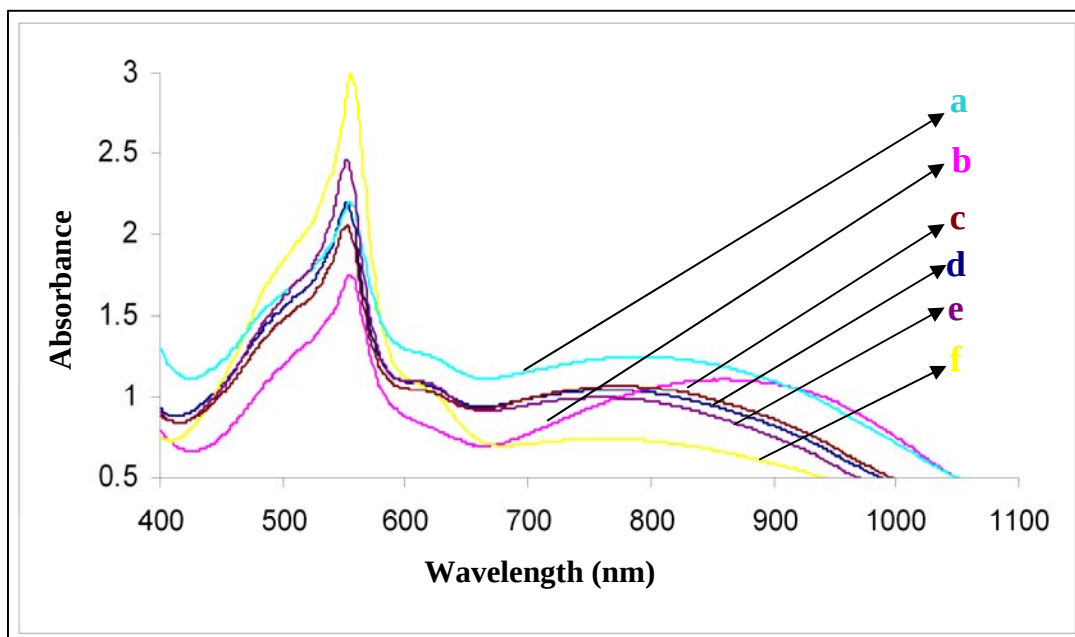
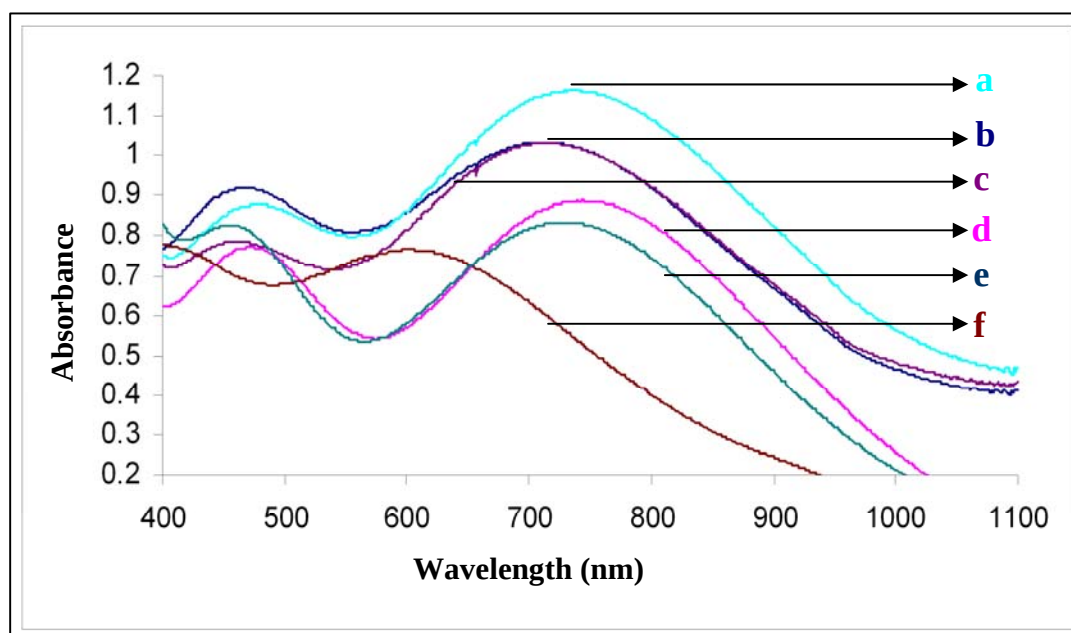
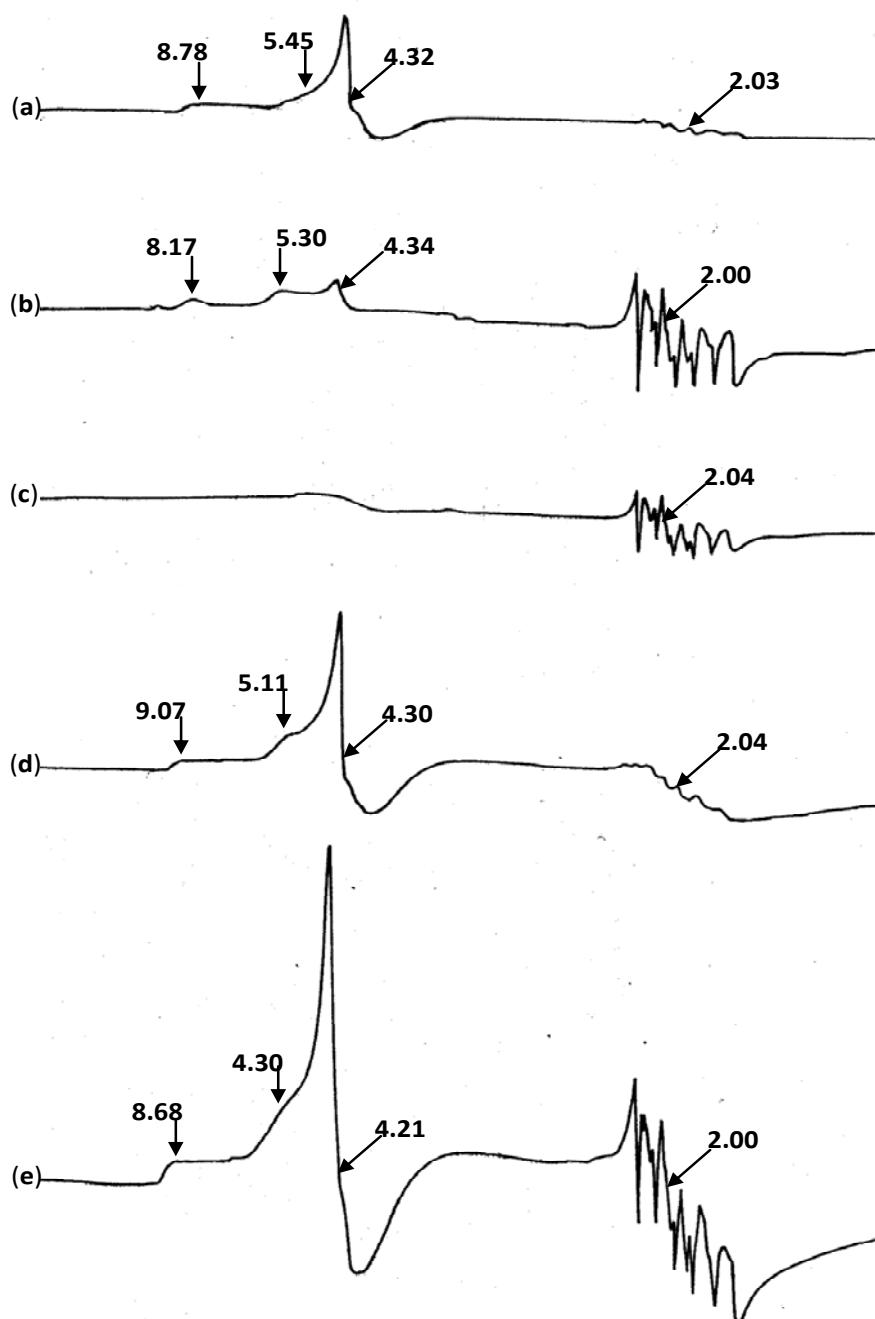




