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Postsynthetic Modification of Metal−Organic Frameworks through Nitrile Oxide−Alkyne Cycloaddition

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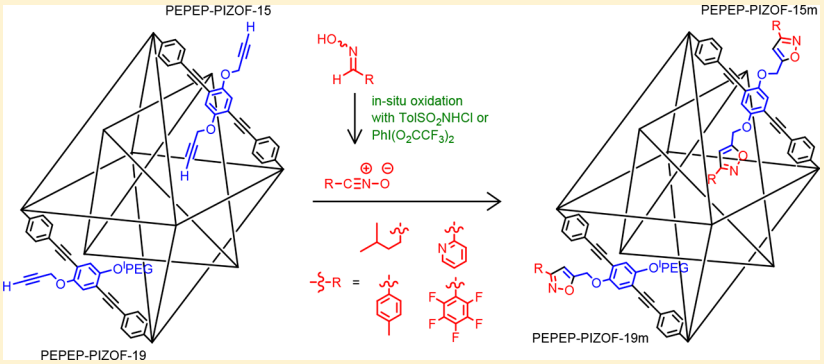
Supporting Information



ABSTRACT: Postsynthetic modification of metal−organic frameworks is an important method to tailor their properties. We report on the nitrile oxide−alkyne cycloaddition (NOAC) as a modification tool, a reaction requiring neither strained alkynes nor a catalyst. This is demonstrated with the reaction of nitrile oxides with PEPEP-PIZOF-15 and -19 at room temperature. PIZOF-15 and -19 are porous Zr-based MOFs (BET surface areas 1740 and 960 $m^2\ g^{-1}$, respectively) consisting of two mutually interpenetrating UiO-type frameworks with linkers of the type $^{-}O_2C[PE\text{-}P(R^1,R^2)\text{-}EP]CO_2^{-}$ (P, phenylene; E, ethynylene; R^1 and R^2, side chains at the central benzene ring with $R^1 = R^2 = OCH_2C{\equiv}CH$ or $R^1 = OCH_2C{\equiv}CH$ and $R^2 = O(CH_2CH_2O)_3Me$). Their syntheses, using benzoic acid as a modulator, and their characterization are reported herein. The propargyloxy ($OCH_2C{\equiv}CH$) side chains contain the ethyne moieties needed for NOAC. Formation of nitrile oxides through oxidation of oximes in aqueous ethanolic solution in the presence of PEPEP-PIZOF-15 and -19 resulted in the reaction of 96−100% of the ethyne moieties to give isoxazoles. Thereby the framework was preserved. The type of nitrile oxide RCNO was greatly varied with R being isopentyl, tolyl, 2-pyridyl, and pentafluorophenyl. A detailed NMR spectroscopic investigation showed the formation of the 3,5-disubstituted isoxazole to be clearly favored (≥96%) over that of the constitutional isomeric 3,4-disubstituted isoxazole, except for one example.

INTRODUCTION

To make porous metal−organic frameworks (MOFs) useful materials, important steps are their equipment with functional moieties and the tuning of the chemical environment within the pores. A powerful tool to tailor MOFs for a concrete application is the postsynthetic modification (PSM) of linker substituents.[1−6] Among the PSM reactions, cycloaddition reactions are especially attractive because they are of maximum atom economy, are highly chemoselective and are thus compatible with many functional groups, and most often provide quantitative conversion. To date, the Diels−Alder reaction[7−9] and azide−alkyne cycloaddition[4,10−25] (the most prominent click reaction) have been applied for PSM at linker substituents. Of the former only three examples have been described, the reaction between an olefin bearing MOF with a tetrazine,[7] the reaction between a furan bearing MOF with maleimides,[8] and, most recently, the reaction of a cyclopentadiene bearing MOF with maleimides,[9] whereas azide−alkyne cycloaddition[4,10−25] has been applied many times to azide group bearing as well as to ethyne group bearing MOFs. Azide−alkyne cycloaddition enjoys great popularity,[26,27] not only for PSM of MOFs but also, for example, in polymer science[28−30] and for bioconjugation,[31−33] because alkynes and organic azides are inert under the conditions of a wide range of reactions and azide−alkyne cycloaddition is compatible with many functional groups and substrate types (aliphatic, aromatic), which allows an unlimited variability of the reaction

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partners. However, the reaction comes with a severe drawback. If not a strained alkyne is used,[24,25] a copper salt is needed as a catalyst for the reaction to proceed quickly under mild conditions.[34−36] To remove the copper salt completely can be a major challenge and may never be achieved. Our experiments with azide−alkyne cycloaddition[8,37] applied to Zr-based MOFs of the PIZOF type[38,39] with propargyloxy substituents at the linker showed us that even washing with EDTA containing diethyl ether was insufficient to remove CuBr and also the replacement of CuBr with $Cu(MeCN)_4PF_6$, a complex soluble in organic solvents, did not provide copper-free PIZOF despite Soxhlet extraction of the postsynthetically modified product with THF and ethanol. As an alternative to increasing the reactivity of the alkyne with the help of ring strain, the reactivity of the dipolarophile can be increased through the change from an azide to a nitrile oxide.[40−44] Nitrile oxide−alkyne cycloaddition (NOAC) neither requires a strained alkyne, nor it requires a catalyst. A shortcoming of NOAC can be that highly reactive nitrile oxides have to be generated in situ in the presence of the alkyne in order to avoid their dimerization to furoxanes.[45,46] On the other hand, recent work shows that even kinetically stable nitrile oxides undergo smooth cycloaddition with terminal alkynes at temperatures as low as those in refluxing CH_2Cl_2.[47] NOAC has been applied e.g. in polymer chemistry as a polymerization method[48,49] and for the modification of polymers,[50,51] for the end-capping of rotaxanes,[47] and for biochemical purposes.[43,52−56] Herein we report on its application for the PSM of terminal alkyne bearing MOFs using highly reactive, in situ generated nitrile oxides.

For the study we used PEPEP-PIZOF-15 and PEPEP-PIZOF-19, which provide propargyloxy substituents as the reaction partner for the nitrile oxide. PEPEP-PIZOFs (porous interpenetrated zirconium−organic frameworks)[38,39] consist of two independent, mutually interpenetrating UiO-type[57] frameworks with $Zr_6O_4(OH)_4(CO_2)_{12}$ as the inorganic building units (also called secondary building units) and the rodlike dicarboxylates $^{-}O_2C[PE\text{-}P(R^1,R^2)\text{-}EP]CO_2^{-}$ with P standing for *p*-phenylene and E for ethynylene, the sequence of the letters resembling the sequence of the corresponding structural units in the backbone and R^1 and R^2 denoting the substituents at the central benzene ring. Although the substituents R^1 and R^2 can be broadly varied[38,39] through using the readily substituted dicarboxylic acids in the PIZOF synthesis, even for PIZOFs, PSM is highly valuable because it enlarges the pool of possible substituents and promises a faster fine-tuning of the pore interior, considering the imponderables of the MOF syntheses. The reaction with nitrile oxides allowed us to modify the PEPEP-PIZOFs with a broad range of substituents: aromatic, heteroaromatic, aliphatic, and highly fluorinated substituents. The very high conversions obtained with NOAC applied to PEPEP-PIZOF-15, which has two propargyloxy substituents ($R^1 = R^2 = OCH_2C{\equiv}CH$) per linker, highlights the efficiency of NOAC for PSM. The successful application of NOAC to PEPEP-PIZOF-19, which carries one propargyloxy substituent and one short linear polyethylene glycol ($O^{l}PEG_3$) substituent per linker, gives an example of the combination of preinstalled substituents of a specific property, here the highly hydrophilic $O^{l}PEG_3$ chain, with substituents introduced in a postsynthetic modification step, e.g. highly fluorinated side chains. Such a combination of incompatible side chains on one linker calls for failure when attempting to assemble the MOF with dicarboxylates already bearing both substituents.

In the following the syntheses and characterization of PEPEP-PIZOF-19 and PEPEP-PIZOF-15 will be presented first, and then their modification through NOAC will be described.

