

Selective Capture of Volatile Iodine using Amorphous Molecular Organic Solid

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Electronic Supporting Information

Materials and Methods

General Information

Solution ^1H NMR spectra were collected on a Bruker Avance 300 spectrometer. Infrared spectra were recorded on a Bio-Rad FTS-185 instrument using KBr discs. The crystals suitable for structure analysis were mounted on a glass fiber with silicone grease and placed in the cold stream of a Bruker APEX II diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073\text{Å}$). The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least squares methods against F^2 with SHELXL-97.¹ Tables of neutral atom scattering factors, f' and f'' , and absorption coefficients are from a standard source.² All atoms except hydrogen atoms were refined with anisotropic displacement parameters. In general, hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model. The crystal structure of **I₂·1** contains heavily disordered solvent molecules in the cavity and void spaces. These disordered solvent molecules were not further identified or refined. Instead, a new set of F^2 (hkl) values with the contribution from solvent molecules withdrawn was obtained by the SQUEEZE procedure implemented in PLATON program.³ Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris 6 Thermogravimetric Analyzer under flowing N_2 gas (40 mL/min), and the heating rate was $5^\circ\text{C}/\text{min}$ from 35 to 900°C . Powder X-ray diffraction (PXRD) measurements were recorded on Shimadzu Lab-X XRD-6000 diffractometer with Cu $K\alpha$, $\lambda = 1.54060\text{Å}$. All PXRD spectra were acquired in a 2θ range from 5 to 90° with a step size of 0.0200° . Elemental analyses were performed on a Heraeus CHN-OS Rapid Elemental Analyzer at the Instruments Center of National Chung Hsing University, Taiwan. Transmission electron microscopy (TEM) and corresponding selected area electron diffraction (SAED) were performed on a JEM-2010 transmission electron microscopy operating at 80-200 KV (JEOL Japan, Co. Ltd). Carbon coated copper grid was used for the sample substrate. A few 8 μl drops of benzene solution of **1** were pipetted onto the sample grid and allowed to dry in air at the ambient temperature. All samples of $\text{I}_{2(\text{g})}$ -treated amorphous powders of **1** were vacuum-dried at 110°C for 1 day to remove any non-specific bonding, before the measurements of solid-state IR, TGA, and EA.

Synthesis of I₂·1: A solution of cage **1** (100 mg, 0.088 mmol) in toluene (15 ml) was layered with iodine (22 mg, 0.088 mmol) solution in diethyl ether (5 ml), and then kept at -20°C for 1 week. The reddish crystals (99 mg, 81 %) of **I₂·1** obtained were suitable for X-ray crystallographic analysis. Anal. Calcd for $\text{C}_{66}\text{H}_{72}\text{I}_2\text{N}_6\text{S}_6$: C, 56.803; H, 5.200; N, 6.022; S, 13.786. Found: C, 56.885; H, 5.237; N, 6.050; S, 13.792. Crystal data: for **I₂·1**: $\text{C}_{66}\text{H}_{72}\text{I}_2\text{N}_6\text{S}_6$, $M = 1395.46$, trigonal, $a = 17.583(3)\text{Å}$, $b = 17.583(3)\text{Å}$, $c = 48.345(10)\text{Å}$, $\alpha = 90.00^\circ$, $\beta = 90.00^\circ$, $\gamma = 120.00^\circ$, $V = 12943(4)\text{Å}^3$, $T = 200(2)\text{K}$, space group $R\bar{3}c$, $Z = 6$, $\mu(\text{MoK}\alpha) = 0.907\text{mm}^{-1}$, 25380 reflections measured, 2548 independent reflections ($R_{\text{int}} = 0.1459$). The final R_1 values were 0.0924 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.2989 ($I > 2\sigma(I)$). The final R_1 values were 0.1417 (all data). The final $wR(F^2)$ values were 0.3261 (all data). The goodness of fit on F^2 was 1.015. CCDC 848479.

The studies of I₂ absorption and desorption kinetics

A vial containing powders of **1** (100 mg, 0.088 mmol) was placed with some crystals of iodine in a closed system at 60°C. The total weight of the powders was monitored day by day. After 12 days absorption, the vial was exposed to air and placed in an oven at 120°C. The molar equivalents of I₂ were calculated based on the increased weights measured.

Supplementary Table and Figures

Table 1. The comparison of **1**-related structures reported.

