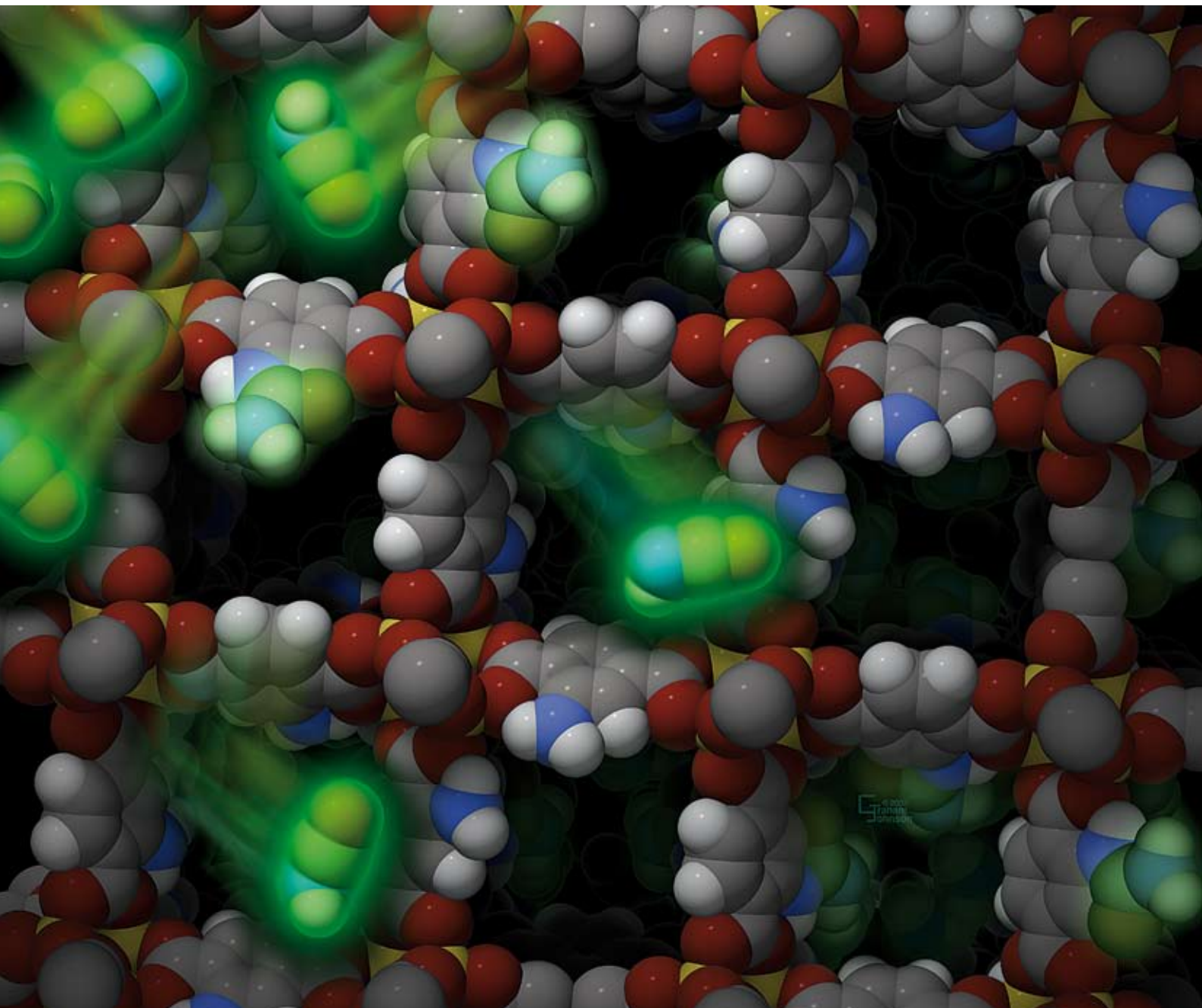


ChemComm

Chemical Communications

www.rsc.org/chemcomm

Number 29 | 7 August 2008 | Pages 3321–3452



ISSN 1359-7345

COMMUNICATION

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FEATURE ARTICLE

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1359-7345(2008)29;1-Y

Covalent modification of a metal–organic framework with isocyanates: probing substrate scope and reactivity†

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Received (in Austin, TX, USA) 10th April 2008, Accepted 29th April 2008

First published as an Advance Article on the web 3rd June 2008

DOI: 10.1039/b806150e

Isorecticular metal–organic framework-3 (IRMOF-3) has been postsynthetically modified with isocyanates to generate unprecedented, microporous urea-functionalized frameworks.