RESULTS AND DISCUSSION

Syntheses of PEPEP-PIZOF-15 and PEPEP-PIZOF-19. The organic building blocks for PEPEP-PIZOF-19 and PEPEP-PIZOF-15, the diacids **4a,b**, were synthesized starting from the 2,5-disubstituted-1,4-diiodobenzenes **1a,b**,[58] which contain propargyloxy groups in a protected form (Scheme 1). Sonogashira−Hagihara coupling of these building blocks with methyl 4-ethynylbenzoate gave the diesters **2**. Deprotection of the ethyne moiety and finally ester hydrolysis yielded the diacids **4**. Whereas diester **2a** was purified by applying our routine protocol of column chromatography,[38] diester **2b** was isolated simply through Soxhlet extraction, as we have recently described for similar diacids.[39] The latter procedure is clearly of advantage with respect to the amount of work and waste and also in the situation when large amounts of the diesters are required. Whether this simple workup procedure can be applied to diester **2a** was not tested. After deprotection of the ethyne moiety through reaction with Bu_4NF in THF, precipitation or recrystallization was sufficient to isolate the diesters **3**. It is important to keep the time in which the diesters are in contact with Bu_4NF short. Otherwise, isomerization of the propargyl into a propa-1,2-dienyl group takes place.[58] For ester hydrolysis the diesters **3** were dissolved in THF and a solution of KOH in methanol was added. The resulting precipitate was isolated. It was suspended in THF, and trifluoroacetic acid (TFA) was added until the solid dissolved (pH 2). Addition of water to the solution resulted in precipitation of the diacid. Results, when the same procedure of diester hydrolysis and product isolation to structurally closely related dicarboxylic acids was applied, strongly indicate that the mixture of THF, trifluoroacetic acid, and water is a good solvent for the diacids, causing occasionally a substantial amount of the diacid to stay in solution. Therefore, if we were to redo the syntheses of diacids **4**, we would remove all volatiles after the treatment with trifluoroacetic acid, suspend the residue in water, and isolate the undissolved diacids **4** by filtration. This procedure was very successful for the isolation of related diacids. Instead of TFA, one could use e.g. HCl for acidification after the basic ester hydrolysis. We prefer TFA because this allows us to detect residual acid simply by ^{19}F NMR spectroscopy. The presence of an acid other than the dicarboxylic acid affects the degree of defects in the UiO framework[59] and is expected to leave similar traces in the PIZOF framework.

The reaction of the diacids **4a,b** with $ZrOCl_2{\cdot}8H_2O$ in DMF in the presence of benzoic acid as modulator under static conditions at 120 °C (Scheme 1) gave PEPEP-PIZOF-19 and PEPEP-PIZOF-15, respectively, as proven by the PXRD diagrams (Figure 1). The synthesis conditions are very similar to those described for other PIZOFs,[38] however using $ZrOCl_2{\cdot}8H_2O$ instead of $ZrCl_4$ as the Zr source. When $ZrCl_4$ was used in the synthesis of PEPEP-PIZOF-15, the PIZOF formation was slow, the solutions turned dark brown, and the precipitated product was brown. The discoloration of the solution and the product were minor when $ZrOCl_2{\cdot}8H_2O$ was employed. The precipitate was washed by suspending it in DMF and then in ethanol and subsequently extracting it with ethanol in a Soxhlet extractor for 1 day. Despite this intensive extraction, some of the benzoic acid remained in the PEPEP-PIZOFs: 9−26 mol %

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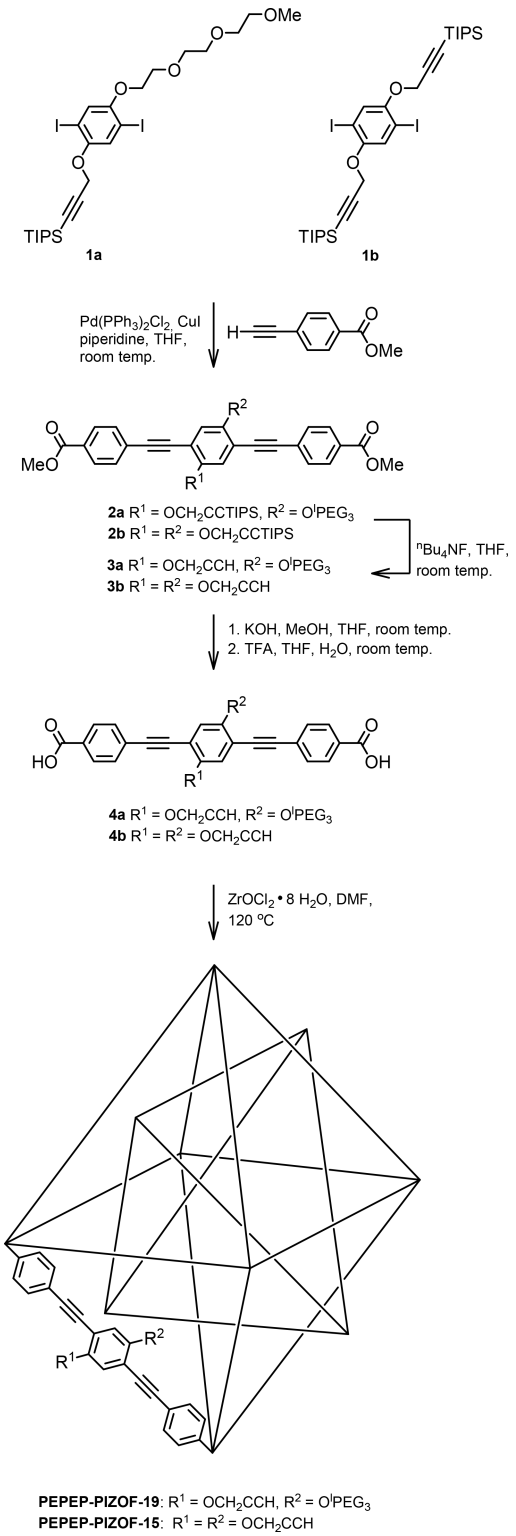
Scheme 1. Syntheses of Diacids 4a,b and of PEPEP-PIZOF-19 and PEPEP-PIZOF-15[a]



[a]The abbreviation $^{1}PEG_3$ stands for $(CH_2CH_2O)_3Me$. For the syntheses of the starting compounds **1a,b**[58] see the literature and the Supporting Information.

relative to the dicarboxylate in the case of PEPEP-PIZOF-19 and 6−10 mol % in the case of PEPEP-PIZOF-15, as was determined by ^{1}H NMR spectroscopy of the disassembled PIZOFs. The content of benzoic acid in PEPEP-PIZOF-19 was

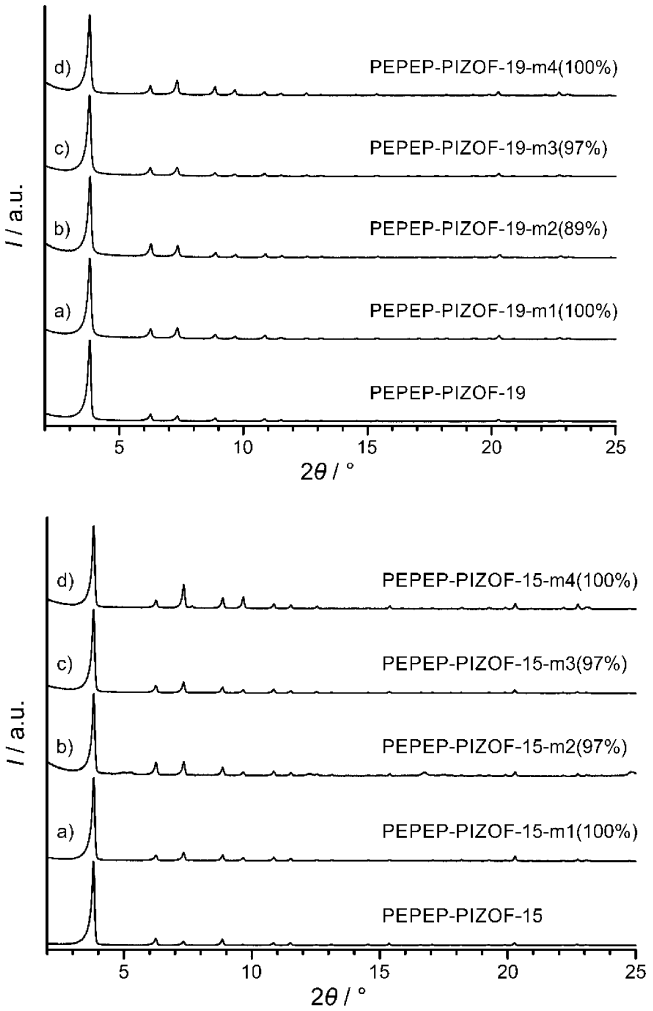


Figure 1. PXRD diagrams of (top) PEPEP-PIZOF-19 and NOAC-modified PEPEP-PIZOF-19-m*n*(conversion of propargyl groups) and (bottom) PEPEP-PIZOF-15 and NOAC-modified PEPEP-PIZOF-15-m*n*(conversion of propargyl groups).

reduced to 0.5−9 mol % by a second Soxhlet extraction with ethanol or methanol for 5−8 days. The PIZOFs used for NOAC contained a maximum of 10 mol % benzoic acid.

