Benzothiazolium-functionalized NU-1000: a versatile material for carbon dioxide adsorption and cyanide luminescence sensing†

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A tailor-made benzothiazolium bromide salt functionality (BzTz) is introduced via solvent-assisted ligand incorporation (SALI) into the mesoporous Zr-based metal–organic framework NU-1000. The resulting NU-1000-BzTz composite has been thoroughly characterized in the solid state. The functional group loading has been determined through 1H NMR analysis of the digested sample (5% HF-DMSO-d6): a maximum value of 1.7 BzTz ligand per [Zr6] node is achieved. The material preserves its pristine crystallinity after SALI, as witnessed by powder X-ray diffraction. The functionalized MOF has a slightly lower thermal stability than its parent material (Tdec = 780 vs. 800 K, respectively). The N2 adsorption isotherm collected at 77 K disclosed that its BET specific surface area (1530 m2 g−1) is lower than that of pristine NU-1000 (2140 m2 g−1), because of the space taken and weight added by the dangling benzothiazolium groups inside the pores. A total CO2 uptake of 2.0 mmol g−1 (8.7 wt% CO2) has been calculated from the CO2 adsorption isotherm collected at T = 298 K and pCO2 = 1 bar. Despite the lower BET area, NU-1000-BzTz shows an increased thermodynamic affinity for CO2 (isosteric heat of adsorption QA = 25 kJ mol−1) if compared with NU-1000 (QA = 17 kJ mol−1), confirming that the presence of a polar functional group in the MOF pores improves the interaction with carbon dioxide. Finally, NU-1000-BzTz has been exploited as a luminescent sensor for polluting anions (CN−, SCN−, OCN−, and SeCN− as sodium or potassium salts) in aqueous solutions, after bromide exchange. A marked reversible blue shift of its emission band from 490 to 450 nm is observed in all cases, with the associated emission color change from light green to blue under a UV lamp. The detection limit of CN− (1.08 × 10−6 M) is much lower than that measured for the other “stick-like” anions considered in this study. The process occurs efficiently even in the presence of other competing ions (i.e. in ordinary tap water), opening promising application perspectives in cyanide luminescence sensing in drinking water.

Introduction

Metal–organic frameworks (MOFs) undoubtedly represent the most widely studied coordination compounds in contemporary materials chemistry research.1–4 Crystalline and often highly porous, their chemical diversity and typically high surface areas give them strength for a broad range of potential applications including gas storage and separation, catalysis,10–13 sensing14–16 and light harvesting.17,18 Besides the infinite metal node-linker combinations conceivable for the construction of
Previously unknown crystalline scaffolds, their versatile nature can be further improved through the post-synthetic modification of already known structures. The introduction of new chemical entities into the MOF framework can be achieved through various approaches like covalent linker modification or partial replacement of the organic linkers using the so-called solvent-assisted linker exchange (SALE) technique. Another promising experimental protocol in this context (especially for the zirconium-based MOFs) is metal node functionalization through chemical modification. Functionalization –OH groups are reactive and present opportunities for channel opening experimental protocol in this context (especially for the zirconium-based MOFs) is metal node functionalization through chemical modification. Functionalization –OH groups are reactive and present opportunities for channel opening.

MOFs derived from carboxylic acid and the hydroxo groups present in the pristine MOF metallic secondary building units. MOFs derived from oxophilic [Zr6O4(OH)4(OH)4(H2O)4]8+ nodes where eight of the twelve coordination sites are occupied by TBAPY4− linkers [H,TBAPY = 1,3,6,8-tetraakis(2-pyridyl-4-carboxylic-acid)pyrene, Fig. 1]. The four terminal –OH groups are reactive and present opportunities for channel chemical modification. Functionalization via SALI leads to the anchorage of ligands strongly bound to the NU-1000 node in a chelating fashion. From the metal node stoichiometric composition, a maximum loading of four functional groups per [Zr6] node is thus possible. The as-synthesised samples retain the same crystallinity of the parent NU-1000 but they generally have a slightly lower surface area, because of the empty volume reduction and added weight upon functionalization. Previous work by some of us has already shown the great potentiality of this technique for the preparation of novel NU-1000-FG (FG = functional group) materials. Some of these compounds have shown excellent performances in carbon dioxide storage, with high absolute uptakes at ambient temperature and pressure conditions and enhanced thermodynamic affinity compared to their parent NU-1000. The improvement of the CO2 isosteric heat of adsorption (Qst) values has been achieved through the introduction of perfluorinated alkyl chains (because of the known affinity of supercritical CO2 for perfluoralkanes) or decoration of the MOF pores with di- or tripeptides that present charge distributions complementary to those of quadrupolar CO2.

