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Bifunctional Porphyrin-Based Nano-Metal–Organic Frameworks: Catalytic and Chemosensing Studies

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Supporting Information

ABSTRACT: The use of 5,10,15,20-tetrakis(*p*-phenylphosphonic acid)porphyrin (H_{10} **TPPA**) as a linker in the preparation of porphyrin-based metal-organic frameworks (Por-MOFs) through coordination to lanthanides cations is reported. The resulting unprecedented materials, formulated as $[M(H_9\text{TPPA})(H_2O)_x]Cl_2\cdot yH_2O$ [x + y = 7; $M^{3+} = La^{3+}$ (1), Yb³⁺ (2), and Y³⁺ (3)], prepared using hydrothermal synthesis, were extensively characterized in the solid-state, for both their structure and thermal robustness, using a myriad of solid-state advanced techniques. Materials were evaluated as heterogeneous catalysts in the oxidation of thioanisole by H_2O_2 and as chemosensors for detection of nitroaromatic compounds (NACs). Nano-Por-MOFs 1–3 proved to be effective as heterogeneous catalysts in the sulfoxidation of thioanisole, with Por-MOF 1 exhibiting the best catalytic performance with a conversion of thioanisole of 89% in the first cycle and with a high selectivity for the sulfoxide derivative (90%). The catalyst maintained its activity roughly constant in three consecutive runs. Por-MOFs 1–3 can be employed as chemosensors because of a measured fluorescence quenching up to 70% for nitrobenzene,



1,4-dinitrobenzene, 4-nitrophenol, and phenol, with 2,4,6-trinitrophenol exhibiting a peculiar fluorescence profile.

■ INTRODUCTION

Metal–organic frameworks (MOFs) nowadays constitute an outstanding class of crystalline materials.^{1–6} These materials are prepared from metal ions or cluster nodes and organic linkers, and because of the endless number of potential combinations between these units, it is easy to imagine the large structural diversity which can be attained. Examination of the various organic linkers employed in the preparation of MOFs shows that porphyrins (Pors) are a fascinating niche in the wide spectrum of MOFs world: porphyrin-based metal–organic frameworks (Por-MOFs).^{7–10} This niche has received increased attention in the past decade because of two main driving forces: Pors have intrinsically remarkable properties,¹¹ and their pivotal role in nature in diverse biological functions is also well-known.^{12–17}

In this sense, the preparation of Por-MOFs to mimic biological functions is of great interest.^{18–20} Por-MOFs have already demonstrated their potential as promising materials for a variety of applications which include, but are not limited to, catalysis,^{7,18–21} gas separation and storage, and light harvesting.^{7,9,22} Our research group has been focused on the development of new MOFs based on linkers bearing phosphonic acid groups coordinated to lanthanide cations.^{23–28} In this manuscript, we describe our most recent efforts to

extend our research to porphyrins in order to prepare novel

materials with peculiar properties and architectures. We employ a new synthetic strategy to obtain $H_{10}TPPA$ (5,10,15,20tetrakis(p-phenylphosphonic acid)porphyrin) which was used for the hydrothermal preparation of the novel materials $[M(H_{9}TPPA)(H_{2}O)_{x}]Cl_{2}\cdot yH_{2}O$ [where x + y = 7; $M^{3+} =$ La^{3+} (1), Yb^{3+} (2), and Y^{3+} (3)] through reaction with the chloride salts of the corresponding lanthanides. We notice, however, that this niche of MOFs remains highly dominated by porphyrins bearing carboxylic/pyridyl moieties which mainly coordinate to transition metals.¹⁰ Therefore, to the best of our knowledge, the present report constitutes the very first study of Por-MOFs comprising a porphyrin functionalized with phosphonic acids as a building block. As in the past, we observed that the isolated products are mainly poorly crystalline materials, typically isolated as powders because of the fast rate of crystal nucleation.^{29,30} We have successfully isolated and characterized 1-3 as nanopowders which proved to simultaneously be effective heterogeneous catalysts in the oxidation of thioanisole by H2O2 and chemosensors for detection of nitroaromatic compounds (NACs) (NB, nitrobenzene; DNB, 1,4-dinitrobenzene; 4-NP, 4-nitrophenol; and TNP, 2,4,6trinitrophenol).

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EXPERIMENTAL SECTION

Chemicals. Pyrrole; boron trifluoride diethyl etherate at \geq 46% boron trifluoride basis; 4-bromobenzaldehyde dimethylacetal of analytical grade; LaCl₃·7H₂O, YbCl₃·6H₂O, and YCl₃·6H₂O (99.9%); hydrochloric acid (37%), thioanisole; and hydrogen peroxide (30% w/ w, Perdrogen aqueous solution) were obtained from Sigma-Aldrich. Bromotrimethylsilane (TMS-Br) and Pd(PPh₃)₄ of analytical grade were obtained from TCI. KBr for infrared spectroscopy was obtained from BDH SpectrosoL. All chemicals were used as received without further purification, except for the pyrrole which was subjected to distillation prior to use.

