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Selective Adsorption Properties of Cationic Metal−Organic Frameworks Based on Imidazolic Linker

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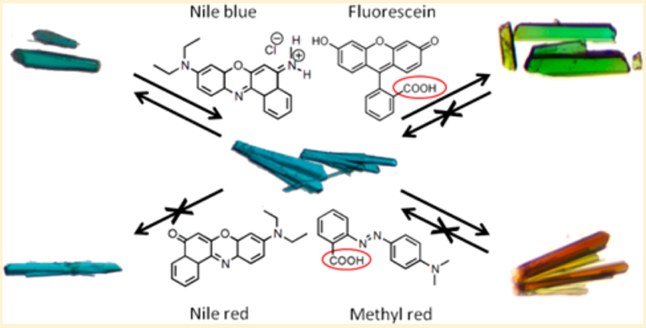
S *Supporting Information*

ABSTRACT: In this work we propose an approach for the controlled synthesis of cationic frameworks by the use of imidazolium salts as linker molecules. The imidazolium salt linker $H_2ImidCl$ was prepared in five steps and converted with zinc and copper nitrate, respectively, to give the two topologically different cationic frameworks $[Cu(Imid)(H_2O)]^+$ and $[Zn_4(Imid)_5]^{3+}$. The framework charge is compensated by anions located in the pores. $[Cu(Imid)(H_2O)]^+$ shows a selective adsorption of organic molecules either bearing a carboxylic group or having an ionic nature. Furthermore, adsorbed molecules featuring a carboxylic group are captured inside the pores, whereas ionic substances can be reversibly adsorbed and desorbed, which was followed by UV/vis spectroscopy.



■ INTRODUCTION

Metal−organic frameworks (MOFs), a class of highly porous materials, exhibit high specific surface areas and allow a controlled pore design.[1,2] The careful selection of building blocks enables the targeted construction as well as incorporation of active sites into the MOF.[3,4] Furthermore these sites are well ordered and can be precisely localized due to the crystallinity of the material. The integrated sites can be active, e.g., for catalysis as intrinsic sites, or used for postfunctionalization.[5,6] Postfunctionalization can be done by attaching molecules to the linkers or by adsorbing (encapsulation) functional molecules. However, adsorption and desorption are in equilibrium and thus noncovalent integration of functional sites may cause leaching of encapsulated species.[7] We focused our investigations on imidazolium salts as building blocks for MOF synthesis. Imidazolium salts are precursors for N-heterocyclic carbenes (NHC), which are known for their attractive properties, being electron-rich and sterically demanding.[8−14] Several attempts were made to immobilize the imidazolium-based NHCs in different materials with high specific surface areas including nanoparticles,[15,16] polymers,[17−19] or SBA-15.[20] Recently, we have developed the synthesis of a porous NHC-based element organic framework (EOF) material, which shows good performance as heterogeneous organocatalyst in the NHC catalyzed conjugated umpolung of unsaturated cinnamic aldehyde and trifluoroacetophenone.[21] Furthermore incorporation of functionalized imidazolium salts and Pd(II)−NHC organometallic complexes as the organic building block into MOFs has also attracted considerable interest.[22−27]

However, the imidazolium salt is not only bearing catalytic potential, it is also an ideal linker for the construction of cationic frameworks. In contrast to zeolites, where only cation exchange is feasible due to the anionic nature of zeolite frameworks, MOFs can undergo both anion and cation exchange depending on their framework charges.[28] Cationic MOFs are usually formed when the positive charge of the metal ions is not completely balanced by the charge of organic linkers. In this case the positive charge of the network should be compensated by guest anions, usually the anions from the metal salt used during the synthesis.[29] However, the targeted synthesis of such compounds is difficult, since the charge balance cannot be easily controlled during the synthetic procedure. The use of a salt as a linker opens the possibility for such controlled design of positively charged frameworks.

