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Immobilization of Volatile and Corrosive Iodine Monochloride (ICl) and I_2 Reagents in a Stable Metal–Organic Framework

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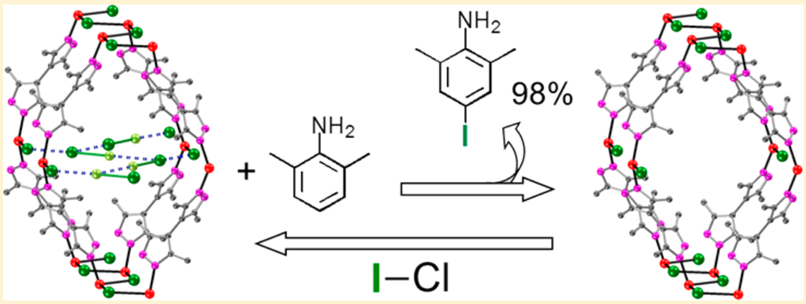
Supporting Information



ABSTRACT: The major discovery here is a robust and water-stable metal–organic framework (MOF) material capable of reversible binding of the volatile and reactive molecules of ICl and I_2. The immobilization of I_2 and ICl, as well as their controllable release thus achieved, is to facilitate the wide-ranging applications of these volatile species as catalysts and reagents in chemical and industrial processes. The framework material TMBP·CuI (hereafter TCuI) can be conveniently prepared in quantitative yields by heating CuI and the organic linker TMBP (3,3′,5,5′-tetramethyl-4,4′-bipyrazol) in acetonitrile. The microporous three-dimensional net of TCuI features CuI chains that contribute to efficient and reversible binding of ICl and I_2 molecules, to result in the stoichiometrically well-defined adducts of TCuI·ICl and TCuI·I_2, respectively. Moreover, the confinement of a volatile compound like ICl within the MOF medium provides unique opportunities to enhance its reactivity and selectivity as a chemical reagent, as is exemplified by the iodination reactions examined herein. With this exemplary study, we intend to stimulate interest in further exploring MOFs and other porous media (e.g., porous polymers) for entrapping ICl and other volatile reagents (e.g., Br_2, SCl_2, S_2Cl_2, and $SOCl_2$) and for potentially novel reactivity associated with the porous medium.

INTRODUCTION

Iodine monochloride (ICl) is a widely used reagent in many chemical and industrial processes (e.g., for iodination and iodine value determination).[1] This reagent, however, is highly volatile and corrosive (e.g., melting point = 27 °C, boiling point = 97 °C, and readily reacting with water), calling for stringent safety measures in storage and handling. A solid-state medium for immobilizing ICl would therefore offer significant operational convenience. Of particular interest would be a structurally regular support capable of stoichiometrically well-defined uptake and easily controllable release, as the resultant ICl/support adduct would then allow one to employ the ICl reagent with convenient control of the rate and quantity of delivery. With this in mind, we look to metal–organic frameworks (MOFs), a versatile class of porous solids,[2] in screening solid support systems for effectively immobilizing ICl and other volatile reagents.

In general, MOF solids are routinely examined in gas adsorption/separation studies (e.g., N_2, H_2, and CO_2),[2p,3] while the uptake of metal species (e.g., by means of thiol/thioether-laced MOFs) has attracted attention of late.[4] More relevant to the present study is the increasing number of MOFs reported to possess various iodine (I_2) uptake properties,[5] including irreversible and reversible trapping and even chemisorptions.[6] On the other hand, no studies on ICl uptake by MOF materials have been reported. This contrast becomes even more worthy of note in light of the more volatile and reactive nature of ICl (relative to I_2) as well as the very broad use of ICl in synthetic chemistry applications, for example, as an iodination reagent.[7]

Filling in this gap, we here report a microporous MOF material (denoted as TCuI) capable of reversible binding of the volatile and reactive molecules of ICl and I_2. The crystal

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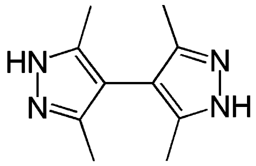
structure of TCuI features distinct CuI moieties (with the organic linker being 3,3′,5,5′-tetramethyl-4,4′-bipyrazol (TMBP),[8] Chart 1) that effectively interact with the ICl and I_2 molecules to form compositionally well-defined adduct products. The practical impacts are also highlighted by the convenient procedure of preparation—simply by heating CuI and TMBP in acetonitrile for a few hours quantitatively yields the crystalline solids of TMBP·CuI (henceforth shortened as TCuI)—no side products are formed, and the atom efficiency is nearly 100%. The open framework of TCuI as formed contains no solvent guests, and therefore no activation step is needed to generate the permanent microporous property. Moreover, the solid sample of TCuI is stable in air and can be immersed in water for days without degrading or decomposition. As will be also described below, the immobilization within the MOF medium can also offer control over the reactivity and selectivity of this commonly used iodinating reagent.