Searching for additional applicative contexts of NU-1000-FG materials besides CO2 storage, we considered luminescent ion sensing. As chemical sensors, luminescent MOFs possess a number of advantages over other luminescent materials. Analyte adsorption within MOF pores allows for its pre-concentration, increasing sensor sensitivity. Selectivity can be achieved by tuning pore dimension and/or by proper functionalization of the linkers or the metallic nodes. In the most interesting cases, the guest molecule induces a shift in the MOF emission frequency. This signal transduction is highly desirable because analyte uptake can be read out as a marked color change by the naked eye (if the emission band falls in the visible region). NU-1000-FG MOFs have already found applications in photocatalysis or in light harvesting. Only recently, a few examples focused on luminescence sensing of dibenzo-p-dioxins, cholesterol and 1-hydroxyypyrene by NU-1000 or NU-1000-FG materials have started to appear in the literature. Our previous experience in MOF synthesis for CO2 storage and luminescence sensing prompted us to design a single NU-1000-FG material suitable for both targets. As (N,S)-containing and intrinsically luminescent heterocycles with basic sites that can interact with acidic CO2, thiazoles and thiazolium salts are the optimal choice in this context. In this work, we present the SALI functionalization of NU-1000 with a monocarboxylic acid decorated with a benzothiazolium tail: BzTz = 3-(4-carboxybenzyl)benzo[d]-thiazolium bromide (Fig. 1). The resulting NU-1000-BzTz composite has been thoroughly characterized in the solid state and successfully exploited in two different applicative contexts: carbon dioxide adsorption and luminescence sensing of polluting anions in aqueous solutions.

![Molecular representations of NU-1000 and schematic representation of its SALI functionalization with a benzothiazolium salt to afford the new material NU-1000-BzTz (idealized structure only, no X-ray data from real sample available).](image)
Experimental section

Materials and methods

All the chemicals and reagents employed were purchased from commercial suppliers and used as received without further purification. **NU-1000** was prepared according to the published procedures. For the organic syntheses, solvents were purified through standard distillation techniques. Deuterated solvents (Sigma Aldrich) were stored over 4 Å molecular sieves and degassed by three freeze–pump–thaw cycles before use. NMR spectra were recorded on a BRUKER AVANCE 400 MHz spectrometer. 1H and 13C{1H} NMR chemical shifts are reported in parts per million (ppm) downfield of tetramethylsilane (TMS) and were calibrated against the residual resonance of the protiated part of the deuterated solvent. FT-IR spectra (KBr pellets) were recorded on a PerkinElmer Spectrum BX Series FTIR spectrometer, in the 4000–400 cm⁻¹ range, with a 2 cm⁻¹ resolution. Thermogravimetric analysis measurements were performed under a N₂ atmosphere (100 mL min⁻¹) at a heating rate of 10 K min⁻¹ on an EXSTAR Thermo Gravimetric Analyzer (TG-DTG) Seiko 6200. The instrument was equipped with a conventional TGA dancer and an evolved gas analyzer. The C, H, N, and S elemental analyses were carried out at ICCOM-CNR using a Thermo FlashEA 1112 elemental analyzer. For the organic syntheses, solvents were purified through standard distillation techniques. Deuterated solvents were degassed by three freeze–pump–thaw cycles before use. NMR spectra were recorded on a BRUKER AVANCE 400 MHz spectrometer, in the 4000–400 cm⁻¹ range, with a 2 cm⁻¹ resolution. Thermogravimetric analysis measurements were performed under a N₂ atmosphere (100 mL min⁻¹) at a heating rate of 10 K min⁻¹ on an EXSTAR Thermo Gravimetric Analyzer (TG-DTG) Seiko 6200. The instrument was equipped with a conventional TGA dancer and an evolved gas analyzer.

