

Supporting Information

Evaluating Host-Guest Interactions in a Metal-Organic Framework Using a Polarity-Sensitive Probe

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Experimental Methods

Synthesis of MOF-177. Submicrometer-sized MOF-177 particles were synthesized according to the procedures reported in literature with some modifications.^{S1} Triethylamine (TEA) (130 μ L, 0.93 mmol) was very slowly added to *N,N*-dimethylformamide (DMF) solution (40 mL) containing $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (0.5 g, 2.64 mmol, Aldrich) and 1,3,5-tris(4-carboxyphenyl)benzene (H_3BTB , 0.2 g, 0.46 mmol, Aldrich). The mixture was allowed to stand for 2 h at room temperature and the resulting solid was collected by centrifugation, washed three times with DMF and chloroform, and then dried in an oven for 12 h at 363 K. MOF-177 is obtained when the $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}/\text{H}_3\text{BTB}$ ratio is 6 and the TEA/ H_3BTB ratio is 2–3.

Characterizations. To confirm the crystal phase and morphology of the prepared MOF-177 particles, powder X-ray diffraction (XRD, Figure S1) and transmission electron microscope (TEM) measurements were performed using a Rigaku RINT2500 XRD spectrometer with a Cu $K\alpha$ source and a Hitachi H-9000 instrument equipped with a tilting device operating at 300 kV, respectively. Scanning electron microscope (SEM) images were also obtained with a Hitachi S-2150 instrument. Steady-state UV-visible absorption and diffuse reflectance spectra were measured with UV-visible-NIR spectrophotometers (Shimadzu, UV-3100, and Jasco, V-570, respectively). Reflectance data were transformed into a Kubelka-Munk function. Steady-state emission spectra were measured by a Hitachi 850 fluorescence spectrophotometer. Measurements for the gas adsorption isotherms of N_2 (77 K) were performed using BELSORP-mini II volumetric adsorption equipment from BEL Japan. MOF-177 powders were placed in a sample tube and dried at 393 K for 6 h under vacuum before the measurements. The BET surface area was calculated from a line regression plot of $1/(V((P_0/P) - 1))$ versus P/P_0 (where V is the total volume absorbed at a particular P/P_0 point and P_0 is 1 atm of pressure) within the range of $0.02 < P/P_0 < 0.05$.

Inclusion of DNS into MOF-177. The synthesized MOF-177 was heated at 393 K for 6 h under vacuum to remove adsorbed solvent and water molecules on the MOF-177 surface. It was immersed in a 1 μ M toluene solution of DNS (Fluka) ($[\text{MOF-177}] = 5 \text{ g L}^{-1}$) at room temperature for 24 h under argon

flow. To completely remove the excess DNS, the resultant material, denoted as DNS@MOF-177, was thoroughly washed with toluene, and then dried at 363 K for 12 h.

All chemicals were purchased from commercial sources (Aldrich, Tokyo Chemical Industry, and Nacalai Tesque) in the highest grade available and used without further purification.

Sample preparations for single-molecule, single-particle experiments. Well-dispersed chloroform suspensions of the MOF samples were spin-coated on cleaned cover glasses. The cover glasses were annealed at 363 K for 30 min to immobilize the particles on the glass surface, and then mounted at the bottom of a single-stream flow cell that allowed the simultaneous exposure of the particles to a liquid medium and the monitoring the fluorescence signal (Scheme S1).^{S2} The position of the particles was determined by the transmission image obtained by illumination from the halogen lamp above the sample and the photoluminescence image under the 365-nm light excitation of MOF-177 (Figure 2B).

