

ELECTRONIC SUPPORTING INFORMATION

Chemical sensing of water contaminants by a
colloid of a fluorescence imine-linked covalent
organic framework

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Section S1. Materials, methods and characterization procedures of the starting materials and IMDEA-COF-1

Most chemicals and solvents were obtained from Aldrich Chemical Co. and used without further purification. The exceptions were Methylene blue, purchased from Fisher Chemicals; Janus Green, obtained from Across Organics and Bromophenol Blue, Crystal Violet and Malachite Green. All dyes and nitroaromatic solutions used in the experiments were obtained by stock solution dilution.

Elemental Analysis were obtained using LECO CHNS-932 elemental analyser UV-vis.

¹H-NMR spectra were recorded on a Bruker Avance III-HD NANOBAAY 300MHz.

Zeta Potential measurements were performed using a Zetasizer Nano ZS90 and a folded capillary zeta cell.

Excitation-Emission Matrix (EMM) and **Emission Spectra** were recorded with a NanoLog 4 HORIBA instrument.

The morphology and microstructure of the prepared material were analysed by **Field Emission Scanning Electron Microscopy (FE-SEM)** (JEOL JM6400) equipped with a 40 kV microprobe.

AFM Measurements. Atomic Force Microscope (AFM) techniques were used in dynamic mode using a Nanotec Electronica system operating at room temperature in ambient air conditions. The images were processed using WSxM (freely downloadable scanning probe microscopy software from www.nanotec.es). For AFM measurements, commercial Olympus Si/N and Ti/Pt cantilevers were used with a nominal force constant of 0.75 N/m and 2 N/m, respectively. The surfaces used for AFM experiments were SiO₂ (300 nm thickness)/Si (IMS Company).

Surface preparations. In order to obtain reproducible results, very flat substrates were used with precisely controlled chemical functionalities, freshly prepared just before the chemical deposition. SiO₂ surfaces were sonicated for 15 min in acetone and 15 min in 2-propanol and then dried under an Argon flow.

Section S2. Synthetic Procedures

IMDEA-COF-1. 27.3 mg of 1,6-diaminopyrene (DAP) and 12.7 mg of benzene-1,3,5-tricarbaldehyde (BTCA) were dissolved in a 10:1 mixture of m-cresol (2.60 mL) and glacial acetic acid (0.26 mL) on a Pyrex vessel. The mixture was heated at 120 °C for 72 hours. The obtained brownish-red precipitate was filtered and washed with abundant methanol and THF. A red product was obtained in a 57 % yield. Elemental analysis found: C, 74.40; H, 3.99; N, 7.60 %. Calculated (C₆₆H₃₆N₆·5CH₃CO₂H): C, 75.17; H, 4.73; N, 6.92 %.

IMDEA-COF-2 was prepared as reported in reference 28 of the body text.

IMDEA-COF-1 and 2 Colloids. 1 mg of material was sonicated at 80 kHz in 25 mL of water at 20 °C for 3 hours. The resulting suspension was diluted until its emission spectra maximum showed an intensity of 1×10^6 count per second (CPS).

Section S3. Atomic Forces Microscopy (AFM)

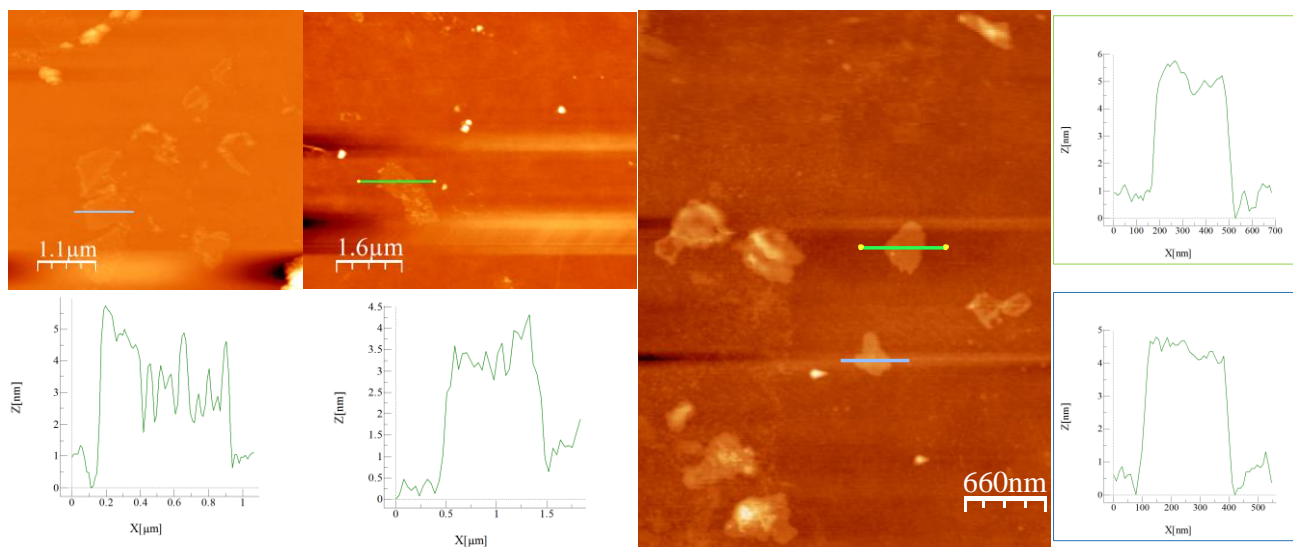


Figure S3.1. Representative topographic AFM images of and the corresponding height profiles along the lines of **IMDEA-COF-1** deposited on SiO₂.

