# Formation of tetrameric water clusters driven by a cavitand template 

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a)

b)


Figure S1. a) Ortep view ( $20 \%$ ellipsoid probability) of the molecular structure of compound Tiiii[H, $\left.\mathbf{C H}_{3}, \mathbf{C H}_{3}\right] \cdot \mathbf{4} \mathbf{H}_{\mathbf{2}} \mathbf{O}$ (1). Symmetry operations: (2) $1 / 2-x$; $1 / 2-y$; z. (3) $1 / 2-y$; x; z. (4) y; $1 / 2-x$; z. Only the hydrogen atoms involved in hydrogen bonds (dotted lines) are drawn; b) CPK top and side views of (1).
a)

b)


Figure S2. a) Ortep view ( $10 \%$ ellipsoid probability) of the molecular structure of compound Tiiii $\left[\mathrm{H}, \mathbf{C H}_{3}, \mathbf{C H}_{3}\right] \cdot \mathbf{C H}_{3} \mathbf{O H} \cdot \mathbf{4} \mathbf{H}_{2} \mathbf{O}$ (2). Symmetry operations: (2) $1 / 2-\mathrm{x}$; $1 / 2-\mathrm{y}$; z. (3) $1 / 2-\mathrm{y}$; x; z. (4) y; $1 / 2-x ; z$. Only one of the four possible orientations of the methanol guest is shown. Hydrogen atoms are omitted for clarity; b) CPK top and side views of (2).


Figure S3. a) Ortep view ( $20 \%$ ellipsoid probability) of the molecular structure of compound Tiiii $\left[\mathbf{H}, \mathbf{C H}_{3}, \mathbf{C H}_{3}\right] \cdot \mathbf{H O C H}_{2} \mathbf{C H}_{2} \mathbf{O H} \cdot \mathbf{4} \mathbf{H}_{2} \mathbf{O}$ (3). The lattice dichloromethane molecule is omitted for clarity. Only the hydrogen atoms involved in hydrogen bonds (dotted lines) are drawn; b) CPK top and side views of (3).


Figure S4. Self-assembly of the Tiiii[ $\left.\mathbf{H}, \mathbf{C H}_{3}, \mathbf{C H}_{3}\right] \cdot \mathbf{C H}_{3} \mathbf{O H} \cdot \mathbf{4} \mathbf{H}_{\mathbf{2}} \mathbf{O}$ (2) complexes in the infinite up-up columnar arrangement running parallel to the crystallographic caxis. Each up-up column is surrounded by four nearest neighboring down-down parallel columns of complexes. Only relevant hydrogen atoms have been reported. Water molecules are represented as red balls.

Materials. The cavitand Tiiii $\left[\mathrm{H}, \mathrm{CH}_{3}, \mathrm{CH}_{3}\right]$ was prepared following a published procedure. ${ }^{1}$
X-ray Crystallographic Studies. Crystal data and experimental details for data collection and structure refinement are reported in Table S1.

The crystal structures of compounds $\mathbf{1}, \mathbf{2}$, and $\mathbf{3}$ were determined by X-ray diffraction methods. Intensity data and cell parameters were recorded at room temperature for $\mathbf{1}$ and $\mathbf{2}$ and at 173 K for 3 (due to the instability of the crystal at room temperature) on a Bruker AXS Smart 1000 single-crystal diffractometer ( $\mathrm{MoK}_{\alpha}$ radiation) equipped with a CCD area detector. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. ${ }^{2}$ The structures was solved by Direct Methods using the SIR97 program ${ }^{3}$ and refined on $F_{o}{ }^{2}$ by full-matrix least-squares procedures, using the SHELXL-97 program. ${ }^{4}$

The PLATON SQUEEZE procedure ${ }^{5}$ was used for compound 3 to treat regions of diffuse solvent which could not be sensibly modelled in terms of atomic sites. Their contribution to the diffraction pattern was removed and modified $F_{o}{ }^{2}$ written to a new HKL file. The number of electrons thus located, 80 per unit cell, are included in the formula, formula weight, calculated density, $\mu$ and $\mathrm{F}(000)$. This residual electron density was assigned to two molecules of dichloromethane solvent per unit cell (two molecules of dichloromethane would give 84 e).

