

A Highly Stable Nonhysteretic {Cu₂(tebpz) MOF + water} Molecular Spring**

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In memory of Professor Valentine A. Eroshenko

A molecular spring formed by a hydrophobic metal–organic framework Cu₂(tebpz) (tebpz = 3,3',5,5'-tetraethyl-4,4'-bipyrazolate) and water is presented. This nanoporous heterogeneous lyophobic system (HLS) has exceptional properties compared to numerous reported systems of such type in terms of stability, efficiency, and operating pressure. Mechanical and thermal energetic characteristics as well as stability of the system are discussed and compared in detail with those of other previously reported HLS.

Development of efficient energy storage is an urgent need of humanity on its way to a sustainable future. Indeed, the global energy consumption trend and predictions of global CO₂ emissions are truly disturbing.^[1] A desirable shift from fossil-fuel energy to renewable energy is highly dependent on efficient energy-storage technology that is able to compensate temporal mismatch between energy production and demand for today's most promising technologies (e.g. solar, wind, and hydro energy). Among electrical, thermal, chemical, and mechanical energy storage, the last-named can be considered to be the least developed, despite the fact that for energy sources that use mechanical energy as a primary source for electricity production (wind and hydro energy) direct mechanical-to-mechanical energy storage offers obvious advantages in terms of efficiency, simplicity of design, and hence lower price and environmental impact. Mainly three technologies are used so far: flywheel, compressed air, and pumped hydro energy.^[2]

The flywheel, which is certainly the most advanced technology, provides very high energy density, efficiency, and good durability.^[2,3] However, such excellent performance comes with a high price,^[3] especially compared to compressed-air and pumped hydro energy technologies,^[3,4] for both of which appropriate geographical location is a serious limitation to usage. Clearly, even though mechanical energy storage in the field of renewable energy has great potential to improve the characteristics and lower the price of existing technology, it suffers from a lack of technological diversity, which limits the full use of this potential.^[2-4] Novel methods of mechanical energy storage that have the following properties would be highly desirable: high energy capacity, high efficiency of energy transformation, durability, low price, environmentally friendly, nonflammable, and nonexplosive. The ability to work under constant pressure (force) would be an additional technical advantage.

A system consisting of a porous material immersed in a nonwetting liquid can be used for energy applications.^[5-9] Thus, mechanical energy can be stored/restored in the form of solid/liquid interfacial energy in the reversible cycle of intrusion/extrusion of the nonwetting liquid: energy must be supplied to the system for penetration of the nonwetting liquid into the lyophobic pores (charging) and is released on spontaneous extrusion of the liquid from the pores (discharging). Such porous heterogeneous lyophobic systems (HLSs) have some notable advantages for mechanical energy storage compared to conventional methods: high energy density,^[10-12] the possibility to accumulate mechanical energy at constant pressure,^[6,7,12] the ability to sustain unprecedented frequencies of charging/discharging,^[8,13,14] and the ability to be scaled down to nanosize, as in most cases the system is in the form of a suspension. Since the introduction of the HLS concept by Eroshenko^[5, 15] such systems have received considerable attention,^[6-48] and two main types thereof are considered to have desirable properties.

The first type comprises HLSs with pronounced pressure hysteresis loop in the *PV* isotherm caused by a large difference between the pressure at which liquid penetrates the pores *P_i* and the pressure at which liquid is expelled from the pores by capillary forces *P_e*. Such hysteresis allows the mechanical energy of a shock to be dissipated (the energy that the system absorbs on forced compression is much larger than the energy released on spontaneous decompression after the shock). Such systems are mostly represented by grafted silica gels + water/aqueous solutions^[16-23] and recently extension was made to MOFs + water/aqueous solution systems (MOF = metal–organic

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[**] MOF = metal–organic framework; tepbz = 3,3',5,5'-tetraethyl-4,4'-bipyrazolate.

framework).^[24] A scarce few works used an ionic liquid,^[25] ferro-magnetic fluids,^[26] or glycerin and glycerol^[27,28] as nonwetting liquid. Such systems demonstrated good reproducibility and durability^[8,14,29] and were rather quickly used as a basis to construct novel shock absorbers and bumpers.^[13,30,31]

