# The Effect of Coinage Transition Metal (Cu, Ag, Au) Substitutions on Two-electron Redox Potential of Quinones

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Quinones are a class of compounds which have widespread importance in chemistry, biology and medicine. Because of their appropriate performance in electron transferring rate, quinones are among the most applicable mediators in biosensors. Recently, the effects of different non-metal substitutions on redox potential of quinone have been investigated to design suitable mediators for different electrochemical measurements. In the present study, the effect of coinage transition metal (TM) substitutions (Cu, Ag, Au) alone or together with other functional group substitutions such as -OH, -Cl, -CH$_3$, -NO$_2$ and -CO$_2$H on lowering or raising the redox potential of quinone was investigated. The range of calculated redox potential was from 0.193 to 1.056 volts in comparison with unsubstituted benzoquinone which is 0.7 volts. We found that coinage TMs, similar to electron donating groups (EDGs), cause lowering effect on redox potential of quinones. Our findings reveal that the copper and hydroxyl groups have the most decreasing effect on redox potential. Calculations were performed through density functional theory with B3LYP xc-functional and mixed basis set 6-31+G** + LANL2DZ.

## INTRODUCTION

Mediator, one of the main parts of biosensor, is a chemical compound used as an electron transferring agent. It shuttles electron between electrode and desired compound at a lower potential which cannot be done easily without the presence of a mediator. Therefore, finding a mediator with the most suitable redox potential is very important for the fabrication of electrochemical sensors and biosensors. On the other hand, the measurement of redox potential *via* the experiments faces many problems and disappointing efforts [1-3]. Because of these problems, many theoretical investigations have been performed to calculate the redox potential of compounds [4-18].

Quinones are a class of compounds which play important role in chemistry, biology and medicine [19-23]. The biological activity of this class of compounds is often linked to their electron transferring rates and redox

potentials [24-26]. Quinones have been used as mediators and electron transferring agents in different biosensors. For example, benzoquinone and its derivatives are among the most applicable and effective mediators for glucose oxidase (GOD) based glucose sensor [27-30]. Quinones also play important role in tyrosinase biosensor [31], DNA sensor [32], and in the horseradish peroxidase electrode [33].

The electronic structure of a quinone can be changed by suitable substitutions to find a desired potential region. Therefore, many theoretical investigations have been performed to calculate the redox potential of substituted quinones [34-40]. So, the study of different structures of these compounds and getting the especial region of potential due to our necessities is of interest.

In the present research quantum mechanical procedure was used, as previously introduced [40], to show the effect of substituting TMs (Cu, Ag, Au) and non-metal groups, -OH, -Cl, -CH$_3$, -NO$_2$ and -COOH, on the two-electron redox potentials of quinones such as 1,4-benzoquinone (briefly benzoquinone), 1,4-naphthoquinone (briefly

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naphthoquinone) and anthraquinone 2-carboxylic acid (briefly anthraquinone). The effect of small TM clusters (copper clusters) on redox potential of benzoquinone was also studied. Selection of Cu, Ag and Au is due to their ability to interact with biological compounds such as amino acids [41]. We followed the trend of lowering or raising the redox potential of quinones which might be helpful in analytical, organic and biological chemistry to predict which compounds are suitable to synthesis and then to be used as mediator for a particular measurement of interest.

## COMPUTATIONAL METHODS

The theoretical aspect is the same as our previous calculation [40]. Isodesmic reaction was used to calculate two-electron redox potentials of compounds belonging to one family by choosing one of them as a reference [35]. To calculate the redox potentials, we applied the reaction equation,

$$QH_2 \quad +Q' \quad \rightarrow Q \quad +Q'H_2 \qquad (1)$$
$$\text{Re}duced \quad Oxidized \quad Oxidized \quad \text{Re}duced$$
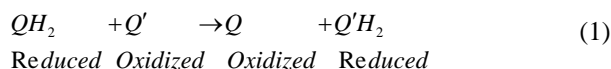
In this method a compound with a known experimental redox potential is selected as a reference molecule and the redox potentials of its derivatives are calculated. According to the Eq. (1), the reference molecule, unsubstituted benzoquinone (hydroquinone, $QH_2$), is oxidized and other quinone derivatives ($Q'$) are reduced.

