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Zirconium metal–organic frameworks containing a biselenophene linker: Synthesis, characterization, and luminescent properties

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Zirconium Metal-Organic Frameworks containing a biselenophene linker: synthesis, characterization and luminescent properties

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Abstract. The bicyclic ditopic linker 2,2'-biselenophene-5,5'-dicarboxylic acid (**H₂SpSp**) specifically designed for MOFs construction has been synthesized in good yields and fully characterized. The corresponding zirconium MOF [Zr₆O₄(OH)₄(SpSp)_{3.8}Cl_{4.4}] (**1**) (where missing linkers are replaced by chloride anions as shown by XRF and elemental analysis) is isostructural with its bithiophene and bithiazole analogues. Starting from **1**, an extension of the biselenophene-based zirconium MOFs family has been successfully achieved exploiting the structural analogy of the five-membered heterocycles selenophene, thiophene and thiazole. Thus, three mixed-linker MOFs containing variable amounts of different bis(heterocyclic) dicarboxylic acids have been prepared and fully characterized: the two double-mixed [Zr₆O₄(OH)₄(SpSp)_{2.6}(ThTh)_{1.3}Cl_{4.2}] (**2**; **H₂ThTh** = 2,2'-bithiophene-5,5'-dicarboxylic acid) and [Zr₆O₄(OH)₄(SpSp)₂(TzTz)_{1.8}Cl_{4.4}] (**3**; **H₂TzTz** = 2,2'-bithiazole-5,5'-dicarboxylic acid) materials, as well as the triple-mixed [Zr₆O₄(OH)₄(SpSp)_{1.6}(ThTh)_{1.2}(TzTz)_{1.4}Cl_{3.6}] (**4**) compound. The four MOFs are luminescent under UV irradiation, exhibiting emission wavelengths falling in the blue-green visible region, as observed for their constitutive linkers. These materials open new horizons in the preparation of porous luminescent sensors or multicolor emitters for LEDs.

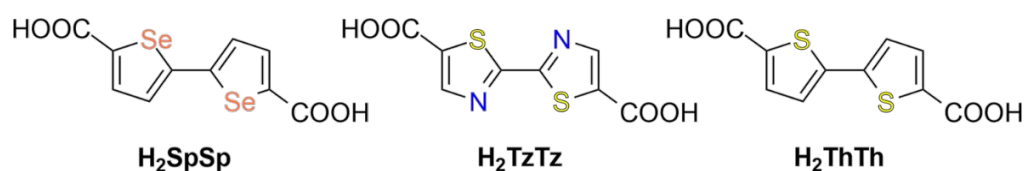
Keywords

Metal-Organic Frameworks (MOFs) – porous materials – zirconium(IV) – biselenophene – bithiazole – bithiophene – luminescence

Introduction

The design, synthesis and characterization of Metal-Organic Frameworks (MOFs) for assorted applications is nowadays one of the most fruitful research fields in inorganic chemistry and materials science.¹ The extreme versatility in MOFs design, obtained through a judicious combination of metallic nodes and organic linkers, and their high crystallinity degree are key features that can be exploited in a plethora of applicative fields. While MOFs featuring fully carbocyclic or nitrogen-containing heterocyclic spacers are ubiquitous, much fewer examples are found with sulphur- or selenium-based heterocycles like thiophene, thiazole and selenophene. The latter in particular has been very little explored as organic building block for MOFs construction. To date, the only literature examples are limited to the simple selenophene-2,5-dicarboxylic acid in combination with Zn^{II} and Cd^{II}, as reported by the group of D'Alessandro and co-workers.² Fully organic selenophene-based polymers are attracting much attention in materials science for their potential technological applications in light-emitting diodes (LEDs), organic solar cells and other electronic components, since they have appropriate absorption and emission band ranges and suitable HOMO-LUMO energy levels.³ Given the peculiar luminescence properties of selenophene, it would be desirable to incorporate it into tailor-made linkers for MOFs construction. Inspired by this idea and following our recent preparation of a bithiazole linker and the related zirconium MOF,⁴ in this work we describe the preparation of the new 2,2'-biselenophene-5,5'-dicarboxylic acid (**H₂SpSp**, Scheme 1). Successively, we tested its coordination ability towards zirconium: combination with Zr^{IV} sources under solvothermal conditions has led to the obtainment of the related MOF of general formula [Zr₆O₄(OH)₄(SpSp)_{3,8}Cl_{4,4}] (**1**, Figure 1) sharing the same structural motif of UiO-67⁵ and isostructural with the already known bithiophene⁶ and bithiazole⁴ analogues. **1** has been fully characterized in the solid state. In the MOFs world, the introduction of chemically different but structurally similar linkers within the same MOF crystal structure leads to the so-called mixed Metal-Organic Frameworks [MIXMOFs or Multivariate (MTV)-MOFs].⁷ MIXMOFs grant pore walls heterogeneity, preserving at the same time the structural motif of the parent single-linker homologue.

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2
3 Aiming at extending the biselenophene-based MOF family (and given the structural analogy between
4 biselenophene, bithiophene and bithiazole), we have also synthesized three Zr^{IV} MIXMOFs
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6
7 isostructural with **1**: the two double-mixed biselenophene-bithiophene
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9
10 [Zr₆O₄(OH)₄(SpSp)_{2.6}(ThTh)_{1.3}Cl_{4.2}] (**2**; **H₂ThTh** = 2,2'-bithiophene-5,5'-dicarboxylic acid, Scheme
11 1) and biselenophene-bithiazole [Zr₆O₄(OH)₄(SpSp)₂(TzTz)_{1.8}Cl_{4.4}] (**3**; **H₂TzTz** = 2,2'-bithiazole-
12 5,5'-dicarboxylic acid, Scheme 1) materials, as well as the triple-mixed
13
14 [Zr₆O₄(OH)₄(SpSp)_{1.6}(ThTh)_{1.2}(TzTz)_{1.4}Cl_{3.6}] (**4**) compound. All the samples are defective; missing
15
16
17 linkers are balanced by chloride anions bound to zirconium, as inferred from elemental analysis, XRF
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19 spectroscopy and powder X-ray diffraction structure determination. The actual ligand composition
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21
22 within the MIXMOFs has been assessed *via* ¹H NMR signal integration after sample digestion in
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24 acidic solution. The luminescent properties of **1-4** have been finally investigated and compared. As
25
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27 their constitutive linkers, all (MIX)MOF samples in DMF suspensions are featured by emissions
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30 falling in the blue-green visible range (λ_{em} between 450 and 510 nm).
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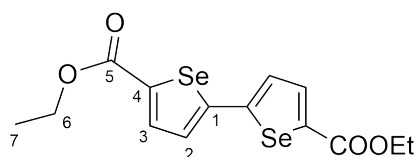
42 **Scheme 1.** Molecular structures of the linkers used in this study: 2,2'-biselenophene-5,5'-dicarboxylic acid
43 (**H₂SpSp**), 2,2'-bithiazole-5,5'-dicarboxylic acid (**H₂TzTz**) and 2,2'-bithiophene-5,5'-dicarboxylic acid
44 (**H₂ThTh**).
45

