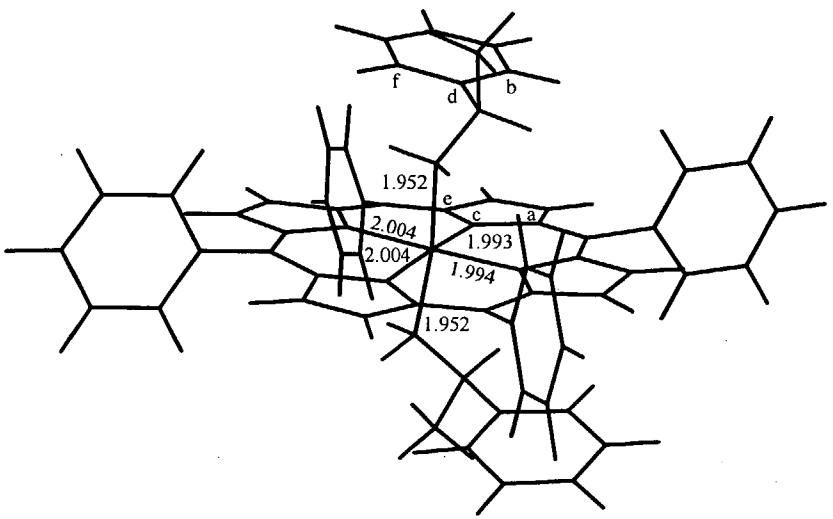
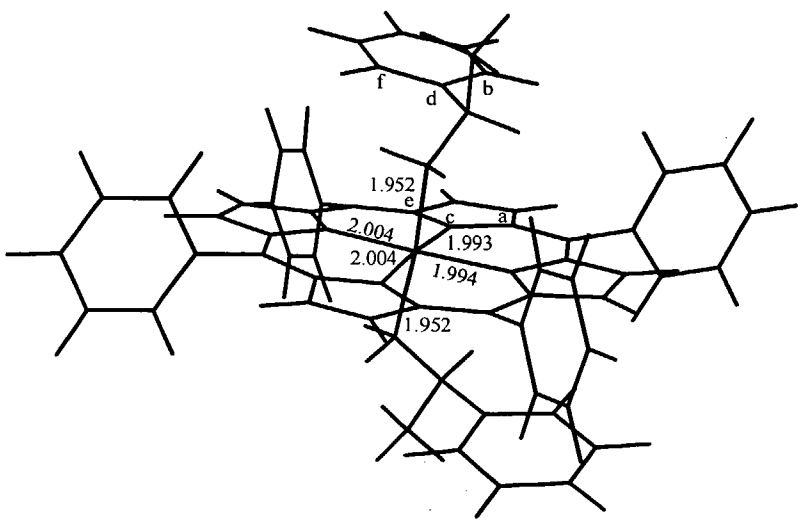


Contact:	Distance (Å):
a···b	3.30
c···d	3.13
e···f	3.68



Contact:	Distance (Å):
a···b	3.30
c···d	3.13
e···f	3.68

Figure S2. Stereoview of the MM-calculated lowest energy conformation of [Fe(TPP)(*R*-[+]-α-MeBzNH$_2$)$_2$]. The coordination group distances (Å) are shown. The ligand phenyl groups are in van der Waals contact with the porphyrin pyrrole rings over which they are positioned. Selected nonbonded contact distances are indicated.

