Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supporting information

The effect of PEG length on the size and guest uptake of PEG-capped MIL-88A particles

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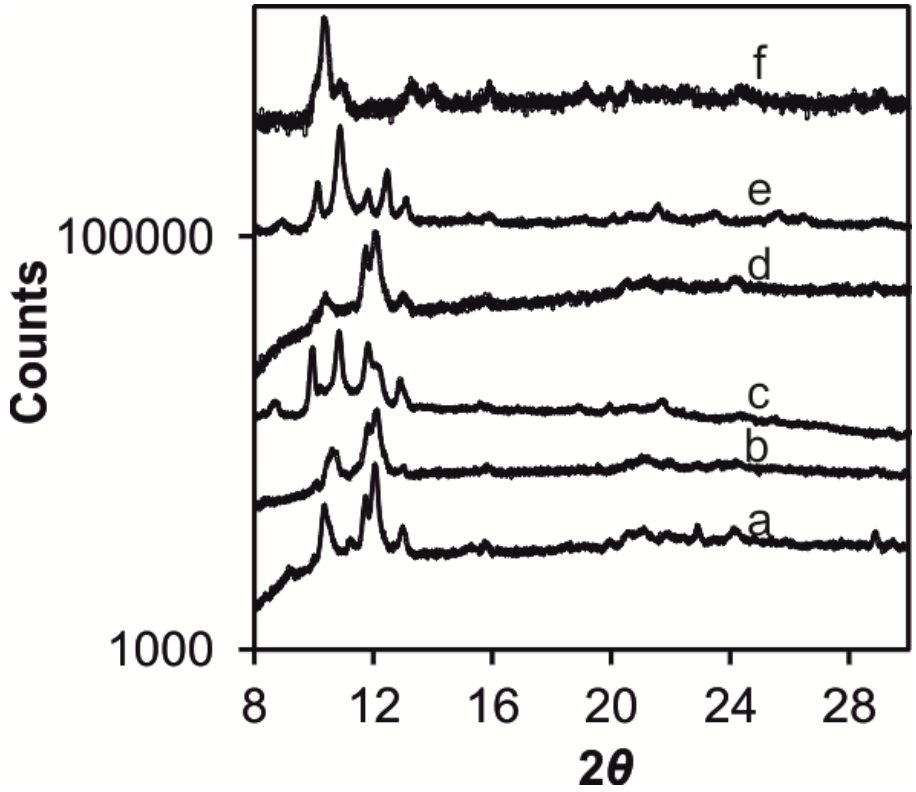


Fig. S1 XRD spectra of a) MIL-88A, and MIL-88A functionalized with 1% of PEG-COOH capping ligand as a function of MWPEG for b) 178, c) 588 Da, d) 2, e) 5, and f) 20 kDa.