PEPEP-PIZOF-19 and PEPEP-PIZOF-15 were characterized with respect to porosity and composition through argon sorption measurements (Figure 2 and Table 1) and thermogravimetric analysis (TGA; Figures S1−S7 and Table 2), respectively. The sorption isotherm of PEPEP-PIZOF-19 shows a distinct hysteresis, whereas that of PIZOF-15 shows only a very minor hysteresis. The latter displays clearly a two-step adsorption and desorption, as has been found for PEPEP-PIZOF-2 and PPPP−PIZOF-1.[39] The BET specific surface area (Table 1) of PEPEP-PIZOF-19 (960 $m^2\ g^{-1}$) is significantly smaller than that of PEPEP-PIZOF-15 (1740 $m^2\ g^{-1}$), and both are significantly smaller than that of PEPEP-PIZOF-2 (2350 $m^2\ g^{-1}$).[39] Obviously, the size increase of the substituents at the linkers from methoxy, which is the substituent of PEPEP-PIZOF-2, to propargyloxy and finally to $O^{1}PEG_3$ leads to a decrease in pore volume and accessible surface. TGA in air (Figures S1 and S6 and Table 2) revealed degradation of the PIZOFs accompanied by mass loss to start at around 230 °C. Mass loss up to 200 °C is considered to be due to the removal of guest molecules and the further mass loss (exp w/o guests in

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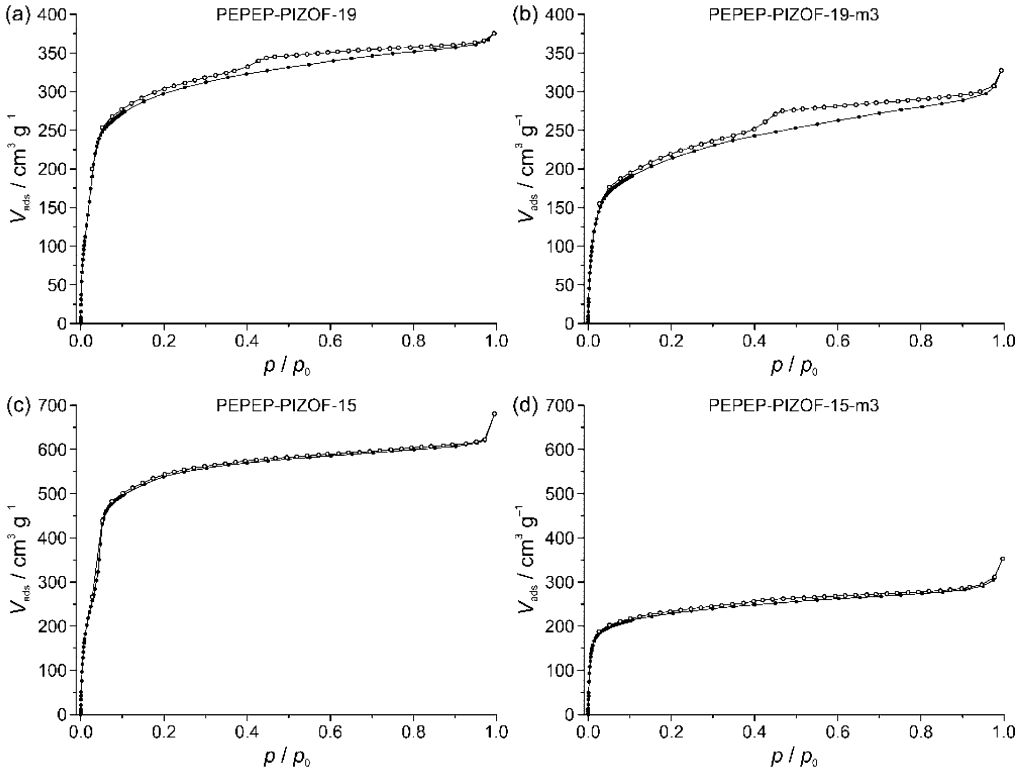

Figure 2. Linear scale plot of the argon sorption isotherms at 87 K (filled circles, adsorption; open circles, desorption): (a) PEPEP-PIZOF-19; (b) PEPEP-PIZOF-19-m3(97%); (c) PEPEP-PIZOF-15 (this batch was extracted with ethanol in a Soxhlet extractor for 5 days prior to the sorption experiment and was used for the preparation of PEPEP-PIZOF-15-m3(97%)); (d) PEPEP-PIZOF-15-m3(97%). The sorption isotherms of PEPEP-PIZOF-19-m1, PEPEP-PIZOF-19-m2, and PEPEP-PIZOF-19-m4 are very similar to that of PEPEP-PIZOF-19-m3(97%). They are presented in Figures S9, S10, and S12 in the Supporting Information, as are the pore size distributions of all of the studied materials (Figures S8–S14).

Table 1. Mass-Specific Surface Areas and Pore Volumes of Unmodified and NOAC-Modified PEPEP-PIZOFs

PEPEP-PIZOF(conversion of propargyl groups)	S_{BET} (m^2 g^{-1})	pore volume (cm^3 g^{-1})
-19	960	0.47
-19-m1(100%)	610	0.35
-19-m2(89%)	580	0.33
-19-m3(97%)	680	0.39
-19-m4(100%)	590	0.34
-15	1740	0.79
-15-m3(97%)	730	0.38

Table 2) to the dehydration of the inorganic building unit[57,60] and the combustion of the linker. The residue of the thermal decomposition in air is assumed to be ZrO_2. The surprising mass increase in the case of PEPEP-PIZOF-15 at 230 °C, a phenomenon which occurred with all of the analyzed batches of PEPEP-PIZOF-15, is assigned to the oxidation of the ethyne groups. Table 2 presents the experimentally determined data and the data calculated for the defect-free PIZOFs with the sum formula $Zr_6O_4(OH)_4$(dicarboxylate)$_{12/2}$. In the case of PEPEP-PIZOF-19, the experimentally determined amount of residue is considerably larger than the calculated amount. Obviously, PEPEP-PIZOF-19 contains defects. This conclusion is corroborated by the hysteresis found in the sorption isotherm of PEPEP-PIZOF-19 (Figure 2) as well as by the large amount of benzoic acid in the samples of PEPEP-PIZOF-19 and the tenacity with which the benzoic acid stayed in the material during Soxhlet extraction. Benzoic acid is thought to coordinate to the inorganic building units at sites where dicarboxylates are

Table 2. Experimentally (exp) Determined Mass Losses (%) upon Heating of PEPEP-PIZOFs in Flowing Air and Data Calculated for Defect-Free PEPEP-PIZOFs (calcd)[a]

PEPEP-PIZOF(conversion of propargyl groups)		exp	exp w/o guests	calcd
-19	guests	2.9		
	linker	75.4	77.7	82.2
	residue	21.7	22.3	17.8
-19-m1(100%)	guests	3.7		
	linker	75.0	77.9	84.7
	residue	21.3	22.1	15.3
-19-m2(89%)	guests	4.2		
	linker	77.7	81.1	84.8
	residue	18.1	18.9	15.2
-19-m3(97%)	guests	3.1		
	linker	77.7	80.2	84.8
	residue	19.2	19.8	15.2
-19-m4(100%)	guests	2.8		
	linker	80.6	82.9	86.4
	residue	16.6	17.1	13.6
-15	guests	3.1		
	linker	77.1	79.6	79.0
	residue	19.8	20.4	21.0
-15-m3(97%)	guests	3.5		
	linker	83.3	86.2	84.9
	residue	13.3	13.8	15.1

[a]Details on the analysis of the TGA curves (Figures S1–S7) are provided in the text and the Supporting Information.