The two-electron redox potential of substituted quinones ($E_{Q'}$) can be calculated through,

$$E_{Q'} - E_Q = -\frac{\Delta G_{rxn}}{|Z|F} \qquad (2)$$

where $E_Q$ is the experimental redox potential of the reference molecule, $|Z|$ is the number of electrons transferred (here equals two), $F$ is the Faraday constant (96485.3399 C mol$^{-1}$) and $\Delta G_{rxn}$ is the differences of Gibbs free energies of products and substrates,

$$\Delta G_{rxn} = \Delta G_{products} - \Delta G_{substrates} \qquad (3)$$

DFT procedure, B3LYP method and mixed basis set 6-

31+G** + LANL2DZ were used in this study. LANL2DZ pseudopotential basis set was applied only for TMs. In this research we are dealing with difference of energies rather than total energy and hence using LANL2DZ basis set for three metals does not make significant error in calculations. For instance, the two-electron redox potential of 2-Cu-Q is 0.586 volts using LANL2DZ while it is 0.592 volts by applying 6-31+g** (1% difference). Although relativistic effect should be included in calculations for gold atom, here it is ignored since the error in energy changes ($\Delta G_{rxn}$) and hence in potential values is insignificant. For example, the calculated redox potential of gold-substituted quinone (*2-Au-Q*) by including relativistic effect is 0.682 volt while it is 0.687 volt without considering this effect. The geometries of all quinones were fully optimized using G09 program [42] and the frequency test was carried out to ensure of being in real minimum and to gain the Gibbs free energies. All calculations were performed in the gas phase.

## NOMENCLATURES

From now on, M represent TMs (Cu, Ag, Au), Q stands for benzoquinone, and G for non-metal group such as -OH, -Cl *etc*. Standard labeling is used for hydrocarbon rings (benzoquinone, naphthoquinone and anthraquinone). Labeling of these compounds has been illustrated in Fig. 1.
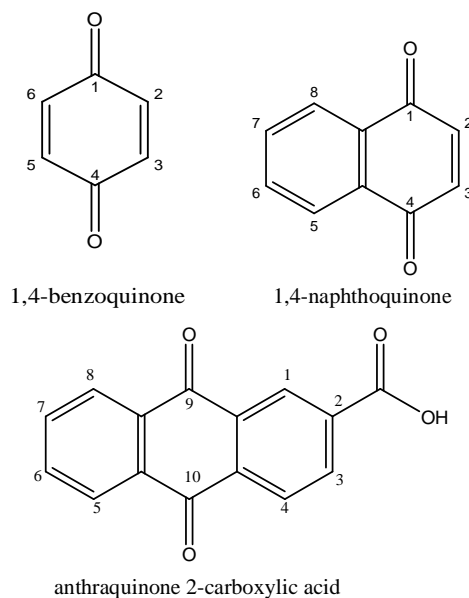
1,4-benzoquinone          1,4-naphthoquinone

anthraquinone 2-carboxylic acid

**Fig. 1.** Labeling of quinone structures.

In general, TM substituted benzoquinone is called $n_1, n_2, n_3, n_4$-M,M',M'',M'''-Q which $n_1$ represents the label of carbon atom that metal M has connected with, $n_2$ is the label of carbon atom that metal M′ has connected with and so on. For instance, in *2,3-Cu-Ag-Q* compound Cu and Ag atoms are connected to carbon numbers 2 and 3, respectively. If *M, M′, M″ and M‴* are the same, the compound is called $n_1, n_2, n_3, n_4$-M-Q as in *2,5-Cu-Q* showing that carbon numbers 2 and 3 are connected to Cu atom. For combination of metal and non-metal substitutions similar nomenclature is used. For instance, *3,6-OH-2,5-M-Q* shows that two hydroxyl groups are connected to carbon numbers 3 and 6 and also two metals M are connected to carbon numbers 2 and 5. This type of nomenclature is applied for small TM cluster substituted quinone in the form of $2$-$(Cu)_n$-$Q$, n is the number of metals in cluster.

## RESULTS AND DISCUSSION

Although the present research is a theoretical investigation, it is worth mentioning that the organometallic compounds used in this article can be synthesized by first halogenations of hydroquinone (reduced form of quinone) through an electrophilic substitution reaction and then exchange of halogen with metal. This type of reaction is very obvious in organic and organometallic chemistry textbooks [43,44], and is also well-known in literature [45,46].

**Two-Electron Redox Potential of Substituted Benzoquinone**

The experimental value of two-electron redox potential

of unsubstituted benzoquinone (the reference molecule) has been reported as 0.7 volt [2]. As mentioned, the redox potential of each quinone derivative is calculated relative to the experimental redox potential of reference molecule. The redox potential of this reference molecule has been previously calculated using direct mechanism [40] as 0.703, in agreement with experimental value with the error of 0.43%.