Single-molecule, single-particle measurements. The experimental setup was based on an Olympus IX71 inverted fluorescence microscope.^{S3} A circular-polarized continuous wave (CW) light emitted from a 488-nm Ar⁺ laser (Melles Griot, 35LAS450; 50 mW; $\sim 2 \text{ kWcm}^{-2}$, at the cover glass surface) that passed through an oil-immersion objective lens (Olympus, UPlanSApo, 1.40 NA, 100 $\times$) after reflection by a dichroic mirror (Olympus, DM505) was used to excite the sample. The emission from single particles on the cover glass was collected by using the same objective lens, and passed through an emission filter (Olympus, BA510IF) to remove undesired scattered light; the emission image was captured by imaged by an electron-multiplying charge-coupled device (EM-CCD) camera (Roper Scientific, Cascade II:512). The images were processed with Image J software (<http://rsb.info.nih.gov/ij/>). The background threshold was modified by the shot noise in each image above the background. Counts above the threshold were then considered to be the fluorescence signal. For spectroscopy, only the emissions that passed through a slit entered the imaging spectrograph (Acton Research, SP-2356); it was equipped with an EM-CCD camera (Princeton Instruments, PhotonMAX:512B). The width of the slit was 100 μm , which corresponded to 0.6 μm at the specimen because the images at the slit were magnified by the built-in 1.6 $\times$ changer. The spectra were typically

integrated for 5 s. The spectrum detected by the EM-CCD camera was stored in and analyzed with a personal computer. All experimental data were obtained at room temperature. A general approach was used to define the intensity threshold in order to distinguish between the on and off states.^{S4} To determine the threshold that separates these states, the emission intensity distribution was fitted by a sum of two Gaussian functions. To determine the threshold that separates these states, the emission intensity distribution was fitted by a sum of two Gaussian functions. The threshold was chosen to be 3σ greater than the background noise levels. Counts above the threshold were then assigned to the “on state”.

At sufficiently long times, the histograms have only one or no counts per bin time due to finite counting statistics. Therefore, we analyzed the probability density, $P(t_{\text{off}})$, by weighting each point in the on histograms by the average time (Δt_{av}) between the nearest neighbor event bins using the following equation:^{S4}

$$P(t_{\text{off}}) = \frac{N(t_{\text{off}})}{N_{\text{total}}} \times \frac{1}{\Delta t_{\text{av}}} \quad (\text{S1})$$

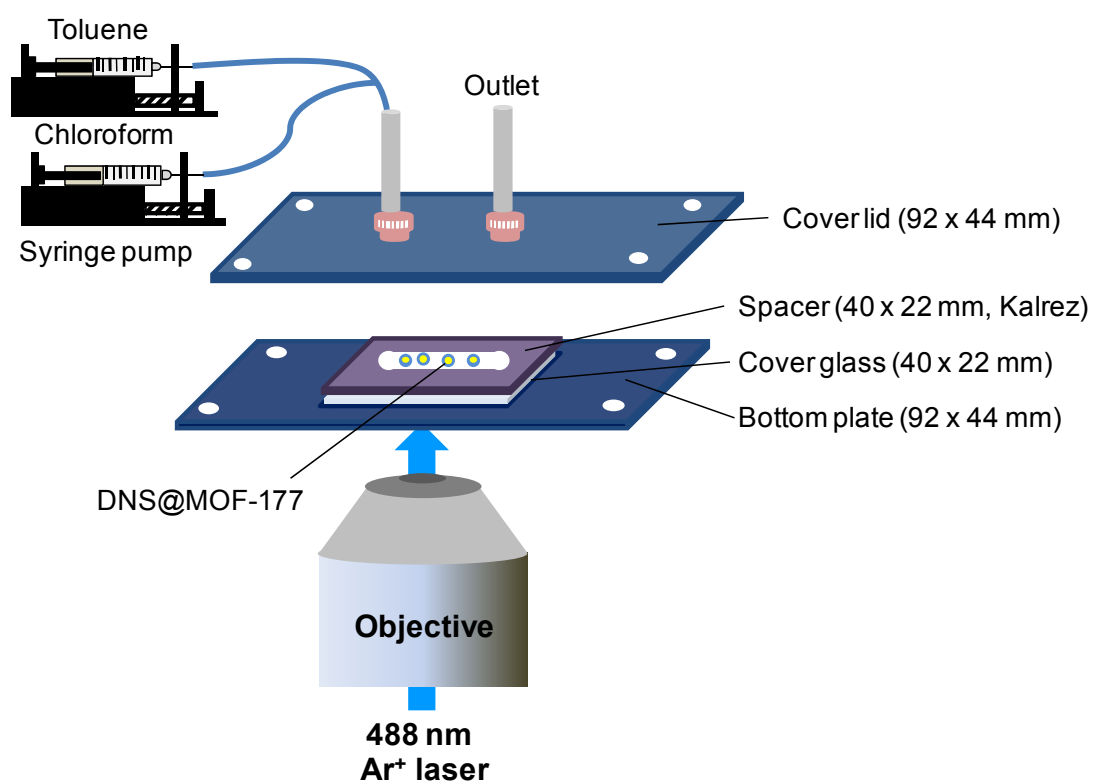
where $N(t_{\text{off}})$ and N_{total} are the number of off events of duration (t_{off}) and the total number of off events, respectively. The time distributions of the off-events follow a simple power law behavior as given by¹

