Supplementary Information for

Facile Supramolecular Strategy to Construct Solid Fluorophore@Metal-Organic Framework Composites

Lavinia A. Trifoi, Gregory K. Hodgson, Nicholas P. Dogantzis, Sumaiya A. Soha, Roya M. Dayam, Costin N. Antonescu, Roberto J. Botelho, R. Stephen Wylie and Stefania Impellizzeri[*]

Laboratory for Nanomaterials and Molecular Plasmonics, Department of Chemistry and Biology, Toronto Metropolitan University, 350 Victoria St., Toronto, ON, M5B 2K3, Canada.

Content

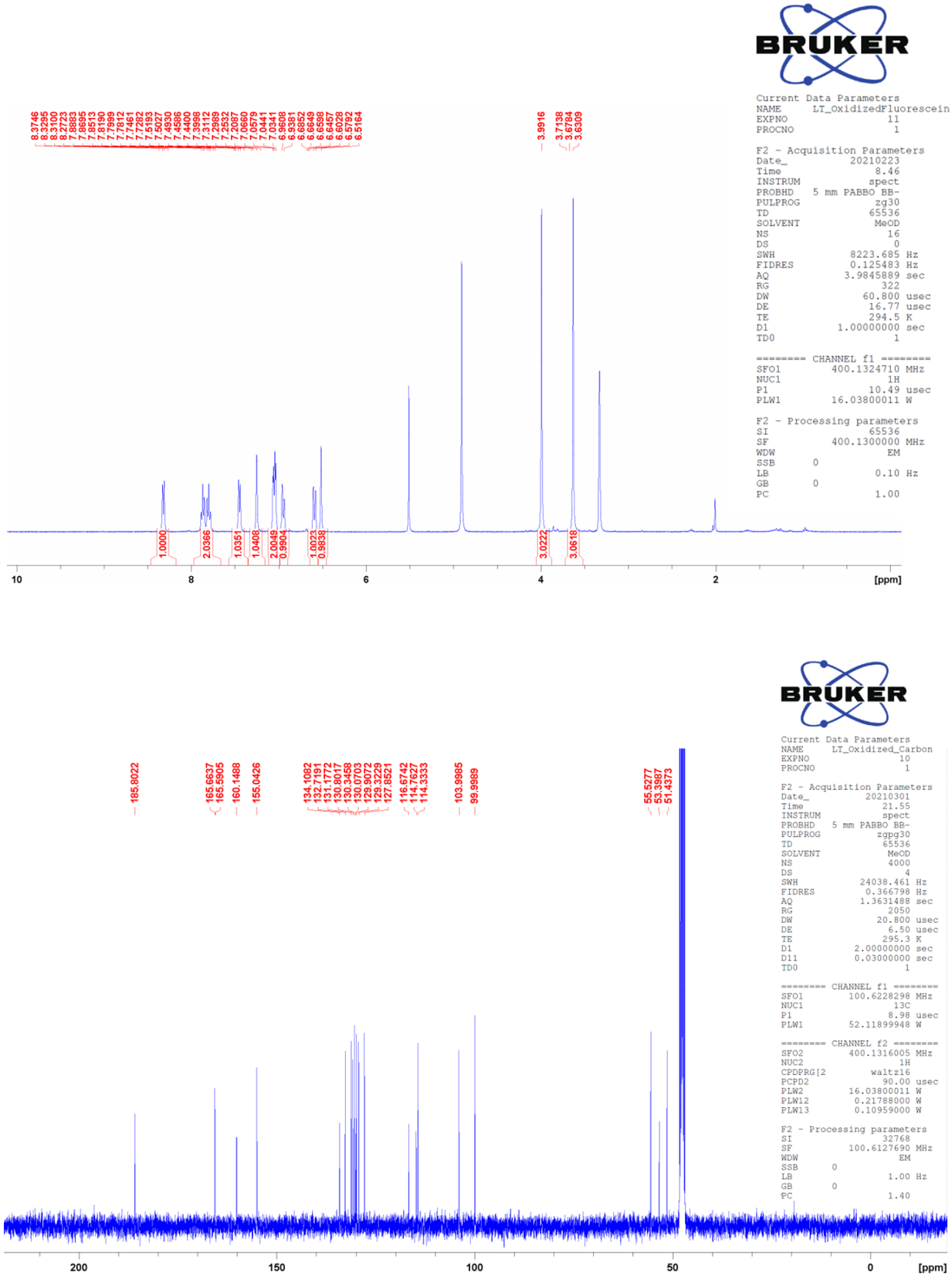


Figure S1. ^{1}H and ^{13}C NMR of **FMe520** in CD_3OD.