46 Experimental Section

47
48 **Materials and Methods.** All the chemicals and reagents employed were purchased from commercial
49 vendors and used as received without further purification. **H₂TzTz**,⁴ **H₂ThTh**⁶ and ethyl
50 selenophene-2-carboxylate⁸ were prepared according to the published procedures. For the
51 organic syntheses, solvents were purified through standard distillation techniques. Deuterated
52 solvents (Sigma Aldrich) were stored over 4 Å molecular sieves and degassed by three freeze-pump-
53 thaw cycles before use. NMR spectra were recorded on a BRUKER AVANCE 400 MHz
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2
3 spectrometer. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts are reported in parts per million (ppm) downfield
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5 of tetramethylsilane (TMS) and were calibrated against the residual resonance of the protiated part of
6
7 the deuterated solvent. FT-IR spectra (KBr pellets) were recorded on a Perkin-Elmer Spectrum BX
8
9 Series FTIR spectrometer, in the $4000\text{--}400\text{ cm}^{-1}$ range, with a 2 cm^{-1} resolution. Thermogravimetric
10
11 analysis (TGA) measurements were performed under N_2 flow (100 mL min^{-1}) at a heating rate of 10
12
13 K min^{-1} on an EXSTAR Thermo Gravimetric Analyzer (TG-DTG) Seiko 6200. Differential scanning
14
15 calorimetry (DSC) measurements were carried out on a NETZSCH STA 409 PC analyzer, heating up
16
17 $\sim 10\text{ mg}$ powdered samples, placed in alumina crucibles, under a N_2 flow (40 mL min^{-1}) from 303 to
18
19 1173 K , with a rate of 10 K min^{-1} . Raw DSC data were corrected based on a background curve
20
21 previously acquired in the same experimental conditions. Elemental analyses were performed at
22
23 ICCOM-CNR using a Thermo FlashEA 1112 Series CHNS-O elemental analyzer with an accepted
24
25 tolerance of $\pm 2\%$. ESI-MS spectra were recorded by direct introduction of the analyte solution (10
26
27 $\mu\text{L/min}$) on a FinniganLTQ mass spectrometer (Thermo, San Jose, CA). The instrument was equipped
28
29 with a conventional ESI source. The working conditions were the following: negative polarity,
30
31 spray voltage 5 kV , capillary voltage -18 V , capillary temperature 563 K and tube lens -87
32
33 V . Sheath gas was set at 10 a.u. and auxiliary gas was kept at 3 a.u. For the acquisitions, the Xcalibur
34
35 2.0 software (Thermo) was used. Aqueous solutions of **H₂SpSp** were prepared using 1 mg/mL and
36
37 then diluting to $10\text{ ng}/\mu\text{L}$ with 95% v/v water and 5% v/v acetonitrile. Powder X-ray diffraction
38
39 (PXRD) qualitative measurements were carried out in the $4\text{--}50^\circ 2\theta$ region with a Panalytical X'PERT
40
41 PRO powder diffractometer equipped with a diffracted beam Ni filter, a PIXcel[©] solid state detector
42
43 and a $\text{Cu K}\alpha$ X-ray source ($\lambda = 1.5418\text{ \AA}$). Slits were used on both the incident (Soller slits aperture
44
45 0.25° ; divergence slit aperture 0.5°) and the diffracted (anti-scatter slit height 7.5 mm) beam. X-ray
46
47 fluorescence (XRF) analyses were performed on powdered batches (*ca.* 10 mg for each MOF sample)
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49 with a Panalytical MINIPAL 2 instrument equipped with a Cr X-ray source.
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Synthesis of diethyl [2,2'-biselenophene]-5,5'-dicarboxylate (Et₂SpSp). The 2,2'-biselenophene-5,5'-diester was prepared through an Ag^I/Pd^{II}-catalysed homocoupling of ethyl selenophene-2-carboxylate, following the literature procedure found for its thiophene analogue.⁹ The full experimental details are reported hereafter, for the sake of completeness. Ethyl selenophene-2-carboxylate (480 mg, 2.36 mmol) was dissolved in freshly distilled dimethyl sulfoxide (DMSO, 14 mL) in a Schlenk round-bottom flask equipped with a magnetic stirring bar. Then, silver fluoride (AgF, 600 mg, 4.72 mmol) and the Pd^{II} catalyst bis(benzonitrile)palladium dichloride [PdCl₂(C₆H₅CN)₂, 27.1 mg, 0.07 mmol] were added to this solution while stirring at ambient temperature. Afterwards, the resulting mixture was heated at 333 K for 5 h. Then, it was cooled to room temperature and passed through a Celite pad, which was successively washed with chloroform (3 × 10 mL). The dark yellow organic filtrate was washed with water (3 × 10 mL) and the aqueous layer extracted with chloroform (3 × 10 mL). The combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude solid that was finally purified through column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 85:15). The dark yellow solid residue obtained after solvent removal was recovered and dried under vacuum. Yield: 405 mg (85%). Single crystals suitable for X-ray diffraction were obtained through ambient temperature slow evaporation of an ethyl acetate concentrated solution. The details of the single-crystal X-ray diffraction data acquisition and treatment as well as the crystal and molecular structure are reported in the Supporting Information (Figure S1 and Table S1).

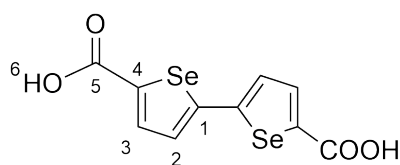


¹H NMR (400 MHz, CD₂Cl₂, 298 K, ppm): δ 1.36 (t, ³J_{HH} = 7.1 Hz, 6H, H⁷), 4.31 (q, ³J_{HH} = 7.1 Hz, 4H, H⁶), 7.37 (d, ³J_{HH} = 3.9 Hz, 2H, H³), 7.90 (d, ³J_{HH} = 3.9 Hz, 2H, H²). ¹³C{¹H} NMR (100

MHz, CD₂Cl₂, 298 K, ppm): δ 14.1 (C⁷), 61.5 (C⁶), 128.3 (C²), 136.2 (C³), 139.1 (C¹), 150.5 (C⁴), 162.9 (C⁵). Elem. Anal. Calc. (%) for **Et₂SpSp**, C₁₄H₁₄O₄Se₂ (FW = 404.18 g/mol): C 41.60, H 3.49;

found C 41.62, H 3.52. IR (KBr pellet, cm^{-1}): $\nu = 3043$ (w), 2988 (w), 2976 (w), 2901 (w), 2867 [w, $\nu(\text{C-H})$], 1685 [s, $\nu(\text{C=O})$], 1525 [m, $\nu(\text{C=C})$], 1442 [s, $\delta(\text{CH}_2/\text{CH}_3)$], 1261 [s, $\delta(\text{O-Et})$], 747 [s, $\gamma(\text{C-H})$].

Synthesis of 2,2'-biselenophene-5,5'-dicarboxylic acid (H_2SpSp). A freshly prepared NaOH 1 M aqueous solution (8.5 mL) was added to a suspension of diethyl [2,2'-biselenophene]-5,5'-dicarboxylate (360 mg, 0.88 mmol) in methanol (8.5 mL), and the resulting mixture was brought to 328 K and kept at this temperature for 2 h. After that time, the clear yellow solution formed was cooled down to ambient temperature. TLC analysis (petroleum ether/ethyl acetate 5:1) showed no more ester starting material. Methanol was removed by rotary evaporation and the residual aqueous phase was acidified with HCl 1 M until very low pH values (3-4). During HCl addition, H_2SpSp started to precipitate. The reaction flask was left at low temperature (277 K) for some hours in order to facilitate the precipitation. The yellow solid recovery was achieved through filtration on filter paper. Yield: 245 mg (80%).



^1H NMR (400 MHz, $\text{DMSO-}d_6$, 298 K, ppm): δ 7.57 (d, $^3J_{\text{HH}} = 4.1$

Hz, 2H, H^3), 7.84 (d, $^3J_{\text{HH}} = 4.1$ Hz, 2H, H^2), 13.25 (s, br, 2H, H^6).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $\text{DMSO-}d_6$, 298 K, ppm): δ 129.4 (C^2),

136.5 (C^3), 140.0 (C^1), 149.6 (C^4), 163.8 (C^5). Elem. Anal. Calc. for H_2SpSp , $\text{C}_{10}\text{H}_6\text{O}_4\text{Se}_2$ (MW = 348.07 g/mol): C, 34.51; H, 1.74. Found: C, 34.53; H, 1.76. ESI-MS/MS: $m/z = 347$ (M-H^-), $m/z = 303$ (M-H-CO_2^-), $m/z = 173$ (M-2H^{2-}). IR (KBr pellet, cm^{-1}): $\nu = 3423$ [s, br, $\nu(\text{O-H})$], 3048 [w, $\nu(\text{C-H})$], 1655 [m, $\nu(\text{C=O})$], 1526 [m, $\nu(\text{C=C})$], 1395 [s, $\delta(\text{CH})$], 763 [m, $\gamma(\text{C-H})$], 466 [w, $\nu(\text{C-Se})$].