$$P(t_{\text{off}}) = A t^{-\alpha} \quad (\text{S2})$$

where A is the scaling coefficient and α is the power-law exponent that describes the distribution.

Fluorescence lifetime measurements. The time-resolved emission spectra and decays were measured by time-correlated single photon counting (TCSPC) using a streak scope (Hamamatsu Photonics, C4334-01) equipped with a polychromator (Acton Research, SpectraPro150). The second harmonic oscillation (450 nm) of the output for the femtosecond laser (Spectra-Physics, Tsunami 3941-M1BB; full width at half-maximum (fwhm), 80 fs; 900 nm) pumped by a diode-pumped solid-state laser (Spectra-Physics, Millennia VIIIs) was used to excite the sample in a quartz cell. The observed temporal emission profiles fitted well to single or double exponential functions. All the measurements were carried out at room temperature.

Scheme S1. Schematic Illustration of Home-Made Single-Stream Flow Cell



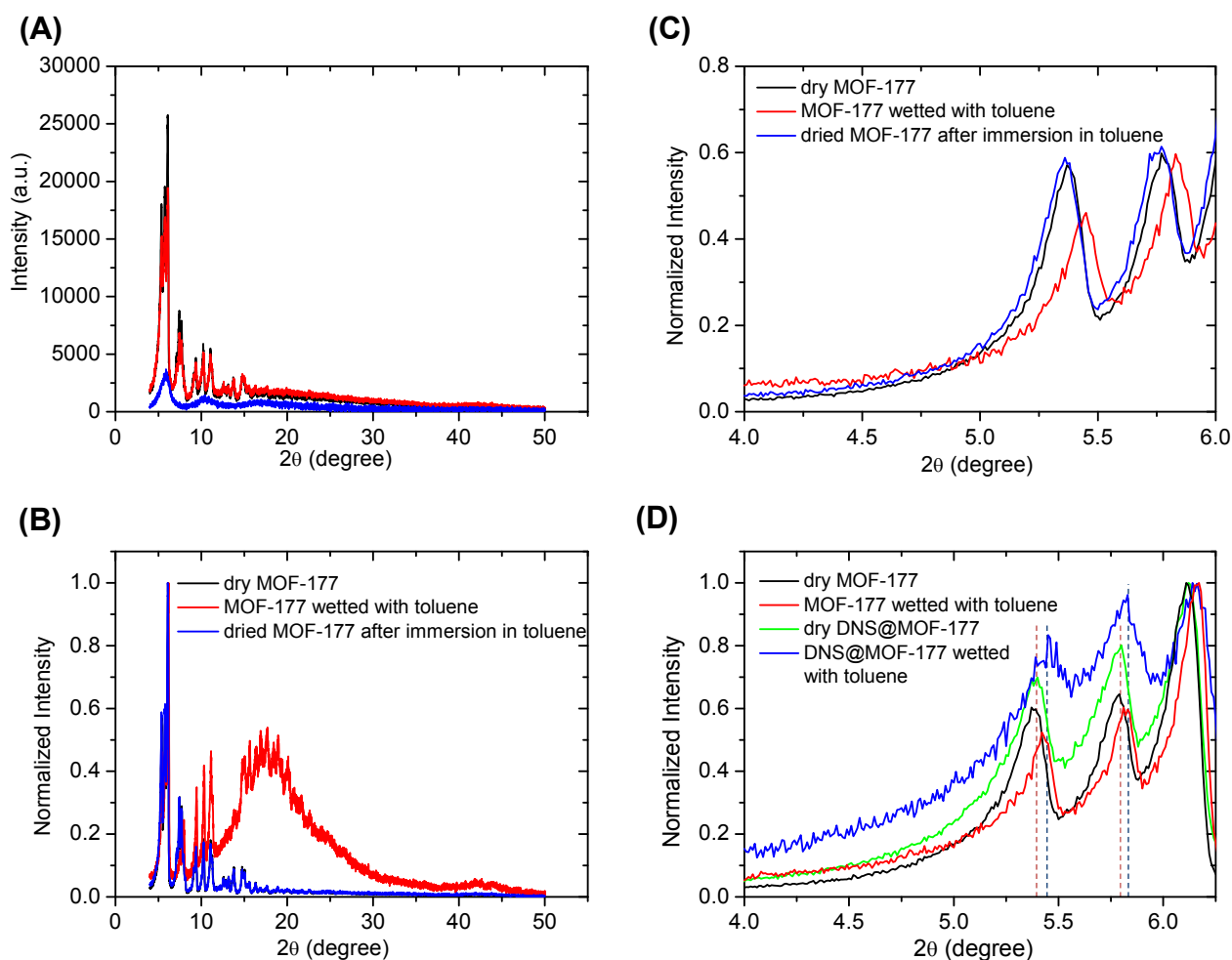


Figure S1. (A) Powder XRD patterns obtained for fresh MOF-177 (black), DNS@MOF-177 (red), and hydrated MOF-177 (blue) powders. There were no apparent changes in the powder XRD patterns during incorporation of DNS into MOF-177; the patterns were almost identical to those reported elsewhere.