

## Electronic Supporting Information (ESI)

### A redox active proton transfer and hydrogen-bonding system of tetrathiafulvalene-dicarboxylic acid and pyridine bases

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**ESI-Table 1.** Crystal Data and Structural Refinement Parameters for compounds **1**~**3**.

**ESI-Table 2.** Data of Intra- and intermolecular hydrogen bonds in the solid state of **1**~**3**.

**ESI-Fig. 1.** Cyclic voltammograms of H<sub>2</sub>L ( $1.0 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$  with  $0.1 \text{ mol}\cdot\text{L}^{-1}$  Bu<sub>4</sub>NClO<sub>4</sub>) in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (8:2 by volume) at a scan rate of  $100 \text{ mV s}^{-1}$ , titrated with 2,2-pyridine (a) and 4,4-bpy (b).

**ESI-Fig. 2.** CV of H<sub>2</sub>L at different scan rates in the presence of 0.2 equiv py: (a) 20 mV, (b) 100 mV, (c) 500 mV and (d) 1000 mV (H<sub>2</sub>L  $1.0 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ , CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN, 8:2 in v/v,  $0.1 \text{ mol}\cdot\text{L}^{-1}$  Bu<sub>4</sub>NClO<sub>4</sub>).

**ESI-Fig. 3.** CV of H<sub>2</sub>L at different scan rates in the presence of (a) 0.2 equiv 2,2'-bpy; (b) 0.2 equiv 4,4'-bpy (H<sub>2</sub>L  $1.0 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ , CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN, 8:2 in v/v,  $0.1 \text{ mol}\cdot\text{L}^{-1}$  Bu<sub>4</sub>NClO<sub>4</sub>).

**ESI-Fig. 4.** Plots of  $E_{\text{pa}}$  and  $E_{\text{pc}}$  of H<sub>2</sub>L versus  $\log \nu$  at different scan rates in the presence of 0.2 equiv. pyridine; Solid lines are linear fits for data.

**ESI-Calculation** of the relative data  $K_{\text{a}2}/K_{\text{a}1}$  and  $K_{\text{a}4}/K_{\text{a}3}$  of the proton transfer equilibriums.

**ESI-Simulation** of the CV behaviours using DigiElch 4.5 ( a demonstrate version, M. Rudolph, *J. Electroanal. Chem.*, 2002, **529**, 97. Also see: <http://www.digiElch.de>).

**ESI-Table 1.** Crystal Data and Structural Refinement Parameters for compounds 1~3.

	1	2	3
formula	C <sub>15</sub> H <sub>13</sub> NO <sub>4</sub> S <sub>6</sub>	C <sub>20</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> S <sub>6</sub>	C <sub>30</sub> H <sub>24</sub> N <sub>2</sub> O <sub>8</sub> S <sub>12</sub>
Fw	463.62	540.71	925.23
cryst size (mm <sup>3</sup> )	0.45 × 0.38 × 0.32	0.80 × 0.32 × 0.18	0.22 × 0.12 × 0.10
cryst syst	monoclinic	monoclinic	triclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>a</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	8.6319(8)	17.140(3)	10.6334(7)
<i>b</i> (Å)	10.0114(9)	7.7891(12)	13.2801(9)
<i>c</i> (Å)	22.265(2)	17.338(3)	13.5988(8)
$\alpha$ (deg)	90.00	90.00	77.855(8)
$\beta$ (deg)	96.953(2)	102.363(4)	78.677(8)
$\gamma$ (deg)	90.00	90.00	79.177(7)
<i>V</i> (Å <sup>3</sup> )	1910.0(3)	2261.1(6)	1819.2(2)
<i>Z</i>	4	4	2
$\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.612	1.588	1.689
<i>F</i> (000)	952	1112	948
$\mu$ (mm <sup>-1</sup> )	0.738	0.637	0.774
<i>T</i> (K)	223(2)	223(2)	223(2)
<i>R</i> <sub>int</sub>	0.0252	0.0515	0.0590
reflns collected	13330	12347	16774
unique reflns	4341	5117	8197
observed reflns	3839	4038	5738
no. params	247	298	486
restraints	2	2	4
GOF on <i>F</i> <sup>2</sup>	1.045	1.066	1.010
<i>R</i> <sub>1</sub> <sup>a</sup> / <i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0495/0.0421	0.0997/ 0.0748	0.1267/ 0.0863
<i>wR</i> <sub>2</sub> <sup>b</sup> / <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.1026/0.0973	0.1436/ 0.1313	0.1504/ 0.1302