Chart 1. TMBP



EXPERIMENTAL SECTION

General Procedure. Starting materials, reagents, and solvents were purchased from commercial sources (e.g., J&K, Aladdin, and Acros) and were used without further purification. Elemental analysis was performed with a Vario Micro CUBE CHN elemental analyzer. Fourier transform infrared (FT-IR) spectra were obtained using a Nicolet Avatar 360 FT-IR spectrophotometer. Solution ^1H and ^{13}C NMR spectra were recorded on a 400 MHz Bruker superconducting magnet high-field NMR spectrometer at room temperature (RT), with tetramethylsilane (TMS) as the internal standard. Thermogravimetric analyses (TGA) were carried out in a nitrogen stream using PerkinElmer Thermal analysis equipment (STA 6000) with a heating rate of 10 °C/min.

The porosity and surface area analysis was performed using a Quantachrome Autosorb iQ gas sorption analyzer. The sample was outgassed at 0.03 Torr with a 5 °C/min ramp to 120 °C and held at 120 °C for 20 h. The sample was then held at vacuum until the analysis was run. Pore analysis was performed using CO_2 at 273 K (pressure range from 8×10^{-3} to 780 mmHg). CO_2 adsorption/desorption isotherms at 273 K were performed on a Quantachrome Autosorb 1MP instrument. Initial data analysis was done using the AS1Win and QuadraWin 5.05 software (both of Quantachrome instruments). High-purity gases were used throughout the analysis. Powder X-ray diffraction data for the TCuI samples were collected in the reflection mode at RT on an Inel Equinox 1000 X-ray diffractometer (Inel, France) equipped with CPS 180 detector using monochromated Cu Kα (λ = 1.5418 Å) radiation. The X-ray tube operated at a voltage of 30 kV and a current of 30 mA.

Single-crystal X-ray diffraction data for TCuI·I_2 were collected on an Agilent Technologies Gemini A System (Mo Kα, λ = 0.710 73 Å) at 298 K. The data were processed using CrysAlisPro.1 and corrected and scaled using the SCALE3 ABSPACK scaling algorithm.[9] Data collection for TCuI was performed on a Bruker Smart Apex CCD diffractometer (Mo Kα radiation, λ = 0.710 73 Å) at T = 298 K using SMART, with the data integrated using SAINT and corrected for absorption and other systematic errors using SADABS.[10] Diffraction data for TCuI·ICl were collected on a Bruker Apex II CCD diffractometer at 100 K using monochromatic Mo Kα radiation with the ω scan technique. Its data were collected and its unit cell determined, and the data were integrated and corrected for absorption and other systematic errors using the Apex2 suite of programs.[11]

The space group of TCuI was assigned using XPREP, and the structure was solved by direct methods using the SHELXS program.[12] The structures of TCuI·I_2 and TCuI·ICl were solved by isomorphous replacement from that of TCuI. All structures were refined by full matrix least-squares against F^2 with all reflections using ShelXL2013.[13] H atoms attached to carbon and nitrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with carbon−hydrogen bond distances of 0.96 Å for CH_3 and 0.86 Å for N−H moieties, respectively, for the RT data sets of TCuI and TCuI·I_2 (0.98 and 0.88 Å for the 100 K data set of TCuI·ICl). Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. The U_{iso}(H) values were set to a multiple of U_{eq}(C/N) with 1.5 for CH_3 and 1.2 for N−H units, respectively. For TCuI·ICl, the ICl adduct was found to be disordered, with near equal probability for I and Cl to be found at the two possible sites. Positions of iodine and chlorine were indistinguishable, and thus I and Cl atom positions and thermal displacement parameters were constrained to be the same for both sites. Subject to these conditions, the I···I−Cl versus I···Cl−I ratio refined to 0.56(1) and 0.44(1).

Preparation of TCuI Single Crystals. A mixture of TMBP (0.019 g, 0.10 mmol), CuI (0.019 g, 0.10 mmol), and CH_3CN (8.0 mL) was stirred in a beaker for about 10 min, and then it was transferred to a 15 mL Teflon container and sealed in an autoclave. The autoclave was heated in an oven at 140 °C for 48 h and then cooled to RT at a rate of 10 °C/h. The light yellow, blocklike crystals (23 mg, 60% yield) were collected by suction filtration, washed with acetonitrile, and dried in air. Chemical analysis of the product $C_{10}H_{14}N_4CuI$ yielded the following: calcd [C (31.55%), H (3.71%), N (14.72%)]; found [C (31.65%), H (3.90%), N (14.65%)]. FT-IR (KBr pellet, $\bar{\nu}$/cm^{-1}): 3309(s), 2920(m), 1671(m), 1632(m), 1459(w), 1419(m), 1385(w), 1281(w), 1028(s), 660(m), 560(m).

