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Supporting Information for "Self-Assembed of Helices from 2,2´-Biimidazoles"

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Ethyl 2-bromo-4-propyl-5-imidazolecarboxylate (14): Ethyl 4-propyl-5-imidazolecarboxylate **2** (3.64 g, 20.0 mmol) was dissolved in 90 mL of glacial acetic acid with stirring. The resulting pale yellow solution was treated with sodium acetate (8.20 g, 100 mmol) in portions. Once the salt had dissolved, a solution of bromine (3.36 g, 21.0 mmol) in 10 mL of glacial acetic acid was added dropwise to the stirred reaction mixture. The bromine addition was complete after 30 min, giving rise to a solution with a persistent orange color. After 18 h, the volatile components were removed *in vacuo* to afford a white solid. Dichloromethane (200 mL) was added to the solid, and the suspension was stirred vigorously for 15 min. After filtering to remove insoluble material(s), the filtrate was evaporated to a white solid. The crude product was purified by flash column chromatography on silica gel using EtOAc as the eluent. After evaporation, a total of 2.93 g (56%) of the product was obtained as a white, crystalline

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solid. TLC (EtOAc): $R_f = 0.62$. ^{1}H NMR ($CDCl_3$): $\delta = 0.92$ (t, 3H, $CH_2CH_2CH_3$), 1.27 (t, 3H, OCH_2CH_3), 1.67 (m, 2H, $CH_2CH_2CH_3$), 2.92 (t, 2H, $CH_2CH_2CH_3$), 4.27 (q, 2H, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): $\delta = 3.7, 14.2, 22.5, 28.4, 60.6, 117.6, 125.9, 146.4, 161.6$. LRMS (CI+): *m/z* 261 [$(M + H)^+$, 100], 263 [$(M + 2 + H)^+$, 100]. HRMS (CI+): calcd for $C_9H_{14}N_2O_2Br$ 261.0239; found 261.0246. Anal. Calcd for $C_9H_{13}N_2O_2Br$: C, 41.40; H, 5.02; N, 10.73. Found: C, 41.46; H, 5.00; N, 10.71.

Ethyl 1-[2-(trimethylsilyl)ethoxymethyl]-5-propyl-4-imidazolecarboxylate (15a): To an oven-dried 250 mL round-bottomed flask containing a stir bar under Ar was added sodium hydride (60% dispersion, 0.96 g, 24.0 mmol) and 50 mL of dry THF. Then, over the course of 30 sec. **2** (3.64 g, 20.0 mmol) was added, causing H_2 to evolve. After several minutes of stirring, gas evolution ceased and the gray-white suspension was treated with 2-(trimethylsilyl)ethoxymethyl chloride (90%, 3.70 g, 20.0 mmol), causing the mixture to take on a green-gold color. After 24 h, the excess NaH was quenched via the slow dropwise addition of water. The volatile components were then removed using a rotary evaporator to afford a gummy gold residue, which was partitioned between EtOAc and water. The organic layer was washed with brine, dried over Na_2SO_4, filtered and evaporated to yield a viscous gold oil. The product was isolated as an almost colorless oil by flash column chromatography on silica gel using EtOAc as the eluent. The yield was 4.05 g (65%). TLC (EtOAc): $R_f = 0.36$. ^{1}H NMR ($CDCl_3$): $\delta = -0.04$ (s, 9H, $Si(CH_3)_3$), 0.87 (t, 2H, OCH_2CH_2Si), 0.96 (t, 3H, $CH_2CH_2CH_3$), 1.37 (t, 3H, OCH_2CH_3), 1.61 (m, 2H, $CH_2CH_2CH_3$), 2.95 (t, 2H, $CH_2CH_2CH_3$), 3.45 (t, 2H, OCH_2CH_2Si), 4.33 (q, 2H, OCH_2CH_3), 5.23 (s, 2H, NCH_2O), 7.50 (s, 1H, imid. C_2H). ^{13}C NMR ($CDCl_3$): $\delta = 1.6, 13.8, 14.3, 17.6, 22.7, 25.5, 60.1, 66.2, 74.0, 129.9, 136.8,$

140.0. 163.3. LRMS (CI+): *m/z* 313 [$(M + H)^+$, 100]. HRMS (CI+): calcd for $C_{15}H_{29}N_2O_3Si$ 313.1947; found 313.1943. Anal. Calcd for $C_{15}H_{28}N_2O_3Si$: C, 57.66; H, 9.03; N, 8.96. Found: C, 57.37; H, 9.06; N, 8.91.

Ethyl 1-[2-(trimethylsilyl)ethoxymethyl]-4-propyl-5-imidazolecarboxylate (15b): The procedure immediately above afforded 1.52 g (24%) of this almost colorless oil, isolated during chromatographic purification of **15a**. TLC (EtOAc): $R_f = 0.55$. ^{1}H NMR ($CDCl_3$): δ = -0.05 (s, 9H, $Si(CH_3)_3$), 0.88 (t, 2H, OCH_2CH_2Si), 0.94 (t, 3H, $CH_2CH_2CH_3$), 1.36 (t, 3H, OCH_2CH_3), 1.68 (m, 2H, $CH_2CH_2CH_3$), 2.84 (t, 2H, $CH_2CH_2CH_3$), 3.52 (t, 2H, OCH_2CH_2Si), 4.32 (q, 2H, OCH_2CH_3), 5.60 (s, 2H, NCH_2O), 7.64 (s, 1H, imid. C_2H). ^{13}C NMR ($CDCl_3$): δ = -1.6, 13.8, 14.1, 17.7, 22.6, 31.2, 60.2, 66.4, 75.8, 118.1, 140.4, 152.8, 160.8.

Ethyl 2-iodo-1-[2-(trimethylsilyl)ethoxymethyl]-5-propyl-4-imidazolecarboxylate (16): In an oven-dried 100 mL round-bottomed flask, SEM-protected imidazole **15a** (1.40 g, 4.48 mmol) was dissolved in 45 mL dry THF with stirring under Ar. *N*-Iodosuccinimide (95%, 1.17 g, 4.93 mmol) was added in one portion, and the flask heated to reflux in the dark. After 3 d, the dark red solution was allowed to cool, and saturated aqueous $Na_2S_2O_3$ was added dropwise until the red color disappeared. The volatile components were removed in vacuo, and the brown oily residue was partitioned between EtOAc and water. The organic phase was washed with brine, dried over Na_2SO_4, filtered and evaporated to yield an orange oil. Flash column chromatography on silica gel using EtOAc as the eluent afforded 1.43 g (73%) of the desired iodide as a very

viscous yellow oil. The product slowly solidified upon standing under vacuum. ^{1}H NMR ($CDCl_3$): δ = -0.07 (s, 9H, Si(CH_3)$_3$), 0.85 (t, 2H, OCH_2CH_2Si), 0.92 (t, 3H, $CH_2CH_2CH_3$), 1.31 (t, 3H, OCH_2CH_3), 1.56 (m, 2H, $CH_2CH_2CH_3$), 2.95 (t, 2H, $CH_2CH_2CH_3$), 3.51 (t, 2H, OCH_2CH_2Si), 4.27 (q, 2H, OCH_2CH_3), 5.20 (s, 2H, NCH_2O). ^{13}C NMR ($CDCl_3$): δ = 1.6, 13.7, 14.3, 17.7, 22.7, 26.4, 60.3, 66.5, 75.4, 91.3, 133.0, 143.8, 162.2. LRMS (CI+): *m*/*z* 439 [$(M + H)^+$, 100]. HRMS (CI+): calcd for $C_{15}H_{28}N_2O_3ISi$ 439.0914; found 439.0906.

X-ray Experimental for $(C_{16}H_{22}N_4O_4)_3\bullet(CH_3OH)_{0.5}$ (12): Crystals grew as thin colorless needles by slow evaporation from a methanol solution. The data crystal was cut from a larger crystal and had approximate dimensions 0.19 × 0.22 × 0.56 mm. The data were collected using the ω-scan technique at 4 - 8°/min, with a scan range of 1.0° in ω to a $2\theta_{max}$ = 50° at 193 K on a Siemens P4 diffractometer, equipped with a Nicolet LT-2 low-temperature device and using a graphite monochromator with MoKαradiation (λ = 0.71073 Å). Details of crystal data, data collection and structure refinement are listed in Table S1. Four reflections (6,-2,-2; 3,-3,4; -4,-6,1; 4,2,-7) were remeasured every 96 reflections to monitor instrument and crystal stability. A smoothed curve of the intensities of these check reflections was used to scale the data. The scaling factor ranged from 0.973 - 1.04. The data were corrected for Lp effects but not for absorption. Data reduction, decay correction, structure solution and refinement were performed using the SHELXTL/PC software package.[1] The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms. The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2 × Ueq of the attached atom (1.5 × Ueq for

methyl hydrogen atoms). On molecule B, one propyl sidechain was disordered about two orientations. The site occupancy was refined while refining a common isotropic displacement parameter for the atoms involved, C23B and C24B, and C23C and C24C. The site occupancy factor for C23B and C24B refined to 66(2)%. Thereafter, the displacement parameters were refined without constraint. The hydrogen atoms on the imidazole nitrogens were observed in a ΔF map and refined with isotropic displacement parameters. One partial occupancy methanol molecule was located in the asymmetric unit. It was assigned a site occupancy factor of 1/2 after refining with unusually high Uiso's when the site occupancy factor was set to 1. The function $\sum w(|F_o|^2 - |F_c|^2)^2$ was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.02*P)^2]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. The data were corrected for secondary extinction effects. The correction takes the form: $F_{corr} = kF_c/[1 + (4.6(3)x10^{-7})* F_c^2 \lambda^3/(\sin 2\theta)]^{0.25}$ where k is the overall scale factor. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography.[2] All figures were generated using SHELXTL/PC. Figure S1 shows the atomic numbering scheme. Positional and thermal parameters and bond lengths and angles are given below in Tables S2-S5. Structure factors are available by request from the authors.

