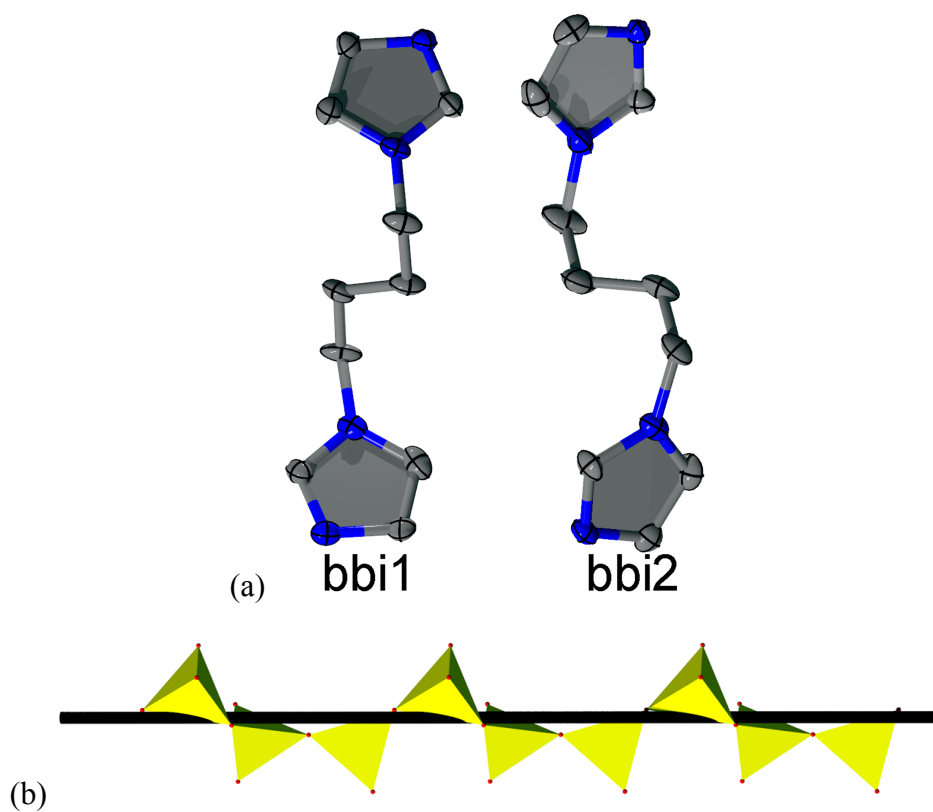


pH-Tuned self-assembly of organic-inorganic hybrids based on different vanadate chains, Zn(II) ions and flexible ligands: crystallizing in polar and centrosymmetric space group

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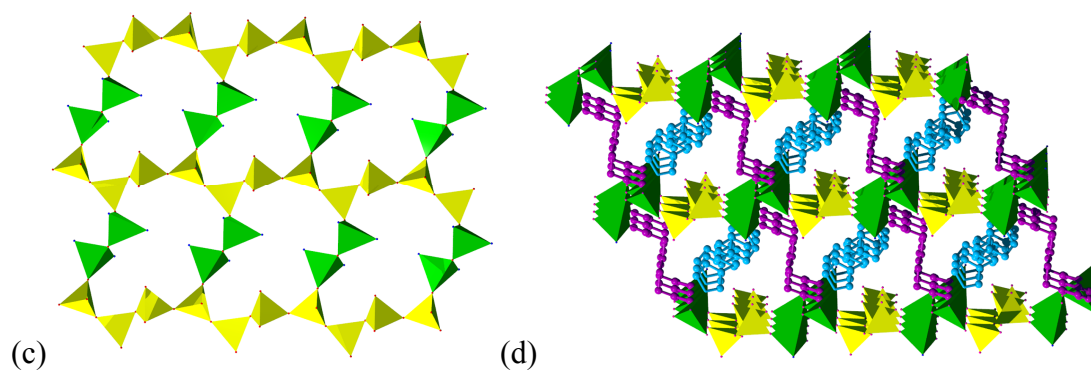


Figure S1. (a) Ball and stick representation of two kinds of bbi ligands in **1**. (b) Polyhedral representation of 1D helical chain of $(V_3O_9)^{3-}$. (c) Polyhedral representation of the $[Zn_2(V_3O_9)(OH)]$ sheet. (d) Polyhedral representation of **1**.