^{S1a,b} These results reveal that the framework structure for MOF-177 was maintained even when DNS was incorporated. (B) Powder XRD patterns of dry MOF-177 powder, MOF-177 powder wetted with toluene, and dried MOF-177 powder after immersion in toluene. A broad peak at around 18 degrees is due to the solvent. (C) Magnified diffraction patterns at low angle region of panel B. XRD peaks were shifted to the higher angle, when MOF-177 powders were immersed in toluene. After the MOF-177 powder in toluene was completely dried up, the peaks returned to their original position (blue line). (D) Powder XRD patterns at low angle region of dry DNS@MOF-177 powder (green line) and DNS@MOF-177 (blue line) powder wetted with toluene. The peak widths at around 5.38 and 5.80 degrees become broad and the peak positions are shifted to the higher angle after immersion in toluene. The results of MOF-177 powders are also shown for comparison.

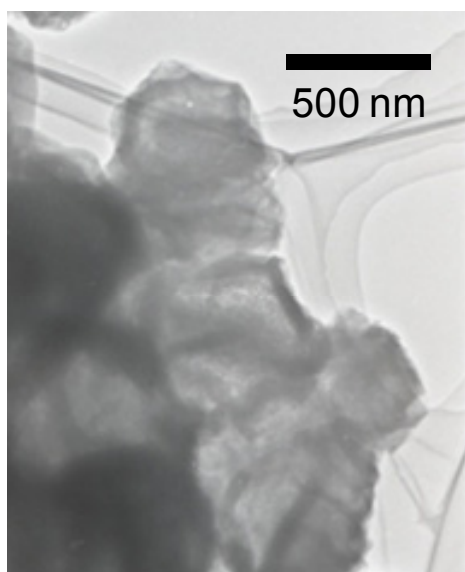


Figure S2. TEM image of MOF-177 particles. The average primary particle size was determined to be around 600 nm.