Prior to study of the TM-substituted quinones, we calculated the two-electron redox potential of benzoquinones with substitutions of only non-metal groups (-OH, -CH$_3$, -Cl, -CO$_2$H and -NO$_2$). The results are presented in Table 1. The calculated redox potentials show that substituting both strongly and weakly electron donating groups (EDGs), -OH and -CH$_3$, lowers the redox potential of benzoquinone. These potential values are in agreement with experiments [2]. However, for strongly and moderately electron withdrawing groups (EWGs), -NO$_2$ and -CO$_2$H, substituting of these groups have raising effect on redox potential of benzoquinone. No experimental data is available for these two compounds. For chlorine substituted benzoquinone, theoretical results show a slightly lowering in potential value (~3%), while the experiment show a slightly increasing in potential value (~2%). In general, halogen substitutions were shown to have dual behavior. As a result of their high electronegativity, they cause inductive withdrawal (withdrawal of electrons from the carbon atom of ring) and because of their non-bonding electrons they can be considered as electron donating groups. The discrepancy between calculated and measured potentials might refer to the dual behavior of halogens.

Different TM-derivatives of benzoquinone were classified into eight groups, which will be explained in the

**Table 1.** Two-Electron Redox Potential of Non-Metal Substituted Benzoquinones

|  | E (this work) | E (exp.) | %Error |
|---|---|---|---|
| *2-OH-Q* | 0.566 | 0.594 | -4.71 |
| *2-CH$_3$-Q* | 0.633 | 0.644 | -1.71 |
| *2-Cl-Q* | 0.678 | 0.712 | -4.78 |
| *2-CO$_2$H-Q* | 0.739 | - |  |
| *2-NO$_2$-Q* | 0.793 | - |  |
| *Q* (reference) | - | 0.7 |  |

following sections. The calculated redox potential and root mean square ($R^2$) of linearity of $E_{Cu}$, $E_{Ag}$, $E_{Au}$ trend was reported, where $E_{Cu}$, $E_{Ag}$ and $E_{Au}$ stand for two-electron redox potential of benzoquinone with substitution of Cu, Ag and Au, respectively. The percentage of potential changes (*%ch.*) with respect to unsubstituted benzoquinone is also presented. Furthermore, we studied the effect of TM substitutions on naphtoquinone and anthraquinone 2-carboxylic acid.

**Type I: The trend of two-electron redox potential of mono-metal, M, substituted benzoquinone.** The calculated two-electron redox potentials of mono-metal substituted benzoquinones are; 0.586, 0.600 and 0.687 volts for Cu, Ag and Au substitutions, respectively. The trend is $E_{Cu} < E_{Ag} < E_{Au} < E_{unsub}$. These results show that these TM substitutions lower the two-electron redox potential of benzoquinone. Therefore, these coinage TM substitutions have the same effect as EDGs.

**Type II: The trend of two-electron redox potential of mono-metal, M, mono-non-metal, G, substituted benzoquinone.** This type contains 45 benzoquinone derivatives. For *2-M-Q* compound there are three available

positions on the quinone ring to be substituted by non-metal groups, position of 3, 5 and 6. These are *ortho*, *para* and *meta* position relative to TM group, respectively. The results of these calculations are presented in Table 2. As expected, simultaneously substituting one TM and one EDG such as hydroxyl or methyl group lowers the two-electron redox potential of benzoquinone much more than type I compounds. This lowering effect was obtained for all positions of the ring. The most lowering in potential values obtained when the EDG was substituted in *para* position relative to TM. For simultaneously substituting one EWG, -$NO_2$ or -$CO_2H$, (with raising effect on redox potential) and one TM (with lowering effect on the redox potential), the potential values do not obey the specific trend. Some of the combinations lead to a potential value lower than the potential of reference molecule while some lead to upper values. The results depend on both the TM type and position of non-metal substitutions. For chlorine substituted compounds the redox potential also depends on both substituent's position and TM type. In spite of the existence of non-metal substitutions, the trend of redox potentials (except for two compounds, *3-NO$_2$-2-M-Q* and *3-CO$_2$H-2-*