The open structures of metal–organic frameworks (MOFs)^{1–4} have been shown to sequester molecules as small as H₂ and as large as C₆₀,^{5,6} suggesting that the voids within these materials can accommodate guests in a liquid-like state. Indeed, Robson and Hoskins suggested more than a decade ago that the channels within these materials would be able to accommodate reagents that could react with the framework.⁷ Recently, our group and others have demonstrated that reactive molecules can access these cavities such that the MOF components can be chemically modified to generate structures with new functionality.^{8,9} The earliest example of such ‘postsynthetic modification’ was from Kim and co-workers, who showed that pendant pyridyl groups could be alkylated in a chiral MOF.¹⁰ Long and Kaye demonstrated that a metal–carbonyl fragment could be installed as an arene complex in isorecticular metal–organic framework-1 (IRMOF-1),¹¹ allowing for photogeneration of open, reactive metal coordination sites. Similarly, a report from Hupp and Mulfort described the reduction of a MOF with lithium, resulting in changes in the gas sorption properties of the framework.⁸ Fujita *et al.* reported that a labile imine species could be formed on a triphenylene template inside of a MOF and that these modifications could be followed using *in situ* crystallography to monitor the mobility of these template molecules within the MOF.¹² Very recently, an interesting study suggested that a lanthanide-based MOF could be modified with an isocyanate,¹³ but carbamate hydrolysis products (not ureas as reported here, *vide infra*) were obtained and no yields were reported. Finally, our group has shown that IRMOF-3, which contains pendant amino groups, could be modified with anhydrides in a single-crystal-to-single-crystal fashion to efficiently generate amide groups within the structure.^{14,15} Herein, we add another reaction, the condensation of IRMOF-3 with isocyanates to generate ureas, to this relatively short list of postsynthetic modification procedures for MOFs (Scheme 1). Furthermore, we have explored the scope of this reaction with different isocyanates and also show an *in situ* reaction/hydrolysis that can be used to generate a MOF with primary (Ar–NHCONH₂) urea groups.

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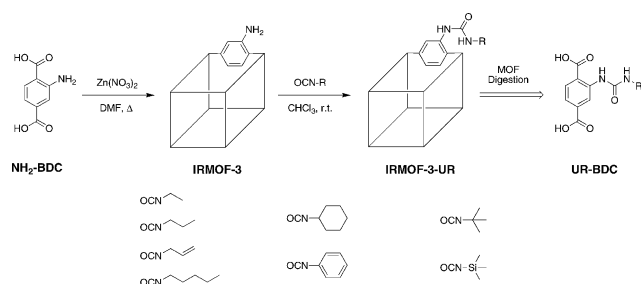
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† Electronic supplementary information (ESI) available: Fig. S1–S6, Table S1, and crystallographic data. CCDC 684721–684722. See DOI: 10.1039/b806150e

IRMOF-3, with a known cubic topology, was prepared from Zn(NO₃)₂·4H₂O and 2-amino-1,4-benzene dicarboxylic acid (NH₂-BDC) as previously described.^{6,16} As shown by Yaghi *et al.*, the 2-amino group of the 1,4-benzene dicarboxylate does not bind to the tetranuclear Zn₄O secondary building units (SBUs), and can undergo organic transformations. Here, IRMOF-3 is used as a model system for postsynthetic covalent modification, but the small number of studies reported to date with different MOFs^{12–15} demonstrates the generality of the covalent postsynthetic approach for the modification of MOFs. In order to optimize the reaction conditions, the reaction with ethyl isocyanate was examined. Crystals of IRMOF-3 (60 mg) were suspended in CHCl₃ (2 mL) and treated with two to eight equiv. of ethyl isocyanate at room temperature for three days. In this study, optimization of both the yield (conversion) and the preservation of single-crystallinity were desired. No difference in crystal quality was observed over the range of equivalents used with ethyl isocyanate. Therefore, in all of the reactions reported here, IRMOF-3 was treated for three days in CHCl₃ (2 mL) with eight equivalents of isocyanate, followed by extensive rinsing to stop the reaction.‡ In the case of cyclohexyl isocyanate and phenyl isocyanate, the reactions were performed with 10% MeOH in CHCl₃ to inhibit crystallization of dicyclohexylurea and diphenylurea side-products, respectively.