Synthesis of **NU-1000-BzTz**

Following the general SALI procedure reported by Hupp, Farha et al., the benzothiazolium salt **BzTz** (0.163 g, 0.46 mmol, 10 eq.) was added to a suspension of benzoate-free **NU-1000** (0.100 g, 0.046 mmol) in a dry and degassed polar solvent mixture (total volume 45 mL, acetonitrile : dimethylsulfoxide = 90:10). The reaction mixture was heated at 353 K for 24 h with occasional gentle swirling. After that time, the mixture was brought back to room temperature and the precipitate was filtered over a 0.2 μm PTFE filter. The bright yellow solid residue was sequentially washed with hot acetonitrile, acetone and dichloromethane (3 × 20 mL each) and finally dried in air. The extent of benzothiazolium salt incorporation was estimated through signal integration of the 1H NMR spectrum of the solution obtained after digesting the sample in a 5% HF-DMSO-d₆ mixture and heating to 343 K for 30 min (see ESI† and Fig. S4). The maximum loading achieved was 1.7(BzTz) per [Zr₆] node. IR (KBr pellet, cm⁻¹): 3387 (w, br) [v(N–H)], 3095 (w) [v(C–Haromatic)], 2928 (w) [v(C–Hsphtalic)], 1655 (vs) [v(C=O)], 1500 (s) [v(C–C=O)], 1435 (w), 1384 (s), 1275 (m), 1250 (m), 1204 (w), 1163 (w), 1123 (s), 1093 (m), 1056 (s), 1014 (w), 946 (s), 839 (m).

Gas adsorption

**NU-1000-BzTz** (~40 mg) was activated at 393 K under high vacuum (10⁻⁶ Torr) for 12 h before each measurement. The textural properties were estimated by volumetric adsorption carried out using an ASAP 2020 Micromeritics instrument, using N₂ as adsorbate at 77 K. For the Brunauer–Emmett–Teller (BET) specific surface area calculation, the 0.01–0.0 p/p° pressure
range of the isotherm was used to fit the data. Within this range, all the Rouquerol consistency criteria are satisfied. The pore size distribution was determined on the basis of the NLDFT method (Tarazona model for cylindrical pores). CO$_2$ adsorption isotherms were recorded at 273 and 298 K at a maximum pressure of 1.2 bar. The isosteric heat of adsorption ($Q_{st}$) was calculated from the CO$_2$ isotherms measured at 273 and 298 K according to a variant of the Clausius–Clapeyron equation:

$$\ln \left( \frac{p_1}{p_2} \right) = \frac{Q_{st}}{R} \times \frac{T_2 - T_1}{T_1 \times T_2}$$

where $p_n (n = 1$ or 2) is the pressure value for isotherm $n$; $T_n (n = 1$ or 2) is the temperature value for isotherm $n$; $R$ is the gas constant (8.314 J K$^{-1}$ mol$^{-1}$).

Luminescence measurements and anion sensing experiments

The experiments were carried out in air-equilibrated water suspensions at 298 K unless otherwise noted. UV-vis absorption spectra were recorded using a PerkinElmer Lambda spectrophotometer using quartz cells with path length of 1.0 cm. Luminescence spectra were recorded using a PerkinElmer LS-50 or an Edinburgh FLS920 spectrofluorimeter equipped with a Hamamatsu R928 phototube. Lifetimes shorter than 10 µs were measured by the above-mentioned Edinburgh FLS920 spectrofluorimeter equipped with a TCC900 card for data acquisition in time-correlated single-photon counting experiments (0.5 ns time resolution). For solid samples, the emission quantum yield was calculated from the corrected emission spectra registered using an Edinburgh FLS920 spectrofluorimeter equipped with a barium sulfate coated integrating sphere (4 inch), a 450 W Xe lamp (λ excitation tunable by a monochromator supplied with the instrument) as light source, and an R928 photomultiplier tube, following the procedure described by De Mello et al. The estimated experimental errors are 2 nm for the band maximum, 5% for the molar absorption coefficient and luminescence lifetime, and 20% for the emission quantum yield of a solid.