Figure S1(a). View of molecule 1 of $(C_{16}H_{22}N_4O_4)4$-1/2CH_3OH showing the atom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

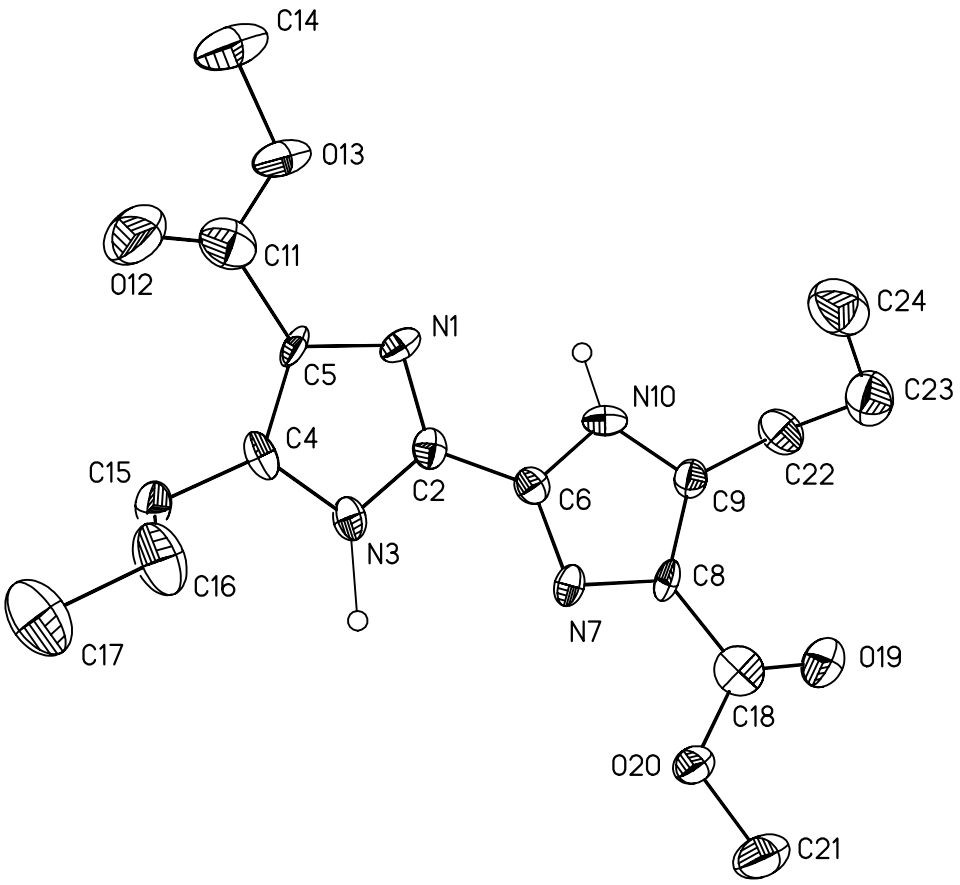


Figure S1(b). View of molecule 2 of $(C_{16}H_{22}N_4O_4)_4$-1/2CH_3OH showing the atom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

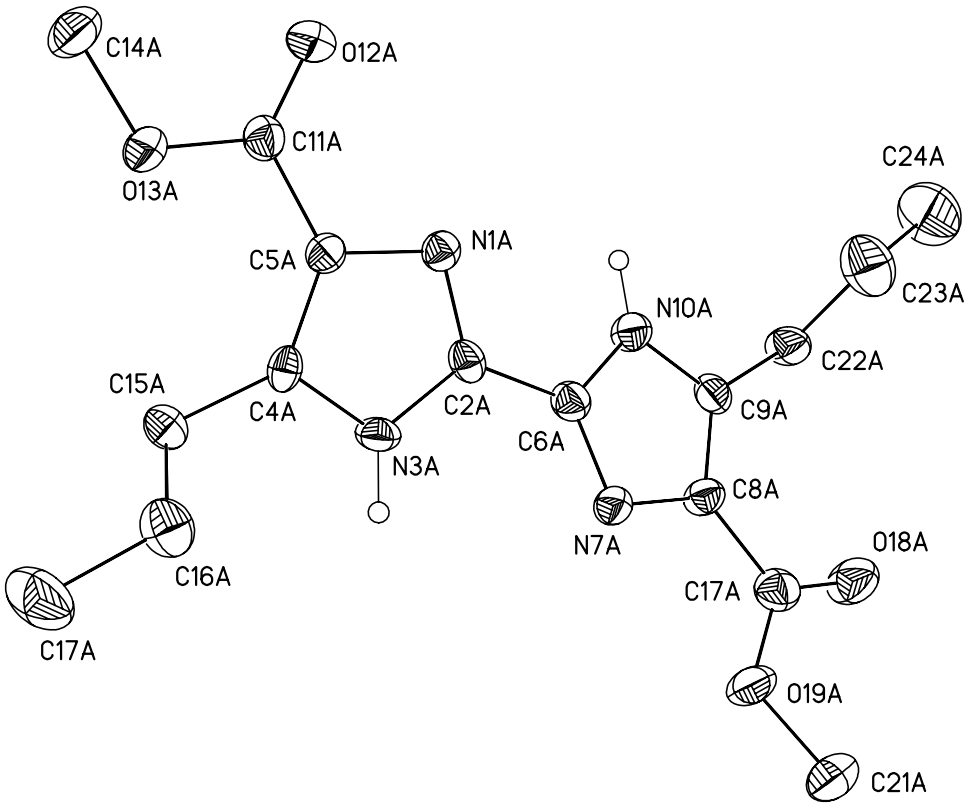


Figure S1(c). View of molecule 3 of $(C_{16}H_{22}N_4O_4)_4$-1/2CH_3OH showing the atom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

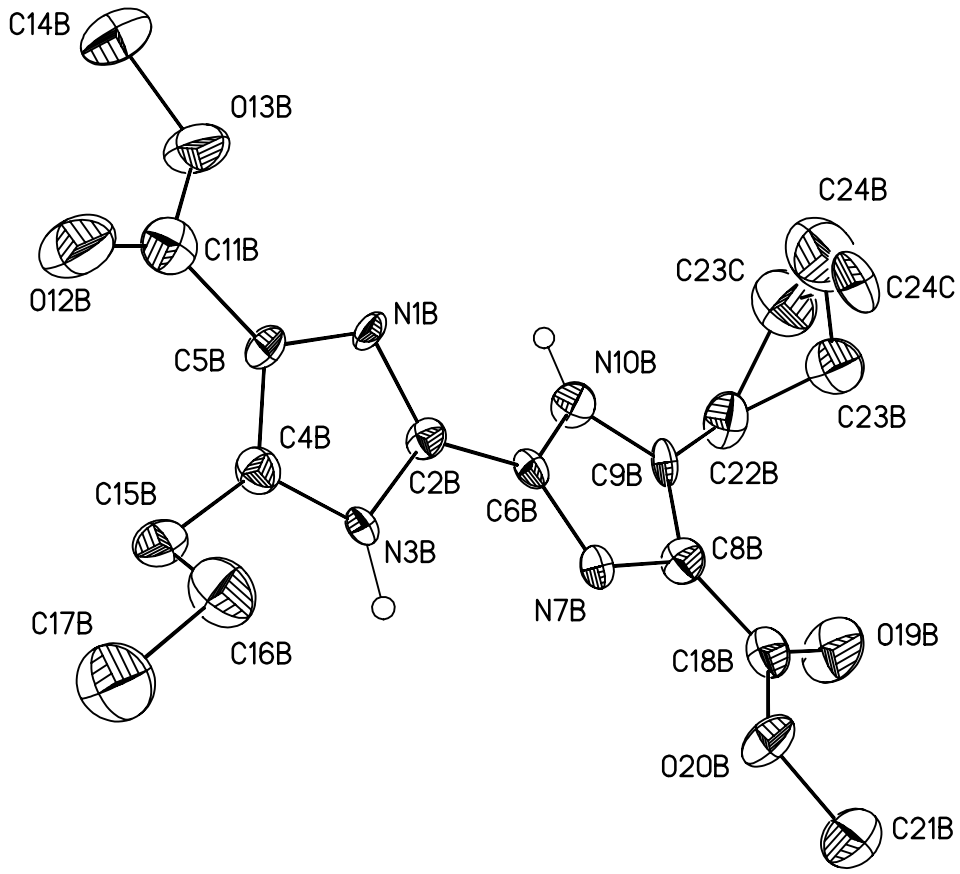


Figure S1(d). View of a portion of one column of H-bound bi-imidazoles. Dashed lines indicate a N-H..N hydrogen bonding interaction. The column extends parallel to the **b** axis.

