

Supporting Information

for

**Turn-on fluorescence chemical sensing through transformation of
self-trapped exciton states at room temperature**

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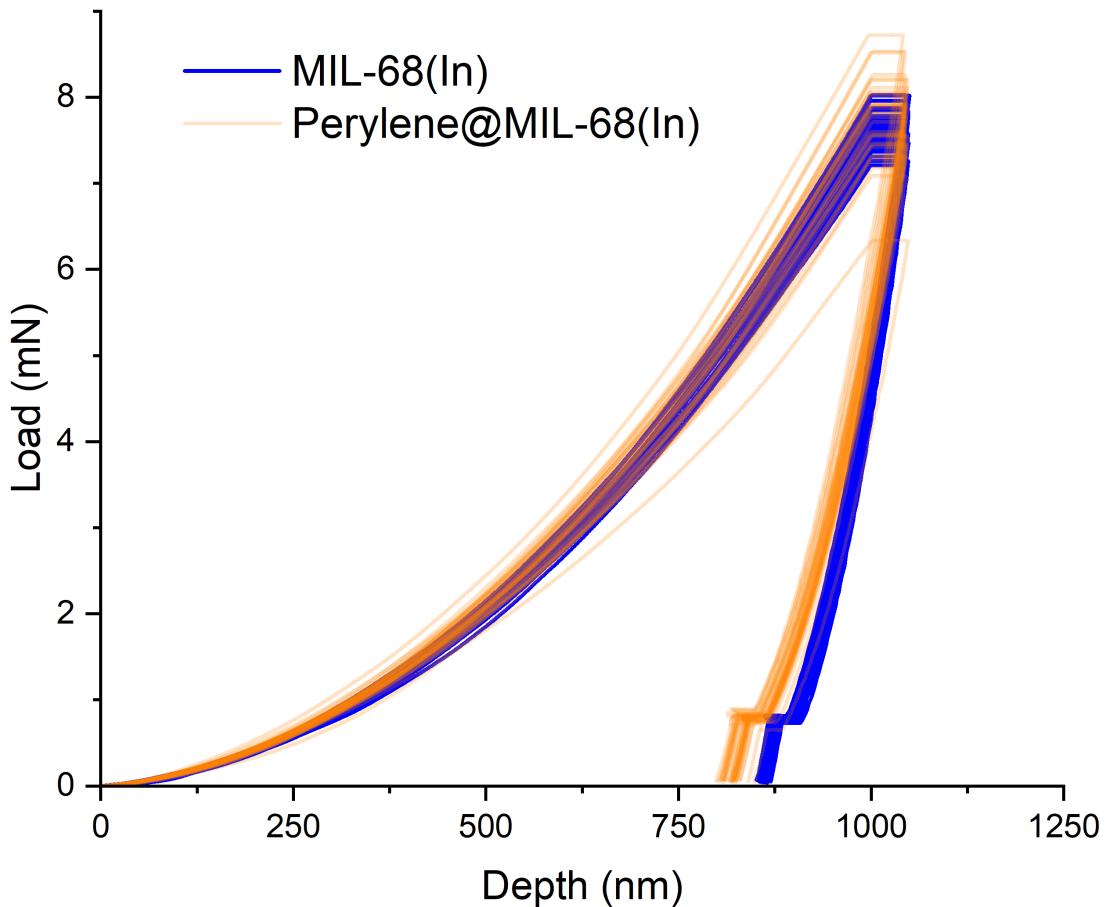


Figure S1. Load-depth curves resulting from nanoindentation tests of MIL-68(In) and perylene@MIL-68(In) with a Berkovich indenter. The results are summarized in Table S1.

Table S1. Indentation modulus and hardness measurements (CSM method) obtained from Berkovich nanoindentation. Mean values and standard deviations from this work were calculated from an indentation depth range of 200 – 1000 nm.

Sample	# of indents	Indentation modulus*, M (GPa)	Hardness, H (MPa)
MIL-68(In)	32	13.24 ± 0.52	402 ± 13
Perylene@MIL-68(In)	32	11.74 ± 0.66	486 ± 32

* Let Poisson's ratio, $\nu = 0$.

