

Supporting Information

Three Metalloporphyrin Frameworks containing imidazole groups: Synthesis, Characterization and Properties

Li Zhang^{1,2}, Lei Hou^{1,*}, Xin Zhao¹, Zengqi Zhang¹, Yongsong Wang¹, Jun Li^{1,*}

¹Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of the Ministry of Education, Shaanxi Key Laboratory of Physico-Inorganic Chemistry, College of Chemistry & Materials Science, Northwest University, Xi'an 710069, China. Email: lhou2009@nwu.edu.cn; junli@nwu.edu.cn

²School of Biological and Chemical Engineering, Nanyang Institute of Technology, Nanyang 473004, China.

Content:

Figure S1: MS of **L**₁: *trans*-(tBu-Ph)₂(Im-Ph)₂Por.

Figure S2: MS of **L**₂: *trans*-(F₃-Ph)₂(Im-Ph)₂Por.

Figure S3: MS of **L**₃: *trans*-(F₅-Ph)₂(Im-Ph)₂Por.

Figure S4: ¹H NMR spectrum of **L**₁: *trans*-(tBu-Ph)₂(Im-Ph)₂Por.

Figure S5: ¹H NMR spectrum of **L**₂: *trans*-(F₃-Ph)₂(Im-Ph)₂Por.

Figure S6: ¹H NMR spectrum of **L**₃: *trans*-(F₅-Ph)₂(Im-Ph)₂Por.

Figure S7: The UV-vis absorption spectrum of **L**₁: *trans*-(tBu-Ph)₂(Im-Ph)₂Por in CH₂Cl₂.

Figure S8: The UV-vis absorption spectrum of **L**₂: *trans*-(F₃-Ph)₂(Im-Ph)₂Por in CH₂Cl₂.

Figure S9: The UV-vis absorption spectrum of **L**₃: *trans*-(F₅-Ph)₂(Im-Ph)₂Por in CH₂Cl₂.

Figure S10: Structural views of complex **2**.

Figure S11: Powder X-ray diffraction pattern of complex **1**.

Figure S12: Powder X-ray diffraction pattern of complex **2**.

Figure S13: Powder X-ray diffraction pattern of complex **3**.

Figure S14: TGA curves for complexes **1-3**.

Figure S15: N₂ adsorption isotherms of complexes **1**, **2** and **3** at 77K

Figure S16: H₂ adsorption isotherms of complexes **1**, **2** and **3** at 77K

Figure S17: Structures of TBHP (a) and ethylbenzene (b) molecules

Table S1. Selected bond lengths (Å) and Angles (°) for the complexes **1-3**.

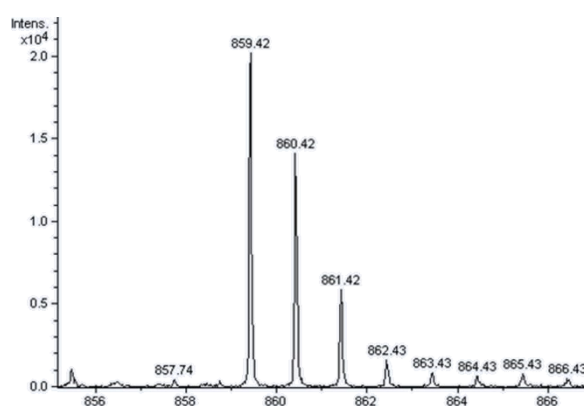


Figure S1. MS of **L₁**: *trans*-(tBu-Ph)₂(Im-Ph)₂Por.

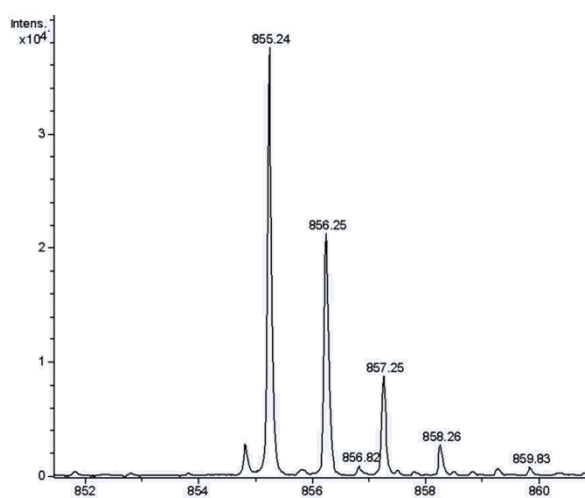


Figure S2. MS of **L₂**: *trans*-(F₃-Ph)₂(Im-Ph)₂Por.