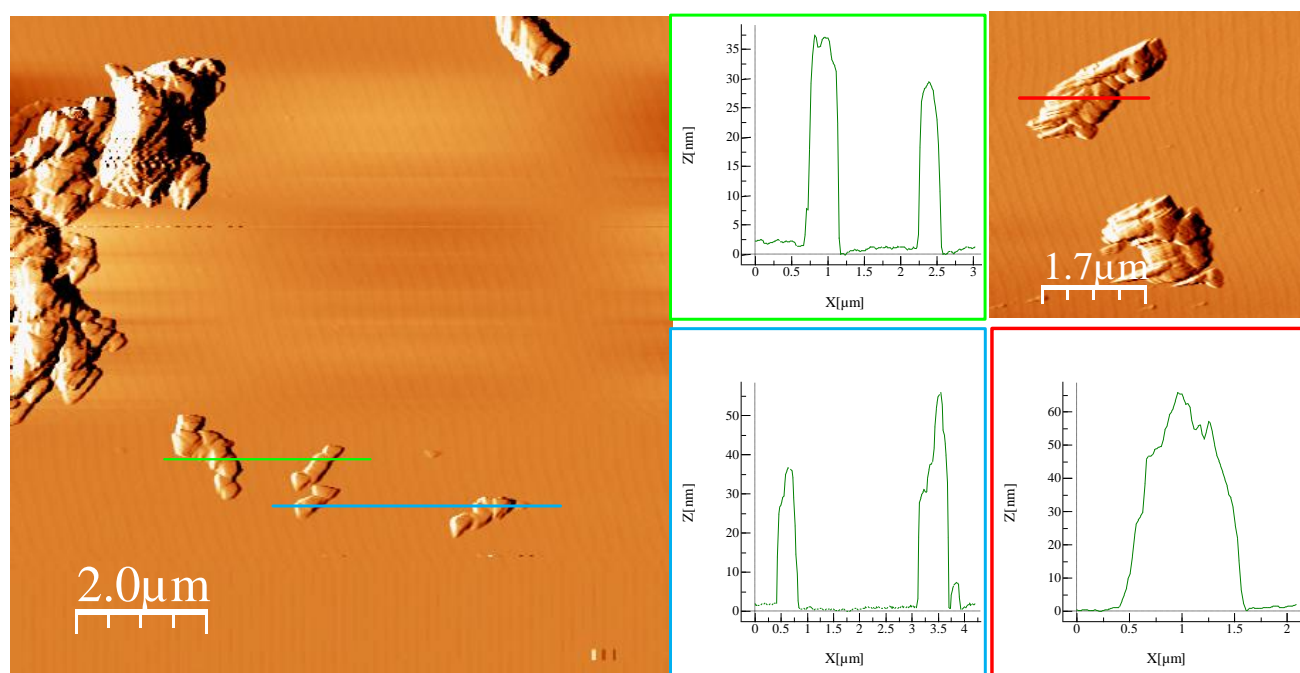


Figure S3.2. Representative topographic AFM images of and the corresponding height profiles along the lines of **IMDEA-COF-2** deposited on SiO₂.

Section S4. Transmission Electron Microscopy (TEM)

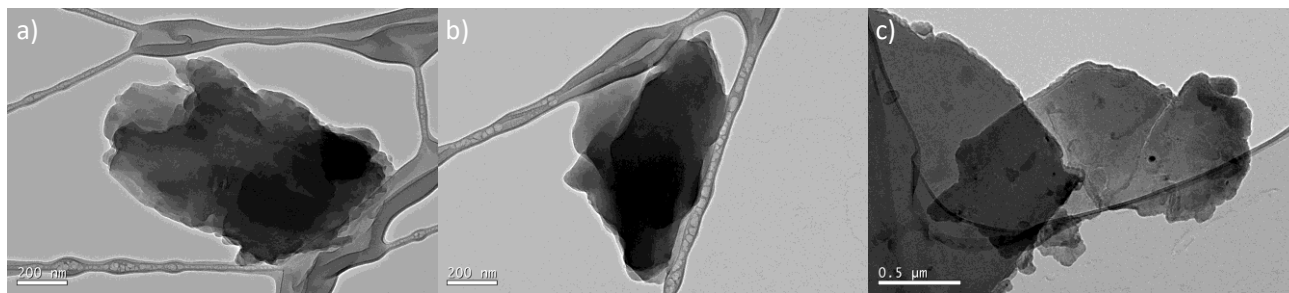


Figure S4.1. Representative TEM micrographs of **IMDEA-COF-1**.

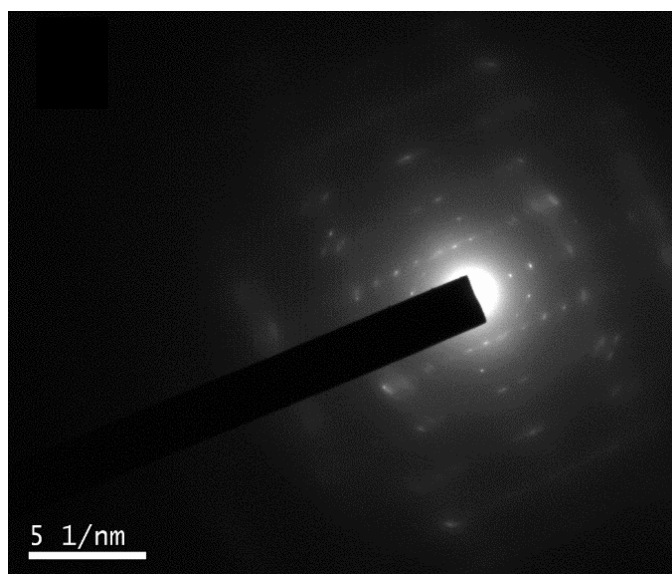


Figure S4.2. Electron diffraction collected on a **IMDEA-COF-1** nano-layer.

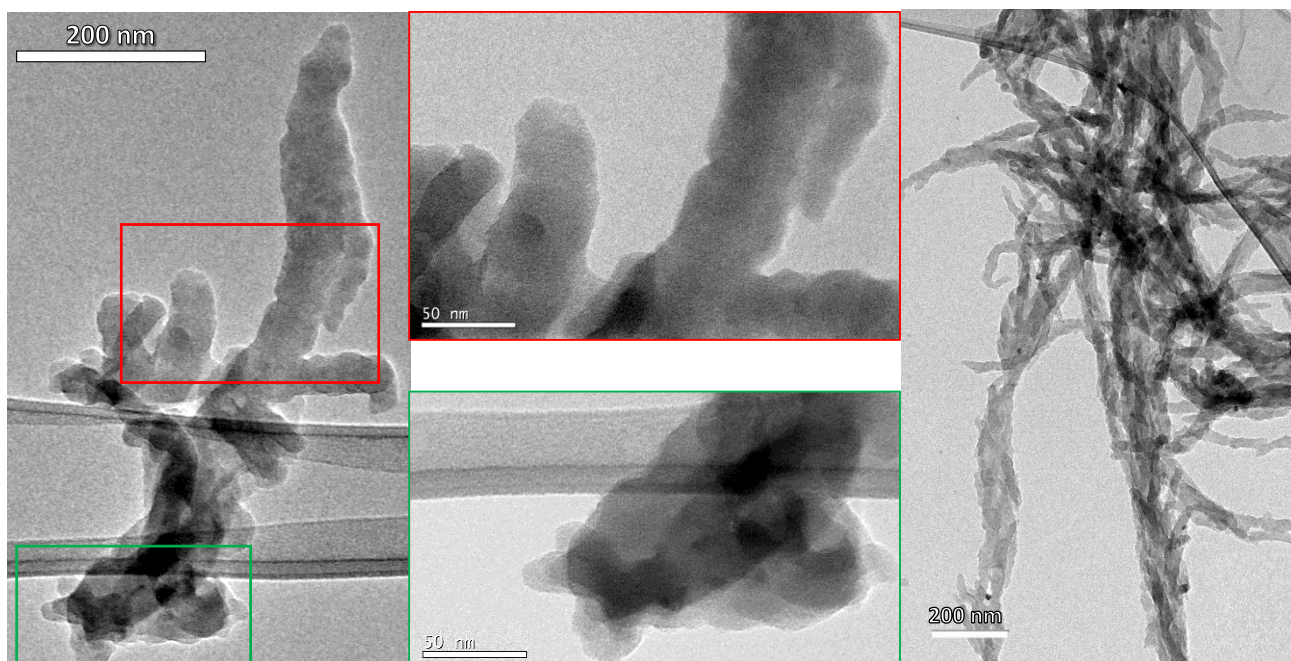


Figure S4.3. Representative TEM micrographs of **IMDEA-COF-2**.

