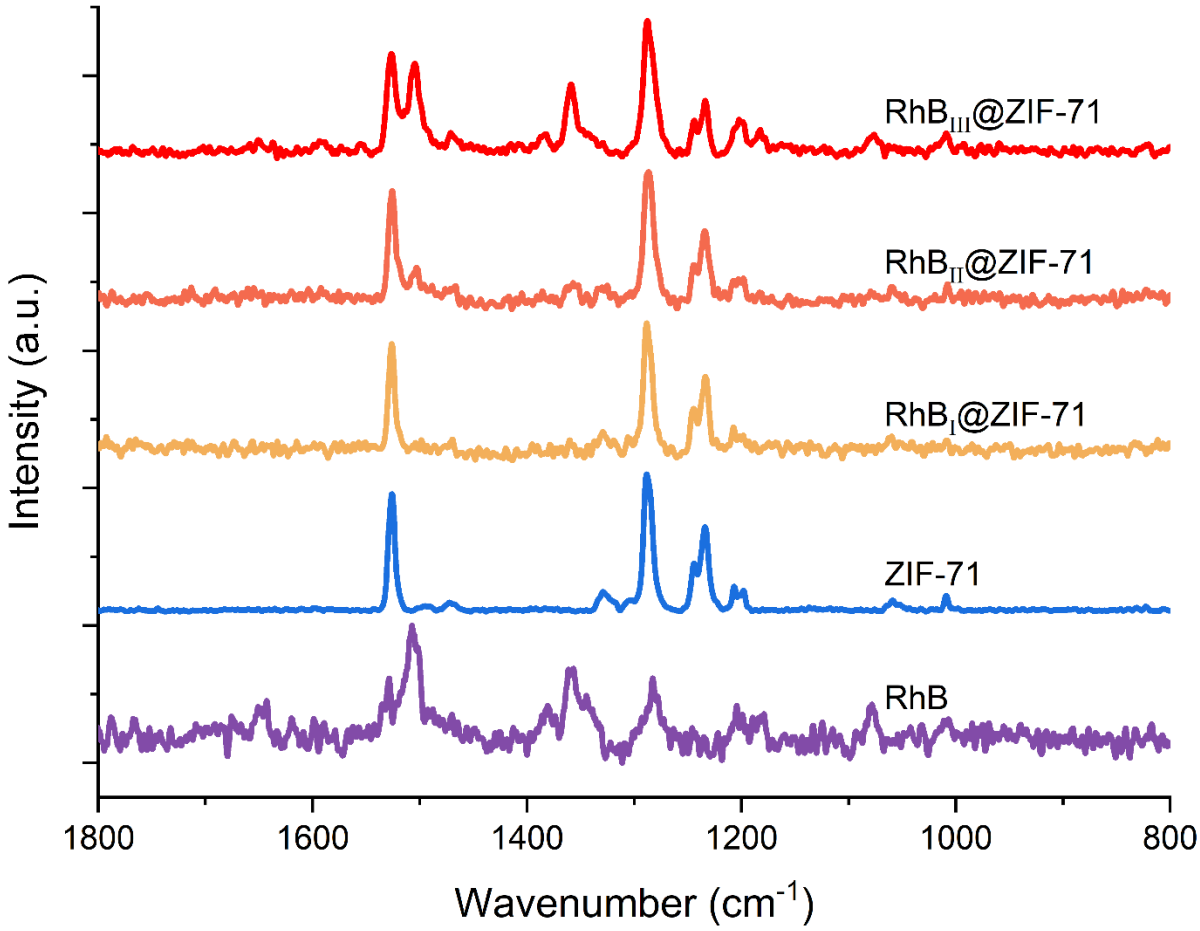

Figure S3. Raman spectra of pure RhB, pristine ZIF-71 crystals, and RhB@ZIF-71 guest-host composites prepared using three different concentrations of RhB guests.