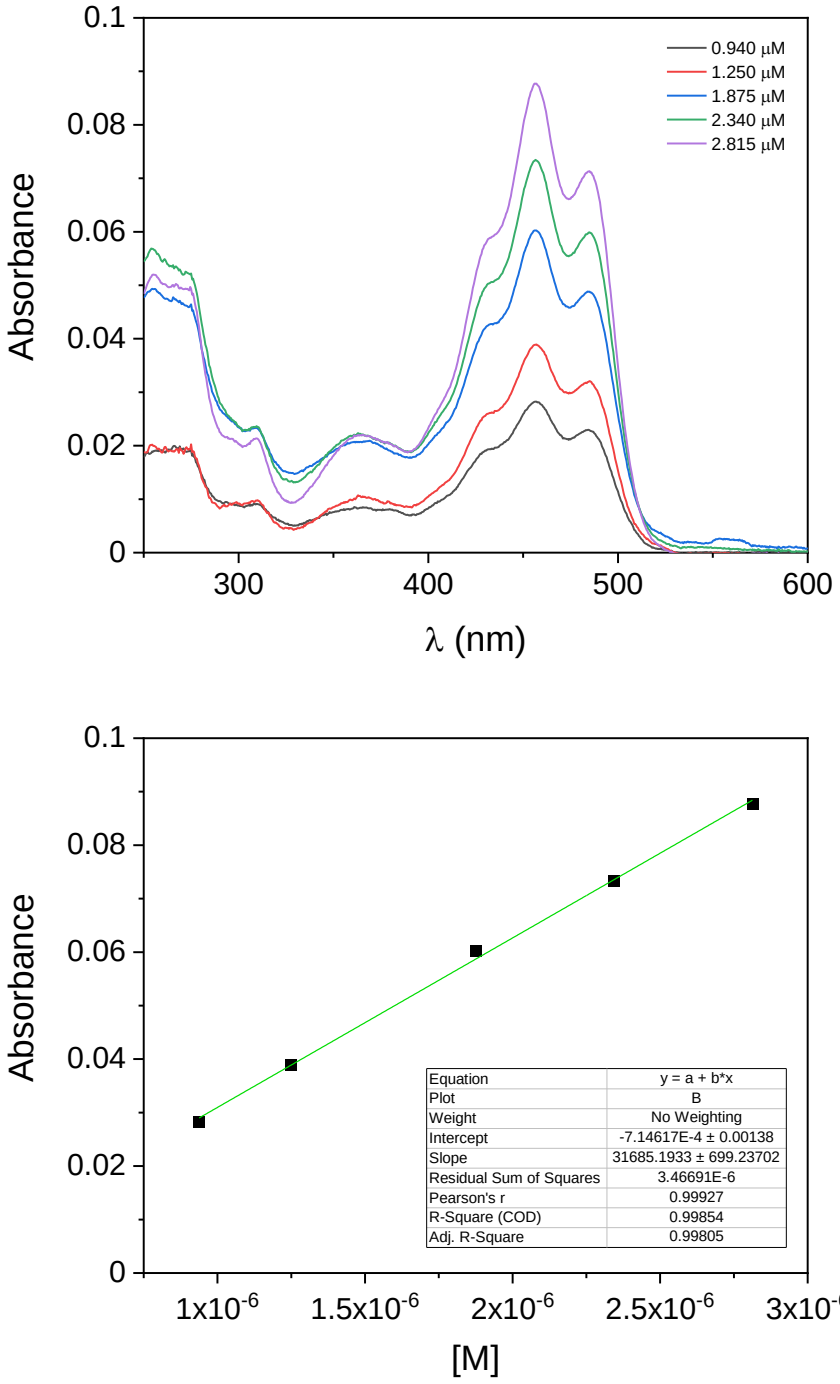


Figure S2. Absorption spectra of a CH_3OH solution of **FMe520** (20°C) at variable concentrations and molar extinction coefficient calculation (λ_{Abs} = 455 nm, the green line represents linear fitting).

Synthesis of FMe520@ZIF-8 and Calculation of the Encapsulation Efficiency

20.7 mg (0.058 mmol) of **FMe520** were placed in a 100 mL round bottom flask. Using a graduated glass pipette, 25 mL of CH_3OH were added to obtain a 2.3 mM stock solution. 12 µL of this solution were then used to prepare 10 mL of a 2.75 µM solution (mass of **FMe520** = 9.9 µg) for spectra analysis (***a*** in Figure S3). In a round bottom flask, we then recombined the diluted solution with the stock to obtain a total volume of 35 mL. To this, 205 mg (2.5 mmol) of 2-methylimidazole were added and the solution was sonicated. In a separate vessel, 246 mg (1.3 mmol) of $Zn(NO_3)_2$ were dissolved in 30 mL of CH_3OH and added to the solution containing the dye and ligand. The mixture was undisturbed for 48 hours to obtain **FMe520**@ZIF-8, which was purified via centrifugation (4 × 9000 rpm, CH_3OH) until no trace of residual dye was detected in the supernatants using absorption and emission spectroscopy. The mass of **FMe520**@ZIF-8 obtained was 43.7 mg. The recovered supernatants were combined, dried under reduced pressure, and diluted as described above (25 mL CH_3OH, of which 12 µL were diluted up to 10 mL for spectral analysis, ***b*** in Figure S3). Knowing that the molar extinction coefficient of **FMe520** in CH_3OH is 31,685 M^{-1} cm^{-1} at 455 nm, we calculated the spectral concentration of non-encapsulated **FMe520** to be 1.58 µM, which can then be reconducted to 0.033 mmol of **FMe520** recovered, indicating that (0.058 – 0.033) = 0.025 mmol, or 9 mg of **FMe520** (43%), were successfully encapsulated within ZIF-8. A consistent result is achieved by extracting the concentration of encapsulated **FMe520** from ΔA at 455 nm in Figure S3 (where $\Delta A = A_{before} - A_{after} = A_{\boldsymbol{a}} - A_{\boldsymbol{b}}$) and resulting in 0.024 mmol = 8.8 mg of **FMe520** (42.5%) effectively encapsulated.

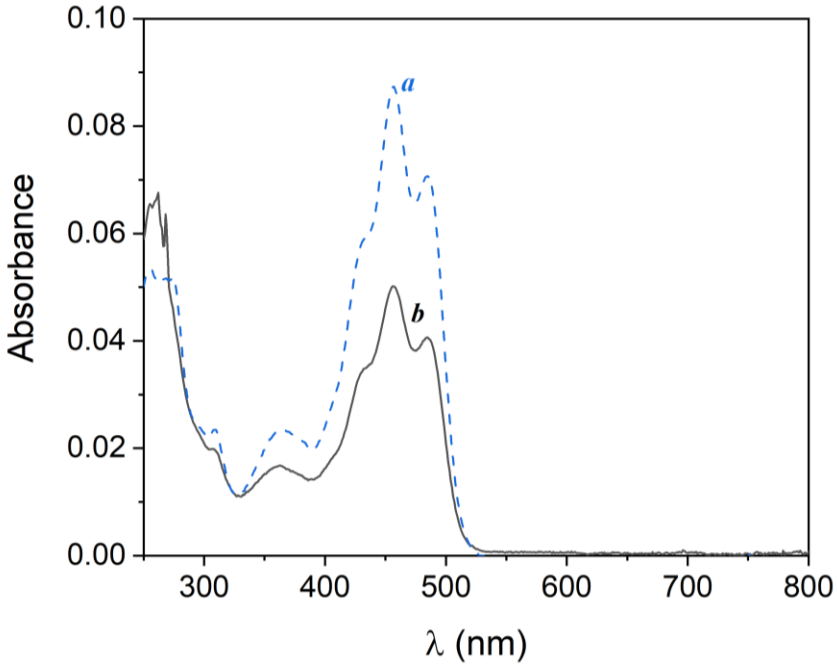


Figure S3. Absorption spectra (20ºC, CH_3OH) of the combined and rediluted supernatants obtained after encapsulation of **FMe520** into ZIF-8.

We repeated the same protocol independently by reducing the crystallization time from 48 to 24 h. Spectroscopic data indicate an encapsulation efficiency of **FMe520** in ZIF-8 of ~22% (average of the two calculation methods which yielded 21.5% and 22%, respectively).

Calculation of the Adsorption Efficiency of FMe520 on Pre-Formed ZIF-8

9.3 mg (0.026 mmol) of **FMe520** were dissolved in 100 mL of CH_3OH to obtain a 0.26 mM stock solution. 330 µL of this solution were then added to 3 mL of CH_3OH to obtain a 26 µM solution for spectra analysis (***a*** in Figure S4). We then recombined the diluted solution with the stock and evaporated all solvent to recover **FMe520** in powder form. Next, 20.4 mg of ZIF-8 were dissolved in 25.0 mL of CH_3OH in a round bottom flask. **FMe520** (9.3 mg) was added to the dispersion of ZIF-8 and stirred for 48 hours. The mixture was then centrifuged (4 × 9000 rpm). The recovered supernatants were combined, dried under reduced pressure, and diluted as described above (100 mL CH_3OH, of which 330 µL were added to 3 mL for spectral analysis, ***b*** in Figure S4). Knowing that the molar extinction coefficient of **FMe520** in CH_3OH is 31,685 M^{-1} cm^{-1} at 455 nm, we calculated the spectral concentration of non-adsorbed **FMe520** to be 23.9 µM, which can then be reconducted to 0.0239 mmol (8.62 mg) of **FMe520** recovered. This indicates that ~0.68 mg of **FMe520** (7.3%), were adsorbed to the external surface of the preformed ZIF-8.