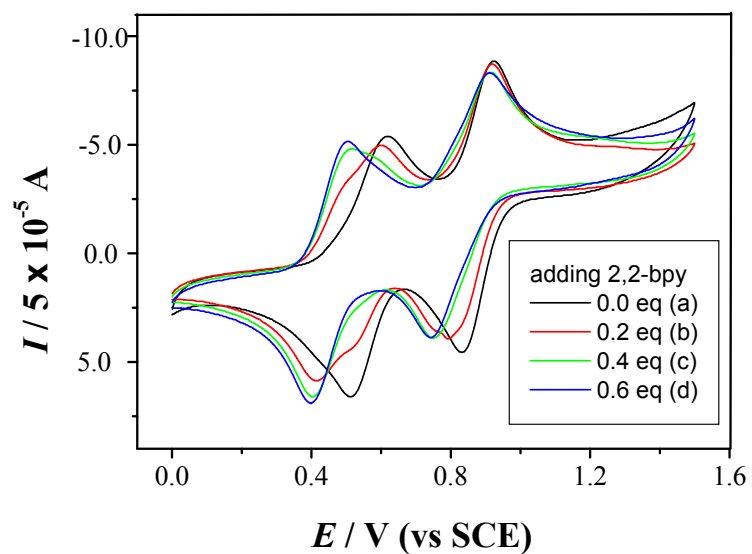
<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ; <sup>b</sup>  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$

**ESI-Table 2.** Data of Intra- and intermolecular hydrogen bonds in the solid state of **1-3**.

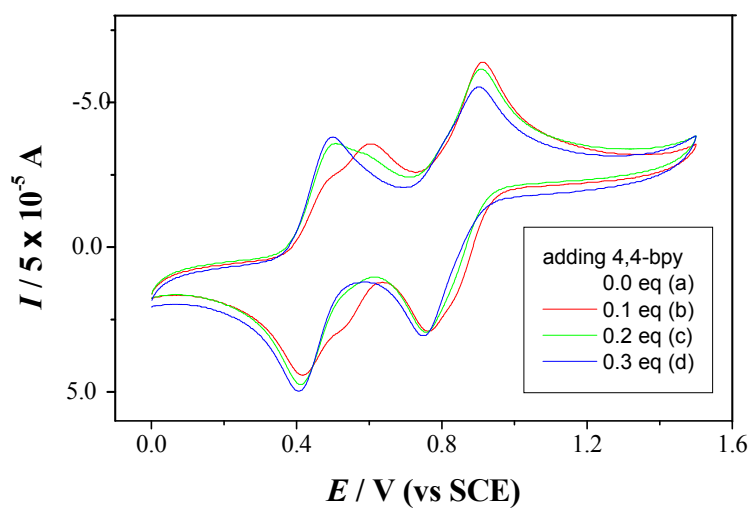
D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	Angle (°)
<b>1</b>				
N(1)–H(1)···O(2) <sup>i</sup>	0.88(2)	1.80(2)	2.674(2)	175(3)
O(4)–H(4)···O(2)	0.85(3)	1.59(3)	2.438(2)	176(3)
C(13)–H(13)···O(3) <sup>ii</sup>	0.94	2.40	3.163(3)	138
C(14)–H(14)···O(3) <sup>iii</sup>	0.94	2.43	3.208(3)	140
C(15)–H(15)···O(4) <sup>iii</sup>	0.94	2.42	3.290(3)	154
<b>2</b>				
N(1)–H(1A)···O(4)	0.87(3)	1.95(3)	2.755(5)	153(3)
O(2)–H(2A)···O(4)	0.83(3)	1.61(3)	2.435(5)	174(3)
C(12)–H(12A)···O(2) <sup>iv</sup>	0.94	2.60	3.392(5)	143
C(13)–H(13A)···O(3) <sup>v</sup>	0.94	2.52	3.198(6)	130
<b>3</b>				
N(1)–H(1)···O(7)	0.88(5)	1.75(5)	2.630(7)	177(6)
N(2)–H(2)···O(1)	0.83(5)	1.76(5)	2.626(6)	169(5)
O(4)–H(4)···O(2)	0.85(5)	1.63(3)	2.458(7)	163(8)
O(6)–H(6)···O(8)	0.85(2)	1.63(4)	2.466(6)	165(8)
C(22)–H(22)···O(5) <sup>vi</sup>	0.94	2.59	3.503(8)	164
C(24)–H(24)···O(3) <sup>vii</sup>	0.94	2.42	3.309(7)	157
C(25)–H(25)···O(4) <sup>vii</sup>	0.94	2.42	3.287(7)	126
C(26)–H(26)···O(6) <sup>vi</sup>	0.94	2.57	3.255(7)	130
C(27)–H(27)···O(5) <sup>vi</sup>	0.94	2.36	3.283(7)	169
C(29)–H(29)···O(3) <sup>vii</sup>	0.94	2.55	3.490(8)	178

