

Electronic Supplementary Information for Dalton Transactions  
This journal is © The Royal Society of Chemistry 2006

**Spectroelectrochemical evidence for communication within a  
laterally-bridged di-manganese(III) bis-porphyrin**

**Robert S. Armstrong, Garry J. Foran, Warren A. Hough, Deanna M. D'Alessandro,  
Peter A. Lay and Maxwell J. Crossley**

**Table S1** Redox potentials of **2** (vs the  $\text{Fc}^+/\text{Fc}$  couple) measured using cyclic voltammetry at Pt working electrode.<sup>a</sup>

CV Peak positions		$E_{1/2}$ /mV	Scan rate /mVs <sup>-1</sup>
Cathodic	Anodic		
~ -310	<sup>b</sup>		200
-890	-820	-855	200
-1070	-1005	-1037	200
-1310	~ -1230	-1270	200
-920	-823	-871	400
-1097	-1007	-1052	400
1067	1147	1107	400

<sup>a</sup> No  $iR$  compensation was applied.

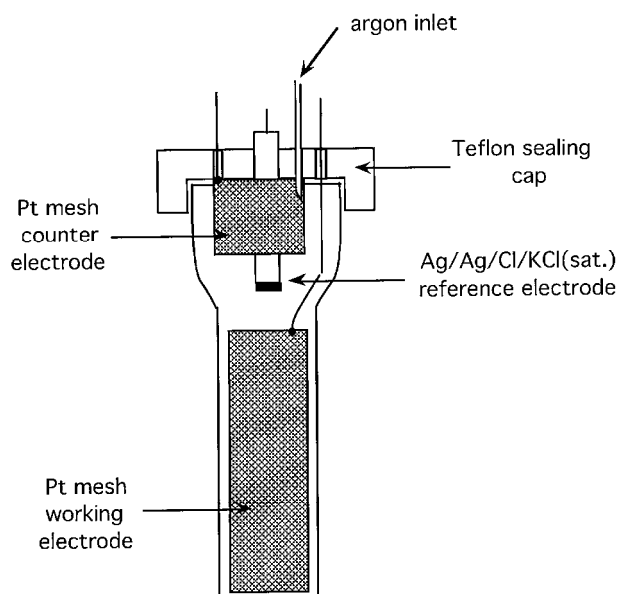
<sup>b</sup> No anodic peak was observed for this couple.

**Table S2** Electronic absorption band positions ( $\times 10^{-3} \text{ cm}^{-1}$ ) and molar absorption coefficients ( $\times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$ ) for dicopper(II) and dizinc(II) bis-porphyrins.

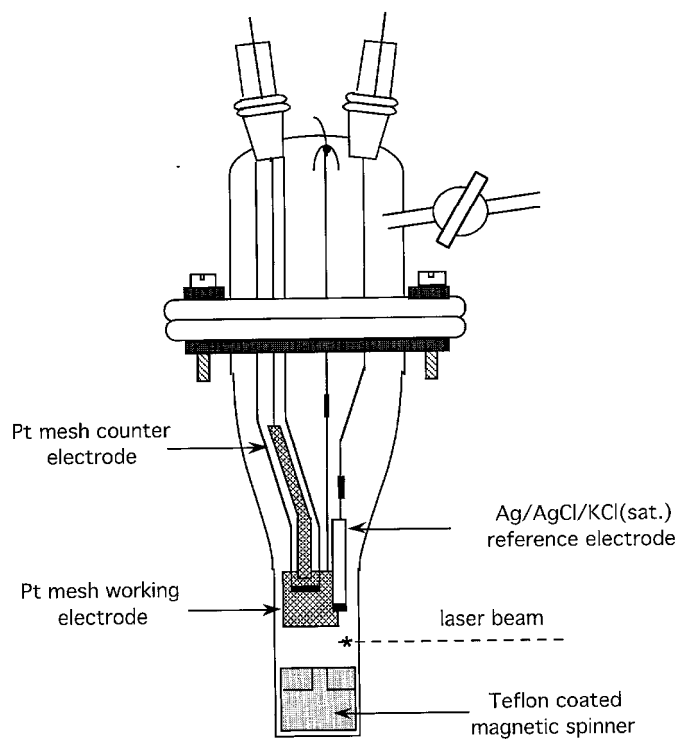
bis-porphyrin	Soret bands	Q bands
$\text{Cu}^{\text{II}}-\text{Cu}^{\text{II}}$	23.58 (5.50), 22.03 (5.40)	19.42 (4.84), 18.62 (4.84), 14.90 (4.40)
$\text{Zn}^{\text{II}}-\text{Zn}^{\text{II}}$	23.26 (5.54), 21.60 (5.52)	19.08 (4.85), 14.99 (4.33), 14.18 (4.30)