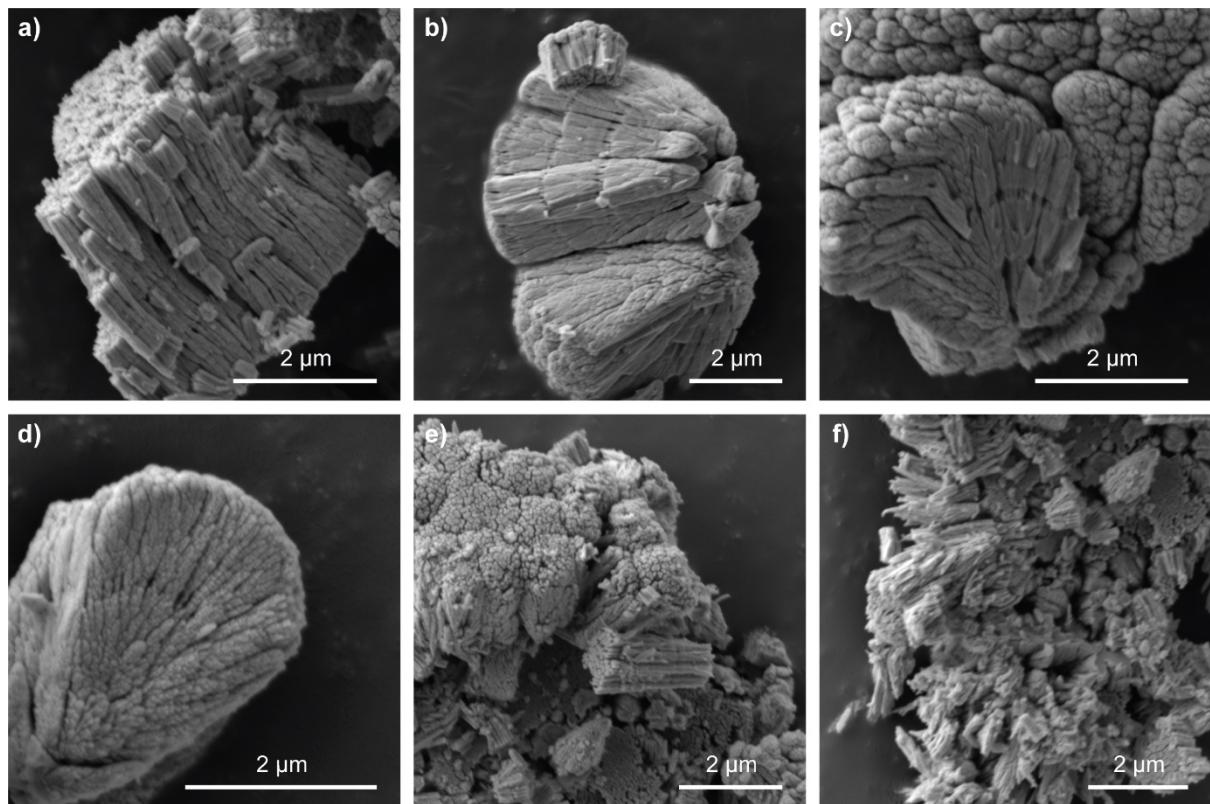


Figure S2. FESEM images of (a-c) MIL-68(In), (d) 025P@MIL-68(In), (e) 05P@MIL-68(In), and (f) 1P@MIL-68(In). 1P, 05P, and 025P designate the amount of perylene used in the synthesis to be 1 mmol, 0.5 mmol, and 0.25 mmol, respectively.

