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1 Evaluating Iodine Uptake in a Crystalline Sponge Using Dynamic 2 X-ray Crystallography

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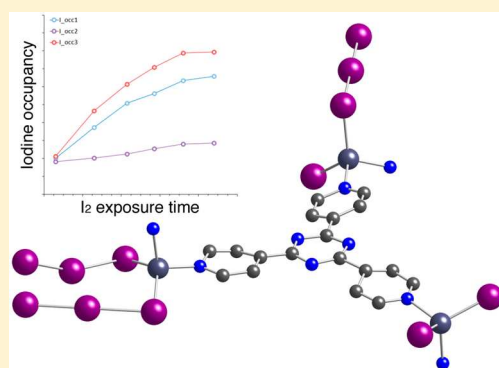
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9 **S** Supporting Information

10 **ABSTRACT:** The uptake of gaseous iodine into the crystalline sponge
11 material $[(\text{ZnI}_2)_3(\text{tpt})_2] \cdot 0.7\text{triphenylene} \cdot 0.3\text{PhNO}_2 \cdot 0.7\text{C}_6\text{H}_{12}$ **1** (tpt = 2,4,6-
12 tris(4-pyridyl)-1,3,5-triazine) has been monitored by dynamic X-ray
13 diffraction and thermogravimetric analysis. The X-ray analyses have enabled
14 the location, quantity, uptake rate, and subsequent chemistry of the iodine
15 upon inclusion into the pores to be determined. An uptake of 6.0 wt % (0.43
16 I_2 per formula unit) was observed crystallographically over a period of 90 min
17 before crystal degradation occurred. The included iodine molecules interact
18 with the iodine atoms of the ZnI_2 nodes at three different sites, forming
19 coordinated I_3^- ions. The results contrast to recent observations on
20 $[(\text{ZnI}_2)_3(\text{tpt})_2]$ without the triphenylene guests which show the presence of
21 I_4^{2-} ions with low quantities of absorbed iodine.



22 ■ INTRODUCTION

23 The capture and immobilization of radioactive iodine¹ is highly
24 topical given the unplanned release of radioactive material from
25 the Fukushima nuclear power plant in 2011.² Concern
26 surrounding the beta-emitting isotopes ¹²⁹I and ¹³¹I stems
27 largely from the volatility of iodine, coupled with its ability to
28 impact upon human metabolic processes.³

29 Metal–organic frameworks (MOFs) are a promising class of
30 materials for the sequestration of iodine, including its
31 radioactive isotopes, owing to their high porosity, tunable
32 pore dimensions, and affinity for a wide range of guests.^{4–6} This
33 has been borne out in a number of MOF systems, including
34 MIL-type aluminum scaffolds,⁷ zinc paddlewheels,⁸ zirconium
35 UiO-66 derivatives,⁹ and zeolitic imidazolate frameworks.¹⁰
36 These studies, combined with *in silico* insights,¹¹ have identified
37 iodine as having an affinity for metal sites and nucleophilic
38 functional groups. Composite materials containing MOFs have
39 been proposed for the sequestration of iodine,¹² as have related
40 materials such as covalent organic frameworks¹³ and other
41 porous organic frameworks.¹⁴ Interest in iodine inclusion is not
42 limited to its radioactive isotopes, and adsorption of iodine can
43 also be used to partially oxidize framework materials and hence
44 introduce electronic conduction.^{15,16}

45 Crystalline sponges are a subset of MOFs that have been
46 tailored to enhance crystallographic investigations by providing
47 a cavity capable of ordering guest molecules.¹⁷ This ordering is
48 driven by the inherent flexibility of the framework, and
49 crystalline sponges have been shown to be effective hosts for

reactive intermediates¹⁸ and difficult to crystallize organic
molecules,¹⁹ allowing structural characterization of molecules
that are not amenable to traditional crystallographic techniques.
When reaction intermediates and/or products are structurally
characterized within the pores, the materials are often referred
to as crystalline molecular flasks (CMFs).^{20,21}