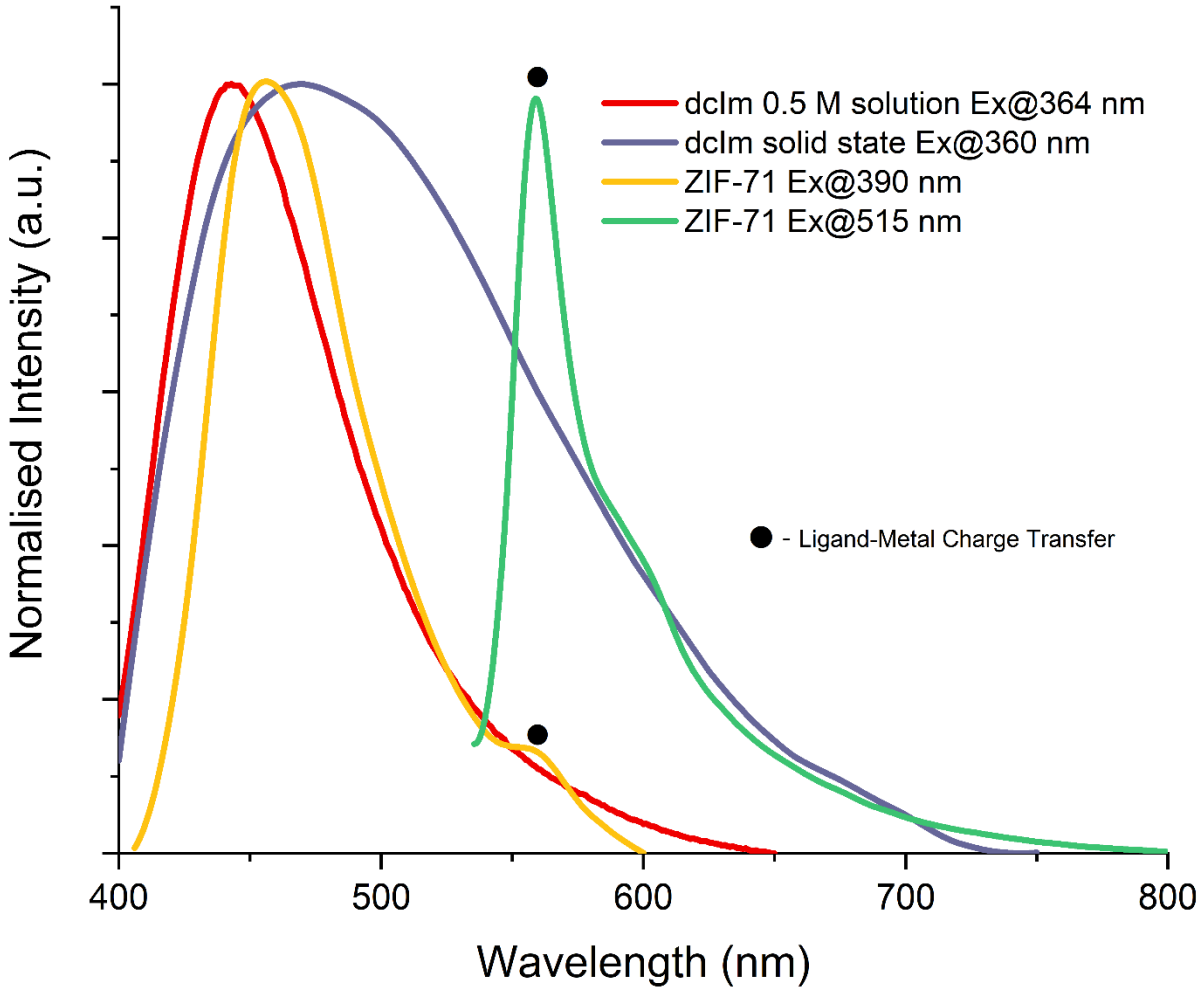

Figure S4. Normalised emission spectra of the dcIm linker in methanol solution (0.5 M) and in the solid state, compared to that of pristine ZIF-71 in solid state excited at 390 nm or 515 nm.

