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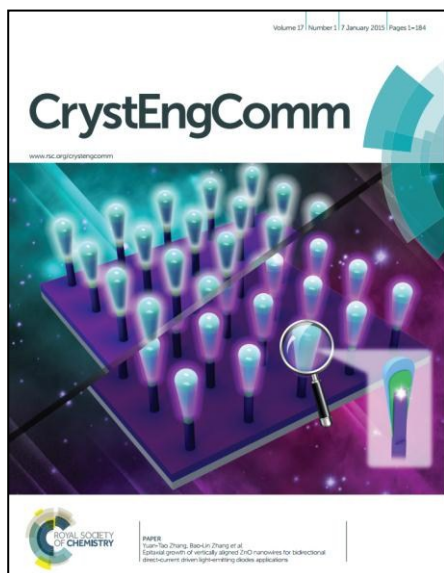
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COMMUNICATION

Charged functional group effects on metal-organic framework for selective organic dye adsorptions†

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A quaternary *N*-alkyl ammonium salt-containing zinc-based metal-organic framework (MOF) was synthesized and tested for selective organic dye adsorptions. Through covalent post-synthetic modification (PSM), the tertiary amine containing MOF was converted into a quaternary *N*-alkyl ammonium salt containing MOF *via* solid-state methylation conditions. The positively charged MOF was found to exclusively adsorb a negatively charged organic dye, while the positively charged organic dye was not adsorbed. This separation experiment revealed that functional group control is an important and critical factor for molecule separations using porous materials.

Metal-organic frameworks (MOFs) are porous hybrid materials constituted by metal clusters and organic linker molecules, which are also called porous coordination polymers (PCPs).[1] The coordination bond between the metal and ligand dictates the resulting structure of the frameworks. Due to the repeating empty space of MOFs known as pores, they demonstrate high porosity and low density. Gas adsorption applications have been widely studied by exploiting the pores in MOFs to capture CO_2, H_2, and etc.[2,3] Other applications, such as sensing, molecule shuttles, and size selective catalysis have also been studied by utilizing the porosity of MOFs.[4-6] Among the many advantages of MOFs, the tunability of the organic linker molecule is one of the most significant and useful features for optimizing these materials for various applications. A variety of organic functional groups can be introduced into the MOF pore (*e.g.,* halides, alcohols, amines, amides, azides, and etc) using a combination of pre-functionalization and post-synthetic modification (PSM).[7] The target functionality could

be introduced via the organic linker molecule first followed by MOF synthesis for incorporation of the functionalized ligand (*i.e.,* pre-functionalization). If the desired functional group is incompatible with direct incorporation into MOF structures (*e.g.,* contains a metal-binding group or is thermally unstable), PSM can be an efficient pathway to introduce the functionality.[7] Although PSM opens avenues to essentially unlimited organic functionalization within MOFs, it has predominately focused on introducing neutral functional groups. Herein, we report the synthesis and characterization of a new quaternary *N*-alkyl ammonium salt-containing MOF obtained through covalent post-synthetic manners followed by its porosity study and an interesting organic dye adsorption property with an unprecedented selectivity in MOFs.

A primary amine group (-NH_2) can be directly introduced into various MOFs since metal-amino group interactions are weaker than metal-carboxylic acid interactions and do not prevent MOF formation. Diverse amino group-containing MOFs including IRMOF-3 (IRMOF = Isoreticular MOF), DMOF-1-NH_2 (DMOF = dabco MOF), MIL-53-NH_2 (MIL = Materials from Institute of Lavoisier), UiO-66-NH_2 (UiO = University of Oslo) have been reported and widely studied for applications such as catalysis and molecule storage capabilities. An amine group can be successfully converted into an amide group via a PSM pathway in the solid-state and subsequently evaluated for applications of interest.[7]

Recently, the functional group tolerance of amines in MOFs has been explored and a unique C-N bond cleavage phenomenon was revealed during MOF synthesis.[8] The C-N bond in the tertiary amine group dissociated during the solvothermal synthesis; however, the C-N bond of the secondary amine group was intact after the MOF synthesis. Specifically, in the zinc-based IRMOF series, IRMOF-NMe_2 was not obtained as the C-N bond cleaved IRMOF-NHMe was synthesized instead. In the case of DMOF, DMOF-1-NMe_2 was successfully synthesized and fully characterized.