Synthesis of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{SpSp})_{3.8}\text{Cl}_{4.4}]\cdot 4(\text{DMF})\cdot 8(\text{H}_2\text{O})$ ($1\cdot\text{S}$).¹⁰ Following the improved preparation of UiO-67 reported by Fahra *et al.*,¹¹ zirconium chloride [ZrCl_4 , 67.6 mg, 0.29 mmol] and a concentrated (12 M) HCl aqueous solution (0.5 mL) were mixed together and diluted with *N,N*-dimethylformamide (DMF, 5 mL). The resulting suspension was sonicated in an ultrasonic bath at

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3 ambient temperature for 15 minutes. After that time, the ligand **H₂SpSp** (100 mg, 0.29 mmol) was
4 added to the clear colorless solution; the mixture was further diluted with fresh DMF (7 mL),
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6 sonicated for additional 15 minutes and finally transferred to a Teflon-lined stainless steel autoclave
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8 (inner Teflon beaker volume ca. 20 mL). The autoclave was sealed and heated at 363 K for 24 h under
9
10 autogenous pressure. After slow overnight cooling, a yellow powder of **1·S** formed at the bottom of
11
12 the beaker. It was collected, washed with ethanol (4 × 10 mL), petroleum ether (4 × 10 mL) and
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14 finally dried under a nitrogen stream at room temperature. Yield: 109 mg (87% based on zirconium).
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16
17 The phase purity of every batch was checked through PXRD. Elemental analysis calcd (%) for **1·S**,
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19 $C_{50}H_{63.2}Cl_{4.4}N_4O_{35.2}Se_{7.6}Zr_6$ (MW = 2586.88 g/mol): C 23.10, H 2.44, N 2.16; found: C 23.09, H 2.41,
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21 N 2.12. IR [$\nu(C=O)$] band (KBr, cm^{-1} , Figure S2): 1651 (m).
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29 **Synthesis of $[Zr_6O_4(OH)_4(SpSp)_{2.6}(ThTh)_{1.3}Cl_{4.2}] \cdot 4(DMF) \cdot 6(H_2O)$ (**2·S**).**¹⁰ Zirconium chloride
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31 $[ZrCl_4$, 70.0 mg, 0.30 mmol] and a concentrated (12 M) HCl aqueous solution (0.5 mL) were mixed
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33 together and diluted with DMF (5 mL). The resulting suspension was sonicated in an ultrasonic bath
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35 at ambient temperature for 15 minutes. After that time, the ligands **H₂SpSp** (52.2 mg, 0.15 mmol)
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37 and **H₂ThTh** (38.1 mg, 0.15 mmol) were added to the clear colorless solution; the mixture was further
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39 diluted with fresh DMF (7 mL), sonicated for additional 15 minutes and finally transferred to a
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41 Teflon-lined stainless steel autoclave (inner Teflon beaker volume ca. 20 mL). The autoclave was
42
43 sealed and heated at 363 K for 24 h under autogenous pressure. After slow overnight cooling, a yellow
44
45 powder of **2·S** formed at the bottom of the beaker. It was collected, washed with ethanol (4 × 10 mL),
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47 petroleum ether (4 × 10 mL) and finally dried under a nitrogen stream at room temperature. Yield:
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49 110 mg (90% based on zirconium). The phase purity of every batch was checked through PXRD.
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51
52 Elemental analysis calcd (%) for **2·S**, $C_{51}H_{59.6}Cl_{4.2}N_4O_{33.6}S_{2.6}Se_{5.2}Zr_6$ (MW = 2456.42 g/mol): C
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54 24.91, H 2.44, N 2.28; S, 3.39; found: C 25.05, H 2.46, N 2.31; S, 3.43. IR [$\nu(C=O)$] bands (KBr,
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56 cm^{-1} , Figure S2): 1704, 1662 (m).
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3 **Synthesis of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{SpSp})_2(\text{TzTz})_{1.8}\text{Cl}_{4.4}]\cdot 4(\text{DMF})\cdot 2(\text{H}_2\text{O})$ (**3·S**).**¹⁰ Zirconium chloride
4 $[\text{ZrCl}_4$, 70.0 mg, 0.30 mmol] and a concentrated (12 M) HCl aqueous solution (0.5 mL) were mixed
5
6 together and diluted with DMF (5 mL). The resulting suspension was sonicated in an ultrasonic bath
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8 at ambient temperature for 15 minutes. After that time, the ligands **H₂SpSp** (52.2 mg, 0.15 mmol)
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10 and **H₂TzTz** (38.4 mg, 0.15 mmol) were added to the clear colorless solution; the mixture was further
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12 diluted with fresh DMF (7 mL), sonicated for additional 15 minutes and finally transferred to a
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14 Teflon-lined stainless steel autoclave (inner Teflon beaker volume ca. 20 mL). The autoclave was
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16 sealed and heated at 363 K for 24 h under autogenous pressure. After slow overnight cooling, a
17
18 microcrystalline yellow powder of **3·S** formed at the bottom of the beaker. It was collected, washed
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20 with ethanol (4×10 mL), petroleum ether (4×10 mL) and finally dried under a nitrogen stream at
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22 room temperature. Yield: 106 mg (92 % based on zirconium). The phase purity of every batch was
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24 checked through PXRD. Elemental analysis calcd (%) for **3·S**, $\text{C}_{46.4}\text{H}_{47.6}\text{Cl}_{4.4}\text{N}_{7.6}\text{O}_{29.2}\text{S}_{3.6}\text{Se}_4\text{Zr}_6$ (MW
25
26 = 2313.51 g/mol): C 24.07, H 2.07, N 4.60; S, 4.99; found: C 24.29, H 2.06, N 4.62; S, 4.97. IR
27
28 $[\nu(\text{C}=\text{O})]$ bands (KBr, cm^{-1} , Figure S2): 1654, 1580 (m).
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38 **Synthesis of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{SpSp})_{1.6}(\text{ThTh})_{1.2}(\text{TzTz})_{1.4}\text{Cl}_{3.6}]\cdot 5(\text{DMF})\cdot 12(\text{H}_2\text{O})$ (**4·S**).**¹⁰ Zirconium
39
40 oxychloride octahydrate $[\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$, 96.7 mg, 0.30 mmol] and a concentrated (12 M) HCl
41
42 aqueous solution (0.5 mL) were mixed together and diluted with DMF (5 mL). The resulting
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44 suspension was sonicated in an ultrasonic bath at ambient temperature for 15 minutes. After that time,
45
46 the ligands **H₂SpSp** (34.8 mg, 0.10 mmol), **H₂TzTz** (25.6 mg, 0.10 mmol) and **H₂ThTh** (25.4 mg,
47
48 0.10 mmol) were added to the clear colorless solution; the mixture was further diluted with fresh
49
50 DMF (7 mL), sonicated for additional 15 minutes and finally transferred to a Teflon-lined stainless
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52 steel autoclave (inner Teflon beaker volume ca. 20 mL). The autoclave was sealed and heated at 363
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54 K for 24 h under autogenous pressure. After slow overnight cooling, a yellow powder of **4·S** formed
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56 at the bottom of the beaker. It was collected, washed with ethanol (4×10 mL), petroleum ether ($4 \times$
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58 10 mL) and finally dried under a nitrogen stream at room temperature. Yield: 110 mg (85% based on
59
60

zirconium). The phase purity of each batch was checked through PXRD. Elemental analysis calcd (%) for **4·S**, $C_{54.2}H_{77}Cl_{3.6}N_{7.8}O_{41.8}S_{5.2}Se_{3.2}Zr_6$ (MW = 2600.99 g/mol): C 25.00, H 2.98, N 4.20; S, 6.41; found: C 25.43, H 3.01, N 4.28; S, 6.38. IR [$\nu(C=O)$] bands (KBr, cm^{-1} , Figure S2): 1658, 1590, 1520 (s).