Symmetry transformations used to generate equivalent atoms:

i: x, 1+y, z ; ii: 1-x, -y, 1-z; iii: 1/2-x, 1/2+y, 3/2-z; iv: 1/2+x, 1/2-y, z ; v: 3/2-x, -1/2+y, 1-z ; vi: x, 1+y, z ; vii: x, -1+y, z.

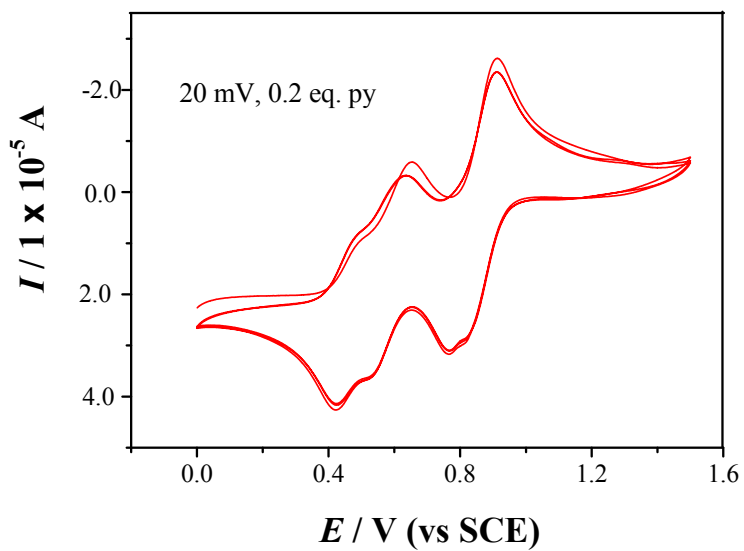


(a) 2,2-bpy

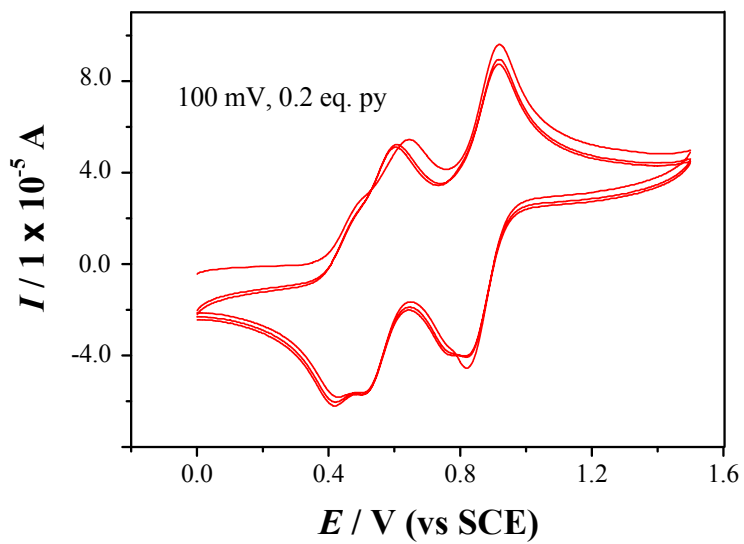


(b) 4,4-bpy

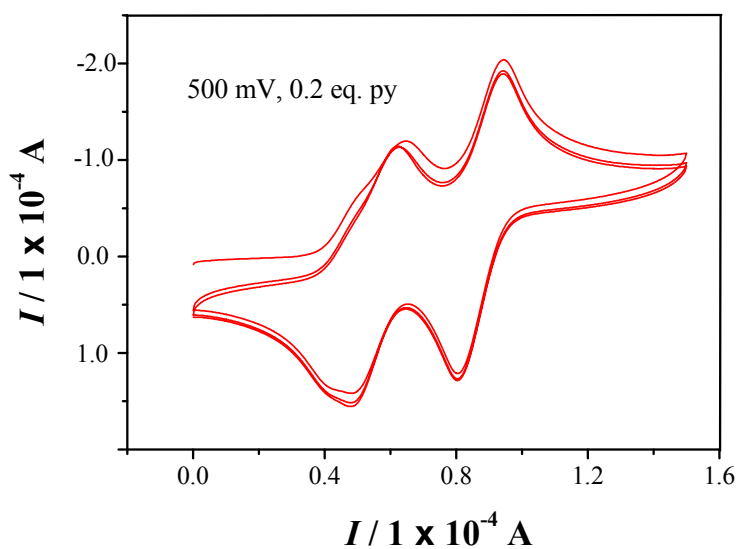
**ESI-Fig. 1.** Cyclic voltammograms of  $\text{H}_2\text{L}$  ( $1.0 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$  with  $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ Bu}_4\text{NClO}_4$ ) in  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  (8:2 by volume) at a scan rate of  $100 \text{ mV s}^{-1}$ , titrated with 2,2-pyridine (a) and 4,4-bpy (b).