Instrumentation. ¹H, ¹³C, and ³¹P nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III 300 spectrometer at 300.13, 125.77 or 75.47, and 121.49 MHz, respectively. Deuterated chloroform or dimethyl sulfoxide- d_6 were used as solvents, and tetramethylsilane or H₃PO₄ (85%) were used as internal references. Chemical shifts (δ) are expressed in ppm and the coupling constants (*J*) in Hz. Mass spectra were collected on a MALDI-TOF/TOF 4800 Applied Biosystems equipment for 5,10,15,20-tetrakis(*p*-(diethoxyphosphoryl)phenyl)porphyrin (H₂TPPE) and collected on a ESI-Q-TOF/TOF Micromass equipment for 4-(diethoxyphosphoryl)benzaldehyde dimethylacetal.

³¹P {¹H} CP MAS spectra were recorded at 9.4 T on a Bruker Avance 400 wide-bore spectrometer (DSX model) on a 4 mm BL cross-polarization magic-angle spinning (CPMAS) VTN probe. For the ³¹P HPDEC spectra, a 90° single pulse excitation of 3.0 μ s was employed; recycle delay: 60 s; $\nu_{\rm R}$ = 8 or 12 kHz. Chemical shifts are quoted in parts per million (ppm) with respect to an 85% H₃PO₄ solution for ³¹P.

Fourier Transform Infrared (FT-IR) spectra in the range of 4000– 350 cm⁻¹ were collected as KBr pellets (2 mg of each sample was milled in a mortar with approximately 200 mg of KBr) using a Bruker Tensor 27 spectrometer by averaging 256 scans at a maximum resolution of 2 cm⁻¹. ATR-FTIR spectra were collected using a FT-IR Bruker Tensor 27 with a ATR accessory (Golden Gate ATR Diamond 45° with KRS-5 Lens, from SPECAC), averaging 256 scans at a maximum resolution of 2 cm⁻¹.

Thermogravimetric analyses (TGA) were performed using a Shimadzu TGA 50 equipment from ambient temperature to ca. 350 °C, with a heating rate of 2 °C/min, under a continuous stream of air at a flow rate of 20 cm³/min.

Elemental analyses for C, H and N were performed with a Truspec Micro CHNS 630–200–200 elemental analyzer at the Department of Chemistry, University of Aveiro. Analysis Parameters: sample amount between 1 and 2 mg; combustion furnace temperature = $1075 \,^{\circ}C$; after burner temperature = $850 \,^{\circ}C$. Detection methods: carbon, infrared absorption; hydrogen, infrared absorption; nitrogen, thermal conductivity. Analysis time = 4 min. Gases required: carrier, helium; combustion, oxygen; pneumatic, compressed air.

SEM (scanning electron microscopy) images were collected using either a Hitachi S-4100 field-emission gun tungsten filament instrument working at 25 kV or a scanning electron microscope SU-70 working at 15 kV. EDS (energy-dispersive X-ray spectroscopy) data was collected using a Esprit 1.9 EDS microanalysis systems. Samples were prepared by deposition on aluminum holders followed by carbon coating using an Emitech K950X carbon evaporator.

Powder X-ray diffraction (PXRD) data were collected at ambient temperature on an Empyrean PANalytical diffractometer (Cu K $\alpha_{1,2}$ X-radiation, $\lambda_1 = 1.540598$ Å; $\lambda_2 = 1.544426$ Å), equipped with a PIXcel 1D detector and a flat-plate sample holder in a Bragg–Brentano parafocusing optics configuration (45 kV, 40 mA). Intensity data were collected by the step-counting method (step 0.01°), in continuous mode, in the ca. $3.5^{\circ} \leq 2\theta \leq 50^{\circ}$ range.

Variable-temperature powder X-ray diffraction data were collected on an PANalytical X'Pert Powder diffractometer (Cu K $\alpha_{1,2}$ X-radiation $\lambda_1 = 1.540598$ Å; $\lambda_2 = 1.544426$ Å), equipped with an PIXcel 1D detector, and a flat-plate sample holder in a Bragg–Brentano parafocusing optics configuration (40 kV, 50 mA), and a high-temperature Anton Paar HKL 16 chamber controlled by an Anton Paar 100 TCU unit. Intensity data were collected in the continuous mode (ca. 100 s data acquisition) in the angular range ca. $3.5^{\circ} \le 2\theta \le 50^{\circ}$.

Absorption and fluorescence spectra were recorded using a Shimadzu UV-2501-PC and FluoroMax3 (Horiba JovinYvon), respectively.