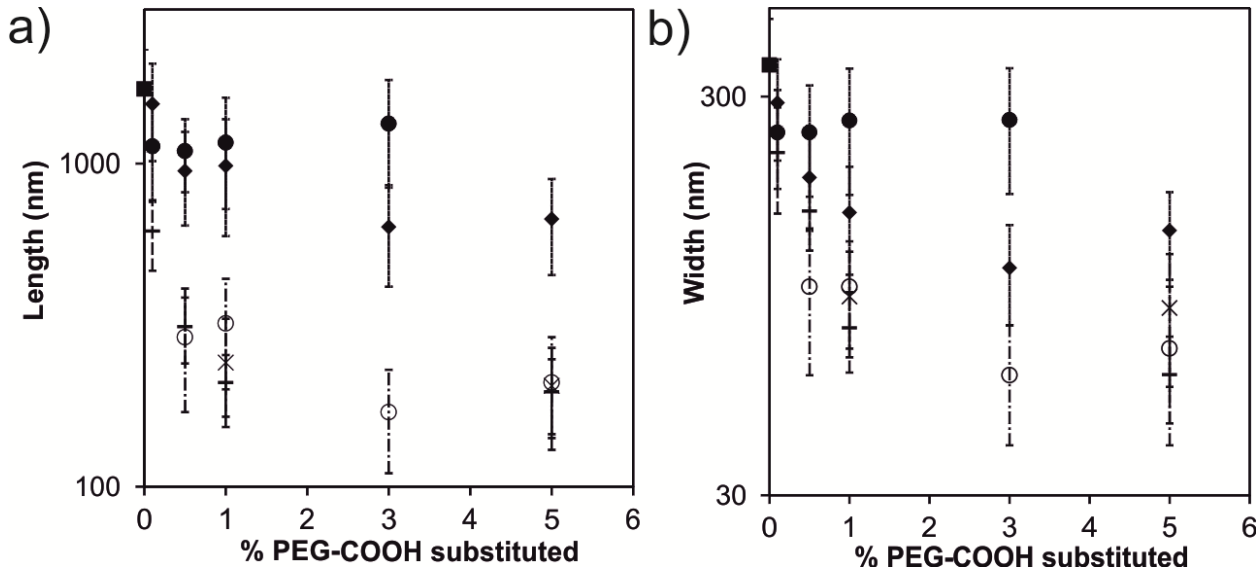


Fig. S2 Particle a) length and b) width as a function of the percentage of PEG-COOH capping ligand from SEM analysis using different MW: 0 (■), 178 (●), 588 Da (♦), 2 (○), 5 (−) and 20 kDa (×).

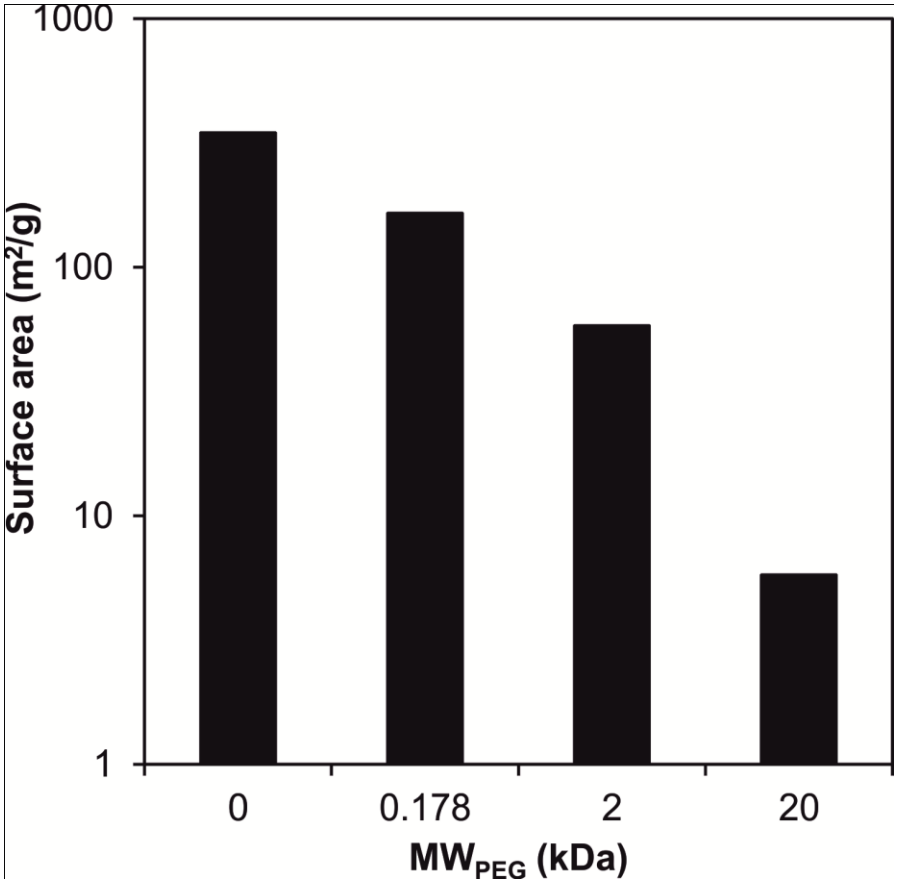


Fig. S3 BET surface areas determined from N_2 sorption experiments for MIL-88A made in the absence or presence of 1% of PEG-COOH capping ligand (MW_{PEG} of 0.178, 2 or 20 kDa).