**Table 2.** Two-Electron Redox Potential Value of Type II Molecules (Units in Volt)

| M | Cu | %Ch. | Ag | %Ch. | Au | %Ch. | $R^2$ |
|---|---|---|---|---|---|---|---|
| *5-OH-2-M-Q* | 0.444 | -37.0 | 0.459 | -34.0 | 0.554 | -21.0 | 0.85 |
| *6-OH-2-M-Q* | 0.473 | -32.0 | 0.481 | -31.0 | 0.568 | -19.0 | 0.81 |
| *3-OH-2-M-Q* | 0.507 | -28.0 | 0.516 | -26.0 | 0.585 | -16.0 | 0.83 |
| *5-CH$_3$-2-M-Q* | 0.528 | -25.0 | 0.541 | -23.0 | 0.627 | -10.0 | 0.85 |
| *3-CH$_3$-2-M-Q* | 0.547 | -22.0 | 0.555 | -21.0 | 0.634 | -9.0 | 0.82 |
| *6-CH$_3$-2-M-Q* | 0.540 | -23.0 | 0.553 | -21.0 | 0.640 | -9.0 | 0.84 |
| *3-Cl-2-M-Q* | 0.595 | -15.0 | 0.600 | -14.0 | 0.676 | -3.0 | 0.80 |
| *6-Cl-2-M-Q* | 0.584 | -17.0 | 0.597 | -15.0 | 0.684 | -2.0 | 0.84 |
| *2-M-Q* | 0.586 | -16.0 | 0.600 | -14.0 | 0.687 | -2.0 | 0.85 |
| *3-CO$_2$H-2-M-Q* | 0.662 | -5.0 | 0.606 | -13.0 | 0.707 | 1.0 | 0.20 |
| *3-NO$_2$-2-M-Q* | 0.758 | 8.0 | 0.685 | -2.0 | 0.725 | 4.0 | 0.20 |
| *5-Cl-M-2-Q* | 0.642 | -8.0 | 0.654 | -7.0 | 0.739 | 6.0 | 0.84 |
| *6-CO$_2$H-2-M-Q* | 0.659 | -6.0 | 0.660 | -6.0 | 0.741 | 6.0 | 0.76 |
| *6-NO$_2$-2-M-Q* | 0.696 | -1.0 | 0.705 | 1.0 | 0.787 | 12.0 | 0.82 |
| *5-CO$_2$H-2-M-Q* | 0.681 | -3.0 | 0.725 | 4.0 | 0.808 | 15.0 | 0.97 |
| *5-NO$_2$-2-M-Q* | 0.908 | 30.0 | 0.917 | 31.0 | 0.997 | 42.0 | 0.82 |

*M-Q*) follows the same trend as Type I, $E_{Cu} < E_{Ag} < E_{Au}$. As the exceptions refer to larger functional groups we suggest that steric effect is the case affecting the redox potential.

**Type III: The trend of two-electron redox potential of mono-metal, M, multi-OH (or -NO2) substituted benzoquinone.** It would be interesting to see the effect of applying the combination of one TM and multi hydroxyl groups as strong EDGs (or multi nitro groups as strong EWGs). The results are presented in Table 3 and Fig. 2. Results show that multi hydroxyl substitutions together with mono-metal substitution makes further decreasing on two-electron redox potential of benzoquinone to maximum 59% while for nitro groups the potential is increased up to 51%. No trend was obtained for adding the non-metal groups.

**Type IV: The trend of two-electron redox potential of two the same metal, M, substituted benzoquinone.** The effect of substituting two the same TMs on different positions of the ring was investigated. The results are presented in Table 4. As it is expected, further decreasing in potential value with respect to mono-metal substituted benzoquinones was obtained. The maximum decreasing in redox potential among copper substituted compounds is 27%, while this value is 26% and 8% among silver and gold substituted compounds, respectively.

**Type V: The trend of two-electron redox potential of two different metals, M and M′, substituted benzoquinone.** This type is similar to type IV but the two substituted TMs are different. According to Table 5, the