Recently, charged metal−organic frameworks have attracted considerable attention due to the possibility to perform postsynthetic modification by ion exchange.[30−34] Pore size and functionality of the material can be tuned in an elegant way by the contribution to these properties of the ionic guest. Additionally, the selective adsorption can be achieved in such ion containing MOFs, since only ionic species can be exchanged, preventing adsorption of neutral species due to reduced pore space.

Here, we report two MOFs incorporating an imidazolium salt linker and copper or zinc as metals, respectively. The

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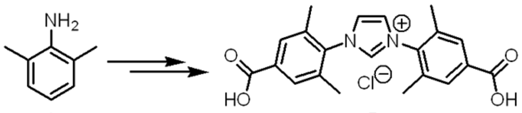
imidazolium salt was synthesized in four steps from 2,6-dimethylaniline (Figure 1). The accessibility of the C2 atom of the imidazolium moiety and ion exchange properties of the MOFs were studied.



1 **5**

Figure 1. 1,3-Bis(4-carboxy-2,6-dimethylphenyl)-1*H*-imidazolium chloride (**5**) was synthesized in four steps starting from 2,6-dimethylaniline (**1**).

EXPERIMENTAL SECTION

A detailed description of the synthesis of 1,3-bis(4-carboxy-2,6-dimethylphenyl)-1*H*-imidazolium chloride (**5**) (H_2ImidCl) starting from 4-bromo-2,6-dimethylaniline (**1**) can be found in section 2 of the Supporting Information.

Synthesis of [Cu(Imid)(H_2O)](Cl)$_x$(NO_3)$_{1-x}$ (6). 1,3-Bis(4-carboxy-2,6-dimethylphenyl)-1*H*-imidazolium chloride (17.0 mg, 0.04 mmol) and $Cu(NO_3)_2{\cdot}3H_2O$ (14.5 mg, 0.06 mmol; 1.5 equiv) were dissolved in 6 mL of ethanol (99%). The resulting solution was heated to 80 °C. After 48 h the mixture was cooled down to room temperature. The turquoise crystals were collected and washed with ethanol. Yield: 73%.

Synthesis of [Zn_4(Imid)$_5$](Cl)$_x$(NO_3)$_{3-x}$ (7). 1,3-Bis(4-carboxy-2,6-dimethylphenyl)-1*H*-imidazolium chloride (17.0 mg, 0.04 mmol) and $Zn(NO_3)_2{\cdot}4H_2O$ (15.7 mg, 0.06 mmol; 1.5 equiv) were dissolved in 6 mL of ethanol (99%). The resulting solution was heated to 90 °C. After 48 h colorless crystals were formed. The resulting solid was collected and washed with ethanol. Yield: 54%.

Crystal Structure Determination. A crystal of [Cu(Imid)(H_2O)](Cl)$_x$(NO_3)$_{1-x}$ (**6**) or [Zn_4(Imid)$_5$](Cl)$_x$(NO_3)$_{3-x}$ (**7**), respectively, was sealed in a glass capillary with a small amount of solvent. X-ray data for [Zn_4(Imid)$_5$](Cl)$_x$(NO_3)$_{3-x}$ were collected at 20 °C by using Mo Kα (λ = 0.71073 Å) radiation with a STOE IPDS imaging plate diffractometer. The data for [Cu(Imid)(H_2O)](Cl)$_x$(NO_3)$_{1-x}$ were collected at 20 °C using synchrotron radiation (λ = 0.88561 Å; 14.0 eV) on beamline 14.2 of Freie Universität Berlin at BESSY (Berlin, Germany) with a MX-225 CCD detector (Rayonics, Illinois).[35] The data were integrated and scaled with the XDS software package.[36] The structures were solved using direct methods with the help of SHELXS-97 and refined by full-matrix least-squares techniques using SHELXL-97.[37] Due to the high disorder and low residual electron density it was impossible to locate counterions (NO_3^- or Cl^-), EtOH, and H_2O guest molecules. Non-hydrogen atoms were refined with anisotropic temperature parameters. The hydrogen atoms were positioned geometrically and refined using a riding model. CCDC 860563 (for **6**) and CCDC 860564 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The topology of the networks was analyzed with the program package TOPOS.

