

## Supporting Information

### **Syn-Anti Conformational Switching in a Ethane-bridged Co(II)bisporphyrin Induced by External Stimuli: Effects of Inter-macrocyclic Interactions, Axial Ligation and Chemical and Electrochemical Oxidations**

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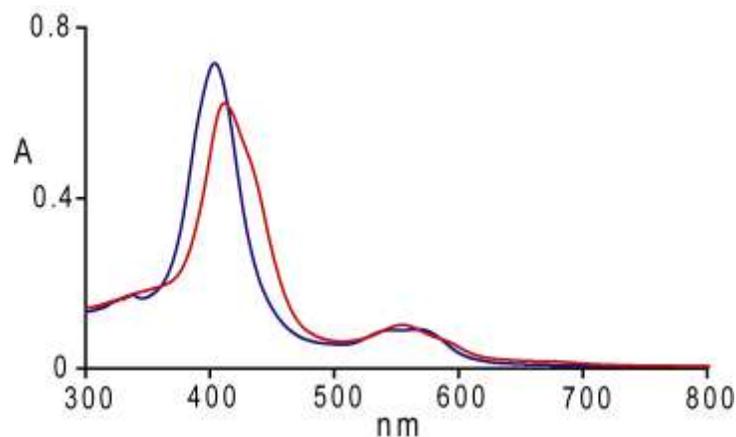


Figure S1. UV-visible spectra (at 295 K) of **2** in  $\text{CHCl}_3$  before (blue-line) and after addition of excess THF (red-line).

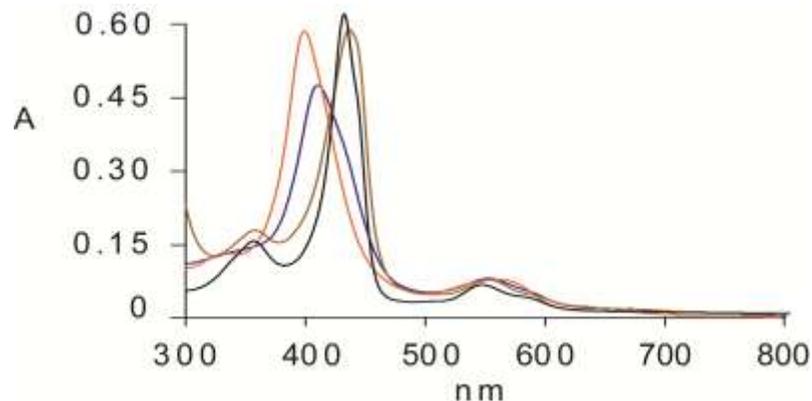


Figure S2. UV-visible spectra (at 295 K) in dichloromethane for **2** (red line), **2**·THF (blue line), **3**·I (black line) and **[3·(py)<sub>2</sub>]<sup>2+</sup>** (brown line).