Materials Preparation. Reactive mixtures composed of H_{10} TPPA (0.0125 g; 0.013 mmol; see Scheme 1 and the structural character-

Scheme 1. Synthetic Route for the Preparation of $H_{10}TPPA^{a}$



^a(i) Diethylphosphite, Et₃N/toluene, 7 mol% Pd(PPh₃)₄, mW (80 °C; 100 psi; 45 W; 45 min.). (ii) (a) pyrrole, BF₃OEt₂, CH₂Cl₂, r.t., 8 h; (b) DDQ, 1 h. (iii) (a) TMS-Br, CH₃CN, 70 °C, 7 days, (b) H₂O.

ization of all compounds in Supporting Information section 1) and the respective metal(III) chloride hydrate (LaCl₃·7H₂O, YbCl₃·6H₂O, or YCl₃·6H₂O; 0.040 mmol) in ca 9.5 mL of distilled water and 500 μ L of hydrochloric acid at 6 M were kept under constant magnetic stirring in open air and at ambient temperature for approximately 30 min. The isolated homogeneous suspensions were transferred to Teflon-lined Parr Instrument reaction vessels and then placed inside a MMM Venticell oven. Reactions took place at 140 °C over a period of 72 h, after which the oven was turned off and the reactors cooled slowly to ambient temperature (while inside the oven). The resulting porphyrinbased nano-MOFs were obtained as dark green powders and recovered by centrifugation, washed with copious amounts of distilled water, and then air-dried at ambient temperature.

[*La*(*H*₉*TPPA*)(*H*₂*O*), *J*[*I*₂, *yH*₂*O* (1) [*where* x + y = 7]. Elemental CHN composition (%). Calcd: C 41.36; H 4.34; N 4.39. Found: C 42.04; H 4.23; N 4.67. Thermogravimetric analysis (TGA) data (weight losses in %) and derivative thermogravimetric peaks (DTG; in italics inside the parentheses): 25–179 °C, -10.6% (38 °C); 179–350 °C, -5.3% (322 °C). Selected FT-IR data (cm⁻¹, from KBr pellets): ν (H₂O) = 3600–3158; ν (N–H) = 3158–2911w-m; ν (POH) = 2911–2688 w-m; δ (H₂O) = 1633 m; δ (phenyl–P) = 1550 m, 1484 m, and 1394m; ν (P=O) = 1265–1093 m-vs; ν (P–O) = 1093–757 vs; ν (phenyl) = 582 m, 570 m, and 522 m.

[*Yb*(*H*₉*TPPA*)(*H*₂*O*)_{*x*}]*Cl*₂·*yH*₂*O* (2) [*where* x + y = 7]. Elemental CHN composition (%). Calcd: C 40.29; H 4.23; N 4.27. Found: C 39.01; H 4.14; N 4.37. Thermogravimetric analysis (TGA) data (weight losses in %) and derivative thermogravimetric peaks (DTG; in italics inside the parentheses): 25–186 °C, -9.6% (44 °C); 186–350 °C, -5.2% (310 °C). Selected FT-IR data (cm⁻¹, from KBr pellets): ν (H₂O) = 3600–3154; ν (N–H) = 3154–2917 w-m; ν (POH) = 2917–2678 w-m; δ (H₂O) = 1633 m; δ (phenyl–P) = 1550 m, 1484 m, and 1394 m; ν (P=O) = 1261–1101 m-vs; ν (P–O) = 1101–779 vs; ν (phenyl) = 584 m, 570 m, and 526 m.

[*Y*(*H*₉*TPPA*)(*H*₂*O*)_{*x}*]*C*[₂·*yH*₂*O* (3) [*where* x + y = 7]. Elemental CHN composition (%). Calcd: C 43.04; H 4.52; N 4.56. Found: C 42.86; H 4.03; N 4.41. Thermogravimetric analysis (TGA) data (weight losses in %) and derivative thermogravimetric peaks (DTG; in italics inside the parentheses): 25–188 °C, -11% (38 °C); 188–350 °C, -5.6% (301 °C). Selected FT-IR data (cm⁻¹, from KBr pellets): ν (H₂O) = 3600–3166; ν (N–H) = 3166–2921 w-m; ν (POH) = 2921–2663 w-m; δ (H₂O) = 1631 m; δ (phenyl–P) = 1550 m, 1484 m, and 1394 m; ν (P==O) = 1263–1097 m-vs; ν (P–O) = 1097–755 vs; ν (phenyl) = 584 m, 570 m, and 524 m.</sub>