S5. Scanning Electron Microscopy (SEM)

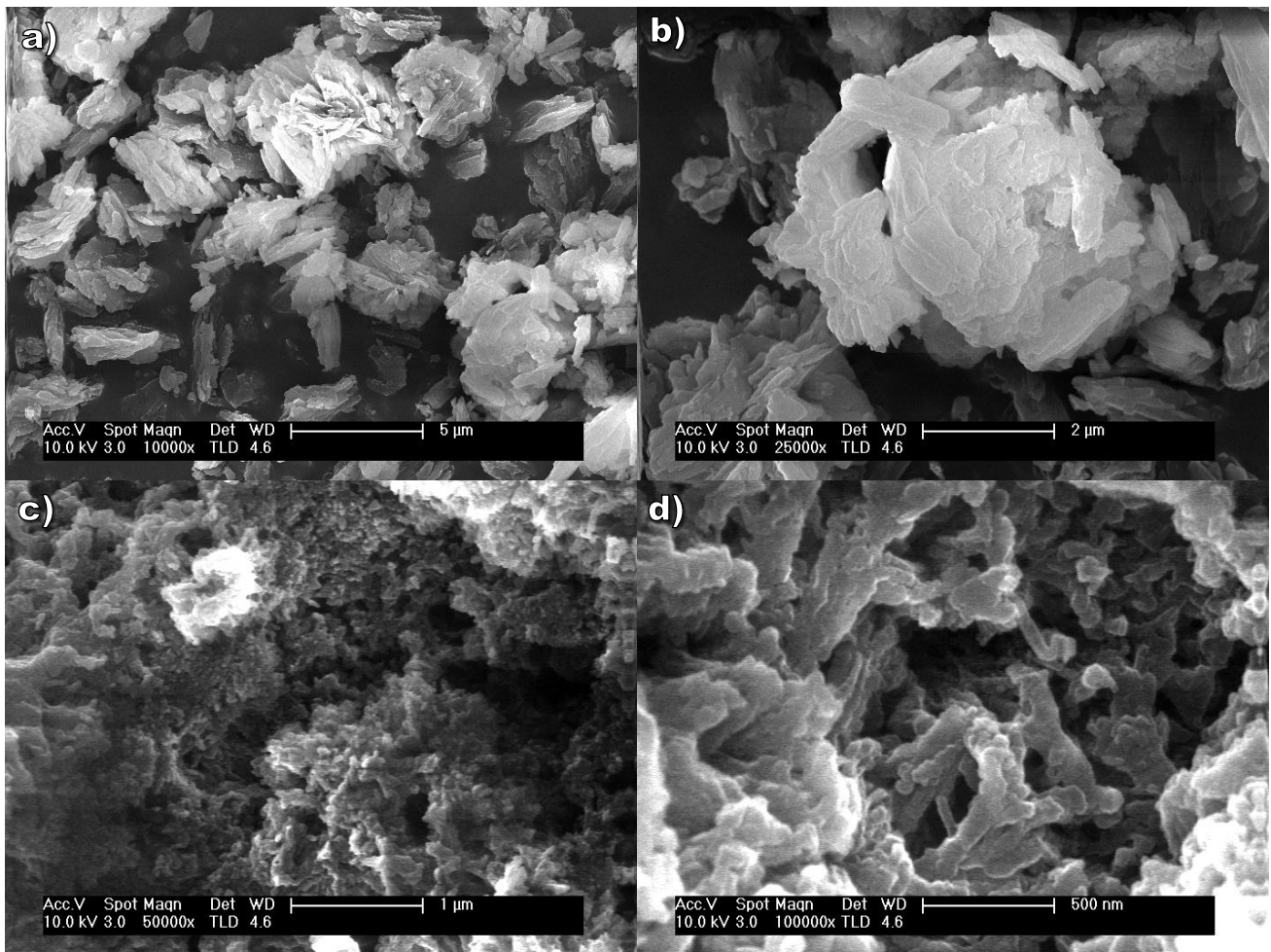


Figure S5.1. SEM images of wide sheets morphology area (a,b) and small sheets morphology area (c,d) of IMDEA-COF-1.

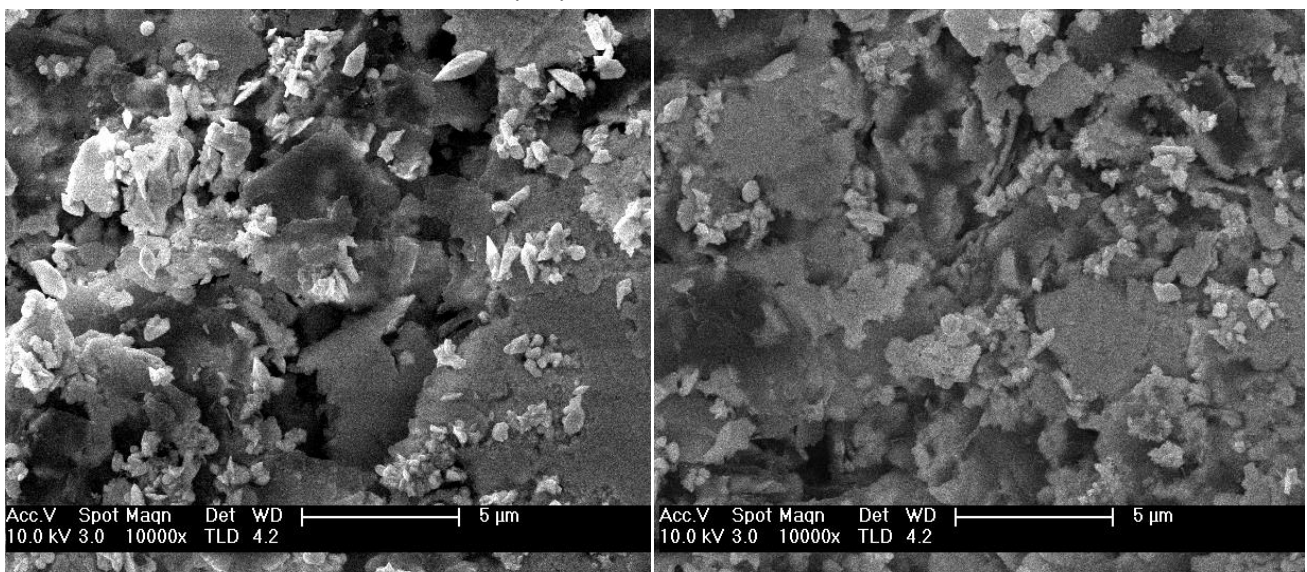


Figure S5.2. SEM images of IMDEA-COF2.