The second type comprises HLSs with small (and preferably negligible) hysteresis in the PV isotherm ($P_i \approx P_e$) for mechanical energy storage.^[7,12,32] Despite the above-mentioned advantages, such HLSs have shown much lower progress in the sense of reaching application status. There may be several reasons for this. First, very few of such systems were reported to have negligible hysteresis in the compression/decompression cycle, which is essential for efficient energy storage (see Table 1 for comparison). Some of the rare examples are {ZSM-5 zeolite + electrolyte solution},^[37] {ITQ-12 zeolite + water},^[32] and {MTT zeolite + water}.^[38] Second, an important factor is the rather high intrusion/extrusion pressures of systems with small hysteresis (Table 1), which limits the range of applications and decreases the overall energy density of a device, for example, because a more constrictive material is required to sustain such high pressures. All of the three above-mentioned HLSs with small hysteresis suffer from this disadvantage. Finally, the third significant reason is the required stability of the porous material under operational conditions, which include not only high pressure, but also temperatures higher than room temperature.

Most of the systems reported so far (Table 1 and Figure 1) were tested only at room temperature, although the effect of temperature may be a serious issue.^[9,39] To the best of our knowledge, the only exception in Table 1 is the {ZSM-5 + water/aqueous solution} HLS, which was tested at 358 K,^[7,37] although it suffers from rather high operating pressure. Note that many of the HLSs based on electrolytes, which were re-

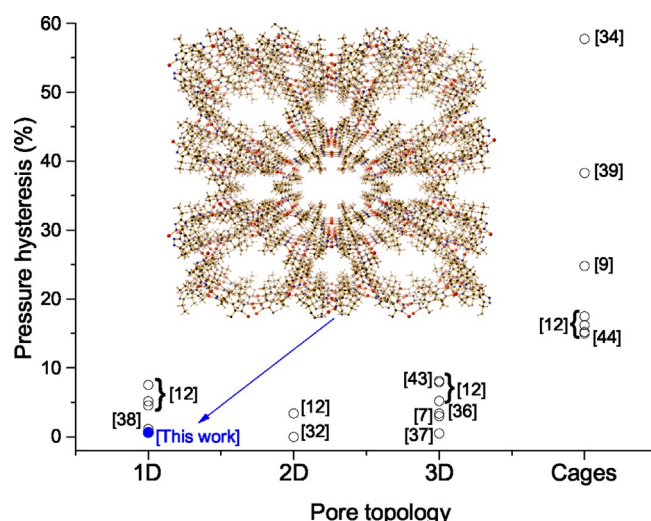


Figure 1. Effect of pore topology on pressure hysteresis of microporous HLSs. Inset: structure of $\text{Cu}_2(\text{tebpbz})$ with Cu in red, N in blue, C in black, H in pink. Dimensions of three sets of pores of $\text{Cu}_2(\text{tebpbz})$ are 1) 5.94, 2) 6.67, and 3) 11.6 Å (not counting the van der Waals radii).

ported to show increased intrusion/extrusion pressure hysteresis at higher electrolyte concentration,^[33–36] are not included in the comparison, as they show lower efficiency of energy storage compared to similar HLSs based on water.

Despite growing interest in HLS properties,^[6–48] high-pressure calorimetric measurements are still very rare,^[9,21,40,41] even though thermal effects on HLS compression/decompression are an essential part of their characterization for practical use and understanding of their operating mechanisms.

Herein we present mechanical and thermal characteristics of a new HLS that has negligible hysteresis, constant intrusion/ex-

Table 1. Characteristics of microporous HLSs.^[a]