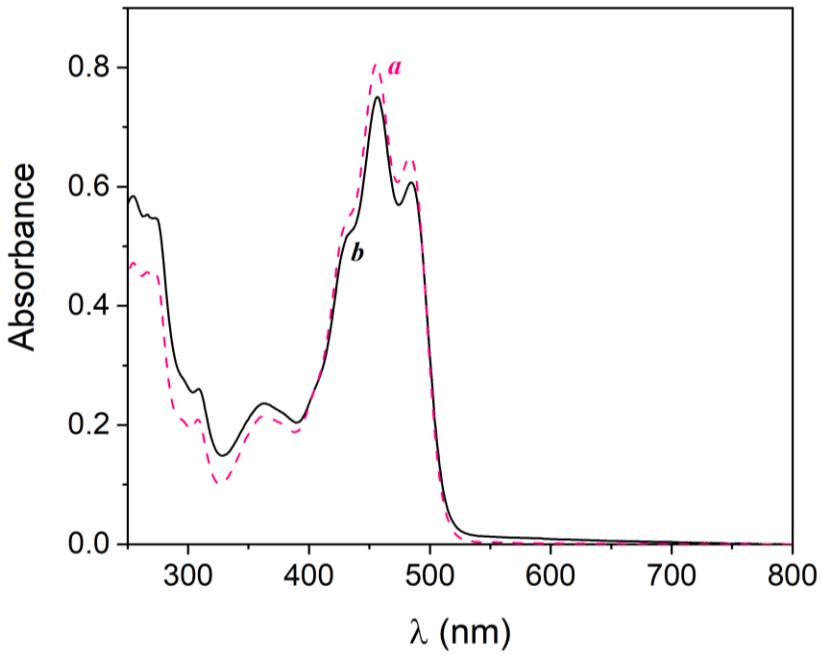


Figure S4. Absorption spectra (20ºC, CH_3OH) of the combined and rediluted supernatants obtained after mixing of **FMe520** with pre-formed ZIF-8 for 48 h.

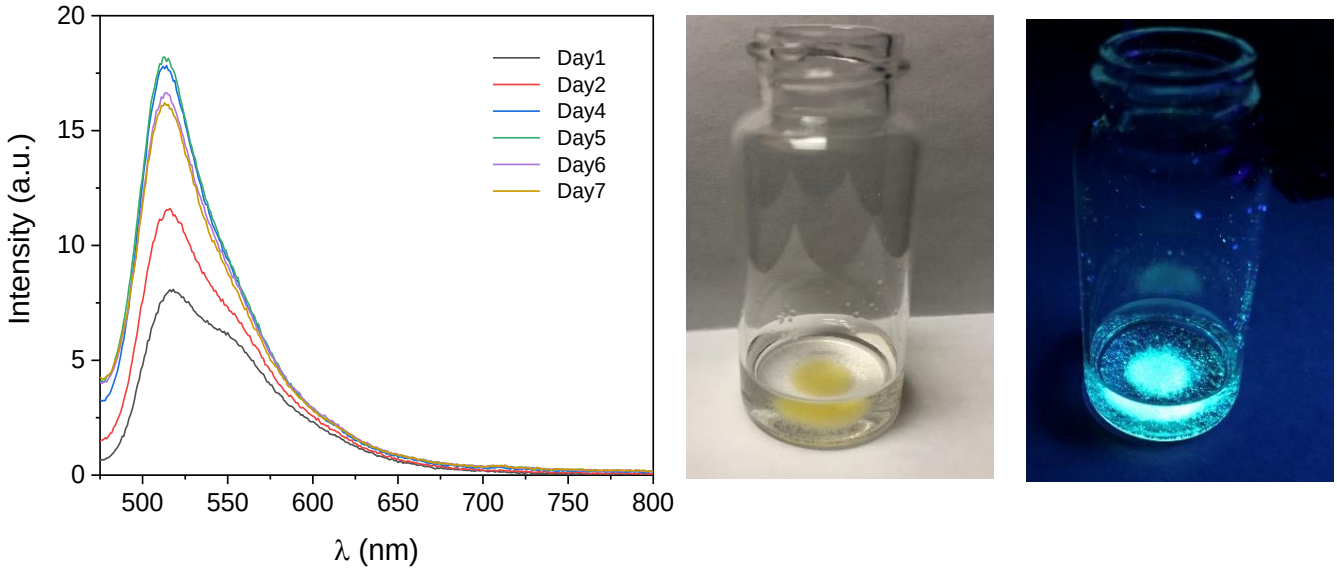


Figure S5. Emission spectra (20ºC, λ_{Ex} = 450 nm) of a dispersion of **FMe520**@ZIF-8 in CH_3OH stirred over a week. Photographs illustrate that **FMe520** encapsulated in ZIF-8 is not soluble in CH_3OH unless released from the metal-organic framework (vide infra).

