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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).

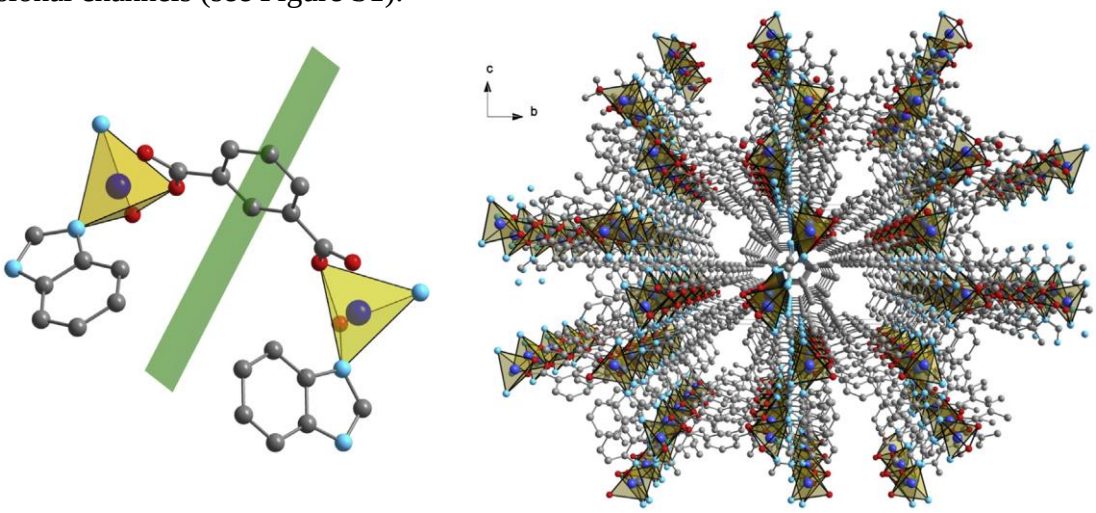

Figure S1. Asymmetric unit with its plane reflection (on the left) and the partially expanded net structure of [Zn(1,3-bdc)$_{0.5}$(bzim)]. Reproduced with permission from reference [1]. Copyright 2015, Elsevier.

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.

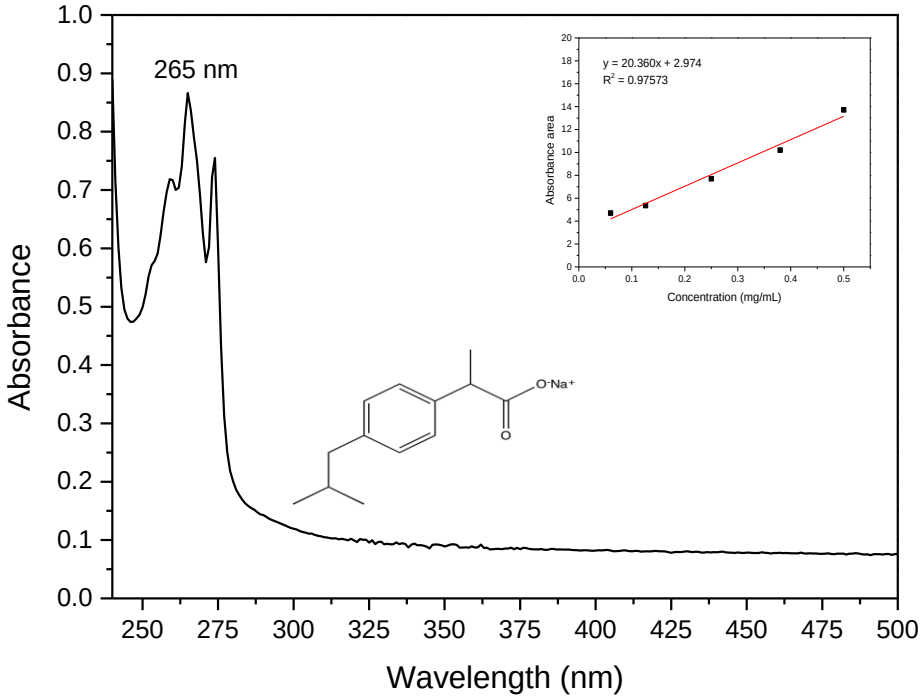

Figure S2. UV-Vis absorption spectrum of the stock solution of Ibuprofen (0.5 mg/mL) and the calibration curve in ethanolic solution (inset).

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 [Zn(1,3-bdc)$_{0.5}$(bzim)].