**Table S3** Correlation table for a change in symmetry from  $D_{4h}$  to  $D_{2h}$ ,  $C_{2v}$ ,  $C_{2h}$  and  $C_s$ .

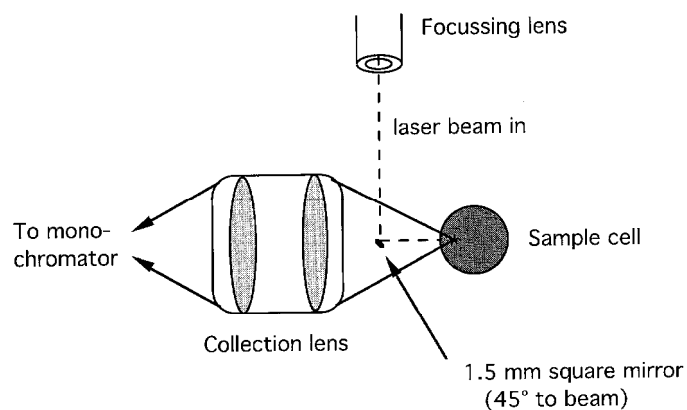
Molecular Symmetry				
$D_{4h}$	$D_{2h}$	$C_{2v}$	$C_{2h}$	$C_s$
$a_{1g}$	$a_g$	$a_1$	$a_g$	$a'$
$a_{2g}$	$b_{1g}$	$a_2$	$b_g$	$a''$
$b_{1g}$	$a_g$	$a_1$	$a_g$	$a'$
$b_{2g}$	$b_{1g}$	$a_2$	$b_g$	$a''$
$e_g$	$b_{2g}$	$b_1$	$b_g$	$a''$
	$b_{3g}$	$b_2$	$a_g$	$a'$
$a_{1u}$	$a_u$	$a_2$	$a_u$	$a''$
$a_{2u}$	$b_{1u}$	$a_1$	$b_u$	$a'$
$b_{1u}$	$a_u$	$a_2$	$a_u$	$a''$
$b_{2u}$	$b_{1u}$	$a_1$	$b_u$	$a'$
$e_u$	$b_{2u}$	$b_2$	$b_u$	$a'$
	$b_{3u}$	$b_1$	$a_u$	$a''$



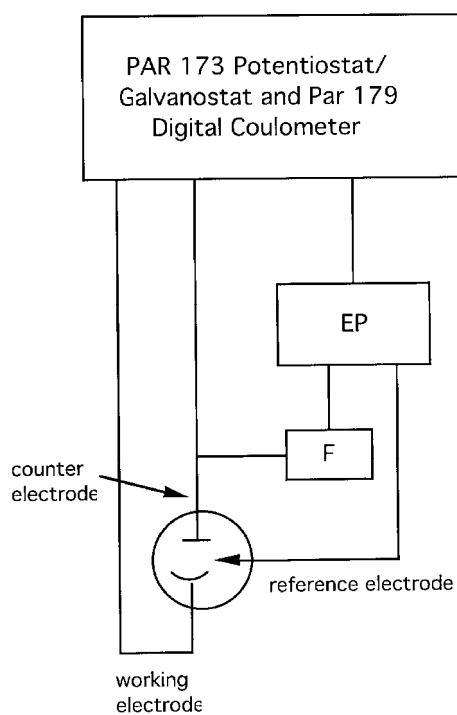
**Fig. S1** Schematic representation of the UV-Vis spectroelectrochemical cell.



