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

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A two-dimensional imine-linked Covalent Organic Framework bearing pyrene has been prepared and exfoliated in water as nanosheets to produce a stable water colloid. This COF water colloid detects the presence of several organic dyes and polynitro-aromatic derivatives. These results show the high potential of these nanomaterials for applications in chemical sensing of pollutants directly in water.

The detection of environmental pollutants in water is an environmental priority. Developing reliable and quantitative determination methods is crucial for properly disposing contaminated environmental and biomedical materials.[1] The use of porous materials with flexible structures and designed pores, such as Metal-Organic Frameworks (MOFs)[2] and Porous Organic Polymers (POPs),[3, 4] have been explored as candidate materials for chemical sensing. Nevertheless, the sensitivity and selectivity of detection in these porous materials is still far from practical applications. Main limitations are associated with poor pollutant-host interactions on the amorphous POP surfaces, or the limited water stability of MOFs.

Covalent organic frameworks (COFs) are alternative porous frameworks for capturing compounds. They are light and crystalline porous materials resulting from the linking of purely organic subunits through covalent bonds. The selection of the building blocks allows predictable control over composition, topology and porosity.[5-10] Although mainly investigated for applications related to their porosity such as catalysis and gas
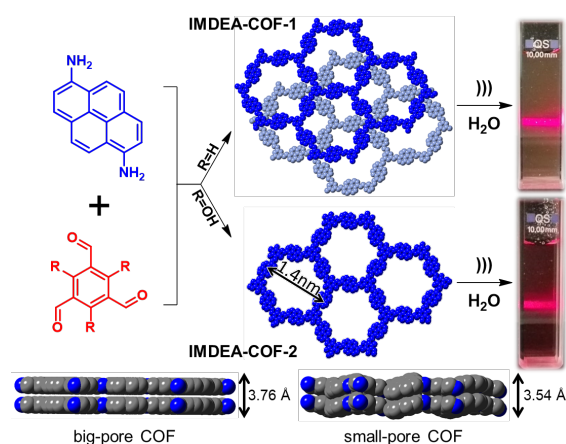
Figure 1. Schematic representation of the two-step procedure followed for the preparation of the water colloids of **IMDEA-COF-1** and **IMDEA-COF-2**, and the main stacking and pore-isomerism features of these structures. The Tyndall effect of the colloids obtained are shown.

storage,[5, 7, 9-19] the incorporation of pre-designed functional molecules within COF materials would open new horizons in chemical sensing, and optoelectronics.[20, 21]

Imine-linked COF materials, synthesised through Schiff condensation reactions, are remarkably chemically robust, thereby reinforcing the potential applications of COFs.[22] When COF constituents or building blocks are electronically switchable molecules (*e.g.* on/off depending on the occurrence of π-π interactions), the resulting materials are good candidates as chemical sensors. Thus, chemo-sensing ability for polynitro-aromatic compounds has been reported using a luminescent azine-linked COF where the azine sites serve as docking sites to lock guest molecules,[23] and a series of imine- or β-ketoenamine linked COFs containing triphenylbenzene as an inherently fluorescent platform.[24, 25] Finally, triazatruxene-based COFs have also recently shown a quick-response fluorescence-on and fluorescence-off nature towards electron rich and deficient arene vapours.[26]

