

## Electronic Supplementary Information

### Long-range electronic connection in Picket-Fence like Ferrocene-Porphyrin Derivatives †

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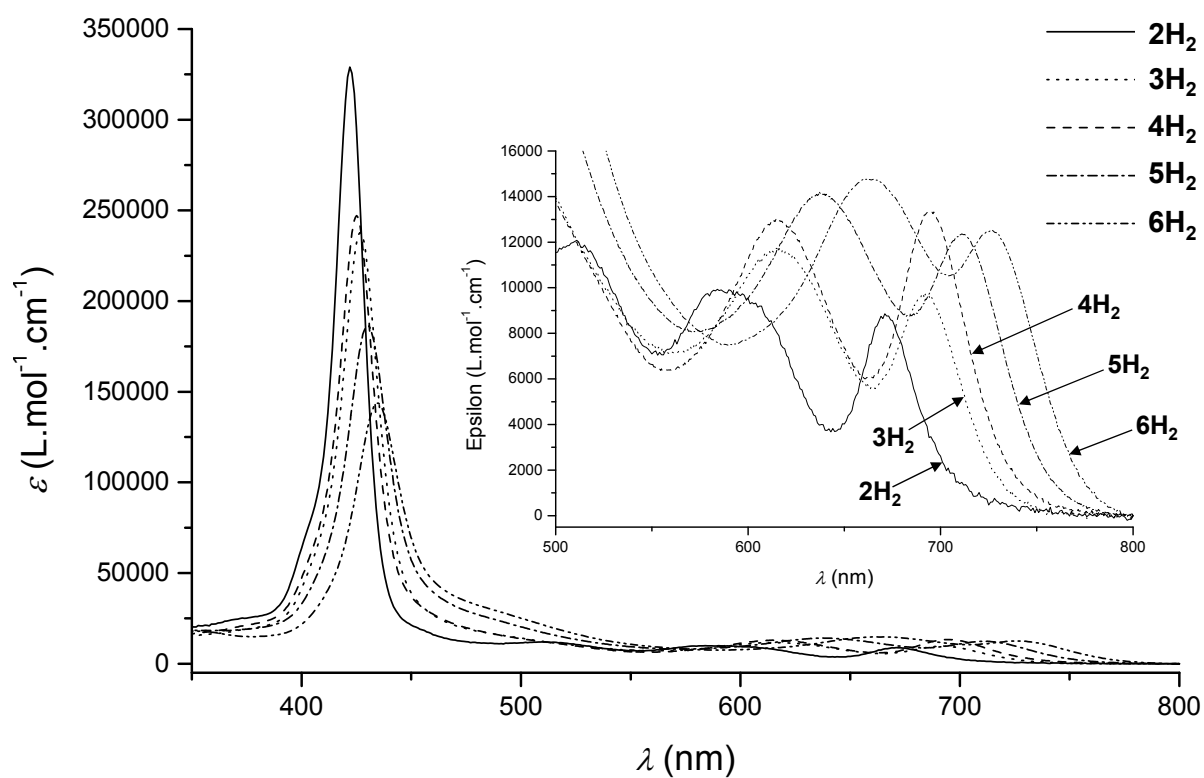
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**Fig. 1** UV-visible absorption spectra of  $2H_2$ - $6H_2$  in  $CH_2Cl_2$  at 295 K.