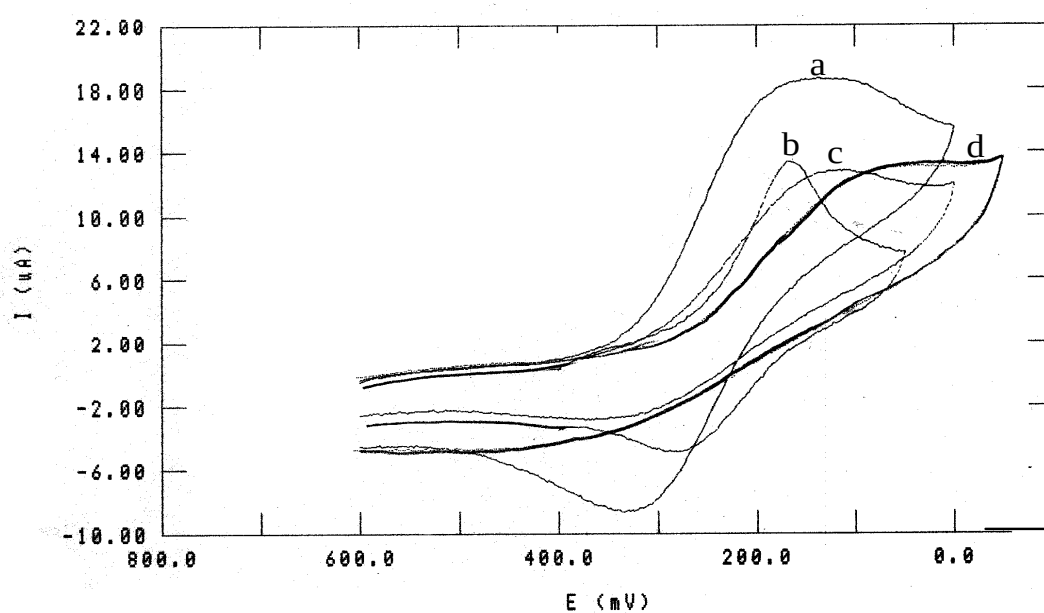
**Figure S1a** Electronic absorption spectra of the adducts of the complex  $[\text{Fe}(\text{L})\text{Cl}_3]$  ( $2 \times 10^{-4} \text{ M}$ ) generated in situ by adding equimolar amount of  $\text{H}_2\text{DBC}$  in SDS (a); DCM (b); CTAB (c); water (d); TX-100 (e) and DMF (f).