The most well-known crystalline sponges are formed from
the linking together of ZnI_2 nodes with 2,4,6-tris(4-pyridyl)-
1,3,5-triazine (tpt) ligands. The compound $[(\text{ZnI}_2)_3(\text{tpt})_2]$,
assembled from the reaction of ZnI_2 with tpt, forms a doubly
interpenetrated (10,3)-b network containing one-dimensional
channels.²² However, when the reaction between ZnI_2 and tpt
takes place in the presence of triphenylene, a different network
is formed. The included triphenylene molecules interact
through $\pi \cdots \pi$ interactions with the tpt linkers forming columns,
and the resultant network, $[(\text{ZnI}_2)_3(\text{tpt})_2] \cdot \text{triphenylene}$,
contains two types of channels.²³ Networks based on ZnI_2
nodes and tpt linkers have previously shown an affinity for
iodine inclusion, resulting in either chemical reaction²⁴ or
structural changes.²⁵

In light of the dynamic nature of crystalline sponges in the
presence of gaseous iodine^{24,25} and the importance of
understanding iodine uptake,¹ the $[(\text{ZnI}_2)_3(\text{tpt})_2] \cdot \text{triphenylene}$
system²³ was targeted for investigation by dynamic X-ray
crystallography. Our objective was to establish (i) the kinetics

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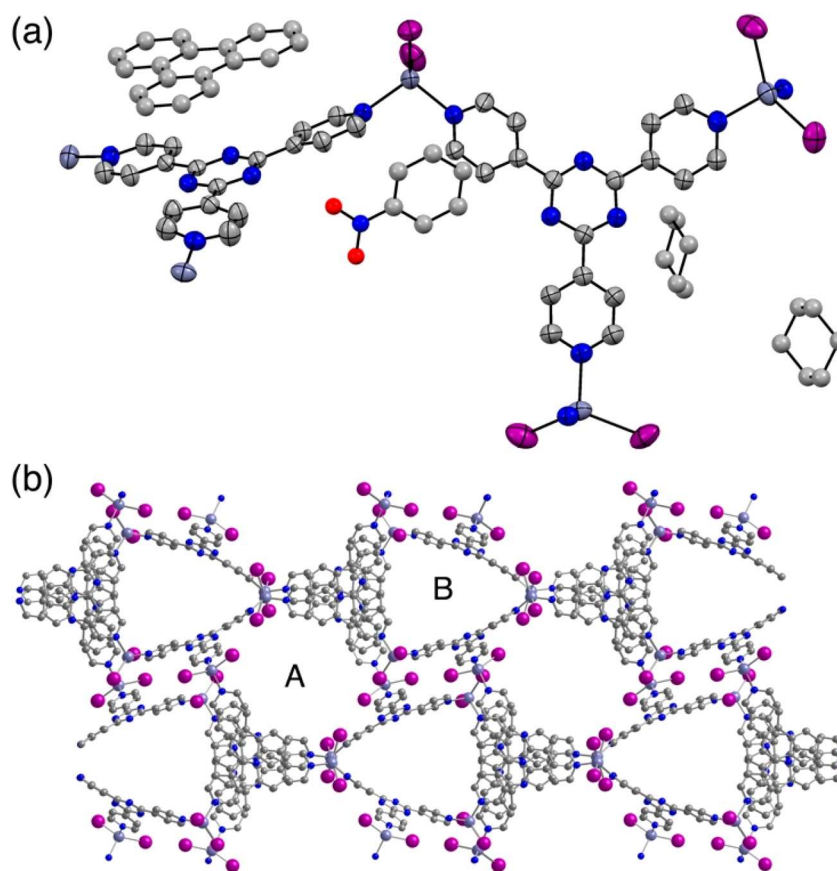


Figure 1. Structure of **1** showing (a) the asymmetric unit, indicating the positions of the triphenylene molecule and the included nitrobenzene and cyclohexane solvent molecules, and (b) the network structure showing the A and B channels, with nitrobenzene and cyclohexane molecules removed for clarity. Hydrogen atoms have been omitted for clarity.

75 of iodine uptake, (ii) the loading of iodine inside the
76 framework, and (iii) the nature of the interaction between
77 the iodine guest molecules, the triphenylene, and host
78 framework. The results of these investigations are reported
79 herein. While this work was being carried out, Woo, Murugesu,
80 and co-workers²⁶ reported the uptake of iodine into
81 $[(\text{ZnI}_2)_3(\text{tpt})_2]$, so we also compare our findings in the related
82 triphenylene-containing framework to their results.