Porous material	Pore topology	Liquid	P_i [MPa]	P_e [MPa]	ΔV [$\text{cm}^3 \text{g}^{-1}$]	$E_i^{[b]}$ [J g^{-1}]	$E_e^{[b]}$ [J g^{-1}]	Energy recovered	P hysteresis ^[c]	Ref.
ITQ-12 zeolite	2D	H_2O	172.0	172.0	0.05	8.1	8.1	100%	0.0%	[32]
ZSM-5 zeolite (318 K)	3D	26 wt% NaCl	98.0	97.5	0.10	9.8	9.75	99%	0.5%	[37]
$\text{Cu}_2(\text{tebpbz})$ MOF	1D	H_2O	35.7	35.4	0.12	4.3	4.3	99%	0.6%	this work
MTT zeolite	1D	H_2O	176.0	174.0	0.03	7.0	5.3	99%	1.1%	[38]
ZSM-5 zeolite (318 K)	3D	H_2O	73.0	70.8	0.12	8.8	8.5	97%	3.0%	[7]
ferrierite zeosil	2D	H_2O	147.0	142.0	0.10	15.0	14.5	97%	3.4%	[12]
SSZ-24 zeolite	1D	H_2O	58.0	55.0	0.10	5.8	5.6	97%	5.2%	[12]
H-BEA-150 Zeolite	3D	20 M LiCl	59.0	57.0	0.09	5.3	5.1	97%	3.4%	[36]
ZSM-12 zeolite	1D	H_2O	132.0	126.0	0.11	15.0	14.4	96%	4.5%	[12]
silicalite-1 zeolite	3D	H_2O	96.0	91.0	0.11	10.6	10.0	94%	5.2%	[12]
zeolite β	3D	15 M LiCl	111.0	102.0	0.16	17.8	16.3	91%	8.1%	[43]
ZSM-22 zeolite	1D	H_2O	186.0	172.0	0.08	14.0	12.7	91%	7.5%	[12]
silicalite-2 zeolite	3D	H_2O	63.0	58.0	0.10	6.5	5.9	91%	7.9%	[12]
DD3R zeolite	cages	H_2O	60.0	51.0	0.11	6.7	5.7	85%	15.0%	[12]
LTA zeolite (2nd cycle)	cages	10 M LiCl	46.0	39.0	0.12	5.5	4.7	85%	15.2%	[44]
chabazite zeolite	cages	H_2O	37.0	31.0	0.15	5.5	4.6	84%	16.2%	[12]
SSZ-23 zeolite	cages	H_2O	40.0	33.0	0.14	7.0	5.6	80%	17.5%	[12]
ZIF-8 MOF	cages	H_2O	23.0	17.3	0.43	9.9	7.4	75%	24.8%	[9]
ZIF-67 MOF	cages	H_2O	18.8	11.6	0.35	6.6	4.1	62%	38.3%	[39]
ZIF-71 MOF	cages	H_2O	71.0	30.0	0.36	25.6	10.8	42%	57.7%	[24]

[a] Results were obtained at room temperature except where indicated. [b] $E_{i,e} = P_{i,e} \Delta V$. [c] P hysteresis = $\frac{(P_i - P_e)}{P_i} \bullet 100\%$.

trusion pressure, operates at pressure suitable for practical applications, and most importantly is stable at temperatures higher than room temperature. This combination of properties in one HLS is currently unique.

From the many reports on the energetic characteristics of HLSs, it is clear that those having a small hysteresis (suitable for energy storage) should be found among microporous systems.^[6–48] Such a search is complicated by the fact that there are no solid models to predict the values of the intrusion and extrusion pressures. Even for HLSs based on mesoporous materials (e.g. grafted silica gels), for which a macroscopic description of the intrusion/extrusion process is acceptable, theoretical prediction strongly suffers from uncertainties due to size effects brought about by confinement.^[17,18,29] For microporous HLSs this is even more complicated due to their extreme confinement and the unsuitability of a macroscopic description. The topology of the porous material used is expected to have an impact on the pressure hysteresis as well. From the analysis of reported data on microporous HLSs in terms of dimensionality of the pores (Table 1 and Figure 1) it is evident that a potential candidate should not have a cage-like structure, as was often stressed in the works of Patarin and co-workers.^[12,32,36,43] On the other hand, it should be highly stable to resist the concomitant effects of pressure and temperature in intrusion/extrusion cycles, which may strongly affect the structure of the porous material.^[9,39] It is also desirable to have the possibility to use water as nonwetting liquid, and thereby take advantage of its low price and no impact on the environment; hence, the porous material must be hydrophobic.

The recently presented MOF $\text{Cu}_2(\text{tebpz})$ ^[49] ($\text{tebpz} = 3,3',5,5'$ -tetraethyl-4,4'-bipyrazolate) meets the above requirements and was chosen as a component of the HLS. $\text{Cu}_2(\text{tebpz})$ has desirable 1D nanoscale channels, which are decorated by hydrophobic ethyl groups. Its water resistance lies among those of several best-performing hydrophobic MOFs.^[50,51] Moreover, the thermal (up to 450 °C) and chemical stabilities of $\text{Cu}_2(\text{tebpz})$ exceed those of most MOFs.^[52] The chemical stability was tested by suspending the material in boiling solvents (THF, toluene, hexane, DMSO, water) and in acidic (0.001 M HCl) or basic (0.001 M NaOH) aqueous solutions for 24 h. The robustness of the material was attributed not only to the greater basicity and coordination strength of pyrazolate, but also to the hydrophobic channels, which preclude hydrolytic attack.^[49]