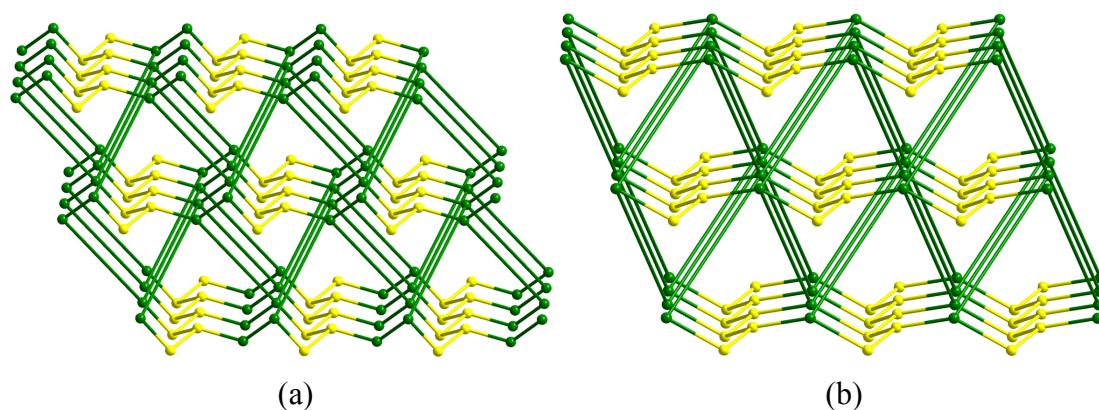
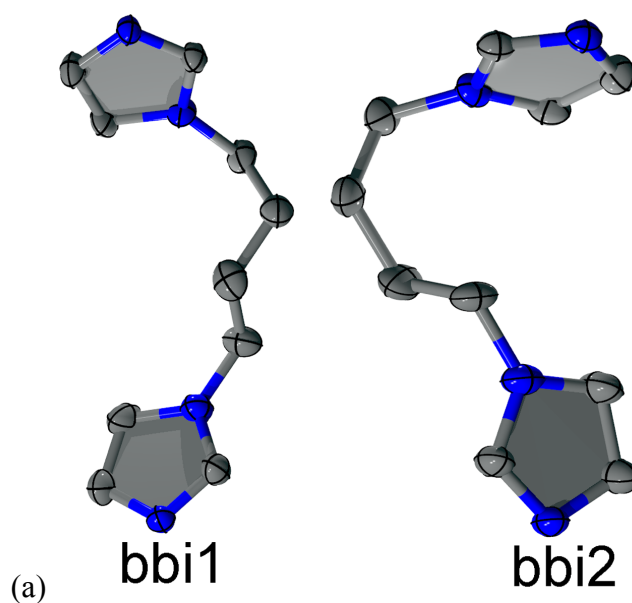


Figure S2. (a) Schematic representation of the (3,4)-connected framework with $(10^3)_2(6^3 \cdot 10^3)_2$ topology of compound **1**. (b) Schematic representation of the (3,6)-connected framework with $(8^3)_2(4^4 \cdot 6^2 \cdot 8^9)$ topology of compound **1**.



