Free energies, kinetics, and photoelectron-transfer properties, and theoretical and quantitative structural relationship studies of $[\text{SWCNT}(5,5)-\text{armchair-C}_n\text{H}_{20}][R]$ ($R = \eta^2-\text{C}_m\text{Pd(dppf)}$, $\eta^2-\text{C}_m\text{Pd(dppr)}$, and $\eta^2-\text{C}_m\text{Pd(dppcym)}$, $n =$ 20 to 300 and $m =$ 60 and 70) nanostructure complexes

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Abstract

Metal complexes containing one or several bis(triorganylphosphine)palladium fragments attached to the $\text{C}_{60}$ core and coordinated in olefinic $\eta^2$ mode have been previously described. The number of carbon atoms of the single-walled carbon nanotubes (SWCNTs) is the useful numerical and structural electrochemical properties contributing to the relationship between the structures of $\eta^2\text{C}_m\text{Pd(dppf)}$, $\eta^2\text{C}_m\text{Pd(dppr)}$, and $\eta^2\text{C}_m\text{Pd(dppcym)}$ ($m =$ 60 and 70) ligands (A to E) and $[\text{SWCNT}(5,5)-\text{armchair-C}_n\text{H}_{20}][R]$ ($R =$ 20 to 190) 1 to 18 and the production of the $[\text{SWCNT}(5,5)-\text{armchair-C}_n\text{H}_{20}][R] (R = \eta^2\text{C}_m\text{Pd(dppf)}$, $\eta^2\text{C}_m\text{Pd(dppr)}$, and $\eta^2\text{C}_m\text{Pd(dppcym)}$, $n =$ 20 to 300 and $m =$ 60 and 70) complexes 30 to 174. In this study, the relationship between the number of carbon atoms index and the first and second free energies of electron transfer ($\Delta G_{\text{et}}(n) =$ 1, 2) using the Rehm-Weller equation based on the first and second oxidation potentials ($\text{ox}E_1$ and $\text{ox}E_2$) of A to E for the predicted complexes 30 to 174 between 1 and 29 with exohedral metallofullerenes A to E, as $[\text{SWCNT}(5,5)-\text{armchair-C}_n\text{H}_{20}][R] (R = \eta^2\text{C}_m\text{Pd(dppf)}$, $\eta^2\text{C}_m\text{Pd(dppr)}$, and $\eta^2\text{C}_m\text{Pd(dppcym)}$, $n =$ 20 to 300 and $m =$ 60 and 70) 30 to 174 was assessed. Here, the first and second free activation energies of electron transfer and the wavelengths of the electromagnetic photons in the photoelectron transfer process, $\Delta G_{\text{et}}(n)$ and $\lambda_{\text{et}}$ (nm), respectively, for 30 to 174 in accordance with the Marcus theory and Planck’s equation were also calculated.

Keywords: Exohedral metallofullerenes, Pd complexes, Single-walled nanotubes, Free energy of electron transfer, Photoelectron transfer, Marcus theory, Planck’s equation

Background

The first metal complexes containing one or several bis(triorganylphosphine)platinum fragments attached to the $\text{C}_{60}$ core and coordinated in olefinic $\eta^2$ mode were described in 1991 [1-3], revealing that fullerenes, at least buckminsterfullerene $\text{C}_{60}$, can function as ligands in reactions with transition metals. Electronic structures of exohedral palladium complexes of [60] and [70] fullerenes with diphenylphosphinoferrocenyl, diphenylphosphinoruthenocenyl, and diphenylphosphinocymantrenyl ligands were studied by cyclic voltammetry and semi-empirical quantum chemical calculations in 2004 [1]. The probable sites of the electronic changes in these complexes under electrochemical oxidation and reduction have also been determined [1-4].

The bulk of fullerene metal complexes consist of heteroligand complexes. The only exceptions known to date are polymeric homoligand complexes of $\text{C}_{60}$ with palladium or platinum, which are prepared by the direct reaction of fullerene with zero-valent complexes of these
metals with a weakly bound ligand, dibenzylideneacetone [1-8]. The platinum and palladium complexes (C_{60})M_{x} (M = Pt and Pd) can also be prepared from the Pt(0) and Pd cyclooctadiene complexes. Two C_{60} molecules are bound to the metal atom in \( \eta^{2} \) mode. However, instead of separate (C_{60})_{2}M molecules, a polymeric chain is formed, which is probably indicative of enhanced reactivity (with respect to ligand-free palladium) of the other fullerene double bonds upon coordination of one bond. If an excess of the M(0) compound is present, the specific content of the metal increases [1-8].

According to elemental analysis, the insoluble precipitates have compositions of (C_{60})PdCl_{x} where \( x = 1, 2, 3 \), and more. Some free metal is always present. C_{60} molecules are presumably linked by metal atoms into one-dimensional chains or two- and three-dimensional frameworks. The palladium (platinum) fullerene polymer reacts heterogeneously with P ligands (tertiary phosphines or tertiary phosphites) in solution to give the C_{60}ML_x complexes, which can also be synthesized by other methods [1-8]. The electrochemical synthesis of the (\( \eta^{2}\)-C_{60}M(PPh_{3})_{2} (M = Pt, Pd) complexes was performed by reacting the dianion of C_{60} prepared by electrochemical reduction (at a Pt electrode in a toluene-acetonitrile solution in the presence of Bu_{3}NBF_{4} as the supporting electrolyte) with the ML_{2}Cl_{2} complex or with a divalent metal chloride in the presence of triphenylphosphine [1-4]. The palladium derivatives of C_{60} and C_{70} with cyamantrenylidiphenylphosphine ligand were prepared in a similar way [7,8]. A series of new exohedral Pd(0) complexes with C_{60} and C_{70} fullerenes containing bisdiphenylphosphinoferrocene (dppf), bisdiphenylphosphinoruthenocene (dppr), or two diphenylphosphinocymantrene (dppcym) molecules as stabilizing ligands have been synthesized. These complexes contain a strongly electron-withdrawing fullerene cage and a metallocene group, which can be either electron releasing (ruthenocene) or electron withdrawing (cyamantrene) and is linked with the cage through a bisdiphenylphosphine palladium bridge. The electrochemical pattern is impeded because the bisdiphenylphosphine palladium fragment linking these terminal groups is also redox active [1-8].

Metal complexes with fullerenes have attracted attention due to the prospects of their application in catalysis, in materials for nonlinear optics, for designing artificial photosynthesis systems, and in the development of supra- and nanomaterials [4]. More specifically, metal-fullerene interactions are of particular importance. Platinum was the first metal found to form \( \pi \)-complexes with fullerenes. However, evidence for the existence of similar complexes for palladium was obtained soon thereafter. The most practical preparation of palladium \( \eta^{2} \) complexes appeared to be by direct synthesis using Pd_{2}(dba)_{3}, fullerene, and a free phosphine ligand. Almost all known complexes of fullerenes with an undisturbed electronic system involve only \( \eta^{2} \) coordination, which is typical of an isolated olefinic double bond. The \( \eta^{2} \) coordination is probably due to the nonplanar surface geometry, which makes the axes of the pseudo-\( \pi \)-orbitals nonparallel and, thus, hampers their bonding to metal orbitals [1-8].

**Nanotubes**

Nanotubes of type (\( n,n \)) are called **armchair nanotubes** because of their ‘W’ shape perpendicular to the tube axis. They are symmetrical along the tube axis, with a short unit cell (0.25 nm or 2.5 Å) that is repeated along the entire section of a long nanotube. All other nanotubes are called **chiral nanotubes** and have longer unit cell sizes along the tube axis [9-11]. The simplest type of nanotube is a cylindrical structure, which conceptually could be formed by folding and gluing a pair of opposite sides of a rectangular graphite sheet [9-24]. If both ends are capped, it will have at least two pentagons and be a type of fullerene. Nanotubes are large, linear fullerenes with aspect ratios as large as 103 to 105 [11]. The walls of such tubes can have various sizes of polygons [25]. Although many nanoscale fullerene materials occur regularly in applications, controlled production of numerous fullerenes and nanotubes with well-defined characteristics has not yet been achieved [16-19,25].

