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Structural Relationships and Theoretical Study of Free Energies of Electron Transfer and Photo Electron Transfer Properties of Enzyme Derivatives with Fullerenes in Nanostructure of [R].C_n (R= Laccase *Coriolus hirsutus* (L*Ch*), Tyrosinase, Laccase *Rhus-vernicifera* (L*Rv*), Cytochrome-c peroxidase, Ascorbate oxidase and Cytochrome-c oxidase) Supramolecular Complexes

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ABSTRACT

The reduction of electron transfer distance leads to an electronic communication between the electrode and redox proteins. This study elaborates upon the relationship between the number of carbon atoms in the fullerenes and the four free energies of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) between the fullerenes C_n (n=60, 70, 76, 82 and 86) and the six most well –known enzyme molecular systems: Laccase *Coriolus hirsutus* (L*Ch*), Tyrosinase, Laccase *Rhus vernicifera* (L*Rv*), Cytochrome c peroxidase, Ascorbate oxidase and Cytochrome c oxidase, numbered 1-6, respectively, in the text. The free energies of electron transfer are based on the four reduction potentials ($^{Red.}E_1$ to $^{Red.}E_4$) of the fullerenes, as assessed by applying the electron transfer (ET) equation to create [Laccase *Coriolus hirsutus* (L*Ch*)].C_n, A-1 to A-5; [Tyrosinase].C_n, B-1 to B-5; [Laccase *Rhus vernicifera* (L*Rv*)].C_n, C-1 to C-5; [Cytochrome c peroxidase].C_n, D-1 to D-5; [Ascorbate oxidase].C_n, E-1 to E-5; and [Cytochrome c oxidase].C_n, F-1 to F-5. The results were extended to calculate the four free energies of the electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) of other supramolecular complexes of each enzyme 1-6, as a class of electron transfer species, with fullerenes C_{60} to C_{120} ([(R)].C_n supramolecular complexes. The study also calculated the first to fourth activation free energies of electron transfer, $\Delta G^{\#}_{et(n)}$ (n=1-4), respectively, as assessed using the *Marcus* theory and the above equations on the basis of the first to fourth reduction potentials ($^{Red.}E_1$ to $^{Red.}E_4$) of fullerenes C_n (n=60, 70, 76, 82 and 86) for the predicted supramolecular complexes [Laccase *Coriolus hirsutus* (L*Ch*)].C_n, A-1 to A-5; [Tyrosinase].C_n, B-1 to B-5; [Laccase *Rhus vernicifera* (L*Rv*)].C_n, C-1 to C-5; [Cytochrome c peroxidase].C_n, D-1 to D-5; [Ascorbate oxidase].C_n, E-1 to E-5; and [Cytochrome c oxidase].C_n, F-1 to F-5. Furthermore, this study determined the wavelengths ($\lambda_{(n)}$; n=1-4; in *nm*) of the electromagnetic photons for the electron transfer processes and in the nanostructure supramolecular complexes.
Keywords: Fullerenes; Hemoglobin A; Rehm-Weller equation; Free energy of electron transfer; Electron transfer properties; Activated free energies of electron transfer

Keywords: Electron transfer; Photo electron transfer; Enzyme; Fullerenes

INTRODUCTION

Hemoglobin The reduction of electron transfer distance leads to an electronic communication between the electrode and redox proteins. Adsorbed proteins are

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available to amplify enzyme actions, and thus, bioelectronic redox chains can be created. However, covalent fixation of redox proteins in an oriented arrangement on alkane thiols self-assembled on gold electrodes is only possible using small signal molecules, a restriction that results from the associated reduction of mobility. A likely solution to this problem involves the use of designed redox proteins and enzymes with engineered electron pathways [1,2].

Laccase was first studied by Gabriel Bertrand in 1894.[1,2a,3] Laccases are copper-containing oxidase enzymes that are found in many plants, fungi, and microorganisms. Laccases act on phenols and similar molecules, performing one-electron oxidations, which remain poorly defined. It has been proposed that laccases play a role in the formation of lignin by promoting the oxidative coupling of lignols, a family of naturally occurring phenols.[1,2a,3] Laccases can be polymeric, and the enzymatically active form can be a dimer or trimer. Other laccases, such as those produced by the fungus *Pleurotus ostreatus*, have roles in the degradation of lignin and can therefore be included in the broad category of ligninases. Laccases can be detected by spectrophotometry using the substrates ABTS, syringaldazine, 2,6-dimethoxyphenol, and dimethyl-p-phenylenediamine. Laccase activity can also be monitored with an oxygen sensor, as the oxidation of the substrate is paired with the reduction of oxygen to water. Laccases have been studied for use as cathodes in enzymatic biofuel cells. They can be paired with electron mediators to facilitate electron transfer to a solid electrode wire.[2a,3] In addition, laccases are among the few oxidoreductases marketed as commercial/industrial catalysts and have been used for textile dyeing/textile finishing, wine cork making, teeth whitening, and many other industrial, environmental, diagnostic, and synthetic applications [2a,3]. Laccases have also been used in bioremediation. In this application, protein ligand docking can be used to predict the putative pollutants that can be degraded by laccase. [2a, 3]

Tyrosinase (monophenol monooxygenase) is an enzyme that catalyses the oxidation of phenols (such as tyrosine) and is widespread in plant and animal tissues. Tyrosinase is a copper-containing enzyme that catalyzes the production of melanin and other pigments from tyrosine by oxidation, as in the blackening of a peeled or sliced potato exposed to air. Tyrosinase oxidizes phenols such as tyrosine and dopamine using dioxygen (O_2). [1,2b,4] In the presence of a catechol, benzoquinone is formed (see reaction below). The hydrogens removed from the catechol combine with oxygen to form water. Tyrosinases have been isolated from a wide variety of plant, animal and fungal species. Tyrosinases from different species are diverse in terms of their structural properties, tissue distribution and cellular location.[1,2b,4] It has been suggested that there is no common tyrosinase protein structure occurring across all species.[2b,c, 4] The enzymes found in plant, animal and fungal tissues frequently differ with respect to their primary structure, size, glycosylation pattern and activation characteristics. However, every tyrosinase has a binuclear type 3 copper center within its active site. In this center, two copper atoms are each coordinated with three histidines. Human tyrosinase is a single membrane spanning transmembrane protein.[2b,c,4] In humans, tyrosinase is sorted into melanosomes, and the catalytically active domain of the protein resides within melanosomes. Only a small

enzymatically non-essential part of the protein extends into the cytoplasm of the melanocyte. [2b,c, 4]

Cytochrome c peroxidase (CCP) was first isolated from baker's yeast by R. A. Altschul, Abrams, and Hogness in 1940 [2d, 5], though not to purity. Takashi Yonetani prepared the first purified yeast CCP in the early 1960s using ion exchange chromatography. Thomas Poulos and coworkers determined the X-ray structure of the protein in the late 1970s. [2d,5] Cytochrome *c* peroxidase (CCP) is a water-soluble, heme-containing enzyme of the peroxidase family that oxidizes cytochrome c by reducing hydrogen peroxide to water. Though cytochrome *c* peroxidase can react with hydroperoxides other than hydrogen peroxide, the reaction rate is greatest with hydrogen peroxide.[2d,5,6] The yeast enzyme is a monomer with a molecular weight of 34,000 that contains 293 amino acids and a single noncovalently bound heme *b*. Unlike most proteins, this enzyme crystallizes when dialyzed against distilled water. Moreover, the enzyme can be purified via crystallization, making cycles of crystallization an effective final purification step. In its resting state, CCP contains a ferric heme, and after the addition of two oxidizing equivalents from a hydroperoxide molecule, it becomes an enzyme of formal oxidation state V. [2d, 5,6] However, both low-temperature magnetic susceptibility measurements and Mössbauer spectroscopy show that the iron in CCP-compound I is a +4 ferryl iron, meaning that it is not in oxidation state V. The other salient feature of CCP-compound I is a long-lived free radical, whose signal suggests a species other than the porphyrin free radicals of other peroxidase compound I species. Early on, this was determined to be an organic free radical, and the bulk of evidence now links it to the side chain of the tryptophan residue (Trp-191). [2d, 5,6]

The enzyme cytochrome c oxidase, or Complex IV, is a large transmembrane protein complex found in bacteria and mitochondria. It is the last enzyme in the respiratory electron transport chain of mitochondria (or bacteria).[2e, 6] It receives an electron from each of four cytochrome c molecules and transfers them to one oxygen molecule, converting molecular oxygen to two molecules of water. In the process, it binds four protons from the inner aqueous phase to make water and translocates four protons across the membrane, helping to establish a transmembrane electrochemical potential difference that is subsequently used by ATP synthase to synthesize ATP. [2e, 6]
In mammals, the cytochrome c oxidase complex is a large integral membrane protein composed of several metal prosthetic sites and 13 protein subunits.[2f,7-9] Ten subunits are nuclear in origin, and three are synthesized in the mitochondria. The complex contains two hemes, a cytochrome a and a cytochrome a_3, and two copper centers, Cu_A and Cu_B.[2f,7] The cytochrome a_3 and Cu_B form a binuclear center that is the site of oxygen reduction. Cytochrome c, which is reduced by the preceding component of the respiratory chain (cytochrome bc1 complex, complex III), docks nearby and passes an electron to the Cu_A binuclear center, oxidizing back to Fe^{3+}-containing cytochrome c. The reduced Cu_A binuclear center now passes an electron to cytochrome a, which in turn passes an electron to the cytochrome a_3-Cu_B binuclear center. [2f,7,8] The two metal ions in this binuclear center are 4.5 Å apart and coordinate a hydroxide ion in the fully oxidized state. Two electrons are passed from two cytochrome c's, through the Cu_A and cytochrome a sites, to the cytochrome

a_3-Cu_B binuclear center, reducing the metals to their Fe^{+2} forms and Cu^{+1}. [2f,7-9] The hydroxide ligand is protonated and lost as water, creating a void between the metals that is filled by O_2. The oxygen is rapidly reduced, with two electrons coming from the Fe^{+2} cytochrome a_3, which is converted to the ferryl oxo form (Fe^{+4}=O).[2f,7-9] The oxygen atom close to Cu_B picks up one electron from Cu^{+1} and a second electron and a proton from the hydroxyl of Tyr(244), which becomes a tyrosyl radical; thus, the second oxygen is converted to a hydroxide ion by picking up two electrons and a proton.[2f,7-9] A third electron, arising from another cytochrome c, is passed through the first two electron carriers to the cytochrome a_3-Cu_B binuclear center, and this electron and two protons convert the tyrosyl radical back to Tyr and the hydroxide bound to Cu_B^{+2} to a water molecule. The fourth electron, from another cytochrome c, flows through Cu_A and cytochrome a to the cytochrome a_3-Cu_B binuclear center, reducing the Fe^{+4}=O to Fe^{+3}, and the oxygen atom simultaneously picks up a proton, converting this oxygen back to a hydroxide ion coordinated within the cytochrome a_3- Cu_B center (as it was at the start of this cycle). The net process utilizes four reduced cytochrome c's and 4 protons to reduce O_2 to two water molecules. [2f,7-9]