**Table 3.** Two-Electron Redox Potential of Type III Molecules (Units in Volt)

| G | NO₂ | | | | | | OH | | | | | |
|---|-----|---|---|---|---|---|-----|---|---|---|---|---|
| M | Cu | %Ch. | Ag | %Ch. | Au | %Ch. | Cu | %Ch. | Ag | %Ch. | Au | %Ch. |
| *3-G-2-M-Q* | 0.758 | 8.0 | 0.685 | -2.0 | 0.725 | 4.0 | 0.473 | -32.0 | 0.481 | -31.0 | 0.568 | -19.0 |
| *6-G-2-M-Q* | 0.696 | -1.0 | 0.705 | 1.0 | 0.787 | 12.0 | 0.507 | -28.0 | 0.516 | -26.0 | 0.585 | -16.0 |
| *3,6-G-2-M-Q* | 0.835 | 19.0 | 0.768 | 10.0 | 0.809 | 16.0 | 0.287 | -59.0 | 0.292 | -58.0 | 0.536 | -23.0 |
| *5-G-2-M-Q* | 0.908 | 30.0 | 0.917 | 31.0 | 0.997 | 42.0 | 0.444 | -37.0 | 0.459 | -34.0 | 0.554 | -21.0 |
| *5,6-G-2-M-Q* | 0.923 | 32.0 | 0.931 | 33.0 | 1.004 | 43.0 | 0.536 | -23.0 | 0.503 | -28.0 | 0.500 | -29.0 |
| *3,5-G-2-M-Q* | 1.050 | 50.0 | 0.983 | 40.0 | 1.010 | 44.0 | 0.519 | -26.0 | 0.461 | -34.0 | 0.621 | -11.0 |
| *3,5,6-G-2-M-Q* | 1.056 | 51.0 | 0.987 | 41.0 | 1.019 | 46.0 | 0.384 | -45.0 | 0.349 | -50.0 | 0.413 | -41.0 |
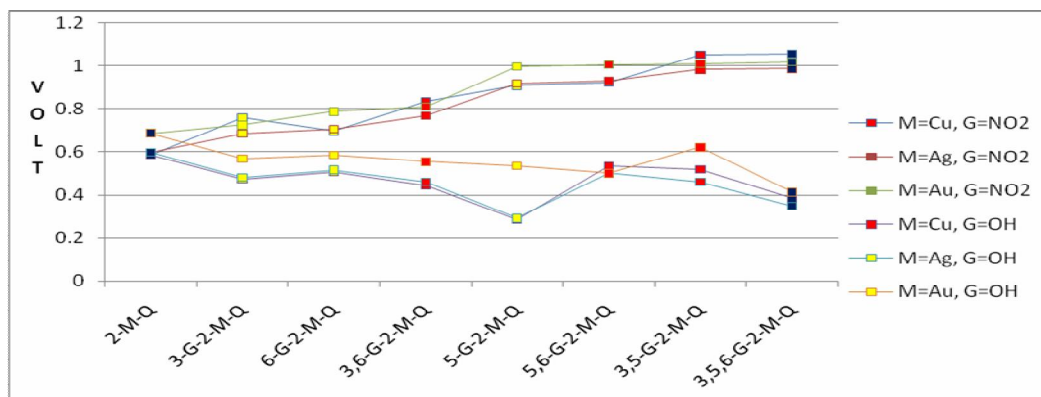


**Fig. 2.** The diagram of two-electron redox potentials of molecules of Type III.

redox potential of *2,6-Cu-Ag-Q* compound is the lowest one confirming the trend $E_{Cu} < E_{Ag} < E_{Au} < E_{unsub}$. Maximum decreasing in redox potential is 29%.

**Type VI: The trend of two-electron redox potential of para-di-metal, M, para-di-non-metal, G, substituted benzoquinones.** Two the same TMs, in *para* position relative to each other, and also two the same non-metal substitutions were used to get a more wide range of potential values. The results are presented in Table 6. The

calculated redox potentials show the trend $E_{Cu} < E_{Ag} < E_{Au}$ (except for two cases, similar to Type II, that $-NO_2$ and $-CO_2H$ groups are located on *ortho* position relative to TM). The range of the potential values is from 0.238 to 1.135 volt representing a 66% decrease and 62% increase in redox potential of benzoquinone, respectively.

**Type VII: The trend of two-electron redox potential of multi-copper (tri and tetra) substituted benzoquinone.** The redox potentials of tri- and tetra-copper substituted

**Table 4.** Two-Electron Redox Potentials of Type IV Molecules (Units in Volt)

| M | Cu | %Ch. | Ag | %Ch. | Au | %Ch. | $R^2$ |
|---|---|---|---|---|---|---|---|
| *2-M-Q* | 0.586 | -16.0 | 0.599 | -14.0 | 0.687 | -2.0 | 0.85 |
| *2,3-M-Q* | 0.533 | -24.0 | 0.525 | -25.0 | 0.649 | -7.0 | 0.70 |
| *2,5-M-Q* | 0.509 | -27.0 | 0.527 | -25.0 | 0.685 | -2.0 | 0.83 |
| *2,6-M-Q* | 0.512 | -27.0 | 0.517 | -26.0 | 0.642 | -8.0 | 0.78 |

**Table 5.** Two-Electron Redox Potentials of Molecules of Type V (Units in Volt)

| | 2,3 | %Ch. | 2,5 | %Ch. | 2,6 | %Ch. | $R^2$ |
|---|---|---|---|---|---|---|---|
| *Cu-Ag-Q* | 0.528 | -24.0 | 0.506 | -28.0 | 0.498 | -29.0 | 0.93 |
| *Cu-Au-Q* | 0.617 | -12.0 | 0.589 | -16.0 | 0.602 | -14.0 | 0.29 |
| *Ag-Au-Q* | 0.616 | -12.0 | 0.600 | -14.0 | 0.604 | -14.0 | 0.52 |