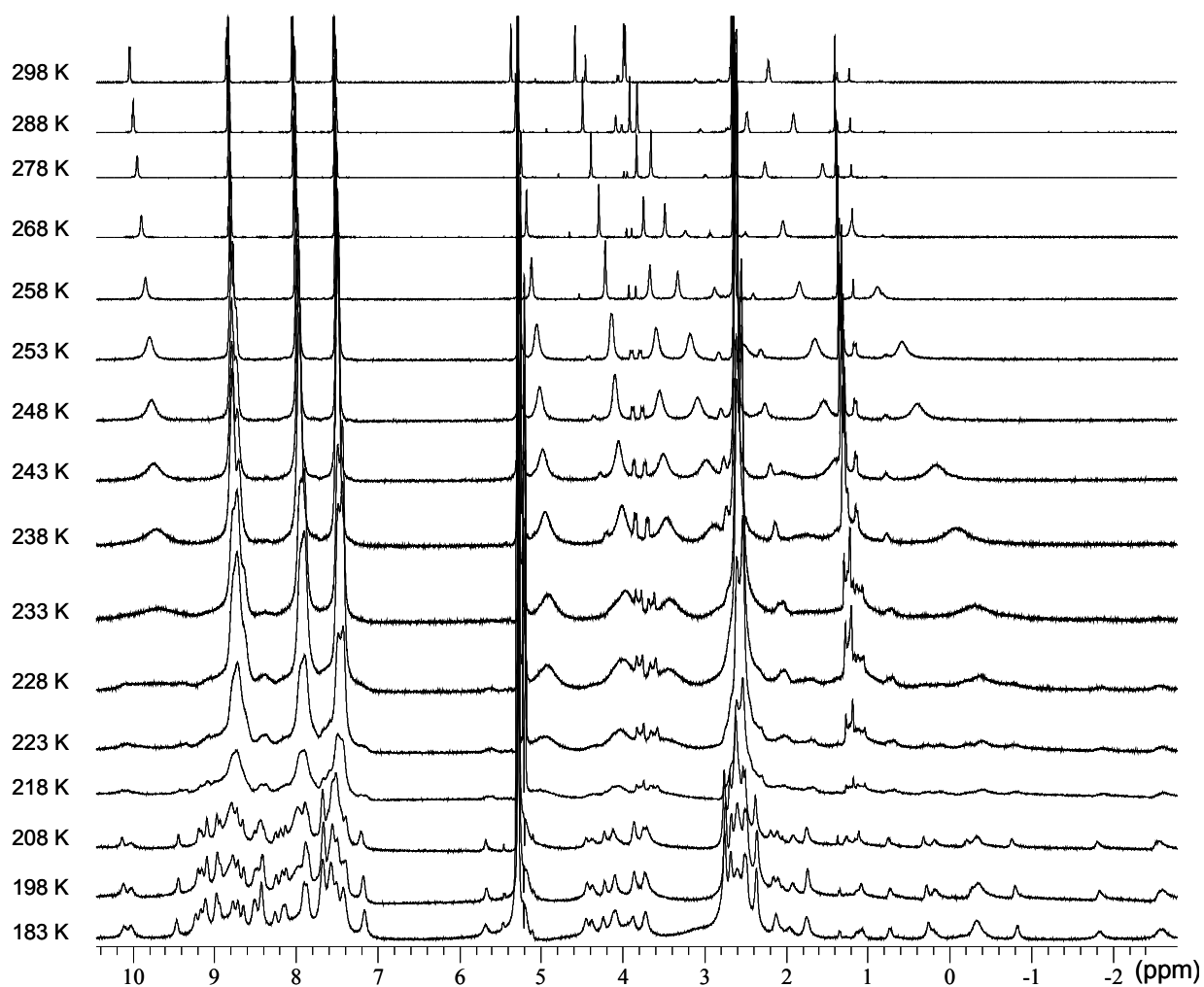
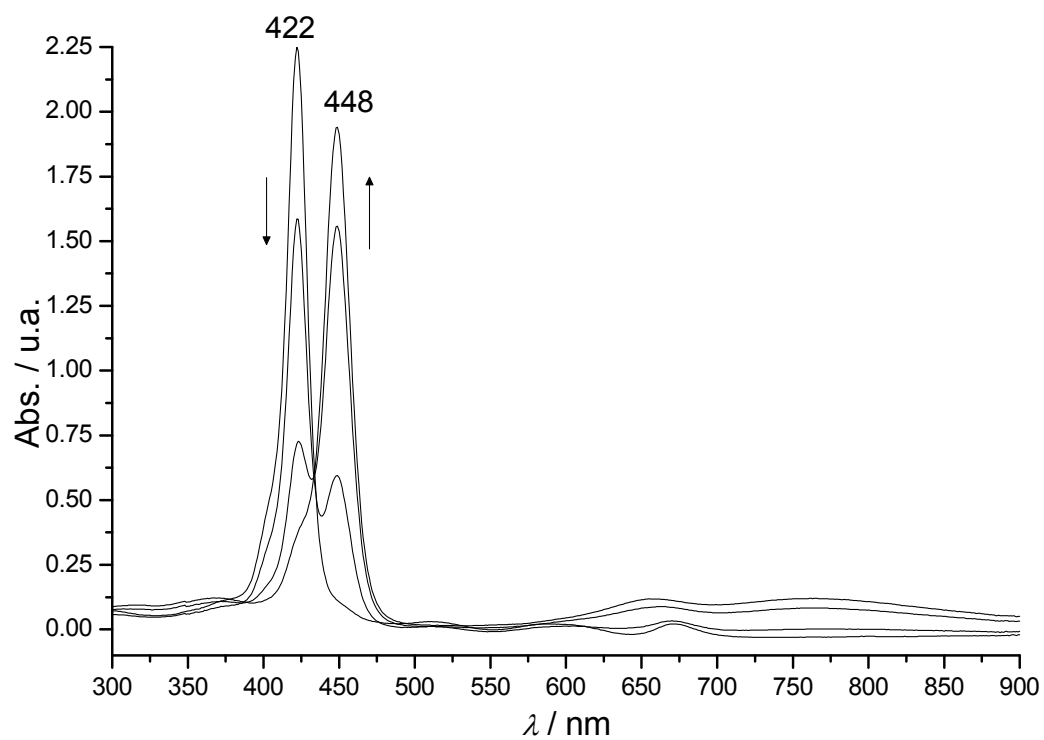
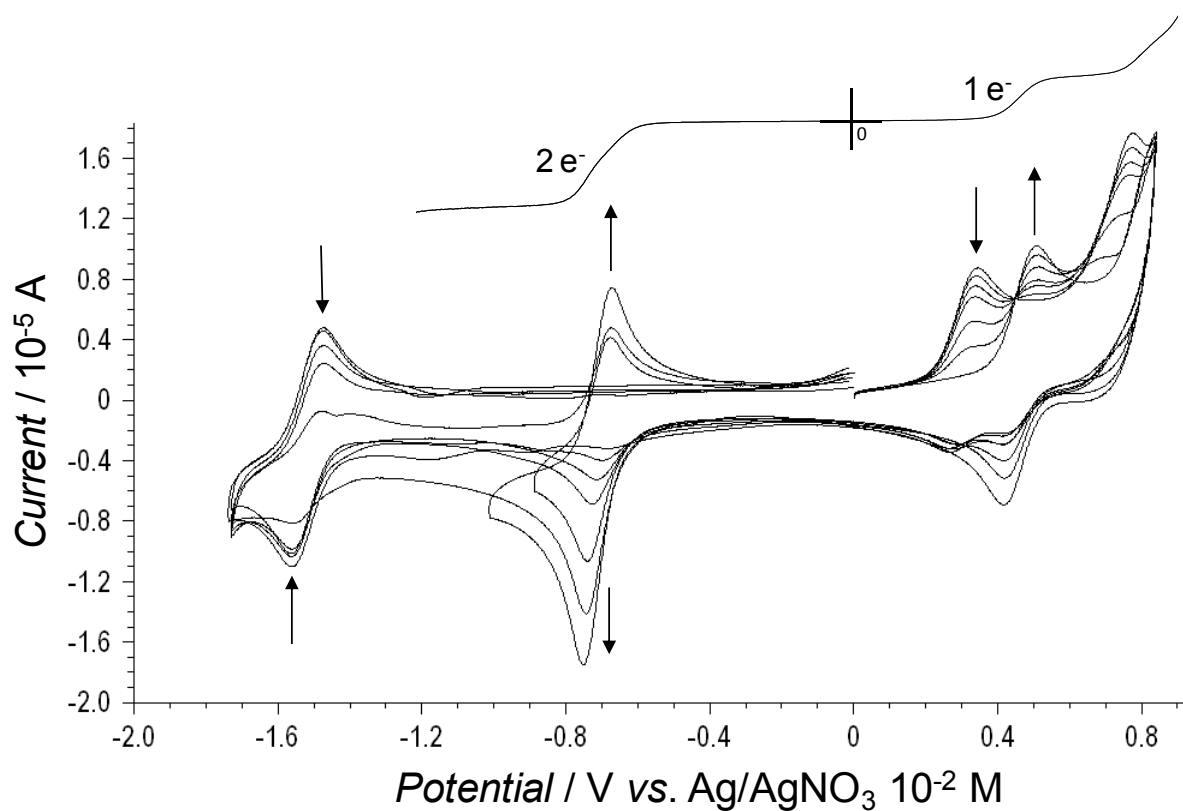