L-ascorbate oxidase is a catalytic enzyme that participates in ascorbate metabolism. Its substrates are L- ascorbate and O_2, its products are dehydroascorbate and H_2O, and it employs one cofactor, copper. [2,6,8,9] This enzyme belongs to the family of oxidoreductases that acts on diphenols and related substances by donating electrons using oxygen as the acceptor.[2,8] The systematic name of this enzyme class is L-ascorbate: oxygen oxidoreductase. Other common names include ascorbase, ascorbic acid oxidase, ascorbate oxidase, ascorbic oxidase, ascorbate dehydrogenase, L-ascorbic acid oxidase, AAO, L-ascorbate: O2 oxidoreductase, and AA oxidase. This enzyme participates in ascorbate metabolism. It employs one cofactor, copper. [2,6,8,9]

Since the discovery of fullerenes (C_n), one of the main classes of carbon compounds, the unusual structures and physiochemical properties of these molecules have been discovered. Potential applications and physicochemical properties of the fullerenes were introduced. Up to now, various empty carbon fullerenes with different numbers "n" such as C_{60}, C_{70}, C_{76}, C_{82} and C_{86}, have been obtained. The chemical, physical and mechanical properties of empty and endohedral fullerenes have been the subject of many studies.[10–24] The compressive mechanical properties of fullerene molecules C_n (n = 20, 60, 80, and 180) were investigated and discussed in detail using a quantum molecular dynamics (QMD) technique by Shen. [11,24] The unique stability of molecular allotropes such as C_{60} and C_{70}, was demonstrated in 1985. [10,11] This event led to the discovery of a whole new set of carbon-based substances, known as fullerenes.

After the discovery of C_{60} peapods by Luzzi *et al.* [12-17], the aligned structure of encapsulated molecules, due to the molecule-molecule and/or molecule-SWNT interactions, has been studied as a new type of hybrid material [14,15]. Zhang *et al.* [12] reported evidence for the latter interaction measuring the thermal stability of C_{60} peapods. [12-16]

The electrochemical properties of the C_{60} fullerene have been studied since the early 1990s, when these materials first became available in macroscopic quantities (for a review, see [14]). [13,14] In 1990, Haufler *et al.* [15] showed that CH_2Cl_2

electrochemically reduces C_{60} to C_{60}^{1-} and C_{60}^{2-}. In 1992, Echegoyen *et al.* [16] cathodically reduced C_{60} in six reversible one-electron steps for -0.97V vs. Fc/Fc^{+} (Fc=ferrocene). This fact, along with the inability to perform anodic electrochemistry on fullerenes, matches the electronic structure of fullerenes: the LUMO of C_{60} can accept up to six electrons to form C_{60}^{6-}, but the position of the HOMO does not allow for hole-doping under the usual reported electrochemical conditions. In 1991, Bard *et al.* [17] first reported on the irreversible electrochemical and structural reorganization of solid fullerenes in acetonitrile. Dunsch *et al.* [18] improved upon the experimental conditions by investigating highly organized C_{60} films on HOPG, in an aqueous medium. The reduction of these films induces a morphological change; they re-structure into conductive nanoclusters of ~100 nm in diameter. [18,19]

Graph theory has been a useful tool in assessing the *QSAR* (Quantitative Structure Activity Relationship) and *QSPR* (Quantitative Structure Property Relationship). [25-36] Numerous studies in different areas have used topological indices (TI).[25-33] Any extrapolation of results from one compound to other compounds must take into account considerations based on a Quantitative Structural Analysis Relationship Study, which mostly depends on how close physical and chemical properties are of the compounds in question. It is important to use effective mathematical methods to make good correlations between several properties of chemicals. In 1993 and 1997, several complex applications of the indices were reported.[25-36] The numbers of carbon atoms at the structures of the fullerenes were utilized here.

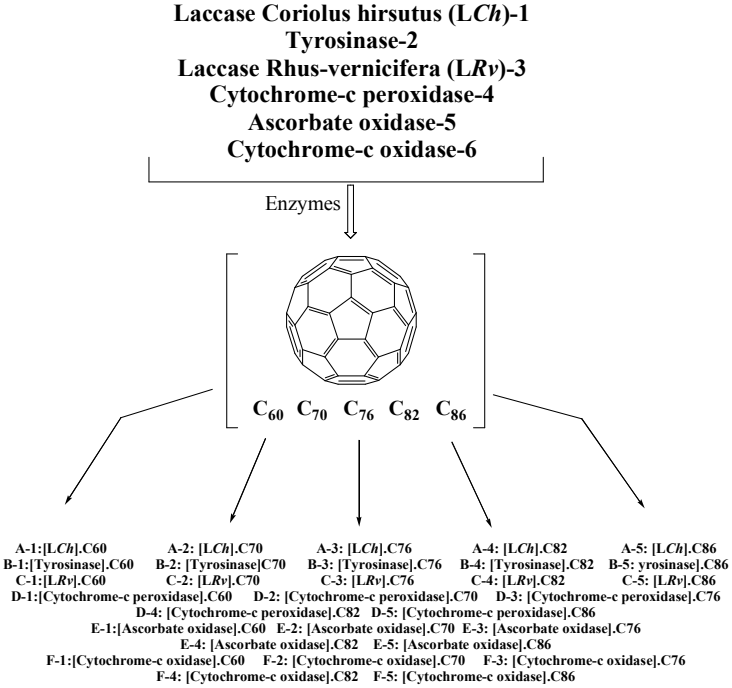

Fig. 1. The conjectured structures of Laccase *Coriolus hirsutus* (L*Ch*), Tyrosinase, Laccase *Rhus-vernicifera* (L*Rv*), Cytochrome-c peroxidase, Ascorbate oxidase and Cytochrome-c oxidase, **1-6** and fullerenes C_n (n=60, 70, 76, 82 and 86) which [Laccase *Coriolus hirsutus* (L*Ch*)].C_n, **A-1** to **A-5**, [Tyrosinase].C_n, **B-1** to **B-5**, [Laccase *Rhus-vernicifera* (L*Rv*)].C_n, **C-1** to **C-5**, [Cytochrome-c peroxidase].C_n, **D-1** to **D-5**, [Ascorbate oxidase].C_n, **E-1** to **E-5** and [Cytochrome-c oxidase].C_n, **F-1** to **F-5**.

This study elaborates upon the relationship between the number of carbon atoms and the four free energies of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) of fullerenes C_n (n=60, 70, 76, 82 and 86) with Laccase *Coriolus hirsutus* (L*Ch*), Tyrosinase, Laccase *Rhus-vernicifera* (L*Rv*), Cytochrome-c peroxidase, Ascorbate oxidase and Cytochrome-c oxidase, 1-6, on the basis of the four reduction potentials ($^{Red.}E_1$ to $^{Red.}E_4$) of the fullerenes, as assessed by applying the *Rehm-Weller* equation [37] to create [Laccase *Coriolus hirsutus* (L*Ch*)].C_n , A-1 to A-5, [Tyrosinase].C_n, B-1 to B-5, [Laccase *Rhus-vernicifera* (L*Rv*)].C_n, C-1 to C-5, [Cytochrome-c peroxidase].C_n, D-1 to D-5, [Ascorbate oxidase].C_n, E-1 to E-5 and [Cytochrome-c oxidase].C_n, F-1 to F-5. The results were extended to calculate the four free energies of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) of other supramolecular complexes of Laccase *Coriolus hirsutus* (L*Ch*), Tyrosinase, Laccase *Rhus-vernicifera* (L*Rv*), Cytochrome-c peroxidase, Ascorbate oxidase and Cytochrome-c oxidase, 1-6 as a class of electron-transfers, with fullerenes C_{60} to C_{120} ([Enzymes].C_n complexes, i.e.: [Laccase *Coriolus hirsutus* (L*Ch*)].C_n; 7-11 & 37-40, [Tyrosinase].C_n, 12-16 & 41-44, [Laccase *Rhus-vernicifera* (L*Rv*)].C_n, 17-21 & 45-48, [Cytochrome-c peroxidase].C_n, 22-26 & 49-52, [Ascorbate oxidase].C_n, 27-31 & 53-56 and [Cytochrome-c oxidase].C_n, 32-36 & 57-60, (supramlecular complexes 7-121). This study calculated the four free energies of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) of A-1 to A-9, B-1 to B-9, C-1 to C-9, D-1 to D-9, E-1 to E-9 and F-1 to F-9. See Equations 1 to 27, Tables 1 to 12 and Figures 1 and 2.
In this study has also calculated the first to fourth activate free energies of electron transfer and kinetic rate constants of the electron transfers, $\Delta G^{\#}_{et(n)}$ and k_{et} (n=1-4), respectively, as assessed using the *Marcus* theory and the equations on the basis of the first to fourth reduction potentials ($^{Red.}E_1$ to $^{Red.}E_4$) of fullerenes C_n (n=60, 70, 76, 82 and 86) for the predicted supramolecular complexes [Laccase *Coriolus hirsutus* (L*Ch*)].C_n; 7-11 & 37-40, [Tyrosinase].C_n, 12-16 & 41-44, [Laccase *Rhus-vernicifera* (L*Rv*)].C_n, 17-21 & 45-48, [Cytochrome-c peroxidase].C_n, 22-26 & 49-52, [Ascorbate oxidase].C_n, 27-31 & 53-56 and [Cytochrome-c oxidase].C_n, 32-36 & 57-60 (supramlecular complexes 7-60). See Equations 2 and 3, Tables 6 to 12 and Figure 3.