The postsynthetic modification of IRMOF-3 (to produce the modified frameworks designated IRMOF-3-UR) was confirmed, as previously described,^{14,15} by electrospray ionization mass spectrometry (ESI-MS) and nuclear magnetic resonance (NMR). Samples of IRMOF-3-UR were digested using dilute acid and DMSO and analyzed by ¹H-NMR spectroscopy, which confirmed the presence of the modified ligand *via* a distinctive downfield shift of the aromatic resonances (Fig. 1). The aromatic resonances of the benzene dicarboxylate starting material (NH₂-BDC) and products (UR-BDC, Scheme 1) were used to calculate the yield for each postsynthetic modification



Scheme 1 Scheme for the postsynthetic modification of IRMOF-3 with isocyanates (top). List of isocyanates examined (bottom).

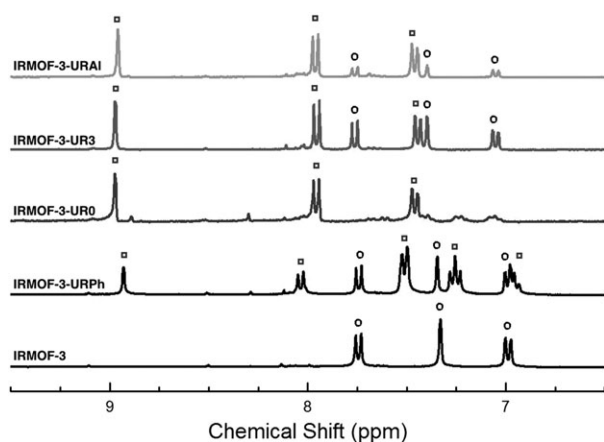


Fig. 1 $^1\text{H-NMR}$ spectra of DCI- D_2O digested IRMOFs in $\text{DMSO-}d_6$ solution. From bottom to top: IRMOF-3, IRMOF-3-URPh, IRMOF-3-UR0, IRMOF-3-UR3, and IRMOF-3-URAl. Squares and circles represent signals of modified and $\text{NH}_2\text{-BDC}$, respectively.

reaction (Table 1). The modification of IRMOF-3 was confirmed by ESI-MS, which showed the expected molecular ion peak for each product compound (*vide infra*).

To determine the generality of this reaction, eight different isocyanates (Scheme 1) were examined under the aforementioned reaction conditions. The results of these studies are summarized in Table 1. The conversion of the amine groups in IRMOF-3 to urea groups by each isocyanate varied significantly with the nature of the substituent. Straight-chain alkyl isocyanates showed decreasing conversion with increasing chain length with yields of 71%, 60%, and 51% for ethyl, propyl and pentyl isocyanate, respectively. Interestingly, bulkier, branched isocyanates, such as cyclohexyl isocyanate and *tert*-butyl isocyanate, gave lower or virtually no modification of IRMOF-3. In contrast, phenyl isocyanate showed $\sim 53\%$ conversion and trimethylsilyl isocyanate showed essentially quantitative conversion at $\sim 99\%$. The latter result was particularly surprising considering the comparable steric bulk of *tert*-butyl isocyanate, which showed essentially no conversion under our reaction conditions; however, $^1\text{H-NMR}$ and ESI-MS analysis revealed that the product of the reaction with trimethylsilyl isocyanate was not the trimethylsilylurea ($\text{R} = \text{Si}(\text{CH}_3)_3$), but rather a simple primary urea ($\text{R} = \text{H}$). Thus, under the present reaction conditions, trimethylsilyl isocyanate reacts with IRMOF-3 and then is hydrolyzed, most likely by residual water, to generate the resulting primary urea framework. The precise mechanism of this process is presently under investigation, but the results to date suggest this is an exciting prospect for the introduction of ever more complex reaction sequences and functionality into MOFs.¹⁵

Photographs of the modified IRMOF-3 suggest that the crystals remain intact after the postsynthetic modification procedure (see ESI).[†] The urea-containing MOFs were examined by thermal gravimetric analysis (TGA) to confirm the thermal and structural stability of the materials. All of the modified MOFs showed good thermal stability, with a weight loss at $\sim 225^\circ\text{C}$ and decomposition temperatures around 475°C . The first significant weight loss (7% to 22% depending on the modification) observed at $\sim 225^\circ\text{C}$ may be due to the

Table 1 Conversion of IRMOF-3 to IRMOF-3-UR with different isocyanates. Percent conversion values are the average of at least three independent experiments