Carbon nanotubes possess many special properties, such as an open mesoporous structure, high electrical conductivity and chemical stability, and extremely high mechanical strength and modulus [11,19-21]. These properties not only help in the transportation of ions but also facilitate the adsorption of the double layer and confer advantages in the development of electrochemical capacitors [22]. Single-walled carbon nanotubes have been recognized as potential electrode materials for electrochemical capacitors [23,24].

One of the most widely recognized structures of nanotubes is the (5,5) tube, which can be built by successively adjoining sections of ten C atoms. In the infinite tube, the periodic unit cell has two sections, each consisting of 20 C atoms [9]. The electronic structures and electrical properties of single-walled nanotubes can be simulated from those of a graphite layer (graphene sheet) [19-24].

**Figure 1** shows the (5,5) **armchair** form with the imaginary structures of the \( \eta^{2}\)C_{m}Pd(dppf), \( \eta^{2}\)C_{m}Pd(dppr), and \( \eta^{2}\)C_{m}Pd(dppcym)\( _{2} \) (\( m = 60 \) and 70) ligands (A to E) and 1 to 174 as \([\text{SWCNT}(5,5)\text{-armchair}-C_{n}H_{20}]\{R\} \) (\( R = \eta^{2}\)C_{m}Pd(dppf), \( \eta^{2}\)C_{m}Pd(dppr), and \( \eta^{2}\)C_{m}Pd(dppcym)\( _{2} \), \( n = 20 \) to 300 and \( m = 60 \) and 70) 30 to 174. The nanotubes may not contain any hydrogen atoms (there is no hydrogen in the electric arc technique), and the nanotubes can be easily closed at both ends.

Electronic structures of tubular aromatic molecules derived from the metallic (5,5) armchair SWCNT for C_{20}H_{20} up to C_{210}H_{20} (see Figure 1) were reported by Zhou et al. in 2004 [9]. The authors considered how the...
electronic structures of short molecular sections of the (5,5) tube relate to, differ from, and asymptotically approach those of an infinite metallic tube [9]. Some of the structural and electronic properties were investigated, such as the ionization potential, electron affinity, Fermi energy, chemical hardness, and relative energetic stability. All of these metrics show the length periodicity in the frontier orbital (i.e., highest occupied molecular orbital-lowest unoccupied molecular orbital) gap, in contrast to the optical ‘charge transfer’ transition and the static axial polarizability [9]. The (5,5) nanotubes have two types of symmetry. For nanotubes with odd identification numbers (1 to 17), the point group is \( D_{5h} \) whereas nanotubes with even identification numbers (2 to 18) have a point group of \( D_{5d} \). Static and time-dependent density function theory calculations were used to independently optimize the structure for neutral, cationic, and anionic complexes [9]. The hybrid nonlocal Becke, three-parameter, Lee-Yang-Parr (B3LYP) function was applied [9].

Infinite-length SWCNTs are \( \pi \)-bonded aromatic structures that can be either semi-conducting or metallic, depending upon the diameter and helical angle of the SWCNTs. In a pioneering 1992 DFT calculation, Mintmire et al. predicted that the infinite length (5,5) armchair SWCNT (6.70 Å diameter) would be metallic with a very low transition temperature separating the uniform (high-temperature) structure from the Peierls bond alternating (low-temperature) structure [25,26]. This specific SWCNT is the elongated tube of the \( C_{60} \), \( C_{70} \), etc. molecular family [9]. Most of the previous studies have dealt with \( C_{60}@SWCNT \) and \( C_{70}@SWCNT \) structures [18,27-30].

Figure 1 Schemes. A to E and \([SWCNT(5,5)-armchair-C_{n}H_{20}]\)(R) (R = \( \eta^2-C_{60}Pd(dppf) \), \( \eta^2-C_{50}Pd(dppr) \), and \( \eta^2-C_{70}Pd(dpccym) \), \( n = 20 \) to 300 and \( m = 60 \) and 70) complexes.
The diameter sizes of C60 and [SWCNT(5,5)-armchair-C6H20] 1 to 18 were reported to be 6.70 and 6.94 Å, respectively [28-30]. With these diameters, C60 and larger fullerenes cannot be encapsulated inside the [SWCNT(5,5)-armchair-C6H20] in the structure of C60@[SWCNT(5,5)-armchair-C6H20].

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 the similarity of the physical and chemical properties of the compounds in question. Numerous studies in the above areas have also used topological indices [31-35]. In previous studies, the relationship between the D_U index and electron affinity, reduction potential (\(E_{1}^{\text{red}}\)) of [SWCNT(5,5)-armchair-C6H20] as well as the free energy of electron transfer (\(\Delta G_{et}\)) between [SWCNT(5,5)-armchair-C6H20] structures and fullerene C60 in C60@[SWCNT(5,5)-armchair-C6H20] complexes was investigated [28]. In some studies, the relationship between the D_U index and the free energy of electron transfer (\(\Delta G_{et}\)) using the Rehm-Weller equation based on the first oxidation potential (\(E_{1}^{\text{ox}}\)) of Sc@C84 and Er2@C82 for the predicted supramolecular complexes between SWCNT(5,5)-armchair-C6H20 and the endohedral metallofullerenes Sc@C84 and Er2@C82 as [M2@C84]@[SWCNT(5,5)-armchair-C6H20] (M = Er and Sc, x = 82 and 84) [28-30,36] was assessed.

To characterize the structural properties of the π-bonds, we investigated the relationship between the number of carbon atoms of the SWCNT (Cn) index and electron affinity, \(E_{1}^{\text{red}}\) of [SWCNT(5,5)-armchair-C6H20] 1 to 18 (and extension of the results to 19 to 29) as well as the first and second free energies of electron transfer (\(\Delta G_{et(1)}\), \(n = 1.2\)) using the Rehm-Weller equation [36] based on the first and second oxidation potential (\(E_{1}^{\text{ox}}\) and \(E_{2}^{\text{ox}}\)) of the \(\eta^{2}-\text{C}_{n}\text{Pd(dppf)}\), \(\eta^{2}-\text{C}_{n}\text{Pd(dppr)}\), and \(\eta^{2}-\text{C}_{n}\text{Pd(dpcym)}\text{)2}\) (m = 60 and 70) ligands (A to E) for the predicted [SWCNT(5,5)-armchair-C6H20][R] (R = \(\eta^{2}-\text{C}_{n}\text{Pd(dppf)}\), \(\eta^{2}-\text{C}_{n}\text{Pd(dppr)}\), and \(\eta^{2}-\text{C}_{n}\text{Pd(dpcym)}\text{)2}\) (n = 20 to 300 and \(m = 60\) and 70) supramolecular complexes 30 to 174. We also calculated the first and second activation free energies of electron transfer and the wavelengths of the electromagnetic photons in the photoelectron transfer process, \(\Delta G_{et(1)(n)}\) and \(\lambda_{(n)}\) (nm) using the Marcus theory, Planck’s equation, and the equations based on the first and second oxidation potentials (\(E_{1}^{\text{ox}}\) and \(E_{2}^{\text{ox}}\)) of A-E for the predicted supramolecular complexes 30 to 174. The Marcus theory is based 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 states 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, as well as the Gibbs free energy. The reorganization energy is defined as the energy required to reorganize the structure of the system from initial to final coordinates without changing the electronic state [37-42].