Preparation of TCuI Crystalline Powders. Crystalline powder of TCuI can be conveniently prepared by reacting TMBP (0.190 g, 1.0 mmol) and CuI (0.210 g, 1.1 mmol) in refluxing acetonitrile (reagent grade, 25 mL) for about 2 h. The resultant light yellow microcrystalline product (0.365 g, 96% yield as per TMBP) was collected by suction filtration, washed by acetonitrile extensively, and dried in air. Chemical analysis of the product $C_{10}H_{14}N_4CuI$ yielded the following: calcd [C (31.55%), H (3.71%), N (14.72%)]; found [C (31.59%), H (3.85%), N (14.75%)]. X-ray powder diffraction of the bulk sample indicated a pure phase consistent with the single-crystal structure.

Loading of ICl and I_2 into TCuI Powders and Crystals. A small plastic vial containing a TCuI powder sample (100 mg; made from directly reacting TMBP and CuI in refluxing CH_3CN) was placed into a larger vial containing crystallites of I_2 (500 mg), and the larger vial was then capped for I_2 vapor diffusion to occur over a period of 3 d. The resultant solid sample was copiously washed with $CHCl_3$ (to remove I_2 on the exterior) until the filtrate became colorless and then left in air to dry. The same procedure was applied in preparing the X-ray single crystals of TCuI·I_2. Chemical analysis of the TCuI·I_2 samples thus obtained, $C_{10}H_{16}N_4OCuI_3$, corresponding to TMBP·CuI·I_2, yielded the following: calcd [C (18.93%), H (2.22%), N (8.83%)]; found [C (18.69%), H (2.55%), N (8.45%)]. Similar procedures were followed for loading ICl, but this can be completed much faster (e.g., within 1 h). Anhydrous chloroform was also used to wash the powder and single-crystal samples of TCuI·ICl until the filtrate became colorless. The washed samples of TCuI·ICl were evacuated by an oil pump at RT for 30 min to further remove the residual solvent. Chemical analysis of the TCuI·ICl sample $C_{10}H_{14}ClN_4CuI_2$ yielded the following: calcd [C (22.12%), H (2.60%), N (10.32%)]; found [C (21.89%), H (2.59%), N (10.15%)].

Iodination of 2,6-Dimethylaniline (2,6-Xylidine, S1). (1) By free-floating ICl: to a solution of ICl (35 mg, 0.22 mmol) in CH_3CN (2.0 mL, predried by molecular sieves) was added a solution of 2,6-xylidine (24 mg, 0.20 mmol) in CH_3CN (2.0 mL). After being stirred at RT for 10 h, the reaction mixture was washed with a dilute $Na_2S_2O_3$ solution, extracted by dichloromethane (DCM), dried over anhydrous

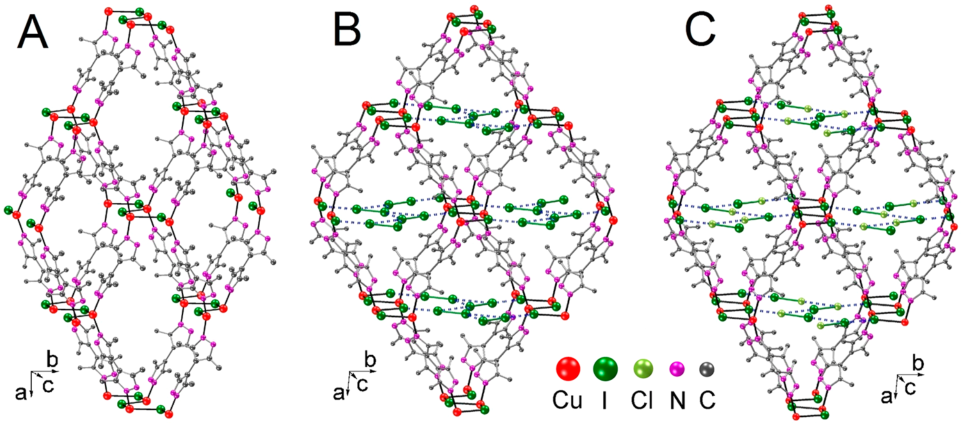


Figure 1. X-ray single crystal structures of (a) TCuI; (b) TCuI·I_2; (c) TCuI·ICl. The dashed lines denote the secondary interactions. The disordering of the ICl molecules in (c) is omitted.