Table S1 Elemental analyses (w%) of MIL-88A made in the absence or presence of 1% of PEG-COOH capping ligand using different MW_{PEG}.

MW_{PEG} (kDa)	C (w%)	H (w%)	Fe (w%)	Cl (w%)	Cl/Fe*	$Fe_3O(OOC\text{-}C_2H_2\text{-}COO)_3\cdot(fumaric\text{-}acid)_x\cdot Cl_z\cdot R\text{-}COO_{1-z}\cdot 3H_2O$ **
0	25.02	2.47	25.33	5.36	1.00	x = 0.4 and z = 1
0.178	24.96	2.57	24.37	5.17	1.00	x = 0.3 and z = 1
0.588	23.97	2.86	27.52	5.53	0.95	x = 0.04 and z = 1
2	24.93	2.74	24.09	4.99	0.98	x = 0.1 and z = 1
20	25.30	3.59	21.81	5.48	1.19	x = 0.03 and z = 1

* atomic ratio = $(w\%Cl/AW_{Cl})/(w\%Fe/AW_{Fe})$ in which AW are the atomic weights (35.45 and 167.55 Da, respectively) ** Fit parameters of the elemental analysis data to the empirical formula.

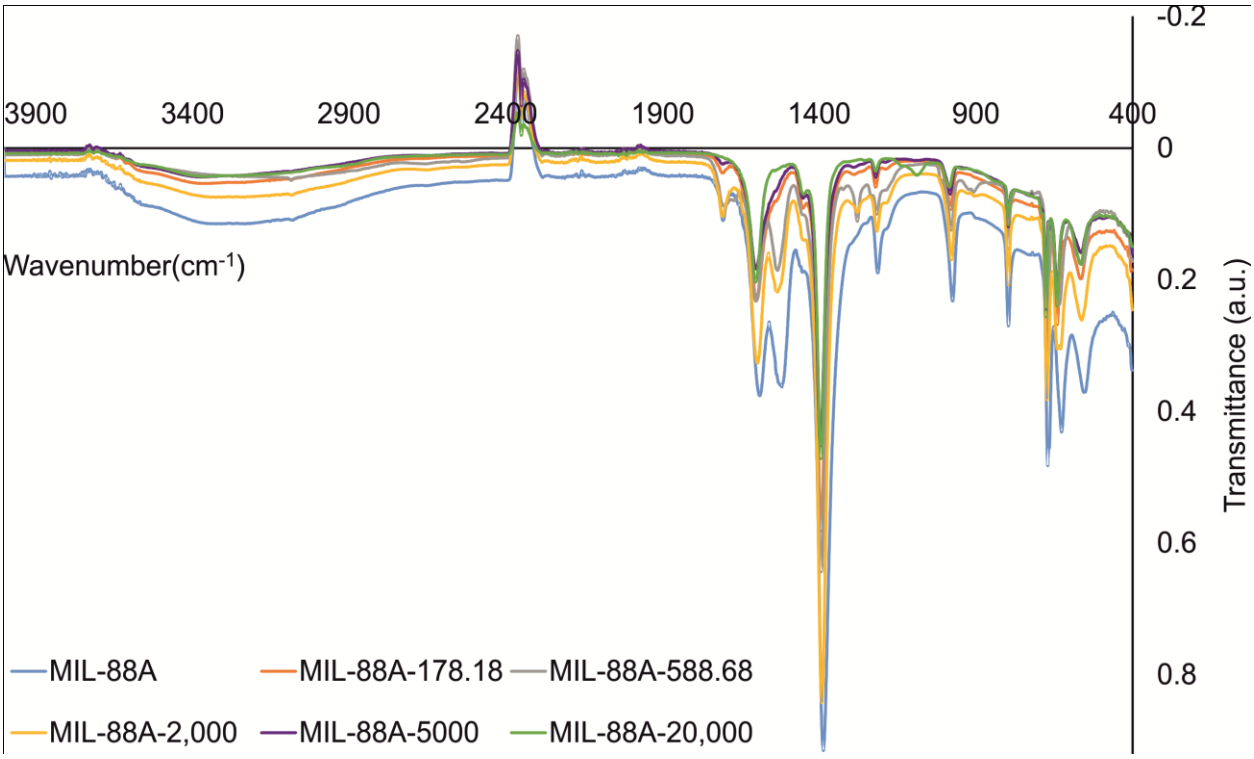
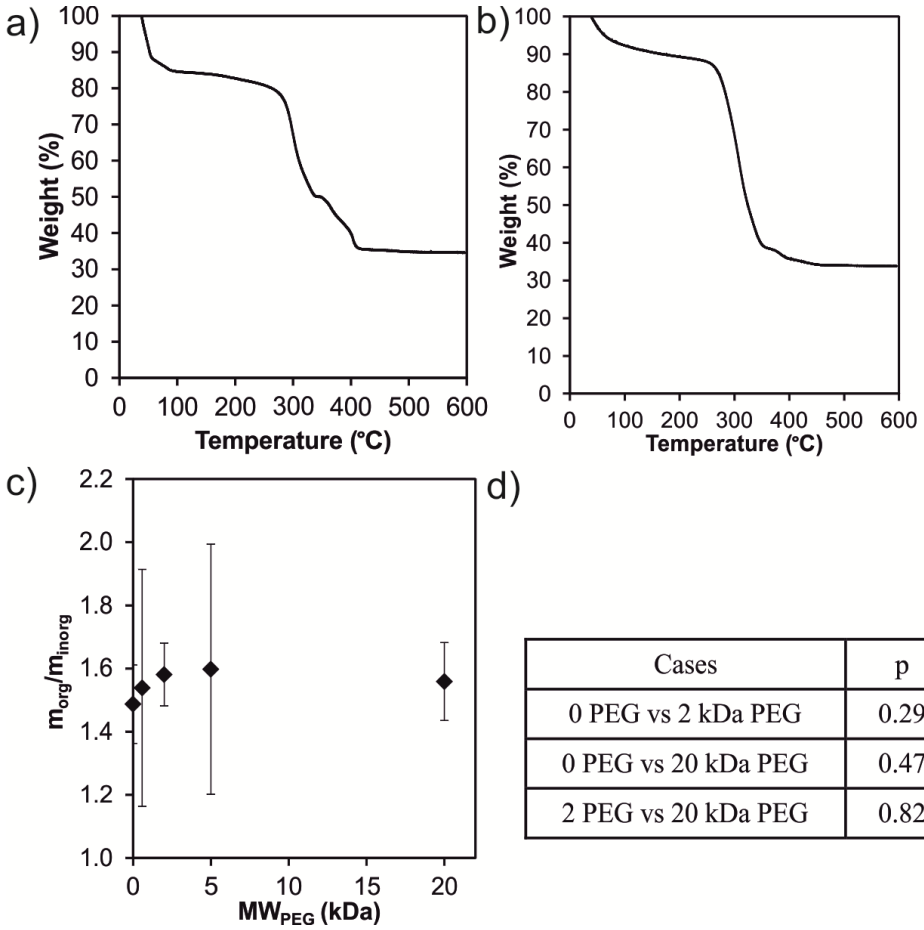


Fig. S4 IR measurements for MIL-88A made in the absence or presence of 1% of PEG-COOH capping ligand (MW_{PEG} of 178, 588 Da, 2, 5 and 20 kDa).



Cases	p
0 PEG vs 2 kDa PEG	0.29
0 PEG vs 20 kDa PEG	0.47
2 PEG vs 20 kDa PEG	0.82

Fig. S5 TGA plots for a) unmodified MIL-88A and b) MIL-88A functionalized with 1% PEG-COOH (MW=20 kDa). c) The m_{org}/m_{inorg} ratios of the TGA results for different MW_{PEG}. d) t-test for unmodified MIL-88A vs MIL-88A functionalized with 1% PEG-COOH (MW = 2 kDa), unmodified MIL-88A vs MIL-88A functionalized with 1% PEG-COOH (MW = 20 kDa) and MIL-88A functionalized with 1% PEG-COOH (MW = 2 kDa) vs MIL-88A functionalized with 1% PEG-COOH (MW = 20 kDa).

