Supplementary Information

Combined Analysis of 1,3-Benzodioxoles by Crystalline Sponge X-ray Crystallography and Laser Desorption Ionization Mass Spectrometry

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Crystallographic data (Table SI1)

Table SI1 Crystallographic data for the Crystalline sponge, CS 1 encapsulating safrole ($2 \subset 1a$), piperonyl acetone ($3 \subset 1b$), piperonyl methyl ketone ($4 \subset 1b$), and piperonylonitrile ($5 \subset 1b$)

<table>
<thead>
<tr>
<th>CS</th>
<th>2 $\subset 1a$</th>
<th>3 $\subset 1b$</th>
<th>4 $\subset 1b$</th>
<th>5 $\subset 1b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>$C_{53.4}H_{41.4}I_{6.0}N_{12}O_{3.5}Zn_{3.0}$</td>
<td>$C_{64.6}H_{58.3}Cl_{6.0}O_{12}Zn_{3.0}$</td>
<td>$C_{76}H_{64}Cl_{6}O_{12}Zn_{3.0}$</td>
<td>$C_{57.1}H_{41.6}Cl_{6}O_{12}Zn_{3.0}$</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$C2/c$</td>
<td>$C2/c$</td>
<td>$C2/c$</td>
<td>$C2/c$</td>
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<tr>
<td>$a$ (Å)</td>
<td>35.0630(15)</td>
<td>33.0803(15)</td>
<td>33.1389(13)</td>
<td>33.0732(15)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>14.7661(5)</td>
<td>14.4234(6)</td>
<td>14.5129(4)</td>
<td>14.4606(5)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>31.2601(12)</td>
<td>32.0307(13)</td>
<td>32.1744(11)</td>
<td>31.2748(12)</td>
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<tr>
<td>$\beta$ (°)</td>
<td>101.654(4)</td>
<td>102.207(3)</td>
<td>102.912(3)</td>
<td>101.909(3)</td>
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<tr>
<td>$V$ (Å$^3$)</td>
<td>15851.1(11)</td>
<td>14937.3(11)</td>
<td>15082.7(9)</td>
<td>14635.5(10)</td>
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<td>$\theta$ range (°)</td>
<td>4.888-65.495</td>
<td>3.355-69.323</td>
<td>2.736-65.342</td>
<td>3.347-65.347</td>
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<tr>
<td>Z</td>
<td>8</td>
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<td>8</td>
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<td>Density (g/cm$^3$)</td>
<td>1.563</td>
<td>1.351</td>
<td>1.538</td>
<td>1.277</td>
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<td>Temperature (K)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
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<tr>
<td>$\mu$ (mm$^{-1}$)</td>
<td>19.735</td>
<td>3.551</td>
<td>3.655</td>
<td>3.569</td>
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<td>$F$ (000)</td>
<td>7054</td>
<td>6207</td>
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<td>$h$, $k$, $l$</td>
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<td>-16 $\leq k \leq$ 16</td>
<td>-16 $\leq k \leq$ 17</td>
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<tr>
<td>$-36 \leq l \leq 36$</td>
<td>$-36 \leq l \leq 37$</td>
<td>$-37 \leq l \leq 37$</td>
<td>$-36 \leq l \leq 36$</td>
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<tr>
<td>Crystal size (mm$^3$)</td>
<td>0.07×0.05×0.03</td>
<td>0.13×0.09×0.03</td>
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<td>Total reflections</td>
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<td>Unique reflections</td>
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<td>13602</td>
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<tr>
<td>$R_{int}$</td>
<td>0.0709</td>
<td>0.0251</td>
<td>0.0608</td>
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<td>Completeness data</td>
<td>0.959</td>
<td>0.986</td>
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<td>restraints</td>
<td>548</td>
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<td>410</td>
<td>700</td>
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<td>parameters</td>
<td>966</td>
<td>1199</td>
<td>982</td>
<td>1095</td>
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<td>GoF (%)</td>
<td>1.022</td>
<td>1.033</td>
<td>1.030</td>
<td>1.013</td>
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<td>$R_1/wR_2$ ($I &gt; 2\sigma(I)$)</td>
<td>0.0574/0.1546</td>
<td>0.0744/0.2442</td>
<td>0.0750/0.2230</td>
<td>0.0601/0.1958</td>
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<tr>
<td>$R_1/wR_2$</td>
<td>0.1018/0.1803</td>
<td>0.0843/0.2629</td>
<td>0.1041/0.2505</td>
<td>0.0723/0.2119</td>
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<tr>
<td>CCDC</td>
<td>1586123</td>
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<td>1586121</td>
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</table>
X-ray structure analysis of 2 ⊂ 1a