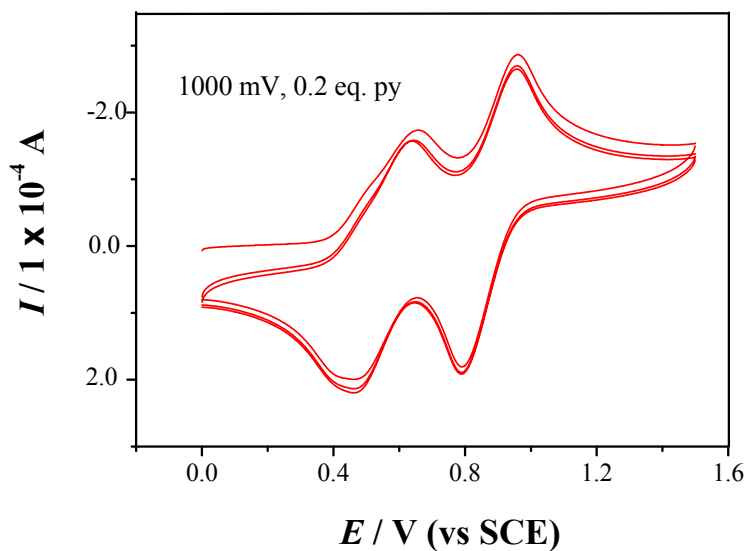
(a)



(b)

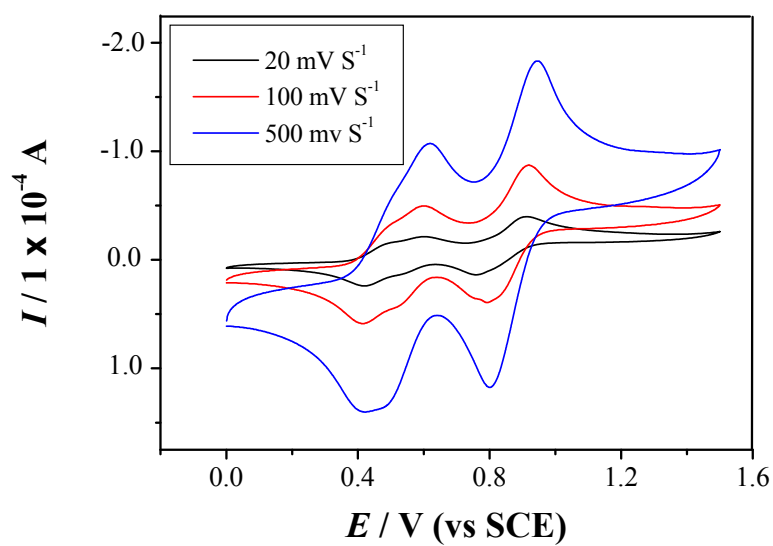


(c)

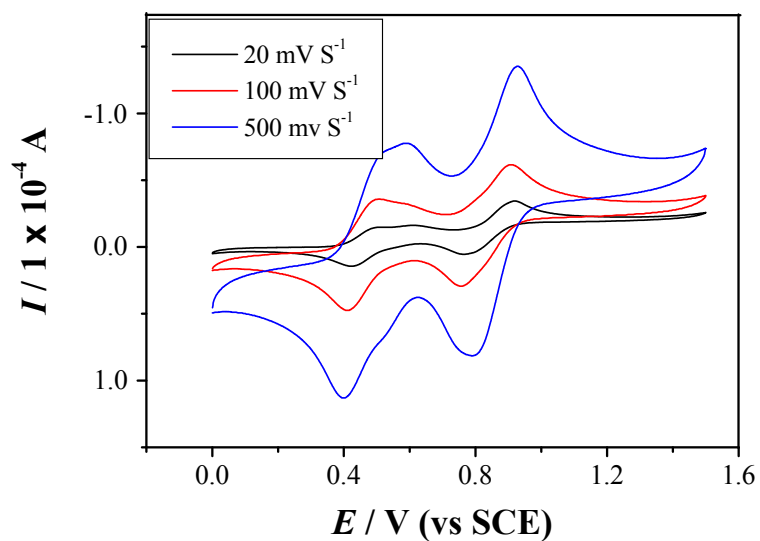


(d)