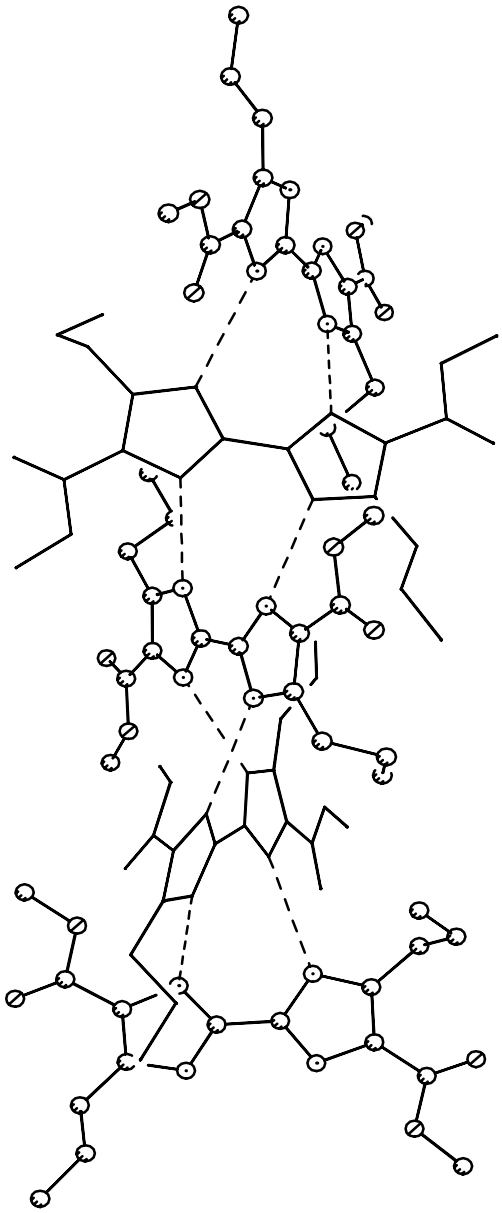
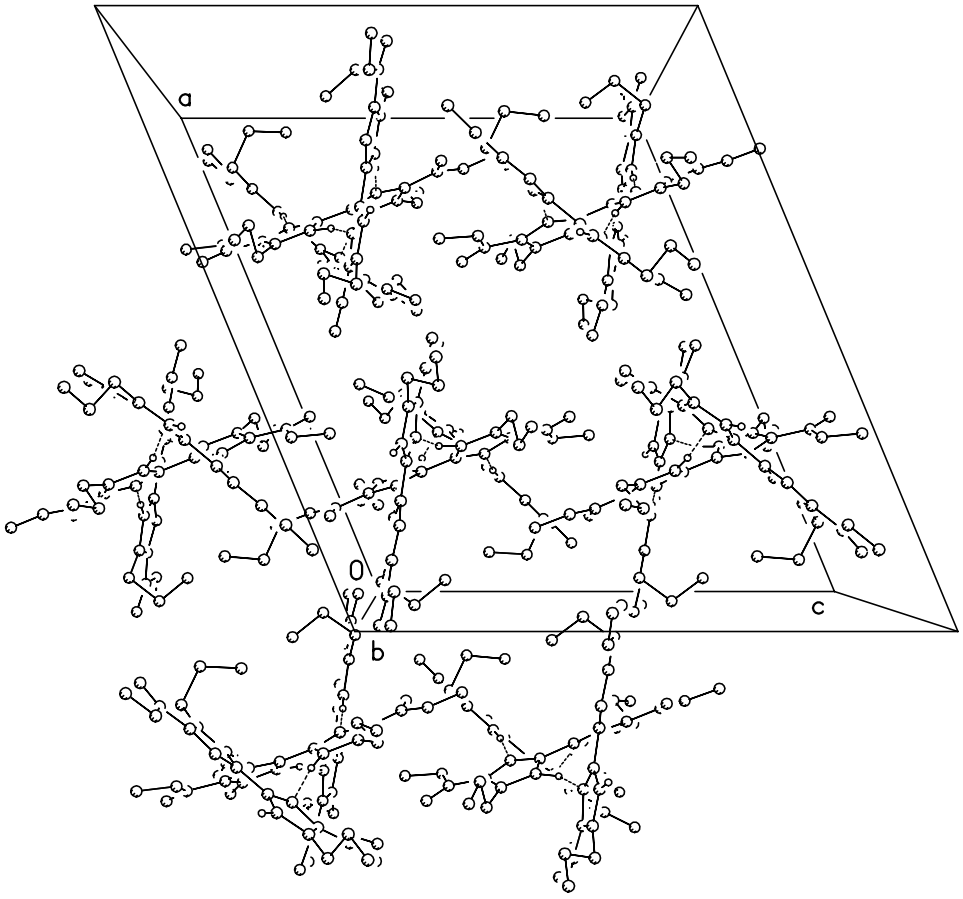


Figure S1(e). Unit cell packing diagram for $(C_{16}H_{22}N_4O_4)_4$-1/2CH_3OH. The view is approximately down the **b** axis. Pairs of molecules are hydrogen bound in infinite columns parallel to **b**. There are two crystallographically unique columns of molecules in the unit cell. Molecules A and B form the columns shown in wire-frame form.



X-ray Experimental for $C_{24}H_{30}N_4O_4$ (11): Crystals grew as colorless prisms by slow evaporation from methanol. The data crystal was cut from a larger crystal and had approximate dimensions 0.20 x 0.30 x 0.35 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073 Å). A total of 199 frames of data were collected using ω-scans with a scan range of 1.9° and a counting time of 119 seconds per frame. The data were collected at –70 °C using a Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table S1. Data reduction were performed using DENZO-SMN.[3] The structure was solved by direct methods using SIR92[4] and refined in blocks by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[5] The anisotropic displacement parameters were restrained during refinement to be approximately isotropic. The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2 x Ueq of the attached atom (1.5 x Ueq for methyl hydrogen atoms). The hydrogen atoms on the imidazole nitrogen atoms were located from a ΔF map but were not subsequently refined. The positions were idealized with Uiso set to 1.2 x Ueq of the bound nitrogen atom. There are six crystallographically independent molecules in the asymmetric unit. These molecules are H-bound in columns via the imidazole groups. Due to the large number of atoms to be refined, the hexyl groups were restrained to have similar bond lengths and angles during refinement. The function $\Sigma w(|F_o|^2 - |F_c|^2)^2$ was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0200*P)^2]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.165, with R(F) equal to 0.096 and a goodness of fit, S, = 1.23. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given below.[6] The data

were corrected for secondary extinction effects. The correction takes the form: $F_{corr} = kF_c/[1 + (1.1(1)x10^{-6})* F_c^2 \lambda^3/(\sin 2\theta)]^{0.25}$ where k is the overall scale factor. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography.[2] All figures were generated using SHELXTL/PC. Figure S2 shows the atomic numbering scheme. Positional and thermal parameters and bond lengths and angles are given below in Tables S6-S9. Structure factors are available by request from the authors.