The *PV* isotherms of $\{\text{Cu}_2(\text{tebpz}) + \text{water}\}$ are presented in Figure 2. This system shows perfect molecular-spring behavior in water intrusion/extrusion steps, which take place around 40 MPa and are associated with $0.12 \text{ cm}^3 \text{ g}^{-1}$ volume variation. The pressure hysteresis is about 0.5% and can be considered to be negligible. To the best of our knowledge, this is the first MOF-based HLS exhibiting negligible hysteresis. Ten compression/decompression cycles at 360 K showed excellent reproducibility, with almost undetectable difference between the first and tenth compression steps (the slight difference of the first cycle is typical for all HLSs). For comparison, ZIF-8, which is known as a MOF with very good stability, shows excellent reproducibility as HLS component at room temperature, but at 360 K one observes degradation after one intrusion/extrusion

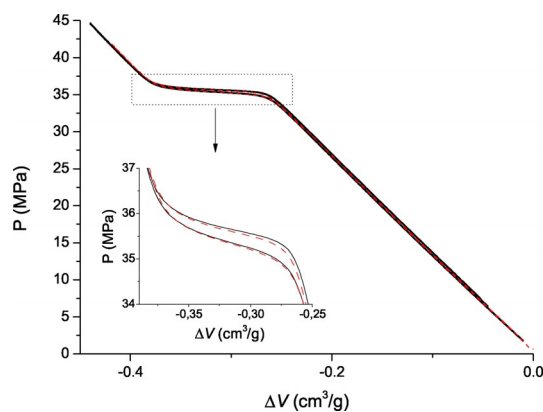


Figure 2. *PV* isotherms (360 K) of $\{\text{Cu}_2(\text{tebpz}) + \text{water}\}$ HLS: comparison of first (solid line) and tenth (dashed line) cycles. Inset: zoom of intrusion/extrusion step.

cycle, and the concomitant effects of pressure and temperature provoked irreversible structural changes.^[9] Even more pronounced effects under such conditions were observed for $\{\text{ZIF-67} + \text{water}\}$.^[39] Apart from the excellent reproducibility of *PV* isotherms (Figure 2), XRD measurements revealed no modification of the structure after high-pressure cycles at 360 K (Figure 3). A similar conclusion can be drawn from the small-angle X-ray scattering (SAXS) data, which were additionally performed in reflection mode in the low-angle range (Figure 3,

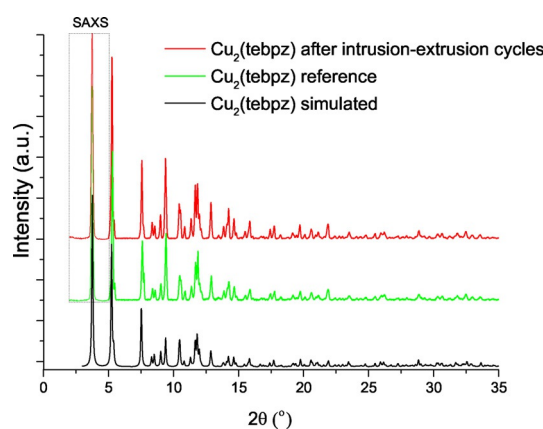


Figure 3. XRD patterns of reference $\text{Cu}_2(\text{tebpz})$ and $\text{Cu}_2(\text{tebpz})$ after ten water intrusion/extrusion cycles at 360 K. Inset: SAXS measurements in the 2–5° range.

inset).

Compared with other HLSs with low hysteresis, such as $\{\text{ITQ-12}^{[32]}/\text{MTT}^{[38]}\}$ zeolites + water and $\{\text{ZSM-5} + 26 \text{ wt} \% \text{ NaCl solution}\}$,^[37] $\{\text{Cu}_2(\text{tebpz}) + \text{water}\}$ has comparable but lower energy capacity (Table 1), albeit not due to smaller volume variation, but due to much lower intrusion/extrusion pressures, which make it much more suitable for practical use. Furthermore, considering that the size and weight of the final application device would strongly depend on the operating pressure of the working body (more material is required to sustain high

pressure), the lower energy capacity of $\{\text{Cu}_2(\text{tebpz}) + \text{water}\}$ due to lower operating pressure should not be regarded as a disadvantage. In terms of stability, it can only be compared with $\{\text{ZSM-5} + \text{water}/26 \text{ wt \% NaCl solution}\}$ HLSs, which were tested at temperatures higher than room temperature (318 K).^[7,37]