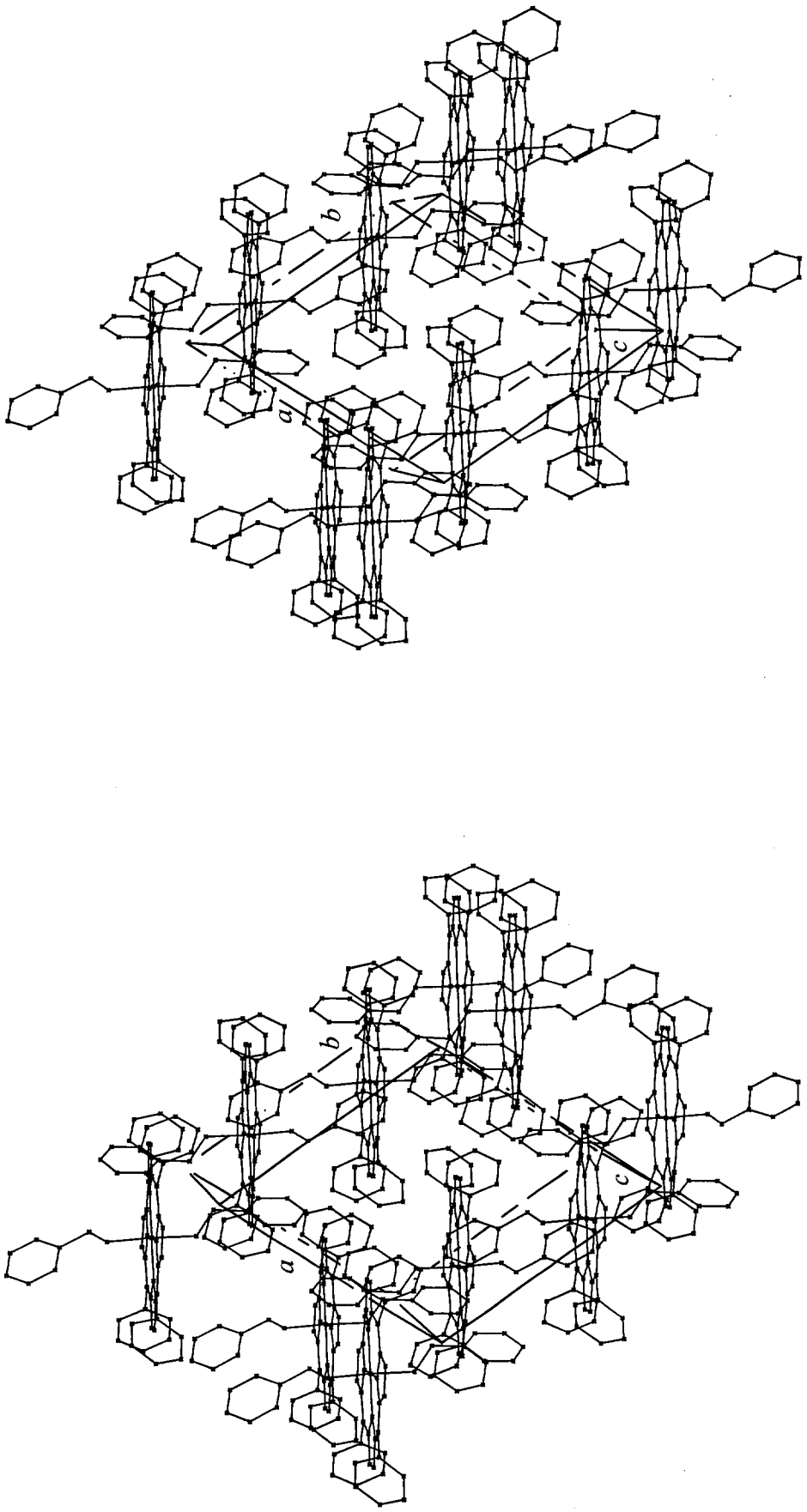
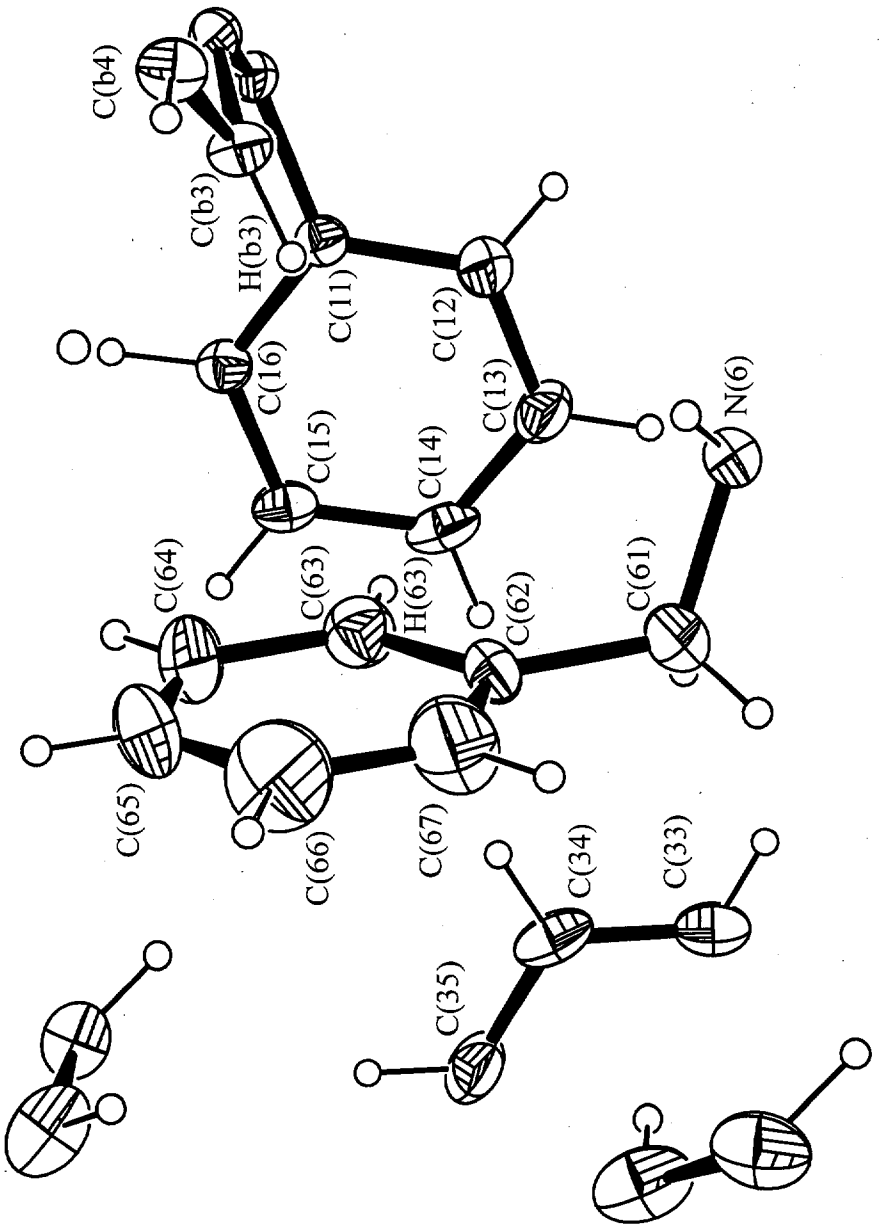