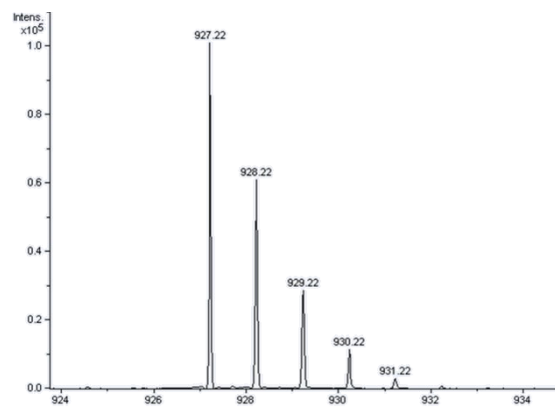


Figure S3. MS of **L**₃: *trans*-(F₅-Ph)₂(Im-Ph)₂Por.

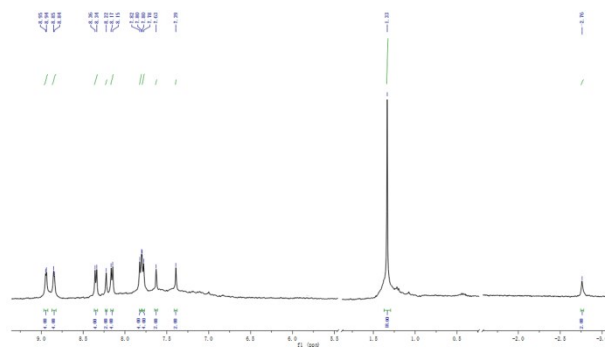


Figure S4. ¹H NMR spectrum of **L**₁: *trans*-(tBu-Ph)₂(Im-Ph)₂Por.

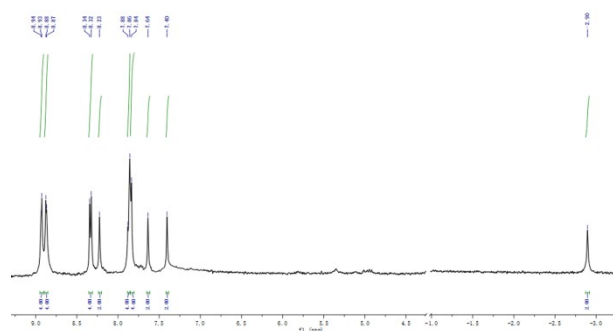


Figure S5. ^1H NMR spectrum of **L**₂: *trans*-(F₃-Ph)₂(Im-Ph)₂Por.

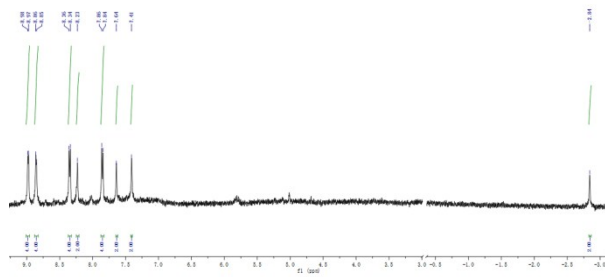


Figure S6. ^1H NMR spectrum of **L**₃: *trans*-(F₅-Ph)₂(Im-Ph)₂Por.