For the brush regime, the PEG spacing and brush thickness are calculated assuming an energy equilibrium of the polymer layer at the surface. Since the radius of the nanoMOF particle is much larger than the brush length, a flat plate approximation is appropriate to estimate the projected size of a PEG brush. The approximation is based on the minimization of free energy of PEG at the interface.[1,2] The free energy (F) is composed of (1) a surface energy term and (2) an entropic contribution term due to the stretching of the polymer chain and is given by: [2,3]

$$\mathbf{F} = \boldsymbol{\gamma_{eff}}\boldsymbol{\pi}\frac{\boldsymbol{\xi_{brush}^2}}{\mathbf{4}} + \frac{\mathbf{3}}{\mathbf{2}}\boldsymbol{kT}\frac{\mathbf{d^2}}{\mathbf{Nb^2}} \qquad \textbf{Equation S.1}$$

where γ_{eff} is the effective surface energy, ξ_{brush} is the projected diameter of a PEG molecule in a brush regime, k is the Boltzmann constant, T is the temperature, d is the end-to end distance of a

single PEG brush, *N* is the number of PEG monomers in a chain, and *b* is the Kuhn monomer length of PEG. If *g* is the number of monomers in an extended PEG molecule, then $\xi_{brush} = bg^{v}$, where *v* = 3/5 for a real chain,[3] and *d*, is described as:

$$\boldsymbol{d = \xi_{brush}\frac{N}{g} = \xi_{brush}^{(v-1)/v} N b^{1/v}} \qquad \textbf{Equation S.2}$$

Substituting *d* as described in Equation S.2 into the free energy expression in Equation S.1 the following expression is obtained:

$$\mathbf{F = \gamma_{eff}\pi\frac{\xi_{brush}^2}{4} + \frac{3}{2}kT\frac{\left(\xi_{brush}^{(v-1)/v} Nb^{1/v}\right)^2}{Nb^2}} \qquad \textbf{Equation S.3}$$

Minimizing the free energy expression in Equation S.3 with respect to ξ_{brush} yields the following expression:

$$\mathbf{\xi_{brush} = \left(\frac{4kTNb^{4/3}}{\gamma_{eff}\,\pi}\right)^{3/10}(m)} \qquad \textbf{Equation S.4}$$

The surface tension of a material, γ, consists of two terms: a dispersive term (γ^d) and a polar term (γ^p) and is calculated as follows:[2]

$$\boldsymbol{\gamma = \gamma^p + \gamma^d} \qquad \textbf{Equation S.5}$$

The interfacial tension between the material (a) and water (b), γ_{ab} can be approximated using harmonic mean expression as follows:[3]

$$\boldsymbol{\gamma_{ab} = \gamma_a + \gamma_b - 4\frac{\gamma_a^d\cdot\gamma_b^d}{\gamma_a^d+\gamma_b^d} - 4\frac{\gamma_a^p\cdot\gamma_b^p}{\gamma_a^p+\gamma_b^p}} \qquad \textbf{Equation S.6}$$

Then, the interfacial tension of the MOF functionalized with PEG suspended in water can be represented by:

$$\boldsymbol{\gamma_{eff} = \frac{b^2}{\xi_{brush}^2}\gamma_{magnetite,PEG} + \left(1 - \frac{b^2}{\xi_{brush}^2}\right)\gamma_{magnetite,water}} \qquad \textbf{Equation S.7}$$

Table S.2 Values to calculate ξ_{brush} and surface tension values for PEG,[2] magnetite,[4] and water.[5]

k	1.38×10^{-23} J/K
T	298 K
N	44 g/mol
b	1.1 nm[26]
γ_{PEG}^{p}	12 mN/m
γ_{PEG}^{d}	30.9 mN/m
$\gamma_{magnetite}^{p}$	3.5 mN/m
$\gamma_{magnetite}^{d}$	48.9 mN/m
γ_{water}^{p}	50.7 mN/m
γ_{water}^{d}	22.1 mN/m

