Int. J. Electrochem. Sci., 6 **(2011)** 5482 - 5498

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

Structural Relationships and Theoretical Study of Free Energies of Electron Transfer, Electrochemical Properties, and Electron Transfer Kinetic of *p*-Phenylenediamine Derivatives With Fullerenes in Nanostructure [R].C_n (R= TMPD, DHDMP, TMDAD and DHDAP) Supramolecular Complexes

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Received: 15 August 2011 / *Accepted:* 6 October 2011 / *Published:* 1 November 2011

Fullerenes are a family of carbon allotropes, molecules composed entirely of carbon, that take the forms of spheres, ellipsoids and cylinders. Various empty carbon fullerenes (C_n) with different carbon atoms have been obtained and investigated. The *p*-phenylenediamine derivatives have shown the important electron-transfer properties. Topological indices are purported to correlate chemical structures with various chemical and physical properties. They have been successfully used to construct effective and useful mathematical methods to establish clear relationships between structural data and the physical properties of these materials. In this study, the number of carbon atoms in the fullerenes was used as an index to establish a relationship between the structures of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD), 5,10-dihydro-5,10-dimethylphenazine (DHDMP), *N,N,N',N'*-tetramethyl-3,6-diaminodurene (TMDAD) and dodecahydro-3a,9a-diazaperylene (DHDAP), 1-4 as the most well-known redox systems and fullerenes C_n (n=60, 70, 76, 82 and 86), which create [TMPD].C_n, A-1 to A-5, [DHDMP].C_n, B-1 to B-5, [TMDAD].C_n, C-1 to C-5 and [DHDAP].C_n, D-1 to D-5. The relationship between the number of carbon atoms and the free energies of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) are assessed using the *Rehm-Weller* equation for A-1 to A-5, B-1 to B-5, C-1 to C-5 and D-1 to D-5 supramolecular [R].C_n (R=TMPD, DHDMP, TMDAD and DHDAP) complexes. Calculations are presented for the four reduction potentials (${}^{Red.}E_1$ to ${}^{Red.}E_4$) of fullerenes C_n. The results were used to calculate the four free-energies of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) of supramolecular complexes A-1 to A-5, B-1 to B-5, C-1 to C-5 and D-1 to D-5 (5-40) for fullerenes C_{60} to C_{300}. The first to forth free activation energies of electron transfer and kinetic rate constants of the electron transfers, $\Delta G_{et(n)}^{\#}$ ($\Delta G_{et(1)}^{\#}$ to $\Delta G_{et(4)}^{\#}$) and k_{et} (n=1-4), respectively, were also calculated in this study for A-1 to A-5, B-1 to B-5, C-1 to C-5 and D-1 to D-5 (compounds 5-40) in accordance with the *Marcus* theory.

Keywords: Fullerenes; *p*-Phenylenediamine; Rehm-Weller equation; Free energy of electron transfer; Electron transfer properties; Activated free energies of electron transfer; Kinetic constant of electron transfer; Marcus Theory; Molecular modeling.

1. INTRODUCTION

The *p*-phenylenediamine derivatives have important electron-transfer properties. The most well-known redox molecular systems are *N,N,N',N'*-tetraalkyl-*p*-phenylenediamines, and particularly *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) and their derivatives which typically undergoing two well-separated (*vide infra*) chemically and electrochemically reversible one-electron oxidations.[1,2] This class of compounds had been considered in electrochemical studies [1,3] and photoinduced electron transfer [1,4]. They had been investigated as derivatizing agents for electrodes in conjunction with redox mediation of biological reagents,[1,5] as electrochromic materials,[1,6] and as flow indicators in electrochemically generated magnetohydrodynamic convection.[1,7]

The structures of four representative *p*-phenylenediamines 1-4 to the discussion are: *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD), 5,10-dihydro-5,10-dimethylphenazine (DHDMP), dodecahydro-3a,9a-diazaperylene (DHDAP) and *N,N,N',N'*-tetramethyl-3,6-diaminodurene (TMDAD).[1] The various derivatives of *p*-phenylenediamine have demonstrated the typical pattern of lower redox potentials as the degree of methylation increases.[1] The results had shown that TMPD has been the easiest to oxidize homologue in that series of compounds. In fact it is one of the most easily oxidizable organic compounds.[1] Methylation of the phenyl ring of TMPD did not lower the redox potential any further of the other derivatives. Compound *N,N,N',N'*-tetramethyl-3,6-diaminodurene (TMDAD) was not only more difficult to oxidize than TMPD, but also according to Evans and Hu, the second one-electron oxidation occurred at a less positive potential than the first one.[1,8,9] The electrochemical oxidation of TMDAD yielded directly the two-electron oxidized form. Evans and co-workers had proposed that this redox potential reversal is due to large conformational changes occurring during the oxidation of TMDAD, but not of TMPD.[1,8,9]

Since the discovery of fullerenes (C_n), one of the main classes of carbon compounds, the unusual structures and physicochemical properties of these molecules have been discovered, and many potential applications and physicochemical properties have been 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.