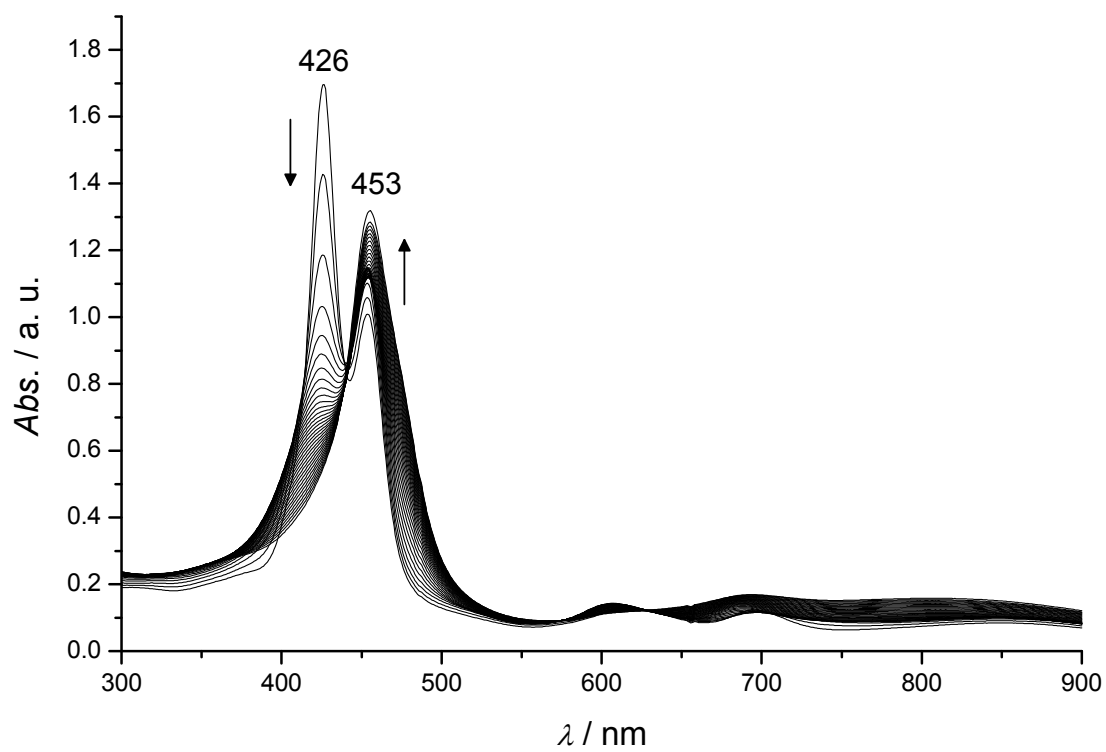
Fig. 2 <sup>1</sup>H NMR spectra of 2Zn in the 183 – 298 K temperature range ( $9 \cdot 10^{-3}$  M, CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz).