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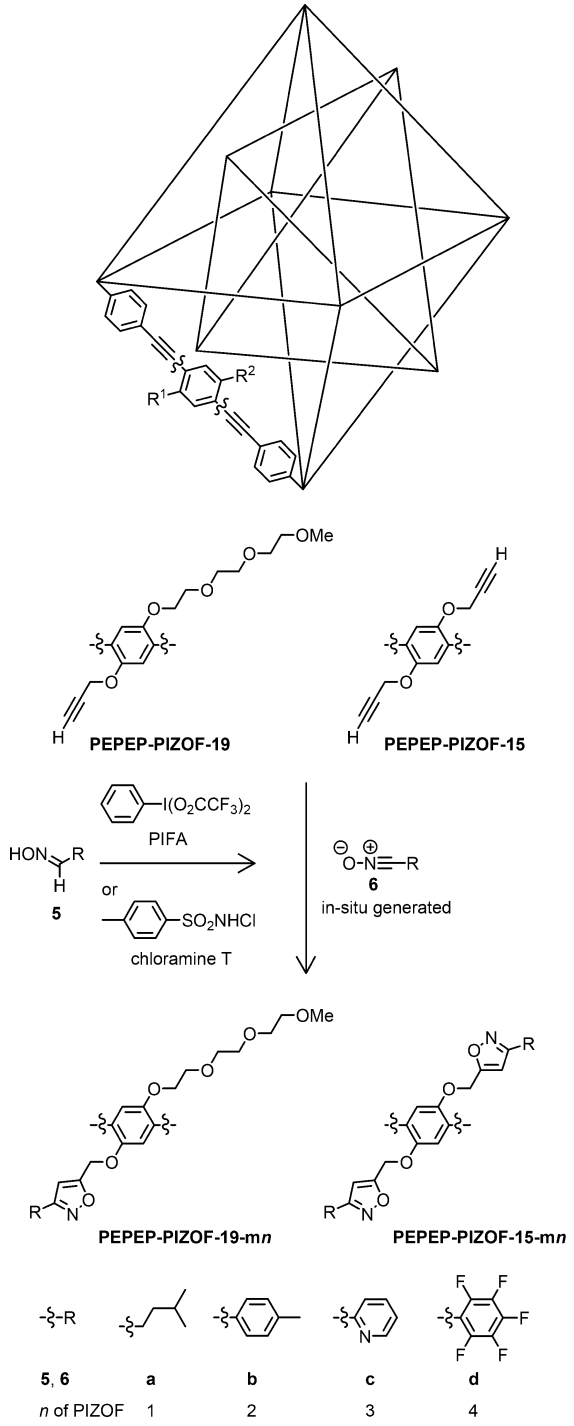
missing. In comparison with PEPEP-PIZOF-19, PEPEP-PIZOF-15 contains much fewer, if any defects, as the experimentally determined and the calculated TGA data match very well, as do the curves of adsorption and desorption. Only the amount of 6−10 mol % of benzoic acid present after 1 day of Soxhlet extraction may hint at structural defects in PIZOF-15.

Nitrile Oxide Click Reaction. To explore the chemical tailoring of PIZOF pores with NOAC, the nitrile oxides **6a−d** were selected as examples for hydrophobic, hydrophilic, highly fluorinated, aliphatic, aromatic, and heterocyclic nitrile oxides (Scheme 2). These nitrile oxides were expected to be unstable, as they lack sterically stabilizing substituents and, therefore, to require an in situ preparation. We opted for their generation via oxidation of the oximes **5a−d**.[45,61,62] Oxime **5c** was purchased; the oximes **5a**,**b**,**d** were synthesized from the corresponding aldehydes, using hydroxylammonium chloride and a base.[63]

Among the several reagents described for the oxidation of oximes to nitrile oxides,[61] our first choice was phenyliodine bis(trifluoroacetate) (PIFA)[63,64] for its low toxicity and instantaneous oxidation of oximes[63] and because we expected iodobenzene and trifluoroacetic acid, which are the two products deriving from PIFA, to be easily removable by extraction of the PIZOFs with an organic solvent. Adding PIFA portionwise to mixtures of PEPEP-PIZOF-19 with the oximes **5a−d** and of PEPEP-PIZOF-15 with the oximes **5b−d** (for the amounts of PIFA and oximes used see Table 3) in aqueous methanol at room temperature gave PEPEP-PIZOF-19-m*n* with n = 1−4 and PEPEP-PIZOF-15-m*n* with n = 2−4 with disubstituted isoxazoles as linker substituents. With the portionwise addition of PIFA the concentration of the generated nitrile oxide and therefore the probability of their dimerization were kept low. Indeed, the conversion of the propargyl groups was significantly lower when all of the PIFA was added at once. To determine the conversions of the propargyl groups, the NOAC-modified PIZOFs were disassembled using CsF and DCl in DMSO-d_6,[8] the ^{1}H NMR spectra of the solutions were recorded, and the intensities of the signals caused by the proton of the isoxazole moiety (isoxazole proton) and of the methylene unit of the propargyl group were determined. The results are given in Table 3. Please note that the reactions have not been optimized with respect to the minimum amount of oxime and/or oxidant. Very high conversions of 89−100% of the propargyl groups were achieved with the aromatic oximes **5b−d**. However, the combination of the aliphatic oxime **5a** with PEPEP-PIZOF-19 resulted in a comparatively low conversion of 68%. A result comparable to the latter finding provided NOAC applied to 1-methoxy-4-(prop-2-yn-1-yloxy)benzene (**7**), which is the most simple cutout of the PIZOF linkers. Using the aliphatic oxime **5a** and PIFA in a 5/1 mixture of methanol and water caused only about 33% of model compound **7** to react, despite 3 equiv of oxime and oxidant being used. In contrast, a complete conversion of model compound **7** into the NOAC product was achieved with sodium *N*-chloro-*p*-toluenesulfonamide (chloramine T) as the oxidant in a 2/1 mixture of ethanol and water. As in the experiment with PIFA, 3 equiv of oxidant and of oxime were used. Interestingly, all of the chloramine T could be added at once, whereas, as mentioned above, PIFA had to be added portionwise. This suggests less competition through nitrile oxide dimerization when chloramine T is used and therefore a distinctly slower rate of oxime oxidation with chloramine T than with PIFA. As in the case of model compound **7**, chloramine T was the reagent of choice for NOAC on PEPEP-PIZOF-15 and -19 with the aliphatic nitrile oxide **6a** to achieve conversions of 98−99% of the propargyl groups (Table 3, experiments 1a, 5a, and 5b). That it is the type

Scheme 2. Postsynthetic Modification of PEPEP-PIZOF-19 and PEPEP-PIZOF-15 through Nitrile Oxide−Alkyne Cycloaddition (NOAC) between the Propargyloxy Substituents at the Linkers and in Situ Generated Nitrile Oxides 6[a]



[a]The reactions were performed in aqueous methanol or aqueous ethanol. Please note that for PEPEP-PIZOF-15-m4 only one of the three isomeric cycloaddition products is shown (see discussion in the text and Figure 3).

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Table 3. Results of NOAC on PEPEP-PIZOF-19 and PEPEP-PIZOF-15 with PIFA in MeOH/H_2O (5/1) or with Chloramine T in EtOH/H_2O (2/1)[a]

exp	PEPEP-PIZOF(conversion of propargyl groups)	oxime (equiv per propargyl group)	oxidant (equiv per propargyl group)	fraction of 3,5-disubstituted isoxazole (%)
1a	-19-m1(100%)	**5a** (10)	chloramine T (10)	99
1b	-19-m1(68%)	**5a** (10)	PIFA (6)	99
2	-19-m2(89%)	**5b** (2)	PIFA (2)	99
3	-19-m3(97%)	**5c** (2)	PIFA (2)	100
4	-19-m4(100%)	**5d** (2)	PIFA (2)	96
5a	-15-m1(99%)	**5a** (10)	chloramine T (6)	98
5b	-15-m1(100%)	**5a** (6)	chloramine T (6)	98
6	-15-m2(97%)	**5b** (4)	PIFA (2)	100
7a	-15-m3(97%)	**5c** (3)	PIFA (2)	99
7b	-15-m3(96%)	**5c** (6)	chloramine T (6)	97
8	-15-m4(100%)	**5d** (3)	PIFA (2)	59[b]

[a]The fractions of the 3,5-disubstituted isoxazole in the mixtures of 3,5- and 3,4-disubstituted isoxazoles and the conversions were determined through ^{1}H NMR spectroscopy. [b]18.5% 3,5/3,5-isomer, 80.5% 3,5/3,4-isomer, <1% 3,4/3,4-isomer.

of oxidant and not the amount that makes the difference can be concluded from a comparison of the results of the experiments 1b and 5a in Table 3. Against our apprehension, the polar toluene sulfonamide, which is the reduction product derived from chloramine T, was nearly quantitatively removed through Soxhlet extraction of the NOAC-modified PIZOFs. Furthermore, chloramine T can also be applied for the aromatic oxime **5c** (the other aromatic oximes **5b,d** were not tested) and gave the same result as PIFA (Table 3, experiment 7b).

^{1}H NMR spectroscopy of the disassembled NOAC-modified PIZOFs (Figure 4), revealed that, except for PEPEP-PIZOF-15-m4, one of the two possible cycloaddition products, 3,5- or 3,4-disubstituted isoxazole, had formed exclusively or nearly exclusively (Table 3). Of these two possible isomers, the former is reported to be the sole or at least main product of the thermal reaction.[53,63,65] However, an influence of the particular environment of a MOF pore on the regioselectivity could not be excluded. As outlined in the Supporting Information, the ^{1}H NMR data of the disassembled NOAC-modified PIZOFs in combination with the ^{1}H NMR data, including a ^{1}H−^{1}H-NOESY spectrum of the NOAC product (model compound **8b**) of diester **3a** with nitrile oxide **6b** (Scheme S1), provided conclusive evidence that the main or sole product was the 3,5-disubstituted isoxazole accompanied, if at all, by a maximum of 3% of 3,4-disubstituted isoxazole. The indicative ^{1}H NMR signals arise from the proton at the isoxazole ring and the protons of the methylene group bound to the isoxazole ring at the 5- or 4-position. As can be seen from Figure 4, the signal shift is very distinct for the two isomeric isoxazoles (see also Table S1).