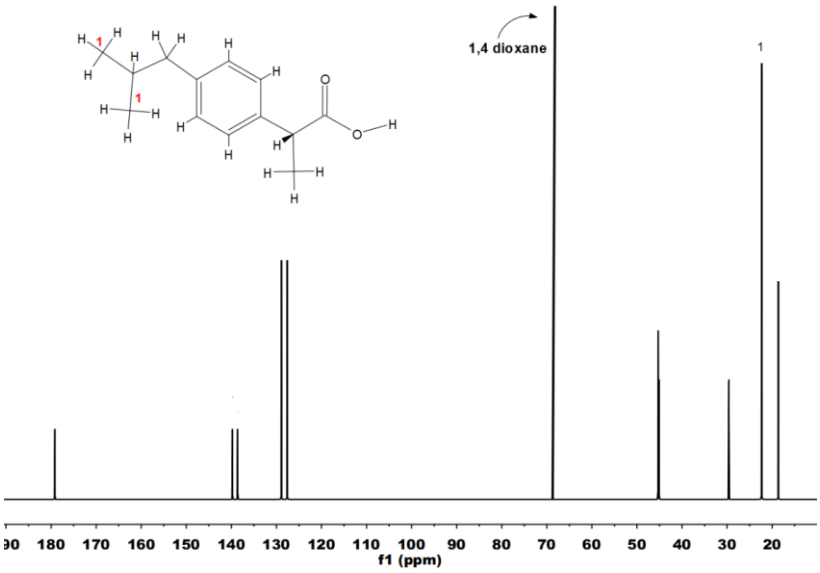

Figure S3. ^{13}C NMR spectrum of Ibuprofen.

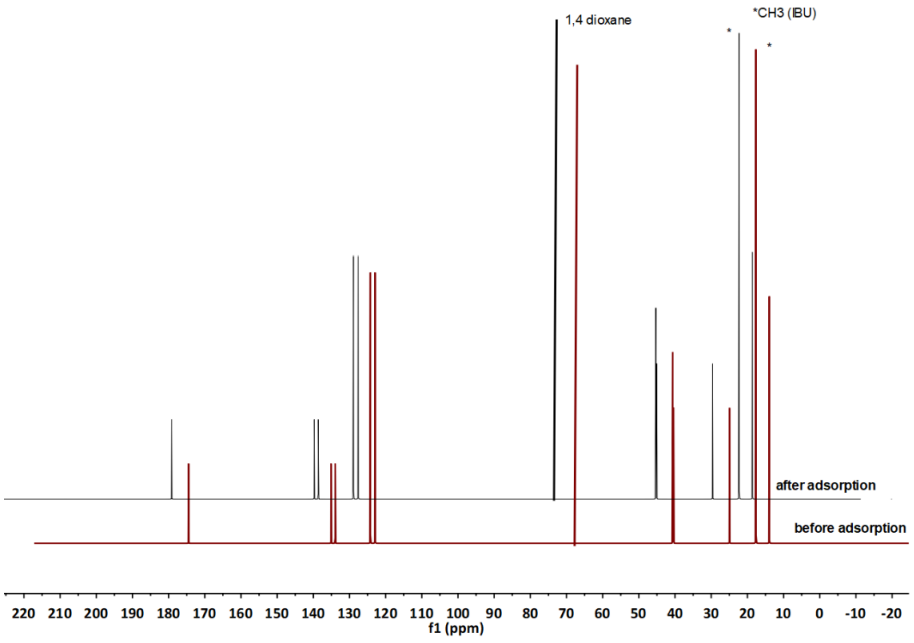

Figure S4. ^{13}C NMR spectrum of Ibuprofen before (red line) and after (black line) adsorption on [Zn(1,3-bdc)$_{0.5}$(bzim)].

Table S1. Data for the quantification by ^{13}C NMR of Ibuprofen adsorbed on [Zn(1,3bdc)$_{0.5}$(bzim)].

Integration area before adsorption (I_{x1})	Integration area after adsorption (I_{x2})	Number of IBU nuclei (N_{IBU})	Number of ref nuclei (N_{ref})*	Quantity of MOF (m_{MOF}) (mg)	Adsorbed quantity (mg/g of MOF)
0.040	0.038	2	4	20	160.7