Marcus's theory builds on the traditional *Arrhenius* equation for the rates of chemical reactions in two ways. First, it provides a formula for the pre-exponential factor in the Arrhenius equation based on the electronic coupling between the initial and final state of the electron transfer reaction (i.e., the overlap of the electronic wave functions of the two states). Second, it provides a formula for the activation energy based on a parameter called the *reorganization energy* and *Gibbs* free energy. The reorganization energy is defined as the energy required to reorganize the system structure from initial to final coordinates without changing the electronic state.

It is common to describe where electrons reside as electron bands in bulk materials and electron orbitals in molecules. For the sake of expedience, the following is described in molecular terms. When a photon excites a molecule, an electron in a ground state orbital can be excited to a higher energy orbital. This excited state leaves a vacancy in a ground state orbital that can be filled by an electron donor. It produces an electron in a high energy orbital that can be donated to an electron acceptor. Photoinduced electron transfer is an electron transfer that

occurs when certain photoactive materials interact with light. Such materials include semiconductors that can be photoactivated like many solar cells, biological systems such as those used in photosynthesis, and small molecules with suitable absorptions and redox states [39,40].

GRAPHING AND MATHEMATICAL METHOD

All graphs were generated using the Microsoft Office Excel 2003 program. Using the number of carbon atoms contained within the Cn fullerenes, several valuable properties of the fullerenes were calculated. These values were used to calculate the four free energies of electron transfer (ΔGet(1) to ΔGet(4)) using the Rehm-Weller equation for [Laccase Coriolus hirsutus (LCh)].Cn, 7-11 & 37-40; [Tyrosinase].Cn, 12-16 & 41-44; [Laccase Rhus vernicifera (LRv)].Cn, 17-21 & 45-48; [Cytochrome-c peroxidase].Cn, 22-26 & 49-52; [Ascorbate oxidase].Cn, 27-31 & 53-56; and [Cytochrome-c oxidase].Cn, 32-36 & 57-60 (supramolecular complexes 7-60).

Equations 1 and 4-27 were utilized to calculate the remaining values of ΔGet(1) to ΔGet(4) for complexes not yet reported in the literature. Some of the other indices were examined, and the best results and equations for extending the physicochemical data were chosen. [31,36]

The Rehm-Weller equation estimates the free energy change between an electron donor (D) and an acceptor (A) as:

$$\Delta G^\circ = e[ED^\circ - EA^\circ] - \Delta E^* + \omega 1 \qquad (1)$$

where e is the unit electrical charge, EDo and EAo are the reduction potentials of the electron donor and acceptor, respectively, ΔE* is the energy of the singlet or triplet excited state, and ω1 is the work required to bring the donor and acceptor to within the electron transfer (ET) distance. If an electrostatic complex forms before the electron transfer, the work term in this expression is zero [37].

The Marcus theory of electron transfer implies rather weak (<0.05 eV) electronic coupling between the initial (locally excited, LE) and final (electron transfer, CT) states and presumes that the transition state is close to the crossing point of the LE and CT terms. The value of the electron transfer is controlled by the activation free energy ΔG#et, which is a function of the reorganization energy (l/4) and electron transfer driving force ΔGet:

$$\Delta G\#et = (l/4)(1+\Delta Get/l)2. \qquad (2)$$

For organic molecules, the reorganization energy was found to be in the range 0.1-0.3 eV. In this study, the minimum amount of reorganization energy was used. [38a-h]

The maximum wavelengths (λ(n), n=1-4) of the electromagnetic photon for the electron transfer process in the nanostructure supramolecular complexes were calculated utilizing Planck's formula,

$$\Delta G\#et = \Delta E = h.c/\lambda(n) \qquad (3)$$

in which the activation free energy of the electron transfer process is used.[39-41]

DISCUSSION

The design of the electrode surface is essential for achievement of fast electron transfer and bioelectrocatalysis. A crucial problem related to the orientation of immobilization of the redox proteins is addressed using electrostatic interaction between unsymmetrical charged proteins and poly ionic surfaces. The reduction of electron transfer distance leads to an electronic communication between the

electrode and redox proteins. Adsorbed proteins are available to amplify enzymatic activity, thereby creating bioelectronic redox chains. However, covalent fixation of a specifically oriented arrangement of redox proteins on gold electrodes containing self-assembled alkane thiols is only possible using small signal molecules. This restriction results from the reduction of the mobility inherent in this type of system. A likely solution to this problem involves the use of designed redox proteins and enzymes with engineered electron pathways enzymatic oxidation techniques show promise within a great variety of industrial fields including the pulp and paper, textile and food industries. Laccases have been reviewed several times in recent years due to their ability to oxidize both phenolic and nonphenolic lignin related compounds as well as highly recalcitrant environmental pollutants, an ability that makes them especially applicable to several biotechnological processes. Laccases are also used as cleaning agents for certain water purification systems, as catalysts for the manufacture of anti-cancer drugs and even as ingredients in cosmetics.[1-9]

The oxidation potentials of Laccase Coriolus hirsutus (LCh), Tyrosinase, Laccase Rhus vernicifera (LRv), Cytochrome c peroxidase, Ascorbate oxidase and Cytochrome c oxidase (referred to as 1-6, respectively), have been reported before, as follows: [1].

No.	The Enzymes	Oxidation potential (^{Ox}E, in Volt)
1	L*Ch*	+0.785
2	Tyrosinase	+0.605
3	L*Rv*	+0.434
4	Cytochrome-*c* peroxidase	+0.740
5	Ascorbate oxidase	+0.350
6	Cytochrome-c oxidase	+0.245

The four reported reduction potentials (Red.E1 to Red.E4) of fullerenes Cn are as follows: for C60 are, -1.12, -1.50, -1.95 and -2.41V, respectively. [42] The RedEn(Volt, n=1-4) for C70 are -1.09, -1.48, -1.87 and -2.30V, respectively. [42] The values of RedEn(Volt, n=1-4) for C76 are -0.94, -1.26, -1.72 and -2.13V, respectively. [45] Four values of RedEn(Volt, n=1-4) for C82 are -0.69, -1.04, -1.58 and -1.94V, respectively. [42] The RedEn(Volt, n=1-4) for C86 are -0.58, -0.85, -1.60 and -1.96V, respectively.[42]
Tables 1-12 contain a summary of the data. They show the calculated values for 7-60 of the four electron transfer free energies and the activation free energies (ΔGet(n) and ΔG#et(n)) between the enzymes 1-6 and fullerenes Cn (n = 60, 70, 76, 82 and 86) as the [Enzymes].Cn complexes. These values were calculated using the Rehm-Weller equation (Eq.-1). The selected enzymes (1-6) were used to model the structural relationship between the number of carbon atoms in the fullerenes and ΔGet(n)(n=1-4). The data of compounds [Laccase Coriolus hirsutus (LCh)].Cn, A-1 to A-5, [Tyrosinase].Cn, B-1 to B-5, [Laccase Rhus-vernicifera (LRv)].Cn, C-1 to C-5, [Cytochrome-c peroxidase].Cn, D-1 to D-5, [Ascorbate oxidase].Cn, E-1 to E-5 and [Cytochrome-c oxidase].Cn, F-1 to F-5 (complexes 7-60) are reported in the appropriate tables. Figure-1 depicts the structures of the supramolecular complexes of [Laccase Coriolus hirsutus (LCh)].Cn, [Tyrosinase].Cn, [Laccase Rhus-vernicifera (LRv)].Cn, [Cytochrome-c peroxidase].Cn, [Ascorbate oxidase].Cn and [Cytochrome-c oxidase].Cn and fullerenes Cn (n=60, 70, 76, 82 and 86).
Fig.-2 (graphs a-d) demonstrate the relationships between the number of carbon atoms of fullerenes “n” and the first, second, third and fourth free-energy of electron transfer (ΔGet(1) to ΔGet(4)) of

[Laccase Coriolus hirsutus (LCh)].Cn (n = 60, 70, 76, 82 and 86). The equations 4-7 correspond to Fig.-2 (graphs a-d). This data was regressed with a second-order polynomial. The R-squared values (R2) for these graphs are 0.9875, 0.9924, 0.9385 and 0.9477, respectively.

$$\Delta G_{et(1)} = -0.0235(n)^2+2.9197(n)-47.256 \quad (4)$$
$$\Delta G_{et(2)} = -0.028(n)^2+3.4999(n)-56.834 \quad (5)$$
$$\Delta G_{et(3)} = -0.0025(n)^2+0.009(n)+71.121 \quad (6)$$
$$\Delta G_{et(4)} = -0.0038(n)^2+0.1084(n)+80.62 \quad (7)$$

By using Equations 4-7, it is possible to calculate the values of $\Delta G_{et(1)}$ to $\Delta G_{et(4)}$ of [Laccase *Coriolus hirsutus* (L*Ch*)].C_n. Table 1 contains the calculated values of the free-energies of electron transfer ($\Delta G_{et(n)}$, n=1-4, in kcal mol^{-1}) between the selected Laccase *Coriolus hirsutus* (L*Ch*) 1 and C_n (as [Laccase *Coriolus hirsutus* (L*Ch*)].C_n compounds A-1 to A-5) 7-11 supramolecular complexes. The $\Delta G_{et(n)}$ (n=1-4) for [[Laccase *Coriolus hirsutus* (L*Ch*)].C_n (C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}, C_{84} and C_{120}) are predicted by using Eq. 4-7 and the *Rehm-Weller* equation (see Table-1).