Compounds	Bond distance of S-S bond (Å)	CSSC torsion angle (°)	Distance between two centroids of aromatic bases (Å)	Reference
DCM 1	2.065(2)	96.8(2)	8.976	(7) in the article
DMF 1	2.049(3)	96.4(2)	9.047	
I ₂ 1	2.028(6)	97.0(5)	9.058	This work

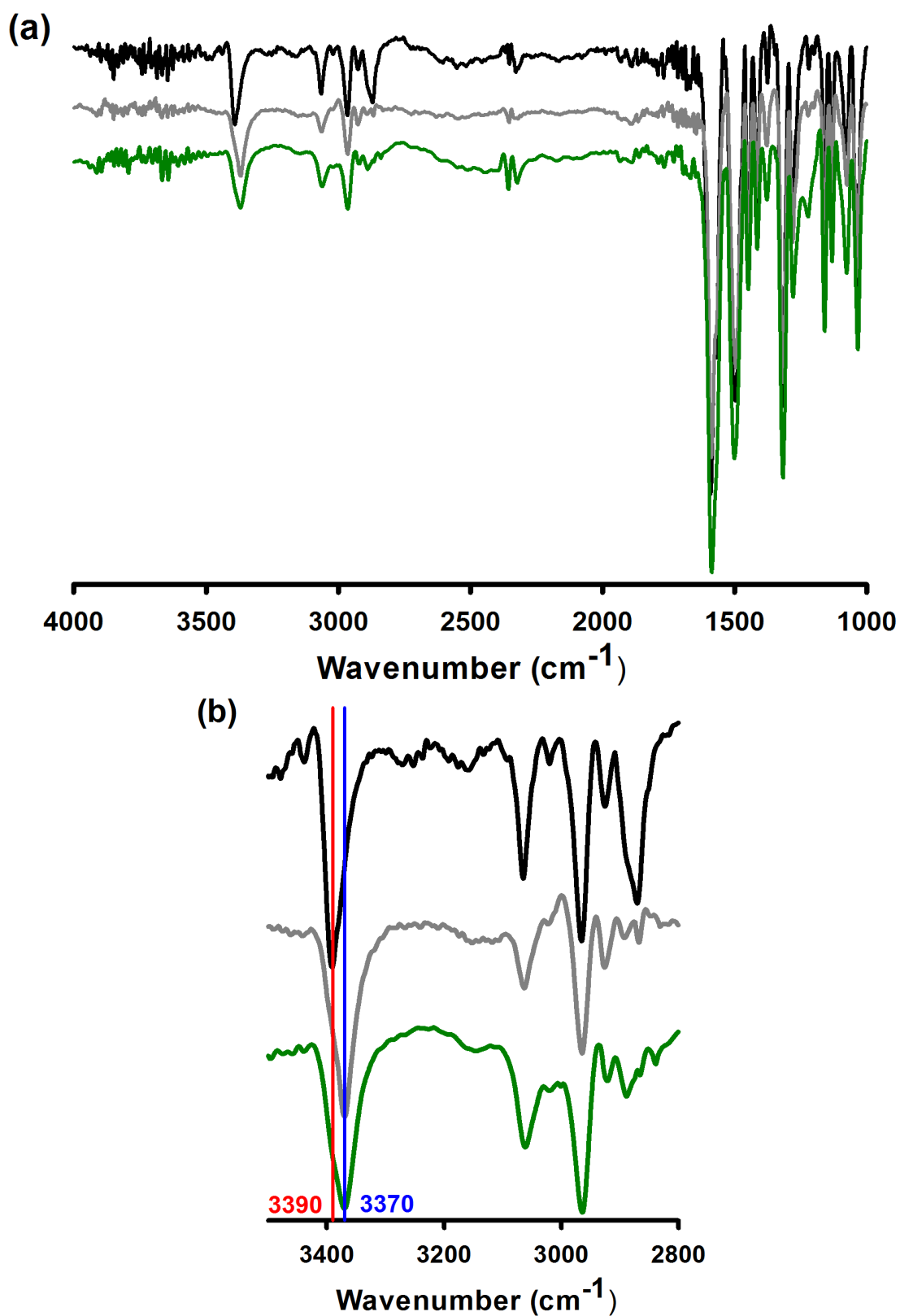


Fig. 1 (a) Solid-state IR spectra of **1** as synthesized (black line), crystalline $\text{I}_2 \cdot \mathbf{1}$ (gray line), and **1** after $\text{I}_{2(g)}$ absorption for 3 days (green line). (b) The same spectra as described above, but only the 2800-3500 cm^{-1} region shown.