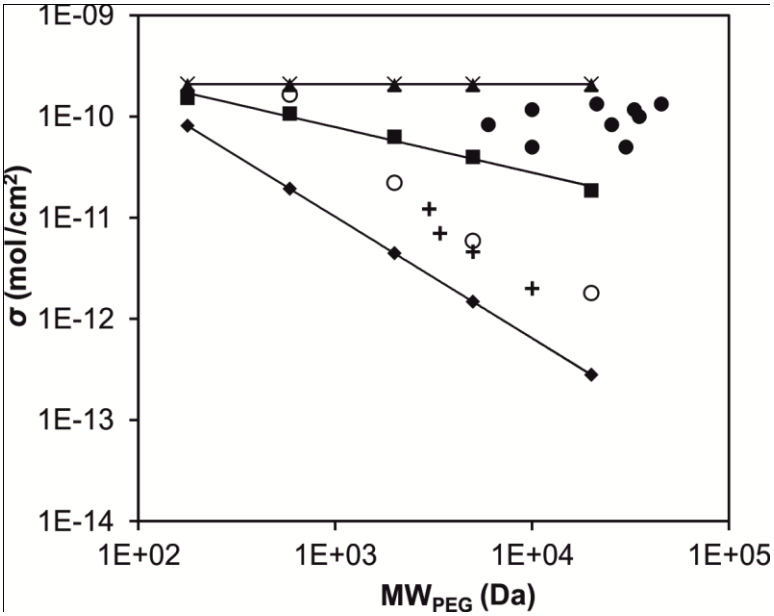


Fig. S6 Packing densities, σ (mol/cm^2), for different models: experimental (○), mushroom (♦), brush (■), coordination sites for the linear and tip sections of a MIL-88A crystal (▲,×), and values in the literature for different brushes on flat surfaces[6] (●) and PEG chains assuming that they are in mushroom regime (+).[1,7] For the mushroom and brush regimes, equation 3 was used: σ = #PEG / ($a_{MOF} \cdot N_A$), where N_A is Avogadro's number. The coordination site values are calculated from previous paper.[8] Trendlines (lines, guide to the eye).

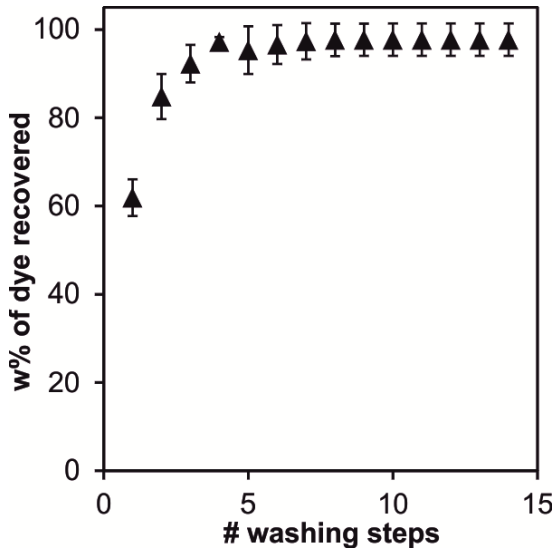


Fig. S7 Monitoring the cumulative leaching of sulforhodamine B from freshly loaded MIL-88A particles (without PEG) as a function of the number of washing steps (with water) using fluorescence spectroscopy. All experiments were carried out in triplicate.