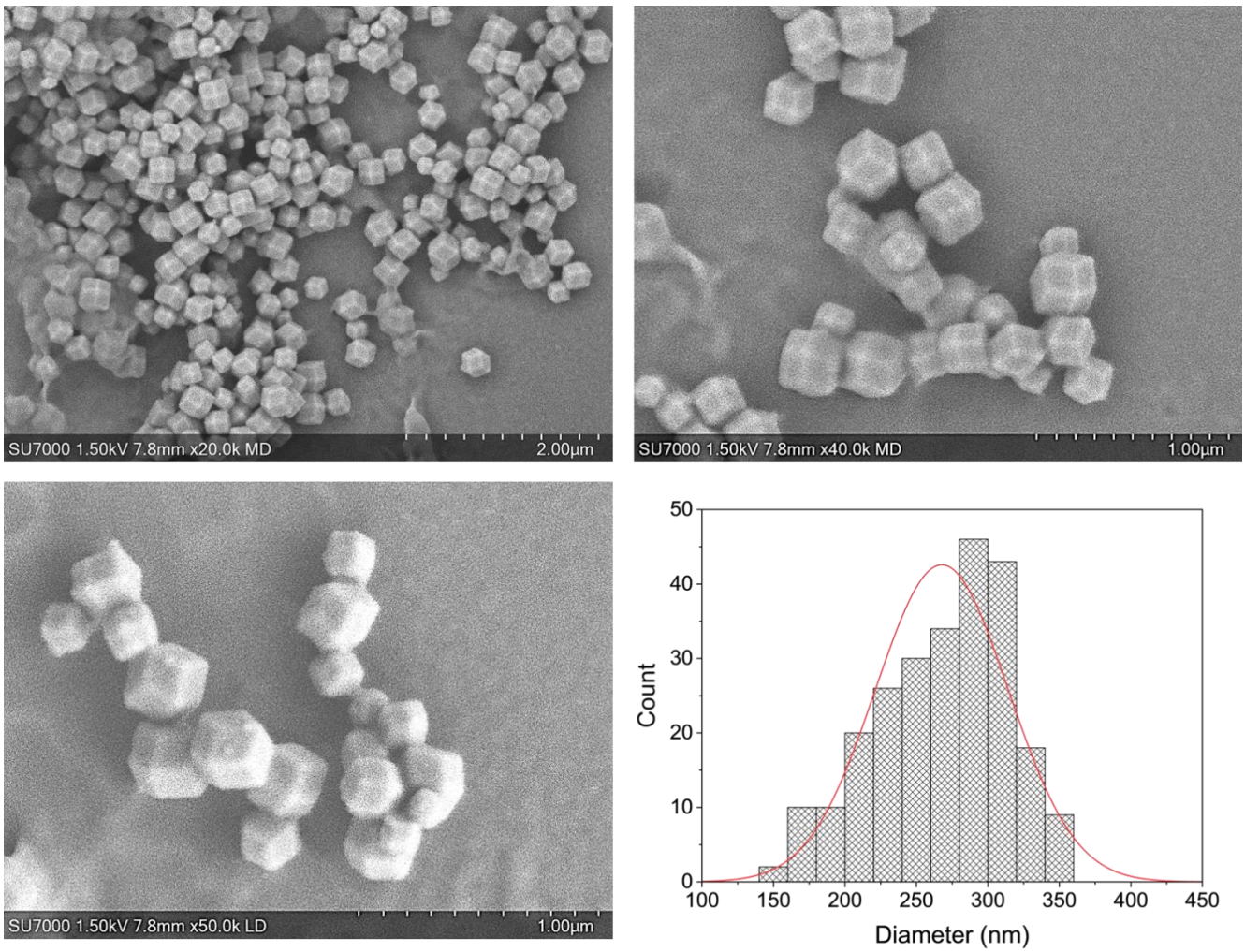


Figure S6. Scanning Electron Microscopy (SEM) of ZIF-8. Histogram showing Gaussian distribution of ZIF-8 particle diameters measured using Fiji (ImageJ).

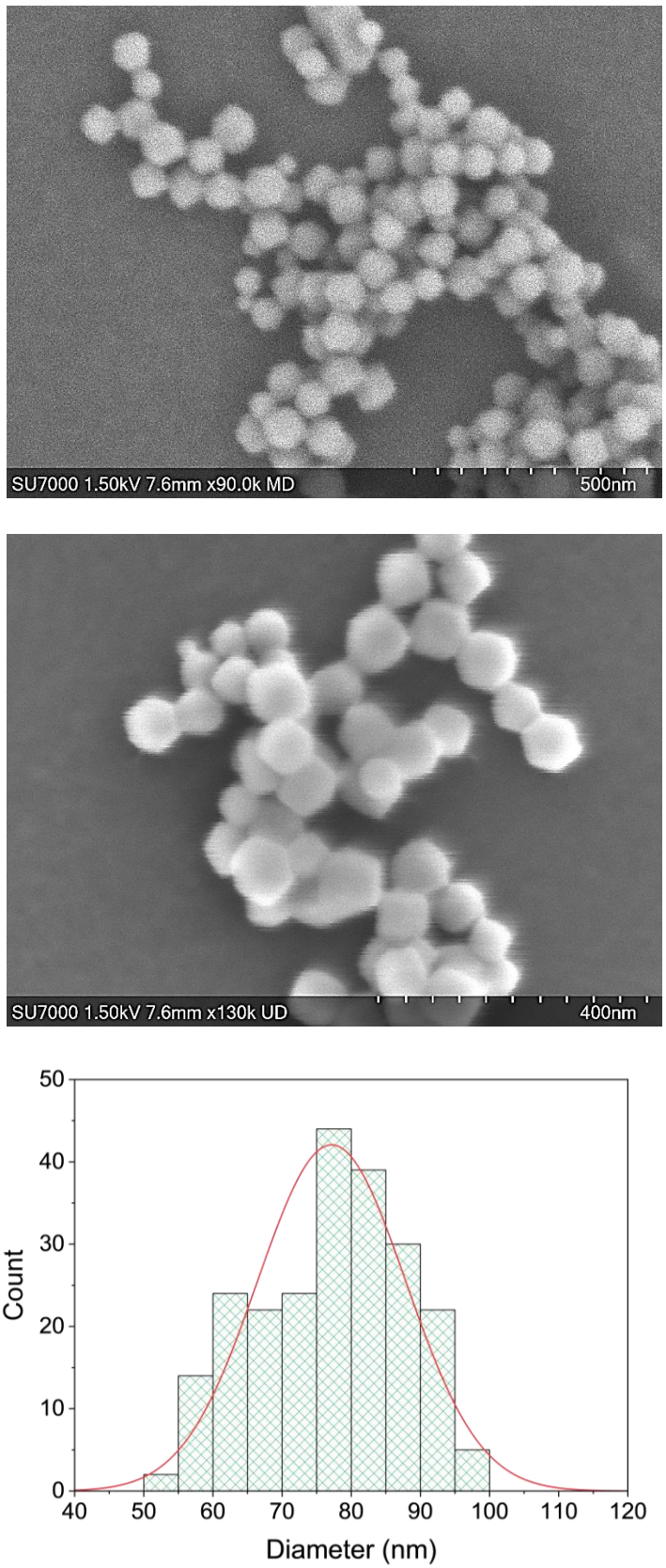


Figure S7. Scanning Electron Microscopy (SEM) of **FMe520**@ZIF-8. Histogram showing Gaussian distribution of ZIF-8 particle diameters measured using Fiji (ImageJ).

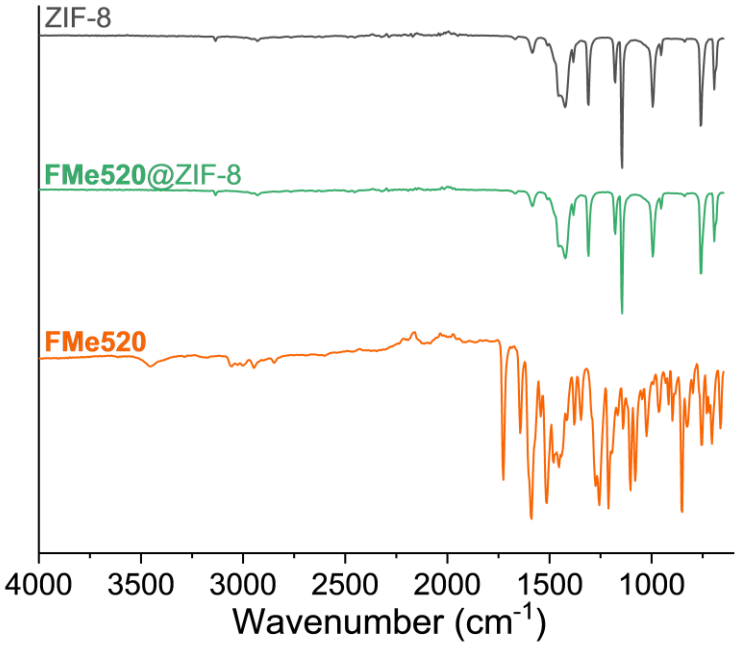
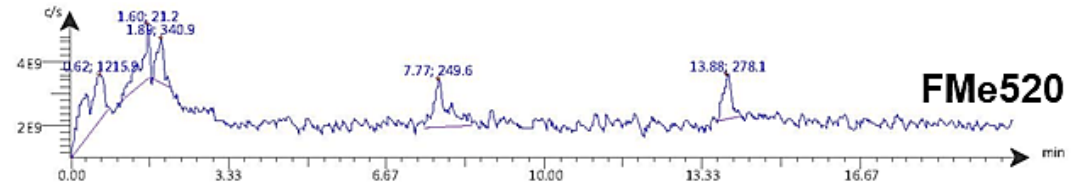
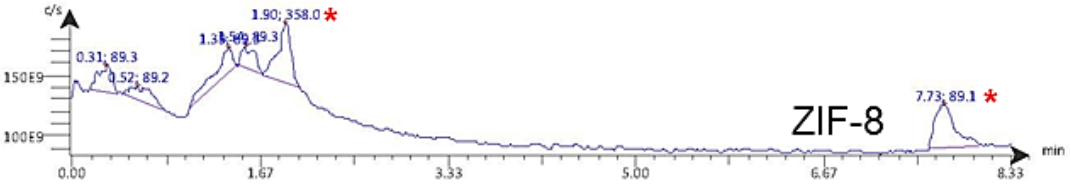