Section S6. Characterization of IMDEA-COFs Water Colloids

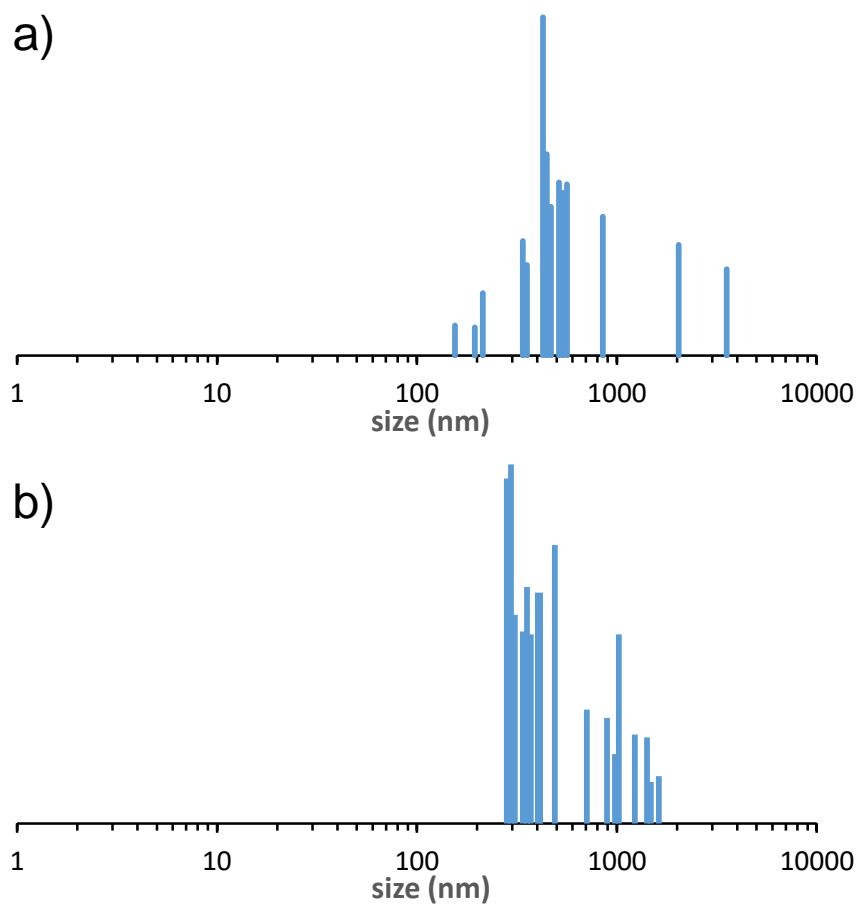


Figure S6.1. DLS of IMDEA-COF-1 (a) and IMDEA-COF-2 (b) water suspensions.



Figure S6.2. Tyndall effect of IMDEA-COF-1 (left) and IMDEA-COF-2 (right) suspensions in water.

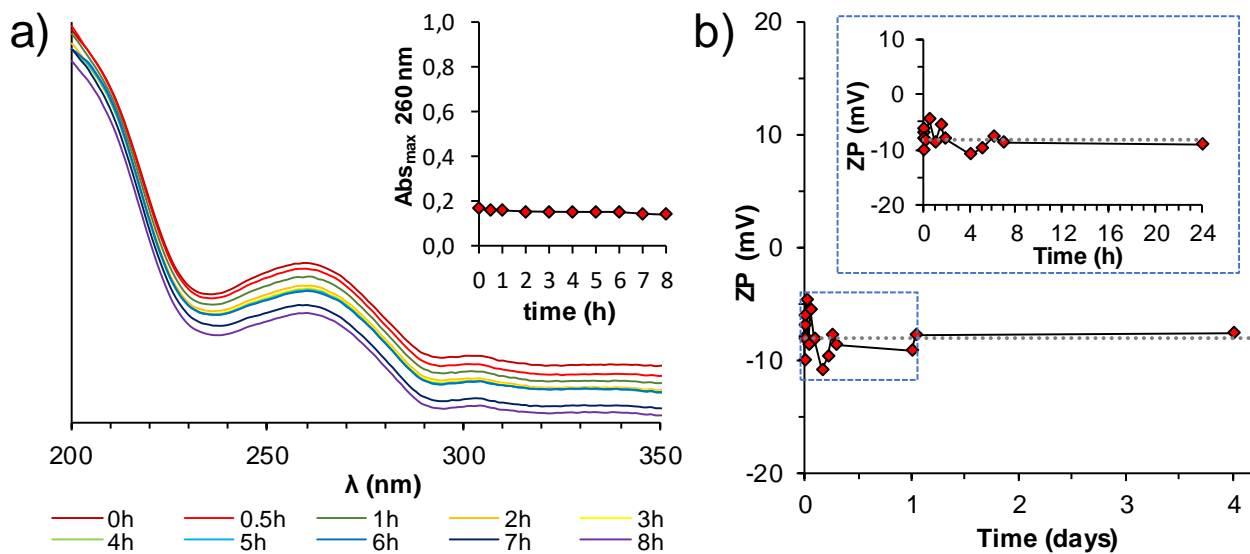


Figure S6.3. (a) UV-Vis spectra and (b) Zeta Potential of **IMDEA-COF-1** suspension in water over time.

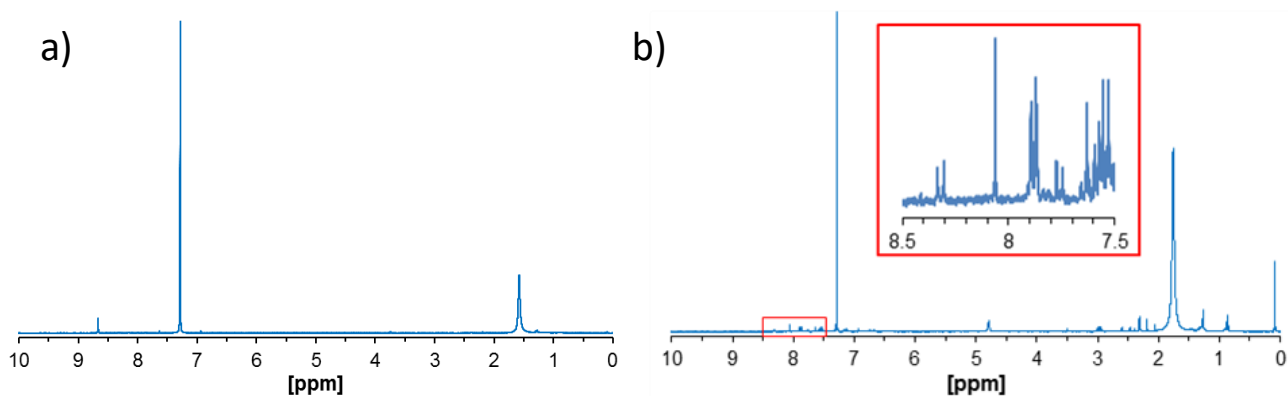


Figure S6.4. ¹H NMR spectra of (a) **IMDEA-COF-1** suspension in CDCl₃. No hydrolysis products signals at the aromatic region. (b) **IMDEA-COF-2** suspension in CDCl₃ and detail of the hydrolysis products signals at the aromatic region.