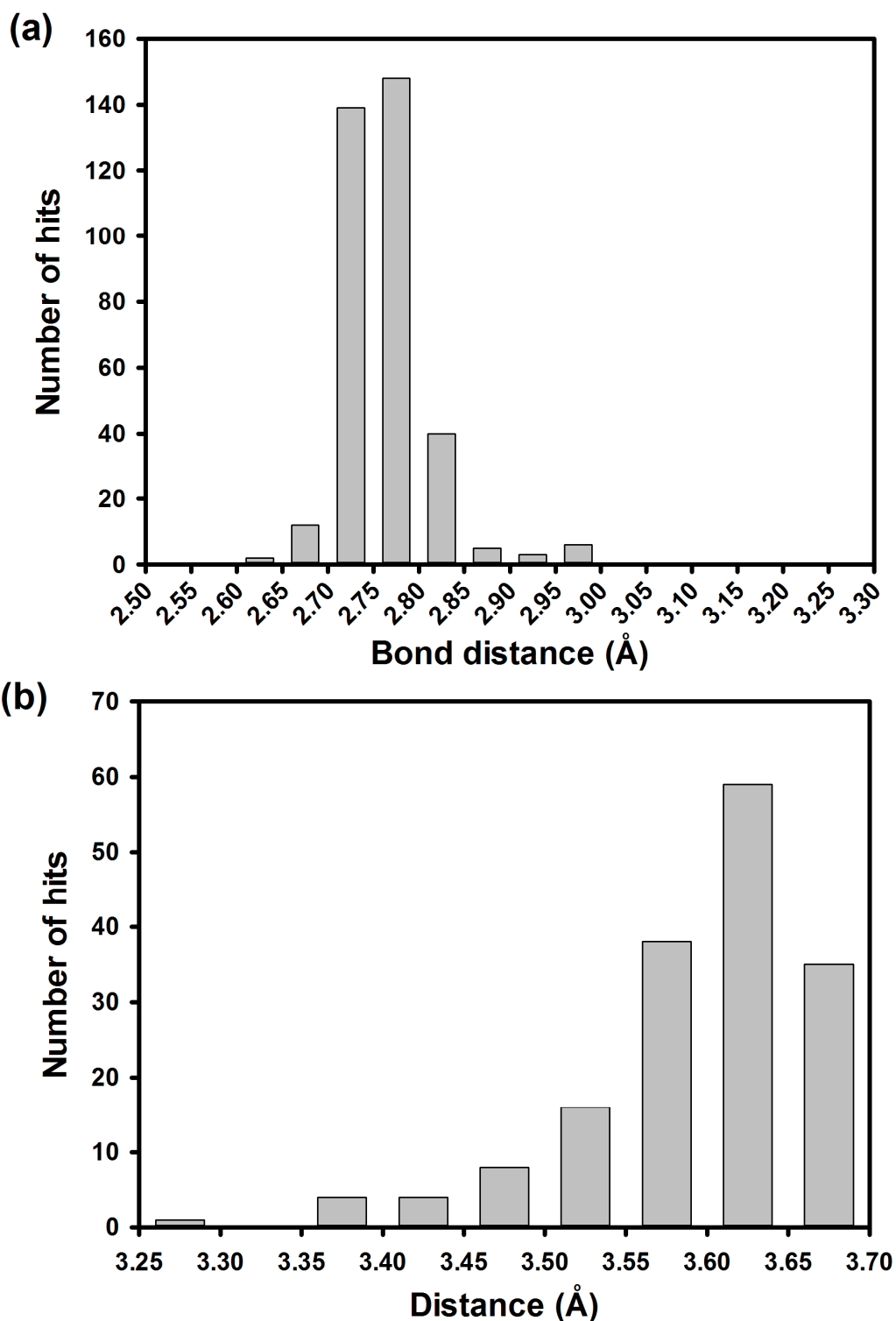


Fig. 2 (a) I-I bond distance histogram. A total of 355 hits with shortest one of 2.633 Å were found from a CSD survey for I-I bond distance (2.5-3.3 Å) using Mogul version 1.3. **(b) I...X (X = centroid of Ph) distance histogram.** The CSD search using ConQuest version 1.13 ($I\cdots X = 2.00\text{-}3.68$ Å, the van der Waals radii: C 1.70 Å; I 1.98 Å) gave 141 entries with 165 hits (the minimum distance = 3.272 Å). No hits were found from 2.00 to 3.25 Å. There are only one hit for I-I...X ($I\cdots X = 3.553$ Å).