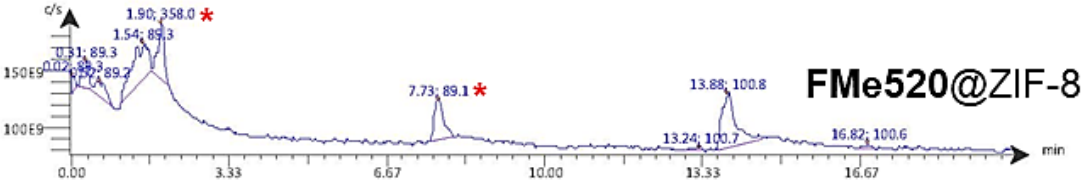
Figure S8. FTIR-ATR spectra of ZIF-8 (black trace), **FMe520**@ZIF-8 (green trace) and **FMe520** (orange trace).



Time (Peak Maximum M:S/Minutes)	Maximum Intensity (c/s)	Time (Peak Centroid M:S/Minutes)	Peak Area	% Peak Area	Peak Resolution	Base Peak Mass (m/z)	Label
0.62	1.4E9	0.60	4.3E10	37.7	13.6	1215.9	
1.60	1.7E9	1.62	1.9E10	16.9	4.3	21.2	
1.89	1.3E9	1.89	1.2E10	10.5	9.2	340.9	
7.77	1.4E9	7.75	2.5E10	22.1	9.0	249.6	
13.88	1.3E9	13.86	1.5E10	12.9	11.0	278.1	



Time (Peak Maximum M:S/Minutes)	Maximum Intensity (c/s)	Time (Peak Centroid M:S/Minutes)	Peak Area	% Peak Area	Peak Resolution	Base Peak Mass (m/z)	Label
0.31	2.2E10	0.29	1.7E11	11.6	9.3	89.3	
0.52	8.6E9	0.57	1.4E11	9.7	11.7	89.2	
1.39	1.8E10	1.38	2.2E11	15.1	4.9	89.3	
1.54	1.7E10	1.55	1.4E11	9.4	12.2	89.3	
1.90	4.9E10	1.89	3.8E11	26.1	6.0	358.0	
7.73	3.4E10	7.74	4.1E11	28.1	10.5	89.1	



Time (Peak Maximum M:S/Minutes)	Maximum Intensity (c/s)	Time (Peak Centroid M:S/Minutes)	Peak Area	% Peak Area	Peak Resolution	Base Peak Mass (m/z)	Label
0.02	1.5E10	0.03	5E10	1.7	4.2	89.3	
0.31	2.3E10	0.29	1.9E11	6.1	9.4	89.3	
0.52	9.6E9	0.57	1.7E11	5.5	13.7	89.2	
1.54	3.1E10	1.50	8E11	26.5	11.0	89.3	
1.90	5E10	1.89	4E11	13.4	6.6	358.0	
7.73	3.5E10	7.74	4.4E11	14.6	10.6	89.1	
13.24	2.9E9	13.25	2.8E10	0.9	5.9	100.7	
13.88	4.8E10	13.85	9.1E11	30.3	15.8	100.8	
16.82	3E9	16.83	2.9E10	0.9	6.7	100.6	

Figure S9. Electrospray ionization mass spectrometry of **FMe520**, ZIF-8, and **FMe520**@ZIF-8.

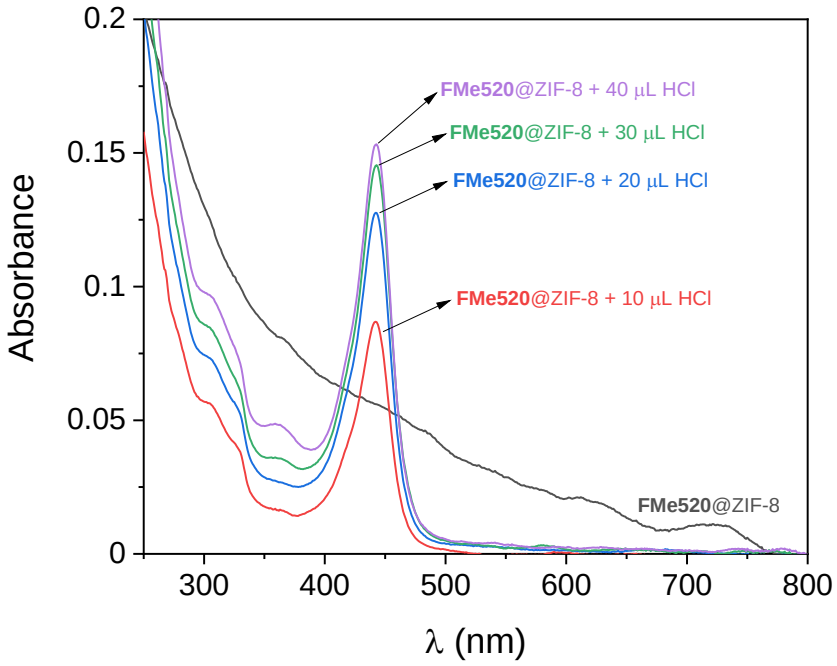


Figure S10. Absorption spectra of a dispersion of **FMe520**@ZIF-8 before and after the addition of incremental amounts of HCl (12 M stock solution). Note that from the absorption values of **FMe520** in acidic environment extracted from Figure S11 below, we recalculated the dye encapsulation percentage to be ~24.8%, in excellent agreement with our previous estimate (Fig. S3 and related discussion).