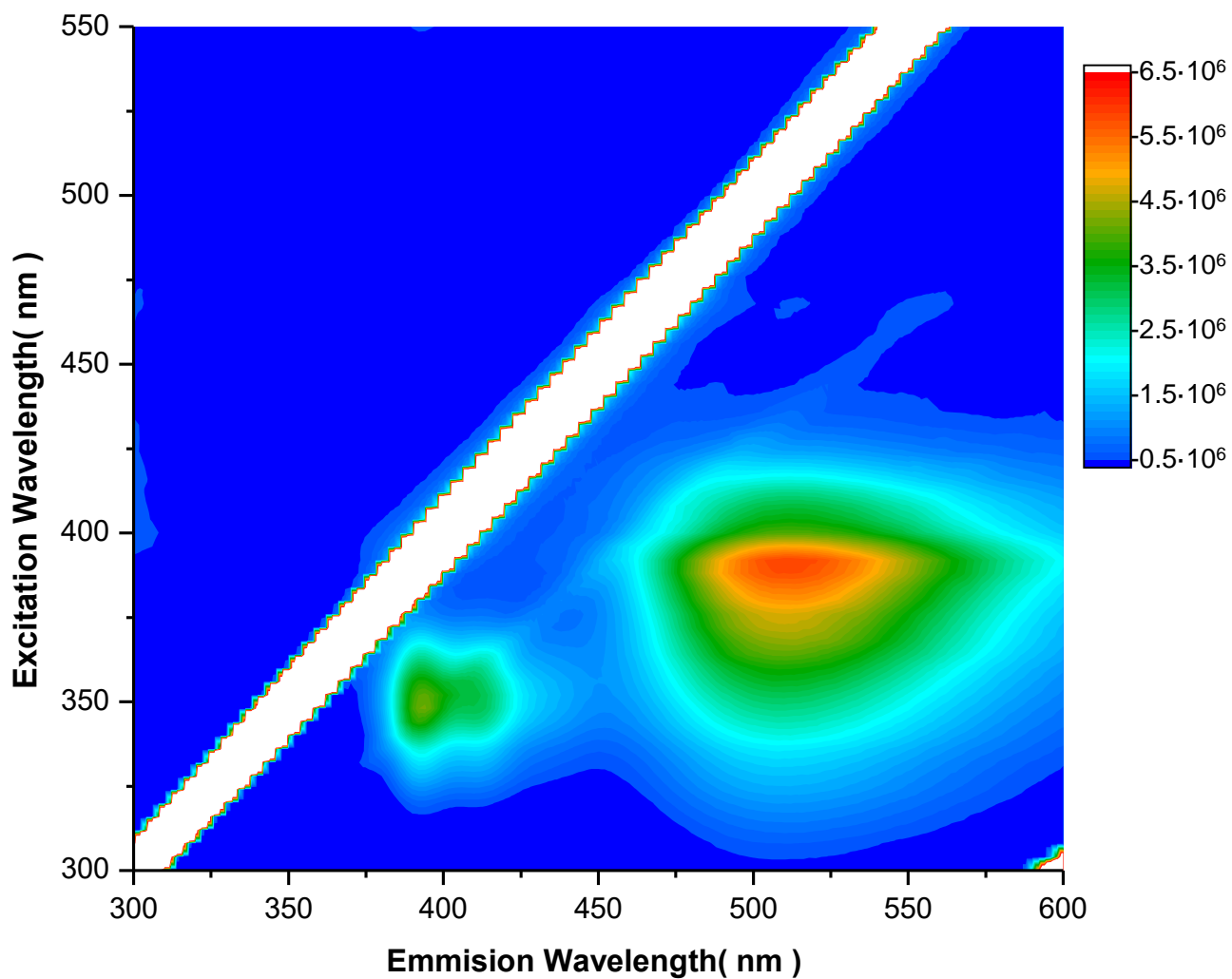


Figure S6.5. Excitation-Emission Matrix (EMM) spectra of **IMDEA-COF-1** suspension in water. The white stripe correspond to the Rayleigh scattering.

Section S7. Chemical Sensing Studies

Stock solutions of all organic dyes and nitroaromatic compounds, which structures are shown in figure S10.1, were prepared with Mili-Q water at 1×10^{-3} M.

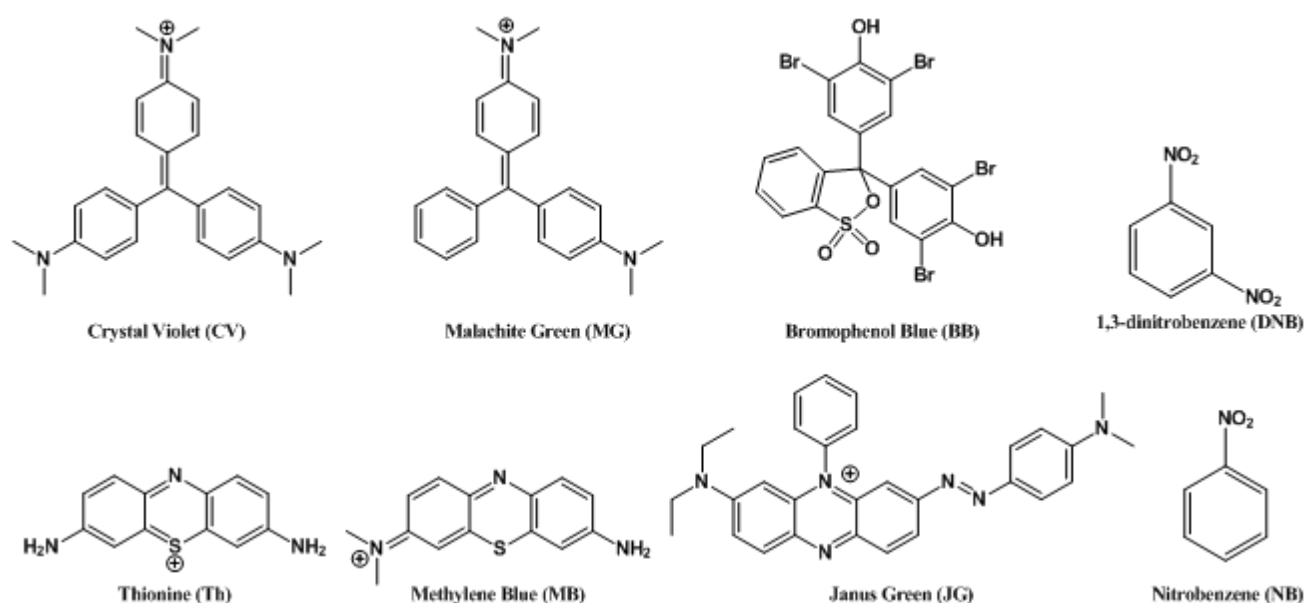


Figure S7.1. Molecular structure of organic dyes and nitroaromatic compounds tested.

IMDEA-COF-1suspension, obtained as is described in section S2, displayed emission maxima at ~ 510 nm upon excitation at 389 nm. Experiments were carried out by spectrofluoremetric titration method. The fluorescence titration experiments were performed by gradually increasing the nitroaromatic and dyes concentration and immediately measuring the emission spectra. Upon addition of analyte to the **IMDEA-COF-1**suspension at different concentration [0 to 1.07×10^{-4} (M)], the fluorescent intensity of the COF gradually decreased with the increasing concentration (Fig S7.2 and S7.3).