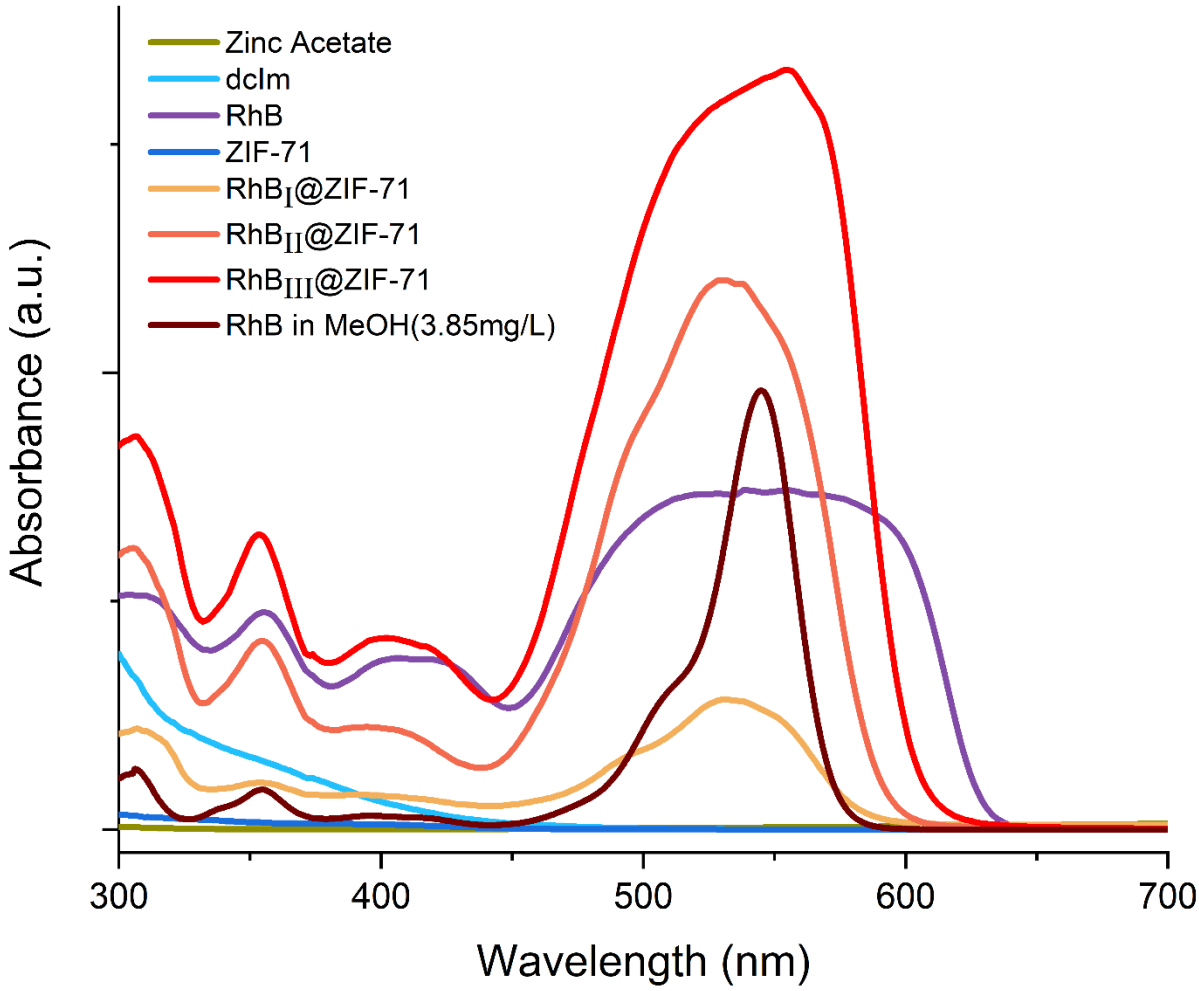

Figure S5. Diffuse reflectance spectra (DRS) of the absorption bands

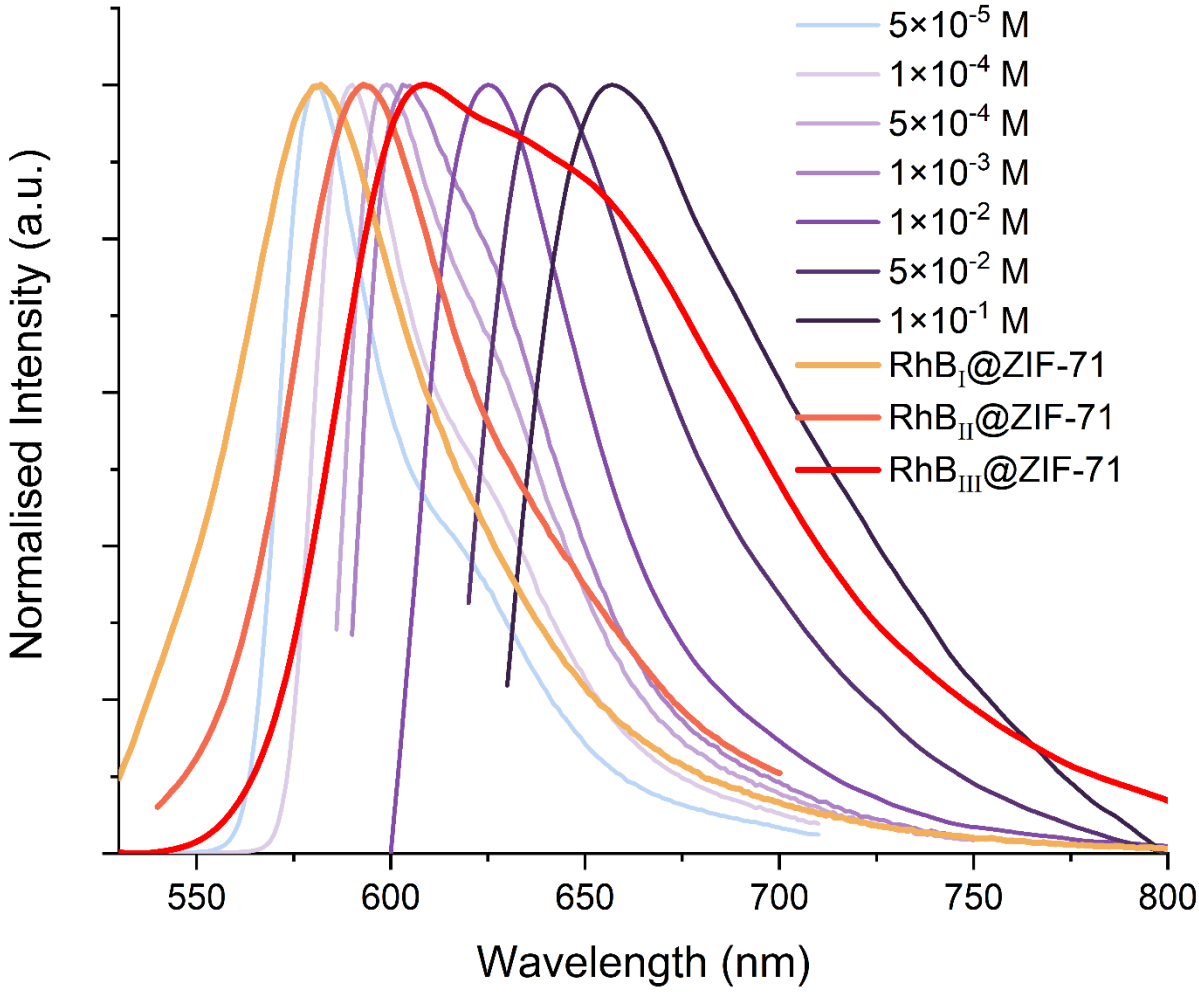

Figure S6. Normalised emission spectra of RhB in MeOH solution (ex@515 nm) of different concentrations, and $RhB_{I/II/III}$@ZIF-71 powders in the solid state.

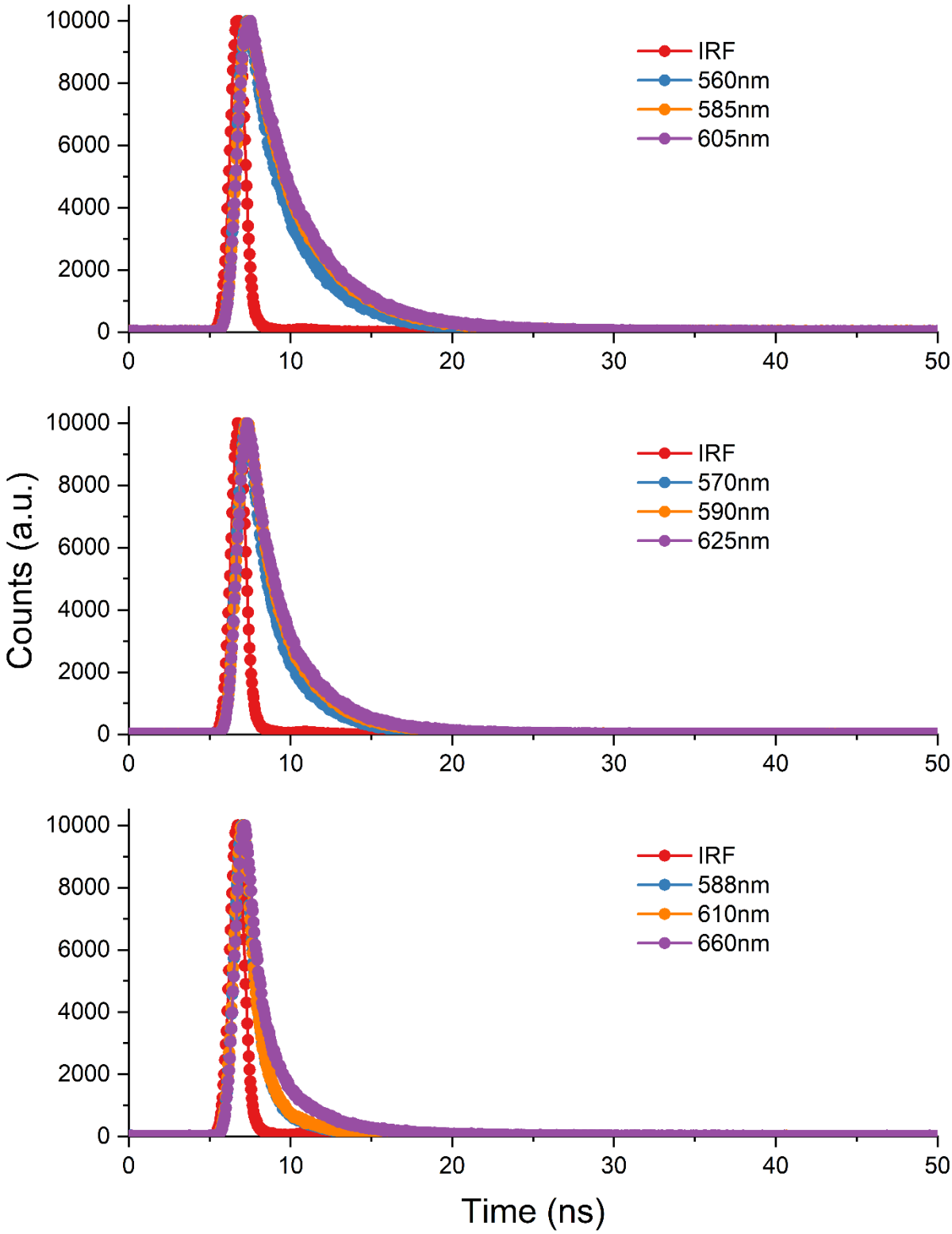

Figure S7. Lifetime emission spectra showing the decays of (a) RhB_I@ZIF-71, (b) RhB_{II}@ZIF-71, (c) RhB_{III}@ZIF-71.