**Figure S1b** Electronic absorption spectra of the adducts of the complex  $[\text{Fe}(\text{L4})\text{Cl}_3]$  ( $2 \times 10^{-4} \text{ M}$ ) generated in situ by adding equimolar amount of  $\text{H}_2\text{DBC}$  in SDS (a); TX-100 (b); CTAB (c); DCM (d); DMF, (e) and water (f).



**Figure S2** EPR spectra of  $[\text{Fe}(\text{L4})(\text{DBC})(\text{H}_2\text{O})]^+$  in (a) Triton X-100; (b)  $[\text{Fe}(\text{L4})(\text{DBC})(\text{H}_2\text{O})]^+$  in aqueous solution; (c)  $[\text{Fe}(\text{L4})(\text{DBC})(\text{H}_2\text{O})]^+$  in SDS; (d)  $[\text{Fe}(\text{L4})(\text{DBC})\text{Br}]$  in CTAB and (e)  $[\text{Fe}(\text{L4})\text{Cl}_3]$  in aqueous solution at 77 K



**Figure S3** Cyclic voltammograms of  $[\text{Fe}(\text{L4})\text{Cl}_3]$  in water (a); SDS (b); TX-100 (c) and CTAB (d) at 25 °C. Complex concentration: 0.001 M, Supporting electrolyte: 0.1 M NaCl, Scan rate 50  $\text{mV s}^{-1}$

**Table S1** Electronic spectral data ( $\lambda_{\max}$  in nm,  $\epsilon_{\max}$  in  $\text{M}^{-1}\text{cm}^{-1}$  in parenthesis) for iron(III) complexes<sup>a</sup> in water and micellar media<sup>b</sup>

|                          | Water       | SDS         | CTAB        | TX-100      |
|--------------------------|-------------|-------------|-------------|-------------|
| [Fe(L1)Cl <sub>3</sub> ] | 380 (7620)  | 389 (5370)  | 377 (5210)  | 376 (3980)  |
|                          | 279 (8870)  | 296(7210)   | 289 (6430)  | 294 (7980)  |
|                          | 243 (15750) | 242 (12580) | 241 (13470) | 245 (14780) |
| [Fe(L2)Cl <sub>3</sub> ] | 366(3850)   | 353 (6270)  | 329 (4280)  | 319 (5380)  |
|                          | 278 (7680)  | 297 (7820)  | 278 (7180)  | 294 (7280)  |
|                          | 240 (16570) | 241 (17320) | 241 (11830) | 247 (12890) |
| [Fe(L3)Cl <sub>3</sub> ] | 316 (3850)  | 377 (4390)  | 366 (4600)  | 360 (3950)  |
|                          | 268 (6580)  | 292 (6720)  | 289 (6920)  | 293 (7820)  |
| [Fe(L4)Cl <sub>3</sub> ] | 356 (3570)  | 330 (5280)  | 324 (5130)  | 352 (4210)  |
|                          | 278 (5540)  | 291 (5620)  | 284 (6790)  | 289 (7940)  |
|                          | 240 (17560) | 238 (11370) | 240 (13720) | 246 (13480) |

<sup>a</sup>Concentration of iron(III) complexes,  $2 \times 10^{-4}$  M.