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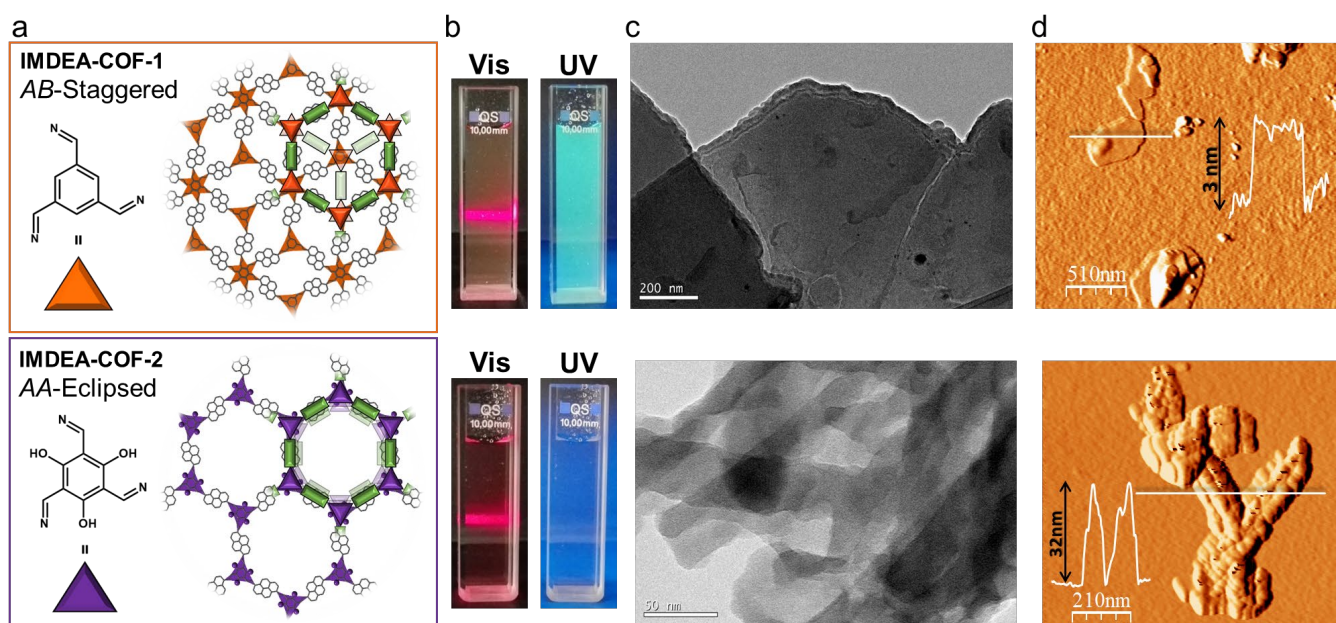
Figure 2. a) Structures of **IMDEA-COF-1** and **IMDEA-COF-2**. b) Emissive properties of the IMDEA-COF water colloids. c) TEM micrographies of representative nanosheets of COF-IMDEA-1 and -2 obtained from water colloid. b) Topographic AFM images of a drop-casted **COF-IMDEA-1** and **-2** water colloid on SiO$_2$ and its corresponding height profile along the represented lines.

To date, COFs have been mainly used to detect organics in organic solvents, while the detection in water still remains a challenge. To overcome this limitation, developing methods to prepare colloidal COFs in water is critical.[27] Our group has recently reported on a pyrene-decorated 2D-COF with layer-stacking-driven fluorescence in solid state.[28] We achieved control over staking by chemical modification of the COF layers, being the COF prepared either in an AA-eclipsed or AB-staggered conformation.

Herein we report the application of our pyrene-**IMDEA-COF** materials in the chemical sensing of pollutants directly in water. We describe the exfoliation of these materials and the formation of stable suspensions in water, suitable to interact and detect a variety of potential water contaminants such as organic dyes and nitro explosive derivatives.

The 2D-**IMDEA-COF** materials were synthesized following the reported procedure.[28] Due to the differences in chemistry of the constituent building blocks used to synthesize **IMDEA-COF-1** and **-2** (Figure 2a), the resulting materials show different stacking patters. This is mainly due to the different nature of the cohesive energy between layers. Thus, AB-staggered-stacking is the thermodynamically favoured structure for **IMDEA-COF-1**, while the AA-eclipsed conformer is observed for **IMDEA-COF-2**.

IMDEA-COF colloids were prepared *via* sonication of 1 mg of the solid in 25 mL of water. The so-formed water COF suspensions are stable for days and show Tyndall effect (Figure 2b), thereby demonstrating the colloidal nature. Dynamic Light Scattering (DLS) measurements showed a homogeneous particle size distribution of *ca.* 430 and 548 nm for **IMDEA-COF-1** and **-2**, respectively (Figure S6.1).

**Table 1.** Cohesive Energy Values (Ec) for the thermodynamically favoured big-pore COF conformations

COF	Stacking	E$_c$ (kcal mol^{-1})
IMDEA-COF-1	AB-staggered	-39.66
IMDEA-COF-2	AA-eclipsed	−48.20[a]/−46.81[b]

[a] Enol-imine form. [b] Keto-amine form.