Na_2SO_4, and filtered. The filtrate was then evacuated on a rotary evaporator, and the resultant crude product was purified via a short silica gel plug (with 1:2 hexane/DCM as the eluent) to provide a brownish oil of **P1** (48 mg, 98% yield based on **S1**). (2) By the TCuI·ICl solid: a TCuI·ICl powder sample (163 mg, 0.30 mmol), **S1** (24 mg, 0.20 mmol), and anhydrous CH_3CN (4 mL) were stirred in a capped glass vial at RT for 10 h, and the same workup as above was applied (48 mg, 96%). The product **P1** is known,[14] and its identity was verified by ^1H NMR (400 MHz, CD_2Cl_2): δ 7.22 (s, 2H, CHAr), 2.11 (s, 6H, CH_3); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 142.81, 136.28, 124.20, 78.55, 16.98.

Iodocyclization of 1-Hydroxyl-3-butyne (S2). (1) By free-floating ICl: a mixture of anhydrous $CHCl_3$ (2 mL), **S2** (14 mg, 0.20 mmol), and a CH_3CN solution (2.0 mL) of ICl (35 mg, 0.22 mmol) in a capped glass vial was stirred first in an ice bath for 10 h and then at 50 °C for another 10 h. After being cooled to RT, a similar workup as above was applied (with 1:2 hexane/DCM remaining the eluent) to provide the product **P2** as a colorless oil (17 mg, 44% yield based on **S2**). (2) By TCuI·ICl: the same procedure was applied to a mixture of anhydrous CH_3CN (2.0 mL), $CHCl_3$ (2.0 mL), **S2** (14 mg, 0.20 mmol), and TCuI·ICl (163 mg, 0.30 mmol) to give **P2** (31 mg, 80%). The product **P2** is known,[15] and its identity was verified by ^1H NMR (400 MHz, CD_2Cl_2): δ 7.01 (s, 1H, CH), 3.77−3.80 (t, 2H, CH_2), 2.76−2.79 (t, 2H, CH_2).

Iodocyclization of 2-Ethynylbenzyl Alcohol (S3). (1) By free-floating ICl: a mixture of anhydrous $CHCl_3$ (2.0 mL), **S3** (28 mg, 0.20 mmol), and a CH_3CN solution (2.0 mL) of ICl (38 mg, 0.24 mmol) in a capped glass vial was stirred in an ice bath for 24 h. A similar workup as above was applied (with 1:2 hexane/DCM as the eluent) to provide the product **P3** as a crystalline brown solid (11 mg, 21% yield based on **S3**). (2) By TCuI·ICl: the same procedure was applied to a mixture of anhydrous CH_3CN (2.0 mL), $CHCl_3$ (2.0 mL), **S3** (28 mg, 0.20 mmol), and TCuI·ICl (163 mg, 0.30 mmol) to give **P3** (33 mg, 63%). The product **P3** is known,[15] and its identity was verified by ^1H NMR (400 MHz, $CDCl_3$): δ 7.54−7.55 (d, 1H, CHAr), 7.41−7.43 (t, 1H, CHAr), 7.39−7.41 (t, 1H, CHAr), 7.32 (s, 1H, CH), 7.12−7.14 (d, 1H, CHAr), 4.60−4.71 (q, 2H, CH_2).

■ RESULTS AND DISCUSSIONS

Structural Studies. The physical origin of I_2 and ICl binding is revealed from the X-ray single-crystal structures before and after the loading of I_2/ICl (i.e., those of TCuI, TCuI·I_2, and TCuI·ICl, respectively; see Experimental Section for the preparative procedures). The crystal structure of TCuI adopts the acentric space group of *Ima*2 (being isostructural to the reported TMBP·CuBr compound[16]), featuring chains of CuI in the shape of a trapezoid waveform (bond angles: ICuI, 110.78°; CuICu, 109.44°). The CuI chains are integrated into a three-dimensional open framework (Figure 1a) by the TMBP molecules as 2-connected (bent) linkers, with the Cu(I) center being coordinated by two crystallographically equivalent TMBP units via Cu−N bonds (1.999 Å). The other N atom on the pyrazole unit is not bonded to Cu(I) (i.e., it remains in the N−H form), and the TMBP molecule features a dihedral angle of 78.30° between the pyrazole units.