Catalytic Studies. In a typical experiment, CH₃CN (2.0 mL) was charged with thioanisole (0.3 mmol) and the catalyst (2 mol %); hydrogen peroxide (30% w/w, Perdrogen aqueous solution) was then added to the previous mixture (2 equiv). Reactions were carried out under constant magnetic stirring and in the absence of light at 50 $^\circ\text{C}.$ Prior to reuse, solid catalysts were separated from the reaction mixture by centrifugation at 6000 rpm, washed with acetonitrile and ethanol, and dried overnight at ambient temperature. Leaching tests were carried out using the reaction conditions mentioned above. When a conversion up to 40% was reached, the solid catalyst was filtered through a 0.20 μ m nylon GVS membrane. The filtrate was transferred to a preheated (50 °C) flask and left to react for further 20 h at the same temperature and in the absence of light. Reactions were followed by GC-FID analyses performed on a Varian 3900 chromatograph using helium as the carrier gas (30 cm/s). GC-MS analyses were performed using an Agilent 6890 gas chromatograph equipped with a mass selective detector (MSD 5973) with electron impact ionization (EI) operating at 70 eV (Agilent Technologies, California, USA). Fused silica DB-5 type capillary columns (30 m \times 0.25 mm i.d.; 0.25 μ m film thickness) were employed in both cases. The gas chromatographic conditions were as follows: initial temperature of 40 °C during 4 min; final temperature of 250 °C with a temperature rate of 25 °C/min; injector temperature of 250 °C; detector temperature of 250 °C. Aliquots were withdrawn from the reaction mixtures and injected directly into the GC injector.

Chemosensing Studies. A 1 mg sample of each Por-MOF (1-3) was dispersed in 3 mL of distilled water. The solution was sonicated for 10 min and used as a stock solution. Then, 100 μ L of the stock solution was taken in a 3 mL of quartz cuvette, and a magnetic bar was placed inside. The mixture was stirred for 1 min to obtain a uniform suspension. Different analytes such as nitroaromatic compounds and phenols were prepared as 1 mM solution. The emission spectra of the suspension were collected before and after the addition of the analyte solution.

RESULTS AND DISCUSSION

Materials Preparation. Por-MOF synthesis started with the design of a more efficient synthetic pathway for the isolation of the organic linker H_{10} TPPA (Scheme 1). The main objective was to isolate the molecule in high yields and in short periods of time.

The first synthetic stage of the new procedure involves the isolation of 5,10,15,20-tetrakis(p-(diethoxyphosphoryl) phenyl)porphyrin (H₂TPPE) based on the Lindsey methodology, 31,32 comprising the condensation of 4-(diethoxyphosphoryl)benzaldehyde dimethylacetal obtained by Hirao cross-coupling³³ and pyrrole, in the presence of BF₃·(OEt)₂, followed by oxidation performed by 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). We stress that this new procedure is significantly more efficient when compared to those reported in the literature,^{34,35} with H₂TPPE being here obtained with a best overall yield (28%) and with a concomitant drastic reduction in the overall reaction time from 2 days (overall yield of 7%),³⁴ or even 68 h (overall yield of 7%),³⁵ to just 9 h (see Scheme 1 and the Supporting Information for further details).

 $H_{10}TPPA$ was obtained in 94% yield from H_2TPPE using the Rabinowitz methodology,^{34,36} typically characterized by the cleavage of the protecting groups through interaction with chlorine or bromine-trialkylsilanes to yield the corresponding trialkylsilyl esters which, in turn, can be readily hydrolyzed to afford the phosphonic acid form.

The isolation of materials $[M(H_9TPPA)(H_2O)_x]Cl_2\cdot yH_2O$ [where x + y = 7; $M^{3+} = La^{3+}$ (1), Yb^{3+} (2), and Y^{3+} (3)] was achieved by employing hydrothermal synthesis using HCl (6 M) as modulator. Systematic modifications in the experimental conditions, namely, temperature and ratios between the metal sources and H_{10} TPPA did not produce any effect on the overall crystallinity, purity, or even in the main structural features of the compounds. All materials were extensively characterized using a myriad of advanced techniques which include PXRD, SEM, STEM, UV–vis, FT-IR, and elemental analysis. Please see Figures S5–S13 for an extensive detailed characterization of the materials.

Figure 1 collects the PXRD patterns of the Por-MOFs and the corresponding SEM images. The particle size of Por-MOFs



Figure 1. (a) Optical photographs of bulk $[M(H_9TPPA)(H_2O)_x]Cl_2$. yH_2O materials; (b) powder X-ray diffraction data and SEM images of $[M(H_9TPPA)(H_2O)_x]Cl_2 \cdot yH_2O$ materials [where x + y = 7; $M^{3+} = La^{3+}$ (1), Yb³⁺ (2), or Y³⁺ (3)]. Color code: red, 1; black, 2; green, 3.

materials 1–3 was determined by the Williamson–Hall method (see Supporting Information section 2.3 for details).^{37,38}

The average crystallite sizes were determined as ca. 13 (\pm 1), 17 (\pm 2), and 15 (\pm 2) nm for 1, 2, and 3, respectively. We note that these average values are in good agreement with the crystal shape and size observed from STEM studies as depicted in Figure 2.