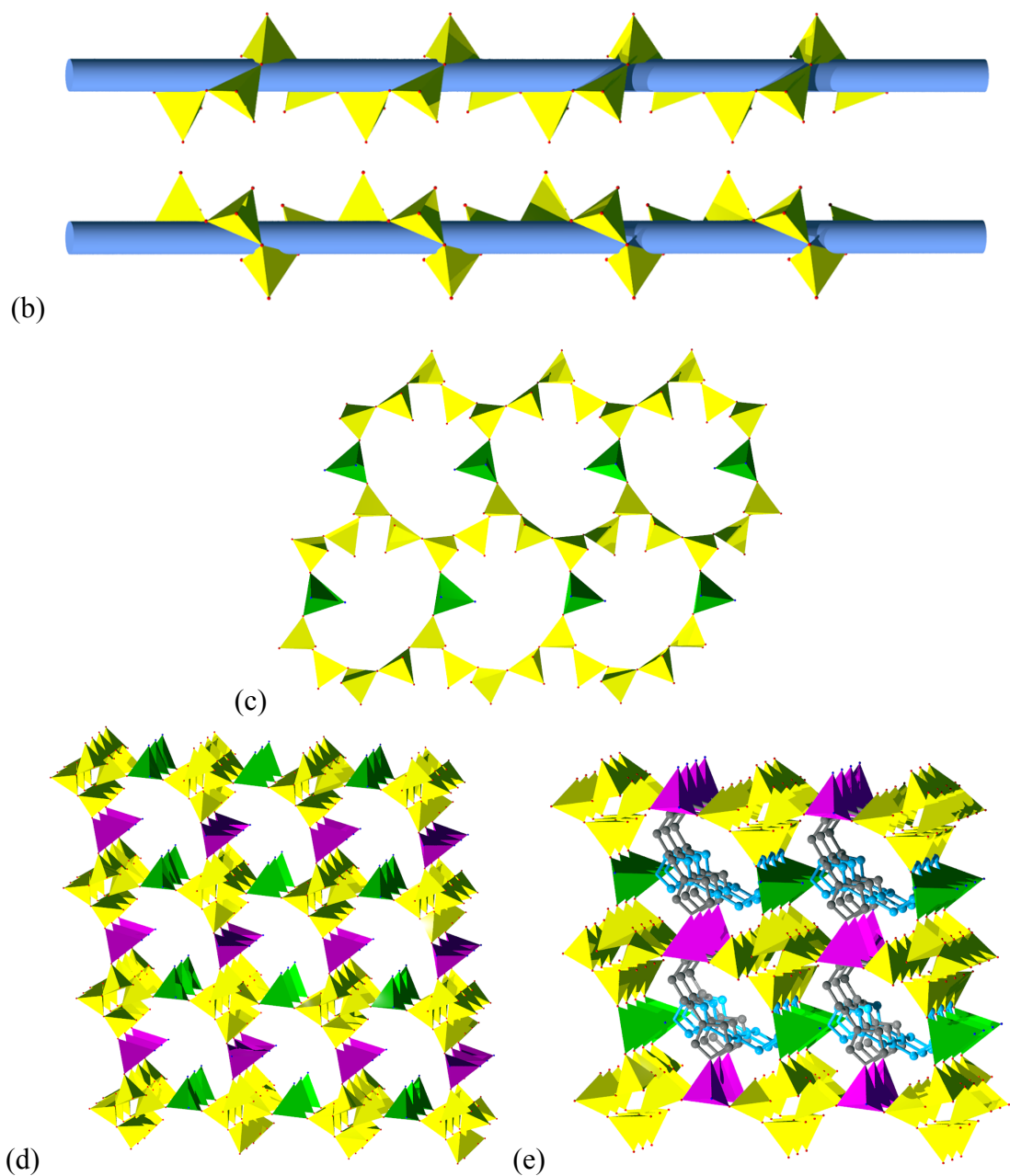


Figure S3. (a) Ball and stick representation of two kinds of bbi ligands in **2**. (b) Polyhedral representation of two kinds of 1D helical chains of $(V_4O_{12})^{4-}$. (c) Polyhedral representation of the sheet by $(V_4O_{12})^{4-}$ and Zn1 atoms. (d) Polyhedral representation of 3D inorganic $[Zn_2(V_4O_{12})]$ framework. (e) Polyhedral representation of **2**.

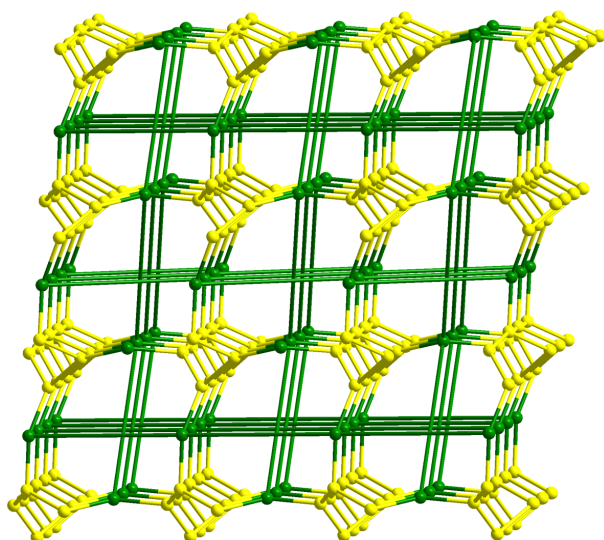


Figure S4. Schematic representation of the (3,4)-connected framework with $(7^2 \cdot 9)_4(7^4 \cdot 9 \cdot 12)(7 \cdot 9^4 \cdot 12)$ topology of compound **2**.