Crystal Data for [Cu(Imid)(H_2O)](Cl)$_x$(NO_3)$_{1-x}$. $C_{42}H_{34}Cu_2N_4O_{10}$: trigonal, $P\bar{3}c1$ (No. 165), a = 27.597(4) Å; c = 21.871(4) Å, V = 14425(4) Å^3, T = 293(2) K, Z = 6, θmax = 35.63°, reflections collected 115363, unique 9952 [R_{int} = 0.0484], final R indices, R_1 = 0.0594, wR_2 = 0.1818; R_1(all data) = 0.0642, wR_2 (all data) = 0.1882, GOF = 1.088.

Crystal Data for [Zn_4(Imid)$_5$](Cl)$_x$(NO_3)$_{3-x}$. $C_{105}H_{95}N_{10}O_{20}Zn_4$: monoclinic, $P2/n$ (No. 13), a = 12.036(2) Å, b = 16.838(3) Å, c = 40.383(8) Å, β = 90.46(3)°, V = 8184(3) Å^3, T = 293(2) K, Z = 2, θmax =20.79°, reflections collected 8101, unique 8101 [R_{int} = 0.0859], final R indices, R_1 = 0.0483, wR_2 = 0.1097; R_1(all data) = 0.0744, wR_2(all data) = 0.1139, GOF = 0.991.

Adsorption Experiments. *Gas Adsorption.* Prior to the gas physisorption measurements the samples were activated using supercritical CO_2 and additionally evacuated at room temperature for 12 h. N_2 physisorption isotherms were measured at 77 K up to 1 bar using a Quantachrome Autosorb 1C apparatus.

Liquid Phase Adsorption. The crystals of the investigated compounds were placed into corresponding dye-containing ethanolic solutions. After three days, the crystals were inspected under the microscope. For desorption experiments the dye loaded crystals were placed in fresh ethanol in a cuvette and the dye release was followed in situ by UV/vis spectroscopy.

RESULTS AND DISCUSSION

For the linker synthesis 2,6-dimethylaniline (**1**) was brominated to 4-bromo-2,6-dimethylaniline (**2**) followed by a copper catalyzed reaction with sodium cyanide to 4-amino-3,5-dimethylbenzonitrile (**3**) in an excellent yield. In the next step the resulting intermediate **3** was treated with paraformaldehyde and glyoxal solution to generate the imidazolium salt (**4**). Finally, hydrolysis with concentrated HCl gave the product 1,3-bis(4-carboxy-2,6-dimethylphenyl)-1*H*-imidazolium chloride (H_2ImidCl) (**5**).

Conversion of linker **5** with copper nitrate in ethanol at 80 °C yielded [Cu(Imid)(H_2O)](Cl)$_x$(NO_3)$_{1-x}$ (**6**) as turquoise crystals. The reaction with zinc nitrate in ethanol at 90 °C results in yellow crystals with the formula [Zn_4(Imid)$_5$](Cl)$_x$(NO_3)$_{3-x}$ (**7**). The chemical compositions of the compounds were determined from representative synthetic batches by means of elemental and thermal analysis as [Cu(Imid)(H_2O)](Cl)$_{0.5}$(NO_3)$_{0.5}$(H_2O)$_{0.5}$(EtOH)$_{0.5}$ for **6** and [Zn_4(Imid)$_5$](NO_3)$_3$(H_2O)$_{12}$ for **7**, respectively. It should be noted that slight variations in composition are probable, due to the possible anion exchange between chloride of the linker and nitrate of metal nitrate used as metal source during the synthesis. Therefore the formulas for the neutral solvent free compounds are formulated as [Cu(Imid)(H_2O)](Cl)$_x$(NO_3)$_{1-x}$ for **6** and [Zn_4(Imid)$_5$](Cl)$_x$(NO_3)$_{3-x}$ for **7**.