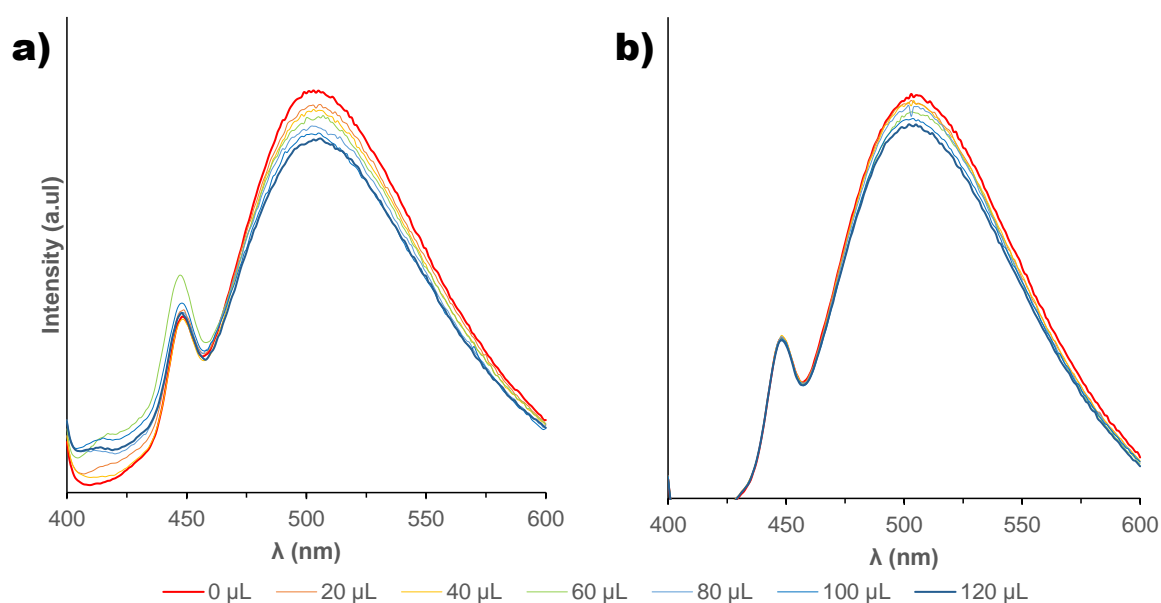


Figure S7.2. Fluorescence quenching of **IMDEA-COF-1** with (A) NB, (B) DNB.

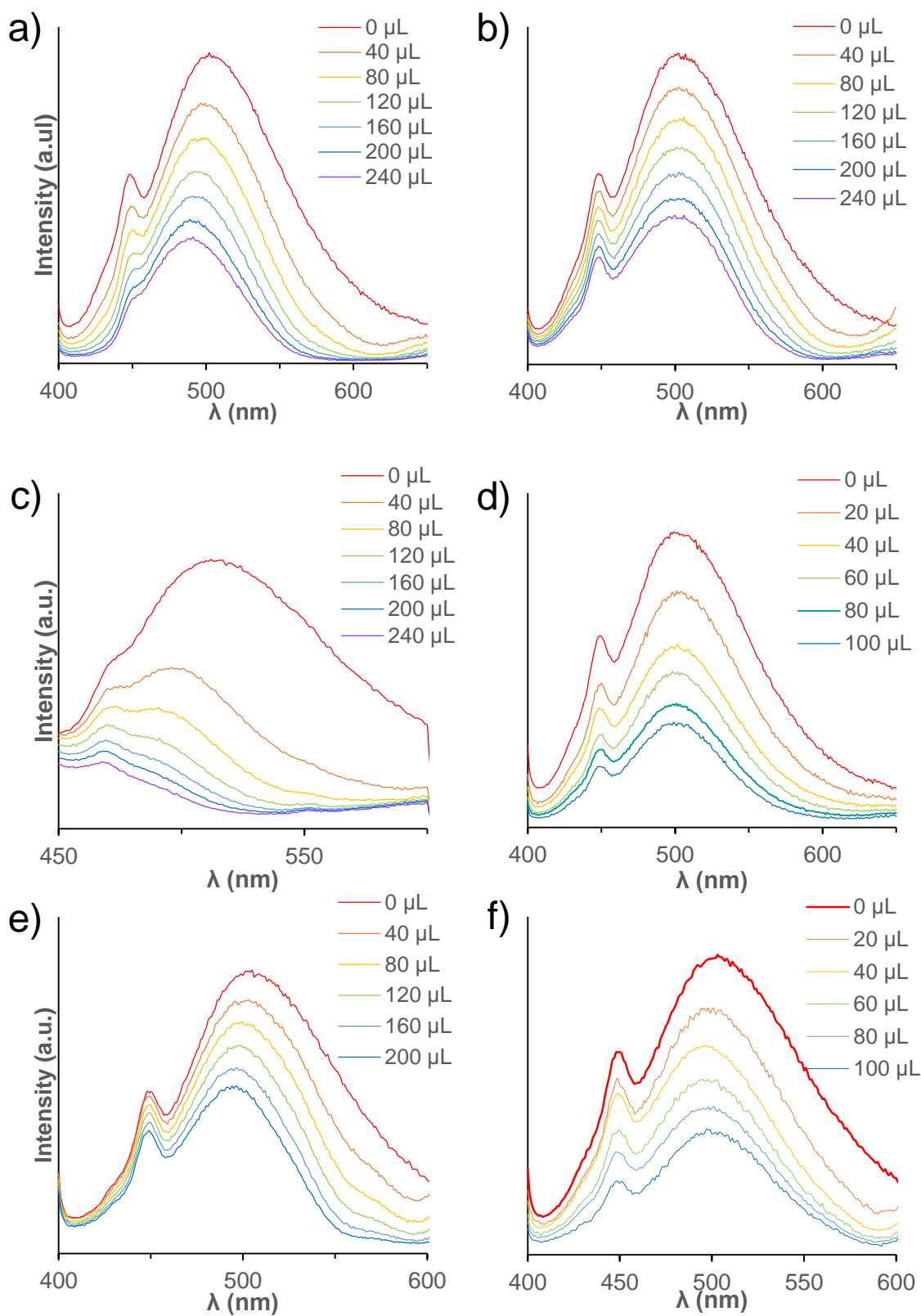


Figure S7.3. Fluorescence quenching of IMDEA-COF-1 with (A) MG, (B) MB, (C) JG, (D) CV, (E) Th and (F) BB, respectively.

The standard curve-linear fitting in the Stern–Volmer (SV) equation was employed to understand the quenching phenomena:

$$\frac{I_0}{I} = 1 + K_{SV} \cdot [Q]$$

Where I_0 is the fluorescence intensity when no quencher is present, I is the intensity with the quencher, K_{SV} is the Stern-Volmer constant $[Q]$ is the concentration of the quencher.