Catalytic Studies. Nano-Por-MOFs materials (1-3) revealed to be effective catalysts in sulfoxidation through green and sustainable procedure. We note that this type of reaction is of great industrial and environmental importance because of the negative impact induced by the presence of sulfur-containing compounds in petroleum products.^{39–45} Remarkably, and to the best of our knowledge, there are only two examples of Por-MOFs reported in the literature which are efficient catalytic systems for the oxidation of organosulfur compounds.^{46,47}

The evaluation of the catalytic activity of materials 1–3 in sulfoxidation was based on previous studies developed in our laboratories.^{48,49} Acetonitrile was employed as the solvent and H_2O_2 as the oxidant (see Supporting Information section 3.1 for the optimization procedure of the catalytic studies). We note that H_2O_2 is the most common oxidant used in the oxidation of sulfur-containing compounds, being considered a



Figure 2. STEM images of: (a) $[La(H_9TPPA)(H_2O)_x]Cl_2\cdot yH_2O$ (1); (b) $[Yb(H_9TPPA)(H_2O)_x]Cl_2\cdot yH_2O$ (2), and (c) $[Y(H_9TPPA)-(H_2O)_x]Cl_2\cdot yH_2O$ (3) [where x + y = 7].

cheap and green oxidant with $\rm H_2O$ being obtained as the sole byproduct. $^{\rm 50,51}$

Because the oxidation reaction of organosulfur compounds proceeds via electrophilic addition of oxygen atoms, sulfides with higher electron density on the sulfur should react more readily, which motivated us to select thioanisole as substrate. The obtained results for the sulfoxidation of thioanisole by H_2O_2 , using the nano-Por-MOFs (1–3) as catalysts, as well as the corresponding building blocks, in acetonitrile at 50 °C are summarized in Table 1.

The catalytic efficiency of the nano-Por-MOFs follows the order 1 > 3 > 2, with average conversions of 89, 79, and 68%, respectively (Table 1). In all cases, a selectivity up to or equal to 90% with respect to the sulfoxide product was observed. The kinetic profiles are depicted in Figure 3. This order of catalytic efficiency agrees well with the observed average crystallite size: Por-MOF (1) has smallest average crystallite size and, consequently, the largest surface area with a concomitant higher availability of catalytic sites to perform the reaction. In the absence of catalyst, and under similar reaction conditions, only 29% of conversion was reached after 24 h.

For comparative purposes, the catalytic activities of the building units were also investigated (LaCl₃·7H₂O, YbCl₃· $6H_2O$, YCl₃· $6H_2O$ and H₁₀TPPA), using equivalent molar

Table 1. Catalytic Activity of the Nano-MOFs 1–3 and of the Corresponding Building Units in the Oxidation of Thioanisole with $H_2O_2^{\ a}$

Catalyst	Conversion (%)	Yield (<i>Selectivity</i>), both in %		
		O S CH ₃	O S CH3	O S CI
1	89	80 (90)	9 (10)	-
2	68	63 (93)	5 (7)	-
3	79	74 (94)	5 (6)	-
LaCl ₃ .7H ₂ O	75	60 (80)	14 (19)	1(1)
YbCl ₃ .6H ₂ O	83	44 (53)	36 (43)	3 (4)
YCl ₃ .6H ₂ O	86	61 (71)	23 (27)	2 (2)
H ₁₀ TPPA	99	96 (97)	3 (3)	-

^{*a*}Thioanisole (0.3 mmol) was dissolved in 2.0 mL of CH₃CN and kept under magnetic stirring at 50 °C for 24 h, in the presence of 2 mol % of catalyst and 2 equiv of H_2O_2 .



Figure 3. Kinetic profiles for the oxidation of thioanisole (0.3 mmol) by H_2O_2 using Por-MOFs 1–3 as catalysts.

ratios (Figure S14). The presence of sulfoxide and sulfone products were observed in all cases. We note that in the studies involving the metal salts, another reaction product was also detected and identified by GC-MS as a chlorine derivative of the sulfoxide (Figure S15).

For the metal salts, the catalytic efficiency follows the order $YCl_3 \cdot 6H_2O > YbCl_3 \cdot 6H_2O > LaCl_3 \cdot 7H_2O$, with average conversions of 86, 83, and 75%, respectively. The oxidation profile is, however, strikingly different concerning selectivity, with the results showing that these precursors are much less selective to the sulfoxide when compared with the nano-MOFs (1-3) (Table 1). When the ligand H_{10} TPPA was evaluated as catalyst, a conversion of 99% was achieved after 24 h, with the sulfoxide being obtained in 97% selectivity.