<sup>b</sup>Surfactant: SDS,  $13.0 \times 10^{-3}$  M ; CTAB,  $6.0 \times 10^{-3}$  M and TX-100,  $12.5 \times 10^{-3}$  M.

**Table S2** Electrochemical data<sup>a</sup> of [Fe(L2)Cl<sub>3</sub>] complexes and its DBC<sup>2-</sup>-adducts in aqueous and aqueous micellar<sup>b</sup> (SDS, CTAB, TX-100) solutions at 25 ± 0.2° C at a scan rate of 50 mV/s

| Complex                                    | $E_{pc}$<br>(V) | $E_{pa}$<br>(V) | $\Delta E$<br>(mV) | $E_{1/2}(\text{V})$ |                  | Redox process                             |
|--------------------------------------------|-----------------|-----------------|--------------------|---------------------|------------------|-------------------------------------------|
|                                            |                 |                 |                    | CV                  | DPV <sup>d</sup> |                                           |
| <b>Water</b>                               |                 |                 |                    |                     |                  |                                           |
| [Fe(L2)Cl <sub>3</sub> ]                   | 0.154           | -               | -                  | 0.231               | 0.304            | C                                         |
|                                            | -               | 0.515           | -                  |                     | 0.232            | Fe <sup>III</sup> → Fe <sup>II</sup>      |
|                                            | -0.626          | -               | -                  | -                   | -0.657           | LR                                        |
| [Fe(L2)Cl <sub>3</sub> ]+DBC <sup>2-</sup> | 0.270           | 0.348           | 78                 | 0.309               | 0.224            | DBSQ → DBC <sup>2-</sup>                  |
|                                            | 0.046           | -               | -                  | -                   | 0.084            | c                                         |
|                                            | -0.668          | -               | -                  | -                   | -0.676           | Fe <sup>III</sup> → Fe <sup>II</sup> + LR |
| <b>SDS</b>                                 |                 |                 |                    |                     |                  |                                           |
| [Fe(L2)Cl <sub>3</sub> ]                   | 0.300           | 0.536           | 236                | 0.418               | 0.426            | Fe <sup>III</sup> → Fe <sup>II</sup>      |
|                                            | -0.664          | -               | -                  | -                   | -0.674           | LR                                        |
| [Fe(L2)Cl <sub>3</sub> ]+DBC <sup>2-</sup> | 0.186           | 0.284           | 98                 | 0.235               | 0.240            | DBSQ → DBC <sup>2-</sup>                  |
|                                            | -0.682          | -               | -                  | -                   | -0.696           | Fe <sup>III</sup> → Fe <sup>II</sup> + LR |
| <b>CTAB</b>                                |                 |                 |                    |                     |                  |                                           |
| [Fe(L2)Cl <sub>3</sub> ]                   | 0.256           | 0.438           | 182                | 0.347               | 0.376            | Fe <sup>III</sup> → Fe <sup>II</sup>      |
|                                            | -0.667          | -               | -                  | -                   | -0.702           | LR                                        |
| [Fe(L2)Cl <sub>3</sub> ]+DBC <sup>2-</sup> | 0.120           | 0.396           | 276                | 0.258               | 0.352            | DBSQ → DBC <sup>2-</sup>                  |
|                                            | -0.720          | -               | -                  | -                   | -0.748           | Fe <sup>III</sup> → Fe <sup>II</sup> + LR |
| <b>TX-100</b>                              |                 |                 |                    |                     |                  |                                           |
| [Fe(L2)Cl <sub>3</sub> ]                   | 0.290           | 0.406           | 116                | 0.348               | 0.378            | Fe <sup>III</sup> → Fe <sup>II</sup>      |
|                                            | -0.612          | -               | -                  | -                   | -0.636           | LR                                        |
| [Fe(L2)Cl <sub>3</sub> ]+DBC <sup>2-</sup> | 0.196           | 0.449           | 253                | 0.302               | 0.338            | DBSQ → DBC <sup>2-</sup>                  |
|                                            | -0.646          | -               | -                  | -                   | -0.665           | Fe <sup>III</sup> → Fe <sup>II</sup> + LR |

<sup>a</sup>Potential measured vs Calomel electrode (0.01 M, 0.1 M NaCl). Add 0.244 V to convert to NHE.