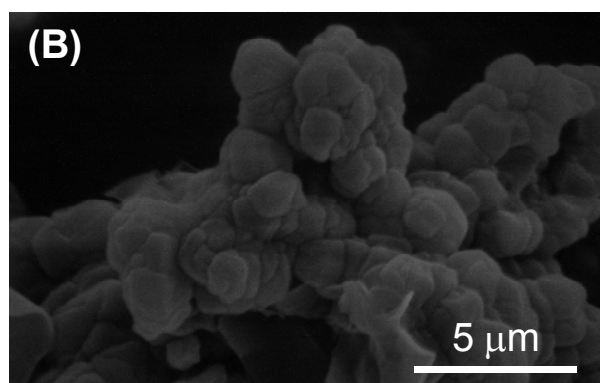
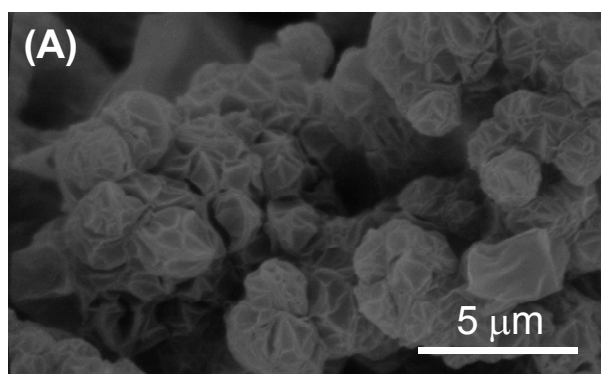


Figure S3. SEM images of freshly-prepared MOF-177 (A) and partially-decomposed (amorphous) MOF-177 (B) powders. These images show agglomerated particles. Fresh MOF-177 showed a regular pattern, while no patterns were observed for the amorphous form. The results can be explained in terms of hydrolysis of the MOFs, which also induces a remarkable reduction in surface area and pore structure by exposure of the MOF samples to moisture.

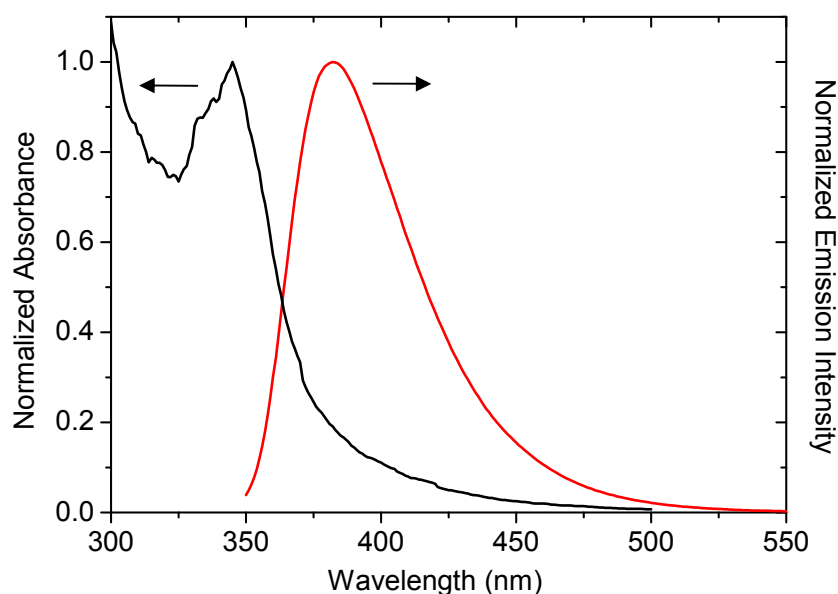


Figure S4. Steady-state UV-Vis diffuse reflectance (black line) and emission (red line) spectra of MOF-177 powder in ambient air.