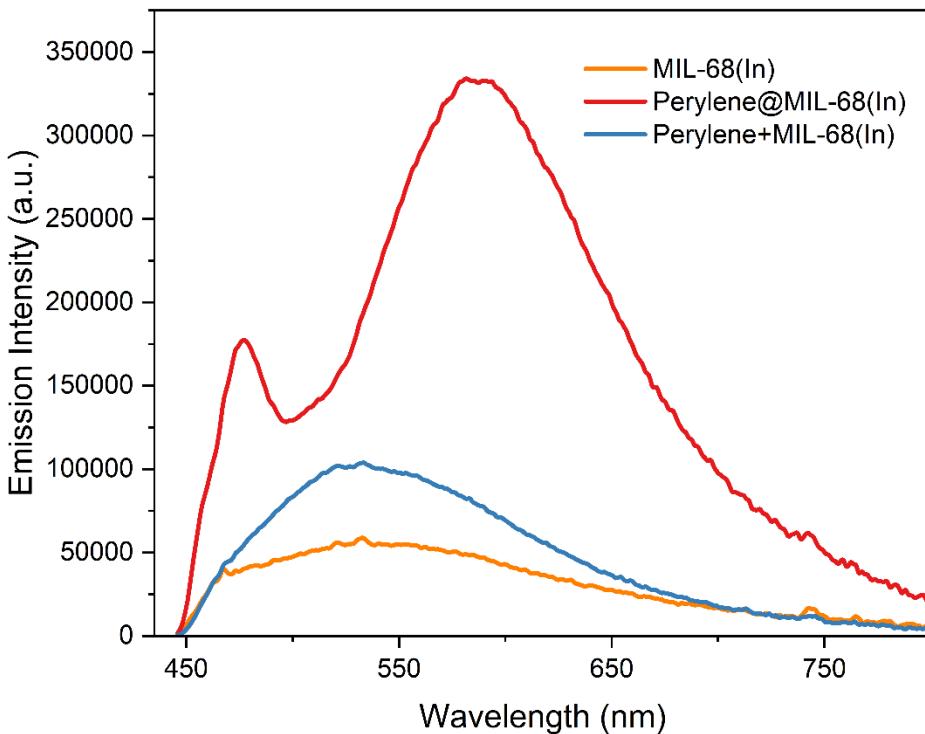


Figure S3. Comparing the emission properties of MIL-68(In), perylene@MIL-68(In), and physically mixed perylene+MIL-68(In) [*i.e.* perylene guests predominantly adhered on the surface of MIL-68(In)]. The perylene+MIL-68(In) was made by simple blending (physical mixing) of the two constituents [in mortar and pestle by maintaining the same guest concentration as 025P@MIL-68(In)]. It is clear that the emission of perylene+MIL-68(In) is different from the perylene@MIL-68(In), which indicates that the perylene guests are mainly confined within the MOF channels in the perylene@MIL-68(In) system.

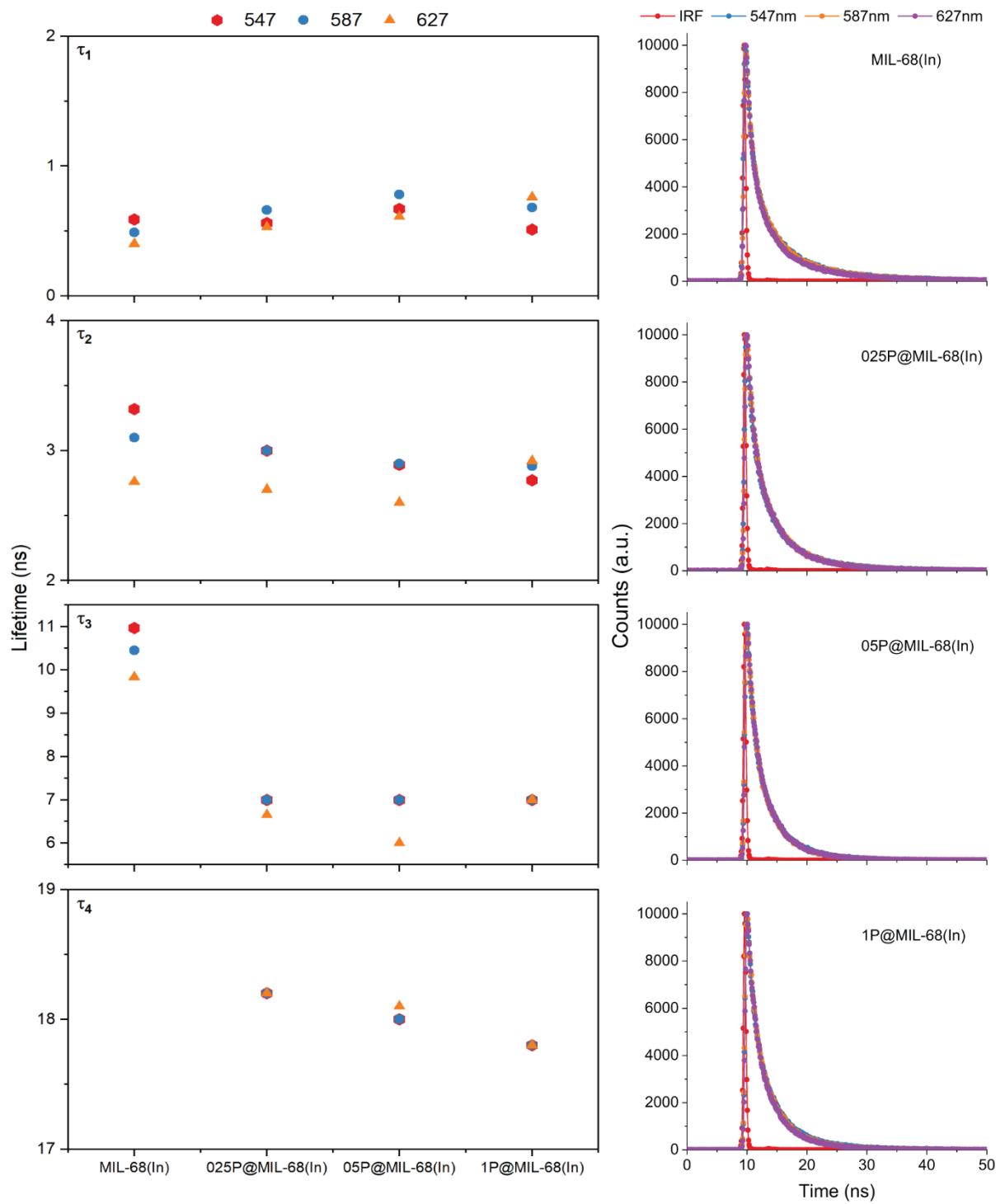
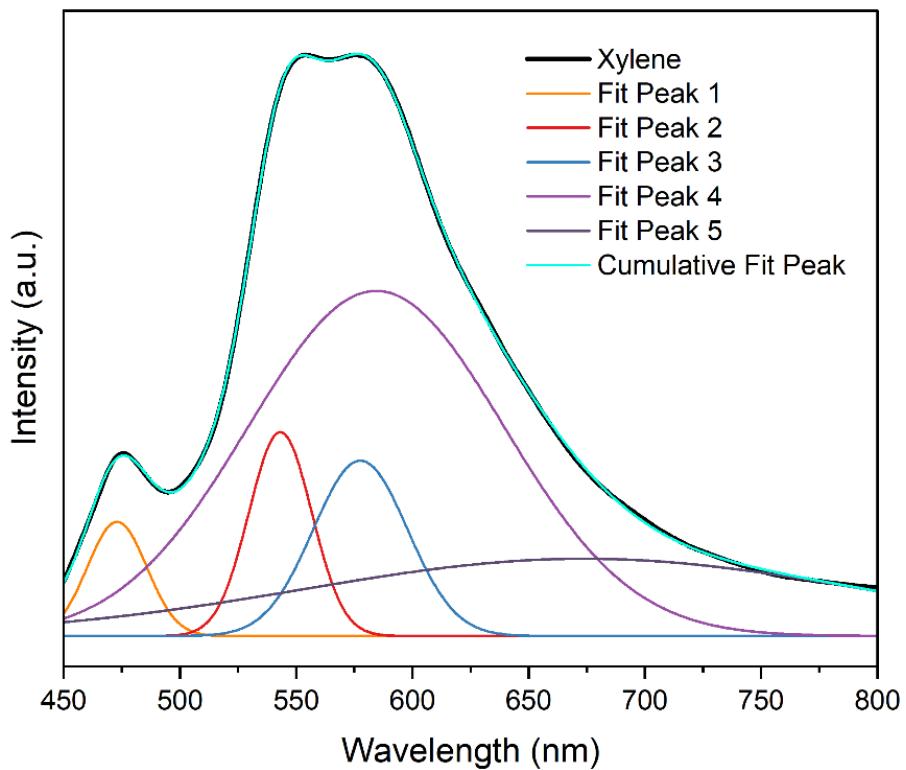