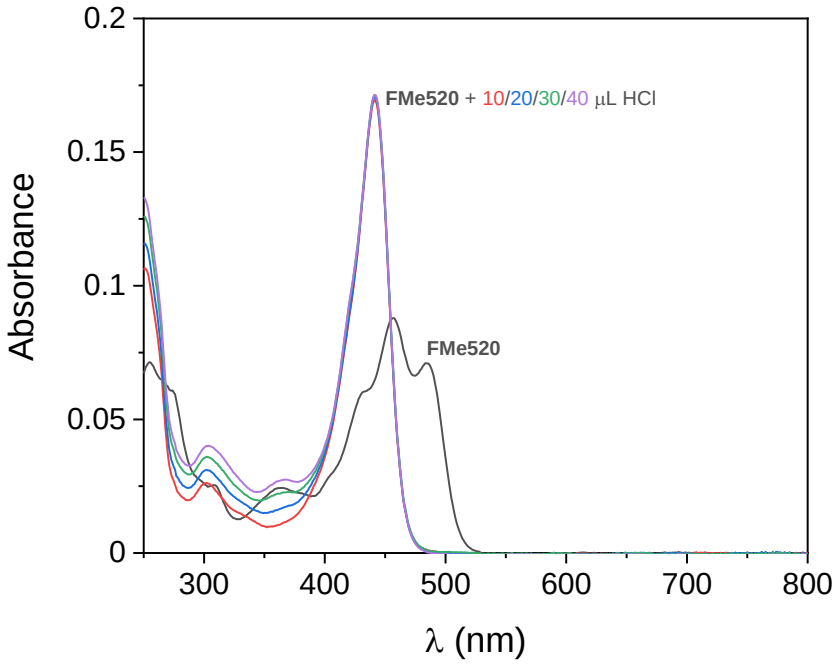


Figure S11. Absorption spectra of a solution of **FMe520** (3 μM, 20ºC, CH_3OH) before and after the addition of incremental amounts of HCl (12 M stock solution).

Figure S12. From left to right: Samples of **FMe520**@ZIF-8, **FMe520**, and ZIF-8 viewed under ultraviolet light.

Table S1. Average fluorescence lifetimes of **FMe520** and **FMe520**@ZIF-8 obtained from five different FLIM regions of interest (ROI, Fig S13 and S14). Note that the mean value and standard deviation from ROIs 1-5 are in good agreement with the data from ROI 6, which corresponds to the entire FLIM field of view and to Figure 5**A** in the main text.

Descriptor	Lifetime (ns) of FMe520	Lifetime (ns) of FMe520@ZIF-8
ROI 1	3.20 ± 0.09	6.23 ± 1.1
ROI 2	3.29 ± 0.09	6.68 ± 0.75
ROI 3	3.18 ± 0.09	6.42 ± 1.1
ROI 4	3.25 ± 0.09	6.61 ± 0.98
ROI 5	3.18 ± 0.09	6.44 ± 0.80
Mean (ROIs 1-5)	**3.22 ± 0.09**	**6.48 ± 0.95**
ROI 6 (Entire Field of View)	**3.22 ± 0.10**	**6.49 ± 0.96**

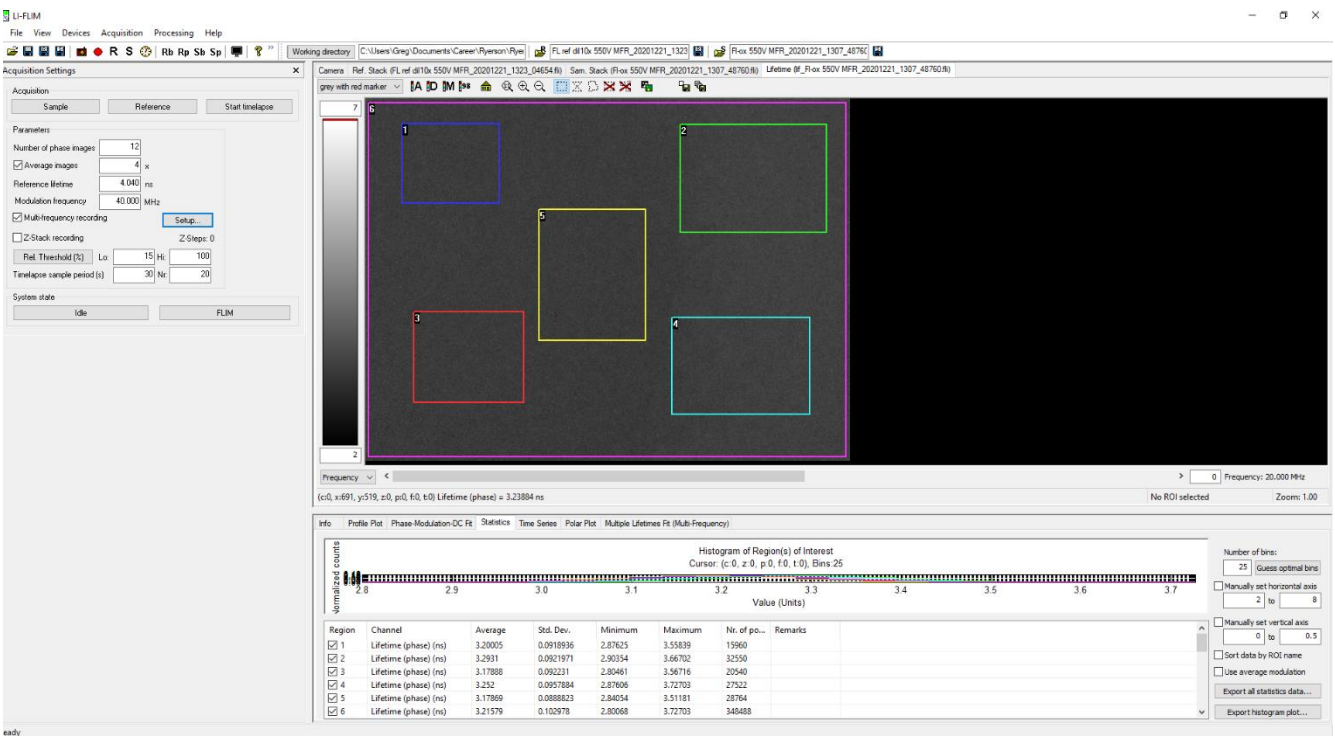


Figure S13. Raw FLIM data for **FMe520** showing ROIs 1-6.