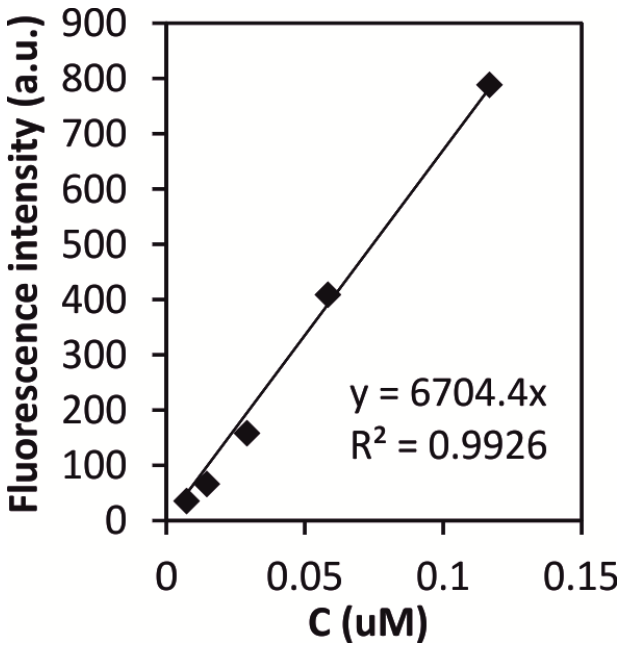


Fig. S8 Fluorescence calibration curve of sulforhodamine B in water.

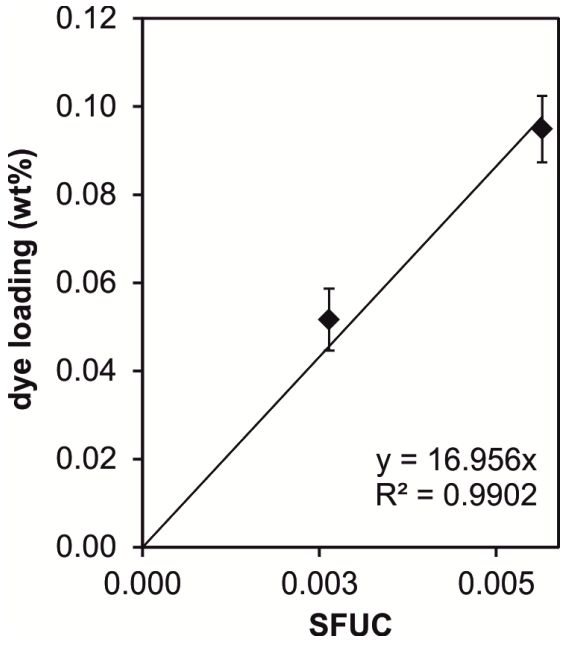


Fig. S9 Dye-loading as a function of the surface fraction of unit cells (SUFC is calculated from equation S13 from our previous finding[8]) for MIL-88A and PEG20k-MIL-88A.

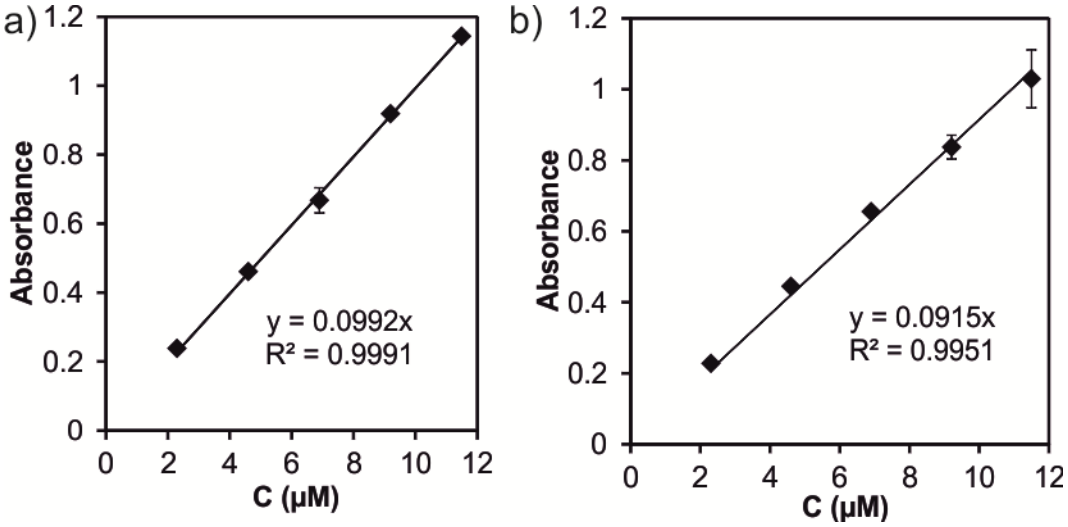


Fig. S10 UV-calibration curves of sulforhodamine B in a) PBS and b) water.

References

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