Figure S4. Lifetime data of MIL-68(In) and perylene@MIL-68(In) powders observed under the 547, 587, and 627 nm emission wavelength. IRF = instrument response function.



Model	Gaussian				
Equation	$y = y_0 + A/(w^*sqrt(pi/(4*ln(2)))) * exp(-4*ln(2)*(x-xc)^2/w^2)$				
Plot	Peak1 (Intensity)	Peak2 (Intensity)	Peak3 (Intensity)	Peak4 (Intensity)	Peak5 (Intensity)
y_0	-26932.8 ± 33059.8	-26932.8 ± 33059.8	-26932.8 ± 33059.8	-26932.8 ± 33059.8	-26932.8 ± 33059.8
x_c	473.0 ± 0.1	543.2 ± 0.1	577.6 ± 0.3	584.4 ± 2.7	674.0 ± 58.2
A	2777278.4 ± 167134.3	5263344.9 ± 182305.5	6808557.9 ± 285976.7	36278100.0 ± 6350215.6	17824000.0 ± 25039400.0
w	30.0 ± 0.6	31.8 ± 0.3	47.9 ± 0.7	129.5 ± 4.9	284.2 ± 187.2
Reduced Chi-Sqr	1551025.018				
R-Square (COD)	0.99992				
Adj. R-Square	0.99992				

Figure S5. Deconvolution of the emission spectrum of perylene@MIL-68(In) in xylene by using the Gaussian method implemented in OriginPro.