IRMOF-3-	Isocyanate	% Conversion	STD
URtBu	<i>tert</i> -Butyl	N.r.	—
UR0 ^a	TMS	~ 99	—
UR2	Ethyl	71	± 5
UR3	Propyl	60	± 7
UR5	Pentyl	51	± 3
URAl	Allyl	75	± 5
URPh	Phenyl	53	± 4
URCy	Cyclohexyl	27	± 4

^a The product was the primary urea, $\text{NH}_2\text{CONH-BDC}$, with no spectroscopic evidence for the TMS group present.

urea functionality, as this is not observed for amide-modified IRMOF-3.^{14,15} Powder X-ray diffraction (PXRD) patterns showed the modified bulk materials possessed the same reflections as unmodified IRMOF-3 (see ESI).[†] Furthermore, single-crystal X-ray diffraction for the modified IRMOFs, as shown in Table 2, indicate that all of the modified IRMOFs retain cell parameters identical to those of the parent material IRMOF-3. A complete dataset was collected for IRMOF-3-URPh and IRMOF-3-URCy,[‡] which when solved gave the expected MOF lattice, although the modified groups could not be located due to the positional disorder of the urea substituent.^{6,14–16} The presence of the urea modifications was confirmed from ESI-MS data obtained on the individual crystals after X-ray data collection was complete (Table 2), which in all cases clearly identified the modified ligand in the spectrum. These data unambiguously show that IRMOF-3 modified by isocyanates maintains good stability and high crystallinity after modification.

To further confirm the modification of the MOF and investigate its effect on porosity, the Brunauer–Emmett–Teller (BET) surface area of two modified samples were measured *via* dinitrogen adsorption at 77 K. The samples showed high BET surface areas of $1660\text{ m}^2\text{ g}^{-1}$ and $1400\text{ m}^2\text{ g}^{-1}$ for IRMOF-3-URPh and IRMOF-3-UR2, respectively. The surface areas are reduced relative to IRMOF-3 ($\sim 2400\text{ m}^2\text{ g}^{-1}$),¹⁶ which is expected as a result of modification, but are still far in excess of typical zeolites. The full dinitrogen adsorption isotherm for IRMOF-3-UR2 is shown in Fig. 2, which generally shows Type I behavior.¹⁷ Near saturation, IRMOF-3-UR2 does show some small deviation from ideal Type I behavior; the

Table 2 Unit cell determinations and mass spectrometry data for modified IRMOF-3 single crystals. Complete structural datasets were collected and solved for IRMOF-3-URCy and IRMOF-3-URPh

IRMOF-3- ^a	Cell setting	$a = b = c/\text{\AA}$	$\alpha = \beta = \gamma/^\circ$	Volume/ \AA^3	ESI-MS(-) (m/z)
UR0	Cubic <i>F</i>	25.14	90	15893	222.98
UR2	Cubic <i>F</i>	25.54	90	16652	251.00
UR3	Cubic <i>F</i>	25.35	90	16283	265.03
UR5	Cubic <i>F</i>	25.58	90	16744	293.05
URAl	Cubic <i>F</i>	25.52	90	16623	263.05
URPh	Cubic <i>F</i>	25.73	90	17041	298.98
URCy	Cubic <i>F</i>	25.73	90	17032	305.08

^a For IRMOF-3, cubic, $Fm\bar{3}m$, $a = b = c = 25.7465(14)\text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 17066.0(16)\text{ \AA}^3$.

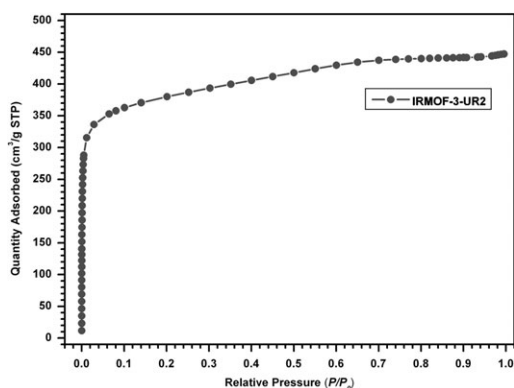


Fig. 2 Dinitrogen adsorption isotherm for IRMOF-3-UR2 at 77 K. From this isotherm the BET surface area was calculated to be 1400 m² g⁻¹, confirming the microporosity of the sample.

origin of this is presently unknown, but is under further investigation. Overall, the gas sorption data obtained clearly show that the modified samples still possess very high surface areas and both the microporosity and functionality desired in next generation MOF materials.

