Voltammetric sensing of chloride based on a redox active complex: a terpyridine-Co(II)-dipyrromethene functionalized anion receptor deposited on a gold electrode

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1. The electroactive surface area of gold working electrode A_{eas} was determined by oxygen adsorption measurement and was calculated by equations:

$$A_{eas} = \frac{Q_{Au}}{Q_H^S} = 0.32 \pm 0.02 \text{ cm}^2 \tag{S1}$$

$$Q_{Au} = \frac{A_{p,c}}{v} \tag{S2}$$

where $A_{p,c}$ is the charge of the gold oxide reduction of the gold working electrode, v is scan rate (0.1 V/s), and Q_H^S is the standard`s reference charge (0.00039 ± 0.00001 C/cm²) suggested for polycrystalline gold [1].

2. The roughness factor (*RF)* was calculated according to equation:

$$RF = \frac{A_{aes}}{A_{geom}} = 10.34 \pm 0.52, \text{ where } A_{geom}= 0.0314 \text{ cm}^2 \tag{S3} [2]$$

3. Calculation procedure for surface coverage Γ [mol/cm³]

Based on the slopes of the relationships presented in Fig. 1B, the surface coverage (Γ) was calculated using the following equation:

$$I_p = \frac{n^2 F^2 v A \Gamma}{4RT} \tag{S4} [3]$$

where n – the number of electrons involved in the oxidation or reduction process; *F =96500 C mol⁻¹* – the Faraday's constant; v – scan rate; A – is the area of the electrode; R – ideal gas constant; T – the temperature in Kelvin.

4. Calculation procedure for α and k [s⁻¹]

To determine the electron transfer coefficient α, the peak potential E_p is plotted *vs.* log v [4]. E_{pa} and E_{pc} are plotted separately in this way to give two branches. The slope of the line is given in equation:

$$slope = -\frac{2.3RT}{\alpha nF} \tag{S5}$$

Determining the x-intercepts of the lines for anodic and cathodic branches provides v_a and v_c, respectively, values that are used in Eq. S5 to determine the electron transfer rate constant k_0 [5]:

$$k = \frac{\alpha nF\vartheta_c}{RT} = \frac{(1-\alpha)nF\vartheta_a}{RT} \tag{S6}$$

where: n is the number of electrons involved in the oxidation or reduction process; $F = 96500$ [C mol^{-1}] – the Faraday constant; $R = 8.3145$ [J mol^{-1}K^{-1}] is the ideal gas constant; $T = 273K$ – room temperature.
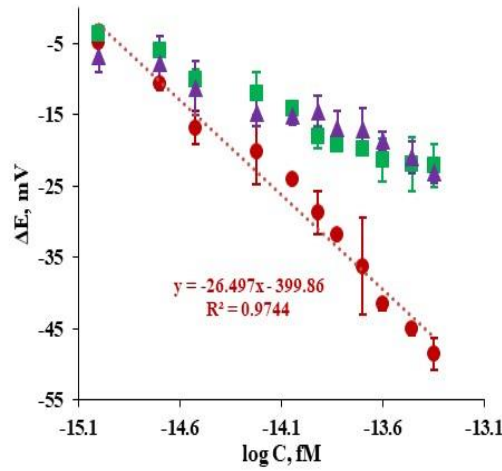

Figure S1: Redox potential differences $\Delta E = E_n - E_0$, mV recorded using SWV for Au/MBL,AHT/TPY/Co(II)/DPM-AR in the presence of chloride.

5. Selectivity $R_{i,j}$ was calculated based on the slope ratio as recommended by Macca and Wang [6], equation:

$$R_{i,j} = \frac{S_j}{S_i} \tag{S7}$$

where: S_i is the slope of the calibration curve for chloride; S_j is the slope of the calibration curve for sulphate/bromide.

6. The selectivity factor α_f of the proposed sensor was estimated by the Equation:

$$\alpha_f = \frac{\left(\frac{\Delta I_n}{I_0}\right)_{Cl-}}{\left(\frac{\Delta I_n}{I_0}\right)_{Int}} \tag{S8}$$

where $\left(\frac{\Delta I_n}{I_0}\right)_{Cl-}$ and $\left(\frac{\Delta I_n}{I_0}\right)_{Int}$ are normalized responses of the Au/ MBL,AHT/TPY/Co(II)/DPM-AR to Cl$^-$ and interfering agents (sulphate and bromide) [7].

7. Limit of detection (*LOD*) was calculated using *IUPAC* (International Union of Pure and Applied Chemistry) definitions according to the equation:

$$LOD = \frac{3.3\sigma}{q} \tag{S9}[8]$$

where σ is the standard deviation of the response and q is the slope of the calibration curve.

Table S1: Response ratio $R_{i,j}$ of the Au/MBL+AHT/TPY-Co(II)/DPM-AR sensor.