Though apparently the precursors appear to be more efficient than the nano-MOFs (1-3), these materials exhibit clear advantages in comparison with the corresponding building units: the metal salts act as homogeneous catalysts, which ultimately requires significantly more demanding separation and purification processes than for the pure heterogeneous catalysis performed by the nano-MOFs, while although $H_{10}TPPA$ was insoluble, the behavior of this molecule as catalyst in two more runs (Figure S16) revealed a significant decrease in conversion from the first to the third run (99–56%). Data from ³¹P NMR (Figure S17) and FT-IR (Figure S18) further suggested the decomposition of this ligand.

The recyclability of nano-Por-MOFs (1-3) was investigated in consecutive batch runs for the oxidation reaction of thioanisole by H_2O_2 at 50 °C (Figure 4). In all cases, the



Figure 4. Catalytic recycling tests for the oxidation of thioanisole using $[La(H_9TPPA)(H_2O)_x]Cl_2 \cdot yH_2O$ (1), $[Yb(H_9TPPA)(H_2O)_x]Cl_2 \cdot yH_2O$ (2), or $[Y(H_9TPPA)(H_2O)_x]Cl_2 \cdot yH_2O$ (3) [with x + y = 7].

solid catalysts were washed and dried under atmospheric conditions prior to reuse. The recyclability of catalyst 1 was investigated in four consecutive batch runs with the catalytic activity remaining roughly constant. Sulfoxide and sulfone were formed in 90 and 10% selectivity, respectively, in the first run, while in the subsequent runs, sulfoxide was formed with a selectivity of 96% and the sulfone product with 4%. In the case of the ytterbium-based Por-MOF 2, a moderate decrease of conversion between the first and second runs (11%) was observed, though selectivity remained constant in both runs. Recycling experiments of material 3 revealed a decrease of conversion from 79% in the first run to 63% in the third run, and a decrease of overall selectivity for the sulfoxide product from 94 to 90% followed by 87% in the first, second, and third runs, respectively. The structural integrity of all materials was deeply evaluated by PXRD, SEM, and FT-IR at the end of each run (Figures S19-S24). Among all Por-MOFs, material 1 showed to be the most promising catalyst keeping the catalytic activity along four consecutive runs with no significant modifications in the structure, even though a small reduction of the overall crystallinity was observed.

In this sense, to ascertain its true heterogeneous nature, a leaching test was performed. After separating the solid catalyst from the reaction mixture (conversion of 42% after 4 h at 50 $^{\circ}$ C), the conversion increase during the period between 4 and 24 h was negligible (42–50%), thus indicating the absence of soluble active species and, ultimately, that 1 is a truly heterogeneous catalyst.

Chemosensing Studies. Nitro explosives constitute a huge threat to homeland security and mankind health, which has recently motivated the development of simple, inexpensive, and fast detection methods.^{52–55} The fluorimetric method is, in this context, an efficient and nondestructive approach with high sensitivity and fast response time.^{54,55} Nitroaromatics, such as NB, DNB, and TNP, are considered as models of the most common nitro explosive molecules and were used to assess the ability of Por-MOFs 1–3 to be used as chemosensors.^{52,55} The absorption spectra of nano-Por-MOFs (1–3) suspended in water exhibit a broad Soret band ca. 415 nm, and when compared with the absorption spectrum of H_{10} TPPA, an alteration of the absorption pattern is observed (Figure S8). The four Q-band pattern of H_{10} TPPA changed to one or two bands, with the new absorption band peaking at 662 nm. The emission spectra (Figure S25) shows a broad emission at 678.7 nm upon excitation at 430 nm.

The variations in the absorption and emission spectral patterns are in good agreement with the dicationic form of $H_{10}TPPA$,⁵⁶ suggesting that the organic linker has the central core protonated while in the composition of the Por-MOFs. As evidenced from our previous work,⁵⁶ protonated porphyrins undergo additional intermolecular hydrogen bonding interactions with nitroaromatic compounds (NACs) and show strong enhancement in its sensitivity.

To explore the ability of the novel nano-Por-MOF materials (1-3) to sense trace amounts of nitro explosive model molecules, luminescence titrations were performed with an incremental addition of 1 mM stock solutions of NB, DNB, and 4-NP (Figures S26–S28) and TNP (Figure 5) to dispersions of each Por-MOF in water. Similar luminescence quenching titrations were carried out with phenol (PhOH) (Figures S26–S28).

Interestingly, most of the tested NACs showed, as expected, fluorescence intensity quenching for this type of interaction in materials 1–3. However, TNP showed a completely distinct profile when compared with the remaining NACs. Figure 5 shows the changes in the luminescence intensity with the incremental addition of TNP (up to 145.2 μ M) to dispersions of the three nano-Por-MOFs. The addition of 0–50.6 μ M TNP to dispersions of Por-MOFs 1 and 3 as well as 0–26.0 μ M TNP to the dispersion of 2 showed an increase in the emission intensity, reaching a saturation point where further addition of TNP (until 145.2 μ M) leads to a fluorescence quenching.