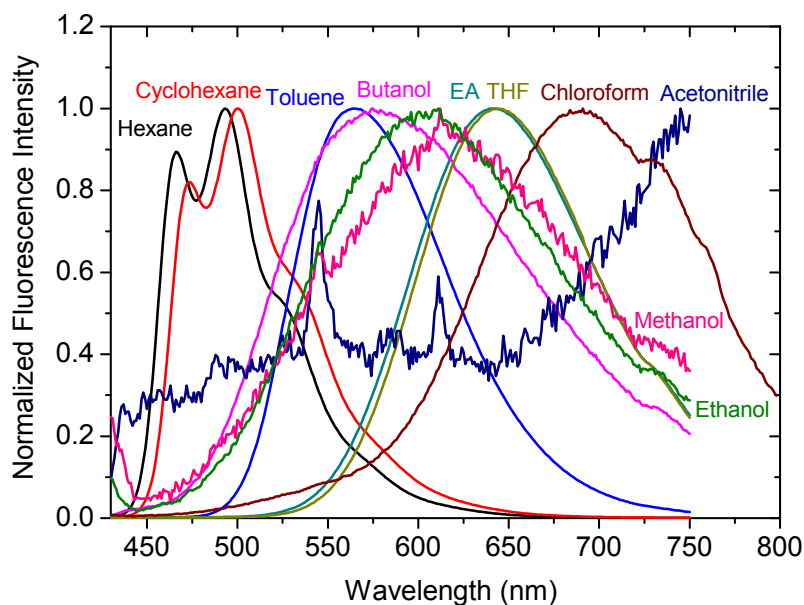


Figure S5. Steady-state fluorescence spectra of DNS in various solvents (EA: ethyl acetate, THF: tetrahydrofuran). The emission spectra shifted dramatically to longer wavelengths as the solvent polarity increased from hexane to acetonitrile. The high sensitivity of emission spectral features for the solvent polarity changes is due to a change of the dipole moment upon excitation.^{S5} This indicates that DNS could be useful as a fluorescent probe for monitoring environmental polarity changes inside the MOF-177 cavity.

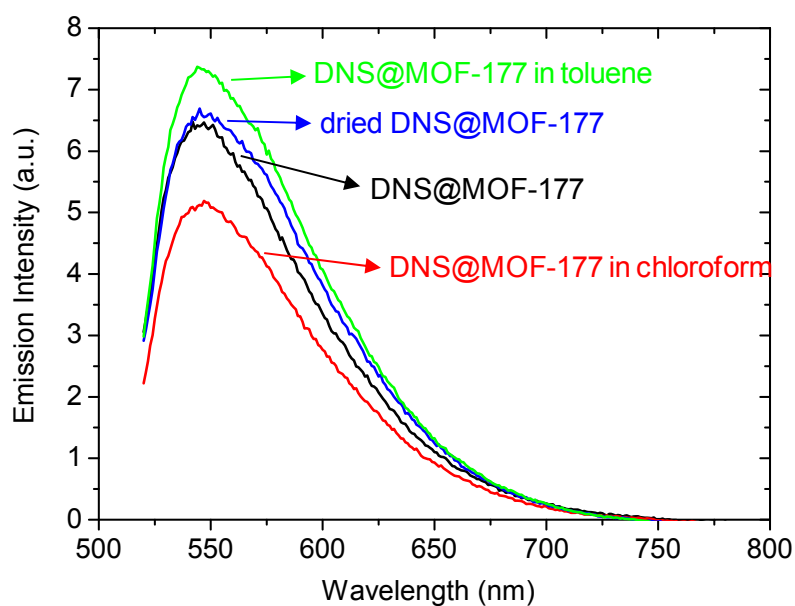


Figure S6. Emission spectra of DNS@MOF-177 in toluene (green line) and in chloroform (red line). After the DNS@MOF-177 powder in chloroform was completely dried up, the emission intensity was recovered (blue line). This result suggests that DNS molecules encapsulated in MOF-177 are hardly desorbed from the MOF framework.