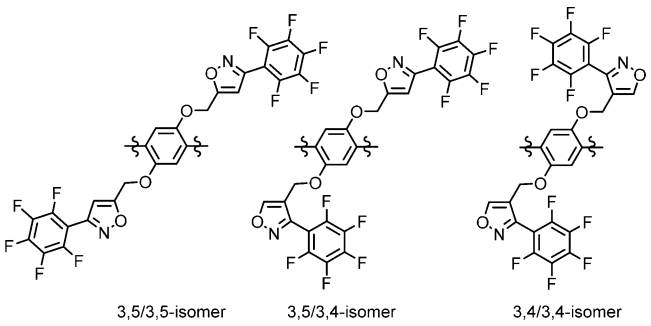

Figure 3. Cutouts of the linkers of PEPEP-PIZOF-15-m4 displaying the 3,5/3,5-, 3,5/3,4-, and 3,4/3,4-isomers, which formed in a ratio of roughly 19/80/1.

Quite a different situation was found for NOAC of PEPEP-PIZOF-15-m4 with nitrile oxide **6d**. The formation of 3,5-disubstituted isoxazole is only slightly favored (59%) over that of the 3,4-disubstituted isoxazole. The result is a PIZOF with three constitutionally isomeric linkers: 3,5/3,5-isomer (18.5%), 3,5/3,4-isomer (80.5%), and 3,4/3,4-isomer (<1%) (Figure 3). Because only very little of the 3,4/3,4-isomer formed and NOAC of PEPEP-PIZOF-19 with nitrile oxide **6d** gave the 3,5-disubstituted isoxazole (96%) nearly exclusively, we assume that the monoaddition product is a 3,5-disubstituted isoxazole and that the isomeric isoxazole moiety is formed predominantly upon the second cycloaddition at the linker. We tried to mimic the 2-fold NOAC with the reaction of nitrile oxide **6d** with diester **3b** in homogeneous solution under otherwise identical conditions. This attempt failed because of an insufficient conversion of the propargyl groups, most probably caused by the low solubility of diester **3b** and of the monoaddition product. Hardly any diaddition product formed. Therefore, the question remains whether the preference for the 3,4-disubstituted isoxazole in the second cycloaddition step of nitrile oxide **6d** is a peculiarity of NOAC on PEPEP-PIZOF-15 or would occur as well in the homogeneous phase. In addition, the cause for the difference in behavior of the perfluorinated nitrile oxime **6d** and the nonfluorinated, aliphatic, and aromatic nitrile oxides **6a−c** remains unknown.

The very close similarity between the powder X-ray diffraction (PXRD) patterns (Figure 1) of all of the NOAC-modified PEPEP-PIZOFs with those of the unmodified PEPEP-PIZOFs strongly suggests that all these materials show the same topology. The degree of crystallinity is, if at all, only very slightly affected by the postsynthetic modification. In contrast to the parent PIZOFs, the NOAC-modified PIZOFs were free of benzoic acid. Argon sorption isotherms proved all NOAC-modified PEPEP-PIZOFs to be porous (Figure 2 and Figures S9−S12 and S14). The significant reduction of the BET surface area and the pore volume upon NOAC (Table 1) is assigned to the filling of the pores with the modified substituents. The similarity of the sorption data for PEPEP-PIZOF-19-m*n* and PEPEP-PIZOF-15-m1 is in line with the nearly quantitative modification of both propargyl groups of the PEPEP-PIZOF-15 linker and supports the aforementioned view that the smaller surface area of PEPEP-PIZOF-19 in comparison to PEPEP-

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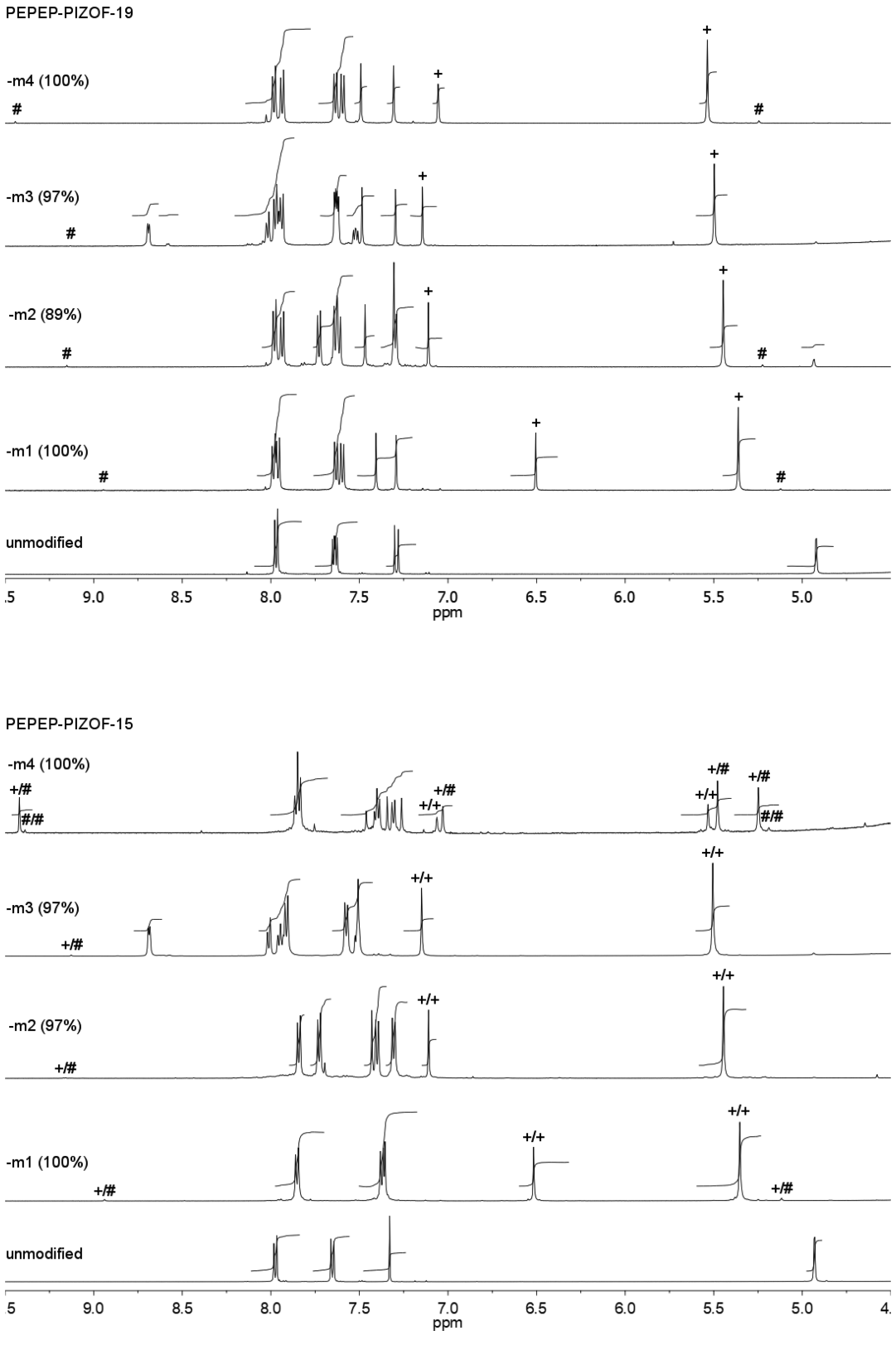

Figure 4. (top) ^{1}H NMR spectra (DMSO-d_6, 500 MHz, room temperature) of disassembled PEPEP-PIZOF-19, PEPEP-PIZOF-19-m1(100%); PEPEP-PIZOF-19-m2(89%), PEPEP-PIZOF-19-m3(97%), and PEPEP-PIZOF-19-m4(100%). (bottom) ^{1}H NMR spectra (DMSO-d_6, 500 MHz, room temperature) of disassembled PEPEP-PIZOF-15, PEPEP-PIZOF-15-m1(100%), PEPEP-PIZOF-15-m2(97%), PEPEP-PIZOF-15-m3(97%), and PEPEP-PIZOF-15-m4(100%). Signals of 3,5-disubstituted isoxazole are indicated with + and those of 3,4-disubstituted isoxazole with #. In the case of PEPEP-PIZOF-15-m*n* the signals assigned to the combinations of 3,5/3,5-, 3,5/3,4-, and 3,4/3,4-isoxazoles are marked with + /+, + /#, and #/#, respectively. The singlets in the range of 5.0−5.5 ppm are the signals of the isoxazole−CH_2O group. The signals in the range of 6.5−7.2 and 8.9−9.4 ppm are the signals of the isoxazole−H.