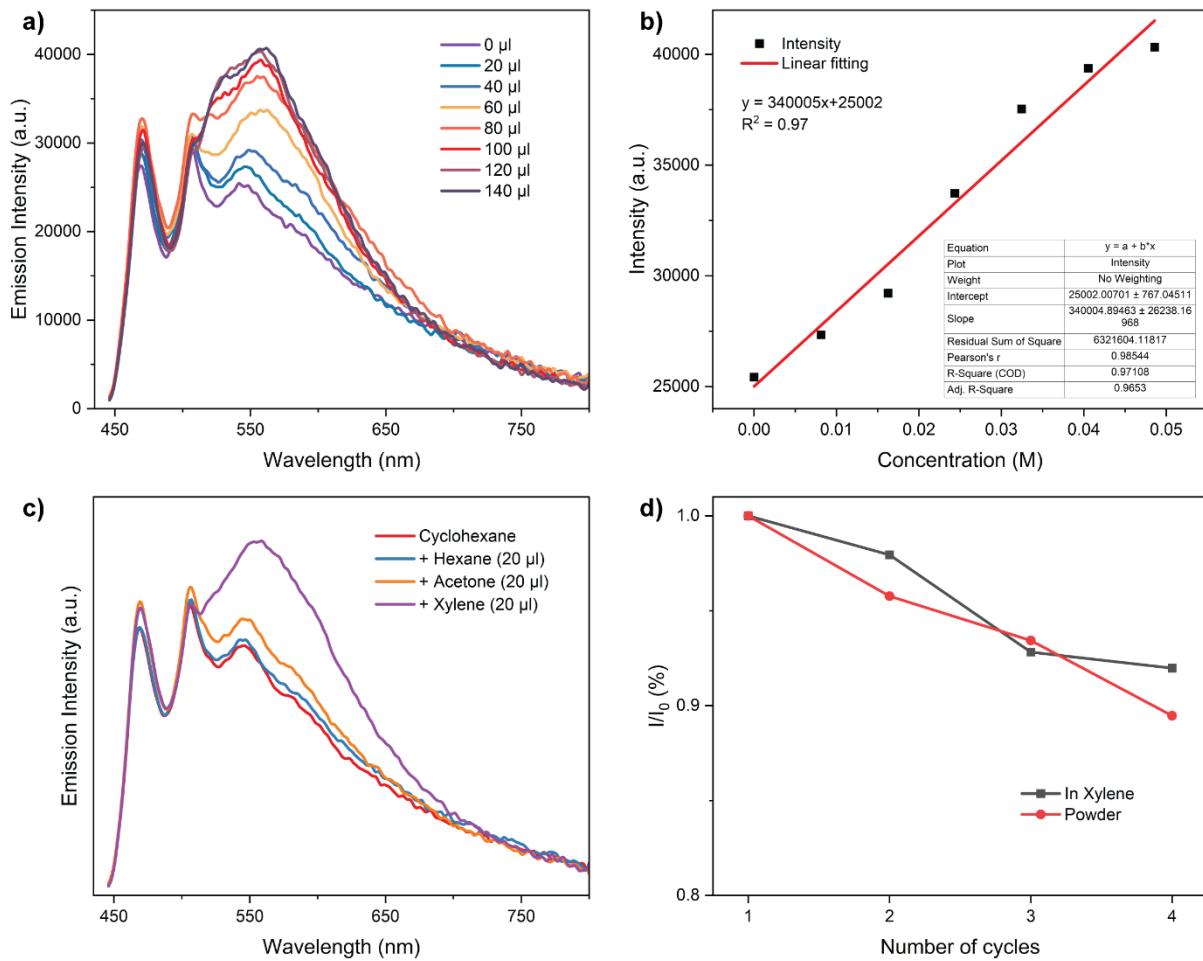


Figure S6. (a) Emission spectra and (b) peak intensities (~ 550 nm) of perylene@MIL-68(In) in cyclohexane in the presence of different concentrations of xylene. (c) Emission spectra of perylene@MIL-68(In) dispersed in cyclohexane and after the addition of different solvent analytes. (d) Reversibility of xylene sensing behavior.

The calculation of the limit of detection (LOD) based on the definition by IUPAC criterion [1]:

$$\text{Detection limit} = 3\sigma / \text{slope}$$

The slope can be obtained from Figure S6(b), and the standard deviation (σ) for the blank probe with the addition of xylene was calculated to be 268.69 (5 repeated measurements). Therefore, the LOD = $3 \cdot 268.69 / 340005 = 0.002$ M = 2 mM.