a)

b)

I3A, I4A / I3B, I4B = 68/32 %

Fig. SI1 ORTEP view (30% probability level) of safrole 2.

a) full structure; b) the host framework.
C1A to O12A 25 %
C1B to O12B 50 %
C1C to O12C 50 %
C1D to O12D 50 %

Fig. SI2 ORTEP view (30% probability level) of safrole 2.
c) Molecule of safrole (position A, B, C, D).
X-ray analysis conditions for guest 2 assigned as A to D.

Some restraints were applied in refinement of a disordered model. By using DFIX restraints, most of the 1,2- and 1,3-distances were restrained to target values based on the standard distance of single and double bonds, and SIMU and DELU were applied for the whole disordered molecule in the pore as shown in Fig. SI3.

Fig. SI3 Restraints applied in the refinement of $2 \subset 1a$. 
X-ray structure analysis of 3 ⊂ 1b

a)

b)

Fig. SI4 ORTEP view (30% probability level) of piperonyl acetone 3.

a) full structure; b) the host framework.
Fig. SI5 ORTEP view (30% probability level) of piperonyl acetone 3.
c) Molecule of piperonyl acetone (position A, B, C, D, E); d) cyclohexane
X-ray structure analysis of 3 ⊂ 1b

C1A to O14A 54 %
C1B to O14B 54 %
C1C to O14C 46 %
C1D to O14D 27 %
C1E to O14E 46 %

C1H to C6H 54 %
X-ray analysis conditions for guest 3 assigned as A to E.

Some restraints were applied in refinement of a disordered model. By using DFIX restraints, most of the 1,2- and 1,3-distances were restrained to target values based on the standard distance of single and double bonds, and SIMU and DELU were applied for the whole disordered molecule in the pore as shown in Fig. SI6.

Fig. SI6 Restraints applied in the refinement of $3 \subset 1b$.
X-ray structure analysis of 4⊂ 1b

Fig. SI7 ORTEP view (30% probability level) of piperonyl methyl ketone 4. 
a) full structure; b) the host framework.
Fig. SI8 ORTEP view (30% probability level) of piperonyl methyl ketone 4.
c) Molecule of piperonyl methyl ketone (position A, B, C, D).

C1A to O13A 100%
C1B to O13B 100%
C1C to O13C 100%
C1D to O13D 100%
X-ray analysis conditions for guest 4 assigned as A to D.

Some restraints were applied in refinement of a disordered model. By using DFIX restraints, most of the 1,2- and 1,3-distances were restrained to target values based on the standard distance of single and double bonds, and SIMU and DELU were applied for the whole disordered molecule in the pore as shown in Fig. SI9.

Fig. SI9 Restraints applied in the refinement of 4 ⊂ 1b.
X-ray structure analysis of $5 \subset 1b$

a)

b)

Zn2A + Zn2B = 70 + 30 %
Cl3A, Cl4A / Cl3B, Cl4B = 70/30 %

Fig. SI10 ORTEP view (30% probability level) of piperonylonitrile 5.
a) full structure; b) the host framework.
Fig. SI11 ORTEP view (30% probability level) of piperonylnitrile (5).
c) Molecule of piperonylnitrile (position A, B, C, D, E); d) cyclohexane
X-ray analysis conditions for guest 5 assigned as A to E.