**ESI-Fig. 2.** CV of H<sub>2</sub>L at different scan rates in the presence of 0.2 equiv py: (a) 20 mV, (b) 100 mV, (c) 500 mV and (d) 1000 mV (H<sub>2</sub>L  $1.0 \times 10^{-3}$  mol·L<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN, 8:2 in v/v, 0.1 mol·L<sup>-1</sup> Bu<sub>4</sub>NClO<sub>4</sub>).

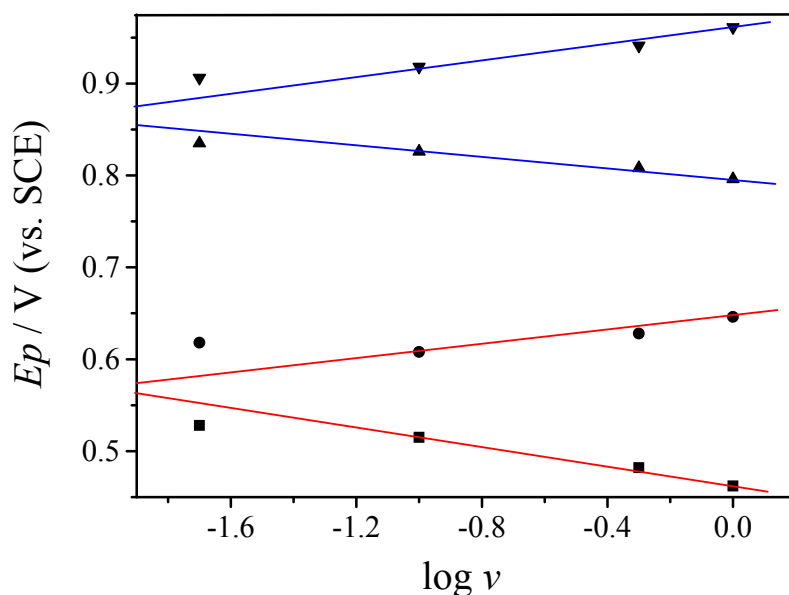


(a)



(b)

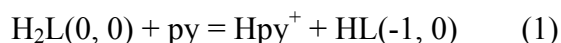
**ESI-Fig. 3.** CV of H<sub>2</sub>L at different scan rates in the presence of (a) 0.2 equiv 2,2'-bpy; (b) 0.2 equiv 4,4'-bpy (H<sub>2</sub>L  $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ , CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN, 8:2 in v/v,  $0.1 \text{ mol} \cdot \text{L}^{-1}$  Bu<sub>4</sub>NClO<sub>4</sub>).



**ESI-Fig. 4.** Plots of  $E_{pa}$  and  $E_{pc}$  of  $H_2L$  versus  $\log \nu$  at different scan rates in the presence of 0.2 equiv. pyridine; Solid lines are linear fits for data.

**Calculation of the relative data  $K_{a2}/K_{a1}$  and  $K_{a4}/K_{a3}$  of the proton transfer equilibriums.**

The relative data  $K_{a2}/K_{a1}$  and  $K_{a4}/K_{a3}$  of the proton transfer equilibriums (Scheme 1) were calculated as follows. The charge and the oxidation state of are presented in parentheses for clarity (charge, oxidation state).



$$K_{a1} = \frac{[Hpy]^+[HL(-1, 0)]}{[H_2L(0, 0)][py]}$$

$$[H_2L(0, 0)] = \frac{[Hpy]^+[HL(-1, 0)]}{K_{a1}[py]} \quad (a)$$



$$K_{a2} = \frac{[Hpy]^+[HL(-1, +I)]}{[H_2L(0, +I)][py]}$$

$$[H_2L(0, +I)] = \frac{[Hpy]^+[HL(-1, +I)]}{K_{a2}[py]} \quad (b)$$



(b)/(a):

$$\frac{[\text{H}_2\text{L}(0, +\text{I})]}{[\text{H}_2\text{L}(0, 0)]} = \frac{K_{a1}}{K_{a2}} \times \frac{[\text{HL}(-1, +\text{I})]}{[\text{HL}(-1, 0)]} \quad (3)$$

$$\varphi_1 = \varphi_1^0 + 0.0592 \lg \frac{[\text{H}_2\text{L}(0, +\text{I})]}{[\text{H}_2\text{L}(0, 0)]}$$

$$\varphi_2 = \varphi_2^0 + 0.0592 \lg \frac{[\text{HL}(-1, +\text{I})]}{[\text{HL}(-1, 0)]}$$