Empty channels are found in the structure parallel to the CuI chains (along the *c* axis), and the iodine atoms are open and accessible from the void domain. The channels are narrow, with the diameter at the "bottleneck" section measured to be about 5.0 Å, and the solvent-accessible region calculated (by PLATON) to be 23.1% of the crystal volume. Brunauer−Emmett−Teller (BET) measurement using N_2 at 77 K did not reveal significant sorption behaviors, presumably due to the small pore size and the lack of lattice dynamics at this low temperature. However, BET measurement using CO_2 at 273 K readily reveals the microporous character of the host framework (Figure 2 and Supporting Information, Figure S1). Specifically, a surface area of 520 m^2/g was determined, with a pore volume of 0.123 cm^3 g^{-1} (i.e., 19.3% of the cell volume). The pore diameter analysis is found to be 5.2 Å, being consistent with the single-crystal structure. The significant sorption for CO_2 uptake is possibly assisted by the N−H unit that might act as a hydrogen bond donor to the CO_2 guest.

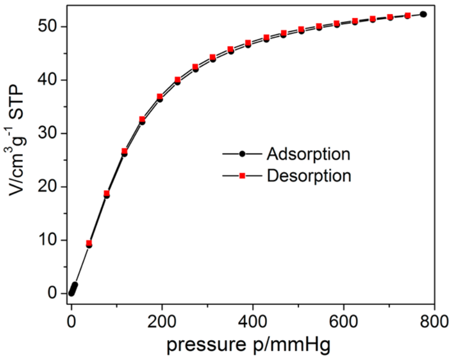


Figure 2. A CO_2 sorption isotherm at 273 K for a TCuI sample.

In the I_2-loaded structure (TCuI·I_2), the I_2 guest is well-ordered, with the host grid little changed from the parent structure of TCuI (Figure 1b). Specifically, one end of the I_2 molecule is in close, end-on contact with an I atom of the framework, with an I—I distance of 3.224 Å (well under the van der Waals distance of 3.8 Å) and an I—I—I angle of 174.6°. The nearly linear I—I—I unit thus observed is reminiscent of a highly asymmetrical I_3^- ion.[17] The significantly longer I—I contact of 3.224 Å (e.g., the corresponding I—I distances in most I_3^- ions are under 3.0 Å),[17] however, indicates that the charge transfer onto the I_2 molecule is likely to be weak. The other terminal iodine of the I_2 guest extends into the channel center and forms side-on contacts with the neighboring I_2 guest at longer I—I distances of 3.843 Å, generating a distinct herringbone pattern for the two rows of parallel I_2 guests planted along the channel.

The ICl-loaded structure (TCuI·ICl) was also solved by single-crystal X-ray diffraction (Figure 1c), and it was found to be similar to that of TCuI·I_2. Herein, two centers of substantial electron densities (2.728 Å apart) were located in the void region, one of which was 3.156 Å away from the I atom in the framework. Such distances closely resemble the corresponding values in the I—I···I motif (2.746 and 3.224 Å) of the above TCuI·I_2. Electron densities at the two positions are nearly identical, with the ICl guests in TCuI·ICl found to be disordered, and the apparent interatomic distances associated with ICl are dominated by the heavy I atom (the Cl atom is largely obscured in this regard; e.g., a typical I—Cl covalent bond is 2.45 Å). In other words, the X-ray data set does not reveal distinct heavy atom positions for atomistically resolving the two possible motifs of I—Cl···I and Cl—I···I. As a result, the coordinates (and anisotropic displacement parameters, see Supporting Information) of the disordered I and Cl atoms occupying close-by positions were constrained to be identical; with the sum of the two motifs constrained to unity, the occupancy rates for Cl—I···I and I—Cl···I refines to 0.56(1) and 0.44(1), respectively. The Raman spectrum of the TCuI solid features distinct peaks below 200 cm^{-1} (e.g., 162 and 175 cm^{-1}, Supporting Information, Figure S2a) that are associated with the Cu—I vibrations.[18] Such peaks become greatly intensified and dominate the Raman spectra of the darkly colored solids of TCuI·I_2 and TCuI·ICl (Supporting Information, Figure S2), apparently because the dark solids strongly absorb the incident laser (632.8 nm) and generate distinct resonance Raman scattering as a result. The present results suggest the CuI components as a key chromophore involved in the electronic transition for the resonance Raman process, whereas the Raman peaks from the I_2 (cf. 180 cm^{-1} in I_2 solid)[17] and ICl (cf. 376 cm^{-1} in CCl_4)[19] guests remain mostly obscured because of the dominant/overlapping peaks from the CuI moiety. Further study to pinpoint the Raman peaks of the I_2 and guests (e.g., using incident lasers with tunable wavelengths) would shed more light on the host—guest interaction in the solids of TCuI·I_2 and TCuI·ICl.