Although electrons are commonly described as residing in electron bands in bulk materials and electron orbitals in molecules, the following description will be 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. An electron is produced in a high-energy orbital and can be donated to an electron acceptor. Photo-induced electron transfer is an electron transfer that occurs when certain photoactive materials interact with light, including semiconductors that can be photo-activated, such as many solar cells, biological systems like those used in photosynthesis, and small molecules with suitable absorptions and redox states [36-42].

### Methods

The number of carbon atoms of the SWCNTs (Cn) was used as a structural index (1 to 29). All mathematical and graphing operations were performed using MATLAB-7.4.0 (R2007a) and Microsoft Office Excel 2003 programs. The number of carbon atoms in the SWCNTs (Cn) is a useful numerical and structural value in characterizing the empty fullerenes. However, we used other selected indices and the best results and equations for extending the physicochemical and electrochemical data.

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

\[
\Delta G_{et} = e(E_{D}^{*} - E_{A}^{*}) - \Delta E^{*} + \omega_{1},
\]

where \(e\) is the unit electrical charge, \(E_{D}^{*}\) and \(E_{A}^{*}\) are the reduction potentials of the electron donor and acceptor, respectively, \(\Delta E^{*}\) is the energy of the singlet or triplet excited state, and \(\omega_{1}\) is the work required to bring the donor and acceptor within the electron transfer (ET) distance. The work term in this expression can be considered to be ‘0’ in so far as an electrostatic complex exists before the electron transfer [36].

The Marcus theory of electron transfer implies rather weak (<0.05 eV) electronic coupling between the initial (locally excited (LE)) and final (ET) states, and assumes that the transition state is close to the crossing point of the LE and CT terms. The value of the electron transfer rate constant \(k_{et}\) is controlled by the activation free energy \(\Delta G^{*}_{et}\), which is a function of the reorganization energy (U/4) and the electron transfer driving force \(\Delta G_{et}\).
\[ \Delta G_{et} = (I/4)(1 + \Delta G_{et}/I)^2, \]  
\[ k_{et} = k_0 \exp(-\Delta G_{et}/RT). \]  

The reorganization energy of organic molecules ranges from 0.1 to 0.3 eV. In this study, we used the minimum amount of reorganization energy [37-42].

To calculate the maximum wavelengths (\(\lambda_{(n)}\); n = 1 to 2 of the electromagnetic photon for the electron transfer process in the nanostructure supramolecular complexes, we used Planck’s formula:

\[ \Delta G_{et} = \Delta E = h.c/\lambda_{(n)}. \]

In this study, this formula was also used to calculate the activation free energy of the electron transfer process [43].

**Results and discussion**

The electronic structures of the exohedral palladium complexes of [60], and [70] fullerenes with diphenylphosphinoferrocenyl, diphenylphosphinoruthenocenyl, and diphenylphosphinocymantrenyl ligands (\(\eta^2-C_mPd(dppf), \eta^2-C_mPd(dppr), \eta^2-C_mPd(dpccym)\)_2 (m = 60 and 70) (A to E), respectively) were studied by cyclic voltammetry and semi-empirical quantum chemical calculations. The C\(_{60}\)Pd(dppf), C\(_{60}\)Pd(dpccym)\(_2\), C\(_{60}\)Pd(dppr), C\(_{70}\)Pd(dpdp), and C\(_{70}\)Pd(dpccym)\(_2\) complexes were synthesized using the Schlenk technique by a previously described method [1,2,5,6]. The reaction required equivalent amounts of the respective fullerene, Pd\(_2(dba)_3\) complex (where dba is \(\eta^5\) phosphinoferrocenyl, diphenylphosphinoruthenocenyl, and diphenylphosphinocymantrenyl ligands) (5,5 armchair SWCNT for C\(_{20}\)H\(_{20}\) up to C\(_{190}\)H\(_{20}\)) 1 to 18 were calculated and presented in Table 1. The absolute redox energy for the above process. The free energy of an electron (e\(^-\)) at rest in the gas phase is set to zero [45,46]. The redox energy of the reaction (A + e\(^-\) \(\rightarrow\) A\(^-\) + E\(_{a}\)) can be calculated using a thermodynamic equation (see Equation 5). In this equation, \(\Delta G_s(A)\) and \(\Delta G_s(A^-)\) are the solvation energies of molecule A and its anion A\(^-\), respectively, and \(\Delta E_g(A \rightarrow A^-)\) is the energy difference between molecule A and its anion (which is defined as the redox energy in the gas phase). Based on this thermodynamic cycle, we can obtain \(\Delta E_g(A \rightarrow A^-)\), the absolute redox energy [45,46]:

\[ \Delta E_g(A \rightarrow A^-) = \Delta E_s(A \rightarrow A^-) + \Delta G_s(A) - AG_s(A^-). \]

By calculating the gas phase energies and solvation energies of molecule A and its anion A\(^-\), the absolute redox potential (scaled) of molecule A in solution can be derived. A scaling coefficient that translates electron affinity into standard redox potentials can be extracted [44-46]. As seen in the results of [16], the static TD-DFT and independently optimized structure were used to calculate the physicochemical and electronic structure of tubular aromatic molecules derived from the metallic (5,5) armchair single-walled carbon nanotubes using the hybrid nonlocal B3LYP function [8,47,48].

The reduction potential (\(\text{Red}E\)) of 1 to 18 can be calculated using the Gibbs equation (\(\Delta G = -nFE\)) and the definition of adiabatic electron affinity. In this equation, \(\Delta G\) is equal to the adiabatic electron affinity (the free energy of electron transfer, \(\Delta G_{et}\) in J mol\(^{-1}\), 1 eV = 96,471 J mol\(^{-1}\), F = 96,495 coulomb, and n = 1). For example, the reduction potentials (\(\text{Red}E\)) of C\(_{20}\)H\(_{20}\) and C\(_{90}\)H\(_{20}\) are equal to –0.34 and –0.89 V, respectively. The \(\text{Red}E\) of [SWCNT(5,5)-armchair-C\(_n\)H\(_{20}\)] (n = 20 to 190) 1 to 18 were calculated and are presented in Table 1. The amount of \(\text{Red}E\) (in V) = \(E_{aa}\) (in eV), where \(E_{aa}\) is the adiabatic electron affinity (see Table 1 for more details).

The values of the relative structural coefficients of the (5,5) armchair SWCNT for C\(_{20}\)H\(_{20}\) up to C\(_{190}\)H\(_{20}\) ([SWCNT(5,5)-armchair-C\(_n\)H\(_{20}\), 1 to 18], the adiabatic electron affinity (\(E_{aa}\) in eV) and the reduction potentials (\(\text{Red}E\)) in V) of 1 to 18 are shown in Table 1. The absolute value of \(E_{aa}\) or \(\text{Red}E\) increases with the number of carbon atoms in 1 to 18. From C\(_{20}\)H\(_{20}\) up to C\(_{190}\)H\(_{20}\), the point groups alternate between \(D_{5h}\) and \(D_{sh}\) [9]. Using the equations 8 to 16 in Table 2, the values in Table 1, and the Rehm-Weller equation, we extended our results to compounds 19 to 29.
Table 1 The values of the coefficients of SWCNT 1 to 18 and the complexes 30 to 119