From (3)

$$\varphi_2^0 = \varphi_1 = \varphi_1^0 + 0.0592 \lg \frac{K_{a1}}{K_{a2}} + 0.0592 \lg \frac{[\text{HL}(-1, +\text{I})]}{[\text{HL}(-1, 0)]}$$

$$\varphi_2^0 = \varphi_1^0 + 0.0592 \lg \frac{K_{a1}}{K_{a2}} \quad (\text{When } [\text{HL}(-1, +\text{I})] = [\text{HL}(-1, 0)] = 1 \text{ mol} \cdot \text{L}^{-1})$$

$$\varphi_1^0 = E_{1/2}(1) = 0.566 \text{ (V)} \quad \varphi_2^0 = E_{1/2}(2) = 0.450 \text{ (V)}$$

$$0.0592 \lg \frac{K_{a1}}{K_{a2}} = \varphi_2^0 - \varphi_1^0 = 0.450 - 0.566 = -0.116$$

$$\lg \frac{K_{a1}}{K_{a2}} = -1.959$$

$$\frac{K_{a1}}{K_{a2}} = 0.011$$

$$\frac{K_{a2}}{K_{a1}} = 91$$

$$\varphi_3^0 = 0.876 \text{ (V)} \quad \varphi_4^0 = 0.786 \text{ (V)} \quad (\text{estimated from } \varphi_3^0 - (E_{pa2} - E_{pa2}^*), \text{ see Fig. 2})$$

$$\lg \frac{K_{a3}}{K_{a4}} = -1.520$$

$$\frac{K_{a4}}{K_{a3}} = 33$$

### Simulation of the CV behaviours

The CV behaviour simulation is carried out by using DigiElch 4.5 (only a demonstrate version, M. Rudolph, *J. Electroanal. Chem.*, 2002, **529**, 97. Also see: <http://www.digiElch.de>). The result (Fig. DigiElch-1), be attention that the coordinates are just opposite to that in the figures in paper) is in accordance with that of the experiment (Fig.2 black line), considering the fast reaction,

$LHH^+ + py = LH^+ + Hpy$  ( $L = TTF\text{COO}$ ,  $+ =$  one electron oxidized). Therefore, the second redox wave is assigned to (HL, -1, +I)/(HL, -1, +I), which is due to the strong acidity of the  $H_2L$  and the positive charge expulsion effect generated from the first oxidation. Being aware that the simulation is carried out with demonstrate version, there are restrictions for detailed application.

The data  $K_{a2}/K_{a1}$  and  $K_{a4}/K_{a3}$  of the proton transfer equilibriums obtained from the simulated results (Fig. DigiElch-1, see table) are the same as the calculated data reported above (Section 3.2).

$$\frac{K_{a2}}{K_{a1}} = \frac{9.13E+007}{1E+006} = 91.3 \quad \frac{K_{a4}}{K_{a3}} = \frac{33.2}{1} = 33.2$$