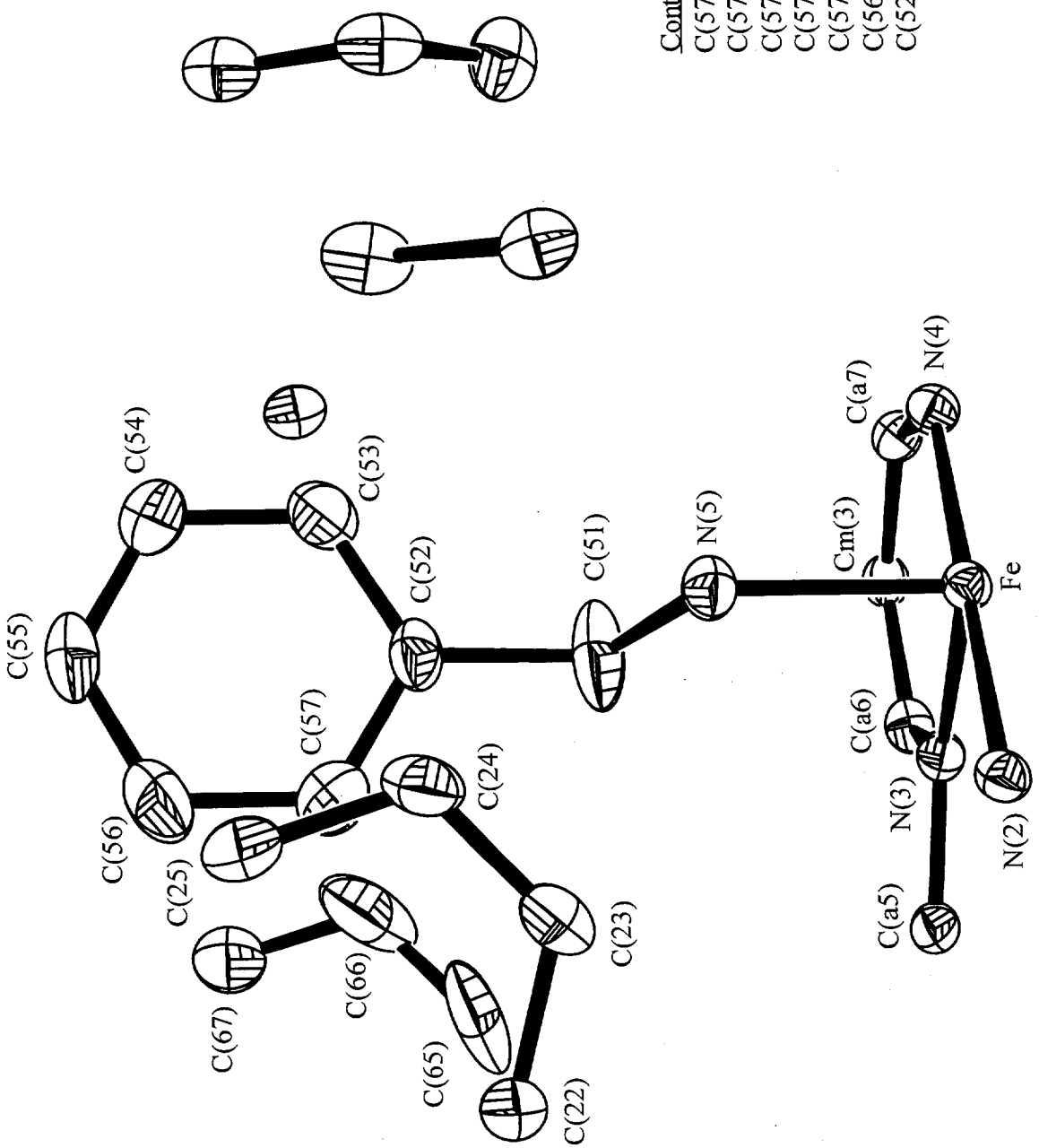