The quaternary *N*-alkyl ammonium-containing BDC ligand (BDC-$NMe_3^+X^-$, X = OTf) is synthesized by an additional methylation from the tertiary amine group-containing ligands

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and then used in MOF synthesis conditions (Scheme 1). However, the charged functional group containing BDC-NMe$_3^+$OTf$^-$ could not be directly incorporated to the MOF structure. Although the Yaghi group reported the existence of BDC-NH$_3^+$Cl$^-$ (33%) during the UiO-66-NH$_2$ synthesis,[9] BDC-NMe$_3^+$X$^-$ was not incorporated into UiO-66-NH$_2$ under standard synthetic conditions. After thorough screening of reaction conditions, it was found that a UiO-66 framework could be synthesized at 150 ^{o}C, with the addition of acetic acid modulators, as evidenced by the powder X-ray diffraction (PXRD) pattern (see ESI, Fig. S1†). However, the C-N bond cleavage occurred during UiO-66-NMe$_3^+$OTf$^-$ synthesis and the secondary amine group-containing BDC (BDC-NHMe) was confirmed by ^{1}H NMR spectrometry after acid digestion (Fig. S2†). Since the C-N bond cleavage phenomenon was nonexistent in DMOF synthesis, the quaternary *N*-alkyl ammonium-containing BDC ligand was first used under DMOF-1 synthetic conditions. Only amorphous and impure materials were obtained from a variety of screening conditions (Scheme 1).
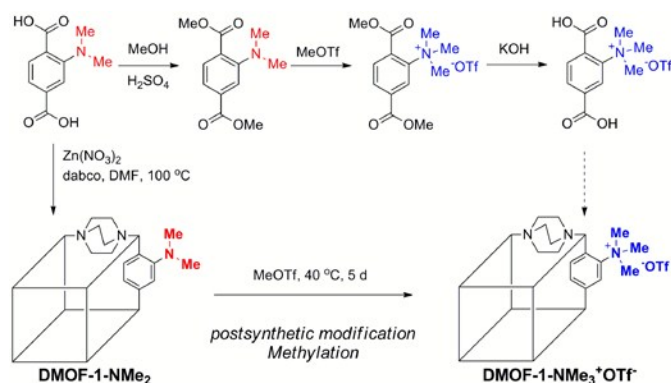
Scheme 1 Direct pre-functionalization versus the post-synthetic modification pathway for DMOF-1-NMe$_3^+$OTf$^-$ synthesis.

Fortuitously, the cationic functional group could be introduced into the MOF pores through *in situ* generation,[9] pre-functionalization, mixed ligand strategy, and post-synthetic approaches. In previous studies, the imidazolium salt (N-Heterocyclic carbene precursor) was incorporated into IRMOF framework *via* a pre-functionalization pathway (IRMOF-76).[10] On the other hand, the *N*-methyl pyridyl functionality was not successfully incorporated into the MOF pores like the present *N*-alkyl ammonium system, and a mixed ligand strategy (*i.e.*, MTV, multivariate strategy) was performed to obtain the cationic functional group-containing MOFs (20% of cationic ligand and 80% of neutral ligand).[11]

In the present system, post-synthetic methylation was also applied towards the synthesis of an ammonium group-containing MOF. From the tertiary amine group-containing DMOF-1-NMe$_2$, the additional methylation was performed as a solid-state transformation (Scheme 1). Wang and co-workers reported an early stage PSM methylation on IRMOF-3 in 2012.[12] In this study, IRMOF-3 (NH$_2$-functionalized MOF) was treated with iodomethane for 4 days, and the modification ratio was determined by element analysis. This material was applied to catalyze a CO$_2$ cycloaddition. However, the

properties of the material were only briefly characterized. In contrast, DMOF-1-NMe$_2$ was not converted to DMOF-1-NMe$_3^+$I$^-$ after treatment with an excess of iodomethane. The methylation by iodomethane was not observed even with an elevated reaction temperature (55 ^{o}C) and increased reaction time (1-5 days). The quaternary *N*-alkyl ammonium salt was successfully introduced into the MOF pore by treating DMOF-1-NMe$_2$ with methyl triflates (MeOTf, methyl trifluoromethanesulfonate) instead of iodomethane. Using triflates, materials could be obtained with 41% conversion to the quaternary *N*-alkyl ammonium group from DMOF-1-NMe$_2$. The conversion of tertiary amines to the quaternary *N*-alkyl ammonium salts was confirmed by ^{1}H NMR spectroscopy after an acid digestion and the ratio between BDC and dabco was also confirmed to be 2:1 (Fig. 1 and S3†). Indeed, Infrared (IR) and High Resolution Mass Spetra (HR-MS) also confirmed the quaternary *N*-alkyl ammonium salt after PSM (Fig. S4†). PXRD showed that the structure of DMOF-1 was retained after methylation (Fig. 1 and S5†) and TGA (Thermogravimetric analysis) showed similar degradation profiles for the fully methylated materials in comparison to the neutral starting MOF (Fig. S5†).

