# Supporting Information

Heterogeneous electron transfer at Au/SAM junctions in a room-temperature ionic liquid under pressure

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a) Materials. The room-temperature ionic liquid (RTIL) 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [bmim][NTf$_2$] (Scheme S1), was synthesized according to a known procedure[S1] and was kept under nitrogen atmosphere. The water content of this ionic liquid was determined by Karl-Fischer titration using a Metrohm 765 KF Coulomb-meter and found to be 55 ppm.

Scheme S1
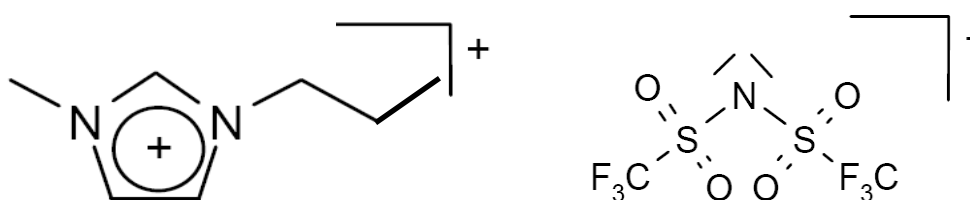
Dicyclopentadienyliron (Ferrocene), [Fe(cp)$_2$]^0 (98 %), tris(2,2–bipyridine)iron(II) hexafluorophosphate, and [Fe(III)meso-tetra(N-methyl-4-pyridyl)porphyrine] (Sigma-Aldrich) were used as received. All solutions were prepared under a nitrogen atmosphere.

b) Electrochemical measurements and data processing. The pressure vessel and electrochemical cell were described in detail before.[S2-S4] The working electrode was a 1.6 mm Ø gold disc electrode sealed in a Teflon cylinder (BAS). The working electrode, together with the auxiliary electrode (platinum wire) and quasi-reference electrode (silver wire, placed in a plastic tube with a Vycor tip at the end) were sealed into the cell cap by two O-rings. The working volume of the high pressure electrochemical cell was 5 ml. The assembled pressure vessel containing the cell was placed in a thermostated water jacket equilibrated at 25 $^{\circ}$C with the accuracy of $\pm$ 0.1 $^{\circ}$C. The variable pressure measurements were performed starting at P = 5 MPa (to eliminate any small bubbles) up to 150 MPa.

In some cases, under ambient pressure conditions electrochemical measurements were performed in a three-electrode cell equipped with a water cooling jacket. The gold (1.6 mm diameter, BAS and 2 mm, and 3 mm, Metrohm) disk electrodes were used as working electrodes, together with a large platinum wire auxiliary electrode. The quasi-reference electrode used was a silver wire, placed in a plastic tube with a Vycor tip at the end. The temperature was controlled within $\pm$ 0.1 $^{\circ}$C using a digital temperature controller. Working solutions were purged with nitrogen at least for 15 min before the experiments.

Gold disk electrodes were treated according the procedures described elsewhere.[S2-S4] In brief the electrode surface was cleaned with successive exposure to 60 $^{\circ}$C sulphochromic acid and 5% HF. This procedure was repeated three times just before the immersion into 30 mM ω-hydroxy-alkanethiol solutions. The electrodes were kept in the coating solutions overnight to allow complete formation of SAM films.

Electrochemical measurements were carried out with an Autolab Electrochemical Analyzer PGSTAT 30, equipped with the General Purpose Electrochemical System (GPES) software for Windows (Version 4.9). Autolab software was used for the "post-measurement" Ohmic potential drop (*IRe, where Re* is solution resistance between reference and working

electrode) corrections of experimental CV response [S5] at ambient as well as at elevated pressures.

Pressure dependence of the solution resistance (Re = 619 Ω at 25 ^{o}C, P = 0,1 MPa)[S5] was

calculated taking into account the matching dependence of viscosity (diffusion coefficient) on

pressure.[S5]

Table S1 Determination of heterogeneous standard rate constans of $[Fe(cp)_2]^{+/0}$ couple at Au

electrode (S = 0.02 cm^2) modified with butanethiol $[CH_3(CH_2)_3SH]$ monolayer .