The emission efficiencies were calculated for each material (1-3). The negative tendency is due to the enhancement profile observed in the emission (Figure 5) for concentrations between 0 and 50.6 μ M of TNP (Figure 6). The response of the materials (1-3) varied with the lanthanide used, with Por-MOF 1 being the most efficient in the initial step of recognition (reactivity order: 1>3>2). This kind of response shows that the acidic nature of the phenolic -OH groups in TNP seems to interact with the porphyrin, providing an initial enhancement in the emission intensity. The efficiency of this behavior was ascribed to be -79, -69, and -76% for 1, 2, and 3, respectively. After reaching the equilibrium, the emission intensity is quenched with the incremental addition of TNP. The second step, which seems to be dependent on the first, is associated with a photoinduced electron transfer process between the electron-deficient TNP and the electron-donating nano-Por-MOFs. It is interesting to note that the initial enhancement step is the more efficient one, whereas the less efficient one corresponds to the quenching step.

To better understand the role of the acidic effect in the first step, a control experiment was performed by adding trifluoroacetic acid (TFA) to the suspension of the nano-MOFs (Figure

Ε



Figure 5. Emission spectra of $[La(H_9TPPA)(H_2O)_x]Cl_2\cdot yH_2O$ (1), $[Yb(H_9TPPA)(H_2O)_x]Cl_2\cdot yH_2O$ (2), and $[Y(H_9TPPA)(H_2O)_x]Cl_2\cdot yH_2O$ (3) [with x + y = 7] dispersed in water upon increasing addition of TNP (6.6 μ M each addition) until a total concentration of 145.2 μ M. Insets: variation in fluorescence upon addition of different aliquots of TNP up to 52.8 μ M.

S29). While TFA has a higher acidic nature than TNP, only a 40% enhancement in the emission intensity was observed. The use of a higher concentration of TFA does not provide the quenching effect. This clearly shows that the enhancement profile observed is intimately associated with the pK_a of the host and rules out its participation in the second step (quenching effect). Plots of the emission variation at 678.7 nm against the concentration of TNP provided a nonlinear variation at lower concentrations of TNP. This kind of behavior prompted us to further study both effects individually, whereas for concentrations above 60 μ M, a Stern–Volmer (SV) analysis



Figure 6. Fluorescence quenching efficiencies of TNP, when using the nano-Por-MOFs $[La(H_9TPPA)(H_2O)_x]Cl_2\cdot yH_2O$ (1), [Yb-(H₉TPPA)(H₂O)_x]Cl₂·yH₂O (2), and $[Y(H_9TPPA)(H_2O)_x]Cl_2\cdot yH_2O$ (3) [with x + y = 7].

can be used to calculate the association constants and sensitivity of the interaction. However, the same cannot be considered for lower concentrations (0–60 μ M), where the curve shape seems to be associated with an equilibrium when TNP interacts with the porphyrin core. Furthermore, materials 1 and 3 show a similar curve shape upon addition of TNP within the same concentration range, while material **2** provides an interaction in a shorter concentration range (0–26.0 μ M) with a completely different curve shape (Figure 7).

A first analysis plotting the emission intensity at 678.7 nm against $1/[\text{TNP}]^2$ (Benesi–Hildebrand approach) fits in a 1:2 stoichiometry, providing a linear progression (Figure 7b). The same fitting procedure to a 1:1 stoichiometry interaction shows a slight curvature instead of the expected linear progression (Figure 8 inset). In fact, porphyrins are well-known to interact in a 1:2 stoichiometry with TNP, where a double protonation of the porphyrin core occurs, maintaining the anionic TNP as counterion in the final structure. The complexity inherent to these equilibria with nano-MOF materials is effectively much higher and provides a behavior which up to now and to the best of our knowledge has not been reported.

The association constants show that 2 has the best association constant (2.91 \times 10¹⁰ M⁻²), followed by 1 and 3 with association constants around 1.43×10^9 and 1.78×10^8 M^{-2} . These values are in good agreement with the corresponding efficiencies of materials 1-3 among the concentration ranges where it is possible to calculate the association constants for each material. The curve shape differences and association constants of materials 1-3 (Figure 7) are highly dependent on the turning point concentration where, inevitably, both effects are present. As these provide opposite responses in emission, the data closer to this concentration does not fit a linear progression in any of the approaches used to calculate the association constants. This variation is even more prominent when plotting the I_0/I versus [TNP] (Figure 8) where it is possible to note that 3 seems to provide a sharper turning point, where only one point is neglected from both steps.