Powder X-ray Diffraction Structure Determination. Powdered samples (~50 mg) of **1·S-4·S** were deposited in the cavity of a silicon free-background sample-holder 0.2 mm deep (Assing Srl, Monterotondo, Italy). Powder X-ray diffraction (PXRD) data acquisitions were carried out with a Bruker AXS D8 Advance vertical-scan $\theta:\theta$ diffractometer, equipped with an X-ray tube (Cu $K\alpha$, $\lambda = 1.5418 \text{ \AA}$), a Bruker Lynxeye linear position-sensitive detector, a filter of nickel in the diffracted beam and the following optical components: primary beam Soller slits (2.5°), fixed divergence slit (0.5°), antiscatter slit (8 mm). The generator was set at 40 kV and 40 mA. Preliminary PXRD analyses to unveil the purity and crystallinity of the samples were performed in the 2θ range $3.0\text{-}35.0^\circ$, with steps of 0.02° and time *per* step of 1 s. PXRD acquisitions for the assessment of the crystal structure were performed overnight with steps of 0.02° and in the 2θ range reported in Table 1.

Table 1. Experimental conditions of the PXRD data acquisitions carried out on **1·S-4·S**.

	1·S	2·S	3·S	4·S
2θ range ($^\circ$)	3.0-105.0	4.5-105.0	5.0-105.0	4.5-105.0

A visual comparison between the PXRD patterns of the MOFs under study with those of the $[Zr_6O_4(OH)_4(L)_6] \cdot n(DMF)$ analogues (L = ThTh²⁻ = [2,2'-bithiophene]-5,5'-dicarboxylate;⁶ L = TzTz²⁻ = [2,2'-bithiazole]-5,5'-dicarboxylate⁴) highlighted that the compounds are isostructural. This suggestion was confirmed by performing a whole powder pattern refinement with the Le Bail approach as implemented in TOPAS-R V3,¹² starting from the unit cell parameters of the parent

1
2
3 bithiophene MOF. The crystallographically independent portion of the ligand and the DMF molecules
4
5 were described using rigid bodies built up through the z-matrix formalism. In the case of **2·S-4·S**, the
6
7 co-presence of the SpSp^{2-} , ThTh^{2-} and TzTz^{2-} ligands was taken into account by including into the
8
9 structural model the rigid body of SpSp^{2-} and inserting proper vicariant atoms (S *vs.* Se for ThTh^{2-} ; S
10
11 *vs.* Se and N *vs.* CH for TzTz^{2-}) setting their molar ratios at the values obtained from the $^1\text{H-NMR}$
12
13 signal integration of the digested samples (see the Supporting Information). In the initial steps of the
14
15 structure determination, both the metal cluster components (i.e. Zr^{4+} , O^{2-} and OH^-) and the spacers
16
17 were positioned according to the crystal structure of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{ThTh})_6] \cdot n(\text{DMF})$. Average values
18
19 were assigned to bond distances and angles.¹³ When allowed by the symmetry, the position and
20
21 orientation of the independent components of the MOFs were let vary. To account for the possibility
22
23 of missing-ligand defects, a known phenomenon for UiO-type materials,¹⁴ the linkers site occupation
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25 factors were refined, reaching in all compounds a value lower than one. As assessed by X-ray
26
27 fluorescence (Figures S3-S6), the missing negative charges are compensated by chloride anions. On
28
29 the basis of a search in the Cambridge Structural Database (v. 2020.1) for Zr_6Cl_x clusters (no $\text{Zr}_6\text{Cl}_x\text{O}_y$
30
31 clusters were found), it was assumed that the chloride anions in **1·S-4·S** are bound to the Zr^{IV} cations
32
33 as terminal ligands vicariant to the oxygen atoms of the carboxylate groups. They were placed
34
35 accordingly in all the positions where their site occupation factor did not refine to zero. The site
36
37 occupation factors of ligands and chloride anions were correlated so that the total negative charges
38
39 were set to -12 , to balance the positive charge coming from the $[\text{Zr}_6\text{O}_4(\text{OH})_4]^{12+}$ metallic node. For
40
41 the sake of simplicity, the smeared electronic density within the cavities was modelled by DMF
42
43 molecules alone. The two crystallographically independent DMF molecules were located using a
44
45 Monte Carlo/Simulated Annealing approach,¹⁵ implemented in TOPAS-R V3. During the
46
47 final structure refinement stages carried out with the Rietveld method ligand and DMF bond
48
49 distances (except for the C-H and C=O bonds) were refined in limited ranges of values,¹⁶
50
51 retrieved carrying out a search in the Cambridge Structural Database (v. 2020.1) for room-
52
53 temperature crystal structures containing the 2,2'-biselenophene, 2-carboxyselenophene, 2,2'-
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1
2
3 bithiophene-5,5'-dicarboxylate or 2,2'-bithiazole fragments. The background was modelled
4
5 through a polynomial function of the Chebyshev-type. An isotropic thermal factor [$B_{\text{iso}}(\text{M})$]
6
7 was refined for the Zr^{IV} metal centre; the isotropic thermal factor of lighter atoms belonging
8
9 to the cluster and the ligands was calculated as $B_{\text{iso}}(\text{L}) = B_{\text{iso}}(\text{M}) + 2.0 \text{ (\AA}^2\text{)}$; the isotropic
10
11 thermal factor of the DMF atoms was calculated as $B_{\text{iso}}(\text{S}) = B_{\text{iso}}(\text{M}) + 3.0 \text{ (\AA}^2\text{)}$. The peak
12
13 profile was modelled through the Fundamental Parameters Approach.¹⁷ The final Rietveld
14
15 refinement plots are shown in Figures S7-S10 of the Supporting Information.
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21
22 Crystal data for **1·S**: cubic, $Pn\bar{3}$, $a = 25.7020(6) \text{ \AA}$, $V = 16979(1) \text{ \AA}^3$, $Z = 24$, $Z' = 4$, $\rho = 0.991$
23
24 g cm^{-3} , $F(000) = 4555.0$, $R_{\text{Bragg}} = 0.011$, $R_{\text{p}} = 0.020$ and $R_{\text{wp}} = 0.028$, for 4986 data and 73
25
26 parameters in the $5.3\text{-}105.0^\circ$ (2θ) range. CCDC No. 2020561
27
28
29

30
31 Crystal data for **2·S**: cubic, $Pn\bar{3}$, $a = 25.546(1) \text{ \AA}$, $V = 16671(3) \text{ \AA}^3$, $Z = 24$, $Z' = 4$, $\rho = 1.005$
32
33 g cm^{-3} , $F(000) = 4925.1$, $R_{\text{Bragg}} = 0.015$, $R_{\text{p}} = 0.025$ and $R_{\text{wp}} = 0.032$, for 4991 data and 86
34
35 parameters in the $5.2\text{-}105.0^\circ$ (2θ) range. CCDC No. 2020562.
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39 Crystal data for **3·S**: cubic, $Pn\bar{3}$, $a = 25.564(1) \text{ \AA}$, $V = 16511(2) \text{ \AA}^3$, $Z = 24$, $Z' = 4$, $\rho = 1.002$
40
41 g cm^{-3} , $F(000) = 4874.4$, $R_{\text{Bragg}} = 0.015$, $R_{\text{p}} = 0.020$ and $R_{\text{wp}} = 0.026$, for 4981 data and 80
42
43 parameters in the $5.4\text{-}105.0^\circ$ (2θ) range. CCDC No. 2020563.
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46
47 Crystal data for **4·S**: cubic, $Pn\bar{3}$, $a = 25.416(2) \text{ \AA}$, $V = 16417(4) \text{ \AA}^3$, $Z = 24$, $Z' = 4$, $\rho = 1.031$
48
49 g cm^{-3} , $F(000) = 5022.6$, $R_{\text{Bragg}} = 0.005$, $R_{\text{p}} = 0.019$ and $R_{\text{wp}} = 0.024$, for 4991 data and 79
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51 parameters in the $5.2\text{-}105.0^\circ$ (2θ) range. CCDC No. 2020564.
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56 **Variable-temperature powder X-ray diffraction.** As a representative example, the thermal
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58 behaviour of **1·S** was investigated *in situ* by variable-temperature powder X-ray diffraction.
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60 A powdered sample (~20 mg) of this MOF was deposited on an aluminium sample-holder and

