Dual-mode humidity detection using a lanthanide-based metal-organic framework: towards multifunctional humidity sensors

Gao, Y.; Jing, P.; Yan, N.; Hilbers, M.; Zhang, H.; Rothenberg, G.; Tanase, S.

DOI
10.1039/C7CC01122A

Publication date
2017

Document Version
Other version

Published in
Chemical Communications

License
Article 25fa Dutch Copyright Act

Link to publication

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: https://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (https://dare.uva.nl)
Dual-mode humidity detection using a lanthanide-based metal-organic framework: towards the development of multifunctional humidity sensors

Yuan Gao,a Pengtao Jing,a,b Ning Yan,a Michiel Hilbers,a Hong Zhang,a,b Gadi Rothenberg,a Stefania Tanasea*

a Van’t Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands. E-mail: s.grecea@uva.nl; h.zhang@uva.nl

b State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, P. R. China

Electronic Supporting Information

Materials and instrumentation

Infrared spectra (4000–400 cm⁻¹, resol. 0.5 cm⁻¹) were recorded on a Varian 660 FTIR spectrometer using KBr pellets and the transmission technique. Powder X–ray diffraction was carried out on a Rigaku Miniflex X-ray Diffractometer. Measurements were done from 3° to 50° with a turning speed of 2.0 °/min. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using a NETZSCH Jupiter® STA 449F3 instrument. The measurements were done under argon (20 mlmin⁻¹) at 35–800 °C. Unless stated otherwise, all chemicals were commercially available (Aldrich, >99% pure) and used as received. The K₂[M(CN)₆]·2H₂O (M⁴⁺ = W, Mo) precursors and the EuM MOFs were synthesized as reported previously.¹,²

Photophysical measurements

Excitation and emission spectra were recorded on a Perkin Elmer LS50B luminescence spectrometer. Measurements were taken on the as-synthesised EuM MOFs (M = Mo, W) and the EuW MOF activated at 80 °C and then exposed to different relative humidity (RH) conditions (in the measuring chamber). The emission spectra intensity was corrected for the sensitivity of the detector. The humidity environment was controlled using different saturated salt solutions.

Luminescence lifetimes were measured using a tunable Nd:YAG-laser system (NT342B, Ekspla) comprising the pump laser (NL300) with harmonics generators (SHG, THG) producing 355 nm to pump an optical parametric oscillator (OPO) with SHG connected in a single device. The excitation energy of laser was 4 mJ/pulse. The laser beam at sample had a diameter of 5 mm without focusing. The laser system was operated at 10 Hz repetition rate with a pulse length of 5 ns. Emission wavelength was selected using a Carl Zeiss M20 single grating monochromator, and the signal is detected using a Hamamatsu PMT type R928P. The luminescence decay curves were recorded every 60 s using a Tektronix 500 MHz digital oscilloscope (Tektronix PDO4054) and a home-written Labview program.

The sample’s stability after each light irradiation measurement is verified by PXRD analysis and also by suspending the sample in water solution. If the burning of the organic portion of the MOFs would occur, this would also result in the formation of free octacyanometallate ions as impurities. Such impurities are very soluble in water and they can be easily identified from the yellow color of the solution or by UV-Vis.
Electrochemical impedance spectroscopy (EIS) measurements.