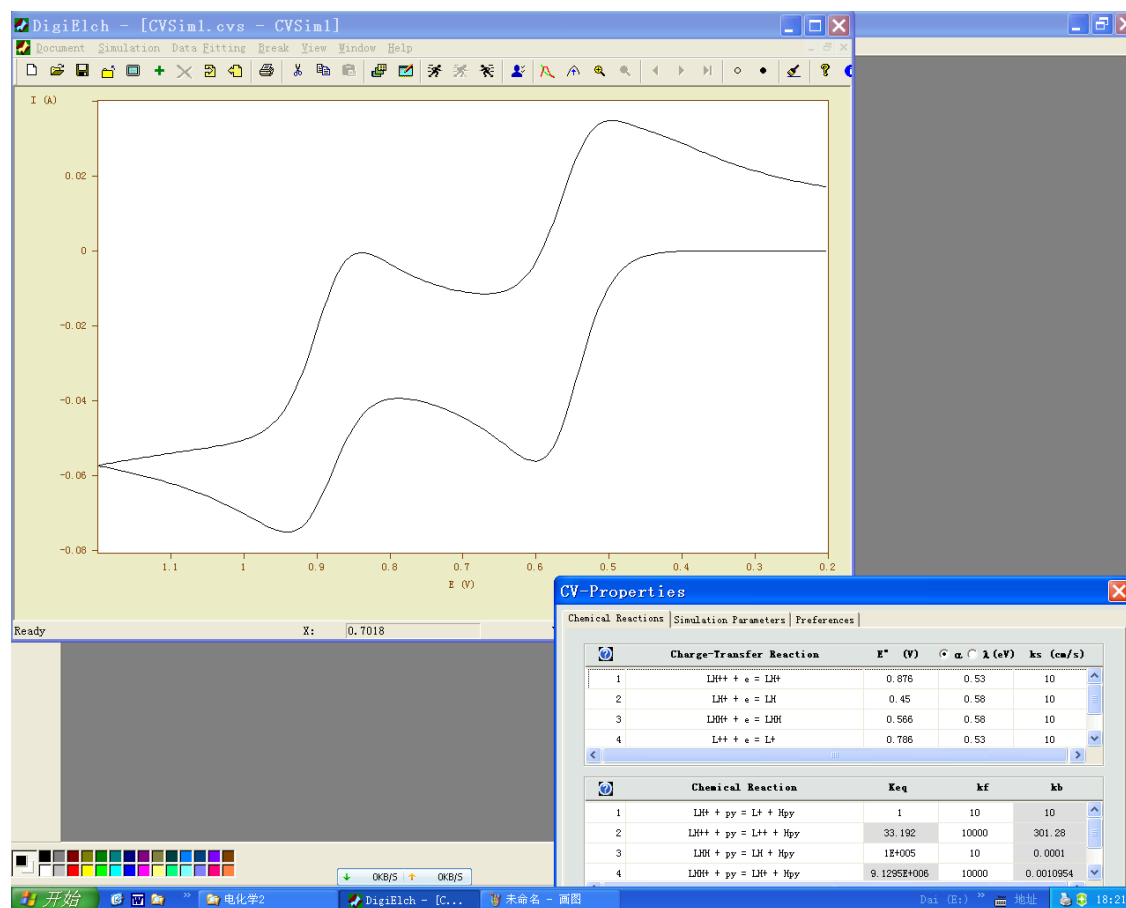


Fig. DigiElch-1.

Fig. DigiElch-2 (first redox step) and 3 (second redox step) show the two steps redox waves in successively increasing the concentration of py. The changes of the two waves are quite different, which is in accordance to that of the experimental results (see section Figure 2 and section 3.2, be attantion the coordinates that are just opposite the figures in paper). The peak of the Epa2 does not change significantly.