Equations 8-11 demonstrate the relationships between the number "n" of carbon atoms in the fullerenes and the first, second, third and fourth free-energy of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) of [Tyrosinase].C_n (n = 60, 70, 76, 82 and 86). These data were regressed with a second-order polynomial. The R-squared values (R^2) for these graphs are: 0.9875, 0.9924, 0.9385 and 0.9477, respectively.

$$\Delta G_{et(1)} = -0.0235(n)^2+2.9197(n)-51.407 \quad (8)$$
$$\Delta G_{et(2)} = -0.028(n)^2+3.4999(n)-60.985 \quad (9)$$
$$\Delta G_{et(3)} = -0.0025(n)^2+0.009(n)+66.97 \quad (10)$$
$$\Delta G_{et(4)} = -0.0038(n)^2+0.108(n)+76.482 \quad (11)$$

By using Equations 1 and 8-11, it is possible to calculate the values of $\Delta G_{et(1)}$ to $\Delta G_{et(4)}$ of [Tyrosinase].C_n. Table-2 contains the thirty-six calculated values of the free energies of electron transfer ($\Delta G_{et(n)}$, n=1-4, in kcal mol^{-1}) between the selected Tyrosinase 2 and the C_n (as [Tyrosinase].C_n compounds B-1 to B-5) 12-16 supramolecular complexes. The $\Delta G_{et(n)}$ (n=1-4) for [Tyrosinase].C_n (C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}, C_{84} and C_{120}) are predicted by using equations 8-11 and the *Rehm-Weller* equation (see Table-2).

The results of *Rehm-Weller* equation shows the free-energies of electron transfer ($\Delta G_{et(n)}$, n=1-4, in kcal mol^{-1}) between Laccase *Rhus-vernicifera* (L*Rv*) 3 and C_n. Equations 12 to 15 show the relationships between the number of carbon atoms of fullerenes "n" and the first, second, third and fourth free-energy of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) of [Laccase *Rhus-vernicifera* (L*Rv*)].C_n (n = 60, 70, 76, 82 and 86). These data were regressed with a second-order polynomial. The R-squared values (R^2) for these graphs are: 0.9875, 0.9924, 0.9385 and 0.9477, respectively.

$$\Delta G_{et(1)} = -0.0235(n)^2+2.9197(n)-55.35 \quad (12)$$
$$\Delta G_{et(2)} = -0.028(n)^2+3.4999(n)-64.928 \quad (13)$$
$$\Delta G_{et(3)} = -0.0025(n)^2+0.009(n)+63.026 \quad (14)$$
$$\Delta G_{et(4)} = -0.0038(n)^2+0.108(n)+72.539 \quad (15)$$

By using Equations 12-15, it is possible to calculate the values of $\Delta G_{et(1)}$ to $\Delta G_{et(4)}$ of [Laccase *Rhus-vernicifera* (L*Rv*)].C_n. Table 3 contains the seventy-six calculated values of the free-energies of electron transfer ($\Delta G_{et(n)}$, n=1-4, in kcal mol^{-1}) between the selected Laccase *Rhus-vernicifera* (L*Rv*) 3 and C_n (as [Laccase *Rhus-vernicifera* (L*Rv*)].C_n C-1 to C-5) 17-21 supramolecular complexes. The $\Delta G_{et(n)}$ (n=1-4) for [Laccase *Rhus-vernicifera* (L*Rv*)].C_n (C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}, C_{84} and C_{120}) are predicted by using Eq. 12-15 and the Rehm-Weller equation (see Table 3).

Equations 16-19 demonstrate the relationships between the number "n" of carbon atoms in the fullerenes and the first, second, third and fourth free-energy of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) of [Cytochrome-c peroxidase].C_n (n = 60, 70, 76, 82 and 86). These data were regressed with a second-order polynomial. The R-squared values (R^2) for these graphs are 0.9874, 0.9923, 0.9385 and 0.9477, respectively.

$$\Delta G_{et(1)}=-0.0236(n)^2+2.9399(n)-49.012 \quad (16)$$
$$\Delta G_{et(2)}=-0.0281(n)^2+3.5011(n)-57.912 \quad (17)$$
$$\Delta G_{et(3)}=-0.0025(n)^2+0.009(n)+70.083 \quad (18)$$
$$G_{et(4)}=-0.0038(n)^2+0.108(n)+79.595 \quad (19)$$

By using Equations 1 and 16-19, it is possible to calculate the values of $\Delta G_{et(1)}$ to $\Delta G_{et(4)}$ of [Cytochrome-c peroxidase].C_n. Table-4 contains the seventy-six calculated values of the free energies of electron transfer ($\Delta G_{et(n)}$, n=1-4, in kcal mol^{-1}) between the selected Cytochrome-c peroxidase 4 and the C_n (as [Cytochrome-c peroxidase].C_n, compounds D-1 to D-5) 22-26 supramolecular complexes. The $\Delta G_{et(n)}$ (n=1-4) for [Cytochrome-c peroxidase].C_n (C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}, C_{84} and C_{120}) are predicted by using equations 16-19 and the Rehm-Weller equation (see Table-4).

Equations 20-23 demonstrate the relationships between the number "n" of carbon atoms in the fullerenes and the first, second, third and fourth free-energy of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) of [Ascorbate oxidase].C_n (n = 60, 70, 76, 82 and 86). These data were regressed with a second-order polynomial. The R-squared values (R^2) for these graphs are: 0.9875, 0.9924, 0.9385 and 0.9477, respectively.

$$\Delta G_{et(1)}= -0.0235(n)^2+2.9197(n)-57.287 \quad (20)$$
$$\Delta G_{et(2)}= -0.028(n)^2+3.4999(n)-66.865 \quad (21)$$
$$\Delta G_{et(3)}= -0.0025(n)^2+0.009(n)+61.089 \quad (22)$$
$$\Delta G_{et(4)}= -0.0038(n)^2+0.108(n)+70.602 \quad (23)$$

By using Equations 1 and 20-23, it is possible to calculate the values of $\Delta G_{et(1)}$ to $\Delta G_{et(4)}$ of [Ascorbate oxidase].C_n. Table-5 contains the seventy-six calculated values of the free energies of electron transfer ($\Delta G_{et(n)}$, n=1-4, in kcal mol^{-1}) between the selected Ascorbate oxidase 5 with fullerenes C_n (as [Ascorbate oxidase].C_n compounds E-1 to E-5) 27-31 supramolecular complexes. The $\Delta G_{et(n)}$ (n=1-4) for [Ascorbate oxidase].C_n (C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}, C_{84} and C_{120}) are predicted by using equations 20-23 and the *Rehm-Weller* equation (see Table-5).

The results of *Rehm-Weller* equation shows the free-energies of electron transfer ($\Delta G_{et(n)}$, n=1-4, in kcal mol^{-1}) between Cytochrome-c oxidase 6 and C_n. Equations 24 to 27 show the relationships between the number of carbon atoms of fullerenes "n" and the first, second, third and fourth free-energy of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) of [Cytochrome-c oxidase].C_n (n = 60, 70, 76, 82 and 86). These data were regressed with a second-order polynomial. The R-squared values (R^2) for these graphs are: 0.9875, 0.9924, 0.9385 and 0.9477, respectively.

$$\Delta G_{et(1)}= -0.0235(n)^2+2.9207(n)-59.742 \quad 24)$$
$$\Delta G_{et(2)}=-0.028(n)^2+3.4999(n)-69.286 \quad (25)$$
$$\Delta G_{et(3)}= -0.0025(n)^2+0.009(n)+58.668 \quad (26)$$
$$\Delta G_{et(4)}= -0.0038(n)^2+0.108(n)+68.181 \quad (27)$$

By using Equations 24-27, it is possible to calculate the values of $\Delta G_{et(1)}$ to $\Delta G_{et(4)}$ of [Cytochrome-c oxidase].C_n. Table 6 contains the thirty-six calculated values of the free-energies of electron transfer ($\Delta G_{et(n)}$, n=1-4, in kcal mol^{-1}) between the selected Cytochrome-c oxidase 6 and C_n (as [Cytochrome-c oxidase].C_n F-1 to F-5) 32-36 supramolecular complexes. The $\Delta G_{et(n)}$ (n=1-4) for [Cytochrome-c

oxidase].C_n (C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}, C_{84} and C_{120}) are predicted by using Eq. 24-27 and the *Rehm-Weller* equation (see Table 6).

By utilizing these results (Eq. 4-27) and the Rehm-Weller equation, the electron transfer energies of $\Delta G_{et(n)}$ (n=1-4) of the complexes between selected class of electron-transfer enzymes 1-6 with fullerenes (C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}, C_{84} and C_{120}) were approximated (Tables 1 to 6). The calculated values of the free electron transfer energies of $\Delta G_{et(n)}$ (n=1-4) for selected [Enzymes 1-6].C_n (n = 60, 70, 76, 82 and 86, compounds 7 to 60) in the *Rehm-Weller* equation and Eq. 4-27, are compared in Tables 1-6. There was good agreement between the calculated and the predicted values. In lieu of increasing the number of carbons atoms in the fullerene structure, the values of $\Delta G_{et(n)}$ (n=1-4) were decreased. It seems that electron transfer increased as the electron population in the C_n structures. See Tables 1-6. It seems that these results are related to the HOMO and LUMO gap of the fullerenes. The Tables also shows that some of the free electron transfer energies $\Delta G_{et(n)}$ (n=1-4) values [Laccase *Coriolus hirsutus* (L*Ch*)].C_n, [Tyrosinase].C_n, [Laccase *Rhus-vernicifera* (L*Rv*)].C_n, [Cytochrome-c peroxidase].C_n, [Ascorbate oxidase].C_n and [Cytochrome-c oxidase].C_n are negative.