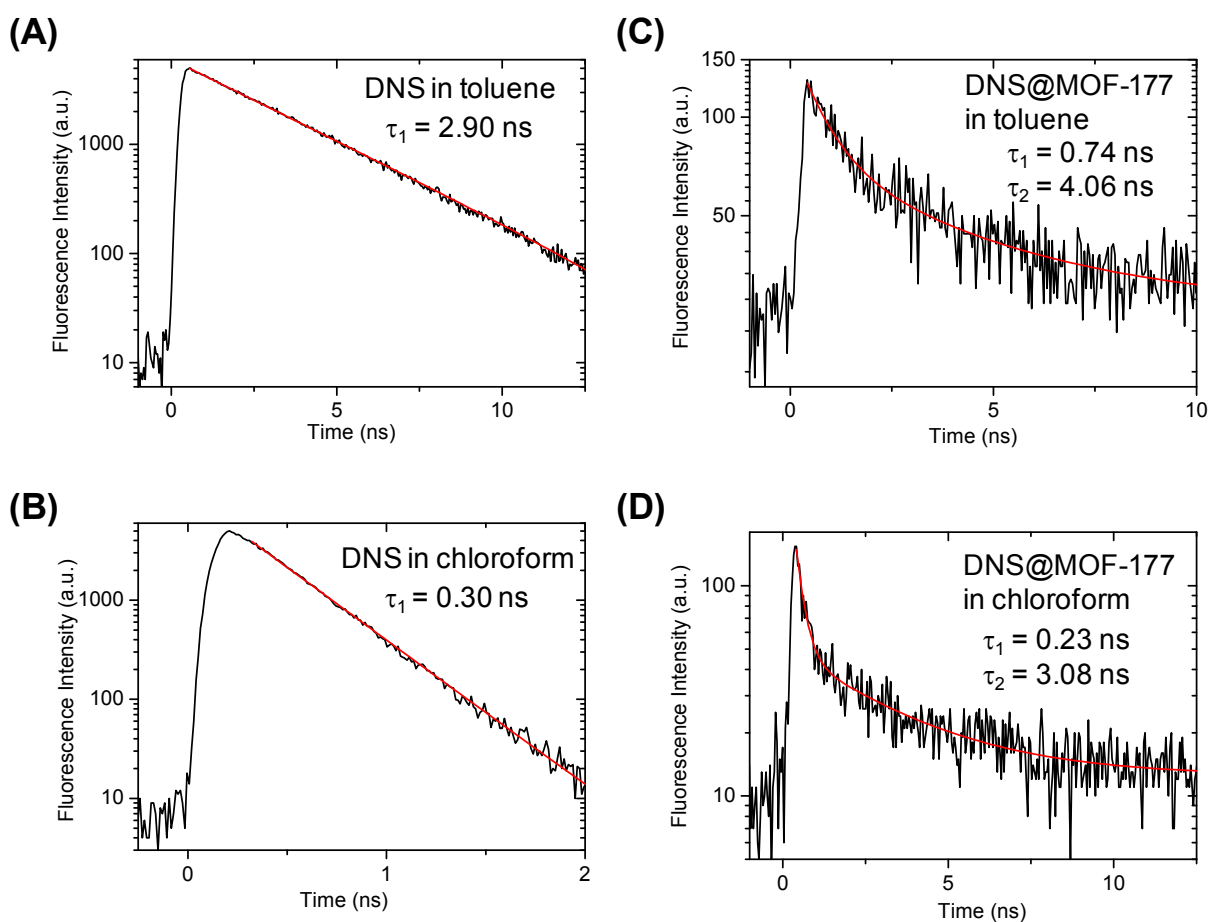


Figure S7. Fluorescence lifetimes observed for DNS in toluene (A) and in chloroform (B) (6 μM), and DNS@MOF-177 suspended in toluene (C) and in chloroform (D) (0.5 g L^{-1}). The excitation wavelength is 450 nm. The red lines indicate single or double exponential curves fitted to the temporal profiles. In a highly polar solvent, the formation of a short-lived nonradiative TICT state is suggested.^{S5} For the DNS@MOF-177 particles in toluene, it is not possible to fit the profile with a single-exponential function because of the distribution of lifetimes of DNS molecules adsorbed on the surface of MOF-177 particles. Therefore, the average lifetime, $\langle\tau\rangle$, was tentatively evaluated to be 3.2 ns (see Table S1). The fast decay component with a lifetime of 0.23 ns observed for the DNS@MOF-177 in chloroform is reasonably assigned to desorbed DNS molecules into the solution and/or surface-adsorbed DNS molecules on the MOF-177 particles.

Table S1. Fluorescence Lifetimes and Maximum Wavelengths of Free DNS Molecules and DNS@MOF-177 Particles in Solutions

sample	τ_1 , ns (a_1 , %)	τ_2 , ns (a_2 , %)	$\langle\tau\rangle$, ns ^c	λ_{max} , nm
DNS in toluene	2.90 ^a	-	-	574 ± 5
DNS in chloroform	0.30 ^a	-	-	703 ± 5
DNS@MOF-177 in toluene	0.74 ^b (64)	4.1 ^b (36)	3.2	560 ± 10
DNS@MOF-177 in chloroform	0.23 ^b	3.1 ^b	-	540 ± 10