Anion	$R_{i,j}$
Cl⁻	1
SO_4^{2-}	0.73
Br⁻	0.47

8. The association constant (K_A) of DPM-AR with chloride was calculated using a Langmuir isotherm approach [9].

$$k_A C = \frac{I_n - I_0}{I_0} \tag{S10}$$

where, C is a concentration of molecules in the solution, and I_0 and I_n mean the peak currents without and in the presence of a particular concentration of chloride, respectively.
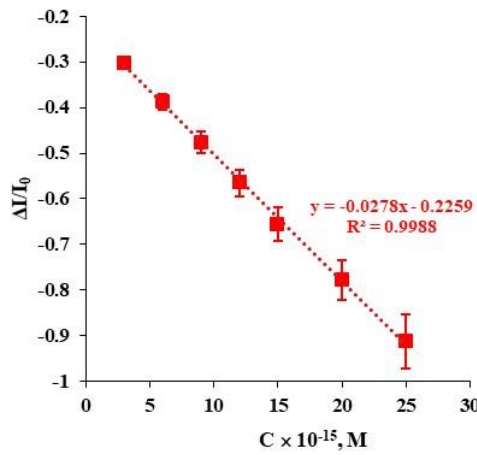

Figure S2: The linear relationship of $(I_n{-}I_0/I_0)$ *vs.* C_{Cl^-} [M] for TPY/Co(II)/DPM-AR modified gold electrode surface.

Based on the obtained results, the dissociation constant K_D was calculated according to the following relationship:

$$K_A = \frac{1}{K_D} \tag{S11}$$

9. Gibbs free energy (ΔG) was calculated using the Van't Hoff equation:

$$\Delta G = -RT\ln K_A \tag{S12}[10]$$

Table S2: The association constant K_A, dissociation constant K_D and Gibbs free energy ΔG calculated for a gold electrode modified with TPY/Co(II)/DPM-AR.

K_A [M⁻¹]	K_D [M]	ΔG [kJ/mol]
$2.78 \pm 0.21 \times 10^{13}$	$6.13 \pm 0.45 \times 10^{-14}$	-69.6 ± 2.0

10. The interface binding constants (K) were estimated according to the procedure reported by Gobi and Ohsaka [11] based on equation:

$$exp\{\Delta E^{\circ\prime}(-nF/RT)\} - 1 = K_1[X] + K_1K_2[X]_2 \tag{S13}$$

where R, F, and T (K) have their usual meaning, n is the number of electrons transferred (in the present case, it is equal to one), and [X] represents the concentration of target anions.
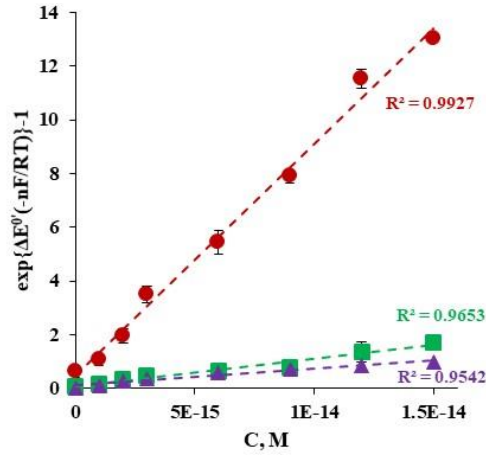

Figure S3: Relationship of $exp\{\Delta E°'(-nF/RT)\}-1$ *vs.* concentration of (●) chloride, (■) sulfate and (▲) bromide.

The formal potential ($E°'$) values were estimated as the average of anodic and cathodic peak potentials. The averages of the anodic and cathodic potential shifts ($\Delta E°'$) were calculated from the CV curves for each anion concentration, and the respective $exp\{\Delta E°'(-nF/RT)\}-1$ values were plotted *vs.* the concentrations of the anions. The corresponding graphs in Fig. S3 show that the relationship is linear, and the slopes accordingly provide access to the interface binding constants of the system under study.

11. In order to confirm the good selectivity of the sensor towards chloride, the reaction coupling efficiency (*RCE*) was calculated using an equation [12]:

$$RCE = \frac{K_1}{K_2} = e^{\frac{nF\Delta E^0}{RT}} \tag{S14}$$

where, K_1 and K_2 are the stability constants of the complex in different redox states, and ΔE^0 is the magnitude of the electrochemical shift.

Table S3: Binding constant (*K*) and Reaction Coupling Efficiency (*RCE*) of the MBL,AHT/TPY/Co(II)/DPM-AR towards chloride, sulfate and bromide (*n* = 5).