All non-hydrogen atoms were refined with anisotropic atomic displacements. The hydrogen atoms were included in the refinement at idealized geometry (C-H $0.95 \AA$ ) and refined "riding" on the corresponding parent atoms. The hydrogen atoms of the water molecules in compound $\mathbf{1}$ were found in the difference Fourier map. In compound 2, the water and methanol hydrogen atoms could neither be found in the difference Fourier map nor calculated. In compound 3, the hydrogen atoms of the ethylene glycol were calculated using the program implemented in WinGX based on the method of M. Nardelli. ${ }^{6}$ The water hydrogen were partly found in the difference Fourier map and partly calculated using the above mentioned program.

The weighting schemes used in the last cycle of refinement were $w=1 /\left[\sigma^{2} F_{o}{ }^{2}+\right.$ $\left.(0.0180 P)^{2}\right], w=1 /\left[\sigma^{2} F_{o}{ }^{2}+(0.1008 P)^{2}\right]$ and $w=1 /\left[\sigma^{2} F_{o}{ }^{2}+(0.0671 P)^{2}\right]$ where $P=\left(F_{o}{ }^{2}+2 F_{c}{ }^{2}\right) / 3$ for $\mathbf{1 , 2} \mathbf{2}$ and $\mathbf{3}$ respectively.

Molecular geometry calculations were carried out using the PARST97 program. ${ }^{7}$ Drawings were obtained by ORTEP3 in the WinGX suite. ${ }^{8}$

Crystallographic data (excluding structure factors) for the structure reported have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-737537 (1) -737538 (2) and -737539 (3) and can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk]

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Table S1. Crystal data and structure refinement information for compounds $\mathbf{T i i i i}\left[\mathbf{H}, \mathbf{C H}_{3}\right.$, $\left.\mathbf{C H}_{3}\right] \cdot \mathbf{4} \mathbf{H}_{2} \mathrm{O} \quad$ (1), Tiiii $\left[\mathrm{H}, \quad \mathbf{C H}_{3}, \quad \mathbf{C H}_{3}\right] \cdot \mathbf{C H}_{3} \mathbf{O H} \cdot \mathbf{4} \mathbf{H}_{2} \mathbf{O} \quad$ (2) and $\quad$ Tiiii $\left[\mathrm{H}, \quad \mathbf{C H}_{3}\right.$, $\left.\mathrm{CH}_{3}\right] \cdot \mathrm{HOCH}_{2} \mathrm{CH}_{2} \mathbf{O H} \cdot 4 \mathrm{H}_{2} \mathrm{O}$ (3)

| Compound | 1 | 2 | 3 |
| :---: | :---: | :---: | :---: |
| Formula | $\mathrm{C}_{36} \mathrm{H}_{44} \mathrm{O}_{16} \mathrm{P}_{4}$ | $\mathrm{C}_{37} \mathrm{H}_{48} \mathrm{O}_{17} \mathrm{P}_{4}$ | $\mathrm{C}_{40} \mathrm{H}_{54} \mathrm{O}_{18} \mathrm{P}_{4} \mathrm{Cl}_{4}$ |
| Molecular weight | 856.59 | 888.63 | 1088.51 |
| Crystal system | Tetragonal | Tetragonal | Triclinic |
| Space group | P4/n | $P 4 / \mathrm{n}$ | $P-1$ |
| $a / \AA$ | 14.396(8) | 14.352(2) | 10.3676(4) |
| $b / \AA$ | - | - | 13.1307(5) |
| c / $\AA$ | 9.799(5) | 9.822(2) | 19.1132(8) |
| $\alpha /{ }^{\circ}$ | - | - | 69.980(1) |
| $\beta /{ }^{\circ}$ | - | - | 88.713(1) |
| $\gamma /{ }^{\circ}$ | - | - | 82.935(1) |
| $\mathrm{V} / \AA^{3}$ | 2031(2) | 2023.2(6) | 2425.6(2) |
| Z | 2 | 2 | 2 |
| T / K | 293(2) | 293(2) | 173(2) |
| $\rho / \mathrm{g} \mathrm{cm}^{-3}$ | 1.401 | 1.459 | 1.490 |
| $\mu / \mathrm{mm}^{-1}$ | 0.256 | 0.262 | 0.448 |
| $F(000)$ | 896 | 932 | 1132 |
| Data / parameters | 2354 / 140 | 2626/144 | 11553 / 611 |
| Total reflections | 11151 | 12598 | 25175 |
| Unique reflections ( $\mathrm{R}_{\text {int }}$ ) | 2354 (0.0994) | 2626 (0.0260) | 11553 (0.0385) |
| Observed reflections $[I>2 \sigma(I)]$ | 1187 | 1836 | 7160 |
| Goodness-of-fit on $F^{2 \mathrm{a}}$ | 1.006 | 1.008 | 0.998 |
| R indices $[1>2 \sigma(I)]^{\mathrm{b}} \mathrm{R} 1$, wR2 | 0.0481, 0.0765 | 0.0467, 0.1417 | 0.0515, 0.1288 |
| Largest diff. peak and hole / $\mathrm{e} \AA^{-3}$ | 0.423, -0.288 | 0.549, -0.228 | 0.709, -0.415 |