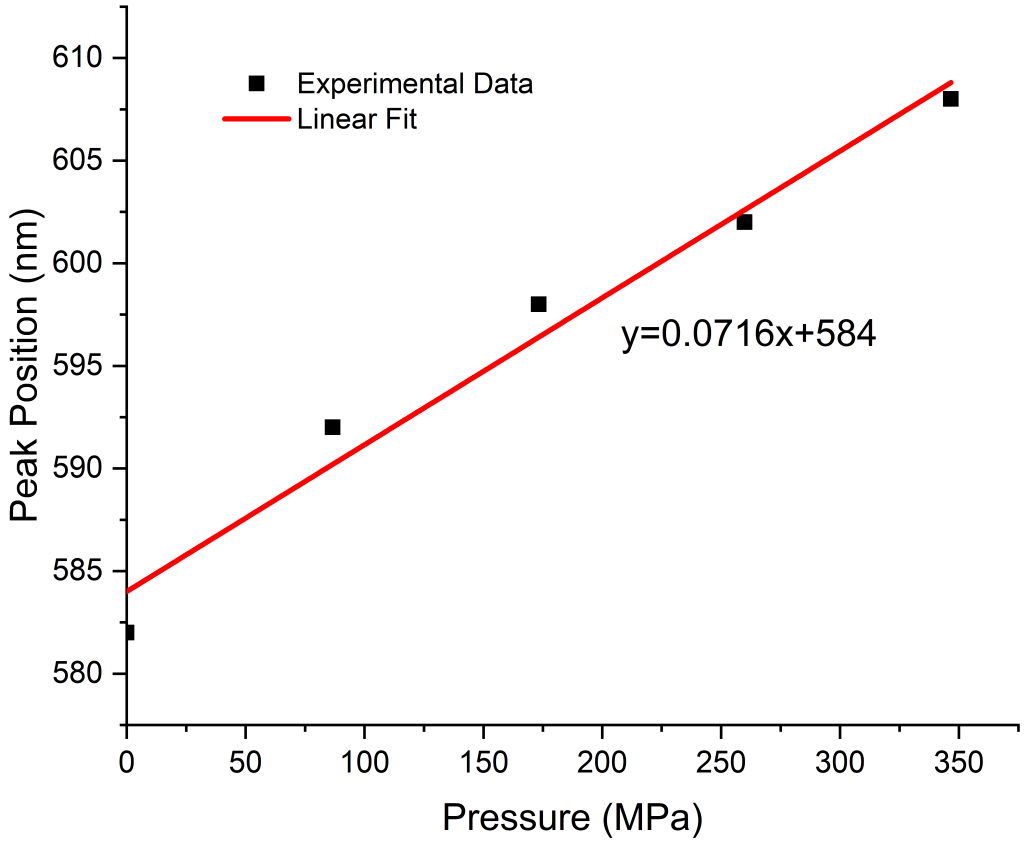

Figure S8. Correlation between the emission peak wavelength and the applied pressure for preparing the RhB_I@ZIF-71 pellets.

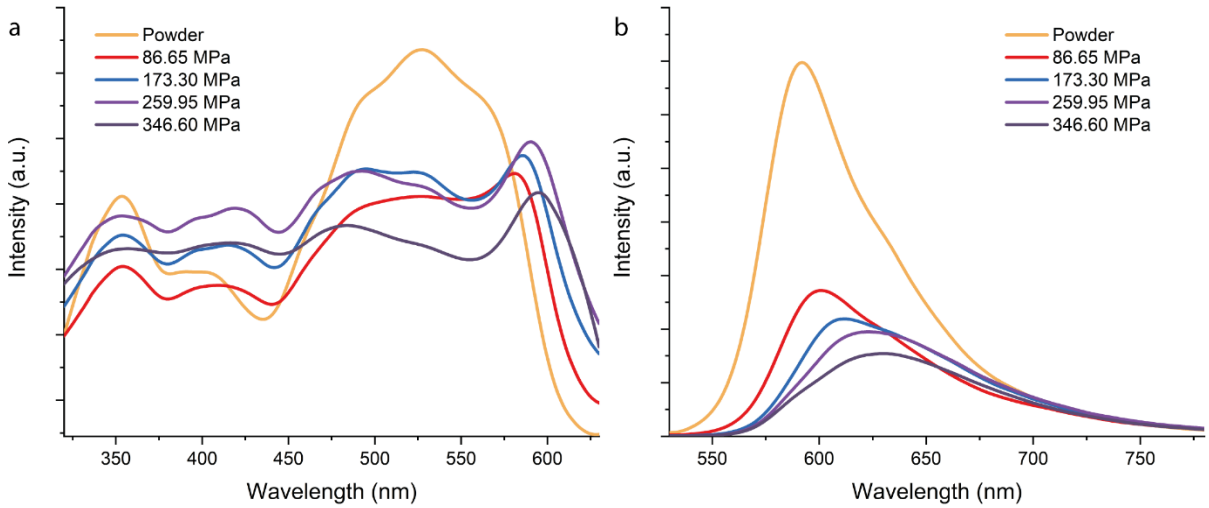

Figure S9. (a) Excitation spectra (measured under em@650 nm), and (b) emission spectra (measured under ex@515 nm) of RhB_{II}@ZIF-71 pellets.