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3 heated using a custom-made sample heater (Officina Elettrotecnica di Tenno, Ponte Arche,
4 Italy) in the temperature range 303-663 K with steps of 20 K. PXRD patterns were acquired
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6 in isothermal conditions in the 2θ range 5.0-25.0°, with steps of 0.02° and a time per step of
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8 1 s, and treated performing a parametric whole powder pattern refinement with the Le Bail
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10 method, as implemented in TOPAS-R V3.
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17 **Gas Adsorption.** Samples of **1·S-4·S** (~40 mg) were activated at 403 K under high vacuum (10^{-6}
18 Torr) for 24 h before each measurement. The textural properties were estimated by volumetric
19 adsorption carried out with an ASAP 2020 Micromeritics instrument, using N₂ as adsorbate at 77 K.
20 For the Brunauer–Emmett–Teller (BET) specific surface area calculation, the 0.01-0.1 p/p⁰ pressure
21 range of the isotherm was used to fit the data. Within this range, all the Rouquerol consistency criteria
22 are satisfied.¹⁸ The pore size distribution was determined on the basis of the NLDFIT method
23 (Tarazona model for cylindrical pores).
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35 **Luminescence measurements.** The experiments were carried out on solids or air-equilibrated DMF
36 suspensions at 298 K unless otherwise noted. UV-vis absorption spectra were recorded with a
37 PerkinElmer λ 40 spectrophotometer using quartz cells with path length of 1.0 cm. Luminescence
38 spectra were collected with a PerkinElmer LS-50 or an Edinburgh FLS920 spectrofluorimeter
39 equipped with a Hamamatsu R928 phototube. For solid samples, the emission quantum yield was
40 calculated from corrected emission spectra registered by an Edinburgh FLS920 spectrofluorimeter
41 equipped with a barium sulfate coated integrating sphere (4 in.), a 450W Xe lamp (λ excitation tunable
42 by a monochromator supplied with the instrument) as light source, and a R928 photomultiplier tube,
43 following the procedure described by de Mello *et al.*¹⁹ The estimated experimental errors are 2 nm
44 on the band maximum, 5% on the molar absorption coefficient, and 20% on the emission quantum
45 yield in the solids.
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Results and Discussion

Synthesis and crystal structure of H₂SpSp and of the related MOFs 1-4. The ditopic linker 2,2'-biselenophene-5,5'-dicarboxylic acid was straightforwardly prepared from ethyl selenophene-2-carboxylate following a literature procedure found for its thiophene analogue⁹ *via* Pd^{II}/Ag^I-catalyzed homocoupling in DMSO. After chromatographic purification, diethyl 2,2'-biselenophene-5,5'-dicarboxylate (**Et₂SpSp**, Scheme S1) was finally converted into the corresponding diacid **H₂SpSp** (Scheme 1) in almost quantitative yield (80%) through a basic hydrolysis (NaOH) in water/methanol mixtures followed by acidification of the concentrated aqueous solution of the corresponding sodium dicarboxylate salt (Scheme S1). This synthetic path was preferred to an alternative methodology successfully exploited for the synthesis of the thiophene analogue **H₂ThTh**,⁶ *i.e.* 2,2'-biselenophene direct carboxylation (treatment of 2,2'-biselenophene with two equivalents of *n*BuLi at 195 K followed by CO₂ bubbling in the reaction mixture and acidification), because of the much higher product yields. Despite the numerous attempts made, it was not possible to grow single crystals of **H₂SpSp** suitable for X-ray diffraction; on the other hand, slow evaporation of ethyl acetate concentrated solutions of the diester **Et₂SpSp** led to the formation of bright yellow platelets that were successfully characterized *via* single-crystal X-ray diffraction. The structural details of **Et₂SpSp** are collected in the Supporting Information (Table S1 and Figure S1). It crystallizes in the triclinic $P\bar{1}$ space group, with half of a molecule, residing on an inversion center, in the asymmetric unit. Consequently, the two selenium atoms lie on the opposite sides of the exocyclic C–C bond (Se–C–C–Se dihedral angle = 180°). This heteroatom reciprocal *trans* arrangement in conjugated bicyclic compounds is somehow expected as it is the lowest energy conformation. As such, it is also typical of 2,2'-biselenophene,²⁰ 2,2'-bithiazole,²¹ 2,2'-bithiophene²² and other bicyclic dicarboxylic acids/esters like **H₂TzTz**⁴ and Hex₂ThTh (Hex = *n*-hexyl).²³

Starting from our optimized synthesis of the thiazole MOF [Zr₆O₄(OH)₄(TzTz)₆],⁴ reaction of **H₂SpSp** with ZrCl₄ in *N,N*-dimethylformamide (DMF) under solvothermal conditions and using