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PIZOF-15 is caused by the space-demanding O^{1}PEG$_3$ substituents.

Like PEPEP-PIZOF-19, all of the four PEPEP-PIZOF-19-m*n* show a sorption isotherm with a hysteresis pointing to the presence of mesopores and therefore framework defects. Another sign of framework defects is the mismatch between experimentally determined and calculated masses for linker and inorganic components (Table 2 and Figures S2–S5 and S7). The courses of hystereses in the sorption isotherms of PEPEP-PIZOF-19 and PEPEP-PIZOF-19-m*n* are very similar. Only the extent of the hystereses varies from material to material. A comparatively very slight hysteresis is found in the sorption isotherm of PEPEP-PIZOF-15-m3 which is slightly larger than that of the parent PEPEP-PIZOF-15. The experimentally determined TGA data of PEPEP-PIZOF-15-m3 agree well with the calculated data. Please note that all of the four PEPEP-PIZOF-19-m*n* were prepared from independent batches of PEPEP-PIZOF-19. Therefore, the differences in sorption isotherms and TGA data may simply be rooted in the variation of defect number among the different batches of PEPEP-PIZOF-19. On the other hand, the sorption isotherm of PEPEP-PIZOF-15 shown in Figure 2 comes from the material that was used to prepare PEPEP-PIZOF-15-m3. Therefore, the slight increase of the hysteresis in this case is understood as an indication that NOAC is not completely harmless. Including PXRD data and TGA data, we estimate the extent of damage to be rather small.

CONCLUSION

The family of PIZOFs has been enlarged by the PEPEP-PIZOFs-15 and -19, which have one and two propargyloxy substituents per linker, respectively. With these MOFs the postsynthetic modification of MOFs through nitrile oxide–alkyne cycloaddition (NOAC) was demonstrated. NOAC works with the unstrained propargyloxy substituent, does not require a catalyst, and yielded conversions of 89–100%. Furthermore, NOAC was found to be applicable to very different types of nitrile oxides—aliphatic, aromatic, heteroaromatic, and highly fluorinated—and thus appears as highly suited for customizing the pore environment for concrete demands, including the introduction of functional groups. The first two examples of the latter are PEPEP-PIZOF-15-m3 and PEPEP-PIZOF-19-m3, which provide a bidentate ligand for metal ions such as palladium and copper ions. Metal ion loaded MOFs are of interest as catalysts.[19,66−70] The modification of PEPEP-PIZOF-15 opens access to a MOF with amphiphilic pores and, in the case of a self-sorting process through rotation of the central benzene ring, to a MOF with alternating pores of e.g. highly polar and fluorophilic pores. We expect post-synthetic modification through NOAC to be applicable to all MOFs which are compatible with aqueous alcoholic solutions. In addition, it may be applicable to MOFs only compatible with water-free solvents, when preformed, kinetically stabilized nitrile oxides are used[47] or one of the other methods to form nitrile oxides is applied.

EXPERIMENTAL SECTION

The syntheses of diacids **4** and of oximes **5** are described in the Supporting Information.

General Considerations. NMR spectra were recorded at room temperature if not otherwise mentioned. They were calibrated using the solvent as an internal standard: $CDCl_3$, 7.25 ppm (^{1}H) and 77.0 ppm (^{13}C); DMSO-d_6, 2.49 ppm (^{1}H) and 39.50 ppm (^{13}C), D_2O, 4.79 ppm (^{1}H). For ^{19}F NMR spectra C_6F_6 ($\delta(^{19}F)$ −169 ppm) was used as an internal standard, however, it was contained in a separate capillary. Signal assignments are supported by DEPT-135 experiments, calculations using increments,[71] and comparison with data from closely related compounds.[38,39,58] All of the named components accompanying the main component, such as a solvent or a side product, were identified and quantified through ^{1}H NMR spectroscopy. Signals assigned to solvents are not listed with the NMR data. The signals listed below are the signals assigned to the highly dominant component.

ESI mass spectra were recorded using an Esquire 3000 ion trap mass spectrometer equipped with a standard ESI source. Samples were introduced by direct infusion with a syringe pump. Nitrogen served as both the nebulizer gas and the dry gas.

Elemental analyses were performed by using HEKAtech EURO EA 2010 CHNS elemental analyzer.

PEPEP-PIZOF-15 and PEPEP-PIZOF-19. $ZrOCl_2 \cdot 8H_2O$ (0.111 g, 0.343 mmol) and benzoic acid (1.256 g, 10.287 mmol) were dissolved in DMF (20 mL) by using ultrasound. Diacid **4b** (0.163 g, 0.343 mmol) or diacid **4a** (0.195 g, 0.343 mmol) was added and dissolved by the application of ultrasound. The screw-capped bottle (100 mL, VWR, Schott, Borosilicate 3.3, ISO 4796; PTFE-coated seal) was tightly closed and put into an oven preheated to 120 °C. The reaction mixture was kept at this temperature under static conditions for 24 h. The suspension was removed from the hot oven and cooled to room temperature. The precipitate was isolated by centrifugation. The yellowish solid was suspended in DMF, the suspension was centrifuged, and the solution was decanted off. The residual solid was washed with ethanol in the same way as described for the washing with DMF. The solid was extracted in a Soxhlet extractor with ethanol for 1 day. The solid was dried at room temperature and reduced pressure. PEPEP-PIZOF-19 was extracted with ethanol or methanol in a Soxhlet device for another 5–8 days. PEPEP-PIZOF-15 contained 6–10 mol % and PEPEP-PIZOF-19 contained 0.5–9 mol % benzoic acid (mol % refers to the moles of the MOF linker).

Disassembly of PEPEP-PIZOFs. PEPEP-PIZOF (1–6 mg) and CsF (6–11 mg) were suspended in DMSO-d_6 (ca. 0.65 mL). A drop of aqueous DCl (35 wt % in D_2O, 20–25 mg) was added. The disappearance of the yellow solid indicated disassembly of the PEPEP-PIZOF (5–15 min). CsF is a white solid and can be easily distinguished from the yellow PEPEP-PIZOF. In some cases, the suspension had to be heated to 80 °C to induce disassembly. Finally, K_2CO_3 (10–15 mg) was added and the solid was removed through decantation.

Nitrile Oxide–Alkyne Cycloaddition (NOAC) with PEPEP-PIZOFs. *General Procedures. Using PIFA.* PIZOF and oxime **5** were suspended in a 5/1 mixture of MeOH and water. [Bis-(trifluoroacetoxy)iodo]benzene (PIFA) was added portionswise, and the suspension was stirred at room temperature for the time stated. The solid was isolated by filtration, if not otherwise stated, and extracted in a Soxhlet extractor.

Using Chloramine T. PIZOF and oxime **5** were suspended in a 2/1 mixture of EtOH and water. Chloramine T·3H_2O was added, and the suspension was stirred at room temperature for the time stated. The solid was isolated by filtration, if not otherwise stated, and extracted in a Soxhlet extractor.