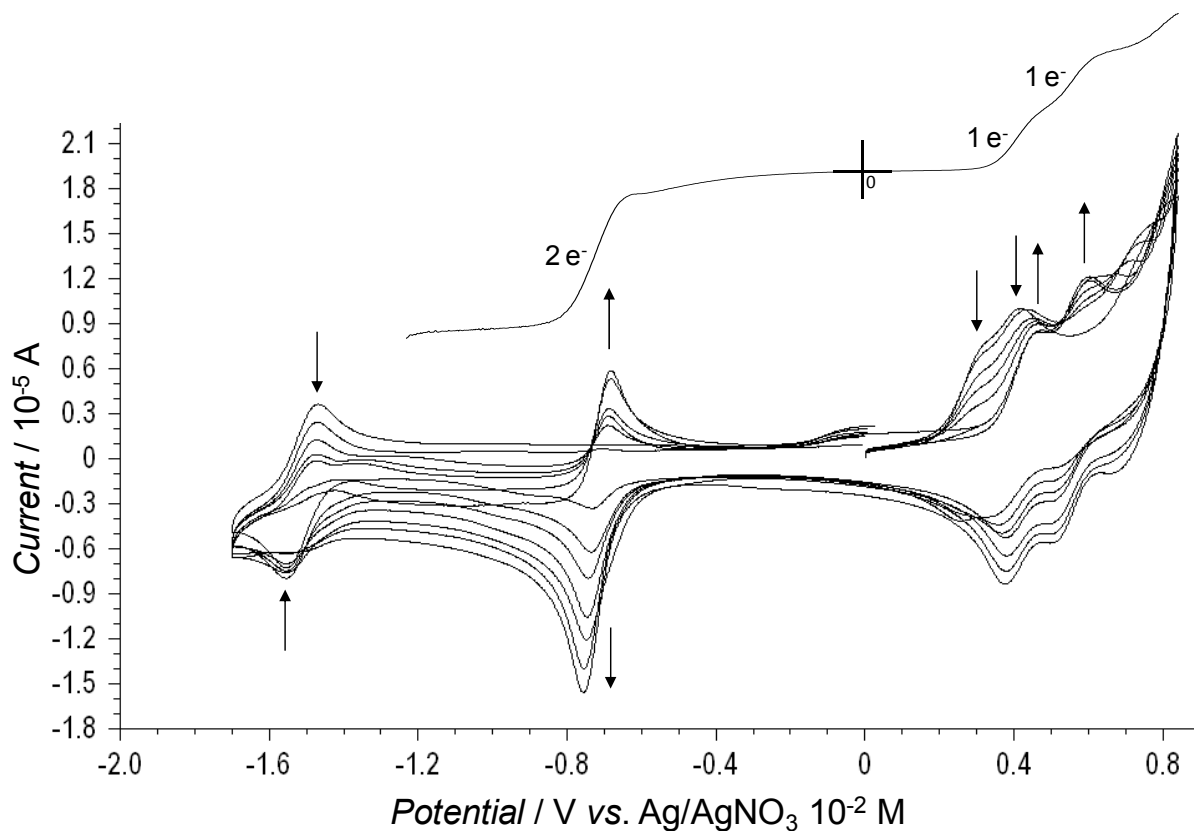
**Fig. 3** Evolution of the UV-visible absorption spectrum of **2H<sub>2</sub>** in CH<sub>2</sub>Cl<sub>2</sub> upon addition of 2 molar equivalents of TFA.



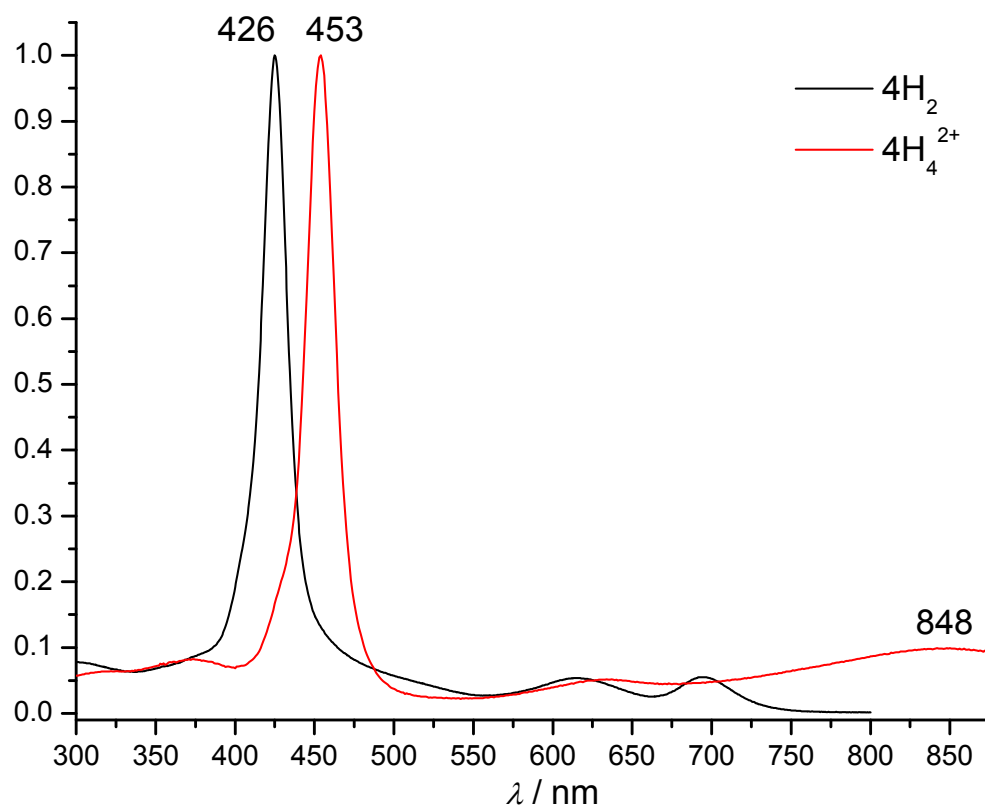
**Fig. 4** Evolution of the CV voltammogram of  $2\mathbf{H}_2$  upon addition of TFA (0 to 2 molar equivalents of TFA,  $[2\mathbf{H}_2] = 5 \times 10^{-4}$  M,  $\text{CH}_2\text{Cl}_2$ , 0.1 M TBAP,  $\nu = 0.1 \text{ V s}^{-1}$ , WE: glassy carbon ( $\text{Ø} = 3 \text{ mm}$ ), CE: Pt wire, RE: Ag/AgNO $_3$   $10^{-2}$  M in  $\text{CH}_3\text{CN}$ ). Inset: RDE voltammogram of  $2\mathbf{H}_2$  after addition of 2 molar equivalents of TFA (same experimental conditions excepted  $\nu = 0.1 \text{ V s}^{-1}$  and  $\omega = 550 \text{ rpm}$ ).