Scan Rate, V s^{-1}	ΔE, mV	Ψ	$k^0_{EXP(cor)} \times 10^2$, cm s^{-1} ($n$ = 3)
20	82	1.054	2.78
30	87	0.840	2.71
40	93	0.670	2.50
			Average Value: 2.66

Cyclic voltammetry was used throughout this work. In the case of thinner SAMs

experimental standard rate constants of electron transfer (k^o_{EXP}) were calculated from the

numerically evaluated relationship between the separation of cathodic and anodic peak potentials

(ΔE_p) and the Ψ function according to the method of Nicholson [S6,S7] using eq. 1 (see Table S1)

$$\Psi = \frac{(D_O/D_R)^{\alpha/2} \; (RT)^{1/2} \; k^o_{EXP}}{(\pi \; n \; F \; D_O \; v)^{1/2}} \tag{1}$$

where α is the transfer coefficient, D_O and D_R are the diffusion coefficients of the oxidized and

reduced forms, respectively, v is the scan rate, F is Faraday constant and n is the number of

transferred electrons. Values of diffusion coefficients for $[Fe(cp)_2]^{+/0}$ and $[Fe(bipy)_3]^{3+/2+}$ couples

at ambient pressure $P = 0.1$ MPa ($T = 25$ °C) were taken from Ref S5. For a $[Fe(cp)_2]^{+/0}$ couple

the values of diffusion coefficients at different pressures at 25 °C (Table 2) were calculated

taking into account the matching values at 20 °C.[S5]

Values of D_O and D_R for the porphyrine complex were evaluated from the experimental

CV data (Fig. S1) using eq. 2 [S6]

$$I_{p(corr)} = -0.446 \quad nF \quad \left(\frac{nF}{RT}\right)^{1/2} C_o \quad D^{1/2} \quad v^{1/2}$$ (2)

where $I_{p(corr)}$ is the background corrected current density and C_o is the reactant concentration. In

the case of thicker SAMs (n = 11) effect of diffusion on the volammetric experimental current

was corrected through convolution technique.[S6] For this purpose background substracted

voltammograms were converted to the sigmoidal-shaped curves by semi-integral convolution

technique [S6] and rate constants at different overvoltages were calculate using eq. 3.[S6,S8,S9]

$$k(E) = D^{1/2} \quad \frac{i(E)}{I_{\lim} - I(E)\left[1 + \exp \quad (nF/RT)(E - E_0)\right]}$$ (3)

where $i(E)$ is the real experimental current, $I(E)$ is the convoluted current and $I_{\lim}$ is convoluted

limiting current $I_{\lim} = n F A D^{-1/2} C_0$. Plots of apparent heterogeneous electron transfer rate

constants for the $[Fe(cp)_2]^{+/0}$ couple against electrode potential at n-dodecanethiol modified Au

electrode at different pressures are presented in Fig. S4.

References:

S1 P. Illner, A. Zahl, R. Puchta, N. van Eikema Hommes, P. Wasserscheid and R. van Eldik, *J. Organometallic Chem*. 2005**, 690**, 3567-3576;

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S3 T. D. Dolidze, D. E. Khoshtariya, D. H. Waldeck, J. Macyk, and R. van Eldik, *J. Phys. Chem. B,* 2003, **107**, 7172-7179;

S4 D. E. Khoshtariya, T. D. Dolidze, D. Sarauli, and R. van Eldik, *Angew. Chem. Int. Ed.*, 2006, **45**, 277-281;

S5 T. D. Dolidze, D. E. Khoshtariya, P. Illner, L. Kulisiewicz, A. Delgado and R. van Eldik, *J. Phys. Chem. B*, 2008, in press.

S6 A. J. Bard and L. R. Faulkner, *Electrochemical Methods. Fundamentals and Applications*, 2nd ed.; John Wiley & Sons, New York, 2001.

S7 R. S. Nicholson, *Anal. Chem*. 1965, **37**, 1351-1355.

S8 J. C. Imbeaux and J. M. Savèant, *J. Electroanal. Chem*., 1973, **44**, 169-187.