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3 concentrated HCl as crystal modulator led to formation of a microcrystalline yellow powder of
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5 formula $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{SpSp})_{3.8}\text{Cl}_{4.4}] \cdot 4(\text{DMF}) \cdot 8(\text{H}_2\text{O})$ (**1·S**). The application of the synthetic protocol
6
7 described above to mixtures of the different (but isostructural) ligands **H₂SpSp**, **H₂ThTh** and **H₂TzTz**
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9 (Scheme 1) allowed for the preparation of the pure phase MIXMOFs **2·S-4·S**. The initial linkers
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11 relative stoichiometric ratio for the syntheses was set to 3:3 for the double-mixed samples and to 2:2:2
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13 for the triple-mixed MOF. Curiously, in the synthesis of the triple-mixed MOF **4·S** the employment
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15 of zirconium oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) instead of simple ZrCl_4 as metal source was of
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17 fundamental importance to get a highly crystalline product (ZrCl_4 only gives amorphous phases under
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19 the same experimental conditions). The presence of the different heterocyclic spacers within the solid
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21 samples is confirmed by the presence of multiple carboxylate stretching bands [$\nu(\text{COO}^-)$] in their IR
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23 spectra (see the Experimental Section and Figure S2). According to a well-established experimental
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25 methodology already applied to other MIXMOFs from the literature,²⁴ the actual linkers composition
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27 in the as-synthesized materials was assessed *via* ¹H NMR signal integration of the digested samples
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29 in acidic solutions (D_2SO_4 in $\text{D}_2\text{O}/\text{DMSO}-d_6$ mixtures), referring to the diagnostic signals of **H₂SpSp**,
30
31 **H₂ThTh** and **H₂TzTz** falling in the $7.0 < \delta_{\text{H}} < 9.0$ ppm range (Figures S11-S13). This spectroscopic
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33 information has been exploited for the refinement of the crystal structures (see the Experimental
34
35 Section and below). The samples are pure unique phases and not mixtures of the single-linker MOF
36
37 components, as witnessed by the DSC traces recorded on **2·S-4·S** (*vide infra*) and by the comparison
38
39 of the PXRD profiles of a specific MIXMOF and of its single-linker counterparts. As a representative
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41 example, the comparison of the powder patterns of the selenophene-thiazole MIXMOF **3·S** and its
42
43 pure linker parent analogues **1·S** and $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{TzTz})_6] \cdot n(\text{DMF})^4$ is shown in Figure S14. As
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45 expected, the main diffraction peaks in **3·S** are unique and fall in between those of its parent materials.
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55 **1·S-4·S** are isostructural with the bithiophene⁶ and bithiazole⁴ MOFs with general formula
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57 $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{L})_6] \cdot n(\text{DMF})$. Hence, in here their crystal structure will be jointly described and
58
59 illustrated by **1·S** as a representative example. For the representation of the crystal structure of **2·S-**
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3 **4·S**, the reader is addressed to Figures S15-S17 of the Supporting Information. For the sake of
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5 simplicity, the discussion is made assuming a perfect crystal without missing ligands and chloride
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7 anions. **1·S** crystallizes in the cubic space group $Pn\bar{3}$ and features $Zr_6O_4(OH)_4$ clusters as secondary
8
9 building units (Figure 1A). The Zr^{IV} metal centres are eight-coordinated, in a square-antiprismatic
10
11 coordination geometry, by eight oxygen atoms, four coming from the carboxylate groups, which
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13 define one square face of the antiprism, and four belonging to μ_3 -O and μ_3 -OH groups, defining the
14
15 other square face. The main Zr–O bond distances between the Zr^{IV} ion and the carboxylate oxygen
16
17 atoms are 2.16 Å (**1·S**), 2.17 Å (**2·S**), 2.15 Å (**3·S**), 2.19 Å (**4·S**). These values are slightly shorter if
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19 compared to those of $[Zr_6O_4(OH)_4(ThTh)_6] \cdot n(DMF)^6$ and $[Zr_6O_4(OH)_4(TzTz)_6] \cdot n(DMF)^4$ (2.23 and
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21 2.22 Å, respectively), proving the existence of a stronger coordinative bond. Each $[Zr_6]$ secondary
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23 building unit is surrounded by twelve carboxylate groups belonging to twelve different ditopic
24
25 ligands, forming a 3D open framework (Figure 1B) of **fcu** topology (assigned with the TOPOS 4.0
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27 software,²⁵ considering the $[Zr_6]$ units as nodes and the ligands as connectors). The structure features
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29 octahedral (~11 Å diameter) (Figure 1C) and tetrahedral (~8 Å diameter) (Figure 1D) cages,²⁶
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31 occupied by solvent molecules. Each octahedral cage is edge-sharing and face-sharing with eight
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33 octahedral and eight tetrahedral cavities, respectively. Two crystallographically distinct DMF solvent
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35 molecules were located within the octahedral and tetrahedral cavities, respectively. Neglecting the
36
37 clathrated solvent, the empty unit cell volume of the four MOFs was estimated with the software
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39 PLATON²⁷ in the range 63-65%, in agreement with the values found in
40
41 $[Zr_6O_4(OH)_4(ThTh)_6] \cdot n(DMF)^6$ and $[Zr_6O_4(OH)_4(TzTz)_6] \cdot n(DMF)^4$ (61 and 62%, respectively);
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43 these values translate into pore volumes of about 0.88 cm³ g⁻¹ (**1·S**), 0.87 cm³ g⁻¹ (**2·S**), 0.99 cm³ g⁻¹
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45 (**3·S**), 0.83 cm³ g⁻¹ (**4·S**). All ligands show a *trans* disposition of their heteroatoms on the two
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47 heterocyclic rings as that found in their uncoordinated form (see also Figure S1 in the Supporting
48
49 Information).^{21-22, 28} Linker deviation from planarity (with dihedral angles between the two
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51 heterocyclic rings falling in the 6-25° range) is observed in all cases, as already found for other
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53 structurally characterized coordination compounds from the literature containing the ThTh²⁻ ligand.²⁹
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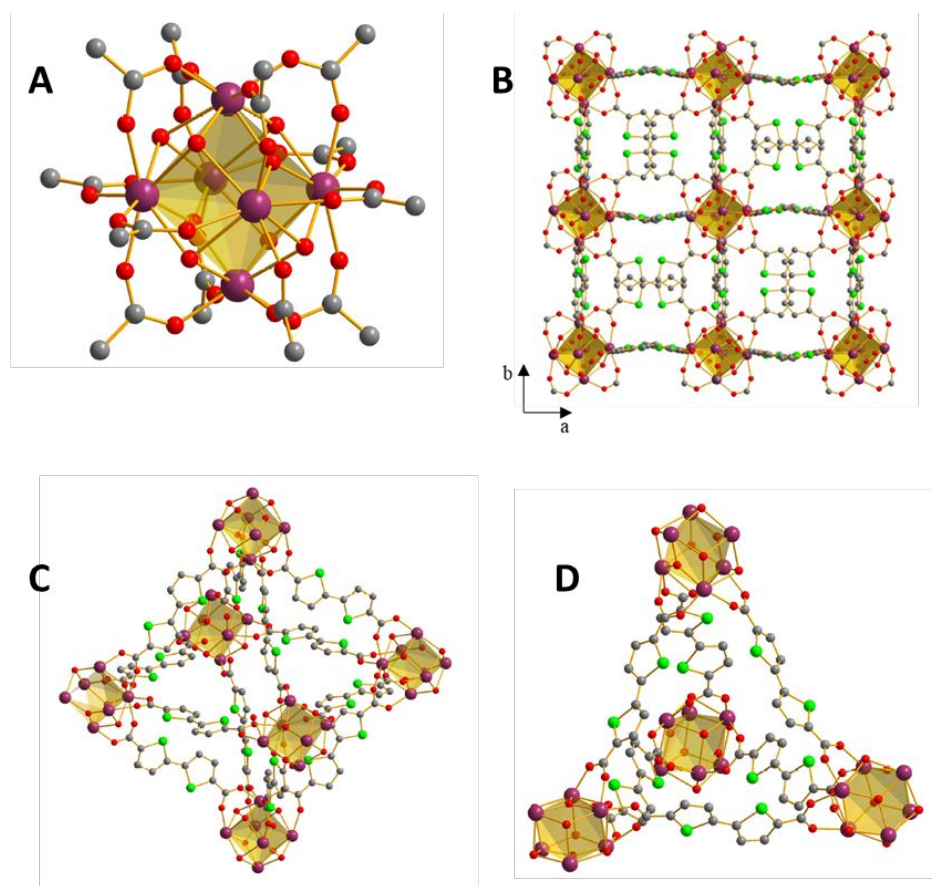


Figure 1. Representation of the crystal structure of **1·S**: (A) the Zr-oxo cluster; (B) portion of the crystal packing viewed along the [100] crystallographic direction; (C) the octahedral cage; (D) the tetrahedral cage. The solvent molecules and hydrogen atoms are omitted. For the sake of simplicity, the graphical model has been built assuming a perfect crystal without missing ligand defects. Atom colour code: carbon, grey; oxygen, red; selenium, light green; zirconium, violet.

Thermal behavior. The thermal analyses (TGA and DSC) carried out under N_2 indicated that **1·S-4·S** undergo the same sequence of events, namely: i) loss of chlatrated solvent; ii) decomposition (Figures S18-S21). The temperature ranges of these events are reported in Table 2.

Table 2. Details of the thermal behaviour of compounds **1·S-4·S**, as observed by TGA under N_2 flow.

		1·S	2·S	3·S	4·S
Loss of solvent	T range (K)	313-473	313-480	313-550	313-600
	Obs. wt. (%)	17.8	16.5	15.7	20.0
	Calc. wt. (%)	16.9	16.3	14.2	22.4
Decomposition	T_{dec} (K)	692	697	676	692
	Res. Mass (%)	24.6	25.0	27.1	29.3
	Chemical residue	$5(ZrC) \cdot ZrO_2$	$6(ZrC)$	$6(ZrC)$	$5(ZrO_2) \cdot ZrS_2$
	(Calc. wt.%)	(24.7)	(25.2)	(26.8)	(29.6)