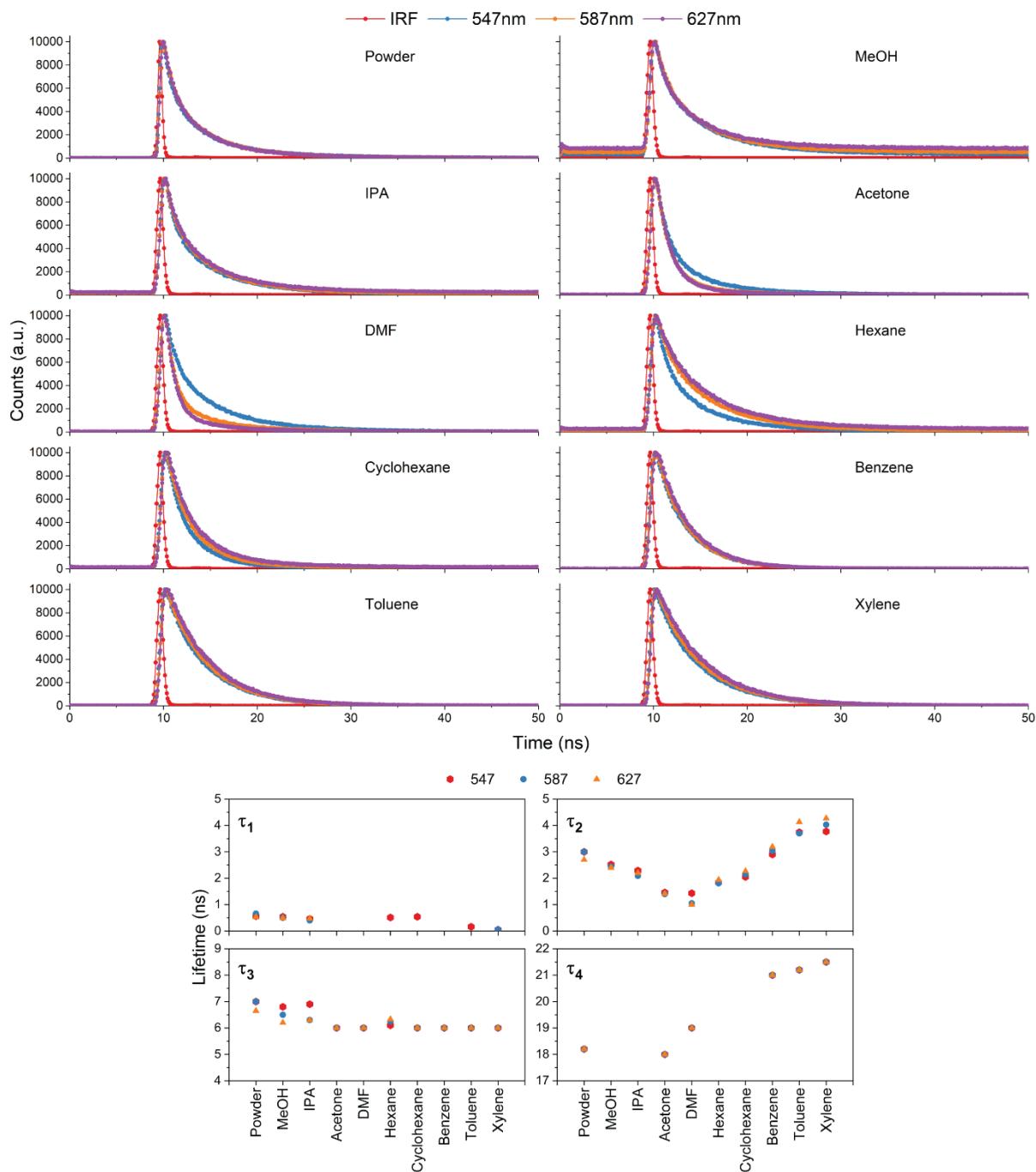


Figure S7. Lifetime data of perylene@MIL-68(In) in different solvents observed under the 547, 587, and 627 nm emission wavelength. IRF = instrument response function.