83 ■ RESULTS AND DISCUSSION

84 Crystals of triphenylene-loaded $[(\text{ZnI}_2)_3(\text{tpt})_2]$ were prepared
85 following the previously reported procedure²⁷ and were
86 suspended in cyclohexane to facilitate solvent exchange. The
87 crystal structure at 290 K demonstrated the presence of both
88 nitrobenzene and cyclohexane solvent molecules in the lattice
89 and the refinement suggested the occupancy of triphenylene
90 was 70% (*vide infra*), giving a formula for **1** of $[(\text{ZnI}_2)_3(\text{tpt})_2] \cdot$
91 $0.7\text{triphenylene} \cdot 0.3\text{PhNO}_2 \cdot 0.7\text{C}_6\text{H}_{12}$. A preliminary test for
92 uptake of gaseous iodine vapor was carried out by monitoring
93 single crystals of **1** in the presence of solid iodine with optical
94 microscopy. The initially yellow single crystals darkened to
95 brown over a 10 min period, with the color change migrating
96 from the crystal edges inward (Figure S3). A sample of **1** was
97 then placed under an atmosphere of iodine vapor for 2 days.
98 The color of the powder changed from yellow to black during
99 this time, and thermogravimetric analysis (TGA) revealed a
100 mass loss of 38.4% when the sample was heated to 200 °C,
101 equivalent to 3.9 molecules of I_2 per formula unit, assuming the
102 same composition as observed in the crystal structure prior to I_2

exposure (*vide infra*) and also loss of the included nitrobenzene
and cyclohexane concurrent with I_2 . This was gauged to be the
maximum uptake for this system (Table S2 and Figure S4).

Having demonstrated that **1** was capable of iodine uptake
over a period of hours, we sought to visualize this process using
dynamic single-crystal X-ray crystallography. Given the
dispersive nature of released vapors, understanding the
behavior of the framework toward volatile iodine over short
time scales is crucial for gas absorption applications. These
experiments were carried out on the single crystal beamline
facility, I19, at the Diamond Light Source. A single crystal of **1**
was mounted in a 1 mm glass capillary, in a static gas cell²⁸
together with several iodine crystals, with **1** and the iodine
being separated by a cotton wool plug (Figure S1). The
temperature of the capillary was maintained at 290 K, with a
stream of gaseous nitrogen, and the iodine allowed to diffuse
within the closed capillary. X-ray data sets, each taking
approximately 20 min to record, were measured sequentially
from the point at which the gas cell was mounted on the
diffractometer. In total, six data sets were measured with a total
X-ray exposure time of 96 min. Over this period, the unit cell
volume increased by 3.9%, from 18204(1) to 18922(5) Å³. For
each data set the structure was refined using the structural
model obtained from the 290 K data obtained before the
absorption of iodine into the crystal (Figure 1).

In all data sets, the atoms of the framework and the
triphenylene molecule were refined anisotropically. Refinement
of the initial data set suggested that triphenylene was present
with only 70% occupancy, and in this and all subsequent data

sets the occupancy was fixed at this level. There is precedence in other structural analyses of $[(\text{ZnI}_2)_3(\text{tpt})_2]$ -triphenylene compounds for triphenylene occupancy of less than 100%.²⁷ To facilitate comparison throughout the series, the same set of constraints and restraints were applied to the solvent atoms; these were subject to an isotropic refinement, with site occupancies fixed to a constant value and isotropic displacement parameters allowed to refine freely. From the X-ray structural analysis, it was clear that iodine was being absorbed into the crystal lattice from the initial measurements, and the percentage absorption increased with time until 96 min, at which point the quality of the diffraction data was such that it could no longer be relied upon. An analysis of the electron density within the crystal lattice using *PLATON SQUEEZE*²⁹ showed an increase in residual electron density with time, as presented in Table 1. In this approach the structure for the

the other ZnI_2 iodine atoms, I(3), I(4), and I(6), no evidence was observed for inclusion into these sites. Analysis of the structures reveals that such adsorption would be sterically hindered by the presence of framework tpt ligands and/or included nitrobenzene molecules.

The framework of **1** contains two different channels (Figure 1).²³ The larger channels (A) are approximately cylindrical and surrounded by hydrogen atoms of the stacked tpt and triphenylene units, while the narrower channels (B) have three walls and are approximately trigonal prismatic. In channel A, the nitrobenzene and cyclohexane guests are severely disordered while channel B is filled with more ordered cyclohexane molecules. All three sites for iodine inclusion are located in channel A (Figure 2b).