Figure S2(a). View of molecule 1 of $C_{24}H_{30}N_4O_4$ showing the atom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

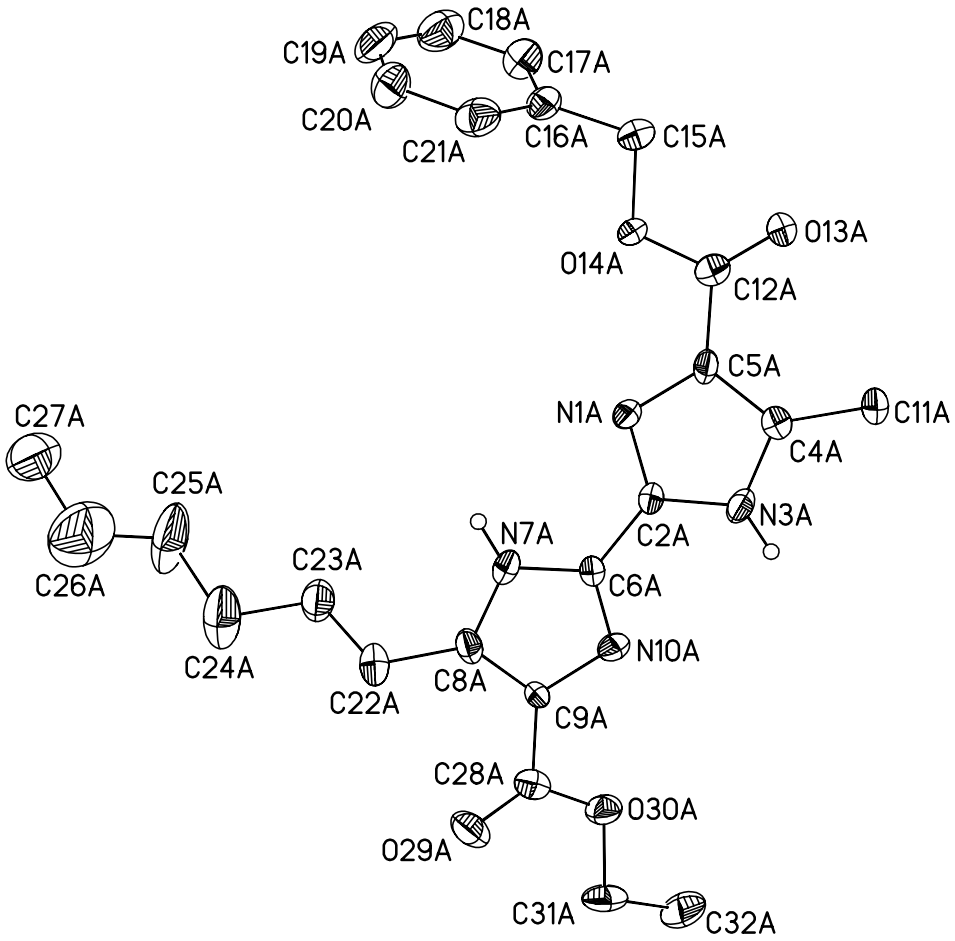


Figure S2(b). View of molecule 2 of $C_{24}H_{30}N_4O_4$ showing the atom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

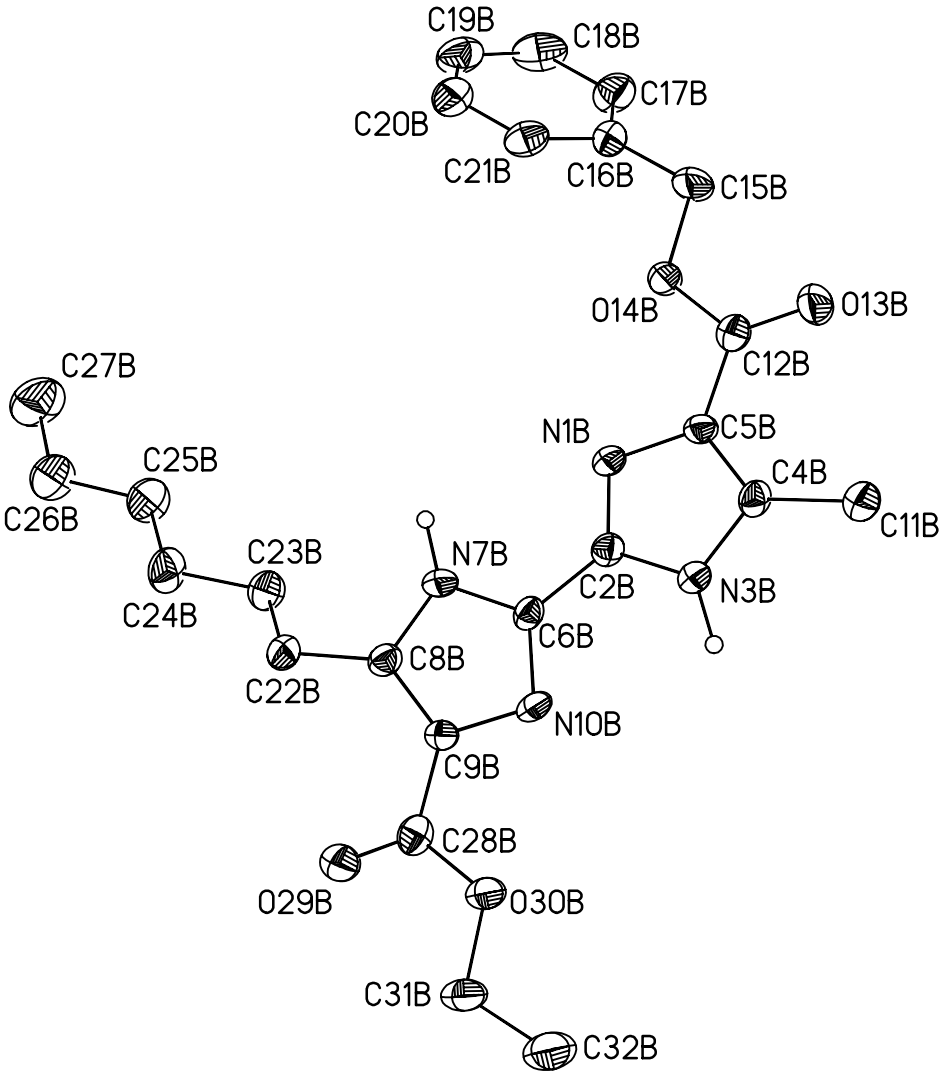


Figure S2(c). View of molecule 3 of $C_{24}H_{30}N_4O_4$ showing the atom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

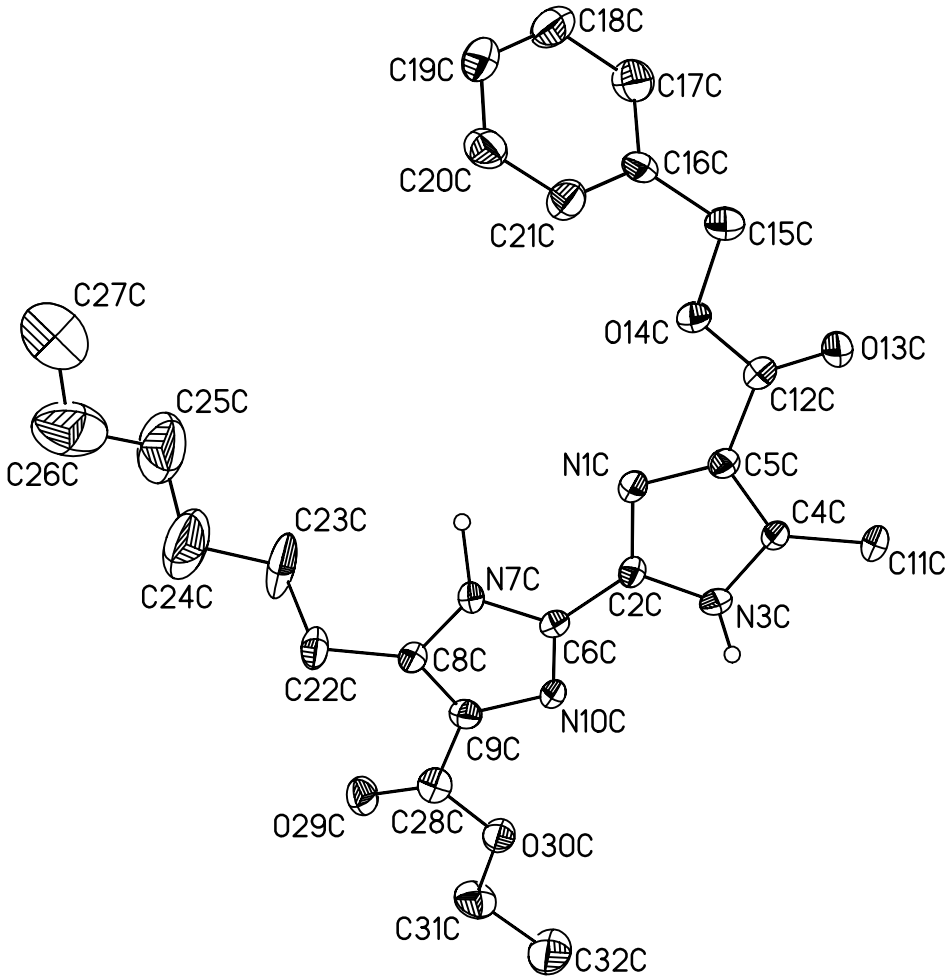


Figure S2(d). View of molecule 4 of $C_{24}H_{30}N_4O_4$ showing the atom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