| Number | Molecular formula | Point group | $E_{aa}$ (eV) | Red $E$ (V) | $[\text{SWCNT}]|^{(30\text{ to 47})}$ | $[\text{SWCNT}]|^{(48\text{ to 65})}$ | $[\text{SWCNT}]|^{(66\text{ to 83})}$ | $[\text{SWCNT}]|^{(84\text{ to 101})}$ | $[\text{SWCNT}]|^{(102\text{ to 119})}$ |
|--------|------------------|-------------|--------------|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1      | $C_{20}H_{30}$   | $D_{5d}$    | 0.34         | $-0.34$     | 27.2108        | 26.5078         | 30.9004         | 960.028         | 90.0940         |
| 2      | $C_{20}H_{30}$   | $D_{5d}$    | 0.89         | $-0.89$     | 39.8938        | 37.3480         | 43.8384         | 53.0380         | 39.6632         |
| 3      | $C_{20}H_{30}$   | $D_{5d}$    | 0.67         | $-0.67$     | 45.8206        | 43.6676         | 48.5603         | 54.9002         | 38.5102         |
| 4      | $C_{20}H_{30}$   | $D_{5d}$    | 1.14         | $-1.14$     | 45.6858        | 43.5245         | 48.3498         | 54.5226         | 38.5102         |
| 5      | $C_{20}H_{30}$   | $D_{5d}$    | 1.56         | $-1.56$     | 55.3440        | 52.0331         | 60.0336         | 64.8882         | 59.0336         |
| 6      | $C_{20}H_{30}$   | $D_{5d}$    | 1.34         | $-1.34$     | 50.2708        | 48.1178         | 53.9604         | 63.4150         | 53.9604         |
| 7      | $C_{20}H_{30}$   | $D_{5d}$    | 1.61         | $-1.61$     | 56.4970        | 54.3480         | 60.1866         | 69.6142         | 60.1866         |
| 8      | $C_{20}H_{30}$   | $D_{5d}$    | 1.98         | $-1.98$     | 60.0292        | 57.8762         | 64.8882         | 71.7166         | 64.8882         |
| 9      | $C_{20}H_{30}$   | $D_{5d}$    | 1.57         | $-1.71$     | 58.8030        | 56.6500         | 63.4926         | 71.9472         | 63.4926         |
| 10     | $C_{20}H_{30}$   | $D_{5d}$    | 1.90         | $-1.91$     | 61.1450        | 58.1441         | 64.8882         | 71.7166         | 64.8882         |
| 11     | $C_{20}H_{30}$   | $D_{5d}$    | 2.24         | $-2.24$     | 71.0248        | 68.9781         | 75.6136         | 82.0182         | 75.6136         |
| 12     | $C_{20}H_{30}$   | $D_{5d}$    | 2.06         | $-2.06$     | 66.8740        | 64.7826         | 71.7166         | 78.1734         | 71.7166         |
| 13     | $C_{20}H_{30}$   | $D_{5d}$    | 2.13         | $-2.13$     | 68.4882        | 66.5595         | 73.2100         | 80.0182         | 73.2100         |
| 14     | $C_{20}H_{30}$   | $D_{5d}$    | 2.43         | $-2.43$     | 75.0662        | 72.7108         | 80.0182         | 86.7056         | 80.0182         |
| 15     | $C_{20}H_{30}$   | $D_{5d}$    | 2.23         | $-2.23$     | 72.7108        | 70.1024         | 77.3308         | 83.7172         | 77.3308         |
| 16     | $C_{20}H_{30}$   | $D_{5d}$    | 2.53         | $-2.53$     | 77.1228        | 75.5652         | 84.3996         | 91.8018         | 84.3996         |

Equations 6 and 7 show the relationship between the number of carbon atoms (n) of [SWCNT(5,5)-armchair] and the adiabatic electron affinity ($E_{aa}$ in eV) and reduction potential ($E_{red}$ in V) of [SWCNT(5,5)-armchair-$C_{20}H_{30}$] (n = 20 to 190) 1 to 18, respectively. Equation 6, like Equation 7, shows the Nieperian logarithmic behavior of the relationship. The R squared value ($R^2$) for the graphs was 0.9461.

$$E_{aa} = 22.4171 \ln(n) - 66.853$$

Table 2 The Nieperian relationship equations 8 to 16

| Complexes 1 to 18 with ligands A to E | [SWCNT(5,5)-armchair-$C_{20}H_{30}$][R] (R = $n^2$-$C_n$Pd(dppf), $n^2$-$C_{30}$Pd(dppr), and $n^2$-$C_{n}$Pd(dppcyml)$_2$, n = 20 to 300 and m = 60 to 70) | Equation | $R^2$ | $\Delta \text{G}_{\text{free}} = a \ln(n) + b$ |
|-------------------------------------|---------------------------------------------------------------------------------|----------|-------|------------------------------------------|
| Stage (n)                          | Ligand                            | a        | b     |                                          |
| 1                                  | A                                  | 8        | 0.9461| 22.416                                   |
| 2                                  | B                                  | 9        | 0.9461| 22.416                                   |
| 1                                  | C                                  | 10       | 0.9461| 22.416                                   |
| 2                                  | D                                  | 11       | 0.9461| 22.416                                   |
| 1                                  | E                                  | 12       | 0.9461| 22.416                                   |

The said equations indicated the relationship between the number of carbon atoms in 1 to 18 and $\Delta \text{G}_{\text{free}}$ (n = 1.2) of [SWCNT(5,5)-armchair-$C_{20}H_{30}$] (n = 20 to 190) 1 to 18, with $n^2$-$C_n$Pd(dppf), $n^2$-$C_{30}$Pd(dppr), and $n^2$-$C_{n}$Pd(dppcyml)$_2$(m = 60 and 70) (A to E) in the complexes [SWCNT(5,5)-armchair-$C_{20}H_{30}$][R] (R = $n^2$-$C_n$Pd(dppf), $n^2$-$C_{30}$Pd(dppr), and $n^2$-$C_{n}$Pd(dppcyml)$_2$, n = 20 to 300 and m = 60 and 70) 30 to 119. The structures concerning these equations are shown in Figure 1.
Using these equations, we derived a good approximation for extending the formulas for the $E_{aa}$ and the $\text{Red} E$ to $[\text{SWCNT(5,5)}]_{\text{armchair-}C_nH_{20}}$ ($n = 200$ to 300) 19 to 29.

The absolute structural coefficients, $E_{aa}$ (in eV), and the $\text{Red} E$ (in V) of $[\text{SWCNT(5,5)}]_{\text{armchair-}C_nH_{20}}$ ($n = 20$ to 190) 1 to 18 are found in Table 1. The relationship between the index and the first and second free energies of electron transfer ($\Delta G_{\text{et}(n)}$, $n = 1,2$), as assessed using the Rehm-Weller equation based on the first and second oxidation potentials ($\alpha^0E_1$ and $\alpha^0E_2$) of A to E for the predicted supramolecular complexes between 1 to 18 with the $\eta^2-C_60Pd(dppf)$, $\eta^2-C_60Pd(dppr)$, and $\eta^2-C_60Pd(dppcym)_2$ ($m = 60$ and 70) ligands (A to E) as $[\text{SWCNT(5,5)}]_{\text{armchair-}C_nH_{20}}$ ($n = 20$ to 190) 1 to 18 to produce $[\text{SWCNT(5,5)}]_{\text{armchair-}C_nH_{20}}[R] (R = \eta^2-C_60Pd(dppf), \eta^2-C_60Pd(dppr)$, and $\eta^2-C_60Pd(dppcym)_2$, $n = 20$ to 300 and $m = 60$ and 70) 30 to 119, is presented.