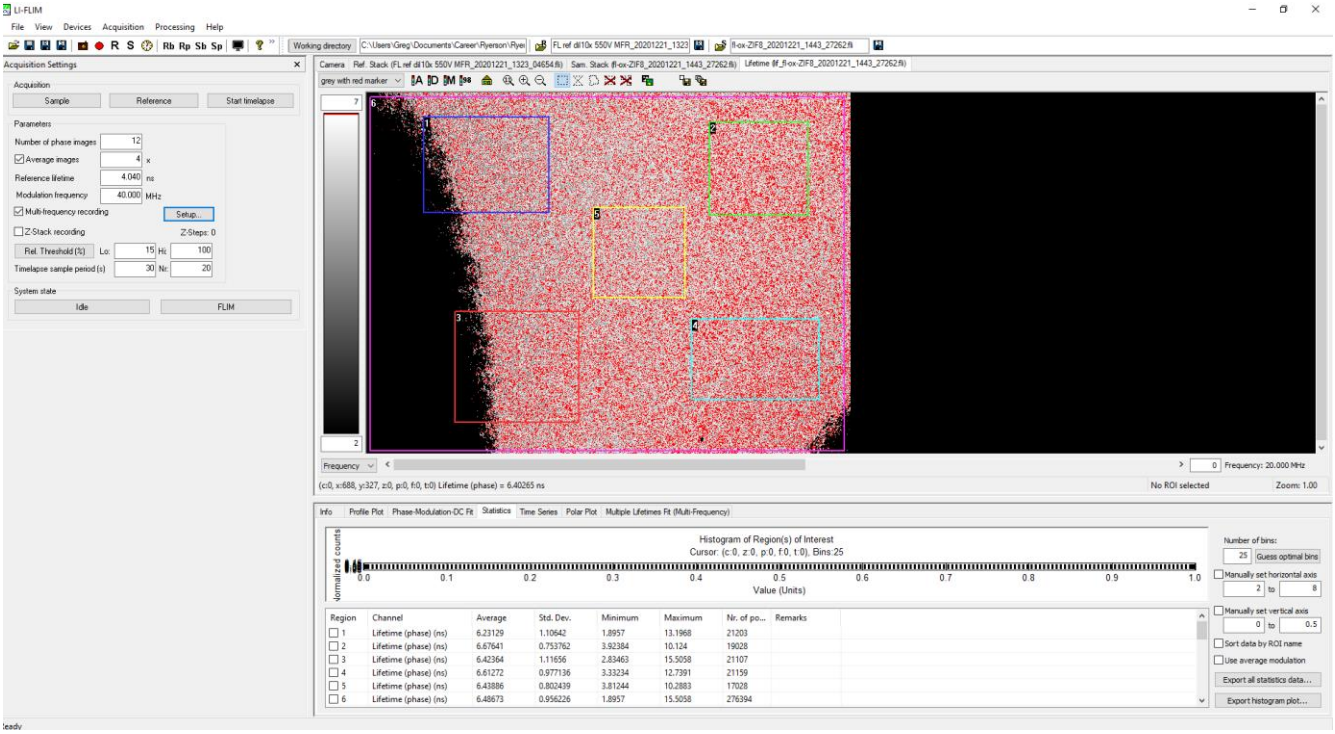


Figure S14. Raw FLIM data for **FMe520**@ZIF-8 showing ROIs 1-6.

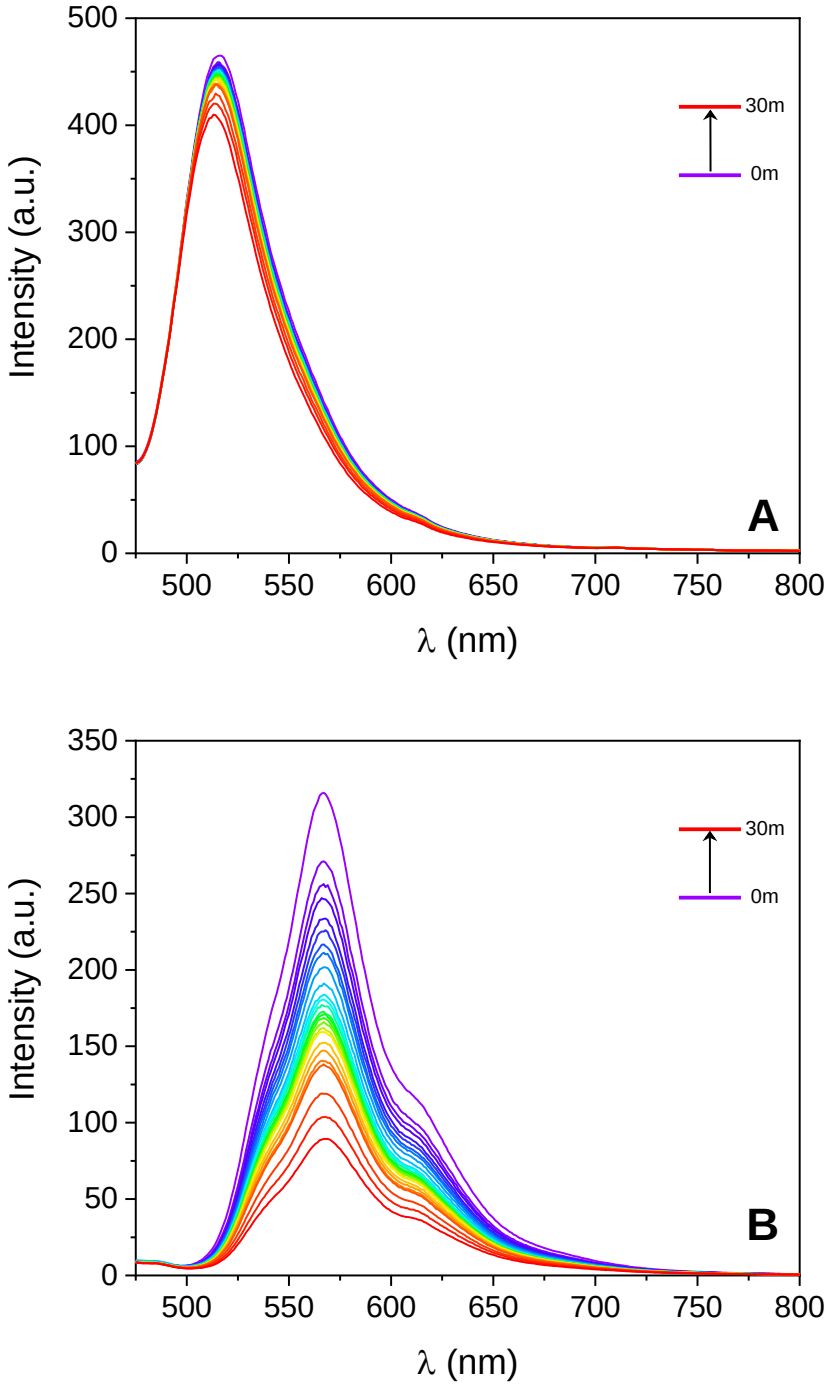


Figure S15. Photobleaching test: emission spectra recorded at the solid state of (**A**) **FMe520**@ZIF-8 and (**B**) **FMe520** before and after irradiation at 455 nm (0 – 30 min).

Table S2. Zn-N bond distances in ZIF-8.