Further information on the iodine adsorption process can be gained by monitoring the rate at which each site in the structure absorbs I_2 molecules. An indication of this is given by the refined site occupancies of the I atoms at the various positions as measured in the six sequential data sets recorded over 90 min. These results are shown in Figure 3. This shows a significant level of I_2 adsorption at $t = 0$ (the start time for the first data collection), which results from the unavoidable, approximately 5 min time delay between sealing the crystal of **1** and iodine in the capillary before mounting it on the diffractometer. Therefore, all three of the located iodine sites start with an occupancy level of 4–7%. All these levels rise with time with the biggest increase occurring between 6 and 45 min. After this, the site occupancies of I_{occ1} and I_{occ3} continue to rise at a slower rate but in parallel. The site occupancy for I_{occ2} rises slightly but levels out at 7% by $t = 90$ min. There is competition between sites I_{occ2} and I_{occ3} as they reside in the same region of the lattice, so full occupancy of both is not possible for steric reasons and their behavior suggests that I_{occ3} takes precedence. The overall uptake of I_2 observed in the dynamic crystallography experiment is 0.43 equiv per formula unit, which corresponds to 6.0 wt %.

In a subsequent set of experiments, a fresh crystal of **1** and an iodine crystal were mounted as before, and the data collections were repeated at 280 K. The results were generally similar to those at 290 K and are presented in the Supporting Information (page S11). The main difference was that the rate of adsorption for all three sites was notably slower at 280 K, reaching occupancies of 9% for I_{occ1} , 3% for I_{occ2} , and 9% for I_{occ3} after 185 min.

While it is known that the absorption of I_2 into a porous material can instigate chemical reactions,²⁴ this is only the second time to our knowledge that chemisorption of gaseous I_2 to form coordinated I_3^- has been visualized and monitored within a porous solid-state framework. Very recently, Woo, Murugesu, and co-workers²⁶ reported the uptake of iodine into $[(\text{ZnI}_2)_3(\text{tpt})_2]$ in the absence of the triphenylene guests. They observed initial incorporation of I_2 at sites bridging between two coordinated iodides, giving rise to I_4^{2-} ions. As greater quantities of iodine were absorbed, these I_4^{2-} bridges were replaced by terminal I_3^- ions, similar to those observed for **1**, and this change in coordination mode allows for greater capacity. The overall uptake of I_2 observed crystallographically in $[(\text{ZnI}_2)_3(\text{tpt})_2]$ is considerably higher than in **1**, consistent with the larger pores present. The nonobservation of I_4^{2-} ions in **1** following exposure to I_2 is likely to relate to the relative positions and orientations of the ZnI_2 units in the structure. In I_2 -loaded $[(\text{ZnI}_2)_3(\text{tpt})_2]$, the distance between the zinc-bound iodine atoms that are bridged by I_2 to form I_4^{2-} is 9.44 Å.

Table 1. Increasing Residual Electron Density with Time Accounting for Solvent Molecules and Iodine as I_2 Is Absorbed into the Crystal of **1 at 290 K**

data set	time (mins)	solvent accessible volume (\AA^3) ^a	no. residual electrons ^b
1	0	8198	1878
2	20	8179	2096
3	36	8362	2382
4	50	8452	2516
5	65	8547	2603
6	81	8787	2682

^aThe solvent accessible volume was calculated using the *SQUEEZE* algorithm, implemented in *PLATON*.²⁹ ^bThe number of residual electrons was calculated using *SQUEEZE*, the calculations were performed on a model containing only the host cage framework and the triphenylene guest. The number of residual electrons calculated by *SQUEEZE* is a measure of all the PhNO_2 , cyclohexane, and iodine present in the lattice at the six time points, though only the electron density corresponding to 0.3 PhNO_2 , 0.7 C_6H_{12} , and the increasing amount of coordinated I_2 is modeled in the six structural analyses. There is additional poorly resolved solvent present in the crystals that cannot be modeled other than by *SQUEEZE*. The key point to note is that the solvent accessible volume and the residual electron density are increasing with time as iodine is absorbed by the crystal.

$[(\text{ZnI}_2)_3(\text{tpt})_2]$ -triphenylene unit, without solvent, was used as the model structure and the residual electron density for each of the six data sets was calculated against this model, accounting for the presence of the included nitrobenzene and cyclohexane solvent molecules and the increasing percentage of iodine.