Uptake of I_2 and ICl Vapor. The robust binding of the I_2 and ICl is reflected in the TGA plots (Figure 3), in which no distinct weight loss was observed for both adducts of TCuI·I_2 and TCuI·ICl under 100 °C. Also, when wet KI starch test paper is placed with the TCuI·I_2 or TCuI·ICl solids in the same chamber, no color change was observed after an extended period of time (e.g., 7.0 h, see Supporting Information, Figures S3 and S4), indicating minimal emission of the I_2 and ICl species at RT. Faster kinetics of I_2 uptake can therefore be achieved under heated conditions. For example, at 77 °C (or up to 95 °C), under ambient pressure (I_2 vapor pressure being 0.014 atm at 77 °C), the TCuI powder adsorbs I_2 and fully reaches the stoichiometric adsorption capacity (as in TCuI·I_2) within half an hour, as indicated by gravimetric methods (e.g., the TGA plot as shown in Figure 3b) and the intensity profile in the PXRD pattern (Figure 4c). The effective uptake of I_2 suggests that the TCuI solid can be used for iodine capturing under relatively mild conditions (e.g., protective masks for workers handling leaks/splashes of iodine agents). For the more demanding applications, for example, capturing radioactive iodine species as nuclear waste under fuel reprocessing conditions (typically at 150 °C, with acids present),[6a,20]the applicability of this material remains unclear.

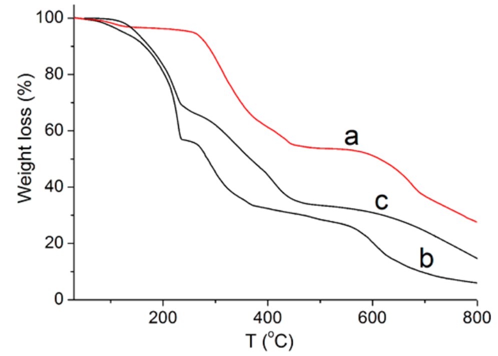


Figure 3. TGA plots of (a) an as-made powder sample of TCuI; (b) TCuI·I_2 (prepared by vapor diffusion at 77 °C); (c) TCuI·ICl (by vapor diffusion at RT).

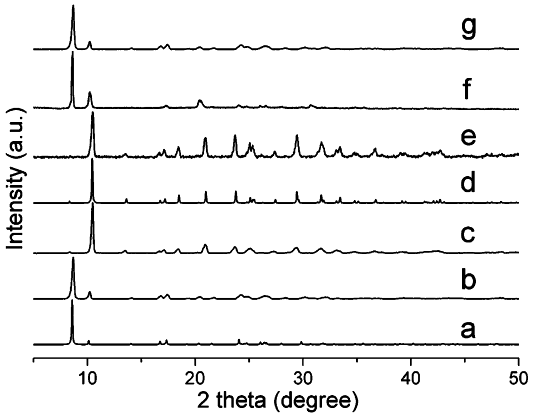


Figure 4. PXRD patterns of TCuI and TCuI·I_2. (a) Calculated from the single-crystal structure of TCuI; (b) as-made bulk powder sample of TCuI; (c) sample from (b) after treatment in I_2 vapor at 77 °C for 0.5 h; (d) calculated from the single-crystal structure of TCuI·I_2; (e) sample from (b) after treatment in an I_2—KI aqueous solution; (f) sample from (e) (or c) evacuated by an oil pump at 120 °C for 2 h; (g) sample from (e) (or c) washed with CH_3CN.

At RT, I_2 upload is slower (e.g., entailing 3 d in saturated I_2 vapor), apparently due to the lower I_2 vapor pressure and the weaker framework dynamics of the TCuI host, as such dynamics generally serves to facilitate the entry of the I_2 guests into the micropores of the TCuI host. The uptake of ICl molecules, by comparison, is more facile: even at RT, the stoichiometric adduct of TCuI·ICl is quickly formed within half an hour (see Figure 3c and PXRD pattern Figure 5b). Notice also that the thermal stability of TCuI·ICl compares well with that of TCuI·I_2 (e.g., no ICl emission under 100 °C; see TGA plot in Figure 3), indicating effective interaction between the polar ICl guests and the TCuI host framework.