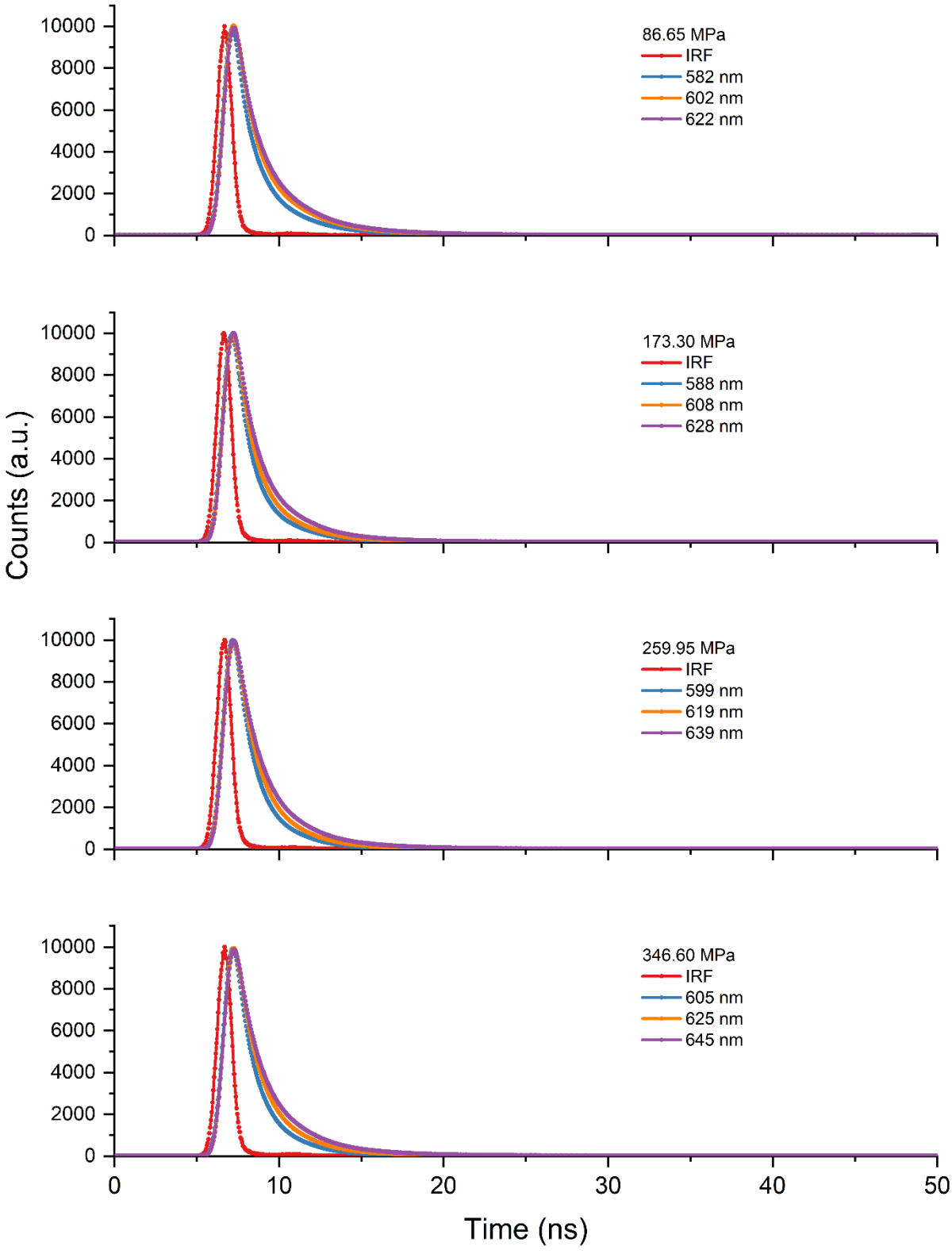

Figure S10. Emission decays of pellets under (a) 86.65 MPa, (b) 173.30 MPa, (c) 259.95 MPa, and (d) 346.60 MPa.

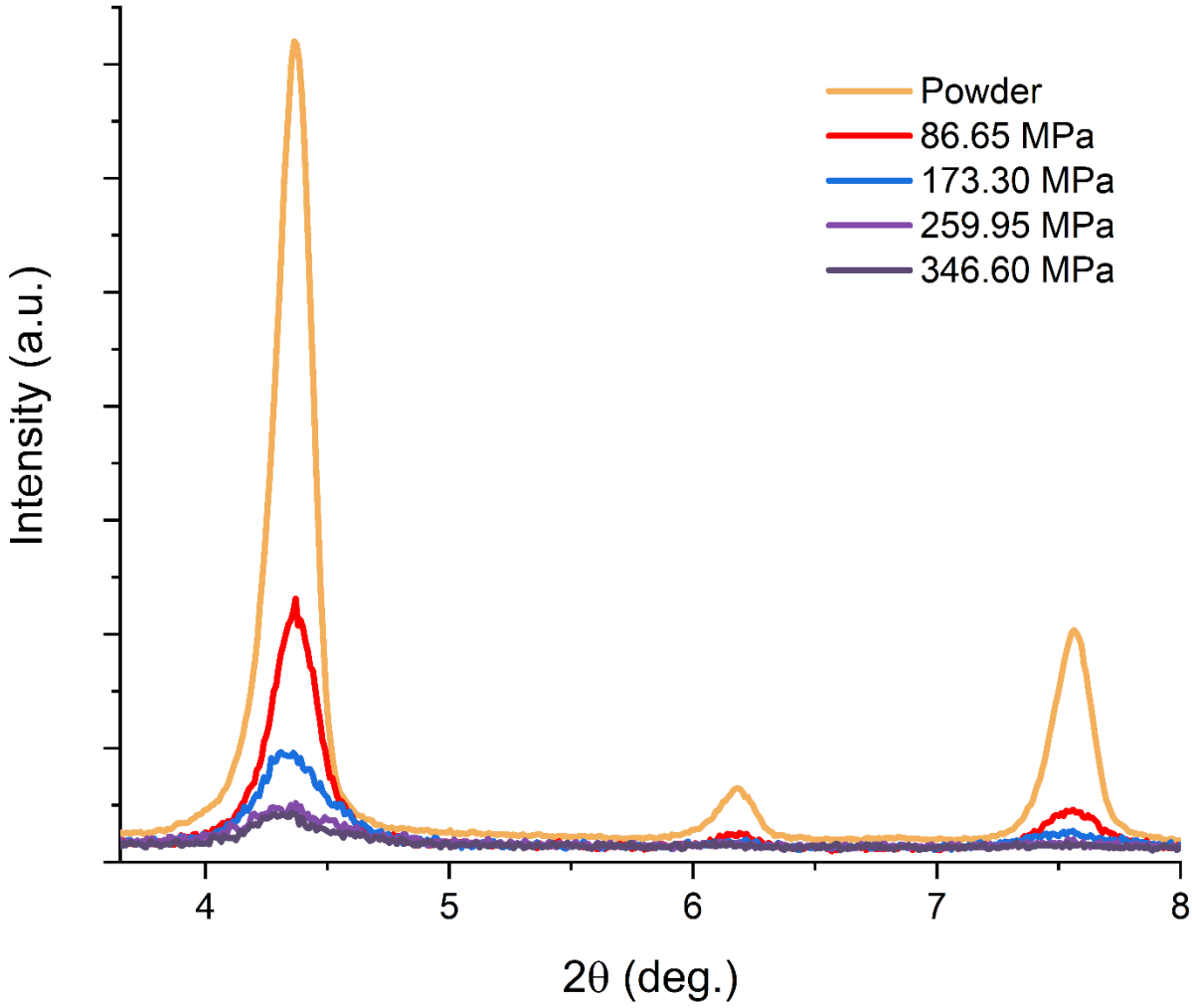

Figure S11. The unnormalized XRD patterns of the RhB_{II}@ZIF-71 pellets.