Carrying out sequential crystal structure determinations during I_2 uptake enabled the rate of inclusion and location of the incoming iodine molecules to be determined. The structure of **1** with the absorbed I_2 after 90 min (data set 6) is shown in Figure 2. I_2 occupies three different sites within the lattice but, in all cases, it links to an iodine atom of one of the “ ZnI_2 ” nodes to form coordinated, linear I_3^- ligands. There are three sites of I_2 occupation: in the final data set, I_{occ1} has 16% occupancy and forms a I_3^- ligand with the Zn-coordinated atom I(5) (I(5)–I(7) 3.055(9), I(7)–I(8) 2.834(12) Å), I_{occ2} has a 7% occupancy and forms a I_3^- ligand with I(1) (I(1)–I(9) 3.018(10), I(9)–I(10) 2.815(19) Å), and I_{occ3} has 20% occupancy and forms a I_3^- ligand with I(2) (I(2)–I(11) 3.324(11), I(11)–I(12) 2.814(14) Å), though with a notably longer $\text{I} \cdots \text{I}_2$ contact than observed for I_{occ1} and I_{occ2} . Although there are potential I_2 adsorption sites proximate to

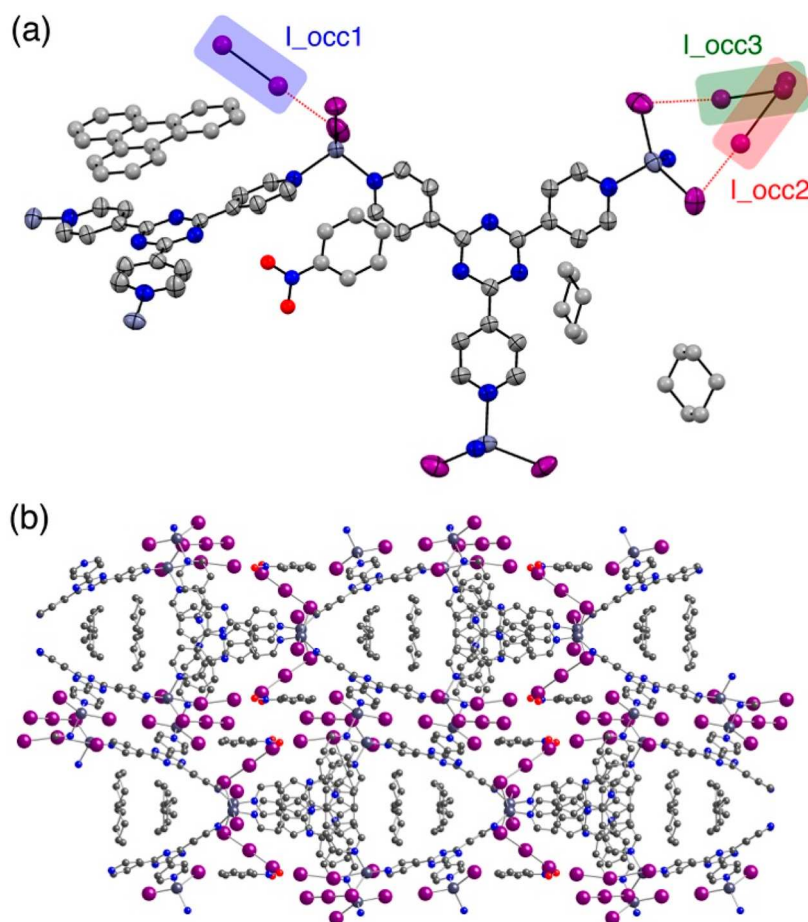


Figure 2. Structure of **1** after 90 min exposure to iodine vapor, showing (a) the asymmetric unit indicating the positions of the absorbed I_2 and (b) the network structure. Hydrogen atoms have been omitted for clarity. The absorbed iodine atoms were refined with partial occupancy as described in the text.

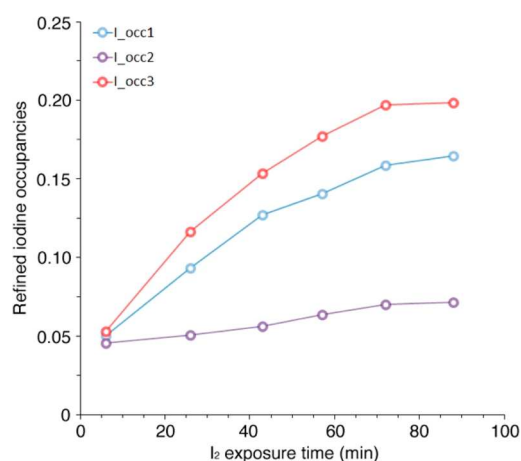


Figure 3. Modeled iodine occupancies, as percentages, for the three sites obtained from refinements of the 6 sequential data sets recorded as the single crystal of **1** absorbed iodine vapor over a 90 min period.