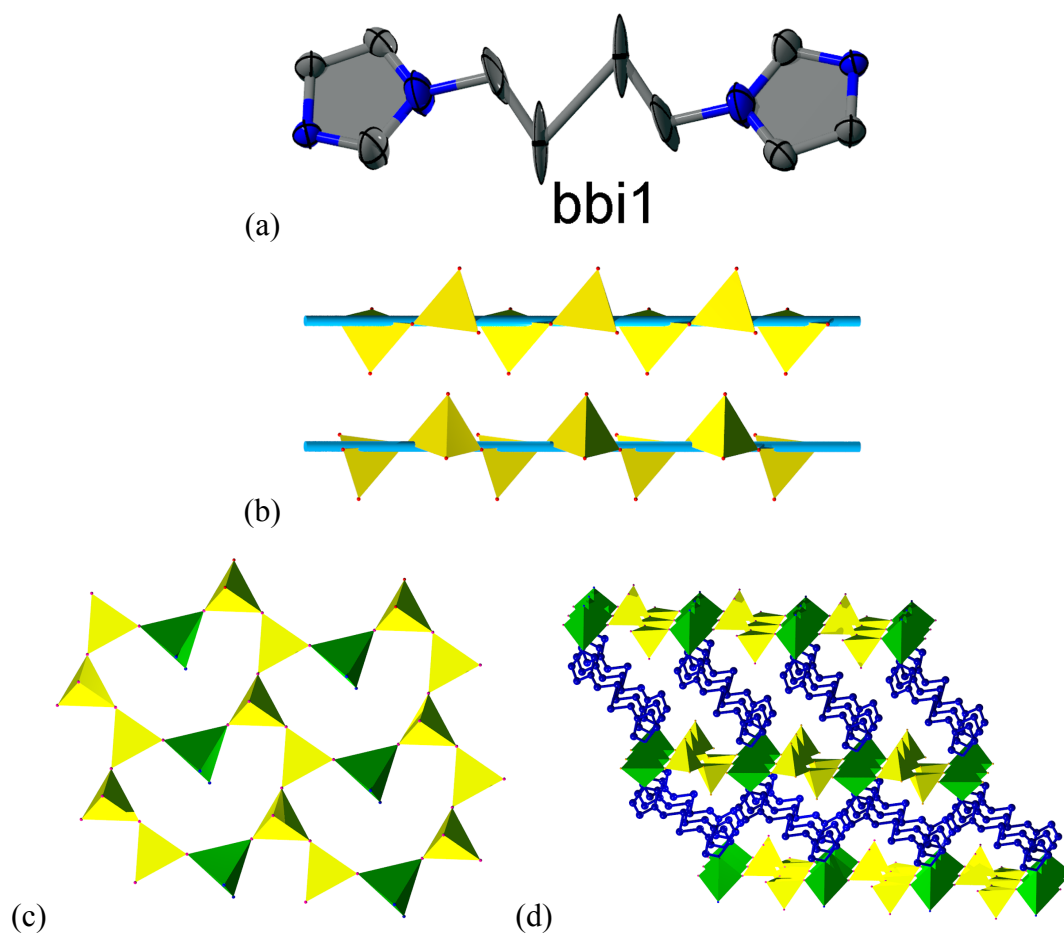


Figure S5. (a) Ball and stick representation of bbi ligand in **3**. (b) Polyhedral representation of 1D helical chains of $(V_2O_6)^{2-}$. (c) Polyhedral representation of the $[Zn(V_2O_6)]$ sheet. (d) Polyhedral representation of **3**.

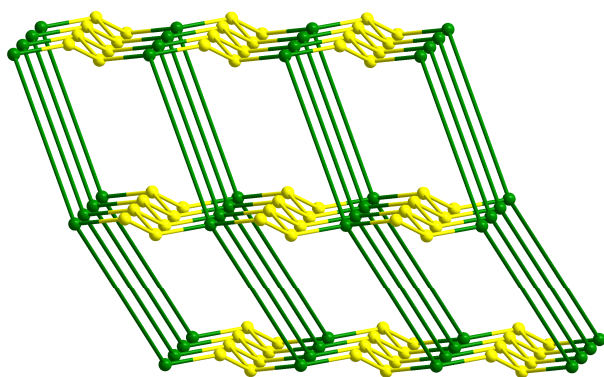


Figure S6. Schematic representation of the (3,4)-connected framework with $(8^2 \cdot 10)(8^5 \cdot 10)$ topology of compound **3**.