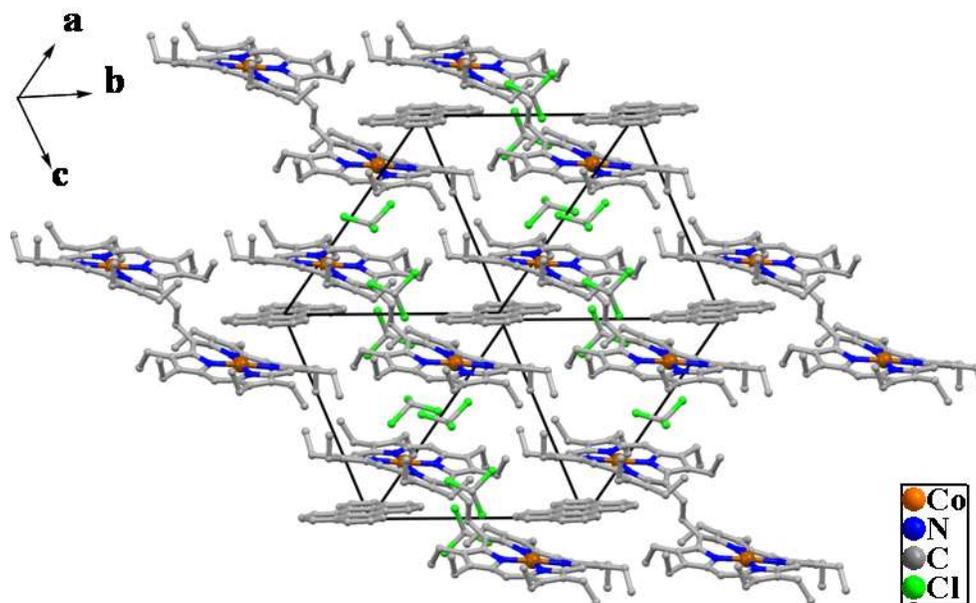


Figure S3. Diagram illustrating the packing of the *anti*-2-perylene in the unit cell at 100 K (H-atoms have been omitted for clarity).

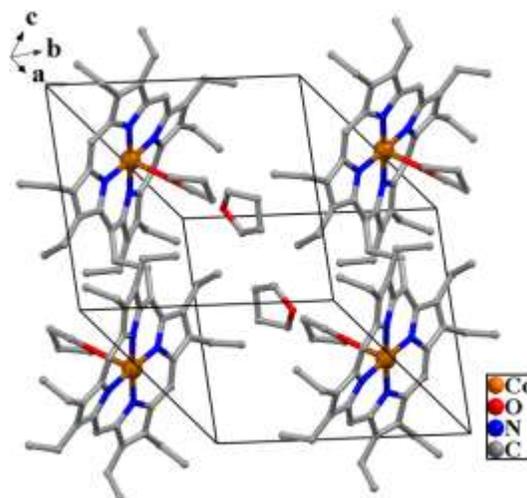


Figure S4. Diagram illustrating the packing of the 2-THF molecules in the unit cell at 100 K (H-atoms have been omitted for clarity).

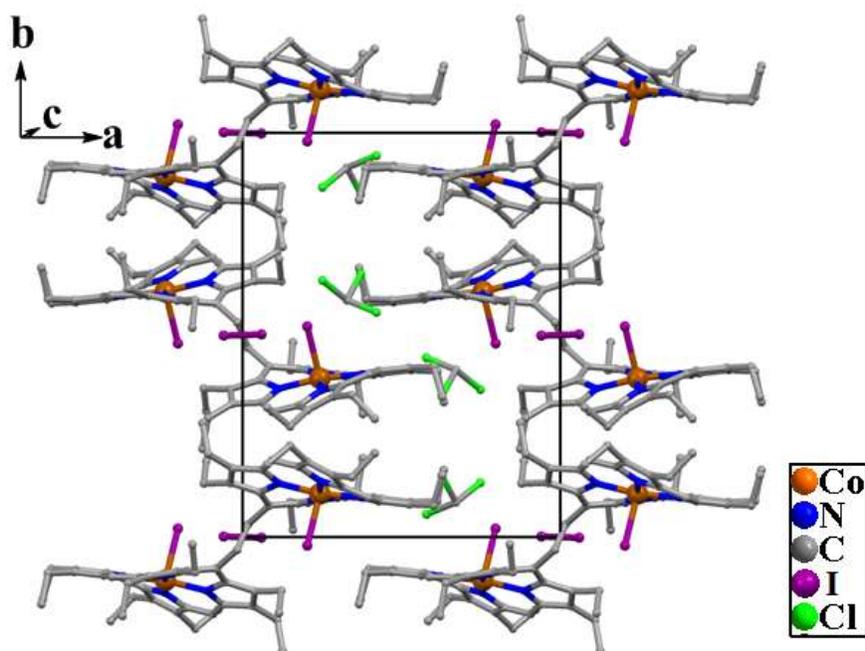


Figure S5. Diagram illustrating the packing of the  $3 \cdot I$  molecules in the unit cell at 100 K (H-atoms have been omitted for clarity).