The nano- and microstructure of the colloids was studied in detail by Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM), evidencing the formation of layers with lateral dimensions of hundreds of nanometres and a typical height of 3 nm for **IMDEA-COF-1** (Figure 2d). These layers characterized by TEM show a complex electron diffraction pattern (Figure S4.2), confirming the crystalline character of the COF-nanolayers after exfoliation (Figure 2c). In case of **IMDEA-COF-2**, colloids are composed of fibres, being the nano-layered nature of the material compromised (Figures 2c and 2d). This is in good agreement with our previous computational studies on these materials,[28] which indicated that the AA-eclipsed **IMDEA-**

COF-2 is more strongly stacked than its counterpart AB-staggered **IMDEA-COF-1**, with a difference of *ca.* 8 kcal mol^{-1} (Table 1). We hypothesize that the higher interaction among layers in **IMDEA-COF-2** favours hydrolysis reactions in water, giving the micro-sized nanofibers overserved (Figure S6.4).

The fluorescence properties of the COF colloids were assessed to explore their potential use as chemical sensors. Thus, emission and absorption spectra of **IMDEA-COF-1** were measured in water suspensions. Upon excitation at 350 nm, **IMDEA-COF-1** water colloids show maxima emission at ~389 nm together with a broad featureless contribution at ~510 nm, indicative of the formation of pyrene excimer species. The formation of pyrene excimers upon excitation can be altered or even cancelled by intercalation of suitable aromatic compounds, which has been exploited in the construction of chemical sensors.[29-31] The counterpart **IMDEA-COF-2** colloid, composed of nano-fibers instead of nano-layers as found for **IMDEA-COF-1,** showed absence of fluorescence properties. These results demonstrated that the COF nanostructure is retained for **IMDEA-COF-1** in water using exfoliation methods.
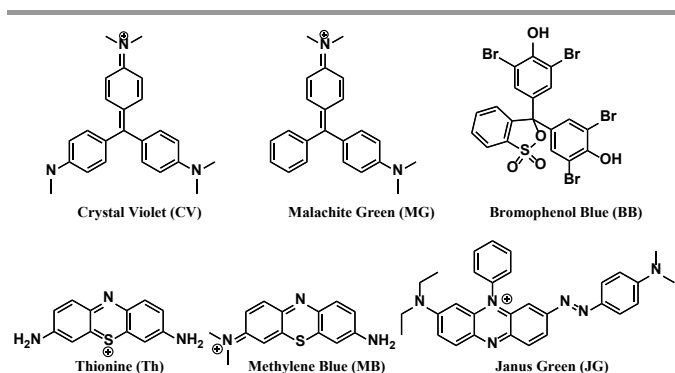

Scheme 1. Schematic representation of organic dyes used in this work.

Despite the successful obtaining of colloidal 2D boronate ester-linked COFs in acetonitrile has been recently reported,[27] the preparation of stable COF colloids in water provides new opportunities for removal of organic pollutants. Considering these features and the lack of research about COFs applications in water, we decided to study the sensing behaviour of **IMDEA-COF-1** in water with different organic pollutants and organic dyes (Scheme 1 and ESI for details): nitrobenzene (NB), dinitrobenzene (DNB), methylene blue (MB), malachite green (MG), janus green (JG), bromophenol blue (BB), crystal violet (CV) and thionin (Th).

The colloidal **IMDEA-COF-1** nano-layers show remarkable chemical sensing properties towards a variety of organic dyes (Scheme 1). Experiments were performed using solutions containing the organic dyes in 1.00×10^{-3} M concentration. Fluorescence emission of colloidal **IMDEA-COF-1** is immediately quenched upon addition of increasing amounts of analyte solution, indicating disruption of the excimer formation. **IMDEA-COF-1** fluorescence emission intensity was significantly quenched upon the addition of dyes solution and exhibit its maximum 81% towards CV at 1.40×10^{-4} M over other dyes (MB: 59%, JG: 64%, MG: 59%, BB: 51% and Th: 41%). The standard linear curve-fitting in the Stern-Volmer (SV) equation was

employed to measure the quenching phenomena. The highest value of Stern-Volmer constant was found to be for JG, 4.72×10^4 M^{-1}, and are in the order JG >CV> BB > MG > Th > MB. These values are close to others recently reported for similar imine-linked COFs but in those cases experiments were carried out in organic solvents.[2]