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5 The decomposition temperature is in the range 675-700 K. The introduction of a bithiophene linker
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7 strengthens the structure stability with respect to the pure biselenophene sample (**2** vs. **1**), while the
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9 opposite occurs with bithiazole (**3** vs. **1**). In the triple-mixed MOF **4**, the two effects mutually vanish,
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11 and the decomposition temperature equals that of **1**. In addition, the pure biselenophene MOF **1** has
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13 a decomposition temperature slightly higher than those of its pure bithiophene $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{ThTh})_6]$
14
15 ($T_{\text{dec}} = 663 \text{ K}$)⁶ or bithiazole $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{TzTz})_6]$ ($T_{\text{dec}} = 673 \text{ K}$)⁴ analogues. This can be related to
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17 the different acidity of the corresponding carboxylic acids and their ability at engaging into
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19 coordination bonds of variable strength with zirconium. Selenium has a higher polarizability and
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21 charge delocalization ability than sulphur, because of its low-energy-lying empty *4d* orbitals.
22
23 Consequently, selenophene carboxylate is slightly more basic than thiophene carboxylate (*pKa* of the
24
25 corresponding acids 10.4 and 10.5, respectively).⁸ Judging from the residual mass values found, the
26
27 solid residues at the end of the decomposition process are likely to be simple binary zirconium
28
29 inorganic compounds like zirconium carbide (ZrC), zirconium oxide (ZrO₂), zirconium sulphide
30
31 (ZrS₂) or their mixtures; tentative compositions are provided in Table 2. Worthy of note, the existence
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33 of a single peak in the DSC curves concomitant with the decomposition of **2·S-4·S** indicates the
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35 presence of a unique phase rather than a solid solution. The variable-temperature PXRD experiment
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37 carried out on **1·S** as a representative example (Figure S22A) highlighted that the MOF gradually
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39 loses its crystallinity starting from room temperature, becoming practically amorphous at 663 K. In
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41 the temperature range 303-423 K, the unit cell volume increment is about 0.4% (Figure S22B); this
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43 low value reveals the high rigidity of the crystal structure when the external stimulus is the
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45 temperature variation.
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55 **N₂ adsorption.** The four MOFs texture and porosity were evaluated through N₂ adsorption
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57 isotherms measured at 77 K. All samples were previously evacuated with a thermal treatment
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59 by heating them at 303 K under high vacuum for 24 h, to remove the solvent inside the pores
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coming from the synthesis. As shown in Figure 2A, **1-4** show type I isotherms, typical of a microporous material, with BET areas in the $300 \div 550 \text{ m}^2/\text{g}$ range. These values are much lower than those found for the pure linker analogues $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{ThTh})_6]$ ($2207 \text{ m}^2/\text{g}$)⁶ or $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{TzTz})_6]$ ($840 \text{ m}^2/\text{g}$),⁴ possibly because of the defective nature of the samples or due to the rapid loss of crystallinity upon heating (see above). The limiting micropore volume estimated through the application of the Dubinin-Astakhov model to the N_2 adsorption isotherm of the real samples equals 0.23, 0.15, 0.12 and $0.19 \text{ cm}^3/\text{g}$ for **1-4**, respectively. The total pore volumes evaluated at $p/p^* = 0.98$ equal 0.26, 0.23, 0.17 and $0.21 \text{ cm}^3/\text{g}$ for **1-4**, respectively. In all samples, there are two different micropore sizes (retrieved from the NLDFT analysis – Tarazona model for cylindrical pores) of *ca.* 18 and 22 Å (Figure 2B), in line with the crystallographic results related to the $\text{Zr} \cdots \text{Zr}$ distances between opposite metallic nodes in the framework and similar to those found for the biphenyl parent MOF UiO-67 (12 and 16 Å).⁵

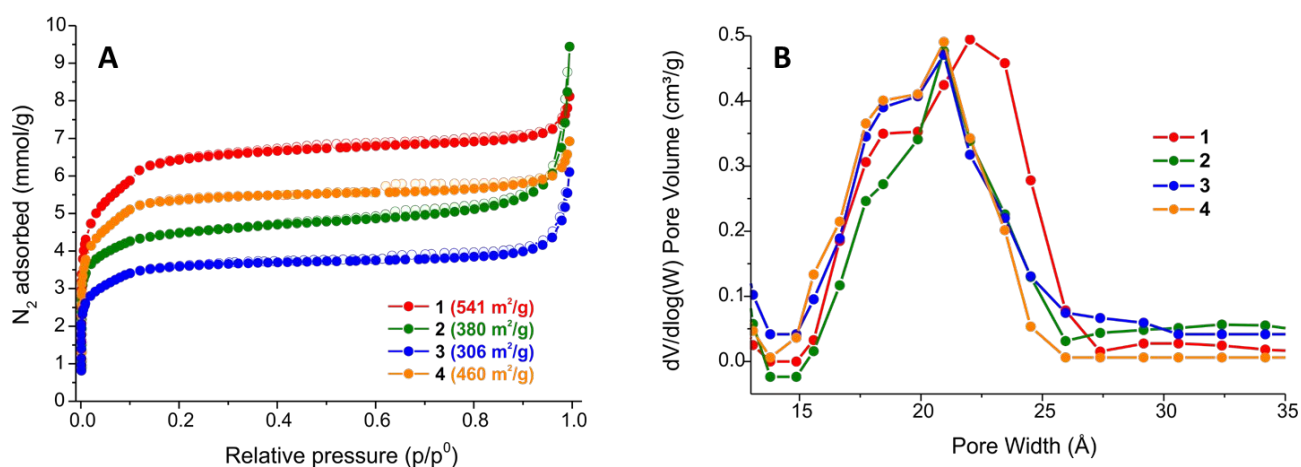


Figure 2. (A) N_2 isotherms measured at 77 K on **1-4**. The desorption isotherm branch is depicted with empty symbols. (B) Pore size distribution (NLDFT – Tarazona model for cylindrical pores) of **1-4**.

Luminescence studies. Initially, the luminescent properties of the bare linkers were studied both in DMF solution and in the solid state. In DMF (Figure 3A), the three absorption and emission maxima of H_2SpSp , H_2ThTh and H_2TzTz are found in the $345 < \lambda_{\text{max,abs}} < 366 \text{ nm}$ and $405 < \lambda_{\text{max,em}} < 435 \text{ nm}$ ranges for absorption and emission, respectively. In the solid state, their emissions are red-

shifted and generate characteristic blue/green colors under a UV lamp, whose CIE chromatic coordinates are shown in Figure 3B.

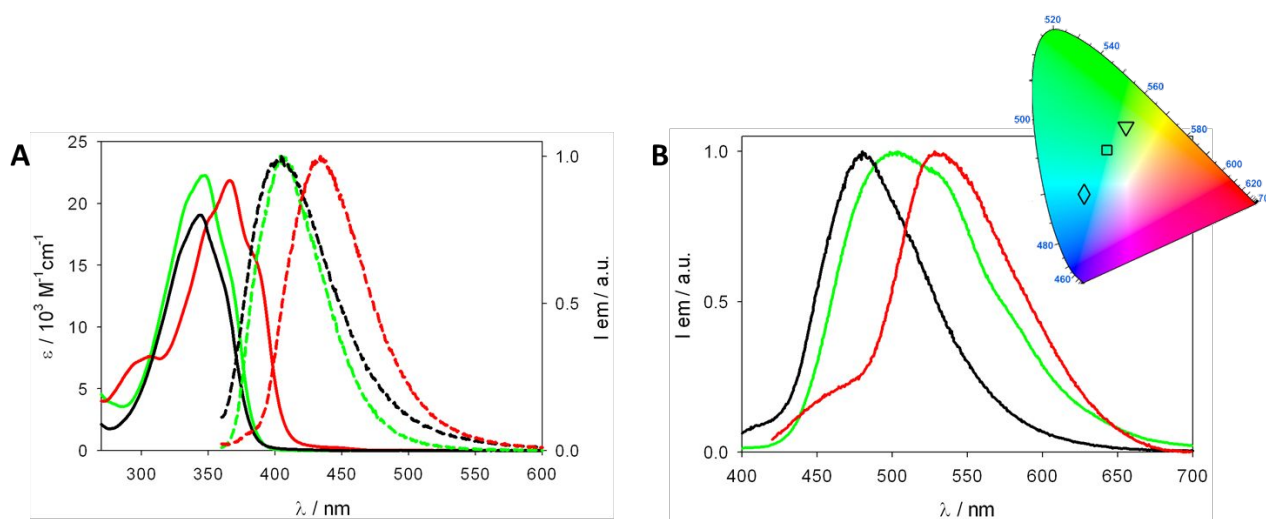


Figure 3. (A) Absorption (solid lines) and normalized emission spectra (dashed lines) of **H₂SpSp** (red), **H₂ThTh** (green) and **H₂TzTz** (black) in DMF solution at r.t. ($\lambda_{\text{ex}}=340$ nm). (B) Normalized emission spectra of the same compounds as powders at r.t. ($\lambda_{\text{ex}}=390, 350$ and 360 nm, respectively). Inset: collective CIE diagram derived from the emission spectra (**H₂SpSp**, triangle; **H₂ThTh**, square; **H₂TzTz**, diamond).