Although post-synthetic methylation provides less than 50% conversion, it has several advantages as a method of incorporating cationic functionalities in MOF chemistry. Even a 50% conversion is higher than the ratio acquired through a MTV strategy (20%), and by adjusting the reaction time and temperature, the conversion could be modulated as needed. Above all, post-synthetic methylation allows for a general approach that may be applicable to other frameworks with tertiary amine functionality in the pores.
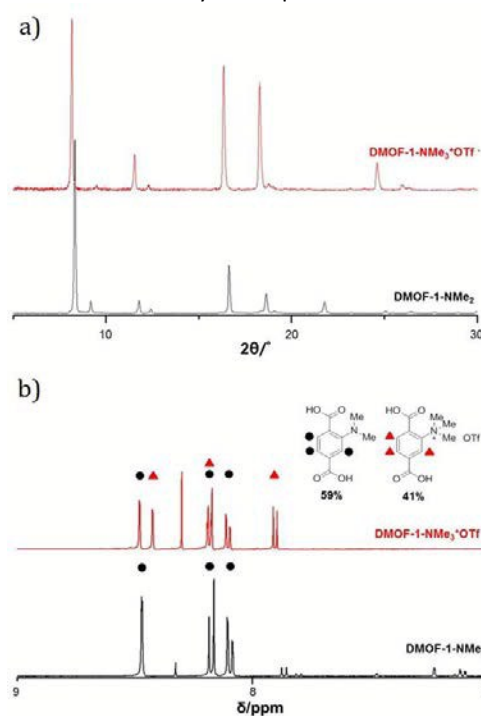

Fig. 1 PXRD pattern (top, a) and ^{1}H NMR spectra (bottom, b) of DMOF-1-NMe$_2$ (before methylation) and DMOF-1-NMe$_3^+$X$^-$ (after methylation) after acid digestion.

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The surface area of both frameworks (before and after methylation) was calculated by the N_2 adsorption isotherm measured at 77 K (Fig. S6†). The calculated BET (Brunauer-Emmett-Teller) surface area decreased with increasing ligand size and was calculated to be 1320 and 718 m^2/g for DMOF-1-NMe_2 and DMOF-1- $NMe_3^+OTf^-$, respectively. Total pore volume and pore size distribution for the frameworks were calculated using NLDFT (non-linear density function theory) method from the Ar adsorption isotherm at 87 K.[13,14] The total pore volume shows the same ligand size dependency as the surface area with values of 0.40 and 0.26 cm^3/g for DMOF-1-NMe_2 and DMOF-1-$NMe_3^+OTf^-$, respectively. Although DMOF-1-NMe_2 showed a narrower pore size distribution with an average pore size of 6.9 Å, DMOF-1-$NMe_3^+OTf^-$ gives a smaller average pore size (6.5 Å) and non-uniform pore size distribution, which is consistent with partial ligand functionalization of the DMOF-1- $NMe_3^+OTf^-$ (Fig. S7†).