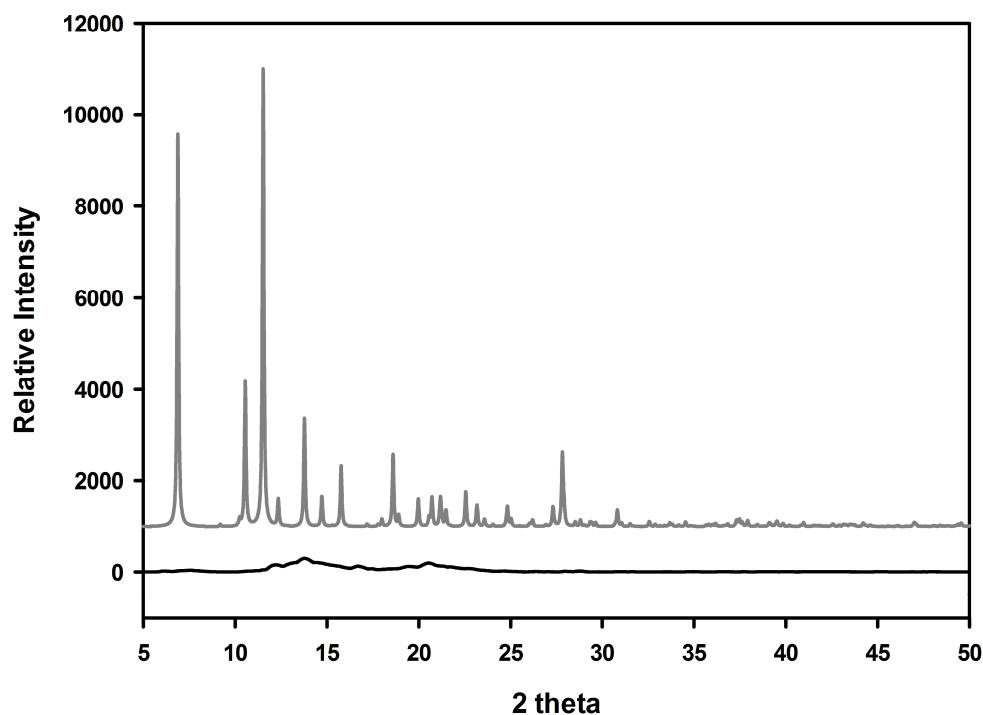


Fig. 3 PXRD profiles of DMF·1 (gray line) and the powders of 1 as synthesized (black line) indicating the amorphism of 1.

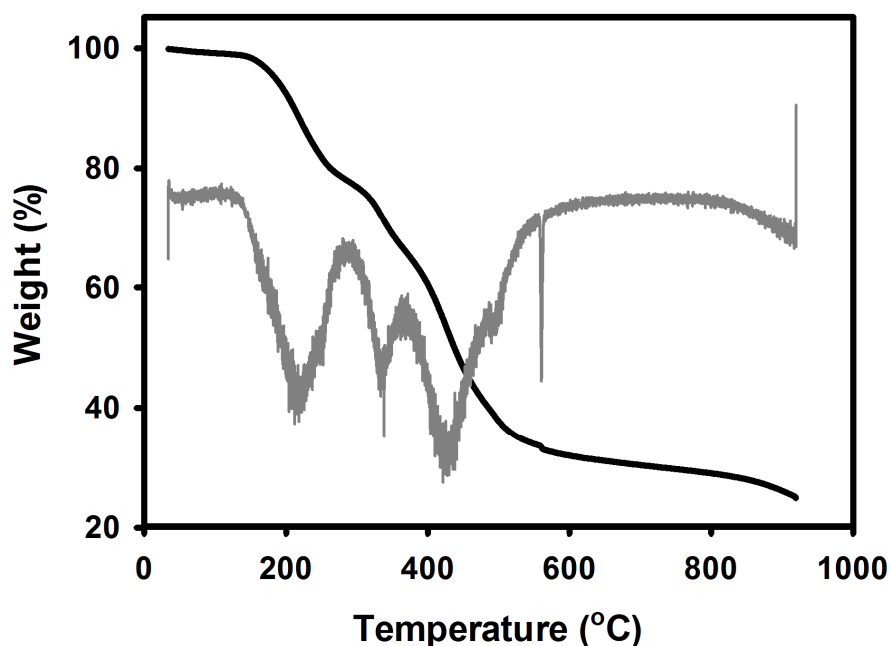


Fig. 4 Thermogravimetric analysis (black line) and corresponding derivative curves (gray line) for the I₂-treated powders of 1 demonstrating a multiple-step process, with the first step related to the loss of iodine in temperature range 140~270°C. The observed I₂ mass loss was 19.6% and the calculated I₂ mass loss was 18.5% for one I₂ per molecule I₂·1. Chemical degradation of 1 started at a temperature above 300°C. The analysis curve is nearly identical to the one for crystalline I₂·1.

Reference

1. G. M. Sheldrick, *SHELXTL, Version 5.1*. Bruker AXS Inc., Madison, WI, 1998.
2. L. E. Sutton, *Tables of Interatomic Distances and Configurations in Molecules and Ions*, Chemical Society Publications, UK, 1965.
3. P. van der Sluis, A. L. Spek, *Acta Cryst.* 1990, **A46**, 194-201.