Figure 2 shows the relationship between the number ($n$) of carbon atoms in the $[\text{SWCNT(5,5)}]_{\text{armchair}}$ 1 to 18 and the first and second free energies of electron transfer ($\Delta G_{\text{et}(n)}$, $n = 1,2$ kcal mol$^{-1}$) of the ligands $\eta^2-C_60Pd(dppf)$ (A). These data were fit using a regression with a second-order polynomial. The $R^2$ values for these graphs were 0.9461. We calculated the values of $\Delta G_{\text{et(1)}}$ and $\Delta G_{\text{et(2)}}$ of $[\text{SWCNT(5,5)}]_{\text{armchair-}C_nH_{20}}[\eta^2-C_60Pd(dppf)] (n = 20$ to 190) 30 to 47 using equations 1, 8, and 9 (see Tables 1 and 2). The predicted values of $\Delta G_{\text{et}(n)}$ ($n = 1,2$) for $[\text{SWCNT(5,5)}]_{\text{armchair-}C_9H_{20}}[\eta^2-C_60Pd(dppf)] (n = 20$ to 300) 30 to 47, and 120 to 130 were calculated using equations 8 and 9 (see Tables 2 and 3).

The first and second free energies of electron transfer ($\Delta G_{\text{et}(n)}$, $n = 1,2$ in kcal mol$^{-1}$) of the supramolecular complexes between the ligand $\eta^2-C_60Pd(dppr)$ B and $[\text{SWCNT(5,5)}]_{\text{armchair-}C_nH_{20}}$ ($n = 20$ to 190) 1 to 18 as presented $[\text{SWCNT(5,5)}]_{\text{armchair-}C_nH_{20}}[\eta^2-C_60Pd(dppr)] (n = 20$ to 190) 48 to 65 are shown in Table 1. Equations 10 and 11 show the second-order polynomial behavior between the number of carbon atoms of 1 to 18 and the free energies of electron transfers in the supramolecular nanostructures of 48 to 65. Using these equations, we achieved a good approximation for extending the first and second free energies of electron transfer ($\Delta G_{\text{et}(n)}; n = 1,2$ in kcal mol$^{-1}$) for the other $[\text{SWCNT(5,5)}]_{\text{armchair-}C_nH_{20}}[\eta^2-C_60Pd(dppr)] (n = 200$ to 300) 131 to 141. The $R^2$ values for the relationships were 0.9461. The predicted values of $\Delta G_{\text{et}(n)} (n = 1,2)$ for $[\text{SWCNT(5,5)}]_{\text{armchair-}C_nH_{20}}[\eta^2-C_60Pd(dppr)] (n = 200$ to 300) 131 to 141 were calculated using equations 10 and 11 (see Tables 2 and 3). Tables 1 and 3 show that the values of the first and second free energies of electron transfer ($\Delta G_{\text{et}(n)}$, $n = 1,2$) increased in the supramolecular complexes of $[\text{SWCNT(5,5)}]_{\text{armchair-}C_nH_{20}}[\eta^2-C_60Pd(dppr)] (n = 20$ to 300) 48 to 65 and 131 to 141 with increasing numbers of carbon atoms in the $[\text{SWCNT(5,5)}]_{\text{armchair-}C_nH_{20}}$ structures.

Figure 2 The relationship between the number of carbon atoms and free energies of ET, $[\text{SWCNT(5,5)}]_{\text{armchair-}C_nH_{20}}[\eta^2-C_60Pd(dppf)]$ complexes 30 to 47. The free energies of ET were calculated using the Rehm-Weller equation. The related curves for other complexes $[\text{SWCNT(5,5)}]_{\text{armchair-}C_nH_{20}}[\eta^2-C_60Pd(dppf)] (n = 20$ to 190) 30 to 47 have similar structures with this figure.
to 190) 1 to 18, as presented in [SWCNT(5,5)-armchair-C\(_n\)H\(_{20}\)]\([\eta^2\text{C}_{70}\text{Pd(dppcm)}]\)\(_2\) (n = 20 to 190) 66 to 83, are shown in Table 1. Equations 12 and 13 show the second-order polynomial relationship between the number of carbon atoms of 1 to 18 and the free energies of electron transfers at the supramolecular nanostructures of 66 to 83. Using these equations, we were able to extend the first and second free energies of electron transfer (\(\Delta G_{\text{et}(n)}\)) (n = 1,2) in kcal mol\(^{-1}\)) for [SWCNT(5,5)-armchair-C\(_n\)H\(_{20}\)]\([\eta^2\text{C}_{60}\text{Pd(dppcy)}]\)\(_2\) (n = 200 to 300) 142 to 152. The \(R^2\) values for the relationships were 0.9461. The predicted values of \(\Delta G_{\text{et}(n)}\) (n = 1,2) in the supramolecular complexes of [SWCNT(5,5)-armchair-C\(_n\)\(_{20}\)]\([\eta^2\text{C}_{60}\text{Pd(dppcy)}]\)\(_2\) (n = 200 to 300) 142 to 152 were calculated using equations 12 and 13 (Tables 2 and 3). The values of the first and second free energies of electron transfer (\(\Delta G_{\text{et}(n)}\)) (n = 1,2) increased in the supramolecular complexes of [SWCNT(5,5)-armchair-C\(_n\)\(_{20}\)]\([\eta^2\text{C}_{60}\text{Pd(dppcy)}]\)\(_2\) (n = 20 to 300) 66 to 83 and 142 to 152 with increasing numbers of carbon atoms in the [SWCNT(5,5)-armchair-C\(_n\)\(_{20}\)]\(_2\) structures (Tables 1 and 3).

The first and second free energies of electron transfer (\(\Delta G_{\text{et}(n)}\)) (n = 1,2) in kcal mol\(^{-1}\)) of the supramolecular complexes between the ligands \([\eta^2\text{C}_{70}\text{Pd(dpp)}]\) \(D\) and \(\eta^2\text{C}_{60}\text{Pd(dppe)}\) \(E\) with [SWCNT(5,5)-armchair-C\(_n\)\(_{20}\)]\(_2\) (n = 20 to 190) 1 to 18 as presented in [SWCNT(5,5)-armchair-C\(_n\)\(_{20}\)]\([\eta^2\text{C}_{60}\text{Pd(dpp)}]\)\(_2\) and [SWCNT(5,5)-armchair-C\(_n\)\(_{20}\)]\([\eta^2\text{C}_{60}\text{Pd(dppcy)}]\)\(_2\) (n = 20 to 190) 84 to 101 and 102 to 119, respectively, are shown in Table 1. Equations 14 to 15 and 16 to 17 show the second-order polynomial relationship between the number of carbon atoms of 1 to 18 and the free energies of electron transfers in the 84 to 101 and 102 to 119 nanostructures. Using these equations, we extended the first and second free energies of electron transfer (\(\Delta G_{\text{et}(n)}\)) (n = 1,2) in kcal mol\(^{-1}\)) for [SWCNT(5,5)-armchair-C\(_n\)\(_{20}\)]\([\eta^2\text{C}_{70}\text{Pd(dpp)}]\)\(_2\) and [SWCNT(5,5)-armchair-C\(_n\)\(_{20}\)]\([\eta^2\text{C}_{60}\text{Pd(dppcy)}]\)\(_2\) 153 to 163 and 164 to 174. The \(R^2\) for the relationships were 0.9461. The predicted values of \(\Delta G_{\text{et}(n)}\) (n = 1,2) in the supramolecular complexes of [SWCNT(5,5)-armchair-C\(_n\)\(_{20}\)]\([\eta^2\text{C}_{70}\text{Pd(dpp)}]\)\(_2\) and [SWCNT(5,5)-armchair-C\(_n\)\(_{20}\)]\([\eta^2\text{C}_{60}\text{Pd(dppcy)}]\)\(_2\) 84 to 119 and 153 to 174 with increasing numbers of carbon atoms in the [SWCNT(5,5)-armchair-C\(_n\)\(_{20}\)]\(_2\) structures (Tables 1 and 3).

The Marcus theory is currently the dominant theory of electron transfer in chemistry. This theory is widely accepted because it accurately predicts electron transfer rates. 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 [37-42].