MOF pores can be considered good candidates for molecular capturing vessels, and therefore organic dye adsorptions with the newly synthesized MOFs were studied.[15] For organic dye adsorptions, the charged frameworks demonstrated interesting selectivity. The negatively-charged frameworks displayed a strong interaction with positively-charged organic dyes such as 'Methylene Blue(MB)' and 'Crystal Violet(CV)'.[16,17] DMOF-1-$NMe_3^+OTf^-$ was synthesized from a well-known neutral framework with newly introduced charged functional groups by covalent bonding thus localizing the charge to the organic ligand. Therefore, we first looked at DMOF-1-$NMe_3^+OTf^-$ for the organic dye adsorption experiments. 'Rhodamine B(RB)' and 'MB' were selected as the positively-charged organic dyes, 'Acid Fuchsin calcium salt(AF)' for the negatively-charged dye, and 'Sudan II(SII)' was chosen as a neutral control dye for the adsorption studies (Table S1†). The adsorption of dye was determined by UV spectrometry in an acetonitrile solution. As expected, the neutral organic dye, 'SII' could be adsorbed in both DMOF-1-NH_2 and DMOF-1-$NMe_3^+OTf^-$.(Fig. 2a, S8 and S9†) On the other hand, the charged organic dyes showed preferred uptake in a single MOF. While DMOF-1-NH_2 showed significant adsorption of 'RB' in solution, DMOF-1-$NMe_3^+OTf^-$ showed no adsorption of 'RB' even after 10 hours (Fig. 2b, S10 and S11†). In other words, although 'RB' could be adsorbed in a DMOF framework, the charged functional groups may have interrupted the adsorption process of the dye molecules. Despite the presence of counter anion (OTf⁻) in the pores of DMOF-1-$NMe_3^+OTf^-$, this work clearly demonstrates the dye adsorption is dominantly affected by surface charge of the framework because the organic dye molecules must initially interact with the surface of the framework.[18,19] In addition, the size of the MOF pore and dye diameter should also be considered. Control experiments of DMOF-1-NMe_2 were performed as proof of size effects on dye uptake. DMOF-1-NMe_2 demonstrated adsorption of 'RB' into the MOF, suggesting that the charged functional group does interrupt the adsorption of charged molecules into MOF pore (Fig. 2b). The effect of contact time on the adsorption of organic dye graphs also displayed this selective adsorption phenomenon (Fig. S9 and S11†).
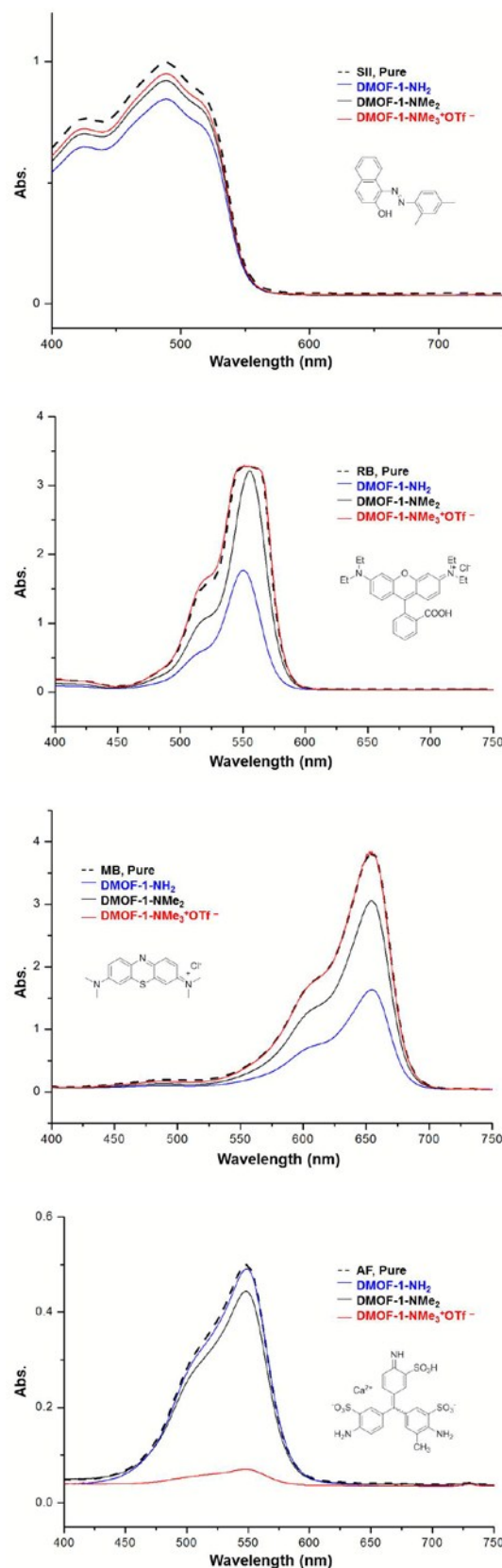

Fig. 2 Organic dye adsorption using DMOF-1-NH_2 (blue solid line), DMOF-1-NMe_2 (black solid line), and DMOF-1-$NMe_3^+OTf^-$ (red solid line) for a) Sudan II, b) Rhodamine B, c) Methylene Blue, and d) Acid Fuchsin calcium salt.