It is worth examining the characteristics of the proposed HLSs in terms of available devices or prototypes based on HLSs. As was described above, HLS energy storage is less developed than energy-dissipation applications. Nevertheless, two types of devices have been developed for energy storage based on HLSs: 1) the rechargeable actuating mechanism, which performs useful work during temperature-induced extrusion of an alloy upon its melting inside pores; a design of such a device was proposed by Eroshenko and Tkachenko^[53] and later patented by Eroshenko^[54] and Egorov et al.^[55] 2) a device for deployment of solar panels of satellites.^[56] Since nonwetting liquids other than water were used for these devices, direct comparison of energetic characteristics may be inappropriate. However, a striking advantage of these devices is a discharge process that takes place at constant pressure with release of the mechanical energy in a smooth, nonexplosive way. In this respect, the proposed system shows very low variation of pressure on intrusion/extrusion (Figure 2).

On the other hand, many works, including prototype development and testing, are dedicated to HLS-based shock absorbers based on water and grafted mesoporous silica.^[16–23] Such HLSs have pronounced hysteresis, which is beneficial for energy dissipation, and about two times greater accumulated energy on intrusion due to higher porosity. Distinctive properties of such systems include the ability to operate at very high frequencies without overheating due to the endothermic effect of intrusion. Below we examine the $\{\text{Cu}_2(\text{tebpz}) + \text{water}\}$ HLS with respect to this property.

Calorimetric measurements were performed for $\{\text{Cu}_2(\text{tebpz}) + \text{water}\}$ (Figure 4). Like for the previously examined MOF-based HLS $\{\text{ZIF-8} + \text{water}\}$,^[9] intrusion is an endothermic process and extrusion is exothermic. The first intrusion is associated with an endothermic effect of 9.6 J g^{-1} , and the endothermic effect of the second to tenth cycles is $7.6 \pm 0.4 \text{ J g}^{-1}$.

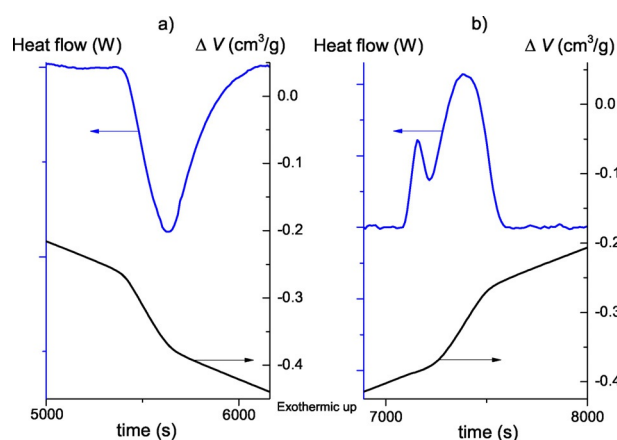


Figure 4. Calorimetric measurements for $\{\text{Cu}_2(\text{tebpz}) + \text{water}\}$, showing a) intrusion and b) extrusion.

The extrusion process is exothermic, and the system generates $-7.2 \pm 0.3 \text{ J g}^{-1}$ of heat for all ten cycles. Such values are quite large and are larger than the mechanical energy stored in the system (Table 1). Considering its negligible hysteresis, $\{\text{Cu}_2(\text{tebpz}) + \text{water}\}$ may potentially be used for thermal energy storage, for example, in applications that operate at high pressures with low variation of intrusion/extrusion pressure.

The observed difference of about 2 J g^{-1} for the thermal effects of the first and successive intrusions is rather large. Considering that the volume of intruded water in the first and successive intrusions is almost the same (Figure 2), it seems that such a difference is not due to incomplete extrusion after the first cycle. A similar difference in the heats of the first and successive intrusions with preservation of the intruded volume was observed by Karbowski et al. for $\{\text{silicalite-1} + \text{water}\}$ ^[40,42] and $\{\text{chabazite} + \text{water}\}$ ^[42] HLSs. Such phenomena were attributed to structural changes of the material, namely, to the formation of silanol defects. As an indication of such hydrophilic defects, they also observed noticeable differences between the intrusion pressures of the first and successive cycles (2 MPa), which is not the case for the $\{\text{Cu}_2(\text{tebpz}) + \text{water}\}$ system (Figure 2). Potentially, the difference between first and successive cycles may be due to the presence of some air molecules in the raw material and their dissolving in water under high pressure after the first intrusion. In principle, gas molecules might change the confinement conditions of water molecules, and such conditions were demonstrated to have a strong influence on the thermal effects of intrusion and extrusion.^[42, 57] In general, a difference between the first and successive intrusions seems to be observed for very different HLSs and is worthy of deeper examination in future work.