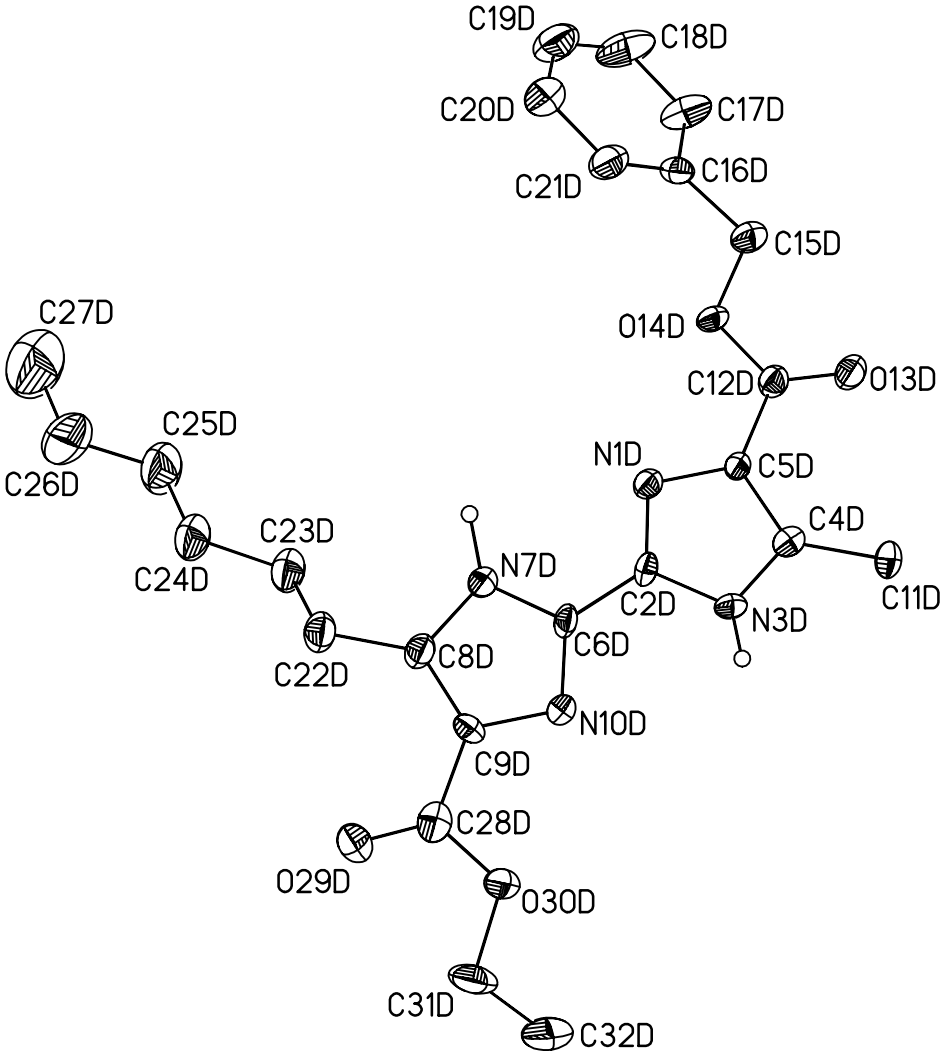


Figure S2(e). View of molecule 5 of $C_{24}H_{30}N_4O_4$ showing the atom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

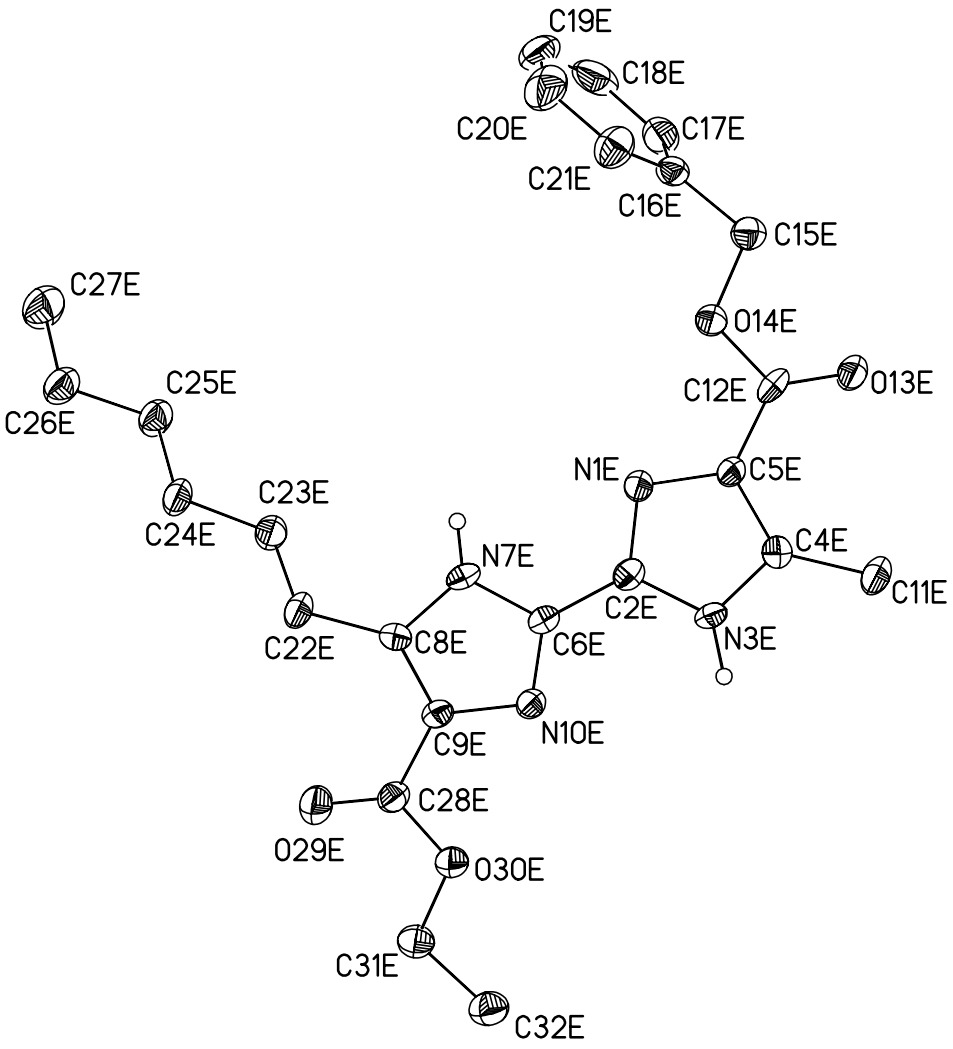


Figure S2(f). View of molecule 6 of $C_{24}H_{30}N_4O_4$ showing the atom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

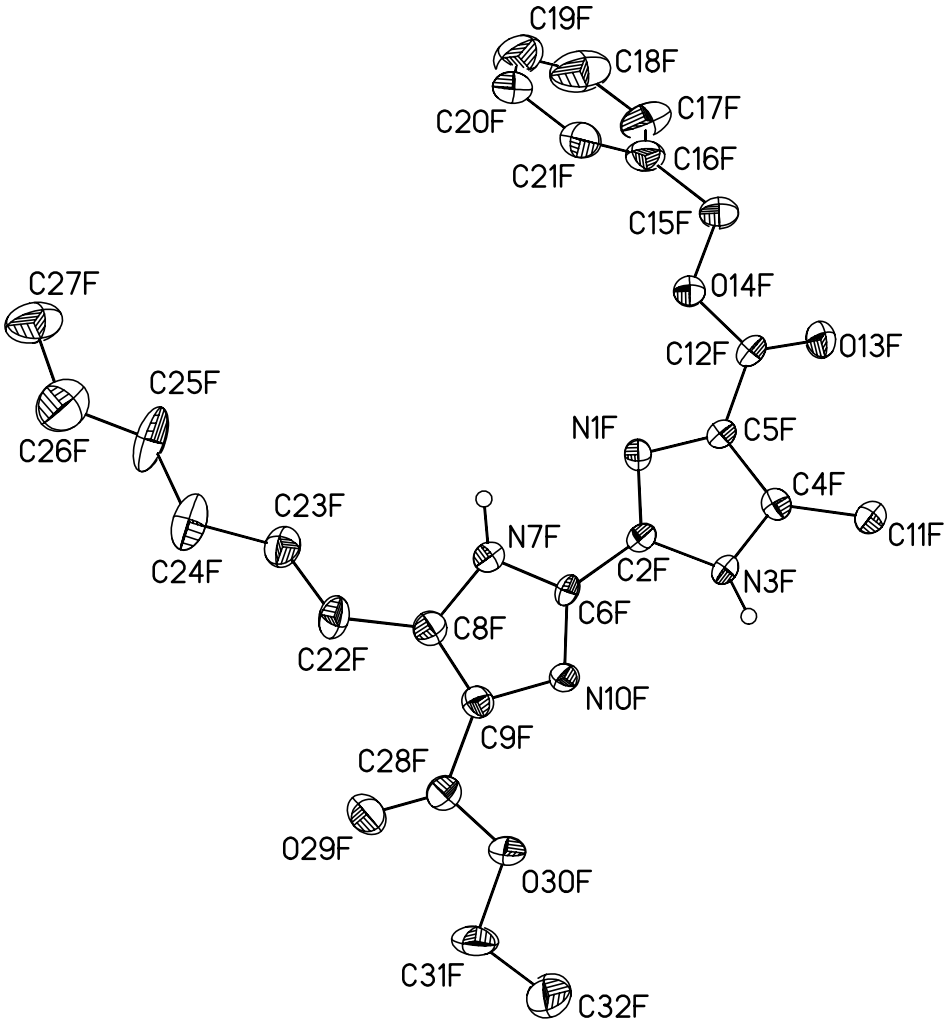


Figure S2(g). View of hydrogen bonding interactions between adjacent molecules of $C_{24}H_{30}N_4O_4$ along one column. Molecules B, D and F are shown in wireframe form.