Results and discussion

Synthesis of NU-1000-BzTz, solid state characterization and CO$_2$ adsorption

After the straightforward preparation of the benzo[18,19]thiazolium salt BzTz through benzo[18,19]thiazole N-alkylation by 4-(bromo- methyl)benzoic acid (Scheme S1, ESI†), the new monocarboxylic ligand was incorporated into activated microcrystalline samples of NU-1000 via SALI by exposing the MOF to solutions of 10 eq. of BzTz per [Zr$_6$] node in a polar solvent mixture of dimethyl sulfoxide (DMSO) and acetonitrile (MeCN) at 353 K for 48 h (see Experimental section for a detailed description). As already noticed for other FGs, SALI was unsuccessful in solvent mixtures containing water. Therefore, it is essential to employ anhydrous solvents to get a good conversion in this step. The extent of FG incorporation was estimated by $^1$H NMR spectroscopy after dissolving NU-1000-BzTz samples in a 5% HF-DMSO-$d_6$ mixture heated to 343 K to promote the digestion process. The corresponding signals of the incorporated FG (Fig. S4, ESI†) were integrated against that of the TBAPy ligand. In our hands and under the same (optimized) experimental conditions, the amount of BzTz incorporated into NU-1000 is reproducible for all the batches prepared. A maximum loading of 1.7 BzTz ligand per [Zr$_6$] node was obtained. This stoichiometry is slightly lower than that observed for other NU-1000-FG samples in the literature (between 2 and 4), possibly due to the big steric hindrance of BzTz that hampers further functionalization of the [Zr$_6$] cluster. The as-obtained NU-1000-BzTz has been thoroughly characterized in the solid state. Powder X-ray diffraction (PXRD) analysis (Fig. 2a) showed that the parent framework

![Fig. 2](image-url)
remains intact after functionalization; only slight differences in relative diffraction peak intensities and positions were observed, due to changes in the electron density introduced by BzTz and to the modification of the unit cell lattice parameters after inclusion of the bulky benzothiazolium groups. The IR spectra (Fig. S5, ESI†) are not informative of the occurred transformation, the main adsorption bands being superimposable for NU-1000 and NU-1000-BzTz in the 2000–400 cm⁻¹ wavenumber range. A more detailed analysis can be made by looking at the difference spectrum [(NU-1000-BzTz)–(NU-1000)] compared with that of pure BzTz (Fig. S6, ESI†). Some of the typical benzothiazolium normal vibrational modes32 can be identified at 1700 cm⁻¹ [ν(COO)], 1609 cm⁻¹ [ν(C–C)], 1417 cm⁻¹ [δ(CH₃)] and 729 cm⁻¹ [γ(CH)]. Thermogravimetric analysis (TGA, Fig. 2b) showed that the thermal stability of NU-1000-BzTz is slightly lower than that of NU-1000 (T_des = 780 vs. 800 K, respectively), possibly because of the (destabilizing) electronic effect caused by the dangling group attached to the metal nodes. An initial weight loss of ca. 22.0 wt% (in line with the stoichiometric 1:1.7 [Zr₆]:BzTz ratio found through ¹H NMR analysis) can be reasonably ascribed to the BzTz dangling group decomposition. In fact, the DTG peak found in this range falls at T = 532 K, a value that is very close to that found for the isolated BzTz decomposition occurring at T = 510 K (Fig. S7, ESI†). In line with this finding, the pore size distribution evaluated through the NLDFT model (Fig. S8, ESI†) shows a slightly reduced mesopore size for the functionalized material (w = 33 vs. 28 Å for NU-1000 and NU-1000-BzTz, respectively), while the micropore size is practically unchanged. This reveals that SAII functionalization occurs in the mesopores only, similar to other NU-1000-FG materials reported in the literature. NU-1000-BzTz showed an increased affinity for carbon dioxide compared with its parent MOF. The total CO₂ uptake at p_CO₂ = 1 bar and T = 298 K and 273 K is 8.7 wt% (2.0 mmol g⁻¹) and 10.8 wt% (2.5 mmol g⁻¹), respectively (Fig. 3b). The absolute gas uptake falls in the same range as that found for other thiazole-containing MOFs like Zr₆(O)₄(OH)₄(TzTz)₆ (7.5 wt%, TzTz = thiazole-5-dicarboxylate),40 but it is lower than that measured for NU-1000 (ca. 3.0 mmol g⁻¹),25 this value being proportional to the respective BET areas. Nevertheless, when the CO₂ isosteric heat of adsorption at zero coverage (Q_st) is considered, the benzothiazolium-functionalized MOF has a higher Q_st value than that found for its parent analogue (25 vs. 17 kJ mol⁻¹, respectively). The isosteric heat of adsorption reflects the interaction strength between CO₂ and the inner MOF pore walls; the introduction of a polar molecule like a benzothiazolium salt into the MOF channels is beneficial for the MOF–CO₂ interaction. The Q_st value found for NU-1000-BzTz is of the same order of magnitude as that calculated for other perfluoroalkane-functionalized25 or peptide-functionalized31 NU-1000 samples of the literature (between 24 and 34 kJ mol⁻¹).