'MB', also a positively-charged organic dye, was also studied for selective adsorption. As expected, while DMOF-1-NH$_2$ and DMOF-1-NMe$_2$ showed the adsorption of 'MB', DMOF-1-NMe$_3^+$OTf$^-$ did not adsorb the positively-charged molecule at all (Fig. 2c, S12 and S13†). In contrast, the negatively-charged organic dye, 'AF', displayed diametrical phenomenon during the sorption experiment. Only small amounts of 'AF' were adsorbed by DMOF-1-NH$_2$ and DMOF-1-NMe$_2$ during the reaction period. However, DMOF-1-NMe$_3^+$OTf$^-$ showed a huge sorption capability towards this negatively-charged organic dye (Fig. 2d, S14 and S15†). Finally, the selective adsorption from a dye mixture solution was performed using DMOF-1-NMe$_3^+$OTf$^-$. The mixture of 'MB' and 'AF' (3:2 molar ratio; for similar absorbance ranges) was prepared and confirmed that there is no direct quenching effect between positive 'MB' and negative 'AF' in a solution. From the mixed dye solution, 'AF' was selectively removed by adsorption on DMOF-1-NMe$_3^+$OTf$^-$ after 10 hours. Therefore, we can conclude that the newly introduced charged-functional group within the MOF plays a key role as DMOF-1-NMe$_2$ showed no selectivity to the organic dye mixture in the control experiment (Fig. 3 and S16†).
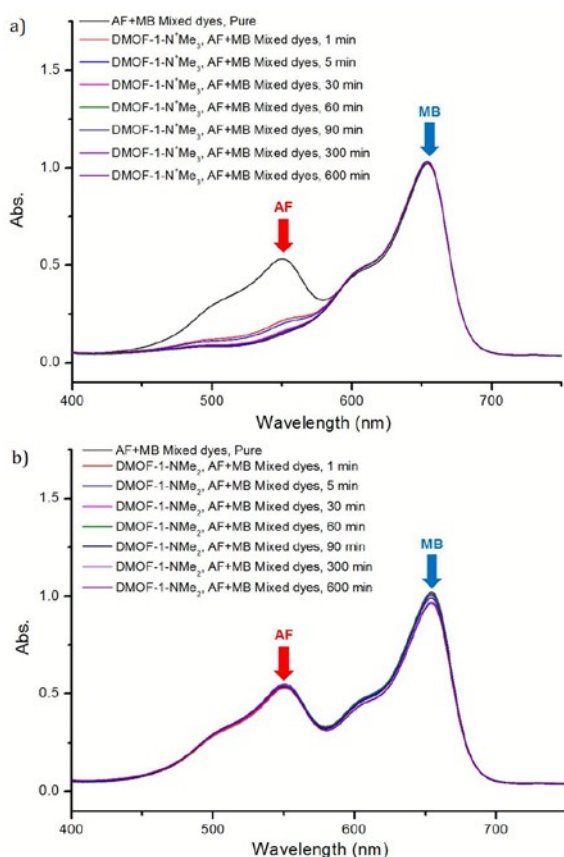
charged functional group-containing MOF confirmed that the material remains porous as well as has identical structures and similar thermal stability to the original DMOF-1-NH$_2$ and DMOF-1-NMe$_2$. Additionally, selective molecular organic dye adsorption was investigated using the charged-functional group-containing DMOF-1-NMe$_3^+$OTf$^-$. While the negatively-charged organic dye molecules were rapidly and strongly adsorbed into the MOF pores, the adsorptions of the positively-charged organic dye molecules were not observed. Finally, the separation of a mixed organic dye solution was achieved by utilizing the charged functional group-containing MOFs.

Fig. 3 Organic dye mixture (MB and AF) separation experiments using DMOF-1-NMe$_3^+$OTf$^-$ (top, a)), and DMOF-1-NMe$_2$ (bottom, b)).
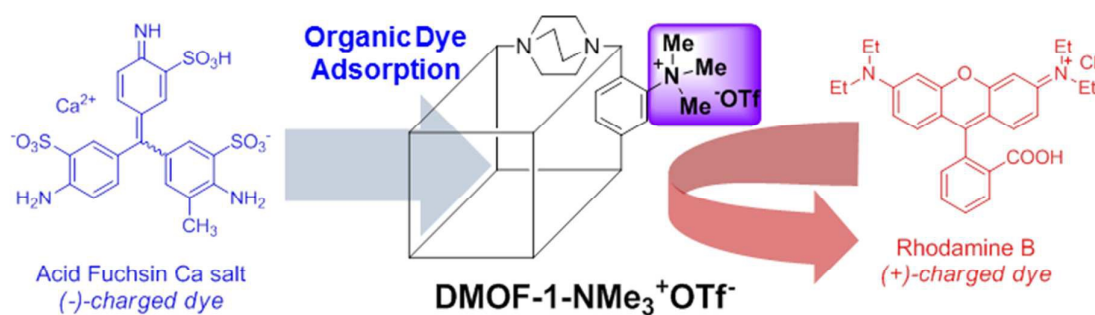
In conclusion, the quaternary *N*-alkyl ammonium salt functionality was successfully introduced into MOF pores through a post-synthetic strategy. Characterization of the new

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