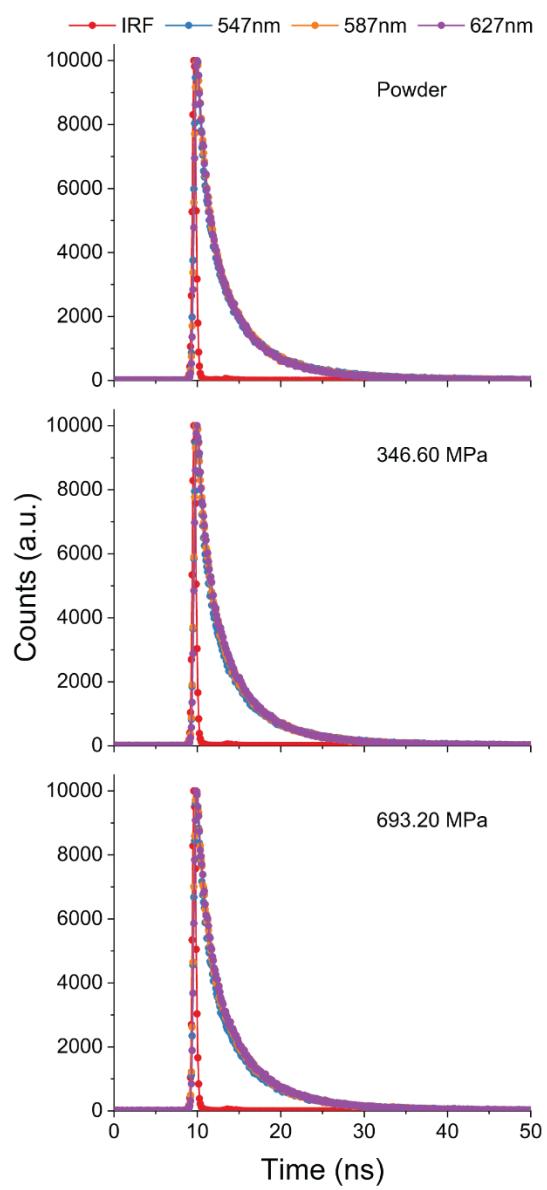
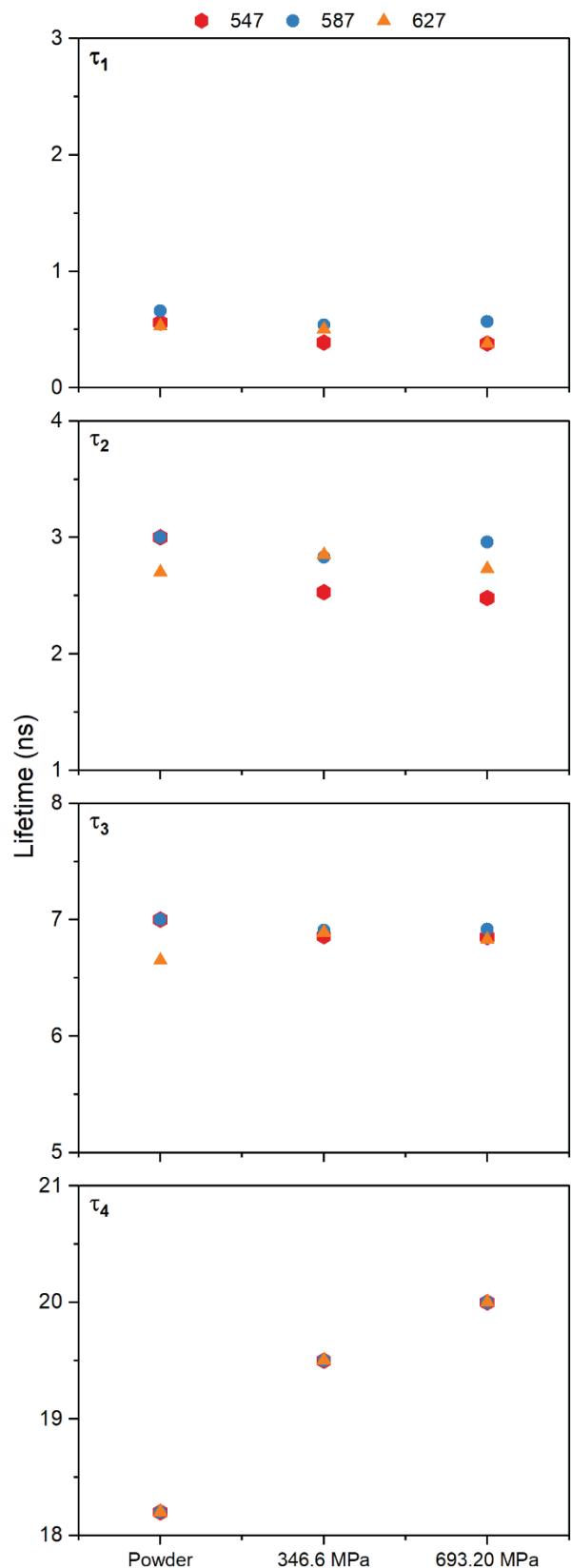


Figure S8. Lifetime data of perylene@MIL-68(In) pellets observed under the 547, 587, and 627 nm emission wavelength. IRF = instrument response function.