**Fig. 5** Electrolysis of a  $10^{-4}$  M solution of **4H<sub>2</sub>** followed by UV-Vis absorption spectroscopy ( $l = 1$  mm, 0.25 M TBAP in  $\text{CH}_2\text{Cl}_2$ ,  $E_{\text{app}} = 0.86$  V, -2.1 e).

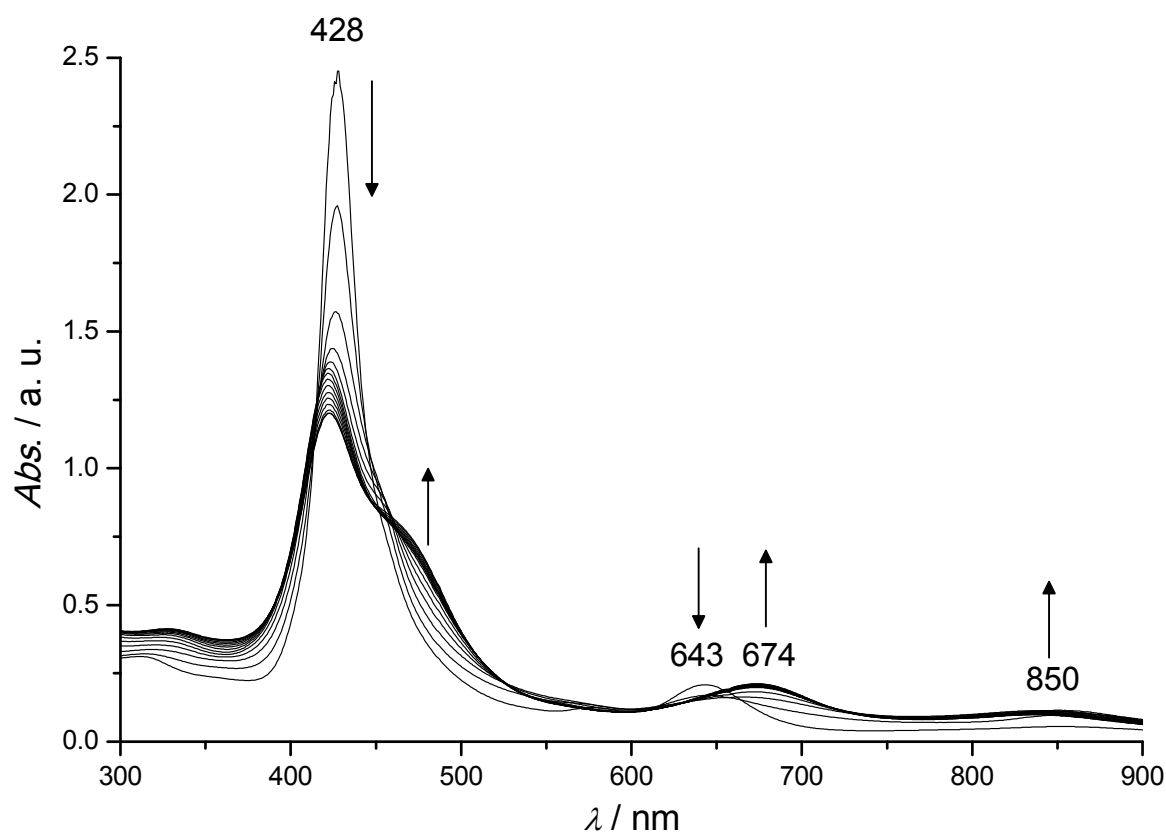


**Fig. 6** Evolution of the CV voltammogram of  $4\mathbf{H}_2$  upon addition of TFA (0 to 2 molar equivalents of TFA,  $[4\mathbf{H}_2] = 5 \times 10^{-4}$  M,  $\text{CH}_2\text{Cl}_2$ , 0.1 M TBAP,  $\nu = 0.1 \text{ V s}^{-1}$ , WE: glassy carbon ( $\text{Ø} = 3$  mm), CE: Pt wire, RE:  $\text{Ag}/\text{AgNO}_3$   $10^{-2}$  M in  $\text{CH}_3\text{CN}$ ). Inset: RDE voltammogram of  $4\mathbf{H}_2$  after addition of 2 molar equivalents of TFA (same experimental conditions excepted  $\nu = 0.1 \text{ V s}^{-1}$  and  $\omega = 550$  rpm).