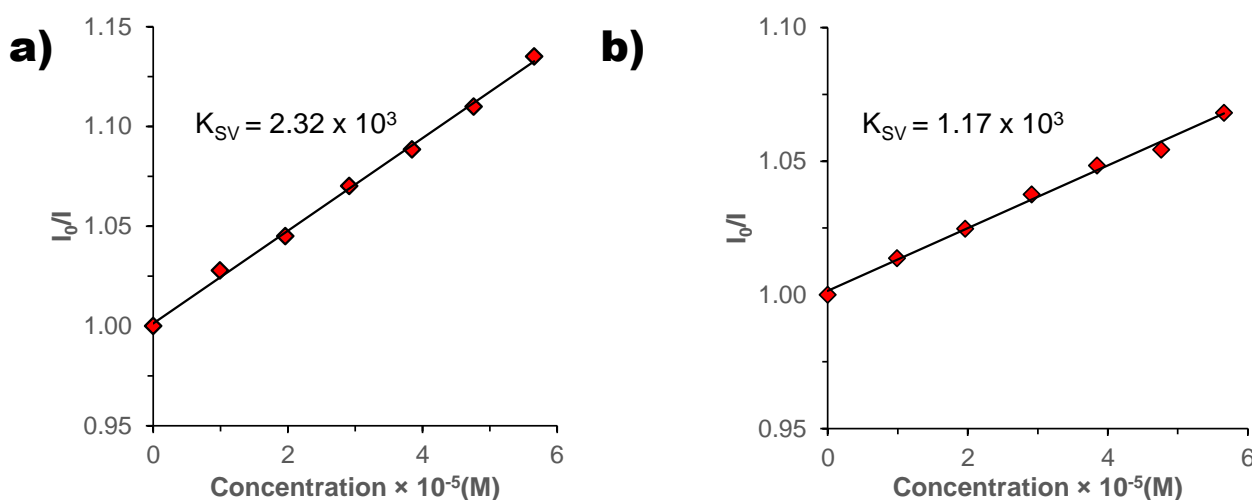


Figure S7.4. Stern-Volmer plots obtained from the titration of **IMDEA-COF-1** with (A) NB and (B) DNB.

On the linear part of the Stern-Volmer linear-curve fitting quenching percentage was calculated according to the formula:

$$\%Quenching = 1 - \frac{I_n}{I_0} \times 100$$

Where I_0 is the fluorescence intensity without quencher, I_n the fluorescence intensity of the sample with the highest quencher concentration with linear response still.

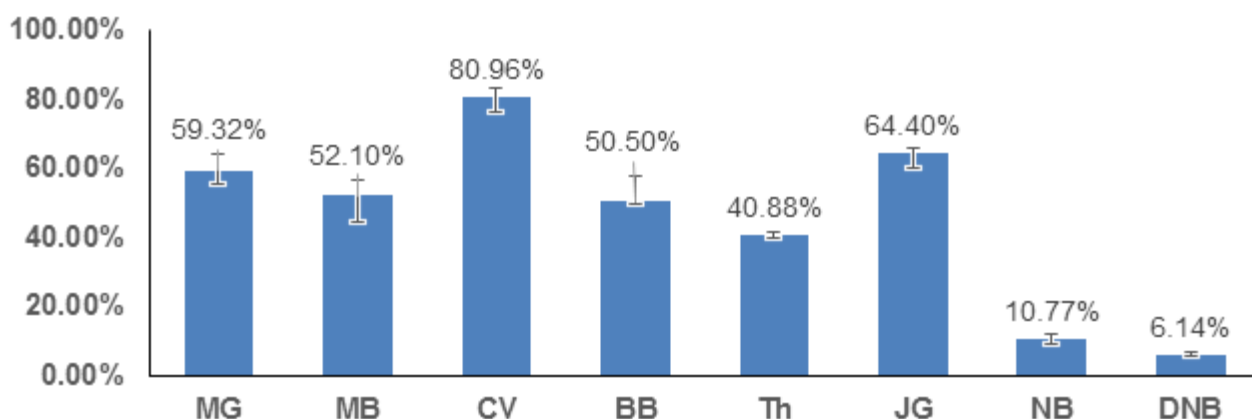


Figure S7.5. Percentage of fluorescence quenching of **IMDEA-COF-1** with analyte. Error bars correspond to the highest and lowest values observed.

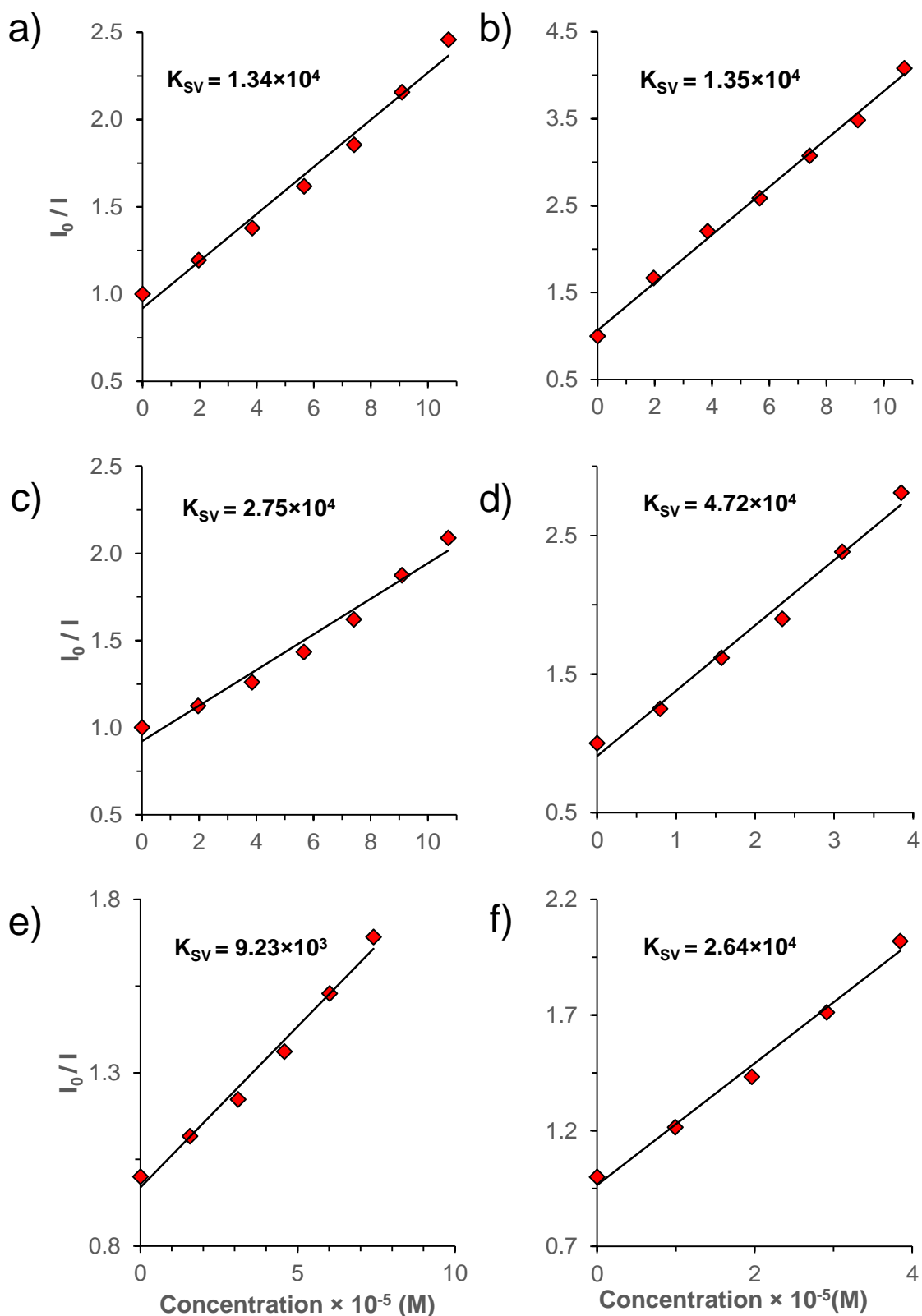


Figure S7.6. Stern-Volmer plots obtained from the titration of IMDEA-COF-1 with (A) MB, (B) MG, (C) CV, (D) JG, (E) Th and (F) BB, respectively.