Parameters	Cl^-	SO_4^{2-}	Br^-
$K\times10^{+13}[M^{-1}]$	20.00	5.13	2.13
RCE	5.2 ± 0.5	2.3 ± 0.6	1.3 ± 0.3

Description of anion receptor synthesis

The synthesis scheme of anionic receptor modified with dipyrromethene ((Z)-4-((1H-Pyrrol-2-yl)(2H-pyrrol-2-ylidene)methyl)-N-(2-(bis(2-(3-hexylureido)ethyl) amino)ethyl)benzamide) is presented on **Scheme S1**. In brief, the compound **1** (Tris-2-aminoethylamine) was mono Boc-protected in dichloromethane according to a previously reported procedure [13] and the compound **2** was formed. The reaction between compound **2** with n-hexyl isocyanate resulted in formation of compound **3**, followed by removing of the Boc protecting group with trifluoroacetic acid in order to obtain compound **4.** The preparation of compound **8** was done by hydrolysis of dipyrromethene methyl ester **7** according to the procedure reported previously using compounds number **5** and **6** [14]. The compound **9** – activated NHS ester was obtained via a DDC mediated coupling reaction in the presence of DMAP. The final step concerned the reaction between compound **9** and **4** and the dipodal anion receptor **10** was formed. The detailed synthesis of dipodal anion receptor (compound **10**) is described in the manuscript by Kaur and co-workers [15].
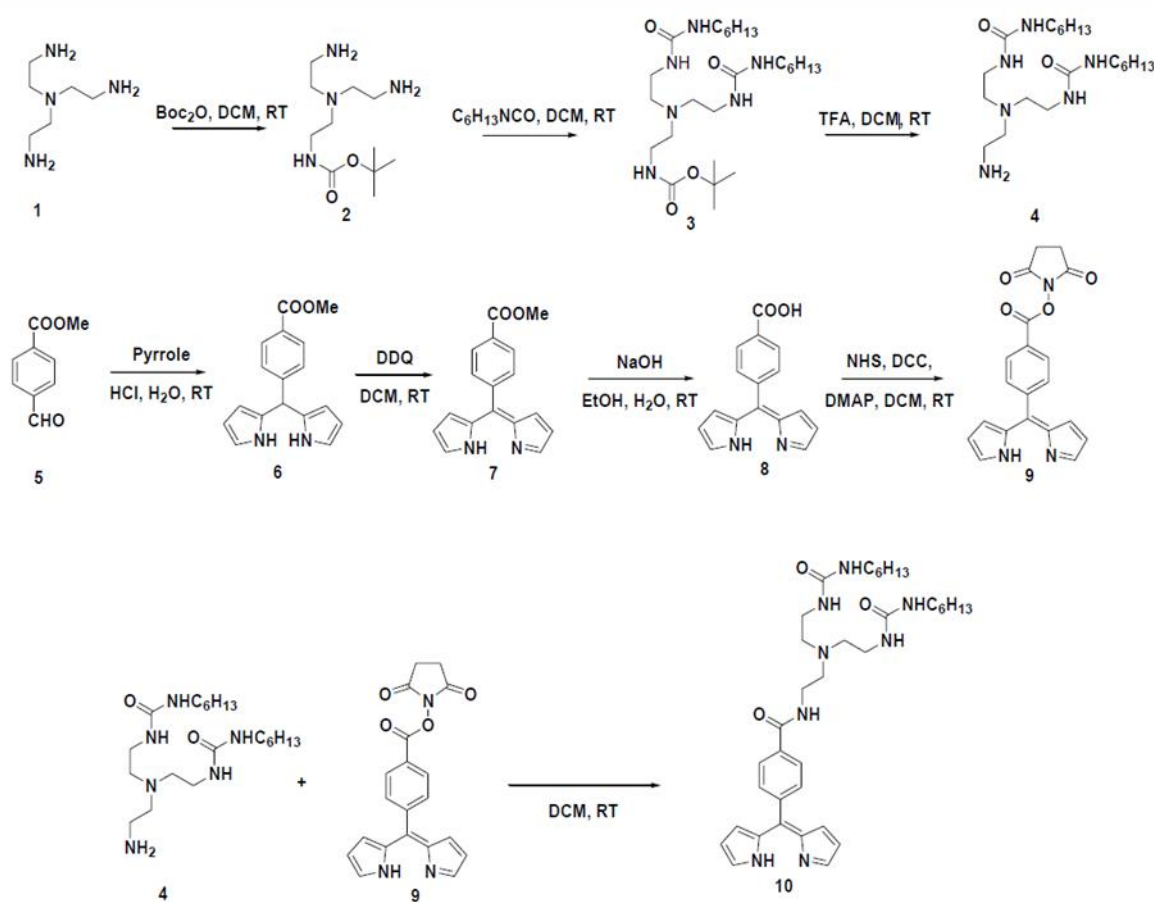
Scheme S1. Synthesis of the dipyrromethene modified dipodal anion receptor.

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