Marcus theory is currently the dominant theory of electron transfer in chemistry. Marcus theory is widely accepted because it makes surprising predictions about electron transfer rates that have been supported experimentally over the last several decades. The most significant prediction is that the rate of electron transfer will increase as the electron transfer reaction becomes more exergonic, but only to a point. [38a-h]

Electron transfer (ET) is one of the most important chemical processes in nature, playing a central role in many biological, physical and chemical (both organic and inorganic) systems. Solid-state electronics depends on controlling ET in semiconductors, and the new area of molecular electronics depends critically on understanding and controlling the transfer of electrons between molecules and nanostructures. In addition, electron transfer is a very simple kind of chemical reaction that, when understood, can give insight into other aspects of biochemistry and chemistry, in general. [38a-h]

The free energy of electron transfer ΔG_{et} is the difference in energy between the reactants on the left and the products on the right, and $\Delta G_{et}^{\#}$ is the activation energy. The reorganization energy is the energy it would take to force the reactants to have the same nuclear configuration as the products without permitting electron transfer. If entropy changes are ignored, the free energy becomes energy or potential energy. [38a-h]

The end result of ET reactions is that an electron is delivered to an orbital that is higher in energy than the one in which it previously resided. When dealing with semiconductors, this is often described as a charge-separated electron-hole pair. In the absence of a proper electron donor or acceptor, it is possible for such molecules to exhibit ordinary fluorescence emission. Electron transfer is one form of photoquenching. In many photo-productive systems, this charge separation is kinetically isolated by the delivery of the electron to a lower energy conductor attached to the p/n junction or into a electron transport chain. In this case, some of the energy can be captured to do work. If the electron is not kinetically isolated, thermodynamics will preside, and the

products will react with each other to regenerate the ground state starting material. This process is called recombination, and the photon's energy is released as heat. The reverse process of photoinduced electron transfer is displayed by light emitting diodes (LED) and chemiluminescence, which demonstrate how potential gradients are used to create excited states that decay by emitting by light.

Tables 7-12 show the calculated values of the first to forth free activation energies of electron transfer and the electromagnetic photon wavelengths corresponding to the electron transfers $\Delta G^{\#}_{et(n)}$ ($\Delta G_{et(1)}{}^{\#}$ to $\Delta G_{et(4)}{}^{\#}$) and $\lambda_{(n)}$ (n=1-4, in *nm*) obtained with equations 2 and 3. Using equations 2 and 3, it is possible to calculate the first to fourth activation free energies of electron transfer and the wavelengths of the electromagnetic photons for the electron transfers $\Delta G^{\#}_{et(n)}$ and $\lambda_{(n)}$ (n=1-4, in *nm*), respectively, for 7-60 in accordance with *Marcus* theory. Figure 3 shows the surfaces of the free energies of electron transfer, $\Delta G_{et(n)}$ and $\Delta G_{et(n)}{}^{\#}$ (n=1-4), between Laccase *Coriolus hirsutus* (L*Ch*), Tyrosinase, Laccase *Rhus vernicifera* (L*Rv*), Cytochrome c peroxidase, Ascorbate oxidase and Cytochrome c oxidase (1-6, respectively) and fullerenes C_n (n=60, 70, 76, 82 and 86), which create [Laccase *Coriolus hirsutus* (L*Ch*)].C_n, A-1 to A-9; [Tyrosinase].C_n, B-1 to B-9; [Laccase *Rhus vernicifera* (L*Rv*)].C_n, C-1 to C-9; [Cytochrome c peroxidase].C_n, D-1 to D-9; [Ascorbate oxidase].C_n, E-1 to E-9; and [Cytochrome c oxidase].C_n, F-1 to F-9, also referred to as 7-60. The values of the first to fourth activated free energies of electron transfer, $\Delta G^{\#}_{et(n)}$ (n=1-4) for 7-60, increase as $\Delta G_{et(n)}$ in each of the complexes.

Using equation 1 (the *Rehm-Weller* equation), equations 2 and 3 (from *Marcus* theory) and Equations 4-27, the values of $\Delta G_{et(n)}$ (n=1-4) and $\Delta G^{\#}_{et(n)}$ (n=1-4) were calculated for 7-60. There is an obvious relationship between the number of carbon atoms (n) and the values of the free energies of electron transfer $\Delta G_{et(n)}$ (n=1-4) and $\Delta G^{\#}_{et(n)}$ (n=1-4) in [Laccase *Coriolus hirsutus* (L*Ch*)].C_n, 7-11 & 37-40; [Tyrosinase].C_n, 12-16 & 41-44; [Laccase *Rhus vernicifera* (L*Rv*)].C_n, 17-21 & 45-48; [Cytochrome c peroxidase].C_n, 22-26 & 49-52; [Ascorbate oxidase].C_n, 27-31 & 53-56; and [Cytochrome c oxidase].C_n, 32-36 & 57-60 (supramolecular complexes 7-60). Figure 3 shows the surfaces of the free energies of electron transfer $\Delta G_{et(n)}$ and $\Delta G^{\#}_{et(n)}$ (n=1,4) between 1-6 and fullerenes (C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}, C_{84} and C_{120}) in the structures of 7-60, which are calculated by Equations 1-27 and shown in Tables 1-12. With the appropriate equations, it is possible to calculate the first to fourth free energies of electron transfer (ΔG_{et} in kcal.mol^{-1}) and the first to fourth activated free energies of electron transfer, $\Delta G^{\#}_{et(n)}$ (n=1-4), respectively, for [Laccase *Coriolus hirsutus* (L*Ch*)].C_n, 7-11 & 37-40; [Tyrosinase].C_n, 12-16 & 41-44; [Laccase *Rhus vernicifera* (L*Rv*)].C_n, 17-21 & 45-48; [Cytochrome-c peroxidase].C_n, 22-26 & 49-52; [Ascorbate oxidase].C_n, 27-31 & 53-56; and [Cytochrome-c oxidase].C_n, 32-36 & 57-60 (supramolecular complexes 7-60), in close accordance with the results of *Marcus* theory.

The values of the maximum wavelengths ($\lambda_{(n)}$; n=1 and 2) were determined for each stage of the electron transfer process in the nanostructure supramolecular complexes 7-60 with *Planck's* formula. Using this formula, we also determined the activation free energy of the electron transfer process. Most of the values were found in the UV-visible

(190-800nm) range of the electromagnetic spectrum. The maximum wavelengths ($\lambda_{(n)}$; n=1 to 4) depended on the $\Delta G^{\#}_{et(n)}$ value in each stage (Equation 3 and Tables 7-12).

Table 1. The data values on the Laccase Coriolus hirsutus (L*Ch*) **1** and the values of the 4 free energies of electron transfer (ΔG_{et}), in kcal mol^{-1}, between Laccase Coriolus hirsutus with C_n (as [Laccase Coriolus hirsutus].C$_n$**; 7-11** & **37-40**) supramolecular complexes. The data of $\Delta G_{et(n)}$ (n=1-4) were predicted by using Eq. 4 to Eq. 7, and those in parentheses were calculated by the Rehm-Weller equation (Eq. 1)

No.	Row	*Formula of [Laccase Coriolus hirsutus].C_n	(ΔG_{et}) in kcal mol^{-1} [Laccase Coriolus hirsutus].C_n			
			$\Delta G_{et(1)}$*	$\Delta G_{et(2)}$*	$\Delta G_{et(3)}$*	$\Delta G_{et(4)}$*
7	A-1	[LCh].C_{60}	43.326 (43.2375)	52.36 (52.0003)	62.661 (62.3773)	73.444 (72.9842)
8	A-2	[LCh].C_{70}	41.973 (42.5457)	50.959 (51.5391)	59.501 (60.5325)	69.588 (70.4483)
9	A-3	[LCh].C_{76}	38.9052 (39.0867)	47.4304 (46.4659)	57.365 (57.0735)	66.9096 (66.5281)
10	A-4	[LCh].C_{82}	34.1454 (33.3217)	41.8858 (41.3927)	55.049 (53.8451)	63.9576 (62.1467)
11	A-5	[LCh].C_{86}	30.0322 (30.7851)	37.0694 (37.0113)	53.405 (54.3063)	61.8376 (62.6079)
37	A-6	[LCh].C_{78}	37.5066	45.8062	56.613	65.956
38	A-7	[LCh].C_{84}	32.1828	39.5896	54.237	62.9128
39	A-8	[LCh].C_{96}	16.4592	21.1084	48.945	56.0056
40	A-9	[LCh].C_{120}	-35.292	-40.046	36.201	38.908

* The data of the free energy of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) for [Laccase Coriolus hirsutus].C_n compounds had not been previously reported

Table 2. The data values on the Tyrosinase **2** and the values of the 4 free energies of electron transfer (ΔG_{et}), in kcal mol^{-1}, between Tyrosinase with C_n (as [Tyrosinase].C$_n$, **12-16** & **41-44**) supramolecular complexes. The data of $\Delta G_{et(n)}$ (n=1-4) were predicted by using Eq. 8 to Eq. 11, and those in parentheses were calculated by the Rehm-Weller equation (Eq. 1)