Uptake from Water and Organic Solvents. Aside from the vapor phase, water also presents an interesting medium in

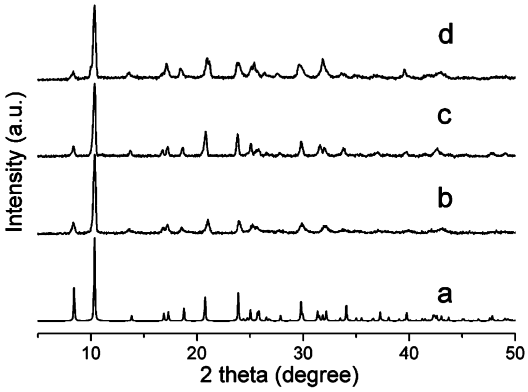


Figure 5. PXRD patterns of TCuI·ICl. (a) Calculated from the single-crystal structure of TCuI·ICl. (b) A bulk powder sample of TCuI after treatment in ICl vapor at RT for 0.5 h. (c) Sample from (b) after standing in open air for 24 h. (d) A TCuI·ICl sample regenerated after three cycles of iodination of 2,6-xylidine.

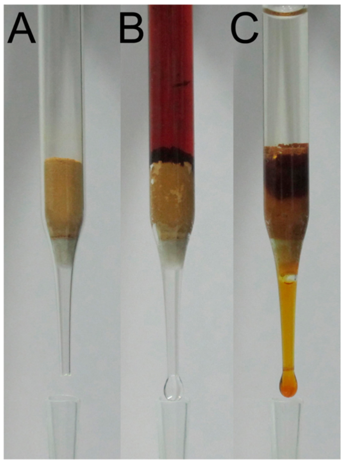


Figure 6. Photographs of a Pasteur pipet column chromatography. (a) A pipet packed with as-made powder of TCuI (with a cotton plug at the base). (b) A 1% Lugol (I_2−KI) solution being gravity-flown through the pipet. (c) The pipet from step (b) being eluted by CH_3CN to regenerate the TCuI.

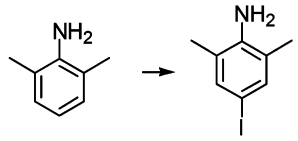
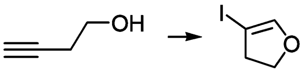
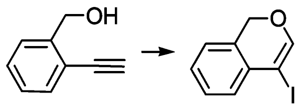
which to test the uptake of I_2 (ICl decomposes in water), because of the relevance to the removal of I_2 contaminants (e.g., the radioactive ^{131}I) that are difficult to remove by ion exchange or reverse osmosis technologies. Also, I_2 uptake from water has been rarely examined for MOF systems,[5h,m] presumably in part due to the water sensitivity so often observed thereof. The TCuI compound therefore stands out as a robust MOF system that efficiently removes I_2 from aqueous solutions. For example, when an I_2−KI solution (2.0 mL, containing 20 mg, 0.079 mmol of I_2 and 40 mg of KI) was shaken with a powder sample of TCuI (24 mg, 0.063 mmol of TCuI unit, 80% of the moles of I_2 in the solution), the TCuI powder can be fully loaded within 1 h, indicating fast kinetics of the uptake process (see the TGA plot in Supporting Information, Figure S5). When an excess of TCuI (36 mg, equivalent to 0.095 mmol of TCuI unit) was shaken with the same I_2−KI solution (also 2.0 mL, like above), the deep brown color of the solution quickly recedes (see Supporting Information, Figure S6 for the photographs) and becomes colorless within 1 h, with spectroscopic measurement of the solutions indicating the uptake of over 99.9% of the I_2 species from the aqueous phase (see Supporting Information, Figures S7 and S8).

Similarly, fast adsorption kinetics are also observed for both the I_2 and ICl molecules in nonpolar solvents (e.g., cyclohexane and chloroform); in general, the adsorption sites can be largely saturated within several hours, and the bulk of the I_2 species can be removed from the solution even within half an hour when a slight excess of TCuI is used (see Supporting Information, Figure S9 for the photographs showing the effective removal of the I_2 from cyclohexane). On the other hand, when the loaded samples of TCuI·I_2 or TCuI·ICl adduct were immersed in hexane or chloroform, no observable color developed in the solution, and no I_2 or ICl was detected by KI starch test paper, pointing to the stability of the adducts under these conditions.

Release of the ICl and I_2 guests, however, can be readily enabled by polar solvents like acetonitrile, methanol, or ethanol, as these solvents instantaneously take on the distinct colors of molecular iodine (or ICl) upon contact with the loaded powder samples of the TCuI·I_2 (or TCuI·ICl). A more visual demonstration is seen in the simple column chromatography experiments in Figure 6. A dark brown Lugol solution (I_2 concentration = 1%) becomes colorless upon passing through the TCuI-loaded pipet, indicating the fast removal of I_2 from the water phase; simultaneously, the top of the TCuI plug starts to exhibit a dark brown band that steadily widens downward, with a sharp boundary with the less-colored, lower portion of TCuI absorbent being maintained in the process. Moreover, as shown in Figure 6c, the molecular iodine thus immobilized in the TCuI phase can be readily eluted by a polar solvent like acetonitrile: the I_2-loaded, dark brown band steadily moves downward, and the eluent takes on the brown-red color indicative of the I_2 molecule. The loading−eluting cycles can be repeated multiple times without compromising the crystal structure of the TCuI host.