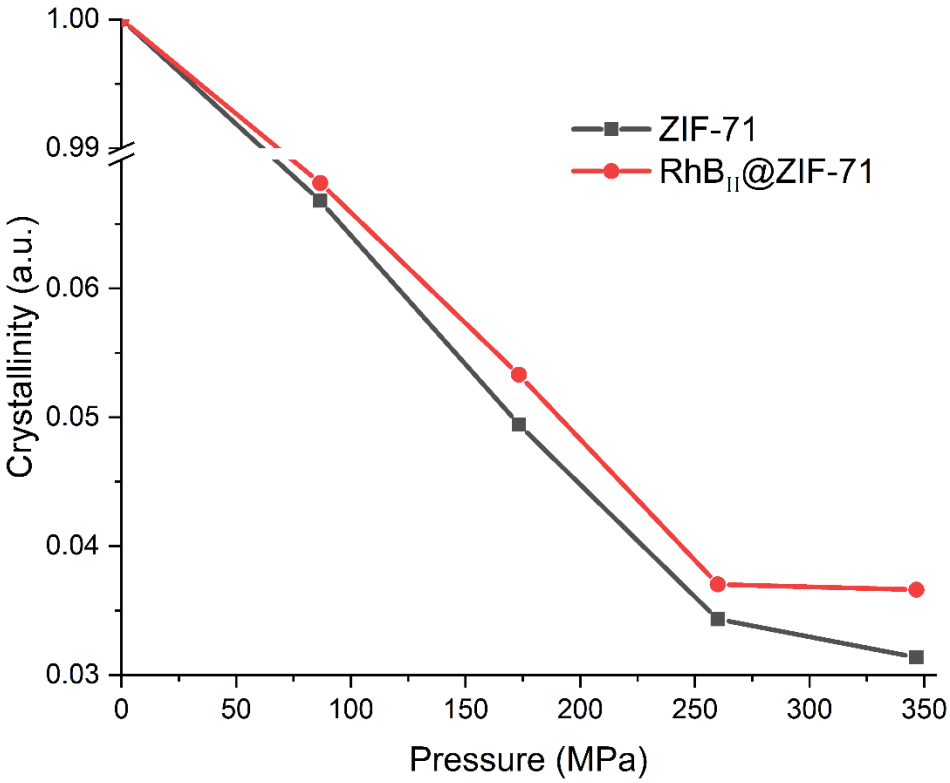

Figure S12. Crystallinity of ZIF-71 and RhB_{II}@ZIF-71 as a function of pressure, where data are presented in Table S4.

According to the Scherrer equation, the size of the crystalline domains D can be calculated by:

$$D = \frac{K\,\lambda}{\Delta \cos\theta}$$

where K is a constant, λ is the wavelength, Δ is the FWHM, and θ is the diffraction angle of the corresponding diffraction peak.

Therefore, the crystallinity can be obtained by using $D_p/D_{initial}$ [1], where D_p is the size of the crystalline domains after being subjected to pressure P, and $D_{initial}$ is the domain size of the pristine powder.

$$\therefore \text{crystallinity} = \frac{D_P}{D_{initial}} = \frac{\frac{K\,\lambda}{\Delta_P \cos\theta}}{\frac{K\,\lambda}{\Delta_{initial} \cos\theta}} = \frac{\Delta_{initial}}{\Delta_P}$$

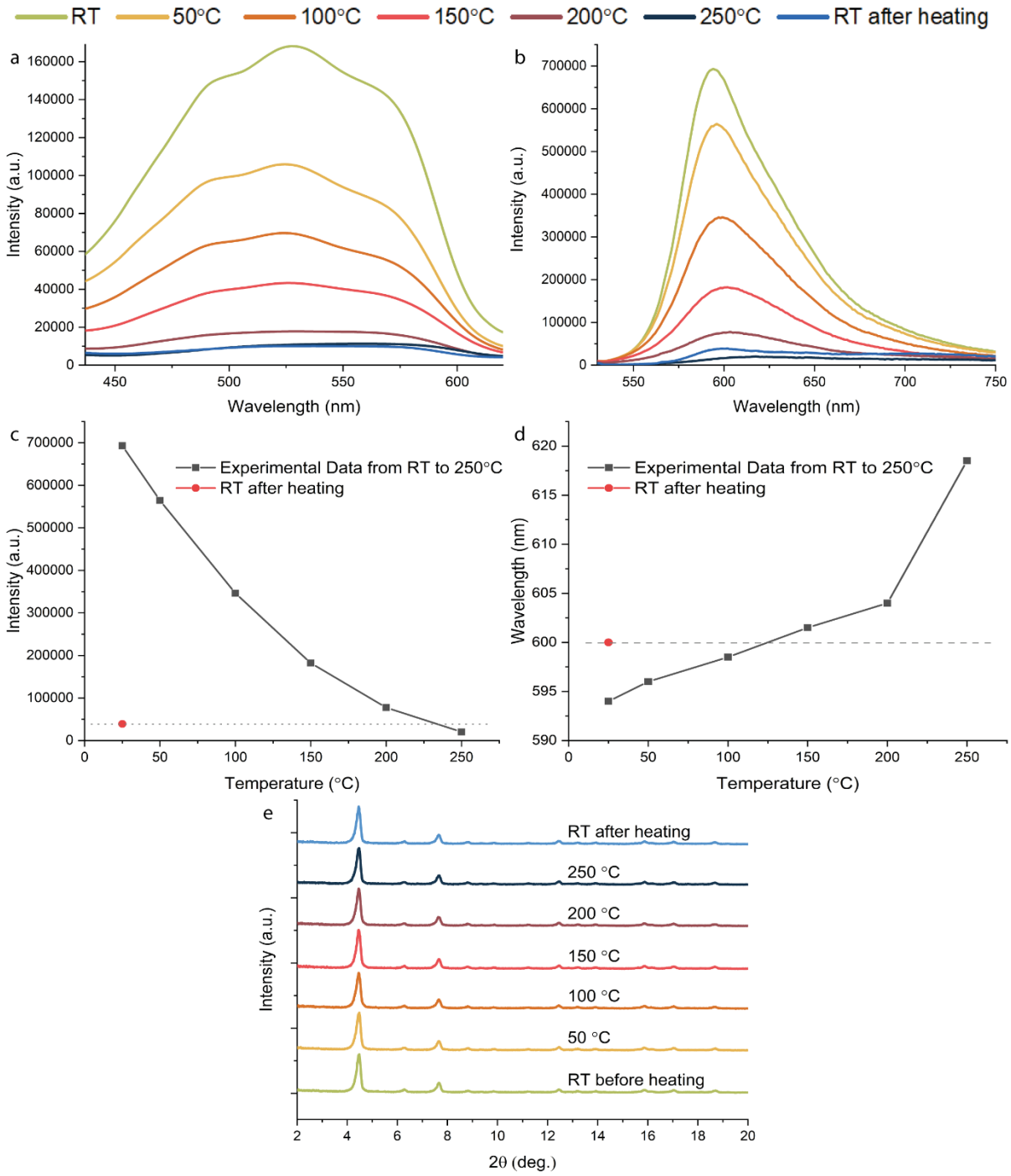

Figure S13. (a) Excitation spectra (measured under em@650 nm) and (b) emission spectra (measured under ex@365 nm) of RhB_{II}@ZIF-71 determined at different temperatures. The variation of (c) peak intensity and (d) peak wavelength as a function of temperature. (e) XRD patterns of RhB_{II}@ZIF-71 at different temperatures.