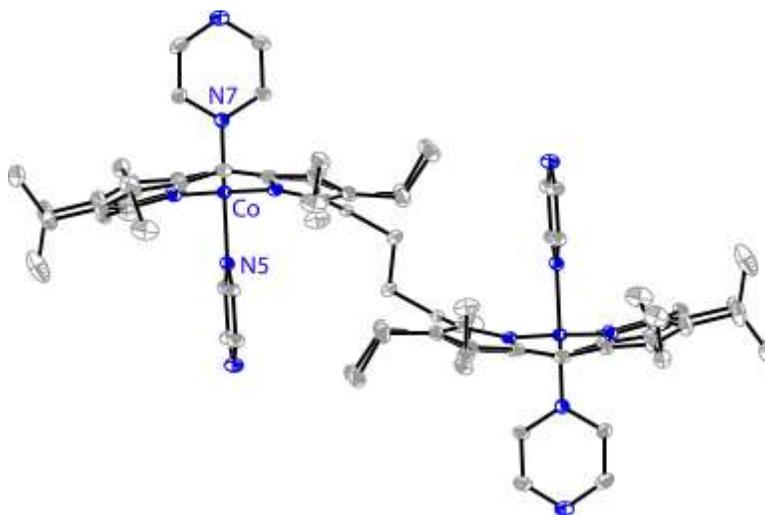


Figure S6. A perspective view of  $[3 \cdot (\text{pyr})_2][\text{Cl}]_2$  showing 50% thermal contours for all non-hydrogen atoms at 100 K (H-atoms, Cl, noncoordinated pyrazine and  $\text{CHCl}_3$  have been omitted for clarity).

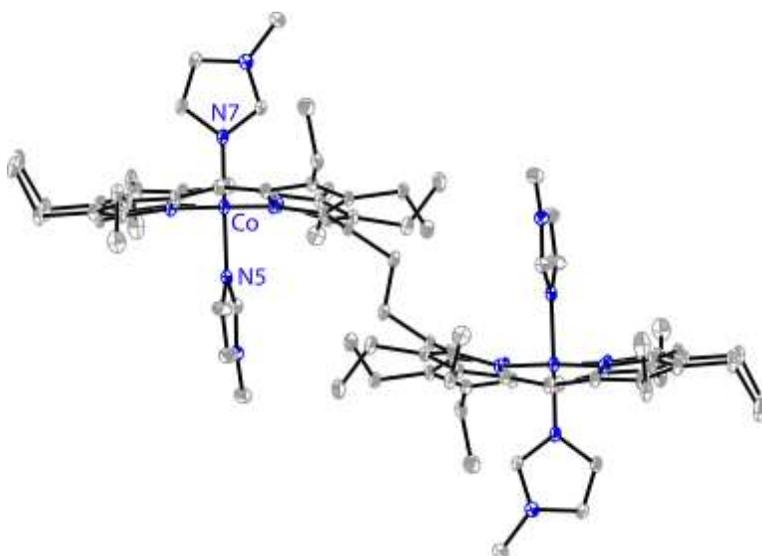


Figure S7. A perspective view of  $[3 \cdot (1\text{-Meim})_2][\text{ClO}_4]_2$  showing 50% thermal contours for all non-hydrogen atoms at 100 K (H-atoms,  $\text{ClO}_4^-$  and benzene have been omitted for clarity).