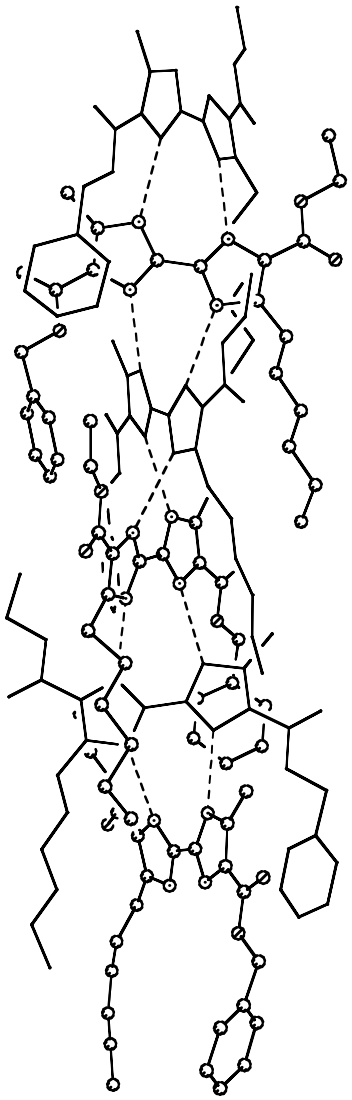
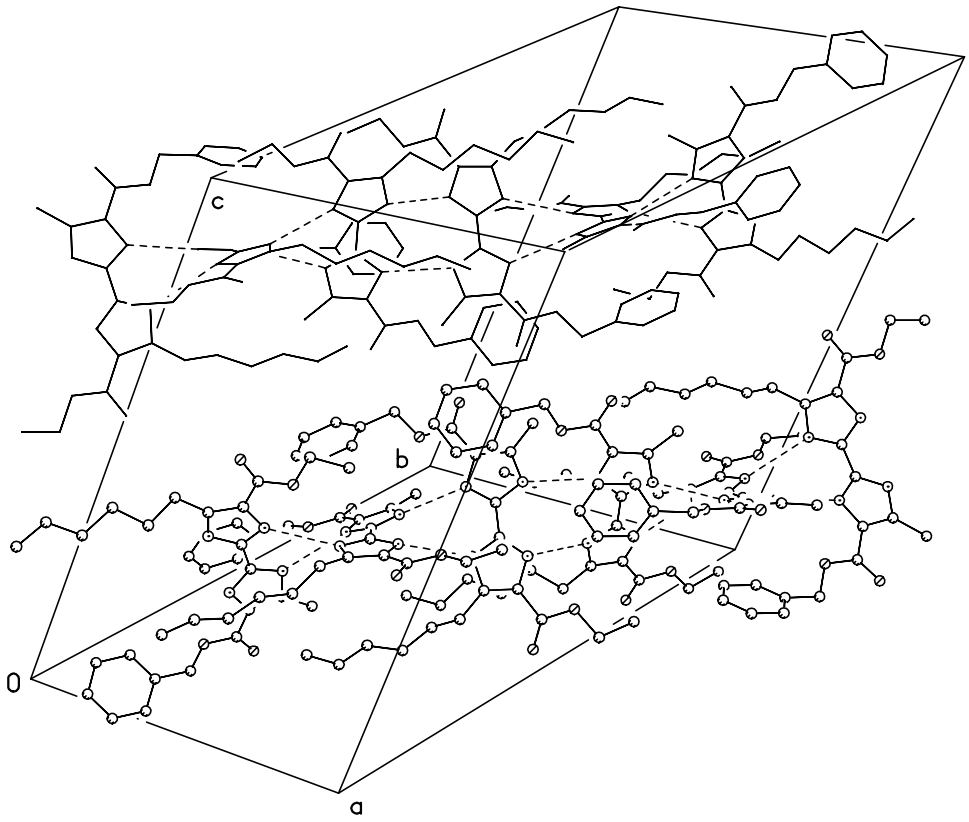


Figure S2(h). Unit cell packing diagram for $C_{24}H_{30}N_4O_4$. The molecules drawn in wireframe form are related by a crystallographic inversion center to those drawn in ball and stick form.



X-ray Experimental for $(C_{24}H_{38}N_4O_4)_4 \bullet (CH_3OH)_{0.5}$ (9): Crystals grew as thin colorless needles by slow cooling of a methanol solution. The data crystal was cut from a larger crystal and had approximate dimensions $0.14 \times 0.26 \times 0.76$ mm. The data were collected using the ω-scan technique at 4 - 10˚/min, with a scan range of 1.0˚ in ω to a $2\theta_{max} = 45^{\circ}$ at 188 K on a Siemens P4 diffractometer, equipped with a Nicolet LT-2 low-temperature device and using a graphite monochromator with MoKα radiation (λ = 0.71073 Å). Details of crystal data, data collection and structure refinement are listed in Table S1. Three reflections (7,2,0; -2,-4,-3; -5,2,2) were remeasured every 96 reflections to monitor instrument and crystal stability. A smoothed curve of the intensities of these check reflections was used to scale the data. The scaling factor ranged from 0.936 - 1.00 with the check reflections showing a slow decrease in intensity throughout the data set. The data were corrected for Lp effects but not for absorption. Data reduction, decay correction, structure solution and refinement were performed using the SHELXTL/PC software package.[1] The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for most of the non-H atoms. There are four molecules of the biimidazole and one-half molecule of methanol per asymmetric unit. Pairs of molecules are hydrogen bound in infinite columns parallel to *b*. Molecules with lables appended by A and B form one pair while molecules appended with labels C and D form a second pair. The N···N distances are all less than 2.9 Å. The hydrogen atoms on carbon were calculated in ideal positions (C-H 0.96 Å) with isotropic displacement parameters set to $1.2 \times$ Ueq of the attached atom ($1.5 \times$ Ueq for methyl hydrogen atoms). The carbon atoms of the hexyl groups did not refine well,

so the C-C bond lengths and angles were constrained to ideal values of 1.54 Å and 109˚, respectively. Initially, all non-H atoms were refined in blocks with anisotropic displacement parameters restrained to be approximately isotropic. However, during the final refinement stages, C9A and N3C refined with non-positive definite temperature factors. These two atoms were subsequently refined isotropically. One imidazole ring defined by atoms C6B, N7B, C8B, C9B and N10B refined poorly, and was idealized and refined as a rigid group. The hydrogen atoms on the imidazole nitrogen atoms could not be found in a difference electron density map after all other atoms were accounted for, and were therefore not included in the final model. The site occupancy factors for the atoms of the methanol molecules were estimated to be 0.5 due to the amount of electron density in the region. These atoms were refined isotropically. The function $\sum w(|F_o|^2 - |F_c|^2)^2$ was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.02*P)^2]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography.[2] All figures were generated using SHELXTL/PC. Figure S3 shows the atomic numbering scheme. Positional and thermal parameters and bond lengths and angles are given below in Tables S10-S13. Structure factors are available by request from the authors.