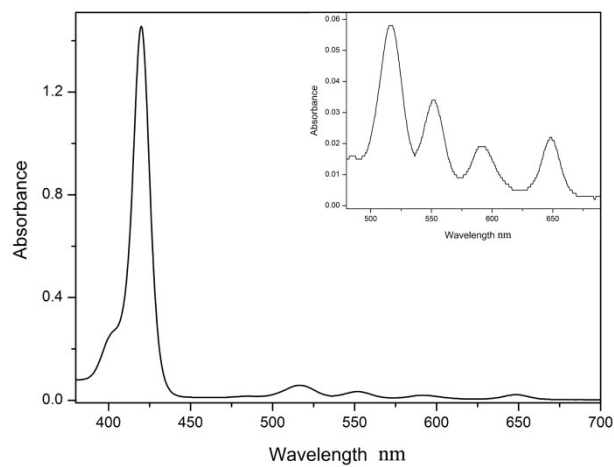


Figure S7. The UV-vis absorption spectrum of **L**₁ in CH_2Cl_2

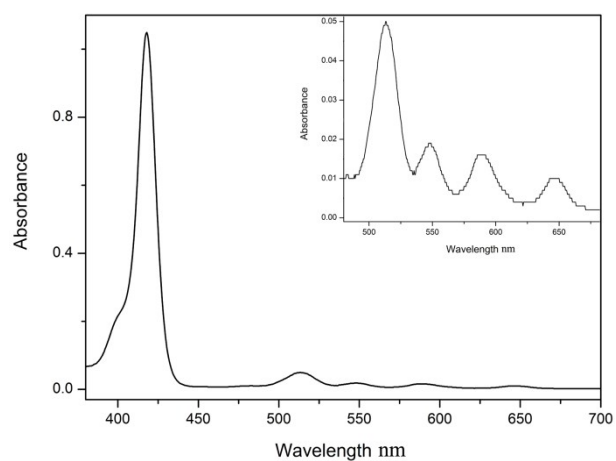


Figure S8: The UV-vis absorption spectrum of **L₂** in CH_2Cl_2

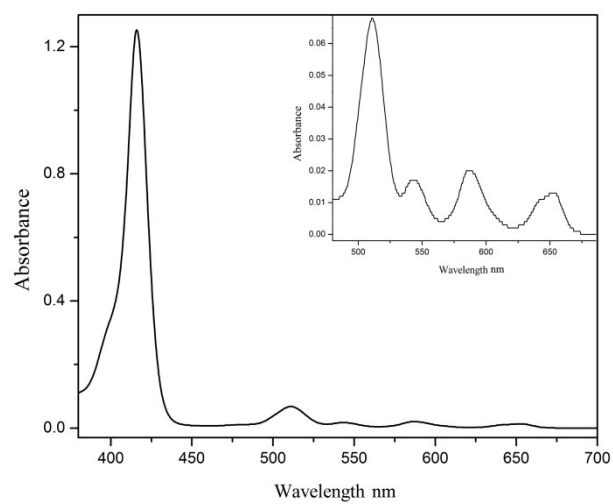


Figure S9. The UV-vis absorption spectrum of **L₃** in CH_2Cl_2

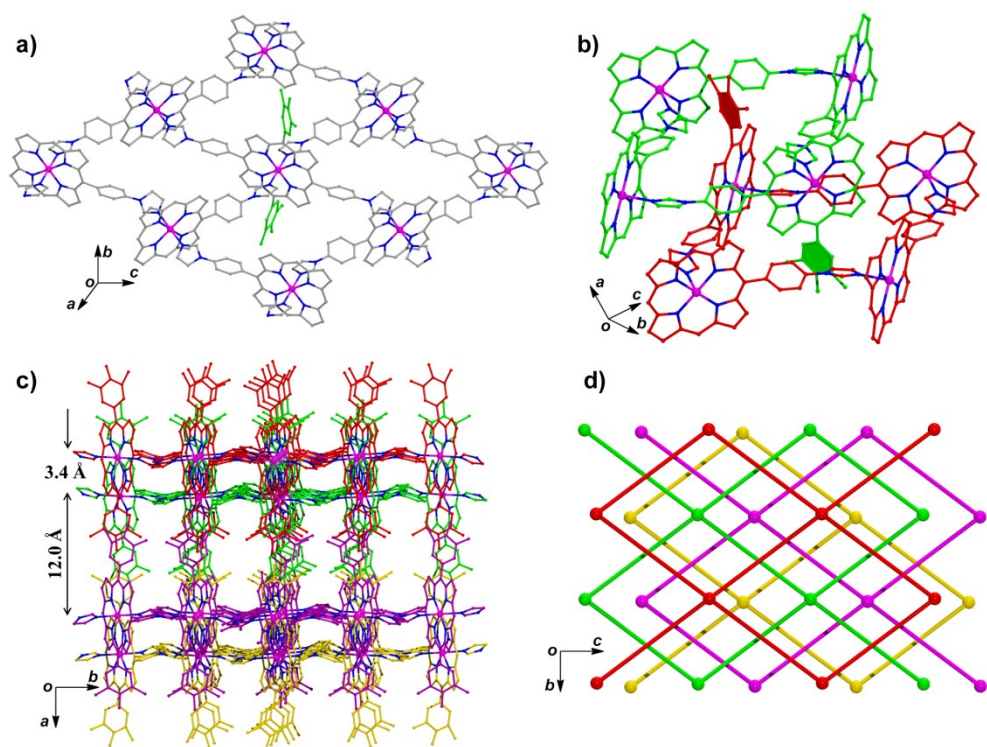


Figure S10. (a) 2D grid layer, b) mutual insertion of 3,4,5-trifluorophenyl groups in **2** between two layers, c) packing diagram of four layers and their topological representation in **2** viewed along the *c* axis, d) Topological graph exhibiting four Stacking layers.