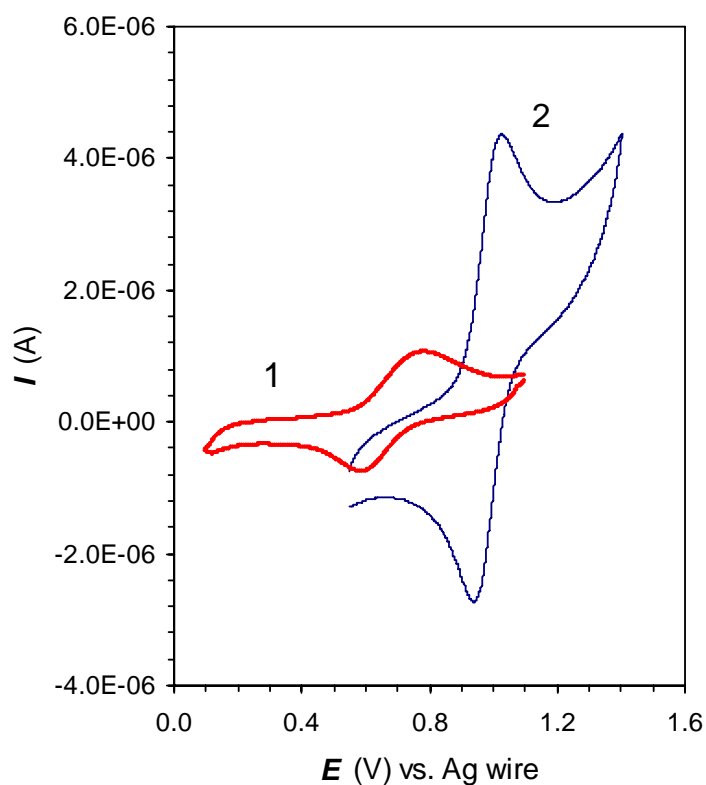S9 C. Cannes, F. Kanoufi and A. J. Bard, *J. Electroanal. Chem*., 2003, **547**, 83-91.

Figure S1. Cyclic voltammograms recorded at ambient pressure ($P = 0.1$ MPa) in [bmim][NTf$_2$] for (Fe III) Porphyrine ($C_{Porph} = 5 \times 10^{-4}$ M,) at gold electrode (S = 0.0314 cm^2) coated with: (1) - [OH$^-$-(CH$_2$)$_3$-SH] monolayer; and (2) [Fe(bipy)$_3$]$^{3+/2+}$ ($C_{Febp} = 3 \times 10^{-3}$ M) at gold electrode (S = 0.04 cm^2) coated with [OH$^-$-(CH$_2$)$_{11}$-SH] monolayer; $v = 0.1$ V s^{-1}, T = 25 ^{0}C
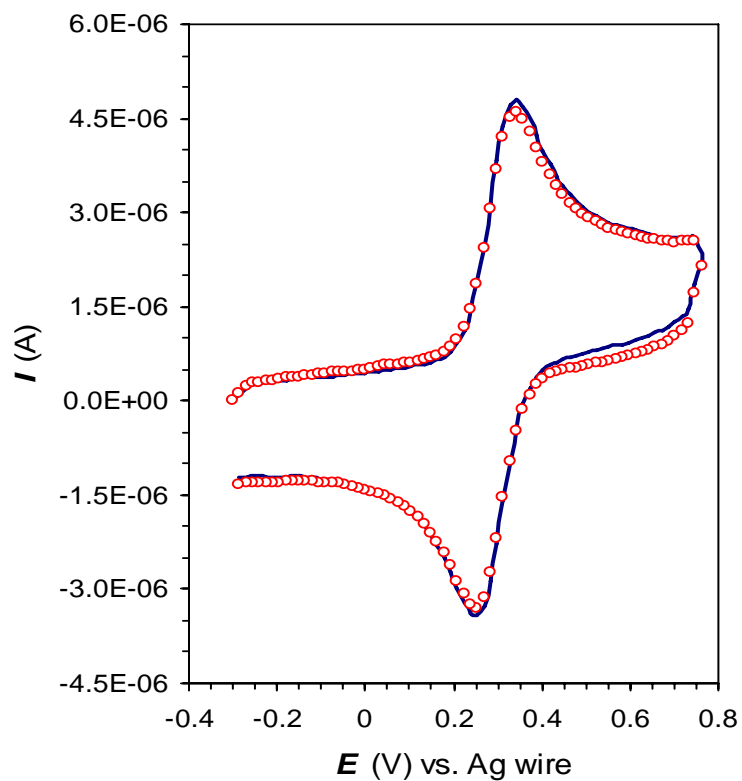
Figure S2. Cyclic voltammograms for the $[Fe(cp)_2]^{+/0}$ couple ($C_{Fec} = 2 \times 10^{-4}$ M) recorded in [bmim][NTf$_2$] at 1-butanethiol([CH$_3$ (CH$_2$)$_3$SH]) modified Au electrode (S = 0.02 cm^2) at $P = 5$ MPa before (−) and after (○) the pressure uprising up to $P = 150$ MPa , $v = 20$ V s^{-1}.