**Fig. 7** Normalized UV-visible absorption spectrum of  $4\text{H}_2$  in  $\text{CH}_2\text{Cl}_2$  before (black line) and after (red line) addition of 2 molar equivalents of TFA.



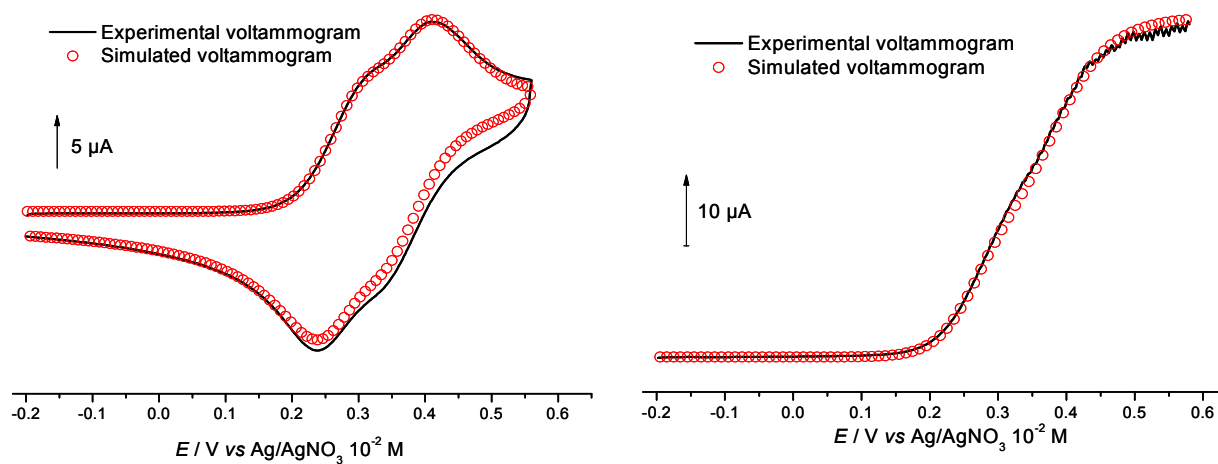


**Fig. 8** Electrolysis of a  $10^{-4}$  M solution of **4Zn** followed by UV-Vis absorption spectroscopy ( $l = 1$  mm, 0.25 M TBAP in  $\text{CH}_2\text{Cl}_2$ ,  $E_{\text{app}} = 1.13$  V, -2.1 e).

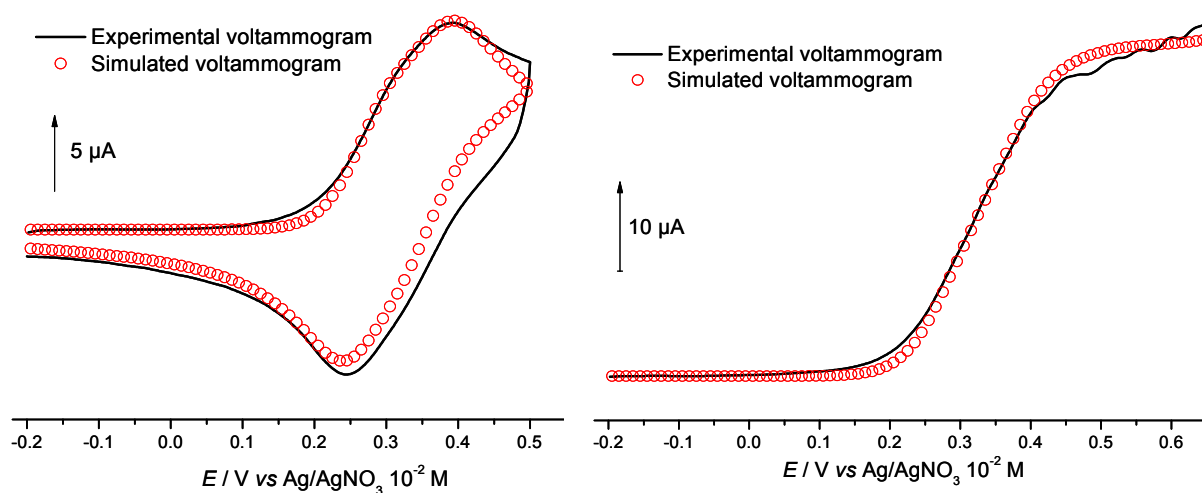
**Table 1:** Key parameters used for the digital simulations of the cyclic and rotating disk electrode voltammograms of **2H<sub>2</sub>-5H<sub>2</sub>** and **2Zn-5Zn**. <sup>a</sup> Potentials are given vs.  $\text{Ag}/\text{AgNO}_3$   $10^{-2}$  M. To be directly compared with those of the manuscript (vs.  $\text{DMFc}/\text{DMFc}^+$ ), +0.345 V must be added to these values.