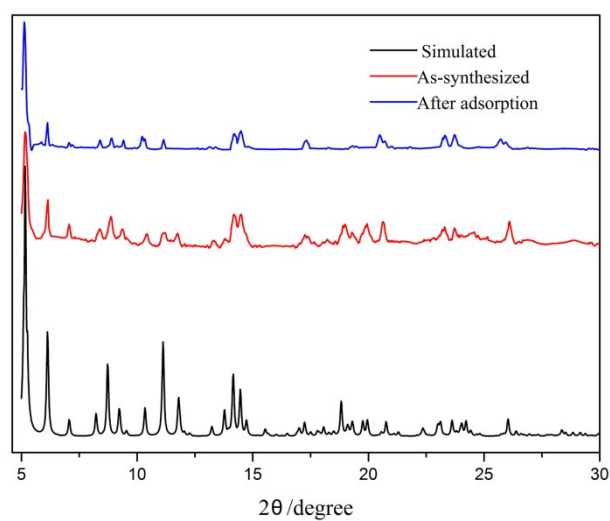


Figure S11. Powder X-ray diffraction pattern of complex **1**

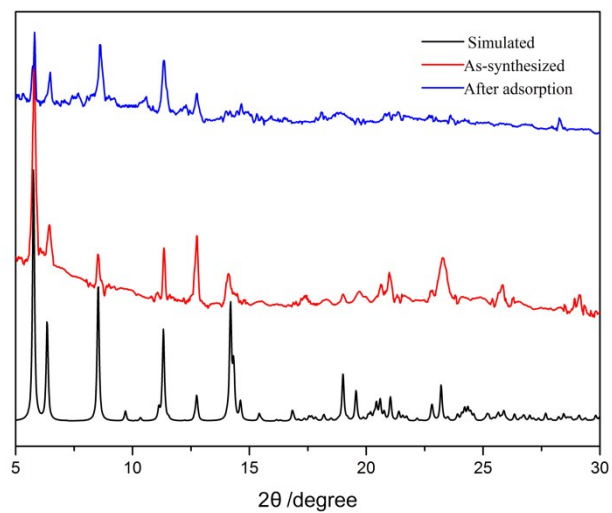


Figure S12. Powder X-ray diffraction pattern of complex **2**

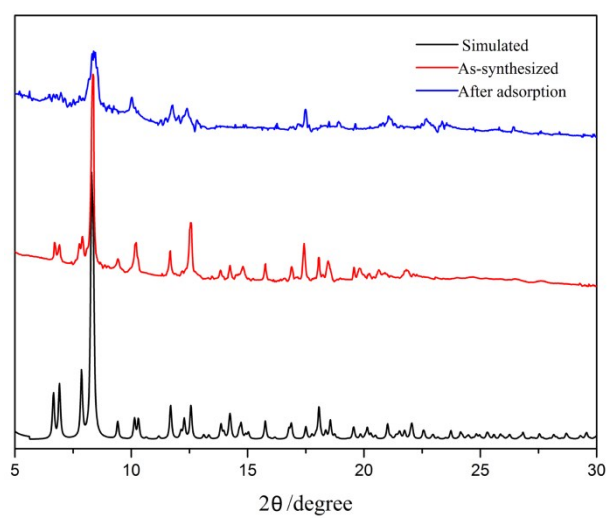


Figure S13. Powder X-ray diffraction pattern of complex **3**

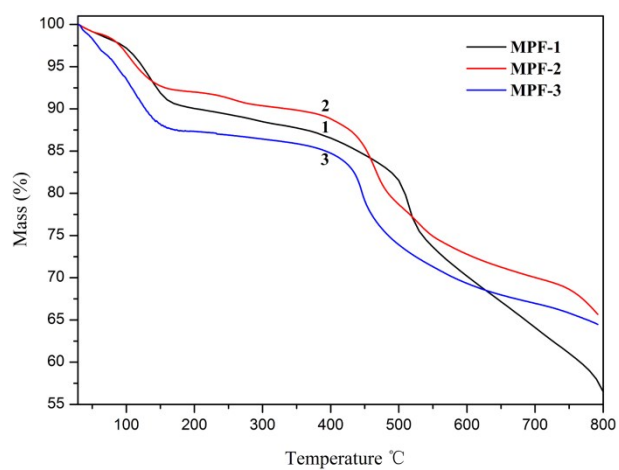


Figure S14. TGA curves for complexes **1-3**

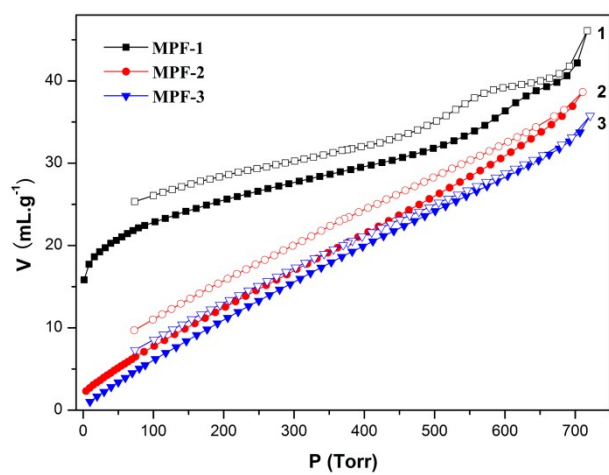