${ }^{\mathrm{a}}$ Goodness-of-fit $\mathrm{S}=\left[\Sigma \mathrm{w}\left(F_{o}{ }^{2}-F_{c}{ }^{2}\right)^{2} /(\mathrm{n}-\mathrm{p})\right]^{1 / 2}$, where n is the number of reflections and p the number of parameters. ${ }^{\mathrm{b}} \mathrm{R} 1=\Sigma\left\|F_{o}\left|-\left|F_{c} \| / \Sigma\right| \mathrm{F}_{\mathrm{o}}\right|\right.$, wR2 $=\left[\Sigma\left[\mathrm{w}\left(F_{o}^{2}-F_{c}^{2}\right)^{2}\right] / \Sigma\left[\mathrm{w}\left(F_{o}^{2}\right)^{2}\right]\right]^{1 / 2}$.

Table S2. H-bonding in Tiiii[ $\left.\mathrm{H}, \mathrm{CH}_{3}, \mathrm{CH}_{3}\right] \cdot \mathbf{4 H _ { 2 }} \mathbf{O}$ (1)

|  | $\mathrm{H} \cdots$ Acceptor $(\AA)$ | Donor-H $(\AA)$ | Donor $\cdots$ Acceptor $(\AA)$ | Donor-H $\cdots$ Acceptor $\left({ }^{\circ}\right)$ |
| :--- | :--- | :--- | :--- | :--- |
| water $/ P=O$ | $1.85(4)$ | $0.99(4)$ | $2.801(5)$ | $159.4(9)$ |
| Water/water | $2.05(4)$ | $0.98(3)$ | $2.858(5)$ | $138.9(9)$ |

Table S3. H-bonding in Tiiii[ $\left.\mathrm{H}, \mathrm{CH}_{3}, \mathrm{CH}_{3}\right] \cdot \mathrm{CH}_{3} \mathbf{O H} \cdot \mathbf{4} \mathrm{H}_{2} \mathrm{O}$ (2)

|  | $\mathrm{H} \cdots$ Acceptor $(\AA)$ | Donor-H $(\AA)$ | Donor $\cdots$ Acceptor $(\AA)$ |
| :--- | :--- | :--- | :--- |
| water $/ P=O$ | Donor-H $\cdots$ Acceptor $\left({ }^{\circ}\right)$ |  |  |
| Water/water |  | $2.807(3)$ |  |
| guest $/ P=O$ | $2.916(5)$ |  |  |
| guest/water | $2.958(8)$ |  |  |
|  |  | $2.796(9)$ |  |

Table S4. H-bonding in Tiiii $\left[\mathrm{H}, \mathrm{CH}_{3}, \mathrm{CH}_{3}\right] \cdot \mathbf{H O C H}_{2} \mathrm{CH}_{2} \mathbf{O H} \cdot \mathbf{4 H _ { 2 }} \mathbf{O}$ (3)

|  | $\mathrm{H} \cdots$ Acceptor $(\AA)$ | Donor-H $(\AA)$ | Donor $\cdots$ Acceptor $(\AA)$ | Donor-H $\cdots$ Acceptor $\left({ }^{\circ}\right)$ |
| :--- | :--- | :--- | :--- | :--- |
| water $/ P=O$ | $1.97(3), 1.87(2)$ | $0.90(3) ; 0.90(2)$ | $2.817(3), 2.762(3)$ | $154.7(9), 168.3(9)$ |
| water/water | $1.85(1), 1.92(3)$, | $0.91(1), 0.90(3)$ <br> $1.93(5), 1.93(3)$ | $2.758(4), 2.786(3)$, | $175.2(9), 160.1(9)$, |
|  |  | $0.90(5), 0.91(3)$ | $2.820(5), 2.831(6)$ | $166.2(9), 177.8(9)$ |
| guest $/ P=O$ | $1.77(4), 1.72(5)$ | $0.95(3), 0.96(5)$ | $2.683(4), 2.662(3)$ | $160.0(9), 168.8(9)$ |
| guest/water | $1.79(1), 1.83(2)$ | $0.91(1), 0.91(2)$ | $2.692(4), 2.660(4)$ | $172.2(9), 150.4(9)$ |