Figure S3. Stereoview of the unit cell of [Fe(TPP)(BzNH$_2$)$_2$]. The upper ligand (C(61) through C(67)) clearly nestles in the space between the phenyl groups of the closest neighbor. The ligand is tilted toward the viewer as a result of close contacts with one of the porphyrin phenyl groups (see Figure S4). The bottom ligand (C(51) through C(57)) is sandwiched between a porphyrin phenyl group of one neighbor and the phenyl ring of another neighbor's top benzylamine ligand (Figure S5). This interaction militates against inversion symmetry about the metal ion for [Fe(TPP)(BzNH$_2$)$_2$].



Contact:	Distance (Å)
H(63)...C(14)	2.915
H(63)...H(14)	3.305
H(63)...C(15)	2.941
H(63)...H(15)	3.337
H(63)...C(13)	3.095
H(63)...H(13)	3.557
H(63)...C(16)	3.191
H(63)...H(b3)	2.801
C(63)...H(b3)	2.926

Figure S4. ORTEP diagram illustrating all atoms within a 5.1-Angstrom radius of C(63) of one of the axial benzylamine ligands of [Fe(TPP)($BzNH_2$)$_2$]. Close contacts leading to the observed Fe-N(6)-C(61)-C(62) dihedral angle of 157.4° are listed at the right side of the diagram. These contacts also favor a N(3)-Fe-N(6)-C(61) dihedral angle (ligand orientation) of 59.9°. Thermal ellipsoids are drawn at the 25% probability level.



Contact:	Distance (Å):
C(57)···C(24)	3.694
C(57)···C(23)	3.911
C(57)···C(25)	3.826
C(57)···C(66)	3.645
C(57)···C(65)	3.914
C(56)···C(25)	3.719
C(52)···C(66)	3.825

Figure S5. ORTEP diagram illustrating all atoms within a 5.1-Angstrom radius of C(52) of one of the axial benzylamine ligands of [Fe(TPP)($BzNH_2$)$_2$]. The contact distances listed at the right of the diagram indicate that the ligand phenyl group is sandwiched between the phenyl ring of a neighboring porphyrin and the phenyl group of one of the axial ligands of a second neighbor close by. This interaction leads to a N(3)-Fe-N(5)-C(51) dihedral angle (ligand orientation) of 18.2° and militates against inversion symmetry about the metal ion. Thermal ellipsoids are drawn at the 25% probability level. Hydrogen atoms have been omitted for clarity.

