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Electronic Supplementary Information

Rapid and efficient electrochemical synthesis of a zinc-based nano-MOF for Ibuprofen adsorption

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Structure

[Zn(1,3-bdc)_{0.5}(bzim)] is a mixed ligand carboxylate/benzimidazolate coordination framework in which these two ligands bridge Zn atoms to form an infinite 3D structure with one-dimensional channels (see Figure S1).

Figure S1. Asymmetric unit with its plane reflection (on the left) and the partially expanded net structure of [Zn(1,3-bdc)_{0.5}(bzim)]. Reproduced with permission from reference 1. Copyright 2015, Elsevier.
**Synthesis**

The quantity of Zn$^{2+}$ ions formed during the electrochemical syntheses was calculated according to the Faraday’s law of electrolysis by the following equation:

\[
n = \frac{i \times t}{z \times F}
\]

where, \(n\) – number of Zn$^{2+}$ mols, \(i\) – current (C.s$^{-1}$), \(t\) – total time the constant current was applied (s), \(z\) – valency number of ions of the substance, \(F\) – Faraday constant, 96 500 C.mol$^{-1}$

**Drug adsorption experiments**

**UV-Vis determination**

To calculate the amount of the drug adsorbed, a calibration curve of the IBU solution of known concentrations was prepared. First, a stock solution of Ibuprofen (0.5 mg/mL) in ethanol was prepared, and from this solution, dilutions were performed, and new concentrations were obtained (0.5, 0.38, 0.25, 0.125, 0.0625 mg/mL). A plot of the area under the curve of absorbance versus concentration was obtained and the equation of the line was used in calculations of concentration of adsorbed drug. **Figure S2** shows an example of absorption spectrum of IBU (C = 0.5 mg/mL) and the inset shows the calibration curve.

![Absorption Spectrum and Calibration Curve](image)

**Figure S2.** UV-Vis absorption spectrum of the stock solution of Ibuprofen (0.5 mg/mL) and the calibration curve in ethanolic solution (inset).

Df – the dilution factor = 76  
V – the solution volume = 1 mL  
m$_{MOF}$ – the amount of MOF used in the adsorption tests = 20 mg
$^{13}$C NMRq

The quantity of Ibuprofen remained in the solution was calculated as a difference of the signal area of the methyl group of the drug (at 22.3 ppm) before and after adsorption. The signal at 67.8 ppm corresponding to the solvent 1,4-dioxane was used as a reference. **Figure S3** presents the $^{13}$C NMR spectrum of the Ibuprofen and **Figure S4** shows the spectrum of Ibuprofen before and after adsorption on $[\text{Zn}(1,3\text{-bdc})_{0.5}\text{(bzim)}]$.

![Figure S3. $^{13}$C NMR spectrum of Ibuprofen.](image1)

![Figure S4. $^{13}$C NMR spectrum of Ibuprofen before (red line) and after (black line) adsorption on $[\text{Zn}(1,3\text{-bdc})_{0.5}\text{(bzim)}]$.](image2)
Table S1. Data for the quantification by $^{13}$C NMR of Ibuprofen adsorbed on [Zn(1,3bdc)$_{0.5}$(bzhim)].

<table>
<thead>
<tr>
<th>Integration area before adsorption ($I_{x1}$)</th>
<th>Integration area after adsorption ($I_{x2}$)</th>
<th>Number of IBU nuclei ($N_{IBU}$)</th>
<th>Number of ref nuclei ($N_{ref}$)*</th>
<th>Quantity of MOF (mMOF) (mg)</th>
<th>Adsorbed quantity (mg/g of MOF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.040</td>
<td>0.038</td>
<td>2</td>
<td>4</td>
<td>20</td>
<td>160.7</td>
</tr>
</tbody>
</table>

*1,4-dioxane was taken as a reference, for which $I_{ref}$ is 1, $MM_{ref} = 88.11$ g.mol$^{-1}$, $d = 1.034$ g.cm$^{-3}$.

**XRD experiments**

![XRD pattern](image)

Figure S5. PXRD pattern of the sample T11 (prepared without benzimidazole) compared to patterns of T2, T4, T6 and T10.
**Figure S6.** PXRD patterns of the sample before (T8) and after Ibuprofen adsorption (IBU@T8).

**FTIR spectra**

**Figure S7.** FTIR spectra of samples obtained via electrochemical synthesis (T2 – T11) and of the reference sample (ST) \(^1\).
$N_2$ adsorption-desorption isotherms

**Figure S8.** $N_2$ adsorption-desorption isotherms of the sample before (T8) and after Ibuprofen adsorption (IBU@T8).

References