

**Supporting information for**

**A supramolecular assembly of side-by-side polyimidazole tripod coils stabilized by  $\pi$ - $\pi$  stacking and unique boric acid templated hydrogen bonding interactions.**

*Lionel E. Cheruzel, Mark S. Mashuta, and Robert M. Buchanan. \**

*\* Department of Chemistry, University of Louisville, 2320 S. Brook Street, Louisville, Kentucky 40292, USA Fax: 502-852-8149.*

[bob.buchanan@louisville.edu](mailto:bob.buchanan@louisville.edu)

## Experimental Section:

All reagents and solvents were purchased from commercial sources and used as received. Elemental analyses were performed by Midwest Analytical, Inc (Indianapolis, IN, USA).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a 3 channel Bruker UnityInova 500 MHz spectrometer complete with pulse field gradient capability with the deuterated solvent as internal standard. The Electrospray Ionization Mass Spectroscopy (ESI-MS) experiments were performed on a Micromass Mass Spectrometer Electrospray Triple Quadrupole Quattro LCZ.

### **(Bis(1-methylimidazol-2-yl)methyl)((1-methyl-4-nitroimidazol-2-yl)methyl)amine (1):**

A dichloroethane solution (20 mL) of 0.78 g of (bis(1-methylimidazol-2-yl)methyl)amine (3.81 mmol) and 0.59 g (3.81 mmol) of 1-methyl-4-nitroimidazole-2-carboxaldehyde was treated with 1.13 g of  $\text{NaHB}(\text{OAc})_3$  (5.33 mmol). After 1.5 h, the reaction mixture was quenched with saturated sodium bicarbonate solution. The dichloroethane was removed under vacuum and the aqueous layer was extracted three times with 20 mL aliquot of ethyl acetate. After drying the organic layer with  $\text{MgSO}_4$ , the solvent was removed under vacuum to yield 0.75 g (58 %) of a pale yellow oil. IR(film):  $\bar{\nu} = 1291$  and  $1503\text{ cm}^{-1}(\text{NO}_2)$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ , TMS):  $\delta = 7.6$  (s, 1H,  $^{\text{nitro}}\text{Im}(\text{H}5))$ , 6.9 (s, 2H,  $\text{Im}(\text{H}5))$ , 6.6 (s, 2H,  $\text{Im}(\text{H}4))$ , 3.9 (s, 2H,  $^{\text{nitro}}\text{Im}(\text{CH}_2))$ , 3.8 (s, 4H,  $\text{Im}(\text{CH}_2))$ , 3.3 (s, 6H,  $\text{Im}(\text{N}-\text{CH}_3))$ , 3.3 (s, 3H,  $^{\text{nitro}}\text{Im}(\text{N}-\text{CH}_3))$ .  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ , TMS):  $\delta = 146.1$  ( $^{\text{nitro}}\text{Im}(\text{C}4))$ , 145.5 ( $^{\text{nitro}}\text{Im}(\text{C}2))$ , 145.0 ( $\text{Im}(\text{C}2))$ , 127.7 ( $^{\text{nitro}}\text{Im}(\text{C}5))$ , 121.8 ( $\text{Im}(\text{C}5))$ , 121.7 ( $\text{Im}(\text{C}4))$ , 49.5 ( $\text{Im}(\text{CH}_2))$ , 49.0 ( $^{\text{nitro}}\text{Im}(\text{CH}_2))$ , 33.5 ( $^{\text{nitro}}\text{Im}(\text{N}-\text{CH}_3))$ , 32.5 ( $\text{Im}(\text{N}-\text{CH}_3))$ ; MS  $m/z$  345.4  $[\text{M}+\text{H}^+]$ .

### **Di[(bis(1-methylimidazol-2-yl)methyl)((1-methyl-4-nitroimidazol-2-yl)methyl)amine]-boric acid (2/1) (2):**

Compound **2** was crystallized by dissolving 0.2 g (0.58 mmol) of **1** with 17 mg (0.29 mmol) of boric acid in 1 mL of ethyl acetate/methanol (1/1) and ether vapors were allowed to slowly diffuse into the solution. Colorless block crystals were isolated from the crystallization solution prior to the x-ray diffraction analysis.