No.	Row	*Formula of [Tyrosinase].C_n	(ΔG_{et}) in kcal mol^{-1} [Tyrosinase].C_n			
			$\Delta G_{et(1)}$*	$\Delta G_{et(2)}$*	$\Delta G_{et(3)}$*	$\Delta G_{et(4)}$*
12	B-1	[Tyrosinase].C_{60}	39.175 (39.0867)	48.209 (47.8495)	58.51 (58.2265)	69.282 (68.8341)
13	B-2	[Tyrosinase].C_{70}	37.822 (38.3949)	46.808 (47.3883)	55.35 (56.3817)	65.422 (66.2975)
14	B-3	[Tyrosinase].C_{76}	34.7542 (34.9359)	43.2794 (42.3151)	53.214 (52.9227)	62.7412 (62.3773)
15	B-4	[Tyrosinase].C_{82}	29.9944 (29.1709)	37.7348 (37.2419)	50.898 (49.6943)	59.7868 (57.9959)
16	B-5	[Tyrosinase].C_{86}	25.8812 (26.6343)	32.9184 (32.8605)	49.254 (50.1555)	57.6652 (58.4571)
41	B-6	[Tyrosinase].C_{78}	33.3556	41.6552	52.462	61.7868
42	B-7	[Tyrosinase].C_{84}	28.0318	35.4386	50.086	58.7412
43	B-8	[Tyrosinase].C_{96}	12.3082	16.9574	44.794	51.8292
44	B-9	[Tyrosinase].C_{120}	-39.443	-44.197	32.05	34.722

*The data of the free energy of electron transfer (ΔGet(1) to ΔGet(4)) for [Tyrosinase].Cn compounds had not been previously reported

Table 3. The data values on the Laccase Rhus vernicifera (L*Rv*) **3** and the values of the 4 free energies of electron transfer (ΔG_{et}), in kcal mol^{-1}, between Laccase Rhus vernicifera with C_n (as [Laccase Rhus vernicifera].C_n, **17-21** & **45-48**) supramolecular complexes. The data of $\Delta G_{et(n)}$ (n=1-4) were predicted by using Eq. 12 to Eq. 15, and those in parentheses were calculated by the Rehm-Weller equation (Eq. 1)

No.	Row	*Formula of [Laccase Rhus vernicifera].C_n	(ΔG_{et}) in kcal mol^{-1} [Laccase Rhus vernicifera].C_n			
			$\Delta G_{et(1)}$*	$\Delta G_{et(2)}$*	$\Delta G_{et(3)}$*	$\Delta G_{et(4)}$*
17	C-1	[LRv].C_{60}	35.232 (35.1434)	44.266 (43.9062)	54.566 (54.2832)	65.339 (64.8908)
18	C-2	[LRv].C_{70}	33.879 (34.4516)	42.865 (43.4450)	51.406 (52.4384)	61.479 (62.3542)
19	C-3	[LRv].C_{76}	30.8112 (30.9926)	39.3364 (38.3718)	49.27 (48.9794)	58.7982 (58.4340)
20	C-4	[LRv].C_{82}	26.0514 (25.2276)	33.7918 (33.2986)	46.954 (45.7510)	55.8438(54.0526)
21	C-5	[LRv].C_{86}	21.9382 (22.6910)	28.9754 (28.9172)	45.31 (46.2122)	53.7222 (54.5138)
45	C-6	[LRv].C_{78}	29.4126	37.7122	48.518	57.8438
46	C-7	[LRv].C_{84}	24.0888	31.4956	46.142	54.7982
47	C-8	[LRv].C_{96}	8.3652	13.0144	40.85	47.8862
48	C-9	[LRv].C_{120}	-43.386	-48.14	28.106	30.779

*The data of the free energy of electron transfer ($\Delta Get(1)$ to $\Delta Get(4)$) for [Laccase Rhus vernicifera].*Cn* compounds had not been previously reported.

Table 4. The data values on the Dodecahydro Cytochrome c peroxidase **4** and the values of the 4 free energies of electron transfer (ΔG_{et}), in kcal mol^{-1}, between Cytochrome c peroxidase with C_n (as [Cytochrome c peroxidase].C_n, **22-26** & **49-52**) supramolecular complexes. The data of $\Delta G_{et(n)}$ (n=1-4) were predicted by using Eq. 16 to Eq. 19, and those in parentheses were calculated by the Rehm-Weller equation (Eq. 1)

No.	Row	*Formula of [Cytochrome c peroxidase].C_n	(ΔG_{et}) in kcal mol^{-1} [Cytochrome c peroxidase].C_n			
			$\Delta G_{et(1)}$*	$\Delta G_{et(2)}$*	$\Delta G_{et(3)}$*	$\Delta G_{et(4)}$*
22	D-1	[CyCP].C_{60}	42.422 (42.1998)	50.994 (50.9626)	61.623 (61.3396)	72.395 (71.9472)
23	D-2	[CyCP].C_{70}	41.141 (41.5080)	49.475 (50.5041)	58.463 (59.4948)	68.535 (69.4106)
24	D-3	[CyCP].C_{76}	38.1068 (38.0940)	45.866 (45.4282)	56.327 (56.0358)	65.8542 (65.4904)
25	D-4	[CyCP].C_{82}	33.3734 (32.2840)	40.2338 (40.3550)	54.011 (52.8074)	62.8998 (61.1090)
26	D-5	[CyCP].C_{86}	29.2738 (29.7474)	35.355 (35.9736)	52.367 (53.2686)	60.7782 (61.5702)
49	D-6	[CyCP].C_{78}	36.7178	44.2134	55.575	64.8998
50	D-7	[CyCP].C_{84}	31.418	37.9068	53.199	61.8542
51	D-8	[CyCP].C_{96}	15.7208	19.224	47.907	54.9422
52	D-9	[CyCP].C_{120}	-36.064	-42.42	35.163	37.835

*The data of the free energy of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) for [Cytochrome c peroxidase].C_n compounds had not been previously reported.

Table 5. The data values on the Dodecahydro Ascorbate oxidase **5** and the values of the 4 free energies of electron transfer (ΔG_{et}), in kcal mol^{-1}, between Ascorbate oxidase with C_n (as [Ascorbate oxidase].C$_n$, **27-31** & **53-56**) supramolecular complexes. The data of $\Delta G_{et(n)}$ (n=1-4) were predicted by using Eq. 16 to Eq. 19, and those in parentheses were calculated by the Rehm-Weller equation (Eq. 1)

No	Row	*Formula of [Ascorbate oxidase].C_n	(ΔG_{et}) in kcal mol^{-1} [Ascorbate oxidase].C_n			
			$\Delta G_{et(1)}$*	$\Delta G_{et(2)}$*	$\Delta G_{et(3)}$*	$\Delta G_{et(4)}$*
27	E-1	[Ascorbate oxidase].C_{60}	33.295 (33.2064)	42.329 (41.9692)	52.629 (52.3462)	63.402 (62.9538)
28	E-2	[Ascorbate oxidase].C_{70}	31.942 (32.5146)	40.928 (41.5080)	49.469 (50.5014)	59.542 (60.4172)
29	E-3	[Ascorbate oxidase].C_{76}	28.8742 (29.0556)	37.3994 (36.4348)	47.333 (47.0424)	56.8612 (56.4970)
30	E-4	[Ascorbate oxidase].C_{82}	24.1144 (23.2906)	31.8548 (31.3616)	45.017 (43.8140)	53.9068 (52.1156)
31	E-5	[Ascorbate oxidase].C_{86}	20.0012 (20.7540)	27.0384 (26.9802)	43.373 (44.2752)	51.7852 (52.5768)
53	E-6	[Ascorbate oxidase].C_{78}	27.4756	35.7752	46.581	55.9068
54	E-7	[Ascorbate oxidase].C_{84}	22.1518	29.5586	44.205	52.8612
55	E-8	[Ascorbate oxidase].C_{96}	6.4282	11.0774	38.913	45.9492
56	E-9	[Ascorbate oxidase].C_{120}	-45.323	-50.077	26.169	28.842

*The data of the free energy of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) for [Ascorbate oxidase].C_n compounds had not been previously reported.

Table 6. The data values on the Dodecahydro Cytochrome c oxidase **6** and the values of the 4 free energies of electron transfer (ΔG_{et}), in kcal mol^{-1}, between Cytochrome c oxidase with C_n (as [Cytochrome c oxidase].C$_n$, **32-36** & **57-60**) supramolecular complexes. The data of $\Delta G_{et(n)}$ (n=1-4) were predicted by using Eq. 16 to Eq. 19, and those in parentheses were calculated by the Rehm-Weller equation (Eq. 1)

No.	Row	*Formula of [Cytochrome c oxidase].C_n	(ΔG_{et}) in kcal mol^{-1} [Cytochrome c oxidase].C_n			
			$\Delta G_{et(1)}$*	$\Delta G_{et(2)}$*	$\Delta G_{et(3)}$*	$\Delta G_{et(4)}$*
32	F-1	[CyCOx].C_{60}	30.9 (30.7851)	39.908 (39.5479)	50.208 (49.9249)	60.981 (60.5325)
33	F-2	[CyCOx].C_{70}	29.557 (30.0933)	38.507 (39.0867)	47.048 (48.0801)	57.121 (57.9959)
34	F-3	[CyCOx].C_{76}	26.4952 (26.6343)	34.9784 (34.0135)	44.912 (44.6211)	54.4402 (54.0757)
35	F-4	[CyCOx].C_{82}	21.7414 (20.8693)	29.4338 (28.9403)	42.596 (41.3927)	51.4858 (49.6943)
36	F-5	[CyCOx].C_{86}	17.6322 (18.3327)	24.6174 (24.5589)	40.952 (41.8539)	49.3642 (50.1555)
57	F-6	[CyCOx].C_{78}	25.0986	33.3542	44.16	53.4858
58	F-7	[CyCOx].C_{84}	19.7808	27.1376	41.784	50.4402
59	F-8	[CyCOx].C_{96}	4.0692	8.6564	36.492	43.5282
60	F-9	[CyCOx].C_{120}	-47.658	-52.498	23.748	26.421

*The data of the free energy of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) for [Cytochrome c oxidase].C_n compounds had not been previously reported.