The turning point for Por-MOFs 1 and 3 is reached at higher concentrations, while 2 has a broad turning point ranging from 26.0 to 50.6 μ M. This behavior might be associated with the crystallite size and shape, where the larger agglomerated



Figure 7. (a) Change in emission at 678.7 nm from materials 1-3 vs [TNP]. (b) Plots of Benesi–Hildebrand equation for materials 1-3 showing the linear dependence in a 1:2 stoichiometry (inset: Benesi–Hildebrand plot with a 1:1 stoichiometry).



Figure 8. I_0/I versus [TNP] and the linear ranges, where K_{sv} can be calculated for materials 1–3.

nanoparticle sizes might affect the TNP diffusion to the material generating a wider concentration turning point between the two steps. In this regard, **3** is highly effective in both processes (emission enhancement and quenching), and a closer analysis shows the dispersed needle shape and size of this material seems to enhance the interaction between the material and TNP.

To gain a better insight on the second step of interaction, a SV analysis was performed to the emission data with concentrations above 50.6 μ M, where only the quenching behavior is observed (Figures S30-S32). With increasing concentrations, the SV plot showed a deviation from linearity and began to bend upward for most of the analytes, at concentrations higher than 50.6 μ M. A linear SV relationship may be observed if either a static or dynamic quenching process is dominant. Thus, in the case of higher concentrations of analytes, the two processes may be competitive, which results in a nonlinear SV relationship. The only exceptions to this upward curvature are 4-NP and TNP (Figure 8, S30, and S31). The linear variation at lower concentration of the analytes in this case can mainly be attributed to static quenching effects (ground state interaction between the analytes and the Por-MOFs). The K_{sy} constants calculated based in this assumption are summarized in Table 2. Material 2, as before, systematically

Table 2. Stern–Volmer Constants for Nano-Por-MOFs 1–3 with Different Analytes

	Stern–Volmer constant (M ⁻¹)				
analyte	1	2	3		
NB	21740	34048	32189		
DNB	15192	26605	17951		
TNP	5600	10930	9904		
4-NP	21531	20813	18060		
PhOH	23583	34203	18581		

provides the best association constants under the Volmer– Stern equation for all the analytes (Table 2), corroborating the quenching efficiencies showed in Figure 9. The SV rate



Figure 9. Fluorescence quenching efficiencies of different analytes when using the nano-Por-MOFs $[La(H_9TPPA)(H_2O)_x]Cl_2:yH_2O(1)$, $[Yb(H_9TPPA)(H_2O)_x]Cl_2:yH_2O(2)$, and $[Y(H_9TPPA)(H_2O)_x]Cl_2:yH_2O(3)$ [with x + y = 7].

constants are of a similar order of magnitude when compared to those of other materials reported in the literature for the nitro-aromatic compounds NB and DNB, with TNP exhibiting moderate SV constants and an unprecedented fluorescence behavior.⁵⁵

All nano-Por-MOFs showed a good sensing behavior toward the studied analytes (Figure 6). Por-MOF 3 proved to be the most efficient chemosensor by quenching the initial fluorescence intensity up to 80% in all analytes, except for TNP where a peculiar profile of initial enhancement followed by quenching demanded a special attention. Even in this special case, Por-MOF 2 experienced a fluorescence quenching of 55%, at concentrations of 145.2 μ M, while Por-MOFs 1 and 3 showed fluorescence quenching of only 34 and 49%, respectively. Furthermore, it was observed that detection of TNP is possible with a detection limit as low as 0.82 ppm with material 3. The remaining materials provided a LOD significantly higher around 19.84 ppm (1) and 21.21 ppm (2). The LODs calculated for the remaining analytes are shown in Table S2. We note, however, that herein a "green" solvent was employed for the detection process (water), contrasting with the toxic nature of the solvents used in the vast majority of the reported studies available in the literature.^{52,54,55}

CONCLUDING REMARKS

In short, we have successfully designed and tested a new and more efficient route for the isolation of porphyrinic molecule $H_{10}TPPA$, which was then employed as a primary building unit in the preparation of novel nanosized Por-MOFs [M-(H₉TPPA)(H₂O)_x]Cl₂·yH₂O [where x + y = 7; $M^{3+} = La^{3+}$ (1), Yb³⁺ (2), or Y³⁺ (3)]. Nano-Por-MOFs 1–3 exhibit true multifunctionality, acting both as efficient heterogeneous catalysts in the sulfoxidation of thioanisole and as chemosensors for the detection of nitroaromatic compounds.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b03214.

Detailed synthesis and structural characterization of the organic compounds; structural studies of the Por-MOF materials (electron microscopy, studies of the protonation of the central porphyrinic core in the MOF materials, determination of the average particle size, TG, FT-IR, and solid-state NMR); additional details on the catalytic studies performed including recycling studies, evaluation of the structural integrity of the recovered catalysts; additional data on the performed chemossensing studies (optical emission spectra, luminescence titrations, SV analysis, Benesi–Hildebrand analysis and determination of the detection limits) (PDF)

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Notes

The authors declare no competing financial interest.

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