Using similar reaction conditions, two different structural building units (SBUs) were obtained and thus two structurally and topologically different MOFs.

The secondary building unit in **7** is a frequently observed assembly in MOF chemistry, a binuclear paddle-wheel cluster consisting of two copper atoms being bridged by four carboxylate groups (Figure 2a). The crystallographic center of symmetry is located between two copper atoms of the paddle-wheel. The Cu−O distances are in the range 1.958(6)−1.979(5) Å.

As a result, two-dimensional cationic layers with uninodal **sql** topology are formed, in which the five membered planar imidazolium ring lies in the plane of the layer (Figure 2b). The counterions could not be located crystallographically. The distance between two C2 atoms of imidazolium units inside the mesh of the net is 21.186 Å. The structure consists of three different intersected 2D layers running perpendicular to [1$\bar{1}$0], [010], and [100] crystallographic directions.

The centers of the mesh are occupied by the knots of the next net (Figure 2c) in such way, that a catenated 3D structure is formed. The framework contains two different kinds of channels along the *c*-axis: smaller trigonal channels and larger hexagonal channels 18.8 Å in size (Figure 2d). The total solvent accessible volume calculated using PLATON is 65.4% of the unit cell volume. According to the orientation of the linker in the structure, the imidazolium unit is hardly accessible.