Figure S3(a). View of molecule 1 of $(C_{24}H_{38}N_4O_4)_4$-1/2CH_3OH showing the atom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

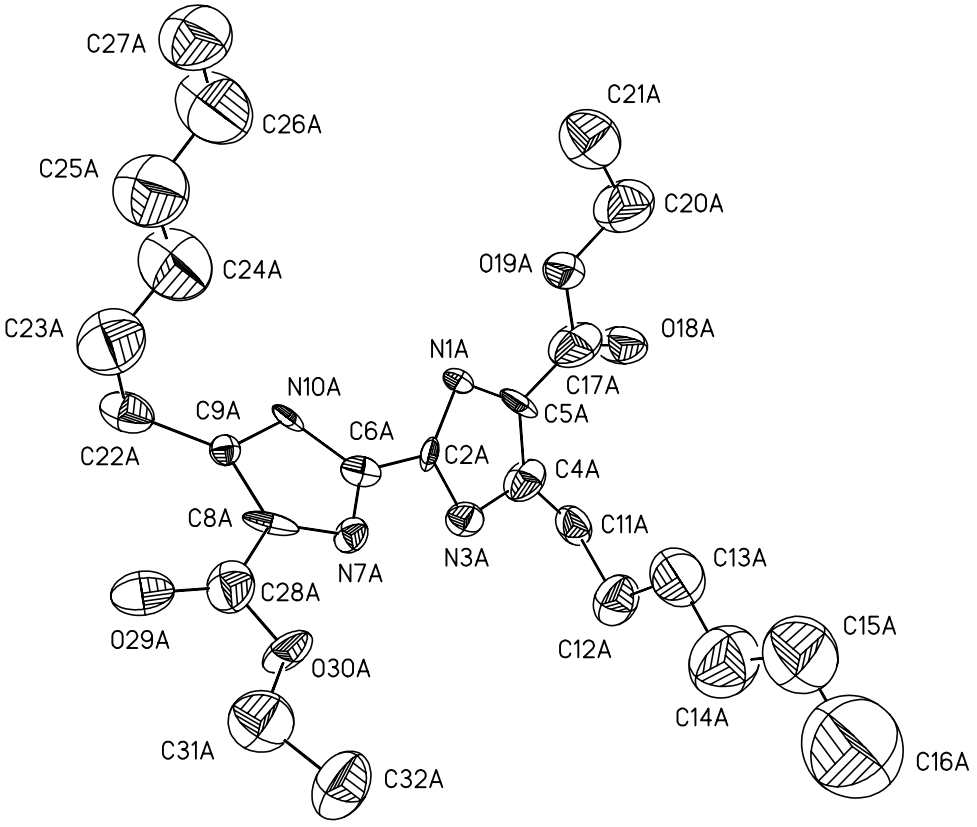


Figure S3(b). View of molecule 2 of $(C_{24}H_{38}N_4O_4)_4$-1/2CH_3OH showing the atom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

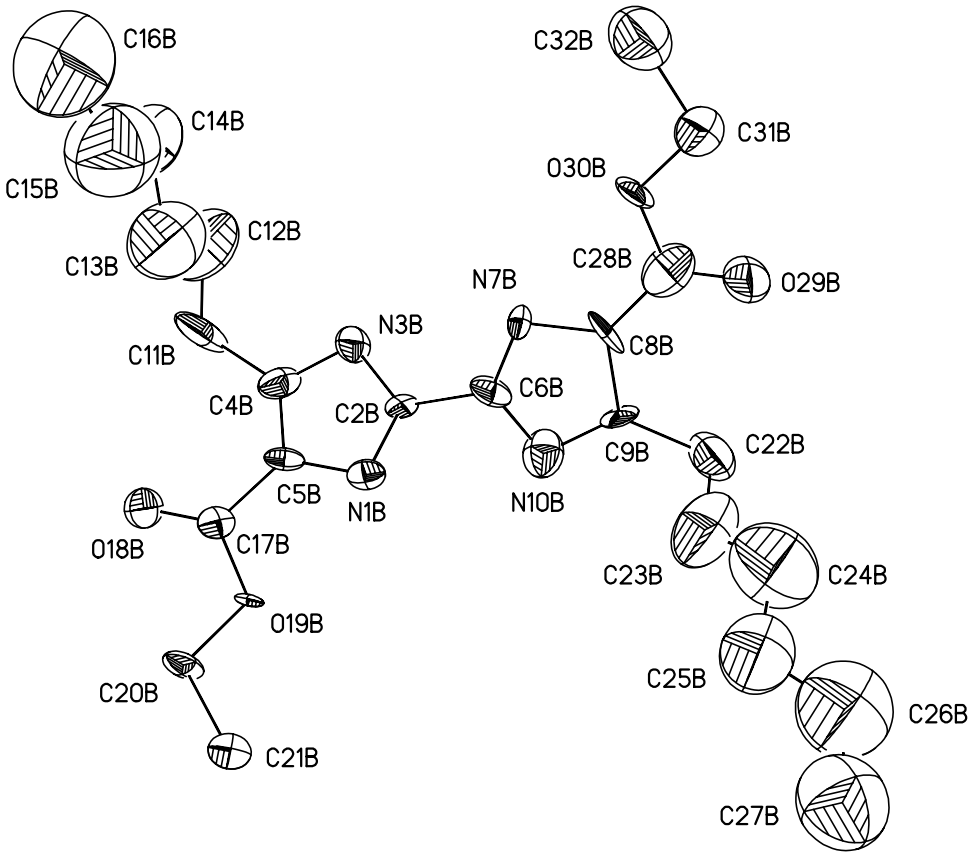


Figure S3(c). View of molecule 3 of $(C_{24}H_{38}N_4O_4)_4$-1/2CH_3OH showing the atom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

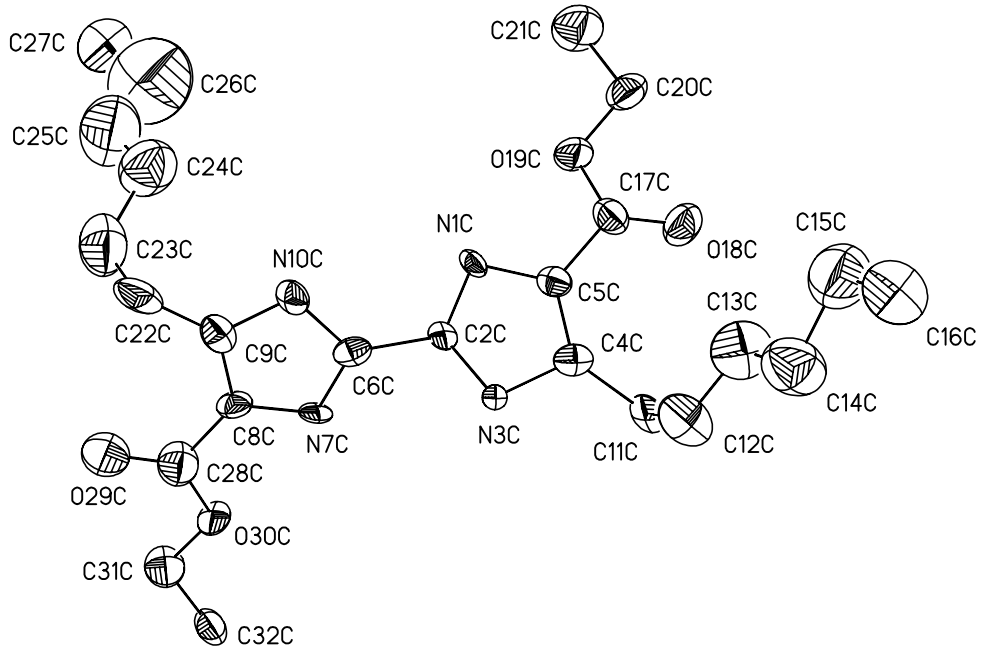


Figure S3(d). View of molecule 4 of $(C_{24}H_{38}N_4O_4)_4$-1/2CH_3OH showing the atom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