Table 7. The values of the first to forth free activation energies of electron transfer and kinetic rate constants of the electron transfers, $\Delta G^{\#}_{et(n)}$ (in kcal mol^{-1}, n=1-4) and the wave length of electron transfer ($\lambda_{(n)}$, in nm), respectively, of [Laccase Coriolus hirsutus].C_n supramolecular complexes (**7-11** and **37-40**) supramolecular complexes

Id.	[Laccase Coriolus hirsutus].C_n *	$\Delta G_{et(1)}^{\neq}$	λ_1 (nm)	$\Delta G_{et(2)}^{\neq}$	λ_2 (nm)	$\Delta G_{et(3)}^{\neq}$	λ_3 (nm)	$\Delta G_{et(4)}^{\neq}$	λ_4 (nm)
7	[Ch].C_{60}	74.59	383	101.59	281	138.95	206	183.17	156
8	[Ch].C_{70}	72.63	393	100.07	286	131.88	217	172.04	166
9	[Ch].C_{76}	63.25	452	84.06	340	119.13	240	155.53	184
10	[Ch].C_{82}	49.06	582	69.44	411	107.81	265	138.06	207
11	[Ch].C_{86}	43.38	659	57.94	493	109.39	261	139.85	204
37	[Ch].C_{78}	59.19	483	82.08	348	117.48	243	153.19	187
38	[Ch].C_{84}	46.47	615	64.58	442	109.15	262	141.04	203
39	[Ch].C_{96}	17.88	1598	24.94	1146	91.71	312	115.32	248
40	[Ch].C_{120}	18.42	1551	25.75	1110	55.93	511	62.79	455

*The data of $\Delta G^{\neq}_{et(n)}$ (in kcal mol^{-1}, n-1-4) and k_{et} (sec^{-1}, n=1-4) for [Laccase Coriolus hirsutus].C_n supramolecular complexes (**7-11** and **37-40**).

Table 8. The values of the first to forth free activation energies of electron transfer and kinetic rate constants of the electron transfers, $\Delta G^{\#}_{et(n)}$ (in kcal mol^{-1}, n-1-4) and the wave length of electron transfer ($\lambda_{(n)}$, in nm), respectively, of [Tyrosinase].C_n supramolecular complexes (**12-16** and **41-44**) supramolecular complexes

Id.	[Tyrosinase].C_n *	$\Delta G_{et(1)}^{\neq}$	λ_1 (nm)	$\Delta G_{et(2)}^{\neq}$	λ_2 (nm)	$\Delta G_{et(3)}^{\neq}$	λ_3 (nm)	$\Delta G_{et(4)}^{\neq}$	λ_4 (nm)
12	[Tyrosinase].C_{60}	63.2568	452	88.2856	324	123.3079	232	165.1417	173
13	[Tyrosinase].C_{70}	61.4581	465	86.8645	329	116.6551	245	154.5831	185
14	[Tyrosinase].C_{76}	52.8539	541	71.9937	397	104.6783	273	138.9513	206
15	[Tyrosinase].C_{82}	39.9547	715	58.5180	488	94.0852	304	122.4663	233
16	[Tyrosinase].C_{86}	34.8498	820	48.0026	595	95.5639	299	124.1525	230
41	[Tyrosinase].C_{78}	49.1387	581	70.1619	407	103.1321	277	136.6688	209
42	[Tyrosinase].C_{84}	37.6191	759	54.0641	528	95.3403	300	125.1970	228
43	[Tyrosinase].C_{96}	12.5660	2274	18.5783	1538	79.0857	361	101.0270	283
44	[Tyrosinase].C_{120}	24.7503	1154	33.1502	862	46.1715	619	52.3431	546

*The data of $\Delta G^{\neq}_{et(n)}$ (in kcal mol^{-1}, n-1-4) and k_{et} (sec^{-1}, n=1-4) for [Tyrosinase].C_n supramolecular complexes (**12-16** and **41-44**).

Table 9. The values of the first to forth free activation energies of electron transfer and kinetic rate constants of the electron transfers, $\Delta G^{\#}_{et(n)}$ (in kcal mol^{-1}, n-1-4) and the wave length of electron transfer ($\lambda_{(n)}$, in nm), respectively, of [Laccase Rhus vernicifera].C_n supramolecular complexes (**17-21** and **45-48**) supramolecular complexes

Id.	[Laccase Rhus vernicifera].C_n*	$\Delta G_{et(1)}^{\neq}$	λ_1 (nm)	$\Delta G_{et(2)}^{\neq}$	λ_2 (nm)	$\Delta G_{et(3)}^{\neq}$	λ_3 (nm)	$\Delta G_{et(4)}^{\neq}$	λ_4 (nm)
17	[LRVe].C_{60}	53.3518	536	76.5075	373	109.3118	261	148.8782	192
18	[LRVe].C_{70}	51.7010	553	75.1851	380	103.0534	277	138.8618	206
19	[LRVe].C_{76}	43.8361	652	61.3986	465	91.8159	311	124.0679	230
20	[LRVe].C_{82}	32.1692	888	49.0073	583	81.9128	349	108.5194	263
21	[LRVe].C_{86}	27.6065	1035	39.4285	725	83.2930	343	110.1071	259
45	[LRVe].C_{78}	40.4593	706	59.7086	479	90.3659	316	121.9127	234
46	[LRVe].C_{84}	30.0776	950	44.9394	636	83.0820	344	111.0918	257
47	[LRVe].C_{96}	8.3852	3407	13.4038	2132	67.9587	420	88.3991	323
48	[LRVe].C_{120}	31.6306	903	41.0466	696	37.7691	756	43.3716	659

*The data of $\Delta G^{\neq}_{et(n)}$ (in kcal mol^{-1}, n-1-4) and k_{et} (sec^{-1}, n=1-4) for [Laccase Rhus vernicifera].C_n supramolecular complexes (**17-21** and **45-48**).

Table 10. The values of the first to forth free activation energies of electron transfer and kinetic rate constants of the electron transfers, $\Delta G^{\#}_{et(n)}$ (in kcal mol^{-1}, n-1-4) and the wave length of electron transfer ($\lambda_{(n)}$, in nm), respectively, of [Cytochrome c peroxidase].C_n supramolecular complexes (**22-26** and **49-52**) supramolecular complexes

Id.	[Cytochrome c peroxidase].C_n*	$\Delta G_{et(1)}^{\neq}$	λ_1 (nm)	$\Delta G_{et(2)}^{\neq}$	λ_2 (nm)	$\Delta G_{et(3)}^{\neq}$	λ_3 (nm)	$\Delta G_{et(4)}^{\neq}$	λ_4 (nm)
22	[CyCP].C_{60}	71.6719	399	98.1794	291	134.9529	212	178.5766	160
23	[CyCP].C_{70}	69.7565	410	96.6805	296	127.9888	223	167.5900	170
24	[CyCP].C_{76}	60.5685	472	80.9536	353	115.4283	248	151.2967	189
25	[CyCP].C_{82}	46.6965	612	66.6218	429	104.2903	274	134.0723	213
26	[CyCP].C_{86}	41.1635	694	55.3671	516	105.8468	270	135.8364	210
49	[CyCP].C_{78}	57.2054	499	77.3947	369	113.8039	251	148.9142	192
50	[CyCP].C_{84}	44.7683	638	60.2047	475	105.6112	271	136.9284	209
51	[CyCP].C_{96}	16.8648	1694	21.9343	1303	88.4636	323	111.5921	256
52	[CyCP].C_{120}	19.5248	1463	29.8670	957	53.3989	535	60.0214	476

*The data of $\Delta G^{\neq}_{et(n)}$ (in kcal mol^{-1}, n-1-4) and k_{et} (sec^{-1}, n=1-4) for [Cytochrome c peroxidase].C_n supramolecular complexes (**22-26** and **49-52**).

Table 11. The values of the first to forth free activation energies of electron transfer and kinetic rate constants of the electron transfers, $\Delta G^{\#}_{et(n)}$ (in kcal mol^{-1}, n-1-4) and the wave length of electron transfer ($\lambda_{(n)}$, in nm), respectively, of [Ascorbate oxidase].C_n supramolecular complexes (**27-31** and **53-56**) supramolecular complexes

Id.	[Ascorbate oxidase].C_n*	$\Delta G_{et(1)}^{\neq}$	λ_1 (nm)	$\Delta G_{et(2)}^{\neq}$	λ_2 (nm)	$\Delta G_{et(3)}^{\neq}$	λ_3 (nm)	$\Delta G_{et(4)}^{\neq}$	λ_4 (nm)
27	[Ascorbate oxidase].C_{60}	48.7950	586	71.0306	402	102.7453	278	141.1978	202
28	[Ascorbate oxidase].C_{70}	47.2168	605	69.7565	410	96.6805	296	131.4478	217
29	[Ascorbate oxidase].C_{76}	39.7151	719	56.5028	506	85.8063	333	117.0655	244
30	[Ascorbate oxidase].C_{82}	28.6535	997	44.6442	640	76.2421	375	101.9771	280
31	[Ascorbate oxidase].C_{86}	24.3571	1173	35.5254	804	77.5738	368	103.5163	276
53	[Ascorbate oxidase].C_{78}	36.5042	783	54.8820	521	84.4048	339	114.9724	249
54	[Ascorbate oxidase].C_{84}	26.6815	1071	40.7657	701	77.3704	369	104.4713	273
55	[Ascorbate oxidase].C_{96}	6.6401	4303	11.1705	2558	62.8028	455	82.5044	346
56	[Ascorbate oxidase].C_{120}	35.3192	809	45.2344	632	33.9512	842	39.2731	728

*The data of $\Delta G^{\neq}_{et(n)}$ (in kcal mol^{-1}, n-1-4) and k_{et} (sec^{-1}, n=1-4) for [Ascorbate oxidase].C_n supramolecular complexes (**27-31** and **53-56**).