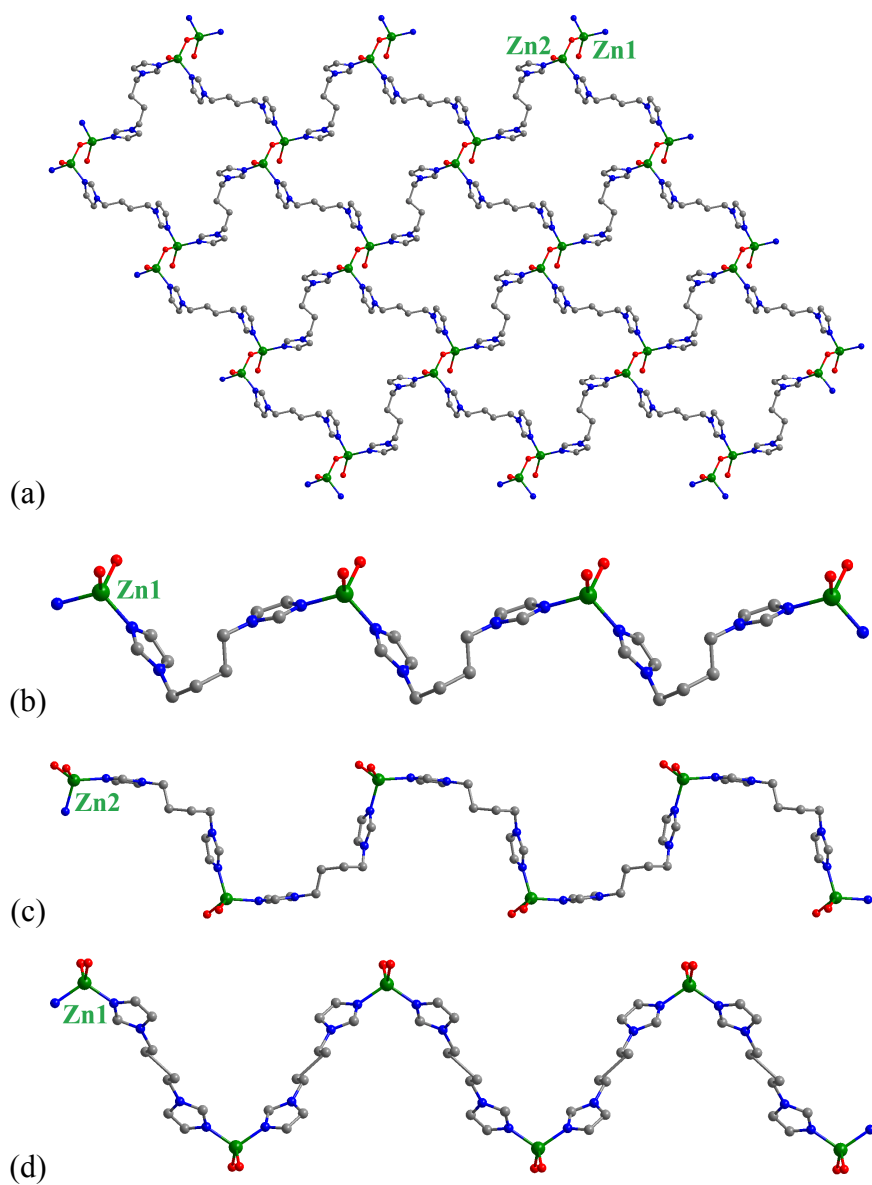


Figure S7. The connectivity modes between Zn atoms and bbi ligands in compounds **1** (a), **2** (b) and (c), **3** (d)