The porosity of NU-1000-BzTz was evaluated by recording the N₂ adsorption isotherm at 77 K on desolvated samples (Fig. 3a). The isotherm shape is the same as that of NU-1000, confirming its mesoporous texture. An obvious reduction in gas uptake and the BET surface area in comparison to that of the parent NU-1000 material was recorded (from 2140 to 1530 m² g⁻¹), because of the reduced empty pore volume after functionalization (the total pore volume at p/p₀ = 0.98 equals 1.53 and 0.93 cm³ g⁻¹ for NU-1000 and NU-1000-BzTz, respectively).

In line with this finding, the pore size distribution evaluated through the NLDFT model (Fig. S8, ESI†) shows a slightly reduced mesopore size for the functionalized material (w = 33 vs. 28 Å for NU-1000 and NU-1000-BzTz, respectively), while the micropore size is practically unchanged. This reveals that SAII functionalization occurs in the mesopores only, similar to other NU-1000-FG materials reported in the literature. NU-1000-BzTz showed an increased affinity for carbon dioxide compared with its parent MOF. The total CO₂ uptake at p_CO₂ = 1 bar and T = 298 K and 273 K is 8.7 wt% (2.0 mmol g⁻¹) and 10.8 wt% (2.5 mmol g⁻¹), respectively (Fig. 3b). The absolute gas uptake falls in the same range as that found for other thiazole-containing MOFs like Zr₆(O)₄(OH)₄(TzTz)₆ (7.5 wt%, TzTz = thiazole-5-dicarboxylate),40 but it is lower than that measured for NU-1000 (ca. 3.0 mmol g⁻¹),25 this value being proportional to the respective BET areas. Nevertheless, when the CO₂ isosteric heat of adsorption at zero coverage (Q_st) is considered, the benzothiazolium-functionalized MOF has a higher Q_st value than that found for its parent analogue (25 vs. 17 kJ mol⁻¹, respectively). The isosteric heat of adsorption reflects the interaction strength between CO₂ and the inner MOF pore walls; the introduction of a polar molecule like a benzothiazolium salt into the MOF channels is beneficial for the MOF–CO₂ interaction. The Q_st value found for NU-1000-BzTz is of the same order of magnitude as that calculated for other perfluoroalkane-functionalized25 or peptide-functionalized31 NU-1000 samples of the literature (between 24 and 34 kJ mol⁻¹).

![Fig. 3](a) N₂ adsorption isotherms of NU-1000 (red diamonds) and NU-1000-BzTz (blue diamonds) for comparison. The desorption branch is depicted with empty symbols. (b) CO₂ adsorption isotherms of NU-1000-BzTz at T = 273 (blue squares) and 298 K (blue circles).
Luminescence anion sensing with NU-1000-BzTz

Before testing NU-1000-BzTz for luminescence ion sensing in aqueous solutions, its water stability was preliminarily assessed. Like its parent MOF NU-1000,53,54 the functionalized MOF maintains its crystallinity degree and structural texture after soaking in water for 24 h, as witnessed by the PXRD control pattern recorded after this time (Fig. S9, ESI†). As observed for NU-1000,27 NU-1000-BzTz shows very weak solubility in pure water, even after heating and thorough sonication. As a consequence, the dissolution of small amounts of the two MOFs in water gives opaque dispersions whose normalized UV-vis absorption spectra display a significant offset and tailed trace due to the particulate scattering (Fig. 4a).