**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

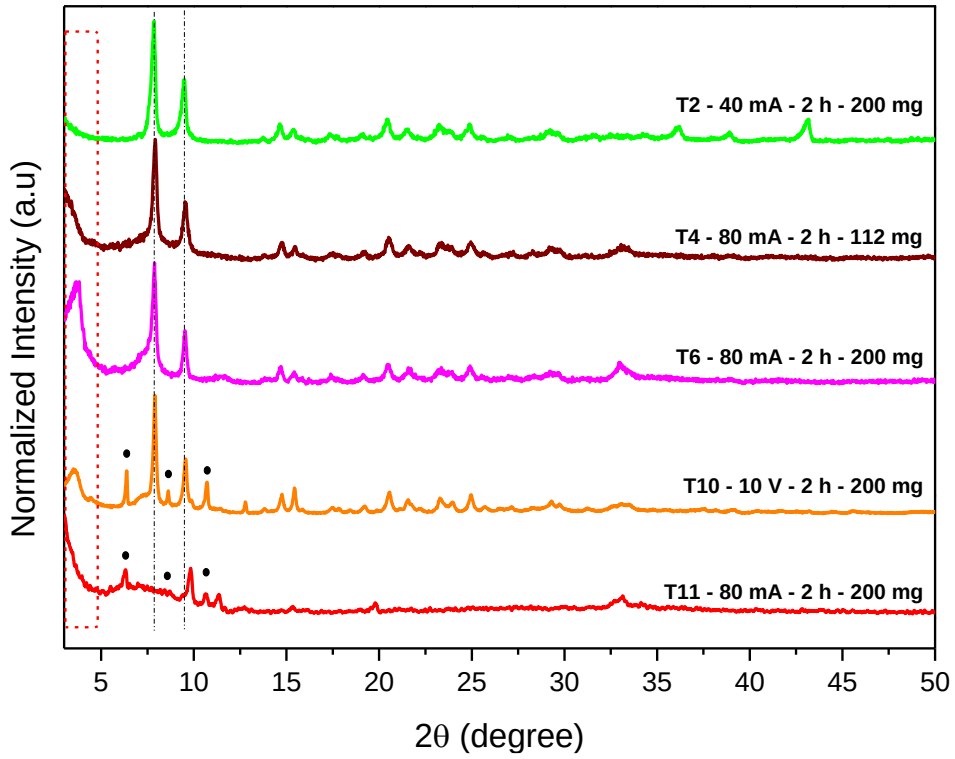

Figure S5. PXRD pattern of the sample T11 (prepared without benzimidazole) compared to patterns of T2, T4, T6 and T10.

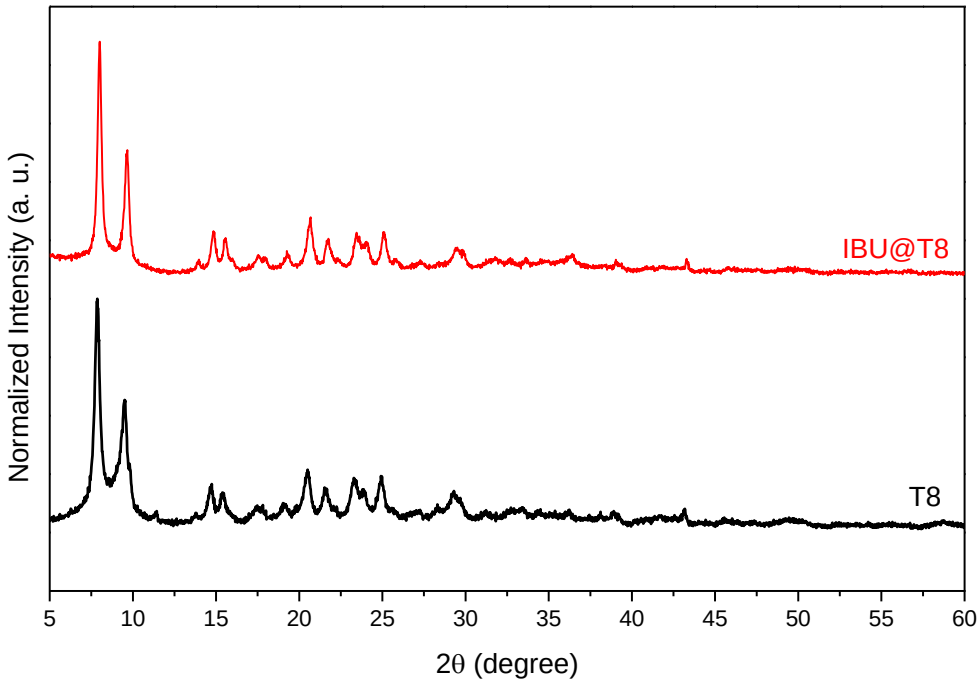

Figure S6. PXRD patterns of the sample before (T8) and after Ibuprofen adsorption (IBU@T8).