Peak Wavelength [nm]	Solvents										
	MeOH	EtOH	IPA	DCM	Acetone	Toluene	Hexane	ACN	DMA	DMF	Cyclohexane
RhB_I@ZIF-71	573	571	571.5	577	575	572.5	569	578	576.5	578.5	572.5
RhB	573	570	564	577	/[a]	/[b]	/[b]	564.5	/[a]	/[a]	/[b]

[a]The signal was too low to be detected. [b]RhB is poorly soluble or insoluble

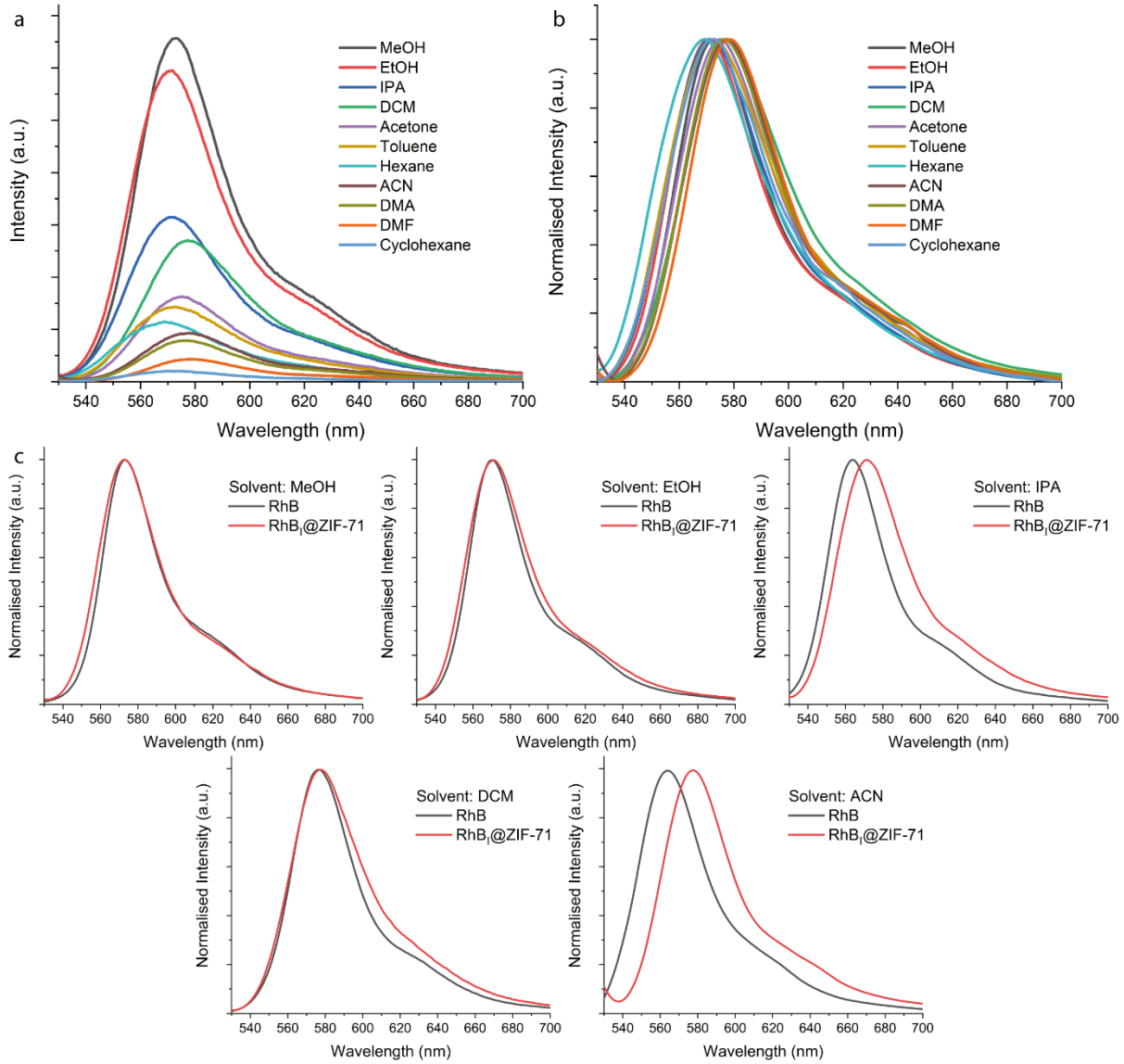

Figure S14. (a) Emission spectra (unnormalized) and (b) normalised emission spectra of RhB_I@ZIF-71 in different solvents (each comprising 1 mg of RhB_I@ZIF-71 in 20 ml solvent; ex@525 nm). (c) Comparison of the emission of RhB_I@ZIF-71 solutions and pure RhB in different solvents (7.5×10^{-6} M, ex@525 nm).