Interestingly, extrusion is associated with a two-peak thermal effect, whereas intrusion takes place with only one peak (Figure 4). Furthermore, a barely detectible but well-reproducible second step of extrusion that matches the smaller exothermic peak in time (Figure 4) is registered. Two-step extrusion was observed for $\{\text{ZIF-8} + \text{water}\}$ HLS^[39] and was suggested to be related to the gate-opening effect. Perhaps for $\{\text{Cu}_2(\text{tebpz}) + \text{water}\}$ the observed phenomena may be related to some reversible structural transition. Maybe such a transition is provoked by the intrusion process, so that its time/pressure matches with the variation in volume and heat flow and is not detected separately in *PV* isotherms or during calorimetric measurements (Figures 2 and 4). However, during decompression, extrusion and reverse transition take place at slightly different pressures and hence are detectible. On the other hand, $\text{Cu}_2(\text{tebpz})$ has pores of three sizes (Figure 1, inset), all of which are accessible to water molecules,^[49] so this double peak may be related to extrusion of the water from pores of different sizes, although this does not explain why there is only one step of volume variation and one endothermic peak for intrusion. Nevertheless, at this point these are just hypotheses, and additional measurements should be performed to clarify the phenomena, preferably by in situ high-pressure XRD and HLS compression/decompression at much higher pressures in order

to detect possible additional steps of intrusion associated with the filling of pores of other sizes.

In conclusion, a highly stable nonhysteretic $\{\text{Cu}_2(\text{tebpz}) + \text{water}\}$ molecular spring with exceptional properties was presented. This is the first MOF-based HLS with negligible hysteresis. The molecular-spring phenomenon takes place at much lower pressure compared to other reported HLSs, and this makes it more suitable for practical applications than previously described equivalent systems. The system is stable at high pressure and temperatures higher than room temperature due to the high stability of the $\text{Cu}_2(\text{tebpz})$ MOF, which is very rare for such operating conditions. Such results also support the hypothesis that the topology of a material used in microporous HLSs is an important parameter defining the intrusion/extrusion pressure hysteresis and hence the efficiency of the system. Upcoming work will be dedicated to further investigations of the $\{\text{Cu}_2(\text{tebpz}) + \text{water}\}$ molecular spring in different operational regimes and in terms of deeper understanding of structural changes during the intrusion/extrusion process.

Experimental Section

$\text{Cu}_2(\text{tebpz})$ MOF was synthesized according to the procedure described elsewhere.^[49] The as-synthesized material was subjected to methanol solvent exchange and then thermally activated at 100 °C for 10 h before the water intrusion/extrusion experiments. An ST-7M transitiometer from BGR-Tech was used for recording the PV isotherms at 360 K in the 0.1–45 MPa pressure range and for the simultaneous registration of associated thermal effects of the HLS compression/decompression according to the experimental procedure given elsewhere.^[41] XRD patterns of pristine $\text{Cu}_2(\text{tebpz})$ and of $\text{Cu}_2(\text{tebpz})$ subjected to intrusion/extrusion cycles were recorded with an X'PertPro PANalytical diffractometer in θ – θ geometry by using $\text{Cu}_{\text{K}\alpha}$ radiation ($\lambda = 1.54184 \text{ \AA}$) at room temperature in the range $5 < 2\theta < 120^\circ$ with a step size of $\Delta 2\theta = 0.0167^\circ$, a counting time of 119 s for each data value, and a total counting time of about 200 min. SAXS measurements were performed by using a Bruker Nanostar U equipped with a $\text{Cu}_{\text{K}\alpha}$ tube source, evacuated beam path, and Vantec 2000 2D detector, with a sample–detector distance of 107 cm. The intensities were corrected for black noise, parasitic signal (empty cell), detector efficiency, spatial distortion, and spherical distortion.

Keywords: energy conversion · heterogeneous lyophobic systems · interfaces · metal–organic frameworks · molecular devices

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