FTIR spectra

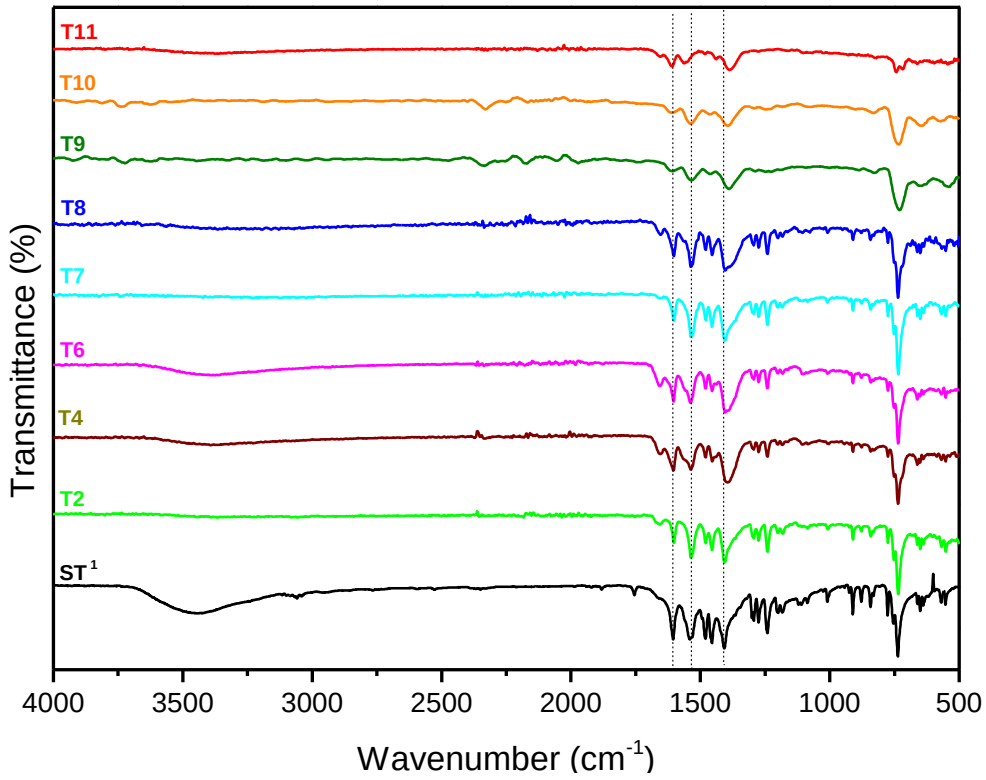

Figure S7. FTIR spectra of samples obtained *via* electrochemical synthesis (T2 – T11) and of the reference sample (ST) [1].

N_2 adsorption-desorption isotherms

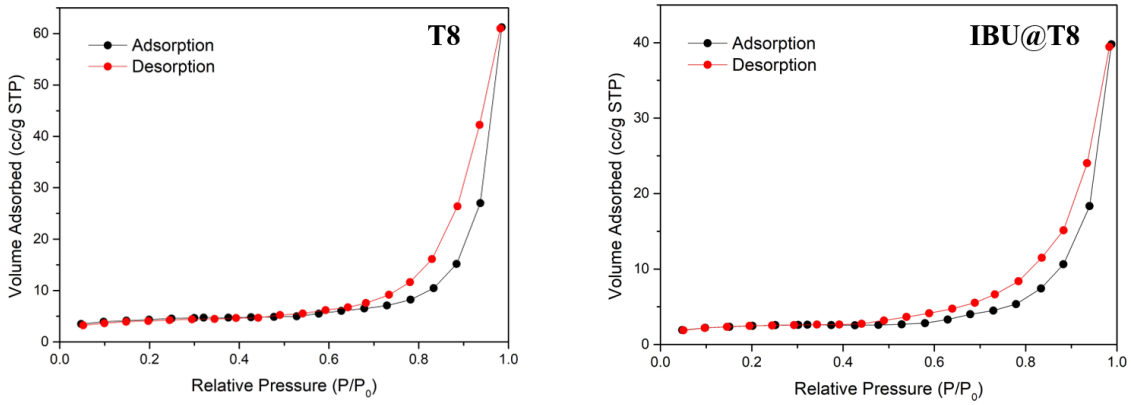

Figure S8. N_2 adsorption-desorption isotherms of the sample before (T8) and after Ibuprofen adsorption (IBU@T8).

References

1 B. S. Barros, J. Chojnacki, A. A. Macêdo Soares, J. Kulesza, L. Lourenço Da Luz and S. A. Júnior, *Mater. Chem. Phys.*, 2015, **162**, 364–371.