ET is one of the most important chemical processes in nature and plays a central role in many biological, physical, and chemical (both organic and inorganic) systems. Solid-state electronics depends on controlling ET in semiconductors. Current molecular electronics depends critically on understanding and controlling the transfer of electrons in and between molecules and nanostructures. Electron transfer is a very simple chemical reaction, which

| Number | Molecular formula | Point group | Adiabatic electron affinity (eV) | \(\Delta G_{\text{et}(n)}\) (120 to 130) | \(\Delta G_{\text{et}(n)}\) (131 to 141) | \(\Delta G_{\text{et}(n)}\) (142 to 152) | \(\Delta G_{\text{et}(n)}\) (153 to 163) | \(\Delta G_{\text{et}(n)}\) (164 to 174) |
|--------|------------------|-------------|-------------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| 19     | C\(_{200}\)H\(_{100}\) | D\(_{5h}\)  | 2.49                          | -2.49                    | 76.7898                  | 84.8608                  | 80.4794                  | 89.9340                  | 80.4794                  | 88.8586                  |
| 20     | C\(_{210}\)H\(_{100}\) | D\(_{5h}\)  | 2.53                          | -2.53                    | 77.1722                  | 85.7832                  | 81.4018                  | 90.8564                  | 81.4018                  | 88.8710                  |
| 21     | C\(_{220}\)H\(_{100}\) | D\(_{5h}\)  | 2.57                          | -2.57                    | 78.6346                  | 86.7056                  | 82.3242                  | 91.7788                  | 82.3242                  | 90.7034                  |
| 22     | C\(_{230}\)H\(_{100}\) | D\(_{5h}\)  | 2.60                          | -2.60                    | 79.2624                  | 87.3974                  | 83.0160                  | 92.4706                  | 83.0160                  | 90.3952                  |
| 23     | C\(_{240}\)H\(_{100}\) | D\(_{5h}\)  | 2.64                          | -2.64                    | 80.2488                  | 88.3198                  | 83.9298                  | 93.4390                  | 83.9298                  | 91.3176                  |
| 24     | C\(_{250}\)H\(_{100}\) | D\(_{5h}\)  | 2.67                          | -2.67                    | 80.9406                  | 89.0116                  | 84.6302                  | 94.0848                  | 84.6302                  | 92.0094                  |
| 25     | C\(_{260}\)H\(_{100}\) | D\(_{5h}\)  | 2.71                          | -2.71                    | 81.6830                  | 89.9340                  | 85.5526                  | 95.0072                  | 85.5526                  | 92.9318                  |
| 26     | C\(_{270}\)H\(_{100}\) | D\(_{5h}\)  | 2.74                          | -2.74                    | 82.5548                  | 90.6258                  | 86.2444                  | 95.6990                  | 86.2444                  | 94.6326                  |
| 27     | C\(_{280}\)H\(_{100}\) | D\(_{5h}\)  | 2.77                          | -2.77                    | 83.2466                  | 91.3176                  | 86.9362                  | 96.0088                  | 86.9362                  | 94.3154                  |
| 28     | C\(_{290}\)H\(_{100}\) | D\(_{5h}\)  | 2.80                          | -2.80                    | 83.9384                  | 92.0094                  | 87.6258                  | 97.0826                  | 87.6258                  | 95.0072                  |
| 29     | C\(_{300}\)H\(_{100}\) | D\(_{5h}\)  | 2.83                          | -2.83                    | 84.6302                  | 92.7012                  | 88.4772                  | 97.7744                  | 88.4772                  | 95.6990                  |
can be used to gain insight into other kinds of chemistry and biochemistry. Electron transfer is fundamental in chemistry [37-42].

The free energy of electron transfer $\Delta G_{et}$ is the difference between the reactants and the products, and $\Delta G^{\neq}$ is the activation energy. The reorganization energy is the energy required to force the reactants to have the same nuclear configuration as the products without permitting the electron transfer. If the entropy changes are ignored, the free energy becomes energy or potential energy [37-42].

Using Equation 2, we calculated the first and second activation free energies of electron transfer, $\Delta G^{et(1)}_{et}$ for 30 to 174 in accordance with the Marcus theory; see Table 4. Figure 3 shows the surfaces of the free energies of electron transfer $\Delta G_{et(n)}$ and $\Delta G^{et(1)}_{et(n)} (n = 1, 2)$ between [SWCNT (5,5)-armchair-C$_6$H$_{20}$] (n = 20 to 300) 1 to 29 and the ligands $\eta^2$-C$_{mn}$Pd(dppf), $\eta^2$-C$_{mp}$Pd(dppp), and $\eta^2$-C$_{nm}$Pd(dppcm)$_2$ (m = 60 and 70) A to E to produce [SWCNT (5,5)-armchair-C$_6$H$_{20}$][R] (R = $\eta^2$-C$_{mn}$Pd(dppf), $\eta^2$-C$_{mp}$Pd(dppp), and $\eta^2$-C$_{nm}$Pd(dppcm)$_2$), n = 20 to 300 and $m = 60$ and 70) 30 to 174. The values of the first and second activation free energies of electron transfer $\Delta G^{et(n)}_{et(1)} (n = 1, 2)$ for 30 to 174 increased with increasing $\Delta G^{et(n)}_{et(1)}$ and the numbers of carbon atoms in the complexes, while the

### Table 4 The values of the first and second free activation energies of electron transfer

| Number of SWCNT (5,5)-armchair-C$_6$H$_{20}$ | $\Delta G^{et(1)}_{et}$ | $\Delta G^{et(n)}_{et}$ |
|---------------------------------------------|------------------------|------------------------|
| (30 to 47)                                  | (48 to 65)             | (66 to 83)             |
|                                             | (84 to 101)            | (102 to 119)           |
| 1                                           | 35.9794                | 53.6851                |
| 2                                           | 65.3881                | 88.6426                |
| 3                                           | 52.5782                | 76.6133                |
| 4                                           | 81.6382                | 107.4149               |
| 5                                           | 112.9940               | 143.0080               |
| 6                                           | 95.9534                | 123.7299               |
| 7                                           | 117.0655               | 147.5840               |
| 8                                           | 149.4346               | 183.6859               |
| 9                                           | 125.4248               | 156.9521               |
| 10                                          | 143.0080               | 175.5331               |
| 11                                          | 174.5111               | 211.4155               |
| 12                                          | 156.9521               | 192.0105               |
| 13                                          | 163.6813               | 199.4459               |
| 14                                          | 141.1025               | 223.9118               |
| 15                                          | 185.7467               | 223.7339               |
| 16                                          | 173.5395               | 210.3310               |
| 17                                          | 204.8434               | 244.6435               |
| 18                                          | 192.4240               | 235.2351               |
| 19                                          | 200.5197               | 239.9162               |
| 20                                          | 124.5481               | 169.5616               |
| 21                                          | 156.9521               | 192.0105               |
| 22                                          | 163.6813               | 199.4459               |
| 23                                          | 141.1025               | 223.9118               |
| 24                                          | 185.7467               | 223.7339               |
| 25                                          | 173.5395               | 210.3310               |
| 26                                          | 204.8434               | 244.6435               |
| 27                                          | 192.4240               | 235.2351               |
| 28                                          | 200.5197               | 239.9162               |
| 29                                          | 238.7416               | 281.5684               |

$\text{[SWCNT(5,5)-armchair-C}_6\text{H}_{20}\text{][R]} (R = \eta^2\text{-C}_{mn}\text{Pd(dppf)}, \eta^2\text{-C}_{mp}\text{Pd(dppp)}, \text{and } \eta^2\text{-C}_{nm}\text{Pd(dppcm)}_2, n = 20 to 190 and m = 60 and 70) \text{ complexes 30 to 119, between 1 to 18 and A to E.}$
kinetic rate constants of the electron transfers decreased with increasing $\Delta G_{et(n)}$ and $\Delta G_{et(n)}^*$ ($n=1,2$) (see Tables 1, 3, and 4, and Figure 3).