**Table 6.** Two-Electron Redox Potentials of Type VI molecules (Units in Volt)

| M | Cu | %Ch. | Ag | %Ch. | Au | %Ch. | $R^2$ |
|---|---|---|---|---|---|---|---|
| *3,6-OH-2,5-M-Q* | 0.238 | -66.0 | 0.238 | -66.0 | 0.370 | -47.0 | 0.75 |
| *3,6-CH₃-2,5-M-Q* | 0.436 | -38.0 | 0.440 | -37.0 | 0.589 | -16.0 | 0.77 |
| *2,5-M-Q* | 0.496 | -30.0 | 0.527 | -24.0 | 0.685 | -2.0 | 0.87 |
| *3,6-Cl-2,5-M-Q* | 0.516 | -26.0 | 0.519 | -26.0 | 0.664 | -5.0 | 0.77 |
| *3,6-CO₂-2,5-M-Q* | 0.697 | -0.42 | 0.641 | -8.0 | 0.764 | 9.0 | 0.30 |
| *3,6-NO₂-2,5-M-Q* | 1.135 | 62.0 | 0.665 | -5.0 | 0.728 | 4.0 | 0.64 |

**Table 7.** Two-Electron Redox Potentials of Type VII Molecules (Units in Volt)

| | Potential | %Ch. |
|---|---|---|
| *2-Cu-Q* | 0.586 | -15.0 |
| *2,5-Cu-Q* | 0.509 | -27.0 |
| *2,3,5-Cu-Q* | 0.453 | -35.0 |
| *2,3,5,6-Cu-Q* | 0.404 | -42.0 |

benzoquinone, *2,3,5-Cu-Q* and *2,3,5,6-Cu-Q*, were calculated. The results of these calculations together with mono- and di-copper benzoquinone are presented in Table 7, showing the effect of adding a TM substitution without any other non-metal group. The results show that the redox potential decreases as the number of *Cu* substitution increases. The $R^2$ of this linearity is 0.98. In this type, the maximum percent of decreasing in potential value is 42%.

**Type VIII: The trend of two-electron redox potential of copper cluster substituted benzoquinone.** In this part the effects of di-, tri- and tetra-copper cluster substitutions on redox potential of benzoquinone were investigated. The results presented in Table 8 show that these clusters also decrease the redox potential of benzoquinone. The redox potentials do not have regular trend by adding a copper atom (in contrast with type VII). The maximum change in redox potential (34%) refers to a tri-copper cluster substituted benzoquinone, *2-(Cu)₃-Q*, although this percent is still less than the potential of *2, 3, 5-tri-Cu-Q* (type VII), 35%. However, one efficiency of using these clusters is that three other positions of the benzoquinone ring still remain unsubstituted and are available to be substituted by other functional groups. We have selected the -OH groups as a strong EDG together with copper clusters to make further decreasing in redox potential of benzoquinone. The *3,5,6-*

*OH-2-(Cu)ₙ-Q* shows the general name of these compounds where n = 2,3,4. Table 8 shows that the maximum decreasing in redox potential (72%) refers to *3,5,6-OH-2-(Cu)₃-Q* compound. This decrease in redox potential of benzoquinone is maximum in comparison with all previous types.

**Generalization of the Trend of Two-Electron Redox Potential of Coinage TM-Substituted Quinines**

Up to now, the calculations were performed for benzoquinones. As mentioned before, to generalize the effect of coinage TM substitutions on two-electron redox potential of quinones, we have studied the effect of substituting these TMs on fused cyclic quinones such as naphthoquinone and anthraqunione. The results will be discussed in the next sections.

**Two-electron redox potential of mono-metal substituted naphthoquinone.** The redox potential of naphthoquinone (0.470 volts) [2] is lower than that of benzoquinone (0.7 volts), because the additional ring acts as EDG. There are three possible positions for a TM to be substituted on naphthoquinone named position of 2, 7 and 8. Unsubstituted benzoquinone was considered as a reference molecule. The calculated potentials are presented in Table 9. Results show

**Table 8.** Two-Electron Potentials of Type VIII Molecules (Units in Volt)

| Clusters | Potential | %Ch. |
|---|---|---|
| *2-(Cu)₂-Q* | 0.608 | -13.0 |
| *2-(Cu)₃-Q* | 0.460 | -34.0 |
| *2-(Cu)₄-Q* | 0.473 | -32.0 |
| *3,5,6-OH-2-(Cu)2-Q* | 0.405 | -42.0 |
| *3,5,6-OH-2-Q(Cu)3-Q* | 0.193 | -72.0 |
| *3,5,6-OH-2-Q(Cu)4-Q* | 0.302 | -57.0 |

**Table 9.** Two Electron Redox Potentials of Mono-Metal Substituted Naphtho and Anthraquinone

| | Cu | %Ch. | Ag | %Ch. | Au | %Ch. | $R^2$ |
|---|---|---|---|---|---|---|---|
| *2-M-naphtho-Q* | 0.314 | -55.0 | 0.330 | -53.0 | 0.415 | -41.0 | 0.87 |
| *7-M-naphtho-Q* | 0.379 | -46.0 | 0.382 | -45.0 | 0.409 | -41.0 | 0.82 |
| *8-M-naphtho-Q* | 0.302 | -57.0 | 0.311 | -55.0 | 0.362 | -48.0 | 0.86 |
| *Anthraquinone2-carboxylic acid* | -0.589 | -23.0 | -0.574 | -20.0 | -0.528 | -10.0 | 0.92 |

that substituting these three metals on all positions of the naphthoquinone ring causes decreasing in redox potential values. The trend is the same as what obtained for benzoquinones.