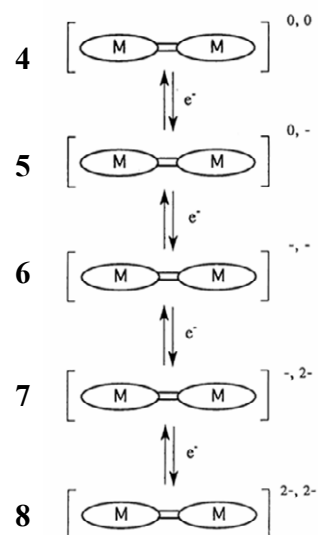
**Fig. S2(a)** Spectroelectrochemical Raman cell.



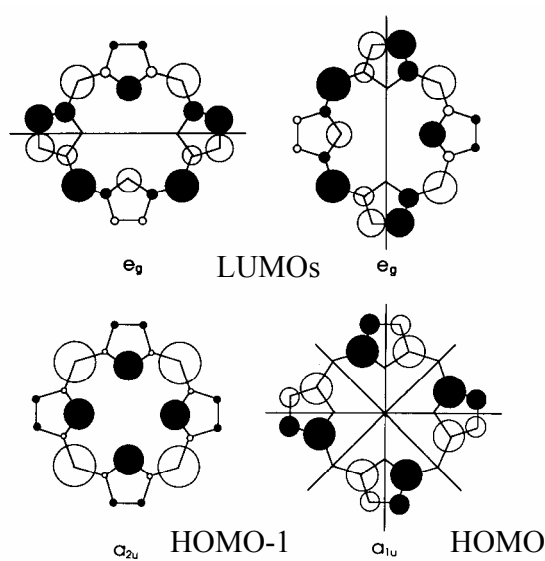
**Fig. S2(b)** Backscattering arrangement of the spectroelectrochemical Raman cell.



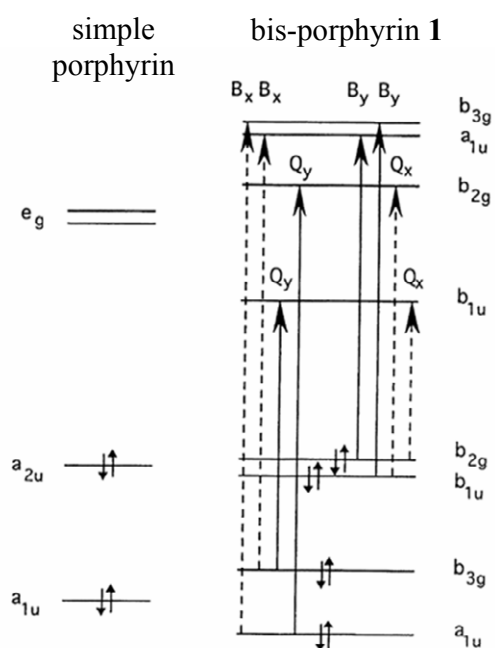
**Fig. S2(c)** Schematic representation of the electrochemical setup for bulk electrolysis. EP = electrometer probe and F = electrical filter.



**Fig. S3** The four electron transfer processes for bis-porphyrin complexes (drawn here in an abbreviated depiction), either in the free-base form or containing metal ions such as Mn(II), Cu(II) or Zn(II).



**Fig. S4** Gouterman's four orbital model for simple porphyrin. Schematic representation of the two highest occupied molecular orbitals (HOMOs:  $a_{1u}$  and  $a_{2u}$ ) and a degenerate pair of lowest unoccupied molecular orbitals (LUMOs). Reproduced from reference 12.



**Fig. S5** Molecular orbital diagram and allowed transitions of simple porphyrin and free-base bis-porphyrin **1** as determined by extended Hückel calculations. Solid arrows represent  $y$ -polarised transitions and dashed arrows represent  $x$ -polarised transitions.