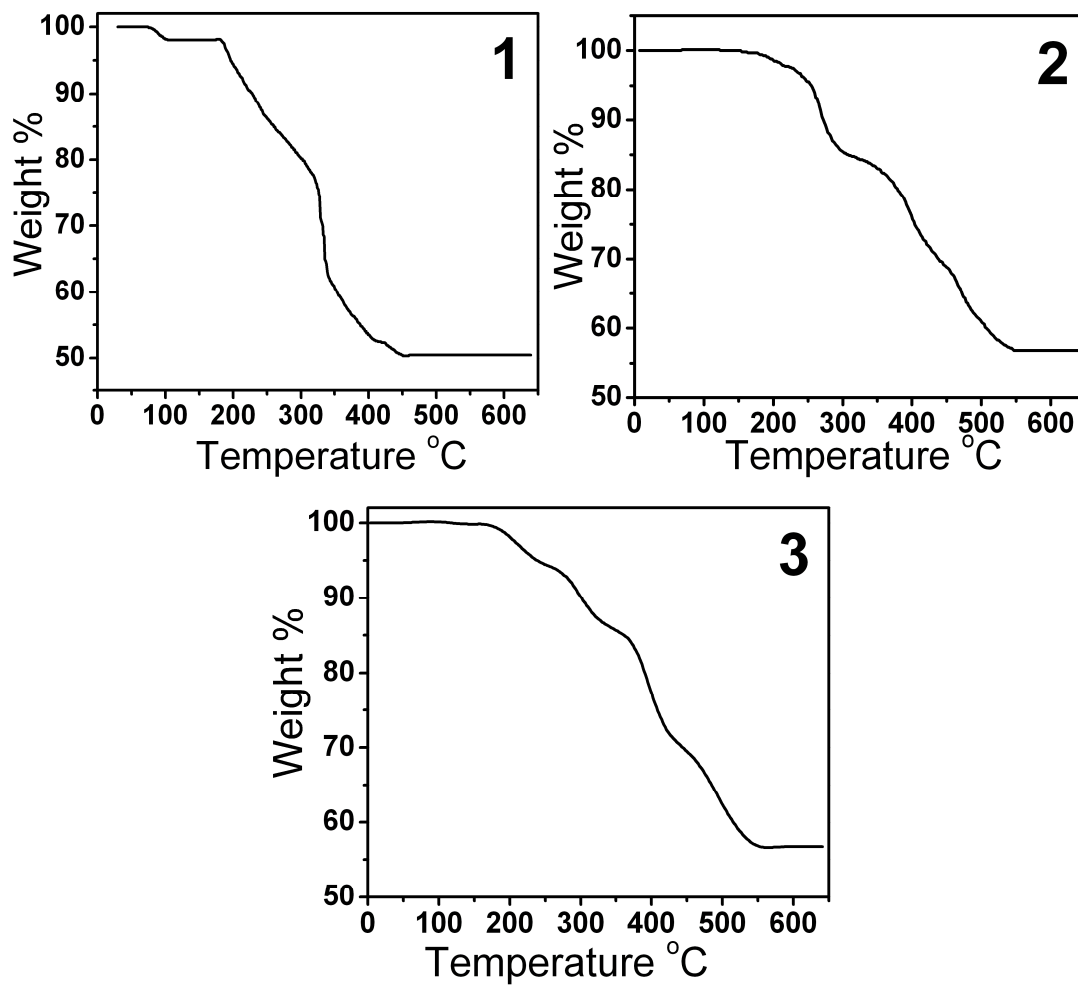


Figure S8. The TGA curves of compounds 1 - 3.

Table S1. Conformation (B) of bbi (A), Dihedral Angle of Two Imidazole Rings (C) (deg), and Torsion Angles (D) (deg) in compounds **1-3**

	A	B	C	D		
1	bbi1	GTG	1.2	N2-C4-C5-C6	C4-C5-C6-C7	C5-C6-C7-N8
				60.76	-179.47	-64.90
	bbi2	GTG	4.9	N4-C14-C15-C16	C14-C15-C16-C17	C15-C16-C17-N6
				58.90	-178.19	-66.00
2	bbi1	TGG	71.9	N2-C4-C5-C6	C4-C5-C6-C7	C5-C6-C7-N3
				-178.40	84.90	75.61
	bbi2	TGG	64.9	N6-C14-C15-C16	C14-C15-C16-C17	C15-C16-C17-N7
				179.78	90.69	-62.22
3	bbi1	TTT	0	N2-C4-C5-C5'	C4-C5-C5'-C4'	C5-C5'-C4'-N2
				169.22	180	-169.22