Samples were prepared using the previous published procedures. The crystalline product was ground with a mortar and pestle to a uniform particle size. The disk-shaped pellets of the EuW MOF were prepared by using a press and a die measuring 13 mm in diameter. The pellet was placed between a pair of parallel copper plates anchored by a clamp. The typical thickness of the sample was ~0.2 mm (±0.05 mm). The electrochemical cell was then fixed with clamp and placed in a humidity-controlled environment which is controlled by different saturated salt solutions. The relative humidity was double checked with the digital sensor. Impedance analysis was measured using 4–points method at different temperatures (30–85 °C) and relative humidities (20–100%). The electrochemical impedance spectroscopy (EIS) tests were carried out under open-circuit voltage (OCV) conditions using a Gamry potentiostat with a frequency range of $10^6$ Hz to 0.1 Hz and voltage amplitude of 10 mV. The impedance response and the recovery time to different relative humidity (RH) values, ranging from 100% to 68% were measured at 500 Hz and 10 mV for powder samples of EuW MOF.
**Figure S1.** (a) The three-dimensional crystal structure of the EuM MOF viewed along the $b$-axis. (b) Close-up view of a single unit cell showing the different coordination environments of the two Eu$^{3+}$ nodes (Eu1 and Eu2).
Figure S2. Excitation ($\lambda_{\text{em}} = 617$ nm, dotted line) and emission ($\lambda_{\text{ex}} = 280$ nm, continuous line) spectra of EuMo (red) and EuW (black) MOFs at room temperature.
Figure S3. UV-Vis spectra of the EuMo (red) and EuW (black) MOFs, $K_4[Mo(CN)_8] \cdot 2H_2O$ (yellow), $K_4[W(CN)_8] \cdot 2H_2O$ (pink) and the Hmpca ligand (orange).
**Figure S4.** The luminescence decay curves of the $^5D_0 \rightarrow ^7F_2$ transition in EuMo (red) and EuW (black) MOFs.
Figure S5. The luminescence decay curves of the $^5D_0 \rightarrow ^7F_2$ transition in EuMo MOF measured within 16 min.
Figure S6. IR spectra of the as-synthesised EuW MOF (black), the EuW MOF activated at 80 °C (red) and its rehydrated form (pink), and the EuW MOF activated at 130 °C (blue) and its rehydrated form (green).
Figure S7. PXRD patterns of the as-synthesised EuW MOF (black), the EuW MOF activated at 80 °C (red) and its rehydrated form (pink), and the EuW MOF activated at 130 °C (blue) and its rehydrated form (green).
Figure S8. Nyquist plots measured at room temperature and different relative humidities.
Figure S9. Nyquist plots measured at 100% relative humidity and different temperatures (top) and the corresponding Arrhenius plot (bottom) for the EuW MOF.
**Table S1.** The response time of lanthanide-based MOFs used for humidity sensing.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Response time (min)</th>
<th>Recovery time (hours)</th>
<th>Characterization method</th>
<th>Rehydration condition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Eu(H₂O)₂(mpca)₂Eu(H₂O)₉W(CN)₆]·nH₂O</td>
<td>5</td>
<td>1</td>
<td>Decay time</td>
<td>Dropwise of water</td>
<td>This work</td>
</tr>
<tr>
<td>[Er₃(fum)₃(H₂O)₆]·8H₂O</td>
<td>n.d.</td>
<td>48</td>
<td>TGA</td>
<td>Water vapor</td>
<td>⁴</td>
</tr>
<tr>
<td>Ba₄(H₂O)₆Eu[L₁]₃(H₂O)₉·(H₂O)Cl</td>
<td>~30</td>
<td>1</td>
<td>TGA</td>
<td>Water vapor</td>
<td>⁵</td>
</tr>
<tr>
<td>[Tb₂(BDOA)₂(H₂O)₆]·6H₂O</td>
<td>n.d.</td>
<td>24</td>
<td>PXRD</td>
<td>Soaked in water</td>
<td>⁸</td>
</tr>
<tr>
<td>[Sm₂(fumarate)₃(H₂O)₉]·3H₂O</td>
<td>n.d.</td>
<td>24</td>
<td>PXRD</td>
<td>Water vapor</td>
<td>⁷</td>
</tr>
<tr>
<td>[Cu₃(bpy)₂Yb₂(ip)₆]·5H₂O</td>
<td>n.d.</td>
<td>24</td>
<td>PXRD</td>
<td>Water vapor</td>
<td>⁸</td>
</tr>
<tr>
<td>[La₂(H₂O)][C₇N₂H₃(COO)₃]·2H₂O</td>
<td>30</td>
<td>~2</td>
<td>PXRD</td>
<td>Ambient conditions</td>
<td>⁹</td>
</tr>
<tr>
<td>[Ln₂(fumarate)₂(ox)₅(H₂O)₄]·4H₂O</td>
<td>n.d.</td>
<td>24</td>
<td>PXRD</td>
<td>Water vapor</td>
<td>¹⁰</td>
</tr>
<tr>
<td>[Gd₂(H₂O)₇Ni(H₂O)₂(bdc)₂(2,5-pydc)₃]·8H₂O</td>
<td>5</td>
<td>1.6</td>
<td>TGA</td>
<td>Water vapor</td>
<td>¹¹</td>
</tr>
<tr>
<td>Eu₃(H₂O)₇PCHOHCOO]·xH₂O</td>
<td>10</td>
<td>2</td>
<td>Decay time</td>
<td>Emission spectra</td>
<td>Water vapor</td>
</tr>
<tr>
<td>[Tb(L₂)(C₇H₄O₆)(H₂O)₆]·H₂O</td>
<td>60</td>
<td>24</td>
<td>Emission spectra</td>
<td>Ambient conditions</td>
<td>¹³</td>
</tr>
<tr>
<td>[Eu₂(CO₃)(ox)₂(H₂O)₇]·4H₂O</td>
<td>n.d.</td>
<td>12</td>
<td>PXRD</td>
<td>90% Relative Humidity</td>
<td>¹⁴</td>
</tr>
<tr>
<td>[{Eu₂(L3)₂(H₂O)₉(Me₂NH)₂}₃]</td>
<td>n.d.</td>
<td>48</td>
<td>PXRD</td>
<td>Refluxed in water</td>
<td>¹⁵</td>
</tr>
<tr>
<td>[{Tb₄(OH)₃(DSOA)₂(H₂O)₉}·(H₂O)₈]</td>
<td>n.d.</td>
<td>24</td>
<td>PXRD</td>
<td>Boiling water</td>
<td>¹⁶</td>
</tr>
</tbody>
</table>

Abbreviations: mpca = 2-pyrazine-5-methyl-carboxylate; fum = fumarate dianion; L₁ = 4,4′-disulfo-2,2′-bipyridine N,N′-dioxide; BDOA = benzene-1,4-dioxylacetate; bpy = 2,2′-bipyridine; ip = isophthalate; ox = oxalate; bdc = benzene-1,2-dicarboxylate; 2,5-pydc = 2,5-pyridinedicarboxylate; HPA = 2-hydroxyphosphonoacetate; L₂ = pyridyl-4,5-imidazole dicarboxylate; L₃ = 5-(3,5-dicarboxybenzoxyl)-isophthalate; DSOA = disodium-2,2′-disulfonate-4,4′-oxydibenzoic acid; n. d. = not determined.
References