<sup>b</sup>Surfactant concentration used for the above studies are SDS, 13.0 × 10<sup>-3</sup> M., CTAB, 6.0 × 10<sup>-3</sup> M. and TX-100, 12.5 × 10<sup>-3</sup> M. <sup>c</sup>Reduction of some dissociated species, LR = Ligand Reduction,

<sup>d</sup>Differential pulse voltammetry scan rate, 5 mV/s

**Table S3** Electrochemical data<sup>a</sup> of [Fe(L3)Cl<sub>3</sub>] complexes and its DBC<sup>2-</sup> adducts in aqueous and aqueous micellar<sup>b</sup> (SDS, CTAB, TX-100) solutions at 25 ± 0.2 °C at a scan rate of 50 mV/s

| Complex                                    | $E_{pc}$<br>(V) | $E_{pa}$<br>(V) | $\Delta E$<br>(mV) | $E_{1/2}$ (V) |                  | Redox process                             |
|--------------------------------------------|-----------------|-----------------|--------------------|---------------|------------------|-------------------------------------------|
|                                            |                 |                 |                    | CV            | DPV <sup>d</sup> |                                           |
| <b>Water</b>                               |                 |                 |                    |               |                  |                                           |
| [Fe(L3)Cl <sub>3</sub> ]                   | 0.128           | 0.322           | 190                | 0.233         | 0.216            | c                                         |
|                                            | 0.436           | -               | -                  |               | 0.450            | Fe <sup>III</sup> → Fe <sup>II</sup>      |
| [Fe(L3)Cl <sub>3</sub> ]+DBC <sup>2-</sup> | -0.627          | -               | -                  | -             | -0.677           | LR                                        |
|                                            | 0.148           | 0.314           | 166                | 0.231         | 0.243            | DBSQ → DBC <sup>2-</sup>                  |
|                                            | -               | -               | -                  | -             | 0.365            | c                                         |
|                                            | -0.664          | -               | -                  | -             | -0.685           | Fe <sup>III</sup> → Fe <sup>II</sup> + LR |
| <b>SDS</b>                                 |                 |                 |                    |               |                  |                                           |
| [Fe(L3)Cl <sub>3</sub> ]                   | 0.184           | 0.280           | 96                 | 0.232         | 0.268            | Fe <sup>III</sup> → Fe <sup>II</sup>      |
|                                            | -0.673          | -               | -                  | -             | -0.689           | LR                                        |
| [Fe(L3)Cl <sub>3</sub> ]+DBC <sup>2-</sup> | 0.132           | 0.270           | 138                | 0.201         | 0.229            | DBSQ → DBC <sup>2-</sup>                  |
|                                            | -0.682          | -               | -                  | -             | -0.701           | Fe <sup>III</sup> → Fe <sup>II</sup> + LR |
| <b>CTAB</b>                                |                 |                 |                    |               |                  |                                           |
| [Fe(L3)Cl <sub>3</sub> ]                   | 0.038           | 0.484           | 446                | 0.223         | 0.226            | Fe <sup>III</sup> → Fe <sup>II</sup>      |
|                                            | -0.701          | -               | -                  | -             | -0.722           | LR                                        |
| [Fe(L3)Cl <sub>3</sub> ]+DBC <sup>2-</sup> | 0.162           | 0.312           | 150                | 0.327         | 0.206            | DBSQ → DBC <sup>2-</sup>                  |
|                                            | -0.726          | -               | -                  | -             | -0.747           | Fe <sup>III</sup> → Fe <sup>II</sup> + LR |
| <b>TX-100</b>                              |                 |                 |                    |               |                  |                                           |
| [Fe(L3)Cl <sub>3</sub> ]                   | 0.114           | 0.354           | 240                | 0.234         | 0.230            | Fe <sup>III</sup> → Fe <sup>II</sup>      |
|                                            | -0.599          | -               | -                  | -             | -0.617           | LR                                        |
| [Fe(L3)Cl <sub>3</sub> ]                   | 0.168           | 0.318           | 150                | 0.243         | 0.208            | DBSQ → DBC <sup>2-</sup>                  |
|                                            | -0.614          | -               | -                  | -             | -0.648           | Fe <sup>III</sup> → Fe <sup>II</sup> + LR |

<sup>a</sup>Potential measured vs Calomel electrode (0.01 M, 0.1 M NaCl). Add 0.244 V to convert to NHE.

<sup>b</sup>Surfactant concentration used for the above studies are SDS, 13.0 × 10<sup>-3</sup> M., CTAB, 6.0 × 10<sup>-3</sup> M. and TX-100, 12.5 × 10<sup>-3</sup> M. <sup>c</sup>Reduction of some aquated/dissociated species, LR = Ligand Reduction,

<sup>d</sup>Differential pulse voltammetry scan rate, 5 mV/s