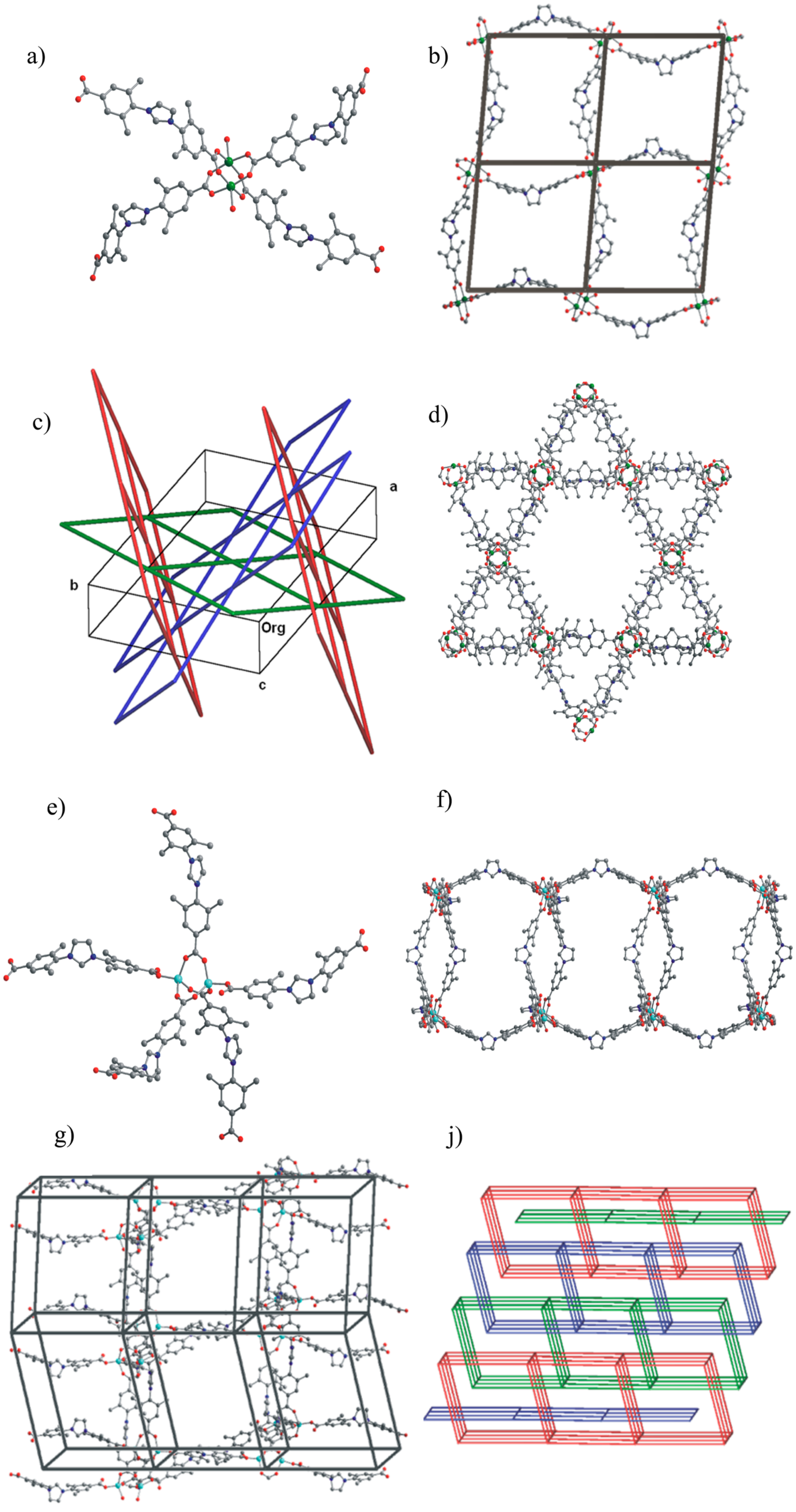


Figure 2. Structures of $[Cu(Imid)(H_2O)]^+$ (**6**) and $[Zn_4(Imid)_5]^{3+}$ (**7**) (color scheme: Cu, green; Zn, light blue; O, red; N, dark blue; C, gray; hydrogen atoms are omitted): (a) paddle-wheel cluster of **6**; (b) two-dimensional layer with **sql** topology of **6** (view along *b*); (c) four catenated layers of **6**; (d) view on the structure of **6** along *c*; (e) secondary building unit of **7**; (f) view along the double layers of **7**; (g) double layer of **7**; (j) intercalation of double layers in the structure of **7**.