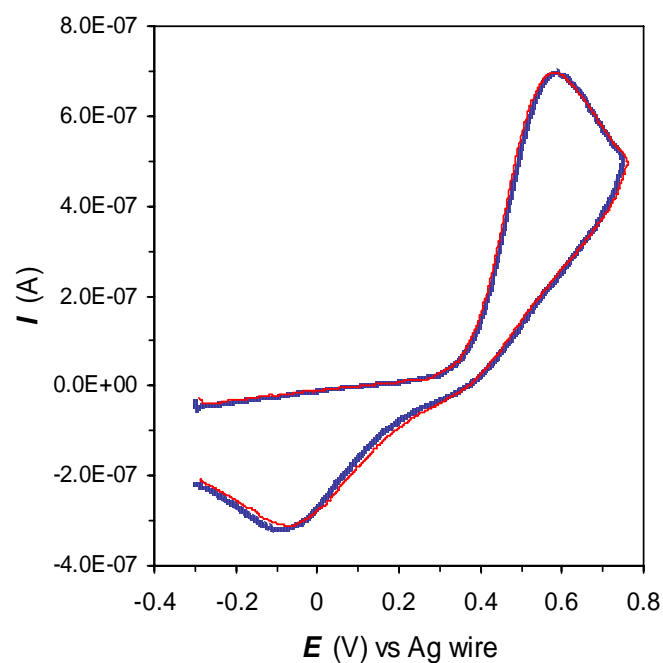**Figure S3.** Cyclic voltammograms for the $[Fe(cp)_2]^{+/0}$ couple ($C_{Fec} = 4\times 10^{-4}$ M) recorded in [bmim][NTf$_2$] at the n-dodecanethiol ([CH$_3$(CH$_2$)$_{11}$SH]) modified Au electrode (S = 0.02 cm^2) at $P = 5$ MPa before (blue) and after (red) the pressure increase to 150 MPa , $v = 0.5$ V s^{-1}.

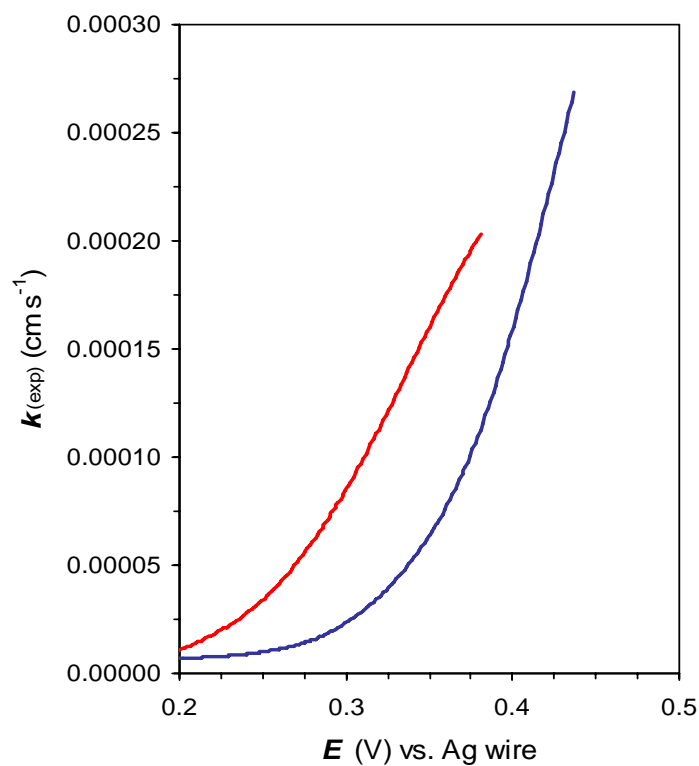**Figure S4.** Plots of apparent heterogeneous electron transfer rate constants for the $[Fe(cp)_2]^{+/0}$ couple ($C_{Fec} = 4 \times 10^{-4}$ M) recorded in [bmim][NTf_2] at the n-dodecanethiol ($[CH_3(CH_2)_{11}SH]$) modified Au electrode (S = 0.02 cm^2) at P = 5 MPa (blue) and P = 150 MPa (red) , v = 0.5 V s^{-1}.