Table S2. Values of time constants (τ_i) of the emission decay of MIL-68(In), 025P@MIL-68(In), 05P@MIL-68(In), and 1P@MIL-68(In) powder upon excitation at 445 nm. Since τ_1 , τ_2 , and τ_3 of the perylene@MIL-68(In) systems are resembling those of MIL-68(In), it was not possible to distinguish the contribution of perylene from τ_1 , τ_2 , and τ_3 . However, τ_4 belongs only to the perylene excimers. $R_t = \sum a_i e^{(-t/\tau_i)}$, R_t is the quantity/counts at time t . The goodness-of-fit is given by χ^2 .

Sample	Wavelength (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	τ_4 (ns)	χ^2
MIL-68(In)	547	0.59	3.32	10.97	-	1.350
	587	0.49	3.10	10.45	-	1.431
	627	0.40	2.76	9.83	-	1.324
025P@MIL-68(In)	547	0.56	3.00	7.00	18.20	1.276
	587	0.66	3.00	7.00	18.20	1.200
	627	0.53	2.70	6.65	18.20	1.332
05P@MIL-68(In)	547	0.67	2.89	7.00	18.00	1.270
	587	0.78	2.90	7.00	18.00	1.205
	627	0.61	2.60	6.00	18.10	1.301
1P@MIL-68(In)	547	0.51	2.77	7.00	17.80	1.172
	587	0.68	2.88	7.00	17.80	1.354
	627	0.76	2.92	7.00	17.80	1.314

Table S3. Quantum yield (QY) of 1P@MIL-68(In), 05P@MIL-68(In), and 025P@MIL-68(In). The QY of each sample was tested three times to determine the average and standard deviation values.

Sample	QY (%)
1P@MIL-68(In)	4.63 ± 0.07
05P@MIL-68(In)	5.14 ± 0.60
025P@MIL-68(In)	14.13 ± 0.74

Table S4. Values of time constants (τ_i) of the emission decay of 025P@MIL-68(In) powder and under different solvents upon excitation at 445 nm.

Sample	Wavelength (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	τ_4 (ns)	χ^2
Powder	547	0.56	3.00	7.00	18.20	1.276
	587	0.66	3.00	7.00	18.20	1.200
	627	0.53	2.70	6.65	18.20	1.332
MeOH	547	0.54	2.52	6.80	-	1.386
	587	0.50	2.44	6.50	-	1.479
	627	0.49	2.40	6.20	-	1.461
IPA	547	0.46	2.29	6.90	-	1.442
	587	0.40	2.09	6.30	-	1.300
	627	0.47	2.20	6.30	-	1.175
Acetone	547	-	1.46	6.00	18.00	1.243
	587	-	1.40	6.00	18.00	1.058
	627	-	1.41	6.00	18.00	1.085
DMF	547	-	1.43	6.00	19.00	1.403
	587	-	1.05	6.00	19.00	1.297
	627	-	1.00	6.00	19.00	1.156
Hexane	547	0.51	1.84	6.10	-	1.222
	587	-	1.81	6.25	-	1.300
	627	-	1.94	6.33	-	1.277
Cyclohexane	547	0.54	2.05	6.00	-	1.324
	587	-	2.15	6.00	-	1.235
	627	-	2.27	6.00	-	1.202
Benzene	547	-	2.90	6.00	21.00	1.212
	587	-	3.04	6.00	21.00	1.207
	627	-	3.19	6.00	21.00	1.209
Toluene	547	0.16	3.74	6.00	21.20	1.145
	587	-	3.70	6.00	21.20	1.176
	627	-	4.13	6.00	21.20	1.122
Xylene	547	0.05	3.77	6.00	21.50	1.245
	587	0.06	4.03	6.00	21.50	1.146
	627	-	4.27	6.00	21.50	1.167

Table S5. Values of time constants (τ_i) of the emission decay of 025P@MIL-68(In) powder and its pellets upon excitation at 445 nm.

Sample	Wavelength (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	τ_4 (ns)	χ^2
Powder	547	0.56	3.00	7.00	18.20	1.276
	587	0.66	3.00	7.00	18.20	1.200
	627	0.53	2.70	6.65	18.20	1.332
346.60 MPa	547	0.39	2.53	6.86	19.50	1.269
	587	0.54	2.83	6.91	19.50	1.280
	627	0.50	2.85	6.89	19.50	1.144
693.20 MPa	547	0.38	2.48	6.85	20.00	1.253
	587	0.57	2.96	6.92	20.00	1.291
	627	0.38	2.73	6.83	20.00	1.260

References:

- [1] Fajal, S.; Mandal, W.; Majumder, D.; Shirolkar, M. M.; More, Y. D.; Ghosh, S. K., Unfolding the Role of Building Units of MOFs with Mechanistic Insight Towards Selective Metal Ions Detection in Water. *Chem. Eur. J.* **2022**, 28, 202104175.