**Two-electron redox potential of mono-metal substituted anthraquinone 2-carboxylic acid.** Anthraquinone 2-carboxylic acid is a compound with a known experimental redox potential (-0.480 volts) which has been used in biosensors [33]. The effects of three mentioned TM substitutions on two-electron redox potential of anthraquinone derivative (reference molecule) have been investigated. The TMs were substituted on position of 5 of this compound. The calculated redox potentials are -0.589, -0.574 and -0.528 volts for Cu, Ag and Au substituted compounds compared to redox potential of reference molecule (-0.480 volts). The results show the trend $E_{Cu} < E_{Ag} < E_{Au}$, in agreement with the trend obtained for the redox potentials of TM-substituted benzo and naphthoquinone.

# GENERAL DISCUSSION

## Part A

**Correlation between experimental Electromotive Force (EMF), Electron Affinity (EA) and Electronegativity (EN) of metals and the two-electron redox potentials of substituted quinones.** This correlation has only checked for those types containing only TMs as substituent, named types I, IV, V, VII and also for naphthoquinone. The experimental EMF [46], EA [47] and EN [46] of TMs are reported in Table 10. We have plotted [48] the diagram of two-electron redox potential of Cu, Ag and Au substituted quinones (y-axis) *vs*. the EMF of Cu, Ag and Au, respectively (x-axis). Similar diagrams were also plotted for EAs and ENs. Linear correlations were obtained for all these diagrams. The $R^2$ values for the linear correlation of type I compounds are 0.994, 0.996 and 0.978 for EMF, EA and EN, respectively. For compounds with more than one TM substitution, sum of the EMFs (or ENs

**Table 10.** The $R^2$ Values for Linear Correlation between Two-Electron Redox Potential and EMF, EA and EN of TMs

| *Experimental* | *Cu* | *Ag* | *Au* | *Average* |
|---|---|---|---|---|
| *EMF (V)* | 0.521 | 0.799 | 1.691 | - |
| *Electron affinity (ev)* | 1.226 | 1.303 | 2.309 | - |
| *Electronegativity (ev)* | 1.900 | 1.930 | 2.540 | - |
| *Type IV* | *2,3-di-M-Q* | *2,5-di-M-Q* | *2,6-di-M-Q* | *Average* |
| $R^2$ *(EMF)* | 0.919 | 0.981 | 0.962 | 0.954 |
| $R^2$ *(Electron affinity)* | 0.986 | 0.999 | 0.999 | 0.994 |
| $R^2$ *(Electronegativity)* | 0.999 | 0.985 | 0.996 | 0.993 |
| *Type V* | *2,3-di-M,M'-Q* | *2,5-di- M,M'-Q* | *2,6-di- M,M'-Q* | *Average* |
| $R^2$ *(EMF)* | 0.943 | 0.985 | 0.955 | 0.961 |
| $R^2$ *(Electron affinity)* | 0.996 | 0.997 | 0.998 | 0.997 |
| $R^2$ *(Electronegativity)* | 0.997 | 0.995 | 0.999 | 0.997 |
| *naphthoquinone* | *2-M-naphtho-Q* | *7-M-naphtho-Q* | *8-M-naphtho-Q* | *Average* |
| $R^2$ *(EMF)* | 0.994 | 0.980 | 0.991 | 0.988 |
| $R^2$ *(Electron affinity)* | 0.990 | 0.999 | 0.993 | 0.994 |
| $R^2$ *(Electronegativity)* | 0.965 | 0.985 | 0.971 | 0.973 |

or EAs) of metals was considered. For example, for the redox potential/EMF correlation of 2,3,5-Cu-Q, three times of the experimental EMF of copper was taken as EMF value since three copper atoms are substituted on the ring. The similar pattern was also used for EAs and ENs. According to above explanation, the $R^2$ values obtained for all correlations of type VII compounds are 0.988 (it is equal for EMF, EA and EN properties). The results of correlations for types IV, V and also for naphthoquinone are reported in Table 10. The $R^2$ values reported in this Table show the linear correlation between the redox potential values of metal-substituted quinone and the experimental EN (or EA or EMF) of the metal substituent. As an example, the diagram of the linear correlation between redox potential values of Type I and experimental EMF of TMs was sketched in Fig. 3. This Figure shows that the TM substituent with the lowest EMF value causes the most decreasing in redox potential of quinone.