The emission spectra and the CIE diagrams of the related MOFs **1·S-4·S** in DMF suspensions are reported in Figure 4. The emission maximum of the pure selenophene MOF **1·S** falls at $\lambda = 510$ nm and it is red-shifted with respect to that of free **H₂SpSp** in DMF; this shift may be caused by the chromophore coordination to Zr^{IV}. In the MIXMOF samples, the emission wavelengths ($\lambda_{\text{max}} = 485, 450$ and 485 nm for **2·S-4·S**, respectively) are associated to blue-green colors. More specifically, the biselenophene/bithiazole MOF **3·S** shows CIE coordinates in the blue region, while the other compounds are closer to green. Blue emitters show applications in displays and solid-state lighting,³⁰ while green-colored LEDs are exploited in medical fields (chromotherapy). Green light helps to lighten hyper-pigmentation spots and has calming and anti-inflammatory properties. In addition, the green color is slightly sedative with beneficial effects for sleep and stress reduction.³¹ Unfortunately, the emission intensity is rather low, falling under the ordinary detection limit set for solid-state materials (luminescence quantum yield < 0.05 found in all samples). This phenomenon is frequently observed in the crystalline solid state, where organic-based multicolor emission is hampered by fluorophores aggregation, phase separation and mutual quenching.³² This problem was also

encountered in other literature MOFs where all the organic linkers in the framework are emissive fluorophores.³³

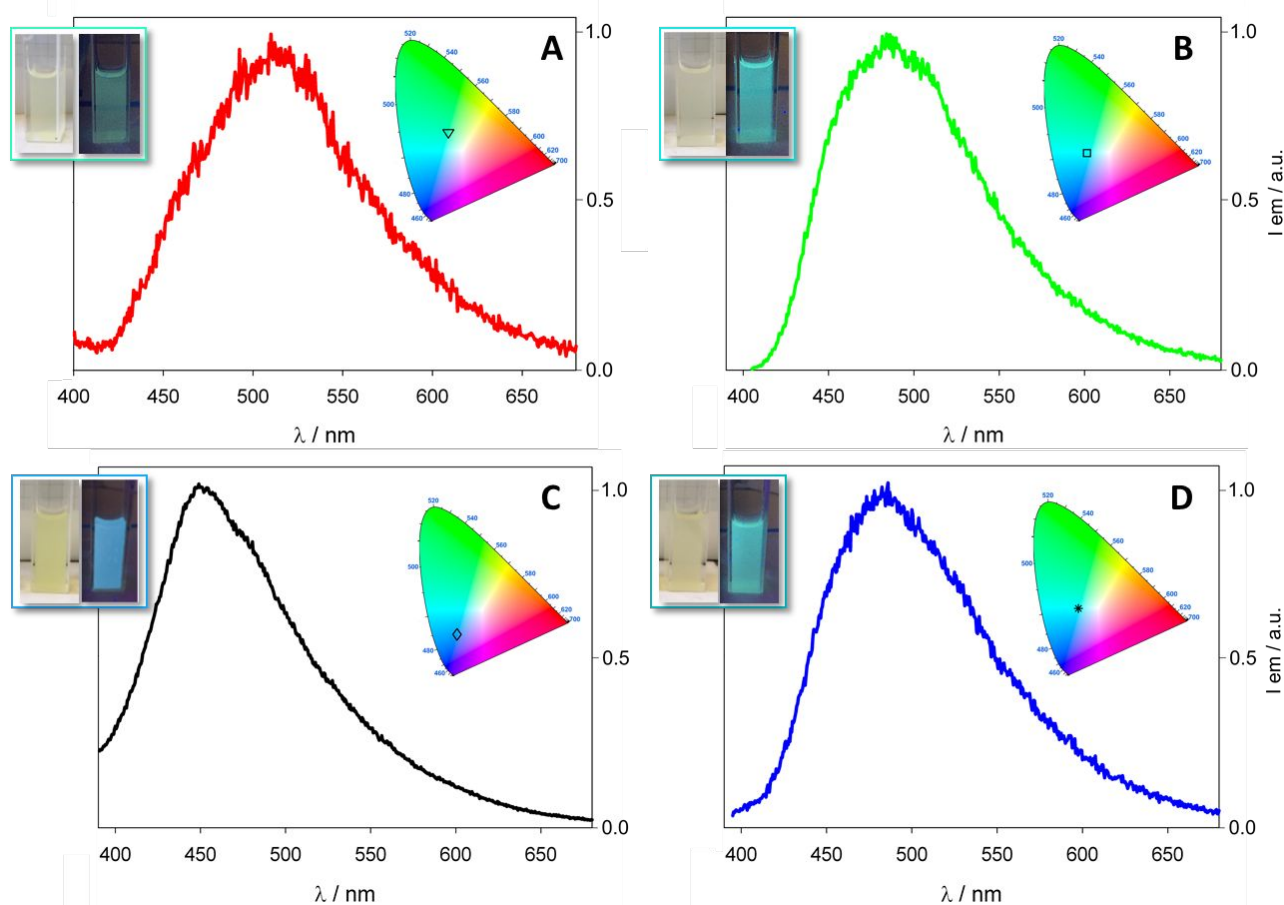


Figure 4. Normalized emission spectra and corresponding CIE diagrams of **1·S-4·S** in DMF suspension. Inset: photos taken on the suspensions under ambient light (left) and under UV excitation (right). A: **1·S**; B: **2·S**; C: **3·S**; D: **4·S**. $360 < \lambda_{\text{ex}} < 380$ nm.

Conclusions

Four novel microporous (MIX)MOFs with five-membered S/Se-containing heterocyclic linkers bound to zirconium nodes have been prepared and fully characterized in the solid state. Selenophene, thiophene and thiazole are luminescent organic molecules that find application in the fields of LEDs and optoelectronics. Their inclusion into an ordered crystalline scaffold kept together by $[\text{Zr}_6]$ secondary building units produces luminescent materials emitting in the blue-green visible range upon excitation by a suitable UV wavelength. The measured emission quantum

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3 yields are low in all cases, because of self-quenching effects coming from the formation of
4 non-fluorescent aggregates in the solid state. This is a proof of evidence that the crystal lattice
5 is made of domains containing the same linker type instead of being distributed randomly
6 within the solid matrix. When chemically different linkers form large clusters within the
7 lattice, the fluorescence is completely quenched, as recently shown in a seminal work
8 published by Zhou and co-workers.³⁴ A viable strategy to solve this problem is the “solid state
9 dilution” of the chromophore using an excess of another non-emissive spacer for the
10 MIXMOF construction.³⁵ This approach is currently being pursued in our laboratories for the
11 preparation of MIXMOFs featured by enhanced luminescence properties.
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26 **Conflicts of Interest.** The authors have no conflicts of interest to declare.
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30 **Associated Content**

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32 **Supporting Information.** Main crystallographic data, experimental details and structure
33 refinement details for **Et₂SpSp**, IR spectra of **1·S-4·S** at comparison, XRF spectra of **1·S-4·S**,
34 graphical results of the structure refinement for **1·S-4·S**, ¹H NMR spectra of the digested mixed
35 samples **2·S-4·S** in D₂SO₄, representation of the crystal structures of **2·S-4·S**, additional PXRD
36 information, TGA-DTG-DSC plots for **1·S-4·S**, VT-PXRD experiment on **1·S**.
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TOC Graphic