^a Errors within ±5%. ^b Errors within ±15%. ^c The average lifetime, $\langle\tau\rangle$, evaluated using the equation:

$$\langle\tau\rangle = \frac{\sum_{i=1}^{i=n} a_i \tau_i^2}{\sum_{i=1}^{i=n} a_i \tau_i} \cdot S_6$$

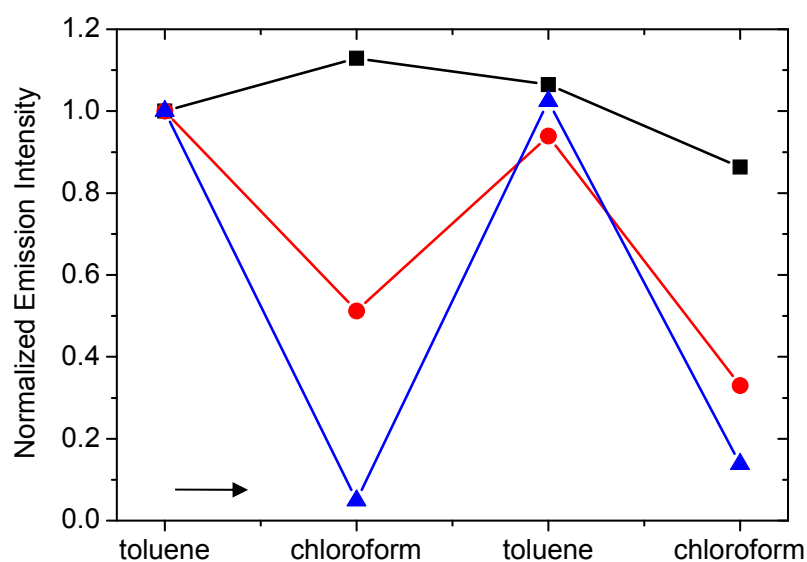


Figure S8. Normalized emission intensity changes observed for single MOF-177 (black) and DNS@MOF-177 (red) particles, and DNS molecules adsorbed on the decomposed MOF-177 (blue) as the solvent was exchanged. The images were captured under static conditions (i.e., without solvent flow).

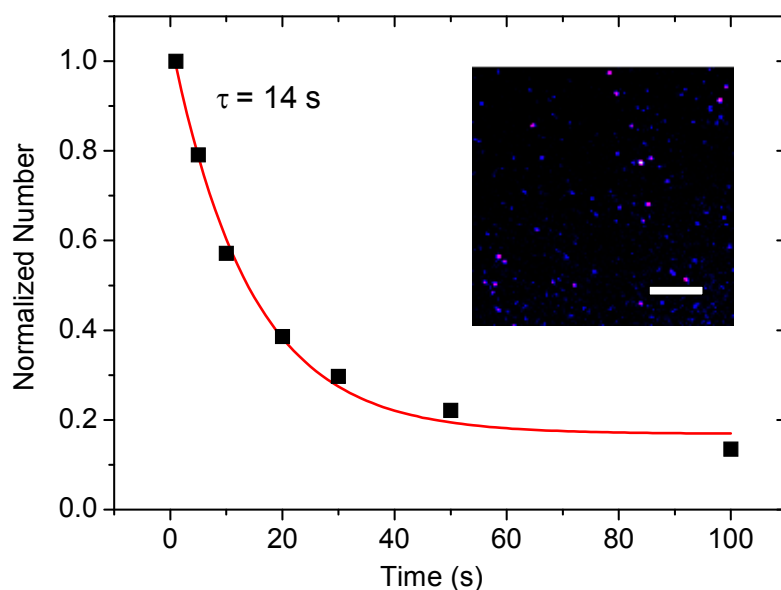


Figure S9. Photoirradiation time dependence of the number of single DNS molecules on the glass surface in ambient air. The bleaching time (τ) of 14 ± 3 s was calculated by using a single-exponential fitting of the number of detected molecules as a function of time (red line). The inset shows the single-molecule fluorescence image observed for DNS molecules coated on a quartz cover glass under the 488-nm laser irradiation in ambient air. The scale bar is 5 μ m.

References

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