## Crystal data and structure refinement for compound 2.

Identification code	compound 2	
Empirical formula	C <sub>30</sub> H <sub>43</sub> B N <sub>16</sub> O <sub>7</sub>	
Formula weight	750.61	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 15.7997(18) Å	$\alpha = 90^\circ$
	b = 8.2540(9) Å	$\beta = 92.861(2)^\circ$
	c = 27.530(3) Å	$\gamma = 90^\circ$
Volume	3585.7(7) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.390 Mg/m <sup>3</sup>	
Absorption coefficient	0.103 mm <sup>-1</sup>	
F(000)	1584	
Crystal size	0.301 x 0.173 x 0.081 mm <sup>3</sup>	
Theta range for data collection	1.52 to 28.30°	
Index ranges	-20 ≤ h ≤ 21, -10 ≤ k ≤ 10, -34 ≤ l ≤ 35	
Reflections collected	29945	
Independent reflections	8345 [R(int) = 0.0273]	
Completeness to theta = 28.30°	93.8 %	
Absorption correction	Sadabs	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	8345 / 0 / 540	
Goodness-of-fit on F <sup>2</sup>	1.097	
Final R indices [I > 2σ(I)]	R1 = 0.043, wR2 = 0.107	
R indices (all data)	R1 = 0.058, wR2 = 0.113	
Extinction coefficient	0.0000(2)	
Largest diff. peak and hole	0.556 and -0.203 e.Å <sup>-3</sup>	

**Atomic coordinates (  $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ).  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.**

	x	y	z	$U(\text{eq})$
O(1)	1760(1)	-3080(1)	2339(1)	29(1)
O(2)	798(1)	-4396(1)	2713(1)	36(1)
O(3)	6850(1)	12771(1)	2303(1)	27(1)
O(4)	5796(1)	14128(1)	2570(1)	34(1)
N(1)	1371(1)	396(1)	3362(1)	19(1)
N(2)	627(1)	-1890(1)	3351(1)	18(1)
N(3)	-1506(1)	3120(1)	3240(1)	19(1)
N(4)	-2272(1)	2589(1)	3871(1)	18(1)
N(5)	256(1)	4876(1)	4361(1)	21(1)
N(6)	1000(1)	3166(1)	4831(1)	23(1)
N(7)	1241(1)	-3196(1)	2659(1)	23(1)
N(8)	-243(1)	1336(1)	3967(1)	15(1)
N(9)	6448(1)	9799(1)	3454(1)	17(1)
N(10)	5623(1)	11953(1)	3312(1)	19(1)
N(11)	5632(1)	5891(1)	4589(1)	21(1)
N(12)	5920(1)	8035(1)	5053(1)	22(1)
N(13)	3734(1)	6689(2)	3297(1)	23(1)
N(14)	2823(1)	7404(1)	3842(1)	20(1)
N(15)	6279(1)	12972(1)	2591(1)	21(1)
N(16)	4814(1)	8890(1)	4002(1)	17(1)
C(1)	763(1)	-504(2)	3578(1)	17(1)
C(2)	1171(1)	-1860(2)	2985(1)	18(1)
C(3)	1643(1)	-476(2)	2982(1)	20(1)
C(4)	1694(1)	1978(2)	3525(1)	26(1)
C(5)	373(1)	18(2)	4035(1)	17(1)
C(6)	-1630(1)	2099(2)	3617(1)	17(1)
C(7)	-2565(1)	3983(2)	3646(1)	20(1)
C(8)	-2101(1)	4327(2)	3258(1)	21(1)
C(9)	-844(1)	2989(2)	2891(1)	26(1)
C(10)	-1055(1)	716(2)	3748(1)	17(1)
C(11)	302(1)	3357(2)	4553(1)	19(1)
C(12)	1410(1)	4641(2)	4817(1)	23(1)
C(13)	964(1)	5691(2)	4532(1)	24(1)
C(14)	-430(1)	5551(2)	4049(1)	27(1)
C(15)	-360(1)	2097(2)	4447(1)	17(1)
C(16)	5787(1)	10720(2)	3605(1)	18(1)
C(17)	6728(1)	10494(2)	3047(1)	18(1)
C(18)	6209(1)	11800(2)	2968(1)	18(1)
C(19)	6824(1)	8398(2)	3708(1)	23(1)
C(20)	5350(1)	10343(2)	4061(1)	20(1)
C(21)	5390(1)	7411(2)	4715(1)	18(1)
C(22)	6521(1)	6854(2)	5146(1)	26(1)
C(23)	6353(1)	5526(2)	4867(1)	25(1)
C(24)	5215(1)	4851(2)	4223(1)	29(1)
C(25)	4632(1)	8237(2)	4489(1)	18(1)
C(26)	3506(1)	7843(2)	3618(1)	19(1)
C(27)	2602(1)	5906(2)	3655(1)	23(1)
C(28)	3159(1)	5450(2)	3321(1)	25(1)
C(29)	4441(1)	6781(2)	2978(1)	33(1)
C(30)	4016(1)	9323(2)	3731(1)	20(1)

B	2295(1)	9474(2)	4976(1)	19(1)
O(5)	2241(1)	9668(1)	4484(1)	21(1)
O(6)	1916(1)	10585(1)	5266(1)	23(1)
O(7)	2692(1)	8167(1)	5183(1)	25(1)

---

Crystallographic Intermolecular Interactions:

Color Code: Nitrogen (blue), Carbon (grey), Oxygen (red), Hydrogen (white).  
Ring labels are consistent with those reported in Figure 1.