Related luminescence spectrometric titration experiments using **IMDEA-COF-1** colloids were also performed for the chemical sensing of di- and nitrobenzene at 1.00×10^{-3} M concentration. It was found that **IMDEA-COF-1** was notably sensitive and 22% quenching efficiency was achieved towards NB addition at 5.66×10^{-5} M over DNB (17%). To quantify the quenching phenomena, standard linear curve-fitting in the Stern Volmer (SV) equation was employed. The quenching constant for NB was found to be 2.32×10^3 M^{-1} while DNB K$_{SV}$ was 1.17×10^3. To verify the goodness of these linear fits, we performed multiwavelength analysis using reactlab, which afforded log K_a values of 2.4 ± 0.1 and 3.14 ± 0.02 for NB and DNB, respectively, in agreement with the calculated K$_{SV}$.
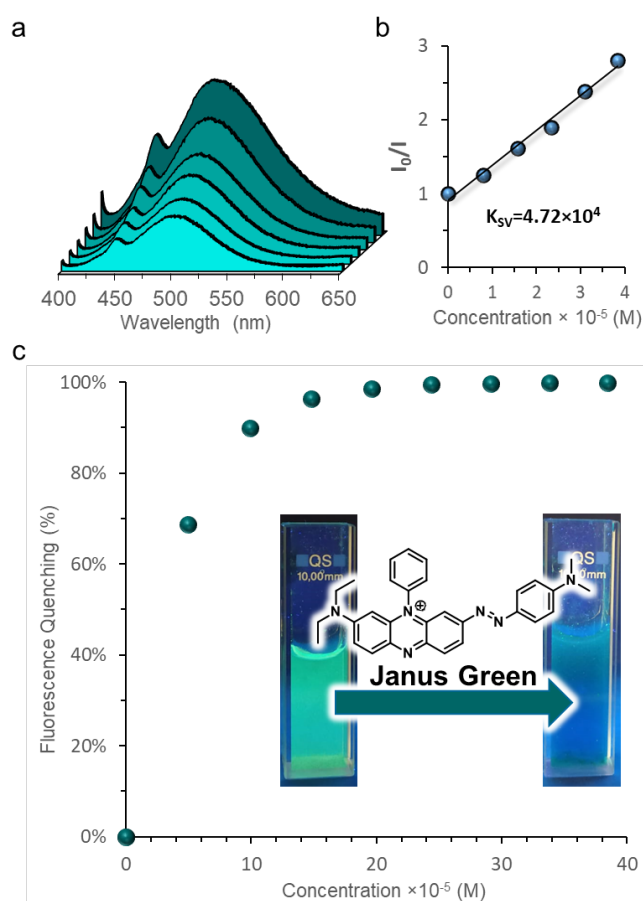
Figure 3. a) Photoluminescence quenching of **IMDEA-COF-1** water colloid upon addition of Janus Green. b) Stern–Volmer plot for the quenching of **IMDEA-COF-1** by Janus Green. c) Quenching data showing vial with **IMDEA-COF-1** water colloid irradiated with UV light before (left) and after (right) Janus Green was added.

In summary, a colloidal two-dimensional pyrene-decorated imine-linked COF material was successfully obtained in water. The **IMDEA-COF-1** material can be easily exfoliated in water upon sonication to originate a stable water colloid formed by

nano-sheets of *ca*. 3 nm thickness and over hundreds of nm in lateral dimensions. This colloidal COFs retain the nanostructure in water therefore, the layer-stacking-driven fluorescence determined in solid-state is kept in water. The easier processibility of the **IMDEA-COF-1** as nano-sheets compared to its counterpart **IMDEA-COF-2** agrees with theory, which indicates a significant difference of *ca*. 8 kcal mol^{-1} in cohesive energies. These results prove that calculated cohesive energies values can be used as a predictive computational tool to assess the feasibility of exfoliation against hydrolysis in COFs. The colloidal **IMDEA-COF-1** is active as chemical-sensor and can detect presence of several organic dyes and polynitro-aromatic derivatives in water. Importantly, this work represents the first example of an imine-based colloidal COF in water.[27] The obtained results show the high potential of water suspensions containing nanostructured COF materials for applications in chemical sensing of pollutants. These results also open new perspectives for potential applications of COFs water colloids as nanocarriers for biomedical applications.

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