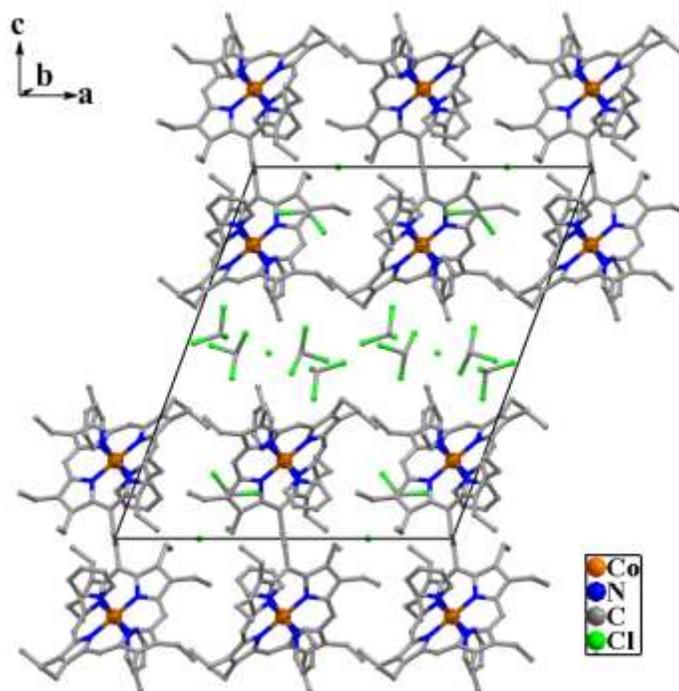


Figure S8. Diagram illustrating the packing of the  $[3 \cdot (\text{py})_2][\text{Cl}]_2$  molecules in the unit cell at 100 K (H-atoms have been omitted for clarity).

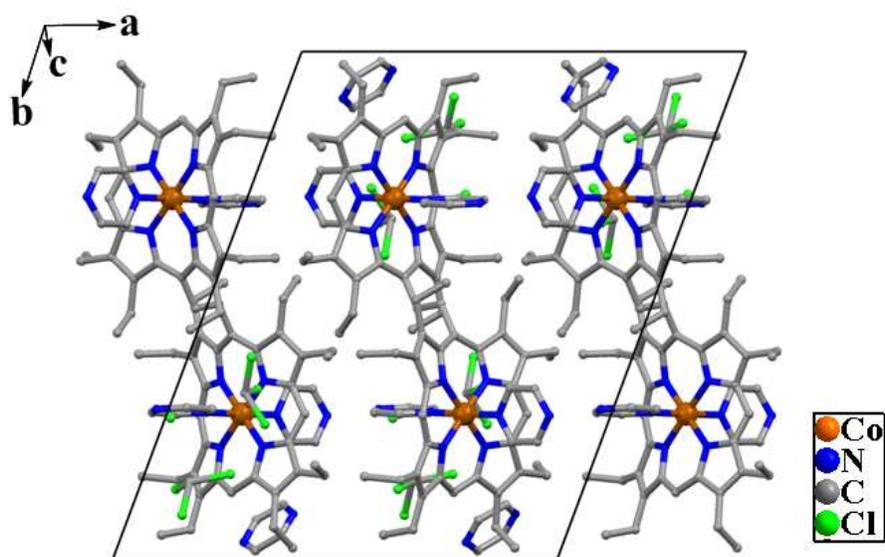


Figure S9. Diagram illustrating the packing of the  $[3 \cdot (\text{pyr})_2][\text{Cl}]_2$  molecules in the unit cell at 100 K (H-atoms have been omitted for clarity).