In summary, we have demonstrated that IRMOF-3 can be postsynthetically modified using a variety of isocyanates. Single-crystal and PXRD studies show that the modified IRMOF-3 retains crystallinity, and gas sorption measurements show retention of microporosity. In at least one case, nearly quantitative conversion is achieved generating a primary urea within the MOF. The previously reported reaction of IRMOF-3 with anhydrides produces acid byproducts that, in some circumstances, can degrade the MOF; in contrast, isocyanates generate no reaction byproducts that can degrade the framework and therefore should allow for the preparation of an even wider-variety of modified MOFs. The strong hydrogen bonding observed for ureas may make MOFs of the type reported here of interest for several applications. First, the use of ureas as anion recognition groups has been widely explored, and a number of excellent examples from Custelcean and co-workers have demonstrated the use of urea-containing MOFs for anion separation.^{18–22} In addition, the use of ureas and urea–base conjugate molecules as organocatalysts²³ bodes well for the use of urea-modified MOFs as solid-state, shape-selective organocatalytic materials. Exploration of the host–guest and catalytic properties of these materials are presently underway and will be reported in due course.

We acknowledge Prof. G. Arrhenius for use of his PXRD, Prof. A. L. Rheingold, Dr A. G. DiPasquale, and Dr J. R. Stork for assistance with the crystallographic studies, and Dr Y. Su for performing the mass spectrometry experiments. This work was supported by U.C.S.D. and the NSF (CHE-0546531).

Notes and references

† Isocyanate modification of IRMOF-3: IRMOF-3 was prepared as previously described (see ref. 6, 15 and 16) from DMF and solvent exchanged with CHCl₃ for 3 d. Approximately 60 mg of IRMOF-3 (0.2 mmol in –NH₂) was suspended in 2 mL of CHCl₃, and 8 equiv. of isocyanate were added to the solution. The mixture was left to stand at room temperature for 3 d, after which the solvent was decanted, and fresh CHCl₃ (4 mL) was added once a day for three days to rinse the crystals free of any excess isocyanate. For phenyl and cyclohexyl

isocyanate, the same procedure was used, except that the reaction was conducted in a mixture of 1.8 mL of CHCl₃ and 0.2 mL of MeOH. Pure CHCl₃ was used for the subsequent washings and soakings.

Crystal data for IRMOF-3-URCy: C_{34.63}H_{28.88}Cl₁₅N_{3.75}O_{13.75}Zn₄, *M* = 1510.72, cubic, space group *Fm* $\bar{3}$ *m*, *a* = *b* = *c* = 25.7262(10) Å, α = β = γ = 90°, *V* = 17026.6(11) Å³, *T* = 100(2) K, *Z* = 8, 123 127 reflections measured, 1101 unique which were used in all data, (*R*_{int} = 0.0803), *R*₁ = 0.0626 (*I* > 2σ(*I*)), *GOF* = 1.234. Analytical data (NMR) indicated that the IRMOF-3 starting material was ~27% modified with cyclohexyl isocyanate to form the cyclohexylurea substituent. However, because of disorder, which includes four-fold positional disorder imposed by the space group, neither the amine nor cyclohexylurea substituents could be located in the difference map. Several partially occupied and disordered chloroform solvent molecules were found. However, acceptable atomic positions could not be ascertained for this solvent or for the amine and phenylurea substituents. These disordered moieties were treated as diffuse contributions using the program SQUEEZE (A. Spek, Platon Library). See the CIF file for more details.

Crystal data for IRMOF-3-URPh: C_{39.13}H₂₇Cl_{11.50}N_{4.63}O_{14.50}Zn₄, *M* = 1463.06, cubic, space group *Fm* $\bar{3}$ *m*, *a* = *b* = *c* = 25.6761(9) Å, α = β = γ = 90°, *V* = 16927.3(10) Å³, *T* = 100(2) K, *Z* = 8, 12 890 reflections measured, 998 unique which were used in all data, (*R*_{int} = 0.0528), *R*₁ = 0.0541 (*I* > 2σ(*I*)), *GOF* = 0.955. Analytical data (NMR) indicated that the IRMOF-3 starting material was ~53% modified with phenyl isocyanate to form the phenylurea substituent. However, because of disorder, which includes four-fold positional disorder imposed by the space group, neither the amine nor phenylurea substituents could be located in the difference map. Several partially occupied and disordered chloroform solvent molecules were found. However, acceptable atomic positions could not be ascertained for this solvent or for the amine and phenylurea substituents. These disordered moieties were treated as diffuse contributions using the program SQUEEZE (A. Spek, Platon Library). See the CIF file for more details.

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