Interestingly, in the absorption spectrum of NU-1000-BzTz, the characteristic absorption band at $\lambda = 280$ nm registered in H$_2$O for the model compound BzTz (Fig. S10, ESI†) does not appear. However, significant differences between the two MOFs are observed in their luminescence properties (e.g. in suspensions, $\lambda_{\text{max,em}}$ = 450 nm and 490 nm for NU-1000 and NU-1000-BzTz, respectively; Fig. 4b). Moreover, both the MOFs show appreciable emission quantum yields in the visible spectrum as powders in the solid phase ($\Phi_{\text{em}}$ = 0.06 and 0.04 for NU-1000 and NU-1000-BzTz, respectively) and in aqueous suspensions, with small discrepancies in the emission maxima and profiles recorded under the two experimental conditions. The small redshift in the absorption and emission spectra of NU-1000-BzTz compared to NU-1000 could be explained by the presence of the positively charged BzTz subunit, which perturbs the electronic environment of the emitting pyrene ligand and slightly stabilizes its excited state.55,56 Analysis of the luminescence lifetimes on powders and aqueous suspensions of both MOFs gives evidence of nanosecond-scale multiexponential decays, corresponding to singlet excited state paths of deactivation (Fig. S11, ESI†).

Given the confinement properties of several other MOFs, which can be modulated by the preferential interactions between the charged cavities of the MOFs and anions,57 we decided to test the uptake of NU-1000 and NU-1000-BzTz towards highly toxic cyanide in aqueous solutions. Initially, the sensing ability and the emission behaviour of bare BzTz in the presence of aqueous cyanide were checked. Consecutive additions of increasing amounts of aqueous KCN (30.5 mM) to a solution of BzTz in H$_2$O (1.05 $\times$ 10$^{-4}$ M) led to small changes in the absorption spectra and to the progressive quenching of its fluorescence. Moreover, we did not record any changes in the emission profile, i.e. no lambda shift in the fluorescence band occurs upon cyanide addition (Fig. S12, ESI†). Hence, the anchoring of the benzothiazolium emitter to a solid MOF support is of fundamental importance to have a better sensing response. In fact, upon addition of KCN, we observed changes in the emission intensity in both MOFs, with NU-1000 exhibiting a steadily increasing emission quantum yield without showing any saturation in the presence of high CN$^-$ concentrations (Fig. 5a). On the other hand, the emission spectrum of NU-1000-BzTz shifts to shorter wavelengths with increasing the concentration of cyanide, restoring the luminescence of the parent MOF NU-1000. This is probably due to the anionic exchange within the framework, promoted by the presence of the positively charged BzTz fragment (Fig. 5b). Analysis of the excitation spectra demonstrates that the strong emission centered at 450 nm likely originates from the tetrasubstituted pyrene subunit (Fig. S13, ESI†). A very similar behaviour was observed when increasing concentrations of analogous “stick-like” anions such as cyanate (OCN$^-$), thiocyanate (SCN$^-$) and selenocyanate (SeCN$^-$) are added to suspensions of NU-1000-BzTz (Fig. S14, ESI†). By comparing the increments of emission intensities at the emission maxima as functions of the anion concentrations, cyanide was found to give the strongest change (Fig. 5c) with an estimated limit of detection (LOD) of 1.08 $\times$ 10$^{-6}$ M (Fig. S15, ESI†), making the MOF suitable for practical application in the detection of cyanide in drinking water (LOD $\leq$ 2 $\times$ 10$^{-6}$ M). The luminescence response is proportional to the relative basicity of the anions, following the order CN$^-$ $\gg$ OCN$^-$ $>$ SCN$^-$59 The direct

![Fig. 4](image_url)