232 Inspection of the structure of **1** reveals that there are no $I \cdots I$
 233 distances between 9 and 10 Å in which the orientation of the
 234 ZnI_2 units could facilitate I_2 bridges. Similar I_4^{2-} ions were
 235 observed by Liao, Zheng, and co-workers in a MOF containing
 236 Cu_4I_4 nodes and isonicotinate ions, though no evidence of I_3^-
 237 ions was reported in this case.³⁰

238 While the interactions between $[(ZnI_2)_3(tpt)_2]$ and **1** with
 239 iodine are the only examples to date of absorption of iodine
 240 with concurrent conversion to I_3^- , previous papers have
 241 reported the direct uptake of triiodide from solution into a
 242 framework,^{31,32} solvent triggered formation of triiodide from
 243 iodine within a framework,³³ and noninnocent redox processes
 244 triggered by iodine in a Fe^{2+} framework.³⁴ A key advantage of
 245 the interaction described in this work is that the solution phase
 246 is bypassed in favor of harnessing reactivity at the gas/solid
 247 interface, which is desirable for materials and applications that
 248 target radioactive iodine vapor absorption.

249 Generally, the rate of iodine uptake for powdered **1** is slower
 250 than that in the single-crystal experiments. The dominant factor
 251 appears to be the accessibility of the material to iodine vapor.
 252 For the single-crystal experiment, the entire surface of the
 253 crystal was exposed to iodine vapor using MiTeGen Micro-
 254 Gripper crystallographic loops when mounting. In contrast,
 255 only the crystallites located at the surface of the bulk powder of
 256 **1** were observed to darken quickly upon exposure to iodine,
 257 signaling rapid uptake. Crystallites located beneath this surface
 258 layer were largely insulated from the iodine vapor. Upon each
 259 sampling, the bulk powder was homogenized with stirring;
 260 however, this insulating behavior persisted throughout the
 261 experiment.

262 Despite the slower kinetics, powdered **1** has a substantially
 263 higher uptake of I_2 than observed in the single crystal X-ray
 264 experiments prior to loss of single crystallinity. A powder 264

sample of **1** was exposed to the normal vapor pressure of solid iodine at 23 °C (3.43×10^{-3} atm),³⁵ and the uptake of iodine was monitored by thermogravimetric analysis hourly for 7 h (Figure 4). To identify the volatile components, continuous

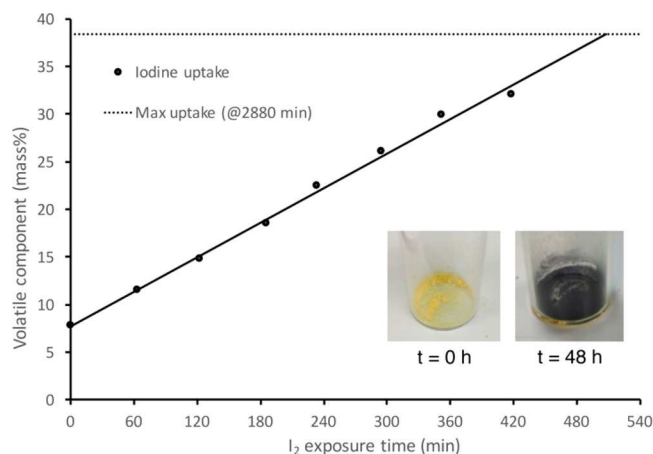


Figure 4. Increasing wt % of the volatile component within **1** upon exposure to iodine vapor as measured by thermogravimetric analysis. The solid black trend-line ($R^2 = 0.9952$) shows a linear relationship up to $t = 6$ h and possibly beyond.