TCuI·ICl as a Solid Iodinating Agent. The controlled release of ICl thus enabled by polar solvents (e.g., acetonitrile) provides the opportunity to explore the solid adduct TCuI·ICl as a potentially safe and convenient iodinating reagent. We start with the iodination of 2,6-xylidine (**S1**, Table 1),[21] which is a conversion that is normally effected by the reagent ICl dissolved in CH_3CN. The reaction is near-quantitative and

Table 1. Reagents (ICl and TCuI·ICl) and the Corresponding Yields for the Three Reactions

	ICl	TCuI·ICl
 **S1** **P1**	98%	98%
 **S2** **P2**	44%	80%
 **S3** **P3**	21%	63%

usually completes overnight (e.g., 10 h) at RT. Replacing the volatile ICl with the TCuI·ICl solid as the iodinating agent, and using similar reaction conditions, we achieved the product **P1** (see Table 1) with a similar yield and purity (see Supporting Information, Figure S10a for the image of the TLC plate for the two protocols). The remaining TCuI host solid can be conveniently filtered off and reloaded with ICl (e.g., in ICl vapor) for further rounds of reactions. The TCuI framework remains crystalline and upstanding after the three cycles that we tested (see the PXRD pattern of Figure 5d).

Additional tests using iodocyclization[22] of alkynyl alcohols serve to highlight further advantages offered by the solid agent TCuI·ICl. For example, in reacting 3-butyn-1-ol (or 1-hydroxyl-3-butyne, **S2**, Table 1) with ICl (in 1:1 $CH_3CN/CHCl_3$), side reactions were severe, and the target molecule **P2** was isolated in a relatively poor yield of 44%. By comparison, with TCuI·ICl used as the iodinating agent and under similar reaction conditions (e.g., in 1:1 $CH_3CN/CHCl_3$, with CH_3CN promoting the release of the ICl guest), the isolated yield of the desired product **P2** jumps to 80%, almost doubling that of the reaction using free ICl as the reagent (see Supporting Information, Figure S10b for the TLC plate for a comparison of the two protocols).

Similarly, in the iodocyclization of 2-ethynylbenzyl alcohol (**S3**, Table 1), ICl gives a low yield of 21% for the target molecule **P3**, with substantial side reactions presumably caused by the very high reactivity of the free-floating ICl molecules. With TCuI·ICl, under similar conditions (e.g., in 1:1 $CH_3CN/CHCl_3$ as the solvent), the yield of **P3** was raised to 63%, three times as high as that from free-floating ICl (see Supporting Information, Figure S10c, where the TLC plate shows a comparison of the two protocols). In both cyclization reactions, the structural integrity of the TCuI solid remains intact, and it can be readily recycled for further rounds of reactions. In general, controlled release of ICl from the immobilizing support serves to maintain the ICl species in rather low concentrations in the reaction medium, thus mitigating the interaction between ICl and the substrate and potentially allowing for better selectivity. In cases where ICl remains associated with the porous support throughout the reaction (i.e., the reaction proceeds in the pores), the confinement effect from the porous medium is likely to be operative. Further studies to examine the effects of the immobilization on reactivity will be especially instructive.

■ CONCLUSIONS

In conclusion, we demonstrated TCuI to be a stable and easy-to-make MOF capable of effective and reversible uptake of the volatile reagents of I_2 and ICl. The practical importance of such properties is obvious, because ICl and I_2 are reagents of wide use in both chemistry and biology, and their immobilization by the porous solid TCuI is to provide significant advantages in storage and applications. Moreover, the immobilization and controlled release of ICl allow for the tempering of its reactivity and selectivity as a chemical reagent, as is exemplified by the improved results observed in the iodination reactions tested. The immobilization properties of the TCuI host point to the effectiveness of the microporous features that provide a snug fit for the guest molecules of ICl and I_2 and of the distinct intermolecular interaction embodied by the halogen−halogen contacts. Further explorations will be conducted on MOFs and other porous media (e.g., porous polymers) for immobilizing a wider range of volatile reagents (e.g., Br_2, SCl_2, S_2Cl_2, and $SOCl_2$) and for uncovering potentially novel reactivity associated with the porous medium.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental procedures, full crystallographic data in CIF format, other related data, and photographs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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