(a) Normalized absorption spectra recorded for suspensions of NU-1000 (red line) and NU-1000-BzTz (blue) in H$_2$O at r.t. (b) Comparison between normalized emission spectra of NU-1000 (red lines) and NU-1000-BzTz (blue lines) recorded on suspensions in H$_2$O at r.t. (solid) and on powders at r.t. (dashed).
The experimental relationship between LOD and anion basicity leads to the hypothesis of the existence of strong hydrogen bonding interactions between the anion and the H atom in the 2-position of the benzothiazolium unit (the most acidic of the whole

![Graphs and images showing emission spectra and experimental results.](image)

Fig. 5 (a) Evolution of the emission spectra recorded for a suspension of NU-1000 upon addition of KCN (from 0 to ca. 1.4 mM, red to orange line, respectively) in H₂O at r.t. λ_ex = 385 nm; A₁₃₈₅nm = 0.38. Inset: Dependence between [CN⁻] and the emission intensity at 450 nm. (b) Evolution of the emission spectra recorded for a suspension of NU-1000-BzTz upon addition of KCN (from 0 to ca. 1.0 mM, blue to green line, respectively) in H₂O at r.t. λ_ex = 385 nm; 0.32 < A₁₃₈₅nm < 0.35. Inset: Dependence between [CN⁻] and the emission intensity at 430 nm. (c) Evolution of the emission intensities recorded at 430 nm for suspensions of NU-1000-BzTz upon addition of KCN, KOCN and NaSCN (λ_ex = 385 nm).

Fig. 6 (a) Evolution of the emission spectra recorded for a suspension of NU-1000-BzTz upon addition of KCN (from 0 to ca. 0.33 mM, blue to turquoise line, respectively) in H₂O at r.t. followed by addition of Ag(CF₃SO₃) (up to ca. 1.3 mM, dark green line). λ_ex = 385 nm; 0.25 < A₁₃₈₅nm < 0.44. Inset: Photos taken of three suspensions of NU-1000-BzTz in pure water (left), 0.5 mM KCN (centre) and 0.5 mM KCN plus excess of Ag(CF₃SO₃) (right), under ambient light (top) and under UV excitation (bottom). (b) Evolution of the emission spectra recorded for a suspension of NU-1000-BzTz upon addition of KCN (from 0 to ca. 1.6 mM, blue to turquoise line, respectively) in tap water at r.t. λ_ex = 385 nm; 0.18 < A₁₃₈₅nm < 0.21.
Interestingly, upon increasing Ag+ concentration, the MOF emits the insoluble AgCN and removes cyanide from the solution.

To test the reversibility of the NU-1000-BzTz sensing in water, the cyanide-containing aqueous suspensions were treated with progressive additions of silver triflate [Ag(CF3SO3)] to form the insoluble AgCN and remove cyanide from the solution. Interestingly, upon increasing Ag+ concentration, the MOF emission decreases in intensity and shifts back to its pristine maximum around 490 nm. This is proof of the cyanide removal and reversible luminescence sensing of NU-1000-BzTz (Fig. 6a); upon repeated additions of KCN and Ag(CF3SO3), the same MOF showed good reversibility, while its fluorescence emission was monitored at 430 nm (Fig. S16–S19 and attached Movie in the ESI†). Finally, NU-1000-BzTz was found to be effectively sensitive to cyanide also in experiments run in ordinary tap water (Fig. 6b), demonstrating its capability to act like a selective cyanide luminescent probe even in complex ion matrices.

**Conclusions**

The SALI technique has been successfully employed to create a new MOF derived from NU-1000 through incorporation of a tailor-made benzothiazoliun salt inside its pores. The as-obtained NU-1000-BzTz is a stable and multifunctional material, which can be exploited in either carbon dioxide storage (owing to its enhanced thermodynamic affinity for CO2 if compared with its parent MOF) or luminescence polluting ion sensing in aqueous solutions. In particular, its emission response is very sensitive to cyanide, and it is totally reversible and selective in aqueous solutions containing other competing anions (complex matrices like ordinary tap water). The emission colour change from light green to blue under a UV lamp in the presence of trace amounts of CN− makes the detection process very straightforward. The extremely low cyanide limit of detection of NU-1000-BzTz opens new horizons to its practical utilization in drinking water samples. To the best of our knowledge, this is the first example of the employment of an NU-1000-derived MOF as a cyanide luminescence sensor. New thiazole-based MOF materials are currently being prepared in our laboratories with the aim of testing them in CO2 storage and luminescence sensing.