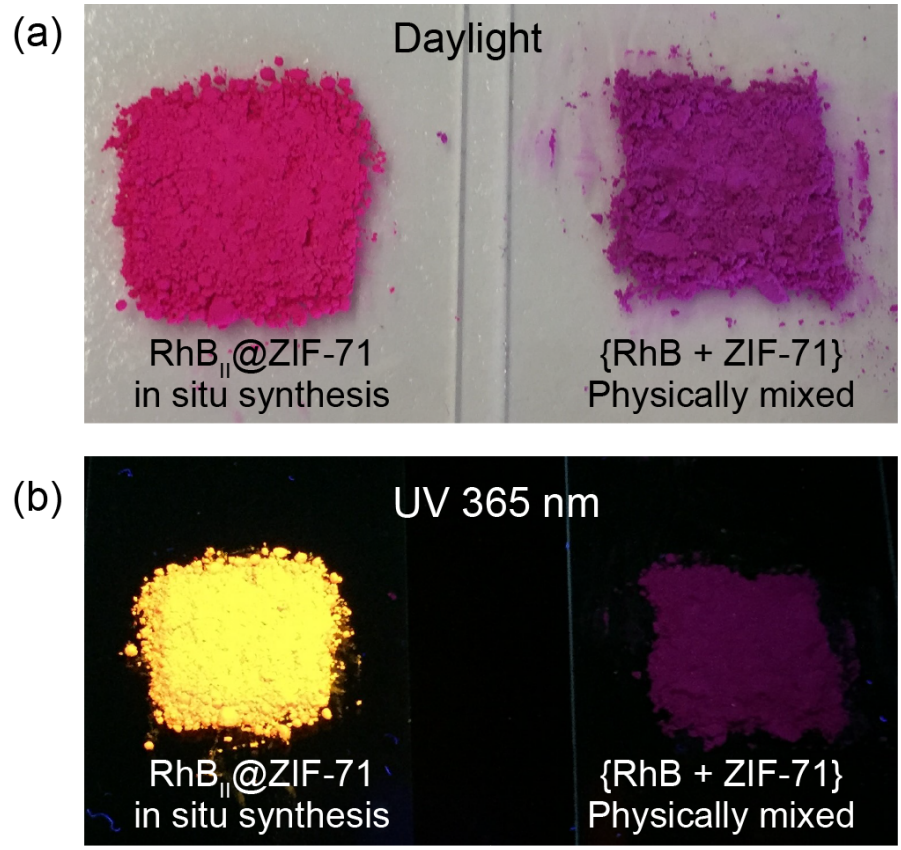

Figure S15. Comparing the sample colour and luminescence behaviour observed (a) under daylight and (b) in UV irradiation. Marked differences can be seen between the samples of RhB_{II}@ZIF-71 derived from *in situ* encapsulation synthesis (see method in manuscript), in contrast to the {RhB + ZIF-71} sample made by simple *physical mixing* or blending of the two constituents (in mortar and pestle by maintaining the same guest concentration as RhB_{II}@ZIF-71). The physically mixed 'composite' is not photoluminescent under UV irradiation due to quenching of the RhB guests aggregating on the outer surface of the ZIF-71 crystals. Conversely, it is clear that the RhB guest molecules confined in the ZIF-71 pores are well isolated and thus highly luminescent under UV excitation.

Table S1. The quantum yield (QY) of ZIF-71 in the solid state.

Sample	QY [%]		
	Ex@385 nm	Ex@485 nm	Ex@525 nm
ZIF-71	9.13	Undetectable[a)]	Undetectable[a)]

[a)]Too weak to be detected

Table S2. Values of time constants (τ_i), normalised pre-exponential factors (a_i), and fractional contributions ($c_i = \tau_i \cdot a_i$) of the emission decay of RhB@ZIF-71 with different concentration of RhB in solid state and in methanol solutions upon excitation at 362.5 nm.

Sample	λ_{obs} [nm]	τ_1 [ns]	a_1	c_1 [%]	τ_2 [ns]	a_2	c_2 [%]	τ_3 [ns]	a_3	c_3 [%]	χ^2
RhB_I@ZIF-71	560	0.28	0.030	5.67	2.08	0.039	54.75	3.88	0.015	39.58	1.098
	585	0.28	0.016	2.50	2.08	0.027	31.41	3.88	0.030	66.09	1.132
	605	0.28	0.015	2.27	2.08	0.024	26.97	3.88	0.034	70.76	1.242
RhB_{II}@ZIF-71	570	0.28	0.060	14.13	1.63	0.043	59.88	3.40	0.009	25.99	1.164
	590	0.28	0.033	6.96	1.63	0.042	52.54	3.40	0.015	40.50	1.114
	625	0.28	0.032	6.24	1.63	0.038	44.73	3.40	0.020	49.03	1.120
RhB_{III}@ZIF-71	588	0.28	0.124	44.27	1.19	0.031	47.49	3.87	0.002	8.24	1.292
	610	0.28	0.121	42.50	1.19	0.031	46.84	3.87	0.002	10.66	1.141
	660	0.28	0.082	22.50	1.19	0.039	45.47	3.87	0.008	32.04	1.154

Table S3. Values of time constants (τ_i), normalised pre-exponential factors (a_i), and fractional contributions ($c_i = \tau_i \cdot a_i$) of the emission decay of RhB_{II}@ZIF-71 pellets upon excitation at 362.5 nm.

Pressure [MPa]	λ_{obs} [nm]	τ_1 [ns]	a_1	c_1 [%]	τ_2 [ns]	a_2	c_2 [%]	τ_3 [ns]	a_3	c_3 [%]	χ^2
86.65	582	0.50	0.053	24.70	1.55	0.036	52.82	3.53	0.007	22.48	1.119
	602	0.50	0.040	16.60	1.55	0.038	49.98	3.53	0.011	33.42	1.113
	622	0.50	0.030	11.81	1.55	0.040	48.66	3.53	0.014	39.52	1.081
173.30	588	0.52	0.059	31.82	1.53	0.037	58.67	3.55	0.003	9.51	1.186
	608	0.52	0.040	20.02	1.53	0.046	66.63	3.55	0.004	13.35	1.104
	628	0.52	0.028	12.57	1.53	0.048	62.93	3.55	0.008	24.50	1.094
259.95	599	0.53	0.052	27.20	1.55	0.043	66.84	3.78	0.002	5.96	1.082
	619	0.53	0.029	14.25	1.55	0.051	72.76	3.78	0.004	12.99	1.085
	639	0.53	0.019	8.32	1.55	0.053	67.34	3.78	0.008	24.34	1.043
346.60	605	0.50	0.040	19.61	1.57	0.048	74.49	4.10	0.001	5.90	1.234
	625	0.50	0.023	10.17	1.57	0.057	77.78	4.10	0.003	12.05	1.146
	645	0.50	0.016	6.55	1.57	0.054	70.72	4.10	0.007	22.73	1.211

Table S4. Comparison of FWHM between pure ZIF-71 and RhB@ZIF-71.

Sample	Pressure [MPa]				
	0	86.65	173.30	259.95	346.60
ZIF-71	0.01610 ±0.00023	0.2410 ±0.0023	0.3257 ±0.0029	0.4690 ±0.0026	0.5130 ±0.0232
RhB_{II}@ZIF-71	0.01625 ±0.0003	0.2383 ±0.0023	0.3048 ±0.0051	0.4387 ±0.0101	0.4437 ±0.0589

References:

[1] Guillerm, V.; Ragon, F.; Dan-Hardi, M.; Devic, T.; Vishnuvarthan, M.; Campo, B.; Vimont, A.; Clet, G.; Yang, Q.; Maurin, G.; Ferey, G.; Vittadini, A.; Gross, S.; Serre, C., A Series of Isoreticular, Highly Stable, Porous Zirconium Oxide Based Metal-Organic Frameworks. *Angew. Chem. Int. Ed.* **2012**, *51*, 9267-9271.