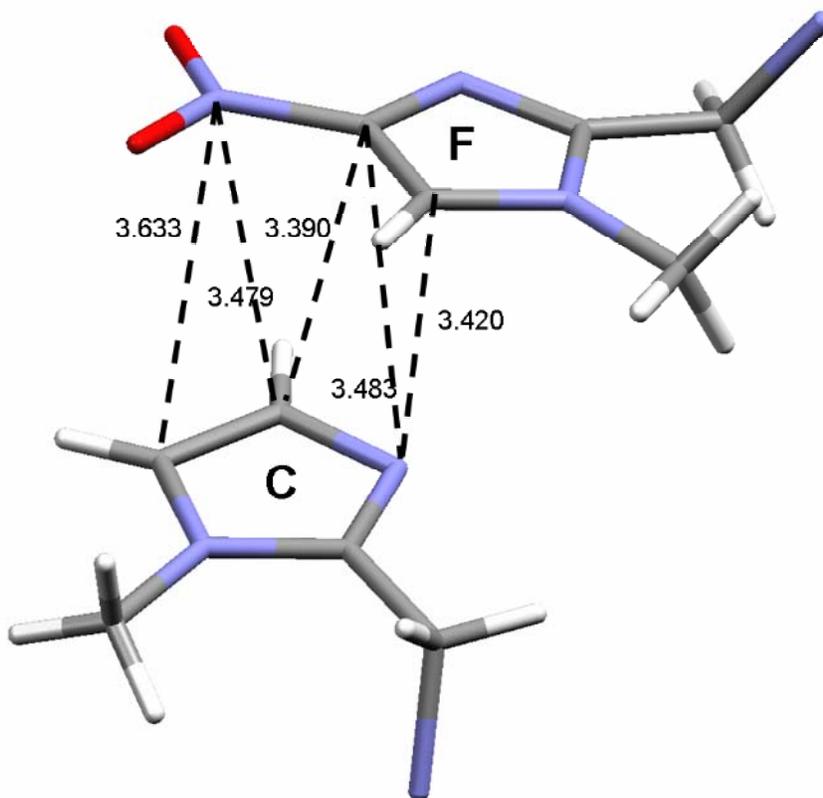


Figure S1: Closest interatomic contacts between  $\pi$ - $\pi$  stacked imidazole molecules associated with rings F and C.

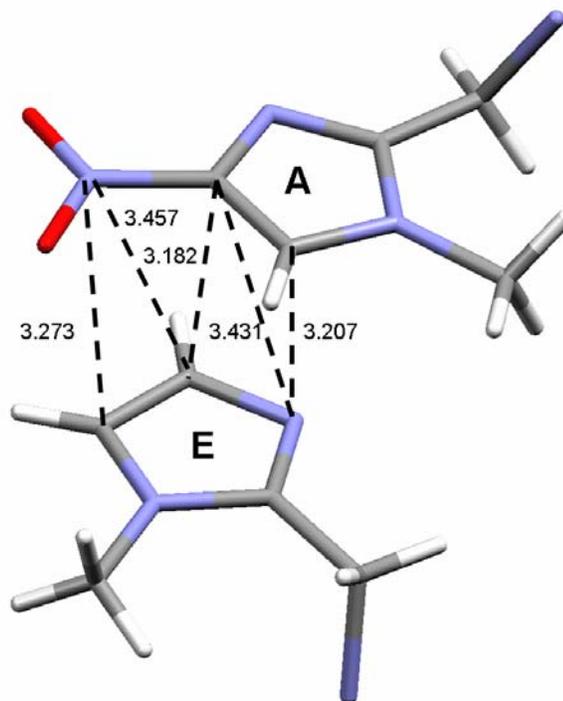


Figure S2: Closest interatomic contacts between  $\pi$ - $\pi$  stacked imidazole molecules associated with rings A and E.