**Conflicts of interest**

The authors have no conflicts of interest to declare.

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**References**

1. L. R. MacGillivray and C. M. Lukehart, Metal-Organic Framework Materials, John Wiley & Sons, New York, 2014.
2. B. Seyyedi, Metal-Organic Frameworks: a New Class of Crystalline Porous Materials, Lambert Academic Publishing, Saarbrücken, 2014.
3. D. Farrusseng, Metal-Organic Frameworks: Applications from Catalysis to Gas Storage, Wiley-VCH Verlag, Weinheim, 2011.
4. M. Schroeder, Functional Metal-organic Frameworks: Gas Storage, Separation and Catalysis, Springer-Verlag, Berlin, Heidelberg, 2010.
5. A. Sturluson, M. T. Huynh, A. R. Kaija, C. Laird, S. Yoon, F. Hou, Z. Feng, C. E. Wilmer, Y. J. Colon, Y. G. Chung, D. W. Siderius and C. M. Simon, Mol. Simul., 2019, 45, 1082–1121.
6. X. Yang and X. Qiang, Cryst. Growth Des., 2017, 17, 1430–1455.
7. H.-C. Zhou, J. R. Long and O. M. Yaghi, Chem. Rev., 2012, 112, 673–674.
8. M. P. Suh, H. J. Park, T. K. Prasad and D. W. Lim, Chem. Rev., 2012, 112, 782–835.
9. O. K. Farha, A. O. Yazaydin, I. Eryazici, C. D. Mallikas, B. G. Hauser, M. G. Kanatzidis, S. T. Nguyen, R. Q. Snurr and J. T. Hupp, Nat. Chem., 2010, 2, 944–948.
10. A. Rossin, G. Tuci, L. Luconi and G. Giambastiani, ACS Catal., 2017, 7, 5035–5045.
11. A. H. Chughtai, N. Ahmad, H. A. Younus, A. Laypkovc and I. Manet, M. Melucci and G. Giambastiani, ACS Catal., 2013, 7, 5035–5045.
12. J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang and C.-Y. Su, Chem. Soc. Rev., 2014, 43, 6011–6061.
13. J. Gascon, A. Corma, F. Kapteijn and F. X. Llabrés i Xamena, ACS Catal., 2014, 4, 6804–6849.
14. Y. Zhang, S. Yuan, G. Day, X. Wang, X. Yang and H.-C. Zhou, Coord. Chem. Rev., 2018, 354, 28–45.
15. F.-Y. Yi, D. Chen, M.-K. Wu, L. Han and H.-L. Jiang, ChemPlusChem, 2016, 81, 675–690.
16. Z. Hu, B. J. Deibert and L. Jing, Chem. Soc. Rev., 2014, 43, 5815–5840.
17. S. Jin, H.-J. Son, O. K. Farha, G. P. Wiederrecht and J. T. Hupp, J. Am. Chem. Soc., 2013, 135, 955–958.
18. H.-J. Son, S. Jin, S. Patwardhan, S. J. Wezenberg, N. C. Jeong, M. So, C. E. Wilmer, A. A. Sarjeant, G. C. Schatz, R. Q. Snurr, O. K. Farha, G. P. Wiederrecht and J. T. Hupp, J. Am. Chem. Soc., 2013, 135, 862–869.
19. G. Tuci, A. Rossin, X. Xu, M. Ranocchiari, J. A. van Bokkoven, L. Luconi, I. Manet, M. Melucci and G. Giambastiani, Chem. Mater., 2013, 25, 2297–2308.
20. S. M. Cohen, Chem. Rev., 2012, 112, 970–1000.
21. W. Bury, D. Fairen-Jimenez, M. B. Lalonde, R. Q. Snurr, O. K. Farha and J. T. Hupp, Chem. Mater., 2013, 25, 739–744.