sampling by mass spectrometry was performed during this experiment (see the Supporting Information). Prior to iodine exposure ($t = 0$ h), a mass loss of 7.8% was recorded on heating to 200 °C. This corresponds to loss of included nitrobenzene and cyclohexane from the pores, with the mass loss suggesting a greater amount of included solvent present than observed in the single crystal X-ray structures, itself consistent with some solvent loss prior to the single crystal study, though no loss of solvent was observed during the single crystal experiments. Once iodine exposure had started, iterative sampling identified a linear increase of approximately 4% by mass of volatile components per hour. This was continued for 7 h, after which time the volatile component of **1** by was 32.0% by mass. This corresponds to between 2.6 and 3.2 molecules of iodine per formula unit under these conditions, depending on whether the nitrobenzene and cyclohexane molecules were displaced by iodine during its uptake and prior to the TGA (i.e., 32.0% mass loss corresponds to I₂) or were retained in the lattice and lost during the TGA along with the iodine (i.e., 32.0–7.8% mass loss corresponds to I₂). We have assumed throughout that triphenylene is not lost through either sublimation or displacement by I₂. Its low volatility (melting point 198 °C, boiling point 438 °C), coupled with its key structural role makes such loss highly unlikely, with no PXRD evidence for the structural change such displacement would lead to.

Over the time scale of the PXRD analyses, the I₂ uptake of **1** is almost identical to that of the more porous triphenylene-free framework [(ZnI₂)₃(tpt)₂].²⁴ These bulk powder results show that **1** is amenable to both scale-up and application beyond the single-crystalline form, both of which are beneficial to device fabrication and practical applications.

CONCLUSIONS

In conclusion, we have found that I₂ is absorbed into crystals of a crystalline sponge, with an uptake of 0.43 molecules of I₂ per formula unit, corresponding to 6.0 wt %, over a 90 min period while retaining crystallinity. Within the crystal structures, I₂

occupies three distinct positions, with significantly different occupancy levels that can be related to the cavity space available within the crystal. In each case chemical reactions occurred and the I₂ molecule has formed a bond to an iodine atom present in the ZnI₂ unit to form a linear triiodide ligand. These interactions indicate that iodine vapor can be removed from the atmosphere and held in solid state materials through covalent bond formation.

Iodine inclusion in organic systems is often assumed to take place near to aromatic systems and accompanied by charge transfer,^{14,36} so direct crystallographic evidence for interaction with ZnI₂ rather than the rings of the tpt ligands is significant. While single crystals of **1** only adsorb 6.0 wt % before loss of single crystallinity, powdered samples of **1** are capable of adsorbing considerably more I₂. From the stoichiometry, it is evident that some of this additional iodine must be included into different sites from those identified in the single crystal experiments, though these X-ray analyses have clearly demonstrated the initial sites of attachment.

These results complement those for the recently published [(ZnI₂)₃(tpt)₂] system,²⁴ particularly in understanding the initial iodine uptake behavior ($t < 90$ min) of crystalline sponges. This work also shows that iodine can be sequestered directly as the triiodide form without first forming I₄²⁻.

EXPERIMENTAL SECTION

Triphenylene-loaded [(ZnI₂)₃(tpt)₂] **1** was synthesized according to the published procedure.²⁷ The identity of individual crystals was confirmed by single-crystal diffraction analysis, and bulk purity was confirmed using powder X-ray diffraction analysis (Figure S2).

X-ray Crystallography. A single crystal of **1** was mounted in a glass capillary together with several crystals of iodine; the crystals of **1** and I₂ were separated by a plug of cotton wool, but iodine vapor could diffuse throughout the capillary. The glass capillary was mounted on a static gas cell, and the assembly immediately mounted on a diffractometer on beamline I19, at the Diamond Light Source. Sequential data sets were recorded approximately every 20 min over a 90 min period, at 290 or 280 K, using monochromated X-ray radiation with $\lambda = 0.6889$ Å, to follow the dynamic absorption of iodine vapor. Data were indexed and integrated in the program *xia2*,³⁷ while structure solutions were performed by dual-space methods in *SHELXT*³⁸ and refined by full matrix least-squares on *F*² in *SHELXL*.³⁹ CCDC 1576326–1576331 (290 K data) and 1576335–1576341 (280 K data) contain the supplementary crystallographic data for all structures in this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b03218.

Details of the crystallographic characterizations and thermogravimetric analyses (PDF)

Accession Codes

CCDC 1576326–1576331 and 1576335–1576341 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or by emailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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373 Author Contributions

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

377 Notes

378 The authors declare no competing financial interest.

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