Because of the good linear correlations between $\Delta G_{et(n)}$ ($n=1,2$), $E_{aa}$ and $RedE$ of 1 to 18 with the ligands A to E, we used the values of $E_{aa}$ and $RedE$ to calculate the free energies of electron transfer ($\Delta G_{et}$ in kcal mol$^{-1}$) of [SWCNT(5,5)-armchair-C$_n$H$_{20}$] ($n=20$ to $190$) 1 to 18 to produce [SWCNT(5,5)-armchair-C$_n$H$_{20}$][R] ($R=\eta^2$-C$_m$Pd(dppf), $\eta^2$-C$_m$Pd(dppr), and $\eta^2$-C$_m$Pd(dpccym)$_2$, $m=60$ and 70) $n=20$ to 190, 30 to 119, and $n=200$ to 300, 120 to 174. The electron affinity and reduction potential have the same magnitude with opposite signs. The free energy of electron transfer can be calculated with the Rehm-Weller equation, which we determined was linearly dependent on the electron affinity of the compounds studied here. In Tables 1 and 3, the values of the first and second free energies of electron transfer ($\Delta G_{et(n)}$, $n=1,2$) obtained for supramolecular complexes 30 to 119 and 120 to 174 from equations 8 to 17 (Table 2) are compared with those obtained with the Rehm-Weller equation.

The number of carbon atoms ($n$), $E_{aa}$, $RedE$, and $\Delta G_{et(n)}$ ($n=1,2$) of [SWCNT(5,5)-armchair-C$_n$H$_{20}$] ($n=20$ to 300) 1 to 29 and their complexes with the ligands $\eta^2$-C$_m$Pd(dppf), $\eta^2$-C$_m$Pd(dppr), and $\eta^2$-C$_m$Pd(dpccym)$_2$ ($m=60$ and 70) (A to E) as [SWCNT(5,5)-armchair-C$_n$H$_{20}$][R] ($R=\eta^2$-C$_m$Pd(dppf), $\eta^2$-C$_m$Pd(dpccym)$_2$, and $\eta^2$-C$_m$Pd(dpccym)$_2$, $m=200$ to 300 and $m=60$ and 70) supramolecular complexes 30 to 174 are shown in Table 3. The $RedE$ were extended for C$_{200}$H$_{20}$ up to C$_{200}$H$_{20}$ ([SWCNT(5,5)-armchair-C$_n$H$_{20}$], 19 to 29). The calculated results for $RedE$ as well as the free energies of electron transfer ($\Delta G_{et(n)}$, $n=1,2$, in kcal mol$^{-1}$) according to the Rehm-Weller equation between A to E with 19 to 29 in structures 120 to 174 are presented in Table 3.

As shown in Figure 2, the periodicity of the plotted points is 3, which is common among benzenoids. Using Equation 1 (Rehm-Weller equation) and equations 2 to 17, the values of $E_{aa}$, $RedE$, $\Delta G_{et(n)}$ ($n=1,2$), $\Delta G_{et(n)}^*$, and $\lambda_{et(n)}$ ($n=1,2$) for 30 to 174 were calculated. The number of carbon atoms showed a good relationship with the values of the $E_{aa}$, the $RedE$ of [SWCNT(5,5)-armchair-C$_n$H$_{20}$] ($n=20$ to 190) 1 to 18 and 19 to 29, and the $\Delta G_{et}$ in [SWCNT(5,5)-armchair-C$_n$H$_{20}$][R] ($R=\eta^2$-C$_m$Pd(dppf), $\eta^2$-C$_m$Pd(dpccym)$_2$, and $\eta^2$-C$_m$Pd(dpccym)$_2$, $n=20$ to 300 and $m=60$ and 70) supramolecular complexes 30 to 174. Figure 3 shows the free energy surfaces of electron transfer $\Delta G_{et(n)}$ and $\Delta G_{et(n)}^*$ ($n=1,2$) between 1 to 29 and the ligands A to E in the structures of 30 to 174, which were calculated using equations 1 to 17 and are shown in Tables 1, 2, 3, 4, and 5. With the appropriate equations, we calculated the $E_{aa}$, the $RedE$ in 1 to 18 and 19 to 29, the first and second free energies of electron transfer ($\Delta G_{et}$ in kcal mol$^{-1}$), and the first and second activation free energies of electron transfer $\Delta G_{et(n)}^*$ for 30 to 174 in accordance with the Marcus theory.

We determined the values of the maximum wavelengths ($\lambda_{et(n)}$, $n=1$ or 2, in nm) for each stage of the electron transfer process in the nanostructure supramolecular complexes 30 to 174 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–vis (190 to 800 nm) range of the
The maximum wavelengths (\(\lambda_{(i)}\); \(n = 1\) or \(2\)) depended on the \(\Delta G_{et(i)}\) value in each stage (Equation 4 and Table 5).

The supramolecular complexes of armchair single-wall nanotubes [SWCNT(5,5)-armchair-C\(_n\)H\(_{20}\)] \((n = 20\) to \(300\)) 1 to 18 and 19 to 29 with the ligands \(\eta^2-C_{60}\)Pd (dppf), \(\eta^2-C_{60}\)Pd (dppr), and \(\eta^2-C_{60}\)Pd (dppcyom) \((m = 60\) and \(70\) \((A \rightarrow E)\) contain a strongly electron-withdrawing fullerene cage and a metallocene group, which can be either electron releasing (ruthenocene) or electron withdrawing (cymantrene) and is linked with the cage through a bisdiphenyl phosphinepalladium bridge. The oxidation potentials

