Utilization of new gold/schiff-base iron(III) complex composite as highly sensitive voltammetric sensor for determination of epinephrine in the presence of ascorbic acid

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From the structural point of view – upon introduction of Au surface – the non-coordinating N-H groups of benzimidazole moiety represent the only possible group that would be responsible for chemisorption of \([\text{Mn}_2(\text{H}_2\text{L})_2]\)(\text{ClO}_4)_2 complex at the electrode surface. Perpendicular chemisorption mode with respect to orientation of Mn(II)-Mn(II) molecular axis was proposed in corroboration to the estimated \(\Gamma\) value of the area per one adsorbed molecule (0.36 nm\(^2\)). [1] (Fig. S1)

**Fig. S1.** Schematic representation of chemisorbed \([\text{Mn}_2(\text{H}_2\text{L})_2]\)(\text{ClO}_4)_2 complex at the gold electrode surface.[1]

Direct comparison of \(\Gamma\) parameter was not possible for \([\text{Fe}_2(\text{H}_3\text{L})_2(\text{MeOH})_2(\mu\text{-OMe})_2]\)(\text{ClO}_4)_4 complex due to the fact that the concentration of iron(III) complex at the electrode is very small, too low to give CV peaks that would be assigned to metal ions. Different conformation of ligand \(\text{H}_3\text{L}\) as well as unambiguously assigned structure of Fe(III) complex by single crystal X-ray diffraction enabled us to anticipate different attachment onto gold electrode, in corroboration with electrochemical data that would explain observed effect.

There is no doubt that \([\text{Fe}_2(\text{H}_3\text{L})_2(\text{MeOH})_2(\mu\text{-OMe})_2]\)(\text{ClO}_4)_4 forms self-assembled monolayers on the Au surface. The electron transfer towards the SAM of complex on the bare gold electrode was confirmed by a sudden shift of the open-circuit potential when a sample of organics was injected into the electrolyte solution. Due to differences in adopted conformation of Schiff base ligand and thus structure, the mode of adsorption found for \([\text{Mn}_2(\text{H}_2\text{L})_2]\)\(^{2+}\) complex would not be possible for \([\text{Fe}_2(\text{H}_3\text{L})_2(\text{MeOH})_2(\mu\text{-OMe})_2]\)\(^{4+}\) system. There reason for this is the fact that the situation when there are two simultaneously chemisorbed benzimidazole moieties – which are crucial for permanent and strong chemisorption – are hindered by methyl and \(t\)-butyl groups of \(\text{H}_3\text{L}\) ligand. However, high degree of planarity of ligands in 1 allows us to assume that one of
them is the source of strong attachment to the electrode, with simultaneous extrusion of coordinated methanol molecule. (Fig. S2)

**Fig. S2.** Postulated schematic representation of chemisorbed $[\text{Fe}_2(\text{H}_3\text{L})_2(\text{MeOH})_2(\mu-\text{OMe})_2][\text{ClO}_4]_4$ complex at the gold electrode surface in present work.

The latter is feasible due to substantial gain in Gibbs free energy for the studied system coming both from N-Au interactions as well as certain degree of non-covalent $\pi$ stacking-Au interactions. Furthermore, rough estimation of the surface covered by one molecule of the complex in the above mentioned planar conformation equals $\sim 3.27$ nm$^2$ on the basis of crystallographic data, what is *ca.* a magnitude higher than for Mn-complex.

Figure S3 presents TEM image of synthesized Fe-complex as well as SEM images of bare gold electrode and its surface after modification with aforementioned metallosupramolecular architecture.
In accordance with previously reported data, the nitrogen-functionalized organic compounds form well-organized compact monolayers on the bare gold electrode [2]. Most probably, such a structure ensures an easier access of possible reactants to the electrode surface. This opinion is supported by the observation that permeability of SAM increases with increasing substrate roughness [3], which was confirmed by infrared reflection-absorption spectroscopy (IRRAS) spectra [4]. Nevertheless, formed self-assembled monolayer effectively protects the metal surface against adsorption of reaction products poisonous for the electrode surface. Modification of the surface electrode not only increases the electrode surface area but also facilitates the charge transfer between the oxidized compound and the gold electrode.
**Table S1.** Relevant geometric parameters (Å, °). A, B, C, D, E – mean planes of subsequent planar fragments: A: N1 – N9; B: C2, N10, N12, C13, C14; C: C14, C15, C17, C18, C19, C24; D: C17, C25, N26, N27, C29; E: C30 – N37.

|    | C-N  | N-N  | C=N  | C-O  | C-N-C | A/B | B/C | C/D | D/E | A/E |
|----|------|------|------|------|-------|-----|-----|-----|-----|-----|
| 1.328 | 1.389 | 1.286 | 1.347 | 108.6 | 6.7  | 1.5 | 1.5 | 6.0 | 13.5 |
| 1.343 | 1.392 | 1.281 | 1.352 | 109.0 | 108.0 | 109.1 | 6.4 | 3.2 | 6.0 |
| 1.344 | 1.397 | 1.288 | 1.347 | 109.0 | 108.0 | 109.1 | 109.0 | 109.1 | 10.2 |
| 1.338 | 1.396 | 1.266 | 1.352 | 109.0 | 108.0 | 109.1 | 109.0 | 109.1 | 10.2 |

**Table S2.** Hydrogen bond data (Å, °)

| D    | H      | A     | D-H   | H···A  | D···A  | D-H···A |
|------|--------|-------|-------|--------|--------|---------|
| N1A  | H1A    | O4C   | 0.86  | 2.02   | 2.87498| 170     |
| N3A  | H3A    | O2D i | 0.86  | 2.07   | 2.852(8)| 151     |
| O16A | H16A   | N26A  | 0.82  | 2.00   | 2.722(6)| 146     |
| N30A | H30A   | O1G   | 0.86  | 1.98   | 2.838(8)| 176     |
| N37A | H37A   | O4D   | 0.86  | 1.97   | 2.754(7)| 152     |
| N1B  | H1B    | O4F   | 0.86  | 1.98   | 2.765(7)| 152     |
| N3B  | H3B    | O1C ii| 0.86  | 2.10   | 2.883(8)| 152     |
| 016B | H16B   | N12B  | 0.82  | 1.99   | 2.697(6)| 144     |
| N30B | H30B   | O1F iii| 0.86 | 2.11   | 2.853(8)| 144     |
| N37B | H37B   | O3E   | 0.86  | 2.02   | 2.869(8)| 169     |
| O1G  | H1G    | O2E   | 0.82  | 2.06   | 2.873(10)| 171    |

Symmetry code: i 1-x,2-y,1-z;

**Table S3.** SHAPE analysis for isoelectronic Mn(II) and Fe(III) complexes, which assumes coordination number 6 for central metal ion

| Shape (CN = 6)            | Symmetry | Fe1A/Fe1B | Mn1A  | Mn1B  |
|---------------------------|----------|-----------|-------|-------|
| Johnson pentagonal pyramid (J2) | C5v      | 25.54     | 16.22 | 15.71 |
| Pentagonal pyramid        | C5v      | 22.09     | 12.130| 12.04 |
| Octahedron                | O6       | 2.04      | 12.45 | 10.55 |
|                |  |  |  |  |
|----------------|---|---|---|---|
| Trigonal prism| $D_{3h}$ | 11.15 | **3.28** | **4.34** |
| Hexagon       | $D_{6h}$ | 31.53 | 32.26 | 30.41 |

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