## Part B

Based on four reasons, B3LYP was chosen for calculations: a- Since there are too many *xc*-functionals for DFT in literature, it would not be possible to examine all of them to see whether it is good for every species in this article or not. b- The characteristic of each species is quite

different from that of any other, so it is not quite possible to find a suitable xc-functional for each species. c- The errors in our results with respect to experimental value are not too bad (see Table 1). d- Our aim was to investigate the decreasing or increasing trend of redox potential values for different substituents. On the other hand, difference of energies has been applied to calculate the redox potential than the total energies. It is worth mentioning that the percentage of deviations, values in Tables 2-10, is reported with respect to the redox potential of quinone (reference molecule).

We do not consider TMs as EDGs, but in terms of electronegativity (EN) and electron affinity (EA) concepts we concluded that the least EN and EA values are related to TM substituent, Cu, which causes the most decreasing effect in redox potential of quinone. They do reduce the redox potential in the same direction as EDG in organic chemistry, for instance OH.

The effect of substitution on the redox potential of quinone is related to the type, site and the number of substitutions. The trend of percentage of changing *(%Ch)* of redox potential from the site point of view for mono-substituted functional group in Table 2, for OH and $CH_3$ group, is 5>6>3. The corresponding values for -Cl, is 6>3>5 for Cu and Ag substitutions and 5>3>6 for Au substitution.
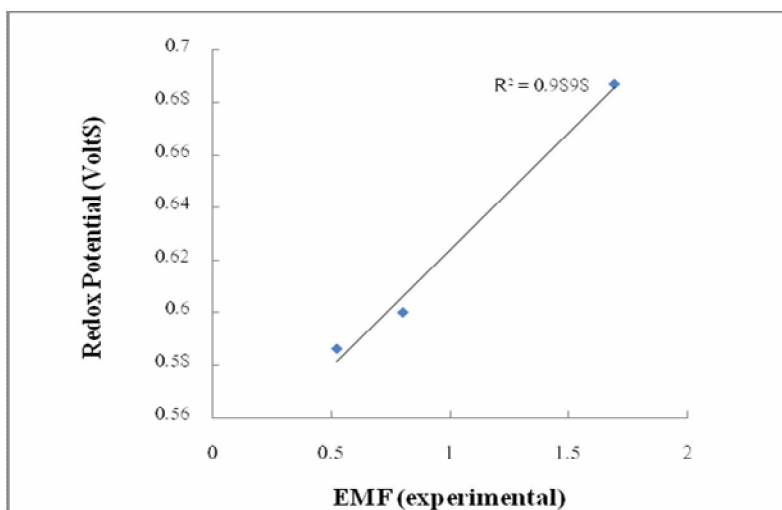


**Fig. 3.** Linear correlation between the two-electron redox potential of type I molecules and experimental EMF of TMs.

For -NO$_2$ the trend is 5>3>6 for Cu and Ag and 5>6>3 for Au substitution. The trend of percentage of changing *(%Ch)* of redox potential from the site point of view for di-substituted functional group in Table 3, for NO$_2$ group, is 3,5,6>3,5>5,6>3,6, and for OH is, 3,6>3,5,6>3,5>5,6 for Cu and Ag substitution and 3,5,6>5,6>3,6>3,5 for Au substitution. The trend of percentage of changing *(%Ch)* of redox potential from the site point of view for di-substituted TM in Table 4, does not show really a significant difference and for Cu and Ag and Au substitution the minimum is observed for the sites 2,6. The maximum percentage of changing (*%Ch*) of redox potential for di-metal substituted compounds in Table 5, relates to combination of Cu and Ag in which their trend is 2,6>2,5>2,3.

## CONCLUSIONS

In the present research, decreasing effect of coinage TM (Cu, Ag, Au) substitutions on two-electron redox potential of benzo-, naphtho- and anthraquinones, which are applicable and suitable candidates for using as mediators in biosensors, was shown. Our results showed that EDG substituents result in a decrease of the redox potential of quinones (in contrast to strong EWGs) and therefore, coinage TM substitutions have the same effect as EDGs. By applying TM substituents, the maximum decrease of 42% in redox potential of benzoquinone was obtained. To obtain a more wide range of potential, the mentioned TMs were applied together with other non-metal functional groups as substitutions on quinones. The decrease of 66% was obtained by applying hydroxyl and copper substituents simultaneously. The effects of copper clusters on the redox potential of benzoquinone have been also investigated. The results showed that the redox potential of benzoquinone is decreased to maximum level, 72%, by applying tri-copper cluster and hydroxyl groups.

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