Experimental /Å	Calculated[a] /Å
1.965	1.931
	1.943
	1.948

[a]SCC-DFTB

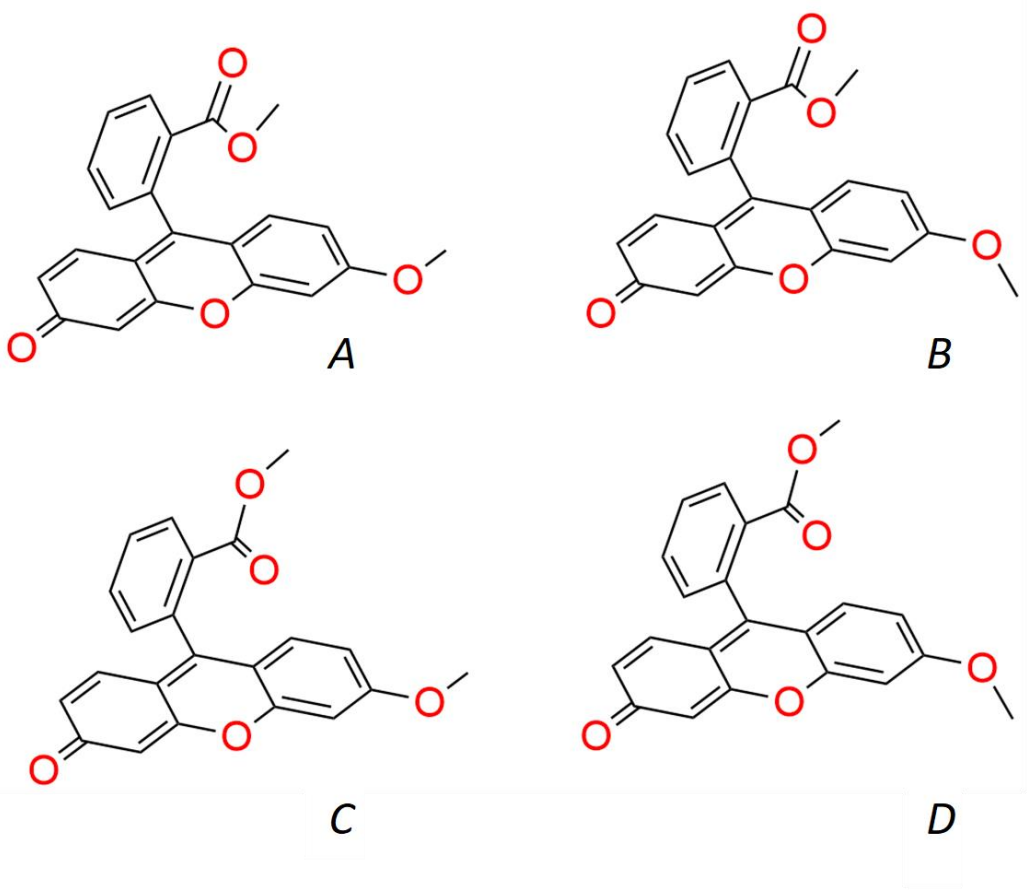


Figure S16. Four conformers of **FMe520**.

Table S3. Boltzmann-averaged fractional abundances of **FeMe520** conformers.

Conformer	Gibbs energy (DFTB) / Hartree	Fraction at 300 K	Gibbs energy (B3LYP/6-311+G(d,p)) / Hartree	Fraction at 300 K
A	-60.206411	0.073	-1224.133037	0.115
B	-60.207221	0.170	-1224.134046	0.335
C	-60.207471	0.221	-1224.133231	0.142
D	-60.208312	0.536	-1224.134234	0.408

Table S4. Energy differences (SCC-DFTB) between optimized **FMeF520** conformer-cage complexes and the sums of the separated components.[a]

FMeF520 conformer in SOD cage	Energy (DFTB) / Hartrees	Δ*E* / Hartrees
cage only	-585.677522	-
A only	-60.477020	-
B only	-60.477610	-
C only	-60.477654	-
D only	-60.478526	-
A	-646.159086	-0.004544
A	-646.143221	0.011321
B	-646.157430	-0.002298
B	-646.151898	0.003234
B	-646.150777	0.004355
B	-646.152560	0.002572
B	-646.150143	0.004989
C	-646.160210	-0.005034
C	-646.150725	0.004451
C	-646.143791	0.011385
D	-646.157110	-0.001062
D	-646.154306	0.001742

[a]ZIF-8 SOD cage omitting coordinatively unsaturated imidazolate ligands with frozen coordinates.

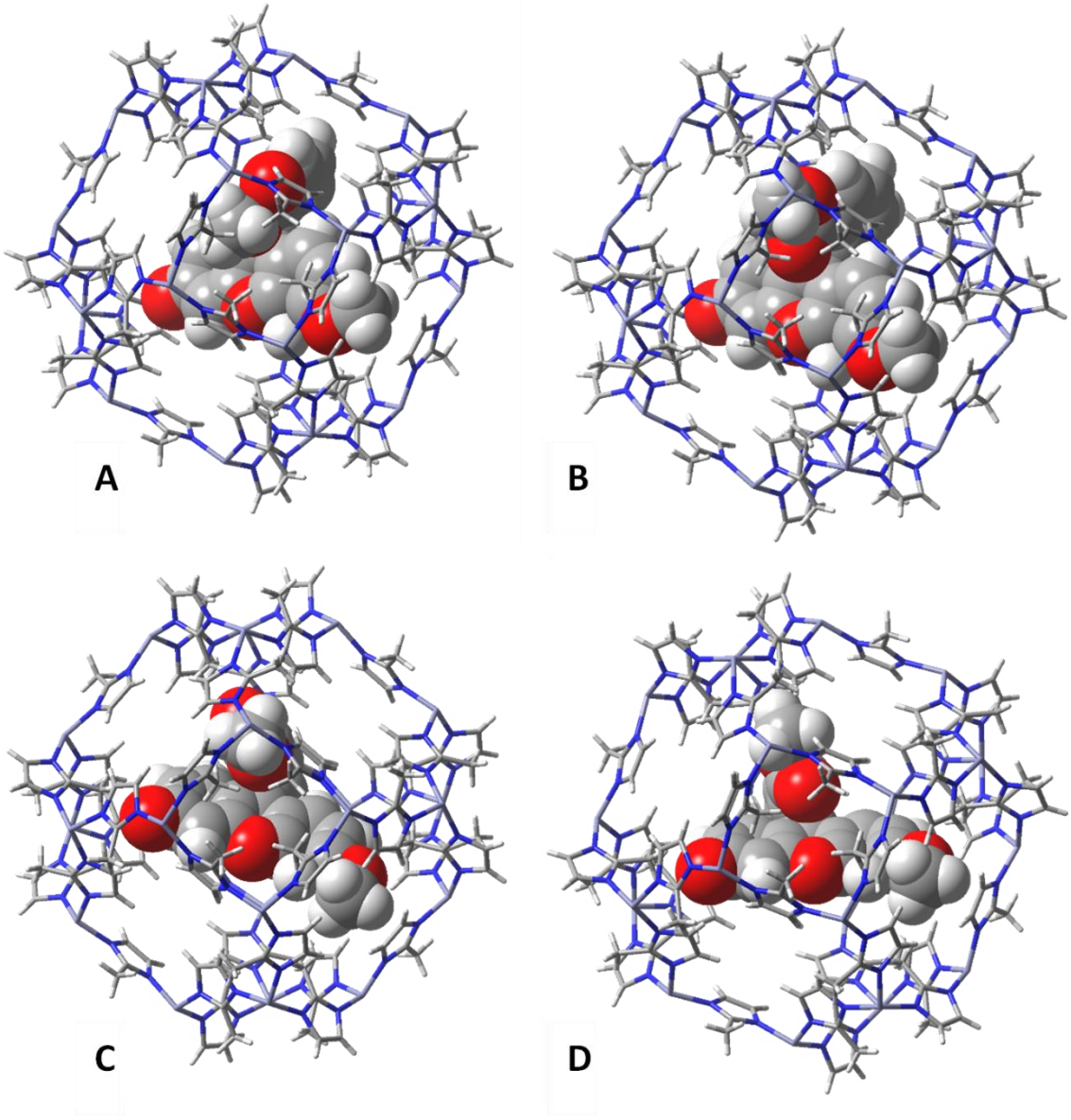


Figure S17. Four examples of stabilized ZIF-8 cage complexes of **FMe520**. **A**: conformer *A*, ΔE = -12 kJ mol^{-1}; **B**: conformer *B*, ΔE = -6 kJ mol^{-1}; **C**: conformer *C*, ΔE = -13 kJ mol^{-1}; **D**: conformer *D*, ΔE = -3 kJ mol^{-1}.

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