| Number of SWCNT (5,5)-armchair-C\(_n\)H\(_{20}\) | Molecular formula | \[SWCNT][\eta^2-C_{60}\]Pd (dppf) \(\lambda_{(1)}\) | \[SWCNT][\eta^2-C_{60}\]Pd (dppr) \(\lambda_{(1)}\) | \[SWCNT][\eta^2-C_{60}\]Pd (dppcyom) \(\lambda_{(1)}\) | \[SWCNT][\eta^2-C_{70}\]Pd (dppr) \(\lambda_{(1)}\) | \[SWCNT][\eta^2-C_{70}\]Pd (dppcyom) \(\lambda_{(1)}\) |
|---|---|---|---|---|---|---|
| 1 | C\(_{20}\)H\(_{20}\) | 794 532 | 847 567 | 655 429 | 804 543 | 655 467 |
| 2 | C\(_{20}\)H\(_{20}\) | 437 322 | 458 339 | 378 272 | 441 328 | 378 291 |
| 3 | C\(_{20}\)H\(_{20}\) | 543 388 | 573 410 | 463 322 | 549 395 | 463 347 |
| 4 | C\(_{20}\)H\(_{20}\) | 350 266 | 365 278 | 307 228 | 353 270 | 307 242 |
| 5 | C\(_{20}\)H\(_{20}\) | 253 200 | 262 208 | 226 175 | 255 202 | 226 184 |
| 6 | C\(_{20}\)H\(_{20}\) | 298 231 | 310 241 | 264 200 | 300 234 | 264 212 |
| 7 | C\(_{20}\)H\(_{20}\) | 244 194 | 253 201 | 219 169 | 246 196 | 219 179 |
| 8 | C\(_{20}\)H\(_{20}\) | 191 156 | 197 161 | 174 138 | 192 157 | 174 145 |
| 9 | C\(_{10}\)H\(_{20}\) | 228 182 | 236 189 | 205 160 | 229 184 | 205 169 |
| 10 | C\(_{11}\)H\(_{20}\) | 200 162 | 206 168 | 181 143 | 201 164 | 181 150 |
| 11 | C\(_{12}\)H\(_{20}\) | 164 135 | 169 139 | 150 121 | 165 137 | 150 126 |
| 12 | C\(_{13}\)H\(_{20}\) | 182 149 | 188 154 | 166 132 | 183 150 | 166 139 |
| 13 | C\(_{14}\)H\(_{20}\) | 175 143 | 180 148 | 159 128 | 176 145 | 159 134 |
| 14 | C\(_{15}\)H\(_{20}\) | 147 123 | 151 126 | 135 110 | 148 124 | 135 115 |
| 15 | C\(_{16}\)H\(_{20}\) | 154 128 | 158 132 | 141 115 | 155 129 | 141 120 |
| 16 | C\(_{17}\)H\(_{20}\) | 165 136 | 169 140 | 150 121 | 166 137 | 150 127 |
| 17 | C\(_{18}\)H\(_{20}\) | 139 117 | 143 120 | 128 105 | 140 118 | 128 110 |
| 18 | C\(_{19}\)H\(_{20}\) | 146 121 | 150 125 | 134 109 | 146 123 | 134 114 |
| 19 | C\(_{20}\)H\(_{20}\) | 142 119 | 146 123 | 131 107 | 143 120 | 131 112 |
| 20 | C\(_{21}\)H\(_{20}\) | 139 117 | 143 120 | 128 105 | 140 118 | 128 110 |
| 21 | C\(_{22}\)H\(_{20}\) | 137 115 | 140 118 | 126 103 | 137 116 | 126 108 |
| 22 | C\(_{23}\)H\(_{20}\) | 134 113 | 138 116 | 124 102 | 135 114 | 124 106 |
| 23 | C\(_{24}\)H\(_{20}\) | 132 111 | 135 114 | 121 100 | 132 112 | 121 104 |
| 24 | C\(_{25}\)H\(_{20}\) | 130 109 | 133 112 | 120 99 | 130 110 | 120 103 |
| 25 | C\(_{26}\)H\(_{20}\) | 127 107 | 130 110 | 117 97 | 128 108 | 117 101 |
| 26 | C\(_{27}\)H\(_{20}\) | 125 106 | 128 109 | 116 96 | 126 107 | 116 100 |
| 27 | C\(_{28}\)H\(_{20}\) | 123 104 | 126 107 | 114 95 | 124 105 | 114 98 |
| 28 | C\(_{29}\)H\(_{20}\) | 121 103 | 125 106 | 112 93 | 122 104 | 112 97 |
| 29 | C\(_{30}\)H\(_{20}\) | 120 101 | 123 104 | 111 92 | 120 102 | 111 96 |

The values are calculated using the Plank's formula. The wavelengths of [SWCNT(5,5)-armchair-C\(_n\)H\(_{20}\)] \([R = \eta^2-C_{60}\]Pd (dppf), \(\eta^2-C_{60}\)Pd (dppr), and \(\eta^2-C_{60}\)Pd (dppcyom) \((n = 20\) to \(300\) and \(m = 60\) to \(70)\) 30 to 174.

Conclusions

The complexes \(\eta^2-C_{60}\)Pd (dppf), \(\eta^2-C_{60}\)Pd (dppr), and \(\eta^2-C_{60}\)Pd (dppcyom) \((m = 60\) and \(70\) \((A \rightarrow E)\) contain a strongly electron-withdrawing fullerene cage and a metallocene group, which can be either electron releasing (ruthenocene) or electron withdrawing (cymantrene) and is linked with the cage through a bisdiphenyl phosphinepalladium bridge. The oxidation potentials
(\alpha E_1 \text{ and } \alpha E_2) \text{ of } \eta^2-C_{n}Pd(dppf), \eta^2-C_{n}Pd(dppr), \text{ and } \eta^2-C_{n}Pd(dppcy)_{2} (m = 60 \text{ and } 70) \text{ (A to E) have been reported. In this study, we identified structural relationships between the number of carbon atoms and the } E_{291}, \text{ the values of the } \text{Red } E \text{ of } [\text{SWCNT } (5,5)-\text{armchair-C}_{n}H_{2n-1} (n = 20 \text{ to } 300)] \text{ 1 to 18 and 19 to 29, the } \Delta G_{et}^{n} \text{ (n), and the } \Delta G_{et}^{n} \text{ for the complexes 30 to 174. The number of carbon atoms is strongly correlated with the values of } E_{291} \text{ and } \text{Red } E \text{ in the } (5,5) \text{ armchair SWCNT 1 to 18 and 19 to 29, which are important factors in characterizing these materials. The values of } \Delta G_{et}^{n} \text{ and } \Delta G_{et}^{n} (n = 1, 2) \text{ were calculated using the Rehm-Weller equation and Equations 2 and 3 for 30 to 119 and 120 to 174 supramolecular nanostructure complexes, respectively. The maximum wavelengths of the electromagnetic photons in the photoelectron transfer process for each stage } (\lambda_{et} (n) \text{ n = 1 to 2, in nm) of the nanostructure complexes 30 to 174 were calculated with Planck's equation. The novel supramolecular complexes and the calculated values have neither been synthesized nor reported previously. Using this model and the associated equations, we can easily calculate the } E_{291}, \text{ Red } E, \Delta G_{et}^{n} (n) \text{ (kcal mol}^{-1}) \text{, and } \lambda_{et} (n) (n = 1, 2; \text{ in nm) of this family of compounds 30 to 174 with good approximation.}

Competing interests
The authors declare that they have no competing interests.

Authors' contributions
AAT carried out the ET investigations. This study was a part of AAT's studies in ET process between important molecules and nanostructures. ZTH participated in the statistical analysis and background part of the study. All authors read and approved the final manuscript.

Authors' information
AAT is professor of Organic Chemistry and is an academic member of the Razi University (Kermanshah-Iran) since 2012. He was the academic member of Islamic Azad University (IAU), Arak, Iran from 1998 to 2012. AAT has spent his post-doctorate at The University of Queensland (UQ), Brisbane, Australia in Reactive Intermediates and Unusual Molecules Group under the supervision of Professor Curt Wentrup in Brisbane, Australia during 2006 and 2007. He has as well developed his scientific activities in Professor Curt Wentrup's laboratory at The University of Queensland and under his supervision in July to September of 2008 and August to September of 2009. Professor AAT has worked in The University of New England (UNE), Armidale, NSW, Australia with a sabbatical opportunity with Professor Stephen Glover’s group from 2011 to 2012. AAT has won national prizes for his scientific paper (ISI, ISC, educational and propagation publication), books, invention, scientific activities, and conferences papers until now. AAT is one of the Members of the Central Committee of the Iranian Chemical Society (CCICS). ZTH has masters degree in Organic Chemistry from Islamic Azad University (IAU), Arak, Iran in 2011. ZTH has studied on theoretical electron transfer process between the exohedral metallofullerenes of Pd and SWCNT(5,5)-armchair nanotubes under the supervision of AAT.

Acknowledgments
The corresponding author gratefully acknowledges his colleagues in the Chemistry Department of The University of New England (UNE), Australia for their useful suggestions.

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Received: 20 March 2012 Accepted: 5 March 2013
Published: 10 April 2013

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doi:10.1186/2228-5326-3-22
Cite this article as: Taherpour and Talebi-Haftadori: Free energies, kinetics, and photoelectron-transfer properties, and theoretical and quantitative structural relationship studies of [SWCNT(5,5)-armchair-CnH20] (R = N=Pd(dppe), N3=Pd(dpdppe), and N3=C-Pd(dpdppe)), n = 20 to 300 and m = 60 and 70) nanostructure complexes. International Nano Letters 2013 3:22

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