Some restraints were applied in refinement of a disordered model. By using DFIX restraints, most of the 1,2- and 1,3-distances were restrained to target values based on the standard distance of single and double bonds, and SIMU and DELU were applied for the whole disordered molecule in the pore as shown in Fig. SI12.

Fig. SI12 Restraints applied in the refinement of 5 ⊂ 1b.
· NMR data of extracts from $X \subset 1$ ($X = 2 - 5$).

Table SI2 Ratios of guest/TPT after decomposition of the CS

<table>
<thead>
<tr>
<th>CS</th>
<th>$2 \subset 1a$</th>
<th>$3 \subset 1b$</th>
<th>$4 \subset 1b$</th>
<th>$5 \subset 1b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMR (guest/TPT ratio)</td>
<td>0.32</td>
<td>1.37</td>
<td>1.66</td>
<td>1.76</td>
</tr>
</tbody>
</table>
Fig. SI13 $^1$H NMR spectrum of safrole 2 extracted from crystalline sponge after decomposition with hydrochloric acid. (CDCl$_3$, 300 K, 400 MHz)
Fig. SI14 $^1$H NMR spectrum of piperonyl acetone 3 extracted from crystalline sponge after decomposition with hydrochloric acid. (CDCl$_3$, 300 K, 400 MHz)
Fig. SI15 $^1$H NMR spectrum of piperonyl methyl ketone 4 extracted from crystalline sponge after decomposition with hydrochloric acid. (CDCl$_3$, 300 K, 400 MHz)
Fig. SI16 $^1$H NMR spectrum of piperonylonitrile 5 extracted from crystalline sponge after decomposition with hydrochloric acid. (CDCl$_3$, 300 K, 400 MHz)
Interaction between the CS frameworks and guests for $X \subseteq 1$ ($X = 2 - 5$)

a) CH-halogen interaction between molecule D and the iodine atom of ZnI$_2$, I4B-C3D 3.82(4) Å, b) CH-$\pi$ interaction between CH of 1,3-benzodioxole group and triazine ring, C6C-N20 3.35(6) Å.

Fig. SI17 Structural analysis drawing of safrole 2.

a) CH-halogen interaction between molecule D and the iodine atom of ZnI$_2$, I4B-C3D 3.82(4) Å, b) CH-$\pi$ interaction between CH of 1,3-benzodioxole group and triazine ring, C6C-N20 3.35(6) Å.
Fig. SI18 Structural analysis drawing of piperonyl acetone 3.
a) CH-O interaction between molecule of B and the TPT ligand, O14B-C27 3.341(15) Å.
b) CH-halogen interaction between molecule of E and the chlorine atom of ZnCl₂, C6E-Cl6 3.49(5) Å.
Fig. SI19 Structural analysis drawing of piperonylonitrile 5.

a) CH-halogen interaction between molecule of A and the chlorine atom of ZnCl$_2$, C6A-Cl6 3.647(19) Å.

b) CH-halogen interaction between molecule of B and the chlorine atom of ZnCl$_2$. C9B-Cl6 3.611(18) Å, and $\pi$-$\pi$ interaction between molecule of B and nitrogen atom of triazine framework, C1B-Cl6 3.57(2) Å.

c) CH-halogen interaction between molecule of C and the chlorine atom of ZnCl$_2$, C1C-Cl2 3.54(3) Å and C9C-Cl1 3.51(3) Å.
1D average spectrum of the guests for $X \subseteq 1$ ($X = 4, 5$)

**Fig. SI20** Optical image a) and IMS at m/z 313.0 b) and 108.0 c), and 1 D mass spectrum obtained from IMS and some assignments of $4 \subseteq 1b$ d)

**Fig. SI21** Optical image a) and IMS at m/z 313.0 b) and 108.0 c), and 1 D mass spectrum obtained from IMS and some assignments of $5 \subseteq 1b$ d).