Saturation point (ST) was measured by adding to the aqueous suspension of **IMDEA-COF-1** increasing amounts of the stock solution until quenching percentage only varies $\pm 0.1\%$ when another aliquot is added, assuming that the decrease in the fluorescence intensity is due to the dilution.

On the other hand, detection limit (DL) was calculated as $DL = 3.3 \cdot \sigma_0$ where σ_0 is the standard deviation of the blank, resulting on a dimensionless number which divided by the K_{SV} gives the DL in molarity units. Blank was measured by repeating the titration experiments adding to the **IMDEA-COF-1** suspension Milli-Q water instead of an analyte stock solution.

Analyte	MG	MB	CV	BB	Th	JG	NB	DNB
$K_{SV} (M^{-1})$	1.02×10^4	8.36×10^3	2.75×10^4	2.64×10^4	9.29×10^3	4.72×10^4	2.32×10^3	1.17×10^3
DL (M)	2.68×10^{-5}	3.55×10^{-5}	1.32×10^{-5}	1.37×10^{-5}	3.89×10^{-5}	7.66×10^{-6}	1.56×10^{-4}	3.09×10^{-4}
SP (M)	9.91×10^{-3}	1.23×10^{-3}	6.54×10^{-4}	9.09×10^{-6}	1.07×10^{-3}	2.91×10^{-3}	1.23×10^{-2}	2.54×10^{-3}

Table S6. Stern-Volmer constant, Detection Limit and Saturation Point of **IMDEA-COF-1** with the different analytes tested.

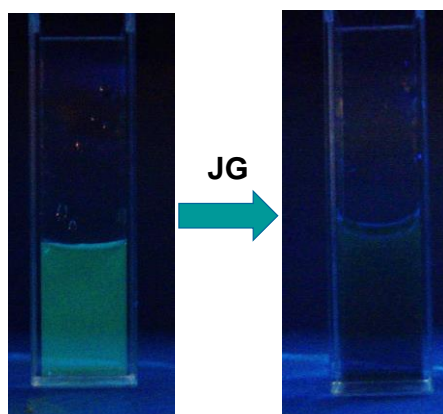


Figure S7.7. Fluorescence quenching of **IMDEA-COF-1** by addition of JG in water

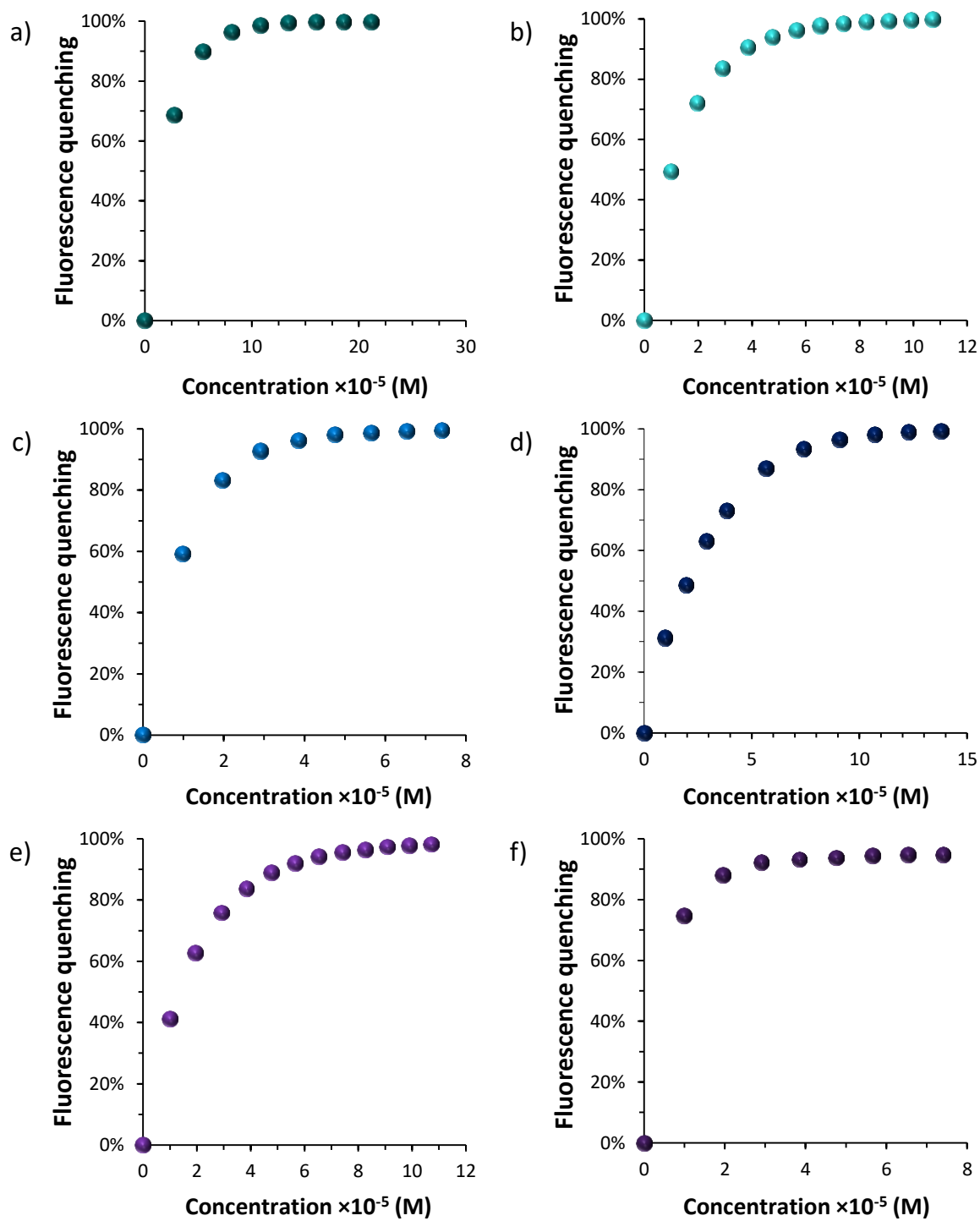


Figure S7.8. Saturation curves of IMDEA-COF-1 upon addition of JG (a), MG (b), BB (c), MB(d), Th(e) and CV (f) in water

References

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