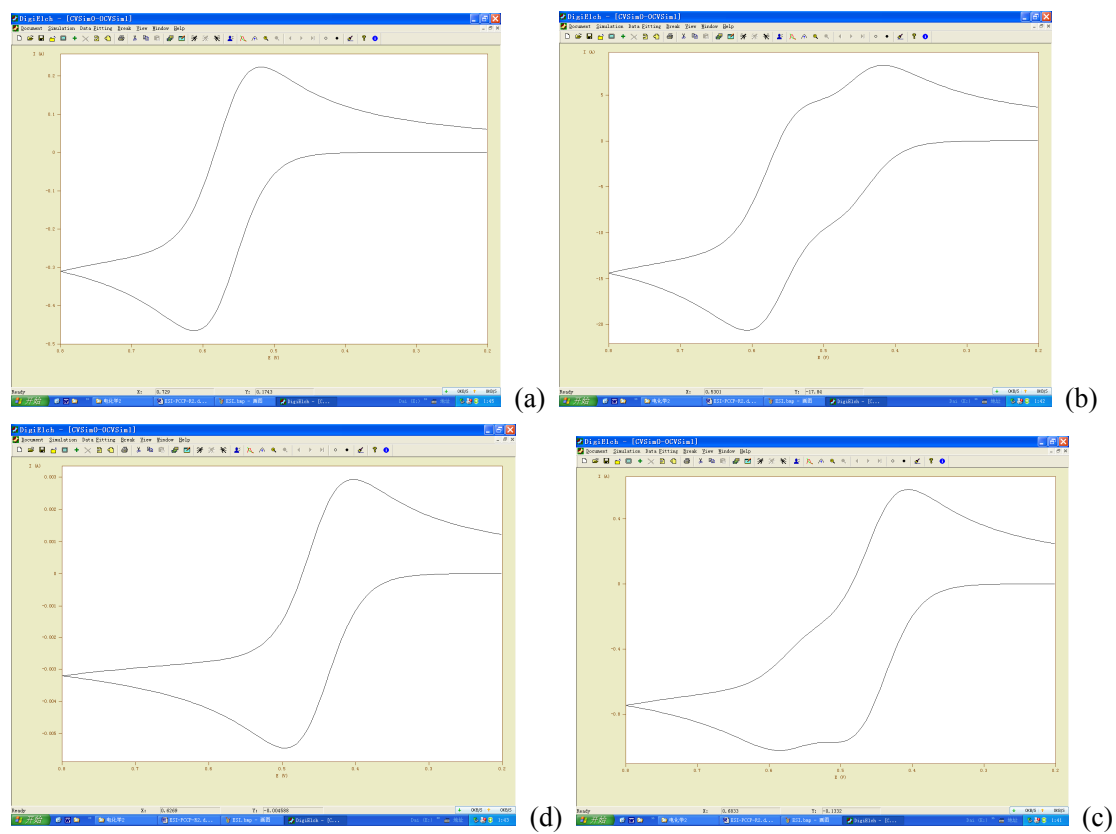


Fig. Digielch-2. (first redox step)

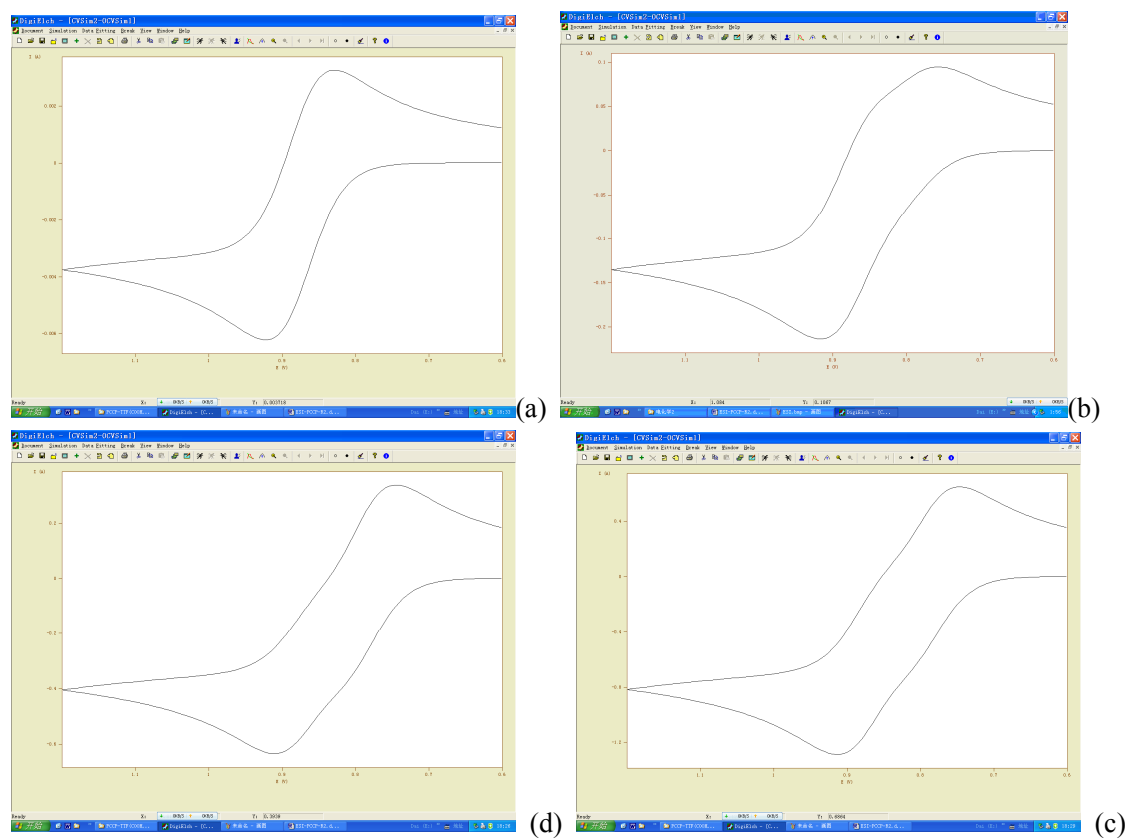


Fig. Digielch-3 (second redox step)