Figure S15. N₂ adsorption isotherms of complexes **1, 2** and **3** at 77K: **1** (black); **2** (red); **3** (blue)

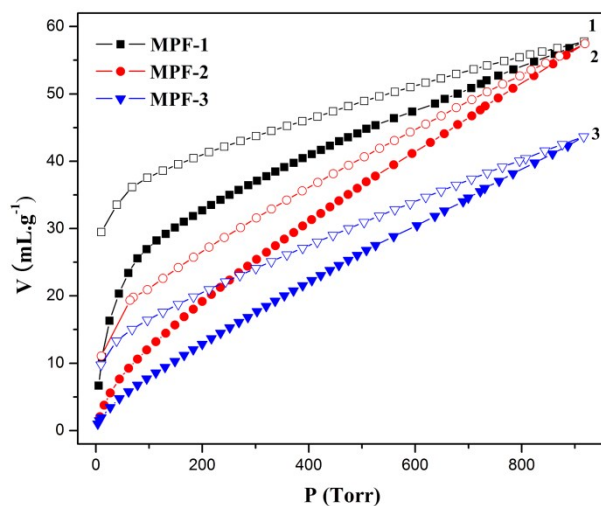


Figure S16. H₂ adsorption isotherms of complexes **1**, **2** and **3** at 77K: **1** (black); **2** (red); **3** (blue)

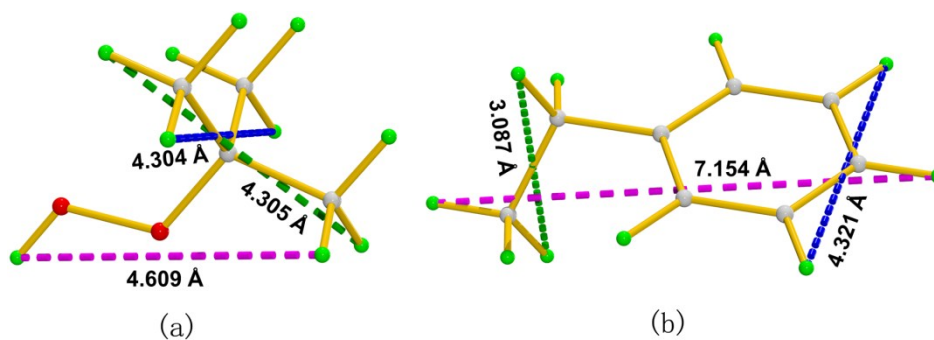


Figure S16. Structure of TBHP (a) and ethylbenzene (b) molecules

Table S1. Selected bond lengths (Å) and Angles (°) for complexes **1-3**

Complex 1			
Co(1)-N(1)	1.980(4)	Co(1)-N(3)	1.973(4)
Co(1)-N(2)	1.979(4)	Co(1)-N(4)	1.976(4)