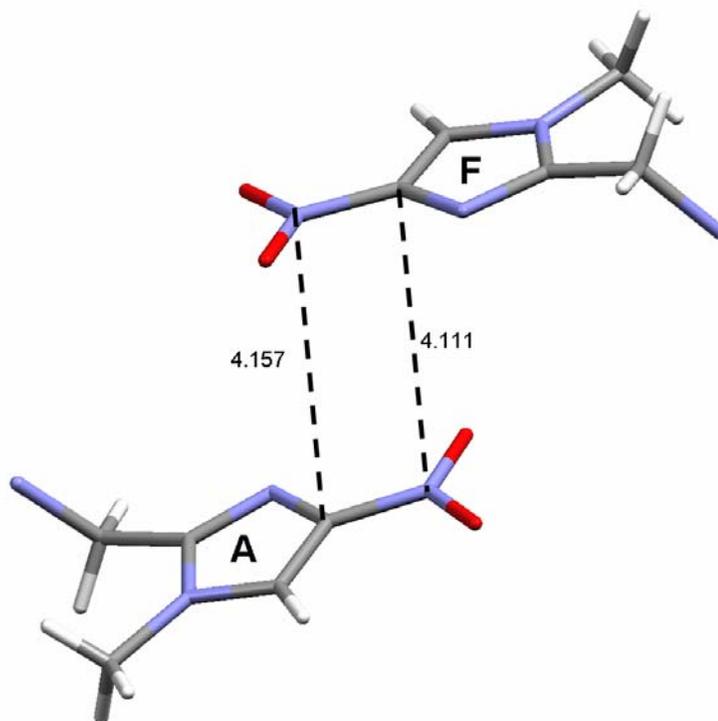


Figure S3: Closest interatomic contacts between  $\pi$ - $\pi$  stacked imidazole molecules associated with rings A and F.

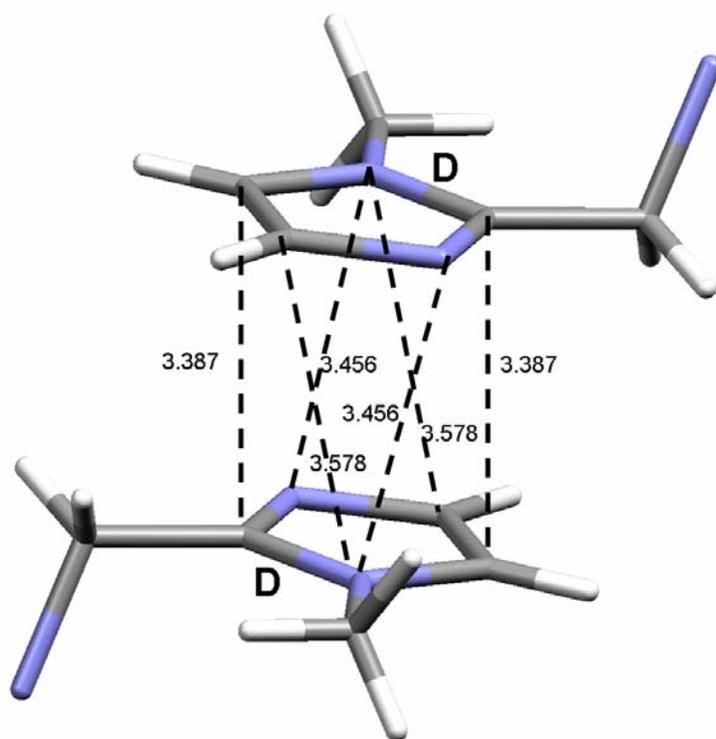


Figure S4: Closest interatomic contacts between  $\pi$ - $\pi$  stacked imidazole molecules associated with rings D and D.