	<b>2H<sub>2</sub></b>	<b>3H<sub>2</sub></b>	<b>4H<sub>2</sub></b>	<b>5H<sub>2</sub></b>	<b>2Zn</b>	<b>3Zn</b>	<b>4Zn</b>	<b>5Zn</b>
$E_0$ (V)	0.295	0.270 0.355	0.260 0.375	0.240 0.350 0.380	0.241	0.200 0.290	0.190 0.300	0.155 0.310 0.330
$k_s$ (cm/s)	0.015	0.012 0.008	0.012 0.012	0.012 0.009 0.006	0.01	0.012 0.008	0.0125 0.008	0.012 0.012 0.012
$D$ (cm <sup>2</sup> /s)	$1.9 \times 10^{-5}$	$1.7 \times 10^{-5}$	$1.7 \times 10^{-5}$	$1.5 \times 10^{-5}$	$1.9 \times 10^{-5}$	$1.7 \times 10^{-5}$	$1.7 \times 10^{-5}$	$1.5 \times 10^{-5}$

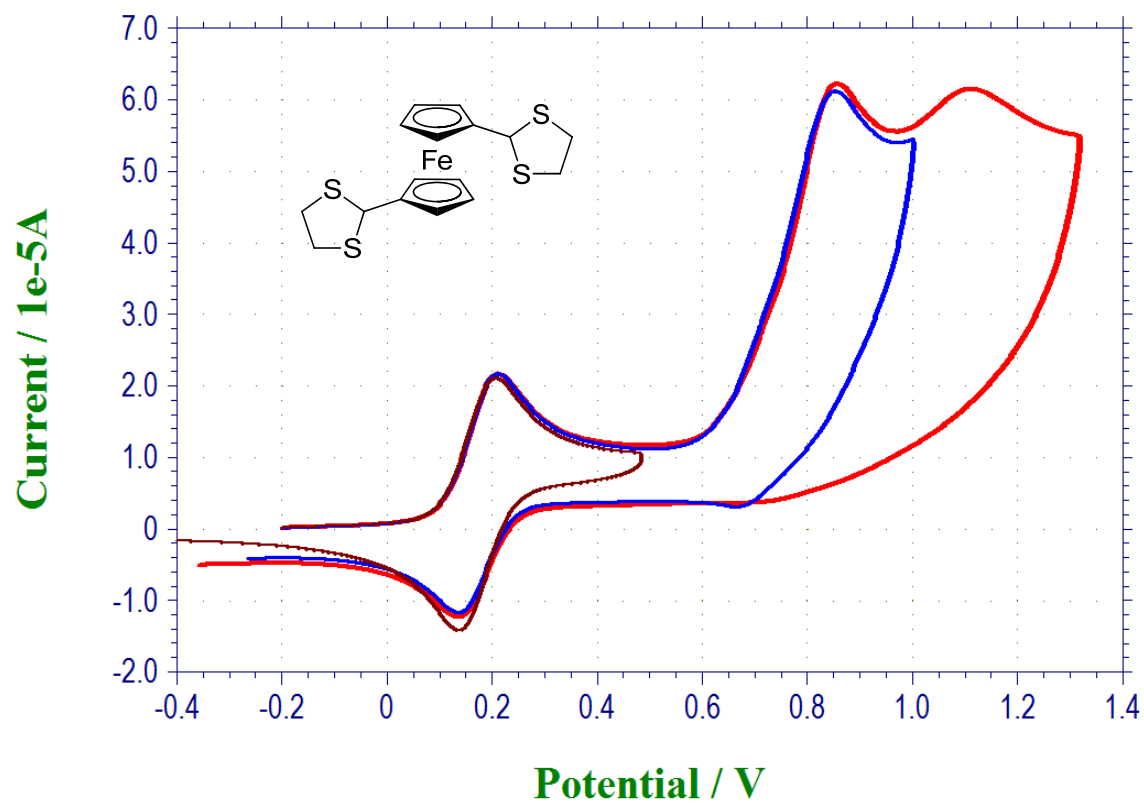
<sup>a</sup> The common parameters used for the digital simulations of the cyclic and rotating disk electrode voltammograms of **2H<sub>2</sub>-5H<sub>2</sub>** and **2Zn-5Zn** are:  $R_u$  ( $\Omega$ ) = 0;  $Cdl$  (F) =  $1 \times 10^{-6}$ ;  $\nu$  (V/s) = 0.1; *disk area* (cm<sup>2</sup>) = 0.07; *Concentration of porphyrins* (mol/L) =  $5 \times 10^{-4}$ ;  $\alpha/\lambda$  (eV) = 0.5;  $\omega$  (rad/s) = 57.6;  $\nu_k(\text{CH}_2\text{Cl}_2)$  (cm<sup>2</sup>/s) = 0.003327. Examples of digital simulations are presented in Fig. 9 and Fig. 10.



**Fig. 9** Comparison between experimental (black line) and simulated voltammograms (red circles) of  $4\text{H}_2$  using parameters presented in Table 1. Left: cyclic voltammetry, right: rotating disk electrode voltammetry.