Table-12: The values of the first to forth free activation energies of electron transfer and kinetic rate constants of the electron transfers, $\Delta G^{\#}_{et(n)}$ (in kcal mol^{-1}, n-1-4) and the wave length of electron transfer ($\lambda_{(n)}$, in nm), respectively, of [Cytochrome c oxidase].C_n supramolecular complexes (**32-36** and **57-60**) supramolecular complexes

Id.	[Cytochrome c oxidase].C_n*	$\Delta G_{et(1)}^{\neq}$	λ_1 (nm)	$\Delta G_{et(2)}^{\neq}$	λ_2 (nm)	$\Delta G_{et(3)}^{\neq}$	λ_3 (nm)	$\Delta G_{et(4)}^{\neq}$	λ_4 (nm)
32	[CyCOx].C_{60}	43.3849	659	64.4704	443	94.8231	301	131.8834	217
33	[CyCOx].C_{70}	41.8975	682	63.2568	452	89.0004	321	122.4663	233
34	[CyCOx].C_{76}	34.8498	820	50.6689	564	78.5802	364	108.5985	263
35	[CyCOx].C_{82}	24.5448	1164	39.4762	724	69.4398	411	94.0852	304
36	[CyCOx].C_{86}	20.5814	1388	30.9325	924	70.7110	404	95.5639	299
57	[CyCOx].C_{78}	31.9287	895	49.1355	581	77.2401	370	106.5839	268
58	[CyCOx].C_{84}	22.8013	1253	35.8349	797	70.5176	405	96.4825	296
59	[CyCOx].C_{96}	4.7894	5966	8.6651	3297	56.6444	504	75.4227	379
60	[CyCOx].C_{120}	40.0361	714	50.7545	563	29.4653	970	34.4364	830

*The data of $\Delta G^{\neq}_{et(n)}$ (in kcal mol^{-1}, n-1-4) and k_{et} (sec^{-1}, n=1-4) for [Cytochrome c oxidase].C_n supramolecular complexes (**32-36** and **57-60**).

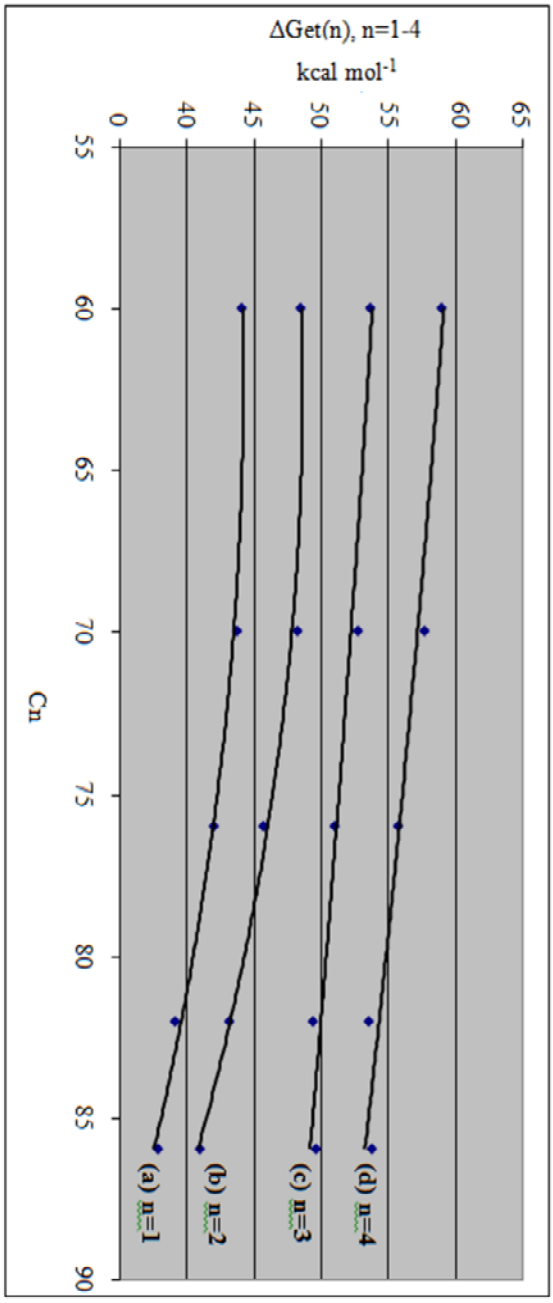

Fig. 2. The relationship between the number "n" of carbon atoms in the fullerenes and the first(a), second(b), third(c) and fourth(d) free-energies of electron transfer ($\Delta G_{et(n)}$, n=1-4) of [Laccase Coriolus hirsutus].C_n (n = 60, 70, 76, 82 and 86), compounds A-1 to A-5 (7-11). (* The related curves for [Tyrosinase].C_n, B-1 to B-5, [Laccase *Rhus-vernicifera* (L*Rv*)].C_n, C-1 to C-5, [Cytochrome-c peroxidase].C_n, D-1 to D-5, [Ascorbate oxidase].C_n, E-1 to E-5 and [Cytochrome-c oxidase].C_n, F-1 to F-5).

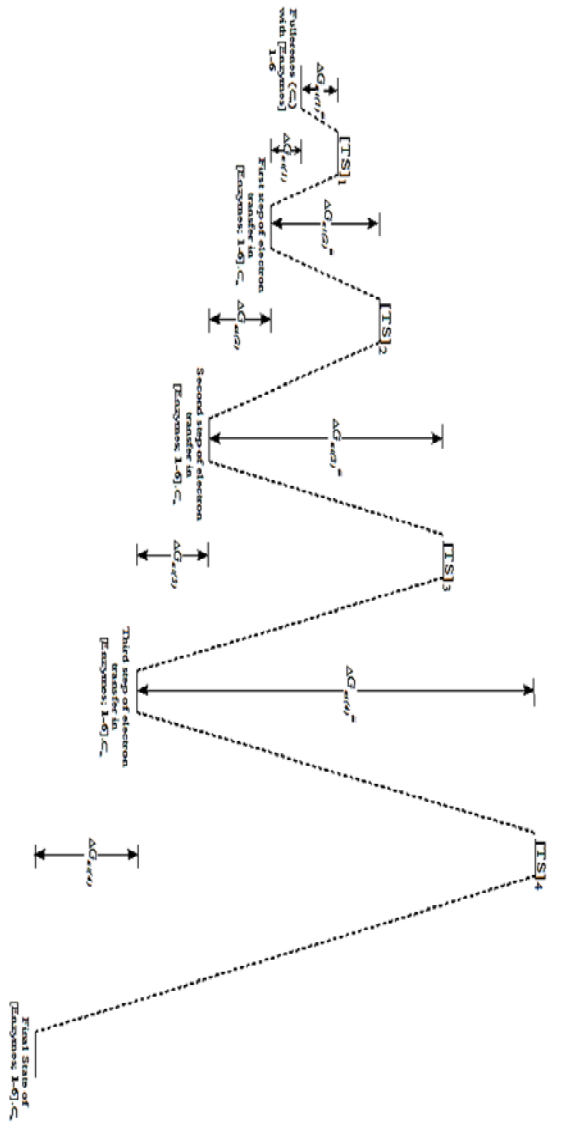

Fig. 3. The surfaces of the free energies of electron transfer $\Delta Get_{(n)}$ and $\Delta Get_{(n)}^{\#}$ (n=1-4) between 1-6 and fullerenes in 7-60.

CONCLUSION

Laccase *Coriolus hirsutus* (L*Ch*), Tyrosinase, Laccase *Rhus-vernicifera* (L*Rv*), Cytochrome-c peroxidase, Ascorbate oxidase and Cytochrome-c oxidase, 1-6 and fullerenes have important electron-transfer properties as the most well-known biomolecules. The electrochemical data of selected enzymes 1-6, i.e [Laccase *Coriolus hirsutus*

(L*Ch*)].C_n; 7-11 & 37-40, [Tyrosinase].C_n; 12-16 & 41-44, [Laccase *Rhus-vernicifera* (L*Rv*)].C_n; 17-21 & 45-48, [Cytochrome-c peroxidase].C_n; 22-26 & 49-52, [Ascorbate oxidase].C_n; 27-31 & 53-56 and [Cytochrome-c oxidase].C_n, 32-36 & 57-60 (supramlecular complexes 7-60) were reported here. These include the four free-energies of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$), calculated using the *Rehm-Weller* equation and $\Delta G^{\#}_{et(n)}$ as well as ($\lambda_{(n)}$; n=1-4; in *nm*) using equations of the *Marcus* theory for the supramolecular complexes 7-60. Using the number of carbon atoms (n), along with the equations of the model, one can derive sound structural relationships between the aforementioned physicochemical data. These equations allow one to calculate $\Delta G_{et(n)}$ (n=1-4), $\Delta G^{\#}_{et(n)}$ and ($\lambda_{(n)}$; n=1-4) for cephalosporin antibiotics 1-6, as [Laccase *Coriolus hirsutus* (L*Ch*)].C_n; 7-11 & 37-40, [Tyrosinase].C_n; 12-16 & 41-44, [Laccase *Rhus-vernicifera* (L*Rv*)].C_n; 17-21 & 45-48, [Cytochrome-c peroxidase].C_n; 22-26 & 49-52, [Ascorbate oxidase].C_n; 27-31 & 53-56 and [Cytochrome-c oxidase].C_n, 32-36 & 57-60 (supramlecular complexes 7-60) of the fullerenes C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}, C_{84} and C_{120}). The values of the maximum wave lengths ($\lambda_{(n)}$; n=1-4) for each stage of the electron transfer process was calculated by the *Planck's* formula in the nanostructure supramolecular complexes 7-60. The novel supramolecular complexes discussed have neither been synthesized nor reported previously.

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211&volume=84&issue=6&startPage=859. c)http://www.biomed.cas.cz/physiolres/pdf/53%20Suppl%201/53_S213.pdf.

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