Co(1)-N(6)#1	2.219(4)	Co(1)-N(8)#2	2.238(4)
N(1)-Co(1)-N(2)	89.70(18)	N(1)-Co(1)-N(4)	89.74(18)
N(3)-Co(1)-N(4)	90.20(18)	N(3)-Co(1)-N(2)	90.42(18)
N(2)-Co(1)-N(8)#2	93.69(17)	N(4)-Co(1)-N(8)#2	87.40(17)
N(1)-Co(1)-N(8)#2	88.64(16)	N(3)-Co(1)-N(8)#2	88.15(16)
N(2)-Co(1)-N(6)#1	88.23(17)	N(4)-Co(1)-N(6)#1	90.68(16)
N(1)-Co(1)-N(6)#1	91.62(16)	N(3)-Co(1)-N(6)#1	91.59(16)
N(3)-Co(1)-N(1)	176.79(17)	N(4)-Co(1)-N(2)	178.77(17)
N(6)#1-Co(1)-N(8)#2	178.06(19)		

Complex 2

Co(1)-N(1)	1.994(4)	Co(1)-N(2)	1.999(4)
Co(1)-N(3)	1.997(4)	Co(1)-N(4)	1.969(4)
Co(1)-N(8)#1	2.249(4)	Co(1)-N(6)#2	2.277(4)
N(1)-Co(1)-N(2)	89.83(18)	N(3)-Co(1)-N(2)	90.44(17)
N(4)-Co(1)-N(1)	90.40(18)	N(4)-Co(1)-N(3)	89.36(17)
N(4)-Co(1)-N(2)	178.83(16)	N(3)-Co(1)-N(1)	178.82(16)
N(1)-Co(1)-N(6)#2	89.44(16)	N(2)-Co(1)-N(6)#2	89.18(16)
N(3)-Co(1)-N(6)#2	91.71(16)	N(4)-Co(1)-N(6)#2	89.67(16)
N(1)-Co(1)-N(8)#1	91.39(16)	N(2)-Co(1)-N(8)#1	91.87(16)
N(3)-Co(1)-N(8)#1	87.46(16)	N(4)-Co(1)-N(8)#1	89.28(16)
N(8)#1-Co(1)-N(6)#2	178.67(16)		

Complex 3

Fe(1)-N(1)	2.003(3)	Fe(1)-N(1)#3	2.003(3)
Fe(1)-N(2)	1.983(3)	Fe(1)-N(2)#3	1.983(3)

Fe(1)-N(3)#1	1.978(4)	Fe(1)-N(3)#2	1.978(4)
N(2)-Fe(1)-N(1)	92.25(15)	N(2)#3- Fe(1)-N(1)	89.75(15)
N(2)-Fe(1)-N(1)#3	89.75(15)	N(2)#3-Fe(1)-N(1)#3	90.25(15)
N(3)#1-Fe(1)-N(1)	91.49(14)	N(3)#2-Fe(1)-N(1)#3	91.49(14)
N(3)#1-Fe(1)-N(2)	90.11(15)	N(3)#2-Fe(1)-N(1)	88.51(14)
N(3)#1-Fe(1)-N(1)#3	88.51(14)	N(3)#2-Fe(1)-N(2)	89.90(15)
N(3)#1-Fe(1)-N(2)#3	89.90(15)	N(3)#2-Fe(1)-N(2)#3	90.10(15)
N(2)-Fe(1)-N(2)#3	180.00(19)	N(1)#3-Fe(1)-N(1)	180.00(18)
N(3)#1-Fe(1)-N(3)#2	180.00(17)		

Symmetry codes used to generate equivalent atoms: Complex **1**: #1 x, -y, z+1/2; #2 x, -y+1, z-1/2; #3 x, -y, z-1/2; #4 x, -y+1, z+1/2. Complex **2**: #1 x, -y, z-1/2; #2 x, -y+1, z+1/2; #3 x, -y+1, z-1/2; #4 x, -y, z+1/2. Complex **3**: #1 y-1/4, -x+3/4, z-1/4; #2 -y+1/4, x+1/4, -z+1/4; #3 -x, -y+1, -z; #4 -y+3/4, x+1/4, z+1/4.