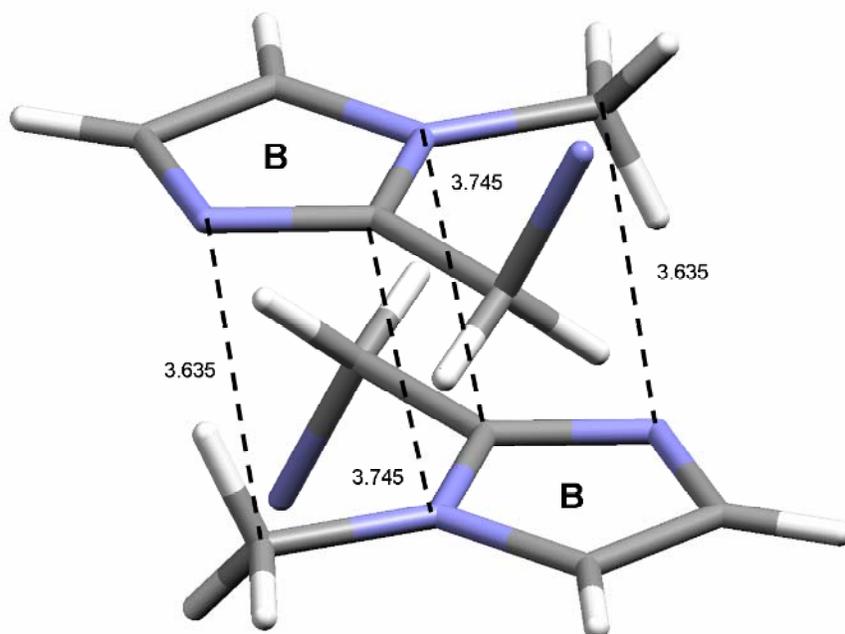


Figure S5: Closest interatomic contacts between  $\pi$ - $\pi$  stacked imidazole molecules associated with rings B and B.

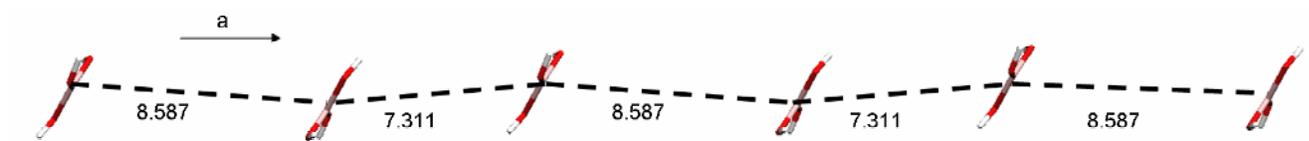


Figure S6: One-dimensional stacking of  $B(OH)_3$  molecules along the crystallographic a axis, separations between the B atoms along the stack and B-B-B angle of  $167.23^\circ$ .

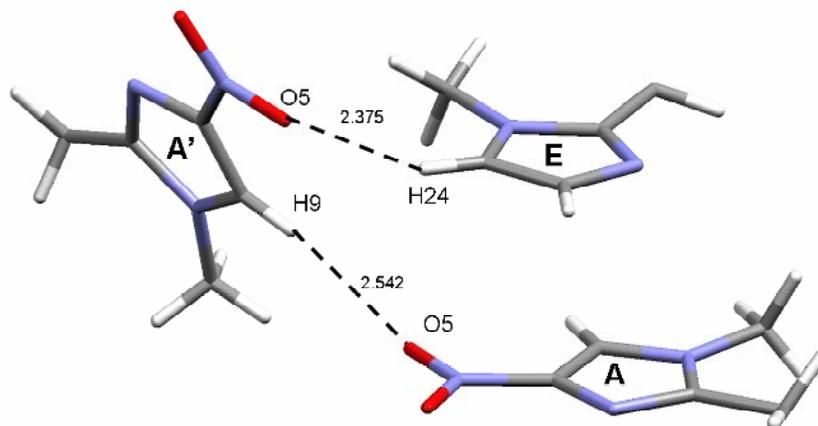


Figure S7: Weak intermolecular H-bonding contacts between O5 of the nitro group of imidazole ring A and H9 of a symmetry related ring A as well as H24 of ring E.

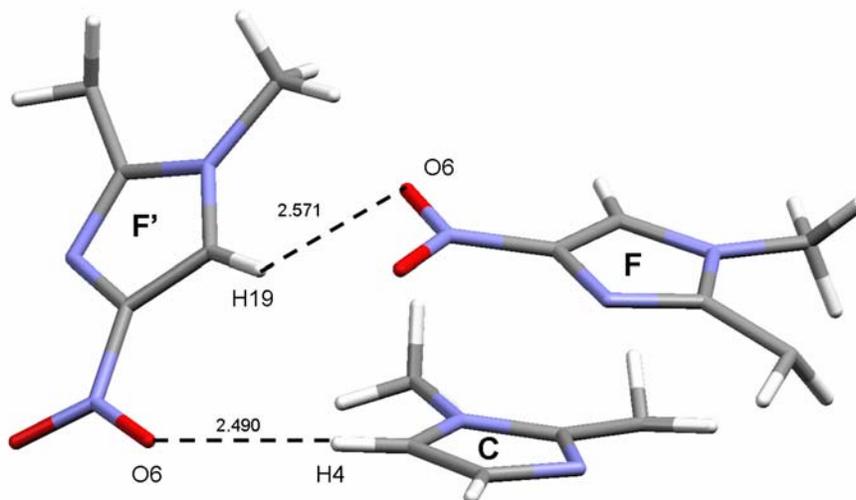


Figure S8: Weak intermolecular H-bonding contacts between O6 of the nitro group of imidazole ring F and H19 of a symmetry related ring F as well as H4 of ring C.