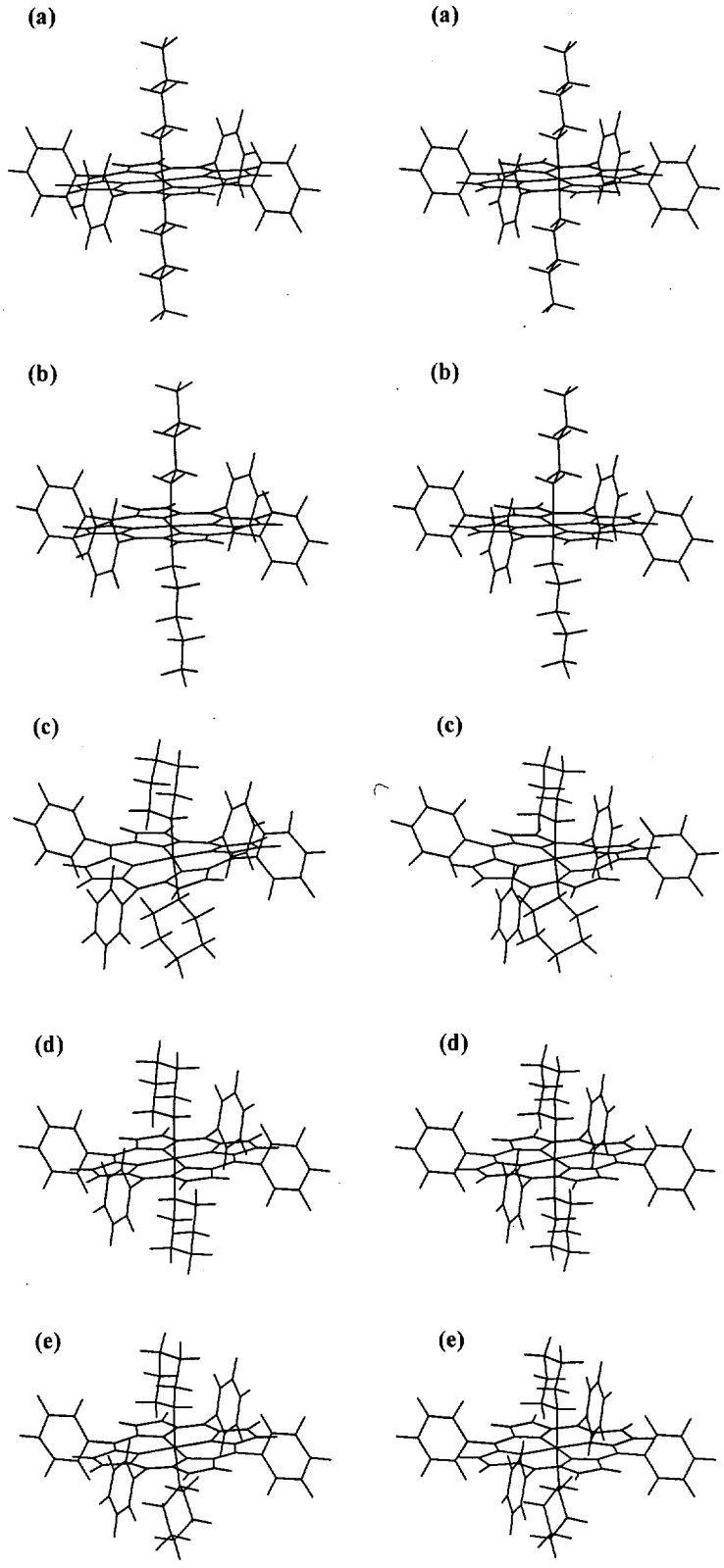


Figure S6. Stereoscopic views of selected calculated minima for [Fe(TPP)(1-BuNH$_2$)$_2$] and [Fe(TPP)(Pip)$_2$] taken from the surfaces in Figure 7 of the main text. The two conformations of [Fe(TPP)(1-BuNH$_2$)$_2$] are (a) a global minimum energy conformation (ϕ_1, ϕ_2 = 0°, 180°; ΔU_T = 0 kcal/mol) and (b) a local minimum energy conformation (ϕ_1, ϕ_2 = 0°, 0°; ΔU_T = 0.14 kcal/mol). The three conformations of [Fe(TPP)(Pip)$_2$] are (c) a global minimum energy conformation (ϕ_1, ϕ_2 = 70°, 20°; ΔU_T = 0 kcal/mol), (d) a local energy minimum (ϕ_1, ϕ_2 = 70°, 110°; ΔU_T = 1.6 kcal/mol), and (e) a higher energy local minimum (ϕ_1, ϕ_2 = 340°, 20°; ΔU_T = ~1.8 kcal/mol).