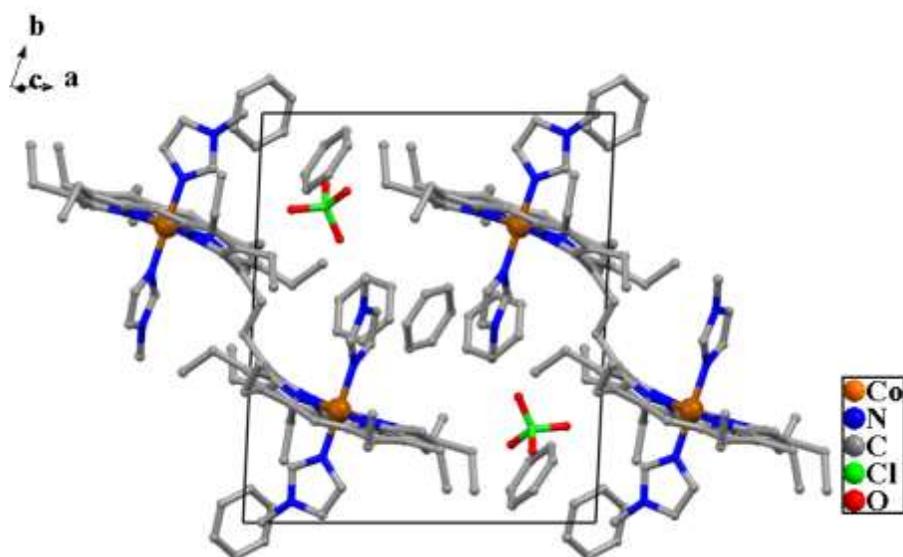


Figure S10. Diagram illustrating the packing of the  $[3 \cdot (1\text{-Meim})_2][\text{ClO}_4]_2$  molecules in the unit cell at 100 K (H-atoms have been omitted for clarity).

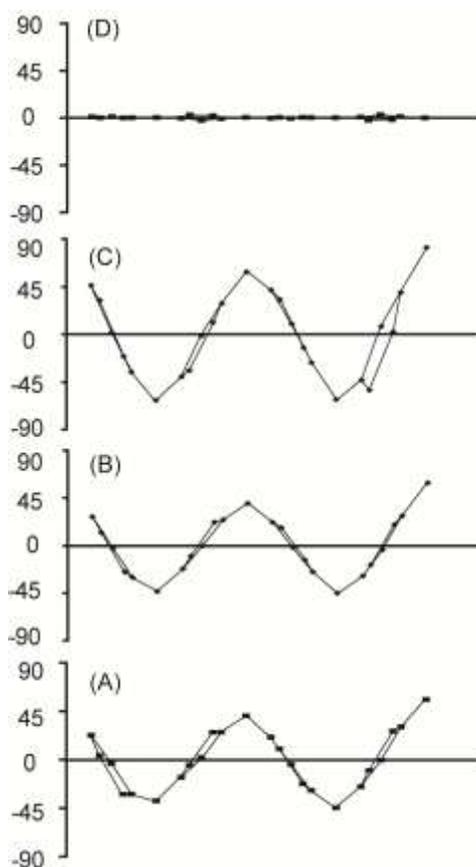


Figure S11. Out-of-plane displacements (in unit of  $0.01 \text{ \AA}$ ) of the porphyrin core atoms of (A) *anti-2*-perylene, (B) **2**·THF, (C)  $[\mathbf{3} \cdot (\text{py})_2][\text{Cl}]_2$  and (D)  $\text{Co}^{\text{II}}(\text{OEP})(3\text{-Mepy})_2$  (taken from R. G. Little and J. A. Ibers, *J. Am. Chem. Soc.*, 1974, **96**, 4440-4446.) from the mean plane of  $\text{C}_{20}\text{N}_4$  porphyrinato core. The horizontal axes show the bond connectivity between atoms.

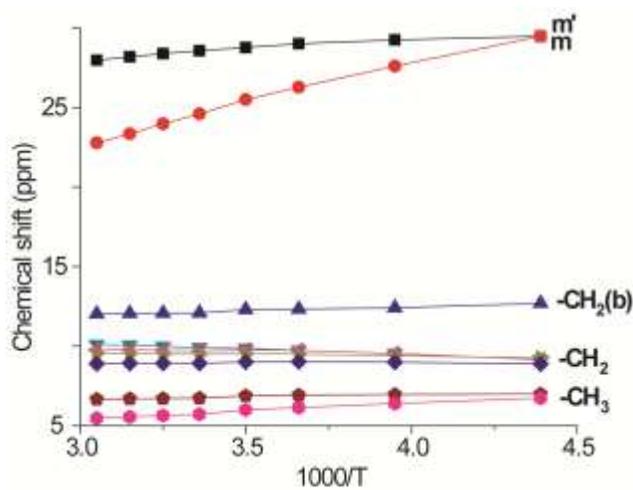


Figure S12. Curie plots (chemical shift versus  $1/T$ ) of the proton signals of **2**.