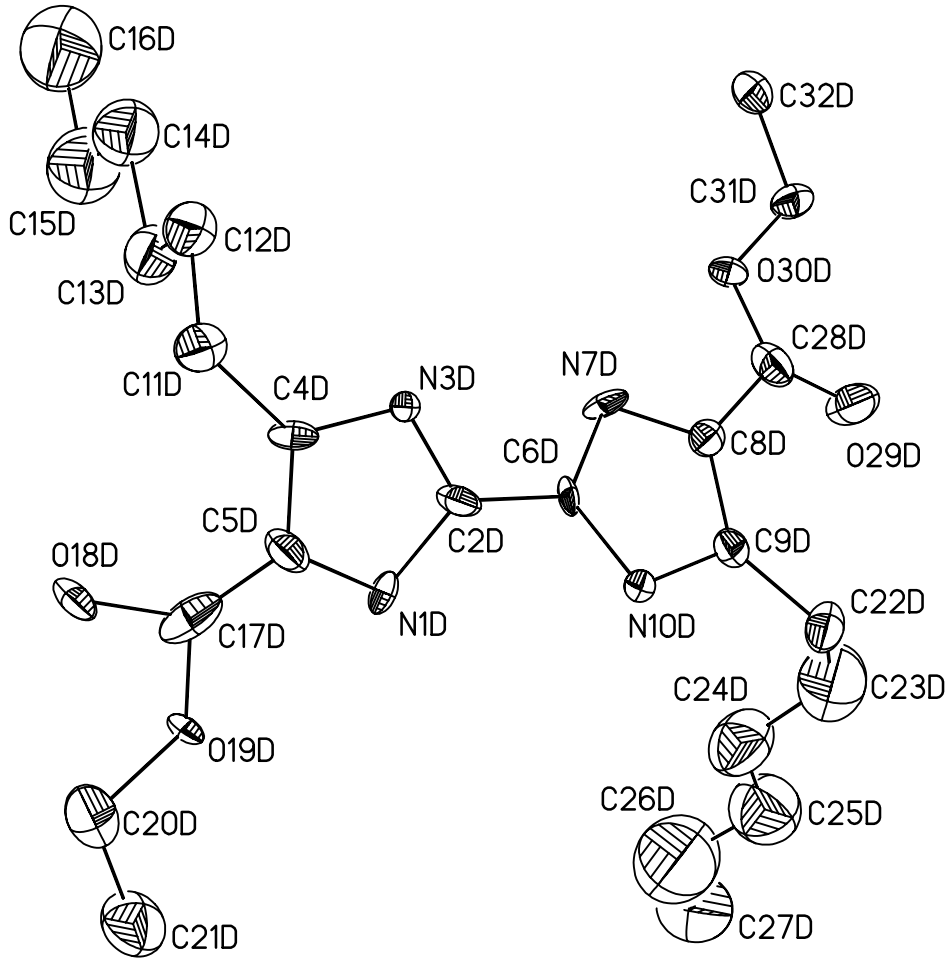


Figure S3(e). View of a portion of one column of H-bound bi-imidazoles. Dashed lines indicate a N-H..N hydrogen bonding interaction. The column extends parallel to the **b** axis.

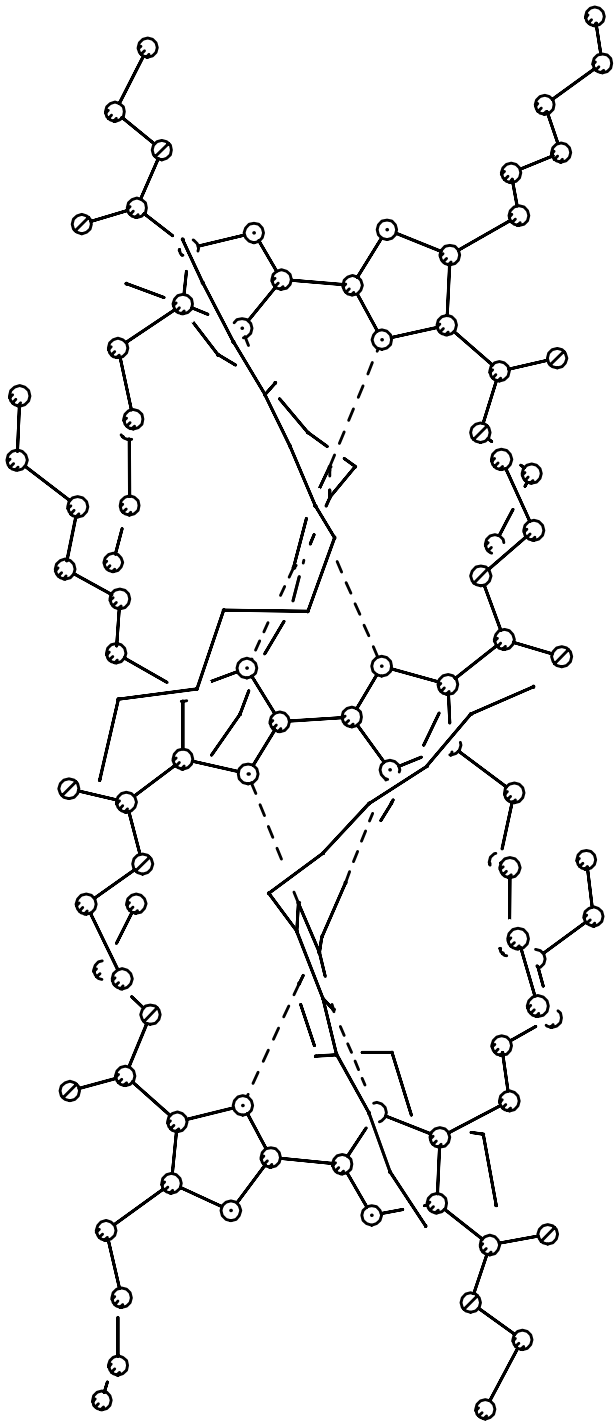
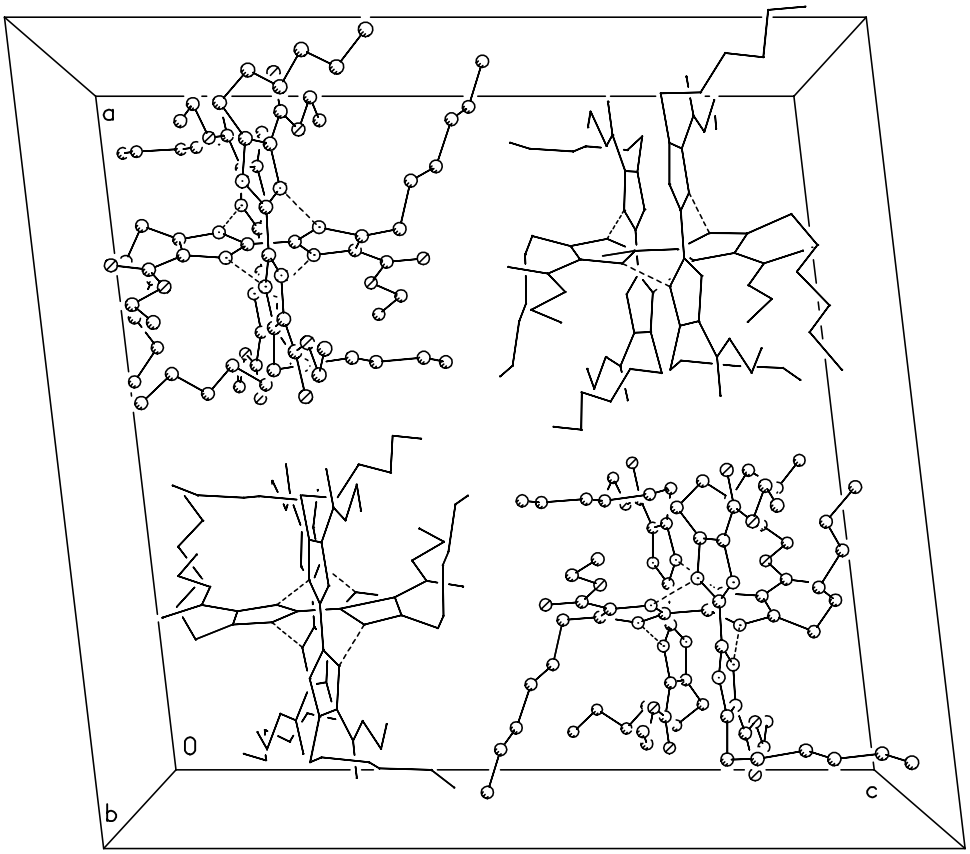


Figure S3(f). Unit cell packing diagram for $(C_{24}H_{38}N_4O_4)_4$-1/2CH_3OH. The view is approximately down the **b** axis. Pairs of molecules are hydrogen bound in infinite columns parallel to **b**. There are two crystallographically unique columns of molecules in the unit cell. Molecules A and B form the columns shown in wire-frame form.



References and Notes

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[6] $R_w(F^2) = \{\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection. $R(F) = \sum(|F_o| - |F_c|)/\sum|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$. $S = [\sum w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

Table S1. Crystal data for $(C_{16}H_{22}N_4O_4)_3 \bullet (CH_3OH)_{0.5}$ (**12**), $C_{24}H_{30}N_4O_4$ (**11**), and $(C_{24}H_{38}N_4O_4)_4 \bullet (CH_3OH)_{0.5}$ (**9**)

	12	**11**	**9**
formula	$C_{48.5}H_{68}N_{12}O_{12.5}$	$C_{24}H_{30}N_4O_4$	$C_{96.5}H_{154}N_{16}O_{16.5}$
fw	1019.15	438.52	1802.36
crystal system	monoclinic	triclinic	monoclinic
space group	*C*2/*c*	$P\bar{1}$	$P2_1/n$
color	colorless	colorless	colorless
a (Å)	21.589(2)	16.0220(5)	24.218(3)
b (Å)	28.437(3)	21.838(1)	17.867(2)
c (Å)	19.203(2)	22.585(1)	24.921(3)
α (deg)	90.0	68.716(2)	90.0
β (deg)	112.57(1)	71.315(3)	96.79(1)
γ (deg)	90.0	80.287(3)	90.0
V (Å^3)	10886(2)	6962.8(5)	10708(2)
Z	8	12	4
temp (K)	193(2)	203(2)	188(2)
R	0.0739	0.0962	0.124
R_W	0.1315	0.120	0.217
GOF	1.521	1.228	1.134