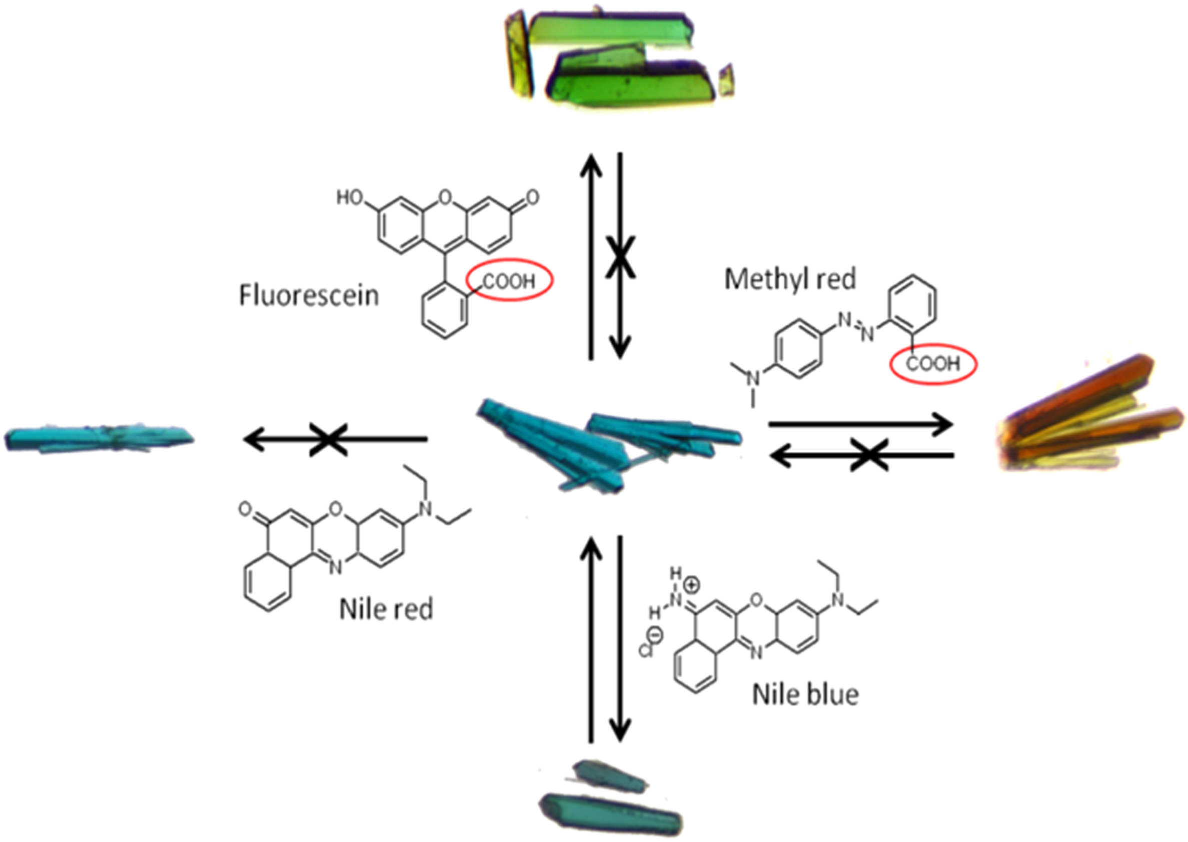


Figure 3. Adsorption of dyes from ethanolic solution on $[Cu(Imid)(H_2O)]^+$. Nile blue can be ad- and desorbed from the framework, whereas fluorescein and methyl red are adsorbed irreversibly. No adsorption of Nile red was observed.

Interestingly, Chun et al. synthesized a similar copper based compound (with isopropyl substituent instead of methyl in the linker) using *N,N*-dimethylformamide as solvent.[22] Similar **sql** layers are present in the structure, but the layers are stacked along one direction resulting in a two-dimensional layered structure. The authors also report the formation of organometallic NHC−copper(I) units during the MOF synthesis, which is obviously not the case during the synthesis in ethanol.

$[Zn_4(Imid)_5](Cl)_x(NO_3)_{3-x}$ consists of binuclear zinc paddle-wheel units being coordinated by three bridging carboxylate groups $(Zn_2(COO)_3)$. The coordination sphere is completed by two more linkers coordinating the zinc atoms in a monodentate fashion on the axial positions of the paddle-wheels (Figure 2e). The bridging dicarboxylates interconnect the SBUs to form layered structural motifs (Figure 2f) interconnected by the monodentate linker molecules to give double layers (Figure 2g). The double layers intercalate to give an extended three-dimensional structure (Figure 2j). The total solvent accessible volume amounts to 49.8% as calculated using PLATON. **7** contains small channels along the *a*-axis with 9.2 Å in diameter (taking van der Waals radii into account). Similar to **6**, the imidazolium units do not point into the open space of the channel, but rather are positioned parallel to the channel walls. In both compounds the conformation of the NHC-linker is indicative for no carbene formation during the synthesis of MOFs. According to the literature, the N−C−N angle in the molecular carbenes is about 101.4°.[38] In **7** this angle is in the range 107.39° and 109.63° and in **6** it is 106.55°. These angle values correspond to the values reported for the imidazolium salt.[39]

Since the linker **5** contains an imidazolium unit, the transformation to an imidazole-2-thione would prove the formation of a carbene (imidazol-2-ylidene) inside the MOF.[40] Imidazole-2-thiones are commonly prepared by reaction of an imidazolium ion with sulfur in the presence of a base, via carbene intermediates. However, in the described reaction of compounds **6** and **7** with sulfur, neither in the supernatant solution nor after digesting the MOF in hydrochloric acid could the derivate of imidazole-2-thiones be detected. This finding confirms the inaccessibility of the C2 atom, expected from crystal structure examination.