PEPEP-PIZOF-19-m1(100%). See the general procedure for NOAC using chloramine T: PEPEP-PIZOF-19 (153 mg, 0.22 mmol propargyl moieties), oxime **5a** (222 mg, 2.19 mmol), EtOH/H_2O 2/1 (20 mL), chloramine T·3H_2O (629 mg, 2.23 mmol). Reaction time: 94 h. Soxhlet extraction with EtOH (70 mL) gave a yellow solid (113 mg). ^{1}H NMR (500 MHz, DMSO-d_6) (Figure S26): δ 7.95 and 7.92 (two halves of two AA′XX′ spin systems, 2 H each, ArH ortho to CO_2), 7.60 and 7.56 (two halves of two AA′XX′ spin systems, 2 H each, ArH meta to CO_2) 7.36 and 7.25 (2 s, 1 H each, ArH ortho to OCH_2), 6.47 (s, 1 H, isoxazole-H), 5.31 (s, 2 H, isoxazole-CH_2O), 4.16, 3.76, 3.63, 3.46, 3.42, and 3.31 (6 t-like, 2 H each, CH_2 of ^{1}PEG$_3$), 3.13 (s, 3 H, OCH_3), 2.45 (d, ^3J = 7.1 Hz, 2 H, CH_2CH(CH$_3$)$_2$), 1.84 (m, 1 H, CH$_2$CH(CH$_3$)$_2$), 0.82 (d, ^3J = 6.7 Hz, 6 H, CH$_2$CH(CH_3)$_2$). ^{13}C NMR (500 MHz, DMSO-d_6) (Figure S27): δ 167.4 (C═N), 166.84

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and 166.80 (CO_2), 163.1 (HC═*C*O), 154.2 and 152.4 ($C_{Ar}OCH_2$), 131.70 and 131.69 (C_{Ar}H meta to CO_2), 130.93 and 130.87 ($C_{Ar}CO_2$), 129.93 and 129.87 (C_{Ar}H ortho to CO_2), 126.9 and 126.8 (C_{Ar} para to CO_2), 118.4 and 117.0 (C_{Ar}H ortho to OCH_2), 114.1 and 113.3 ($C_{Ar}C{\equiv}C$ ortho to OCH_2), 104.5 (HC═*C*O), 94.8 and 88.8 (C≡C), 71.5, 70.5, 70.1, 69.8, 69.4, and 69.3 (CH_2 of $^{l}PEG_3$), 62.5 (isoxazole-CH_2O), 58.3 (OCH_3), 34.3 ($CH_2CH(CH_3)_2$), 27.6 ($CH_2CH(CH_3)_2$), 22.3 ($CH_2CH(CH_3)_2$. MS (ESI): *m*/*z* 704.3 $[M + Na]^+$, 680.2 $[M - H]^-$.

PEPEP-PIZOF-19-m1(68%). See the general procedure for NOAC using PIFA: PIZOF-19 (148 mg, 0.22 mmol propargyl moieties), oxime **5a** (216 mg, 2.13 mmol), MeOH/H_2O 5/1 (20 mL), PIFA (563 mg, 1.31 mmol). PIFA was added in five portions within a period of 4 h and a sixth portion after 18 h. Reaction time after the addition of the last portion of PIFA: 71 h. Soxhlet extraction with EtOH gave a yellow solid (104 mg).

PEPEP-PIZOF-19-m2(89%). See the general procedure for NOAC using PIFA: PEPEP-PIZOF-19 (150 mg, 0.22 mmol propargyl moieties), oxime **5b** (60 mg, 0.44 mmol), MeOH/H_2O 5/1 (15 mL), PIFA (189 mg, 0.44 mmol). PIFA was added in five portions within a period of 4 h and a sixth portion after 17 h. Reaction time after the addition of the last portion of PIFA: 73 h. Soxhlet extraction with EtOH (70 mL) gave a yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) (Figure S28): δ 7.95 and 7.90 (two halves of two AA′XX′ spin systems, 2 H each, ArH ortho to CO_2), 7.68 (half of AA′XX′ spin system, 2 H, ArH of tolyl), 7.61 and 7.58 (two halves of two AA′XX′ spin systems, 2 H each, ArH meta to CO_2), 7.43 and 7.26 (2 s, 1 H each, ArH ortho to OCH_2), 7.26 (half of AA′XX′ spin system, 2 H, ArH of tolyl), 7.08 (s, 1 H, isoxazole-H), 5.40 (s, 2 H, isoxazole-CH_2O), 4.17, 3.77, 3.63, 3.46, 3.42, and 3.31 (6 t-like, 2 H each, CH_2), 3.13 (s, 3 H, OCH_3), 2.31 (s, 3 H, CH_3 of tolyl). ^{13}C NMR (500 MHz, DMSO-d_6) (Figure S29): δ 168.6 (C═N),166.83 and 166.79 (CO_2), 162.1 (HC═CO), 154.3 and 152.4 ($C_{Ar}OCH_2$), 140.4 ($C_{Ar}CH_3$), 131.7 (C_{Ar}H meta to CO_2), 130.79 and 130.75 ($C_{Ar}CO_2$), 129.97, 129.91, and 129.87 (C_{Ar}H ortho to CO_2 and C_{Ar}H of tolyl), 127.2 and 126.9 (C_{Ar} para to CO_2), 126.8 (C_{Ar}H of tolyl), 125.6 (C_{Ar}C═N), 118.5 and 117.1 (C_{Ar}H ortho to OCH_2), 114.2 and 113.6 ($C_{Ar}C{\equiv}C$ ortho to OCH_2),102.5 (HC═CO), 94.8, 94.7, 88.8, and 88.5 (C≡C), 71.4, 70.5, 70.1, 69.8, 69.4, and 69.3 (CH_2 of $^{l}PEG_3$), 62.3 (isoxazole-CH_2O), 58.3 (OCH_3), 23.3 (CH_3 of tolyl). MS (ESI): *m*/*z* 738.2 $[M + Na]^+$, 714.0 $[M - H]^-$.

PEPEP-PIZOF-19-m3(97%). See the general procedure for NOAC using PIFA: PEPEP-PIZOF-19 (120 mg, 0.17 mmol propargyl moieties), oxime **5c** (44 mg, 36 mmol), MeOH/H_2O 5/1 (8 mL), PIFA (153 mg, 0.36 mmol). PIFA was added in six portions within a period of 5 h. Reaction time after the addition of the last portion of PIFA: 115 h. Soxhlet extraction with THF (70 mL) gave a yellow solid (100 mg). ^{1}H NMR (500 MHz, DMSO-d_6) (Figure S30): δ 8.70 (m, 1 H, ArH of pyridine), 8.03 (d, ^3J = 7.8 Hz, 1 H, ArH of pyridine), 7.98 (m partially overlapping with the signal of an AA′XX′ spin system, 1 H, ArH of pyridine), 7.97 and 7.93 (two halves of two AA′XX′ spin systems, 2 H each, ArH ortho to CO_2), 7.63 and 7.61 (two halves of two AA′XX′ spin systems, 2 H each, ArH meta to CO_2), 7.54 (m, 1 H, ArH of pyridine), 7.47 and 7.28 (2 s, 1 H each, ArH ortho to OCH_2), 7.16 (s, 1 H, isoxazole-H), 5.49 (s, 2 H, isoxazole-CH_2O), 4.19, 3.78, 3.65, 3.48, 3.44, and 3.33 (6 t-like, 2 H each, CH_2), 3.14 (s, 3 H, OCH_3). ^{13}C NMR (500 MHz, DMSO-d_6) (Figure S31): δ 169.1 (C═N of isoxazole), 166.79 and 166.75 (CO_2), 162.7 (HC═CO), 154.2 and 152.2 ($C_{Ar}OCH_2$), 149.8 and 147.1 (C_{Ar}H of pyridine and q-C of pyridine), 138.3 (C_{Ar}H of pyridine), 131.7 and 131.6 (C_{Ar}H meta to CO_2), 130.74 and 130.69 ($C_{Ar}CO_2$), 129.84 and 129.80 (C_{Ar}H ortho to CO_2), 126.9 and 126.7 (C_{Ar} para to CO_2), 125.6 and 121.8 (C_{Ar}H of pyridine), 118.3 and 117.0 (C_{Ar}H ortho to OCH_2), 114.1 and 113.3 ($C_{Ar}C{\equiv}C$ ortho to OCH_2), 102.9 (HC═CO), 94.74, 94.66, 88.7, and 88.4 (C≡C), 71.4, 70.4, 70.3, 69.7, 69.3, and 69.2 (CH_2 of $^{l}PEG_3$), 62.4 (isoxazole-CH_2O), 58.2 (OCH_3). MS (ESI): *m*/*z* 725.3 $[M + Na]^+$, 701.1 $[M - H]^-$.