**Fig. 10** Comparison between experimental (black line) and simulated voltammograms (red circles) of  $3\text{H}_2$  using parameters presented in Table 1. Left: cyclic voltammetry, right: rotating disk electrode voltammetry.



**Fig. 11** Cyclic voltammograms of 1,1'-bis[2-(1,3-dithiolanyl)]ferrocene ( $\text{CH}_3\text{CN}$ , 0.1 M TBAP; RE: Ag/AgNO<sub>3</sub> 10<sup>-2</sup> M in  $\text{CH}_3\text{CN}$ ; WE: glassy carbon ( $\text{Ø} = 3$  mm); CE: Pt).

**Table 2.** Summary of the crystallographic data

	<b>2Zn</b>	<b>8Zn</b>	<b>4Zn</b>	<b>10Zn</b>
Empirical formula	C <sub>54</sub> H <sub>42</sub> FeN <sub>4</sub> S <sub>2</sub> Zn	C <sub>58</sub> H <sub>48</sub> Fe <sub>2</sub> N <sub>4</sub> O <sub>4</sub> Zn	C <sub>68</sub> H <sub>64</sub> Fe <sub>2</sub> N <sub>4</sub> O <sub>2</sub> S <sub>4</sub> Zn	C <sub>65</sub> H <sub>55.50</sub> Fe <sub>4</sub> N <sub>4</sub> O <sub>2</sub> Zn
Formula weight	932.26	1042.07	1274.54	1213.40
Temperature (K)	298(2)	223(2)	223(2)	298(2)
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	C2/c	P-1	Pbca	C2/c
Unit cell dimensions (Å, deg)	34.426(16)	8.236(2)	18.415(6)	58.224(18)
	10.100(5)	12.414(4)	12.697(4)	7.400(2)
	32.153(15)	12.620(4)	24.742(8)	27.891(9)
	90	67.731(5)	90	90
	112.358(8)	72.240(5)	90	110.088(5)
	90	76.832(5)	90	90
Volume (Å <sup>3</sup> ), Z	10339(8), 8	1127.9(6), 1	5785(3), 4	11286(6), 8
Density (Mg/m <sup>3</sup> )	1.198	1.534	1.463	1.428
Absorption coefficient (mm <sup>-1</sup> )	0.862	1.219	1.102	1.471
F(000)	3856	538	2648	4988
Crystal size (mm)	0.30 x 0.15 x 0.10	0.30 x 0.05 x 0.05	0.20 x 0.05 x 0.01	0.30 x 0.10 x 0.08
Reflections collected	15373	6557	12817	22893
Independent reflections (R <sub>int</sub> )	7295 (0.0306)	4461 (0.0132)	4773 (0.1441)	8100 (0.0521)
Data / restraints / parameters	7295/0/569	4461/0/409	4773/94/367	8100/285/775
Goodness-of-fit on F <sup>2</sup>	1.124	1.109	0.904	1.296
Final R indices [I>2sigma(I)]	0.0688	0.0418	0.0733	0.1088
R indices (all data)	0.0839	0.0483	0.1892	0.1321

## Details on the *Ab initio* dynamics calculations

The *ab initio* Born-Oppenheimer dynamics calculations were performed using the CP2K-QuickStep program.<sup>i</sup> QuickStep is an implementation of the Gaussian Plane Waves (GPW) method based on the Kohn-Sham formulation of the density functional theory (DFT). The GPW approach is an hybrid method using a linear combination of Gaussian type orbitals to describe the Kohn-Sham orbitals whereas an auxiliary plan waves basis set is employed to expand the electronic charge density. We used the BLYP<sup>ii</sup> functional and the basis set was a double zeta polarized set of gaussian orbitals<sup>iii</sup> for the second and third row atoms, and double zeta for the iron and zinc atom a double in conjunction with the Goedecker-Teter-Hutter<sup>iv</sup> pseudopotentials. The auxiliary PW basis set was defined by a cubic box of 22 (Å)<sup>3</sup> and by a density cutoff of 300 Ry.

Metadynamics<sup>v</sup> has been used to overcome the problem of observing rare events in conventional molecular dynamics. This method has already been successfully used for organometallic<sup>vi</sup> reactivity and organic<sup>vii</sup> reactivity. A series of small repulsive Gaussian potentials centered on the values of some collective variables are added during the dynamics, preventing the system from revisiting the same points in configurational space and creating a history-dependent multidimensional biasing potential. A time step of 1 fs is used for the dynamic performed at 350 K with the H atoms replaced by D atoms and the hills (width 10 degrees, height 0.3 kcal/mol) were added every 10 fs.

In the present study, we explicitly considered the dihedral angle C-C-C-C shown in Fig. 8 (see main text) as a collective variable. During the simulation, the rotation around this angle is effectively observed corresponding to the rotation of one of the ferrocene and around 1200 steps have been necessary to observe the complete rotation and the simulation was stopped after 1600 steps. The free energy surface reconstructed from this simulation is represented in Fig. 8 (see main text). It exhibits a total free energy activation of 10.3 kcal.mol<sup>-1</sup> in very good agreement with the temperature dependent NMR study. We can also note that the free energy difference between the two minima is quite small, a little less than 1 kcal.mol<sup>-1</sup> in agreement with the large distances between the two ferrocenes.

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