To evaluate the porosity of the compounds, nitrogen (at 77 K) and liquid phase (at 298 K) adsorption experiments were performed. Unfortunately, the structures of the compounds undergo significant changes during the sample evacuation at 293 K (Figure S1 in the Supporting Information, ESI). The specific BET surface area calculated from nitrogen adsorption (Figure S7 in the Supporting Information, ESI) isotherm measured at 77 K on an activated and thus structurally changed sample of **6** is only 170 $m^2\ g^{-1}$. For activated **7** no significant nitrogen uptake was observed.

In order to demonstrate pore accessibility without structural transformation and ion exchange properties of **6** and **7**, dye adsorption/desorption experiments were performed with a range of different dyes. **7** showed no dye adsorption under the described conditions regardless of the dye used, which is in accordance with the small pore size of 9.2 Å estimated from crystal structure.

In contrast, **6** adsorbs and desorbs dyes selectively depending on the nature of the dye molecule. $[Cu(Imid)(H_2O)]^+$ (**6**) readily adsorbs fluorescein, methyl red and Nile blue to give fluorescein@[Cu(Imid)(H_2O)], methyl_red@[Cu(Imid)(H_2O)] and Nile_blue@[Cu(Imid)(H_2O)] composites, respectively. Interestingly, Nile red is not adsorbed at all, although it is structurally very similar to Nile blue (Figure 3).

The main difference is the ionic nature of Nile blue compared to Nile red (Figure 3). Apparently the ionic nature of the dye is important to enter the channels of **6** which present an ionic surrounding themselves. Nevertheless upon adding fresh ethanol the Nile blue@[Cu(Imid)(H_2O)] composite releases Nile blue. The desorption process was followed via UV/vis spectroscopy (Figure S9 in the Supporting Information, ESI) until a final equilibrium concentration of dye was reached after 24 h. Also from the solution containing both dyes (Nile blue as well as Nile red) compound **6** selectively adsorbs only Nile blue (Figure S8 in the Supporting Information, ESI).

Methyl red and fluorescein can be adsorbed on compound **6** as well, but cannot be desorbed through exposure to solvent excess. This was proven by monitoring the supernatant solvent via UV/vis spectroscopy. As distinguished from Nile blue, methyl red and fluorescein contain a carboxylic group. Obviously the corresponding anion, formed by deprotonation, is trapped inside the channels by electrostatic interaction or can replace the terminal water molecules coordinated to the copper paddle-wheels. Such coordination leads to the formation of a neutral framework with the composition [Cu(Imid)(dye)]. In this case the dye becomes an integral part of the framework and cannot be desorbed. Such behavior could be useful for noncovalent but nevertheless permanent postfunctionalization by attaching a carboxylic group to the desired functional molecule. In addition, postfunctionalization can be done via a simple adsorption from liquid phase. Furthermore, trapping and thus removal of toxic or undesirable acids, for example 2,4-dichlorophenoxyacetic acid, a widely used herbicide, is an interesting field of application as well.

■ CONCLUSION

We synthesized an imidazolium salt linker, which was successfully incorporated into two metal−organic frameworks. Under similar reaction conditions two different SBUs were obtained resulting in different framework topologies. The cationic nature of the linker causes the formation of positively charged networks. They show a high selectivity in liquid phase adsorption especially with regard to large organic anions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis procedure of 1,3-bis(4-carboxy-2,6-dimethylphenyl)-1*H*-imidazolium chloride, NMR spectra, XRD patterns, IR spectra, TGA data, physisorption data, dye desorption experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

MOF, metal−organic framework; NHC, *N*-heterocyclic carbene; SBA, Santa Barbara amorphous type material; EOF, element organic framework; H_2ImidCl, 1,3-bis(4-carboxy-2,6-dimethylphenyl)-1*H*-imidazolium chloride; SBU, secondary building unit

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