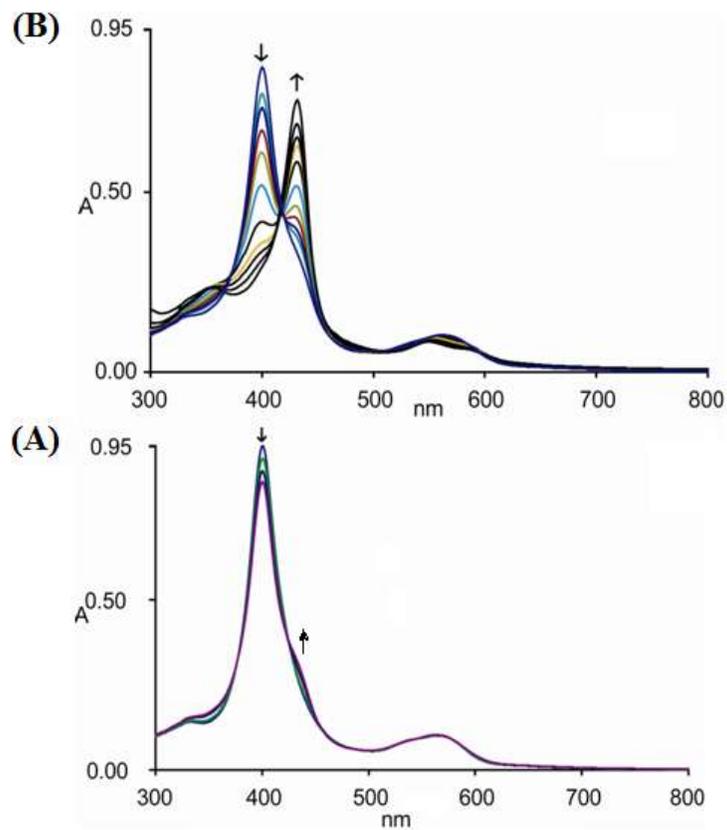


Figure S13. UV-visible spectral changes (in dry  $\text{CH}_2\text{Cl}_2$  under nitrogen at 295 K) of **2** upon oxidations using (A) one molar equivalent of silver tetrafluoroborate and (B) two molar equivalent of silver tetrafluoroborate. The arrows indicate increase or decrease of band intensity.

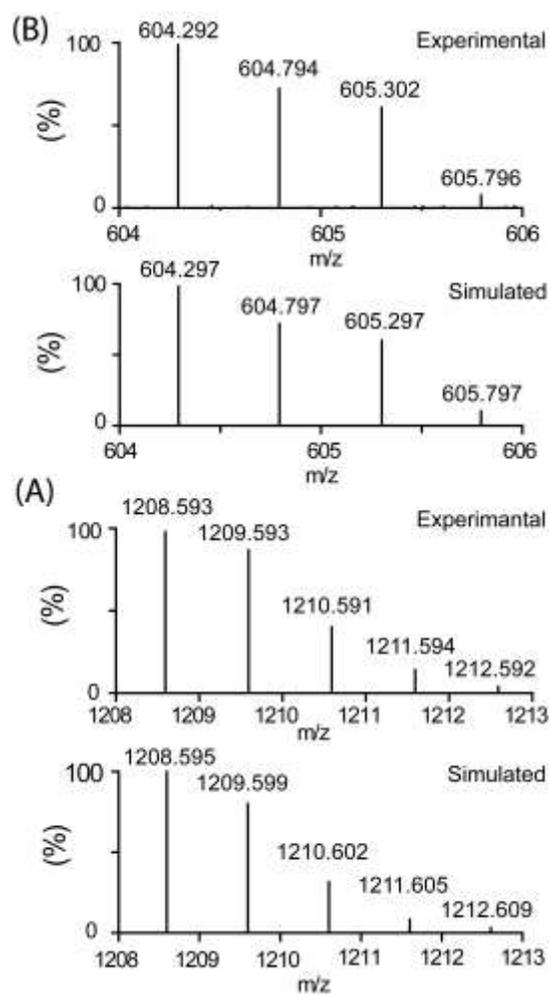


Figure S14. Isotopic distribution in ESI-MS of (A) 2<sup>+</sup> and (B) 2<sup>2+</sup>.