PEPEP-PIZOF-19-m4(100%). See the general procedure for NOAC using PIFA: PEPEP-PIZOF-19 (223 mg, 0.32 mmol propargyl moieties), oxime **5d** (135 mg, 0.64 mmol), MeOH/H_2O 5/1 (15 mL), PIFA (274 mg, 0.64 mmol). PIFA was added in five portions within a period of 4 h and a sixth portion after 21 h. Reaction time after the addition of the last portion of PIFA: 72 h. Soxhlet extraction first with EtOH (70 mL) and then with THF (70 mL) gave a yellow solid (223 mg). ^{1}H NMR (500 MHz, DMSO-d_6) (Figure S32): δ 7.94 and 7.89 (two halves of two AA′XX′ spin systems, 2 H each, ArH ortho to CO_2), 7.60 and 7.55 (two halves of two AA′XX′ spin systems, 2 H each, ArH meta to CO_2) 7.43 and 7.24 (2 s, 1 H each, ArH ortho OCH_2), 7.00 (s, 1 H, isoxazole-H), 5.47 (s, 2 H, isoxazole-CH_2O), 4.16, 3.76, 3.63, 3.46, 3.42, and 3.31 (6 t-like, 2 H each, CH_2), 3.12 (s, 3 H, OCH_3). ^{13}C NMR (500 MHz, DMSO-d_6) (Figure S33): δ 169.4 (C═N), 166.9 and 166.8 (CO_2), 163.3 (HC═CO), 154.4 and 152.3 ($C_{Ar}OCH_2$), 151.6, 145.5, and 143.5 (3 m, CF), 131.72 and 131.70 (C_{Ar}H meta to CO_2), 130.82 and 130.79 ($C_{Ar}CO_2$), 129.9 and 129.8 (C_{Ar}H ortho to CO_2), 126.9 and 126.8 (C_{Ar} para to CO_2), 118.6 and 117.0 (C_{Ar}H ortho to OCH_2), 114.3 and 113.4 ($C_{Ar}C{\equiv}C$ ortho to OCH_2), 105.5 (HC═CO), 99.9 (C_{Ar}C═N), 94.9, 94.8, 88.7, and 88.4 (C≡C), 71.5, 70.5, 70.1, 69.8, 69.5, and 69.3 (CH_2 of $^{l}PEG_3$), 62.6 (isoxazole-CH_2O), 58.3 (OCH_3).

PEPEP-PIZOF-15-m1(100%). See the general procedure for NOAC using chloramine T: PIZOF-15 (30 mg, 0.10 mmol propargyl moieties), oxime **5a** (62 mg, 0.61 mmol), EtOH/H_2O 2/1 (4 mL), chloramine T·3H_2O (176 mg, 0.62 mmol). Reaction time: 72 h. Soxhlet extraction first with EtOH (70 mL) and then with THF (70 mL) gave a yellow solid (17 mg). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.84 and 7.36 (AA′XX′ spin system, 4 H each, ArH ortho and meta to CO_2, respectively), 7.35 (s, 2 H, ArH ortho to OCH_2), 6.51 (s, 2 H, isoxazole-H), 5.34 (s, 4 H, isoxazole-CH_2O), 2.49 (signal strongly overlapping with the signal of DMSO, $CH_2CH(CH_3)_2$), 1.90 (hept, ^3J = 6.5 Hz, 2 H, $CH_2CH(CH_3)_2$), 0.87 (d, ^3J = 6.6 Hz, 6 H, $CH_2CH(CH_3)_2$).

PEPEP-PIZOF-15-m1(99%). See the general procedure for NOAC using chloramine T: PIZOF-15 (30 mg, 0.10 mmol propargyl moieties), oxime **5a** (110 mg, 1.09 mmol), EtOH/H_2O 2/1 (4 mL), chloramine T·3H_2O (176 mg, 0.62 mmol). Reaction time: 68 h. Soxhlet extraction with EtOH (70 mL) gave a yellow solid. ^{1}H NMR (500 MHz, 80 °C, DMSO-d_6) (Figure S38): δ 7.94 and 7.57 (AA′XX′ spin system, 4 H each, ArH ortho and meta to CO_2, respectively), 7.37 (s, 2 H, ArH ortho to OCH_2), 6.43 (s, 2 H, isoxazole-H), 5.33 (s, 4 H, isoxazole-CH_2O), 2.48 (d partially overlapping with the signal of DMSO, $CH_2CH(CH_3)_2$), 1.89 (hept-like, ^3J = 6.7 Hz, 2 H, $CH_2CH(CH_3)_2$), 0.87 (d, ^3J = 6.7 Hz, 12 H, $CH_2CH(CH_3)_2$). The differences in the shifts in comparison to the data reported above for disassembled PEPEP-PIZOF-15-m1(100%) are ascribed to the difference in temperature and pH of the solution.

PEPEP-PIZOF-15-m2(97%). See the general procedure for NOAC using PIFA: PEPEP-PIZOF-15 (30 mg, 0.10 mmol propargyl moieties), oxime **5b** (28 mg, 0.21 mmol), MeOH/H_2O 5/1 (1.5 mL). PIFA (807 mg, 1.88 mmol) was added in five portions within a period of 7 h and a sixth portion after 22 h. Reaction time after the addition of the last portion of PIFA: 3 days. The yellow solid was isolated by centrifugation. Soxhlet extraction with MeOH (70 mL) gave a yellow solid (21 mg). ^{1}H NMR (500 MHz, DMSO-d_6) (Figure S39): δ 7.84 (half of AA′XX′ spin system, 2 H, ArH ortho to CO_2), 7.73 (half of AA′XX′ spin system, 2 H, ArH of tolyl), 7.43 (s, 2 H, ArH ortho to OCH_2), 7.40 (half of AA′XX′ spin system, 2 H, ArH meta to CO_2), 7.31 (half of AA′XX′ spin system, 2 H, ArH of tolyl), 7.11 (s, 2 H, isoxazole-H), 5.45 (s, 4 H, isoxazole-CH_2O), 2.34 (s, 6 H, CH_3).

PEPEP-PIZOF-15-m3(97%). See the general procedure for NOAC using PIFA: PEPEP-PIZOF-15 (90 mg, 0.31 mmol propargyl moieties), oxime **5c** (76 mg, 0.62 mmol), MeOH/H_2O 5/1 (16 mL). PIFA (400 mg, 0.93 mmol) was added in five portions within a period of 5 h and a sixth portion after 18 h. Reaction time after the addition of the last portion of PIFA: 49 h. Soxhlet extraction with EtOH (70 mL) gave a pale yellow solid (84 mg). ^{1}H NMR (500 MHz, DMSO-d_6) (Figure S40): δ 8.69 (d, ^3J = 4.5 Hz, 2 H, ArH of pyridine), 8.01 (d, ^3J = 7.8 Hz, 2 H, ArH of pyridine), 7.94 (t-like, ^3J = 7.8 Hz, 2 H, ArH of pyridine), 7.91 and 7.57 (AA′XX′ spin system, 4 H each, ArH ortho and meta to CO_2, respectively), 7.52−7.51 (m, 3

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H, ArH of pyridine and ArH ortho to OCH_2), 7.15 (s, 2 H, isoxazole-H), 5.51 (isoxazole-CH_2O).

PEPEP-PIZOF-15-m3(96%). See the general procedure for NOAC using chloramine T: PIZOF-15 (30 mg, 0.10 mmol propargyl moieties), oxime **5c** (78 mg, 0.64 mmol), EtOH/H_2O 2/1 (4 mL), chloramine T·3H_2O (176 mg, 0.62 mmol). The yellow solid was isolated by centrifugation. Reaction time after the addition of the last portion of PIFA: 50 h. Soxhlet extraction with EtOH gave a yellow solid (24 mg). For NMR data see PEPEP-PIZOF-15-m3 (97%).

PEPEP-PIZOF-15-m4(100%). See the general procedure for NOAC using PIFA: PEPEP-PIZOF-15 (27 mg, 0.09 mmol propargyl moieties), oxime **5d** (44 mg, 0.21 mmol), MeOH/H_2O 5/1 (4 mL). PIFA (152 mg, 0.32 mmol) was added in five portions within a period of 5 h and a sixth portion after 18 h. Reaction time after the addition of the last portion of PIFA: 48 h. The yellow solid was isolated by centrifugation. Soxhlet extraction with EtOH (70 mL) gave a yellow solid (25 mg). ^{1}H NMR (500 MHz, DMSO-d_6) (Figure S41): signals assigned to the 3,5/3,4-isomer δ 9.42 (s, 1 H, isoxazole-H of the 3,4-isoxazole), 7.86 and 7.41 (AA′XX′ spin system, 4 H each, ArH ortho and meta to CO_2, respectively), 7.34 and 7.26 (2 s, 1 H each, ArH ortho to OCH_2), 7.03 (s, 1 H, isoxazole-H of the 3,5-isoxazole), 5.48 (s, 2 H, isoxazole-CH_2O of the 3,5-isoxazole), 5.25 (s, 2 H, isoxazole-CH_2O of the 3,4-isoxazole); signals assigned to the 3,5/3,5-isomer δ 7.84 and 7.31 (AA′XX′ spin system, 4 H, ArH ortho and meta to CO_2, respectively), 7.40 (s, 2 H, ArH ortho to OCH_2), 7.06 (s, 1 H, isoxazole-H), 5.53 (s, 4 H, isoxazole-CH_2O).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b00126.

Syntheses of diacids **4** and of oximes **5**, PXRD diagrams, and NMR spectra (PDF)

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T.v.Z., L.B., T.P., and M.H. worked on the linker synthesis and developed the PSM. J.L. developed the synthesis of the PIZOFs and characterized the modified PIZOFs. All authors contributed to the interpretation of the data and to the preparation of the manuscript and have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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