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 *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD), 5,10-dihydro-5,10-dimethylphenazine (DHDMP), *N,N,N',N'*-tetramethyl-3,6-diaminodurene (TMDAD) and dodecahydro-3a,9a-diazaperylene (DHDAP), 1-4, 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 [TMPD].C_n, A-1 to A-5, [DHDMP].C_n, B-1 to B-5, [TMDAD].C_n, C-1 to C-5 and [DHDAP].C_n, D-1 to D-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 TMPD, DHDMP, TMDAD and DHDAP 1-4 as a class of electron-transfer radicals, with fullerenes C_{60} to C_{300} ([*p*-phenylenediamine derivatives].C_n complexes), i.e.: [TMPD].C_n; 5-9 & 25-28, [DHDMP].C_n; 10-14 & 29-32, [TMDAD].C_n; 15-19 & 33-36 and [DHDAP].C_n; 20-24 & 37-40 (supramlecular complexes 5-40). 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 and D-1 to D-9. See Equations 1 to 19, Tables 1 to 4 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 [TMPD].C_n; 5-9 & 25-28, [DHDMP].C_n; 10-14 & 29-32, [TMDAD].C_n; 15-19 & 33-36 and

[DHDAP].C_n; 20-24 & 37-40 (supramlecular complexes 5-40). See Equations 2 and 3, Tables 5 to 8 and Figure 3.

Table 1. The data values on the *N*,*N*,*N'*,*N'*-Tetramethyl-para-phenylenediamine (TMPD) **A-1** to **A-5** and the values of the 4 free energies of electron transfer (ΔG_{et}), in kcal mol^{-1}, between TMPD with C_n (as [TMPD].C_n compounds A-6 to A-9) (forms 5-9 and 25-28) 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 [TMPD].C_n**	**(ΔG_{et}) in kcal mol^{-1} [TMPD].C_n**			
			$\Delta G_{et(1)}$*	$\Delta G_{et(2)}$*	$\Delta G_{et(3)}$*	$\Delta G_{et(4)}$*
5	A-1	[TMPD].C_{60}	18.31 (18.22)	27.06 (26.98)	37.51 (37.36)	48.12 (47.96)
6	A-2	[TMPD].C_{70}	16.96 (17.52)	25.55 (26.52)	34.29(35.51)	44.16 (45.43)
7	A-3	[TMPD].C_{76}	13.89 (14.07)	21.96 (21.45)	32.12(32.05)	41.41 (41.51)
8	A-4	[TMPD].C_{82}	9.13 (8.30)	16.33 (16.37)	29.77(28.82)	38.38 (37.13)
9	A-5	[TMPD].C_{86}	5.02 (5.56)	11.46 (11.99)	28.10(29.29)	36.21 (37.59)
25	A-6	[TMPD].C_{78}	12.49	20.31	31.35	40.43
26	A-7	[TMPD].C_{84}	7.17	14.01	28.94	37.31
27	A-8	[TMPD].C_{96}	-8.55	-4.65	23.58	30.22
28	A-9	[TMPD].C_{120}	-60.31	-66.26	10.70	12.67

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

Table 2. The data values on the 5,10-dihydro-5,10-dimethylphenazine (DHDMP) B-1 to B-5 and the values of the 4 free energies of electron transfer (ΔG_{et}), in kcal mol^{-1}, between DHDMP with C_n (as [DHDMP].C_n compounds B-6 to B-9) (forms 10-14 and 29-32) 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 [DHDMP].C_n**	**(ΔG_{et}) in kcal mol^{-1} [DHDMP].C_n**			
			$\Delta G_{et(1)}$*	$\Delta G_{et(2)}$*	$\Delta G_{et(3)}$*	$\Delta G_{et(4)}$*
10	B-1	[DHDMP].C_{60}	19.23 (19.14)	27.98 (27.90)	38.54 (38.28)	49.30 (48.89)
11	B-2	[DHDMP].C_{70}	17.87 (18.45)	26.47 (27.44)	35.37(36.43)	45.43 (46.35)
12	B-3	[DHDMP].C_{76}	14.81 (14.99)	22.87 (22.37)	33.23(32.98)	42.74 (42.43)
13	B-4	[DHDMP].C_{82}	10.05 (9.22)	17.25 (17.29)	30.91(29.75)	39.77 (38.05)
14	B-5	[DHDMP].C_{86}	5.93 (6.39)	12.38 (12.91)	29.26(30.21)	37.65 (38.51)
29	B-6	[DHDMP].C_{78}	13.41	21.23	32.47	41.78
30	B-7	[DHDMP].C_{84}	8.08	14.93	30.09	38.72
31	B-8	[DHDMP].C_{96}	-7.64	-3.73	24.79	31.79
32	B-9	[DHDMP].C_{120}	-59.40	-65.34	12.02	14.65

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

Table 3. The data values on the *N*,*N*,*N'*,*N'*-tetramethyl-3,6-diaminodurene (TMDAD) C-1 to C-5 and the values of the 4 free energies of electron transfer (ΔG_{et}), in kcal mol^{-1}, between TMDAD with C_n (as [TMDAD].C_n compounds C-6 to C-9) (forms 15-19 and 33-36) 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).

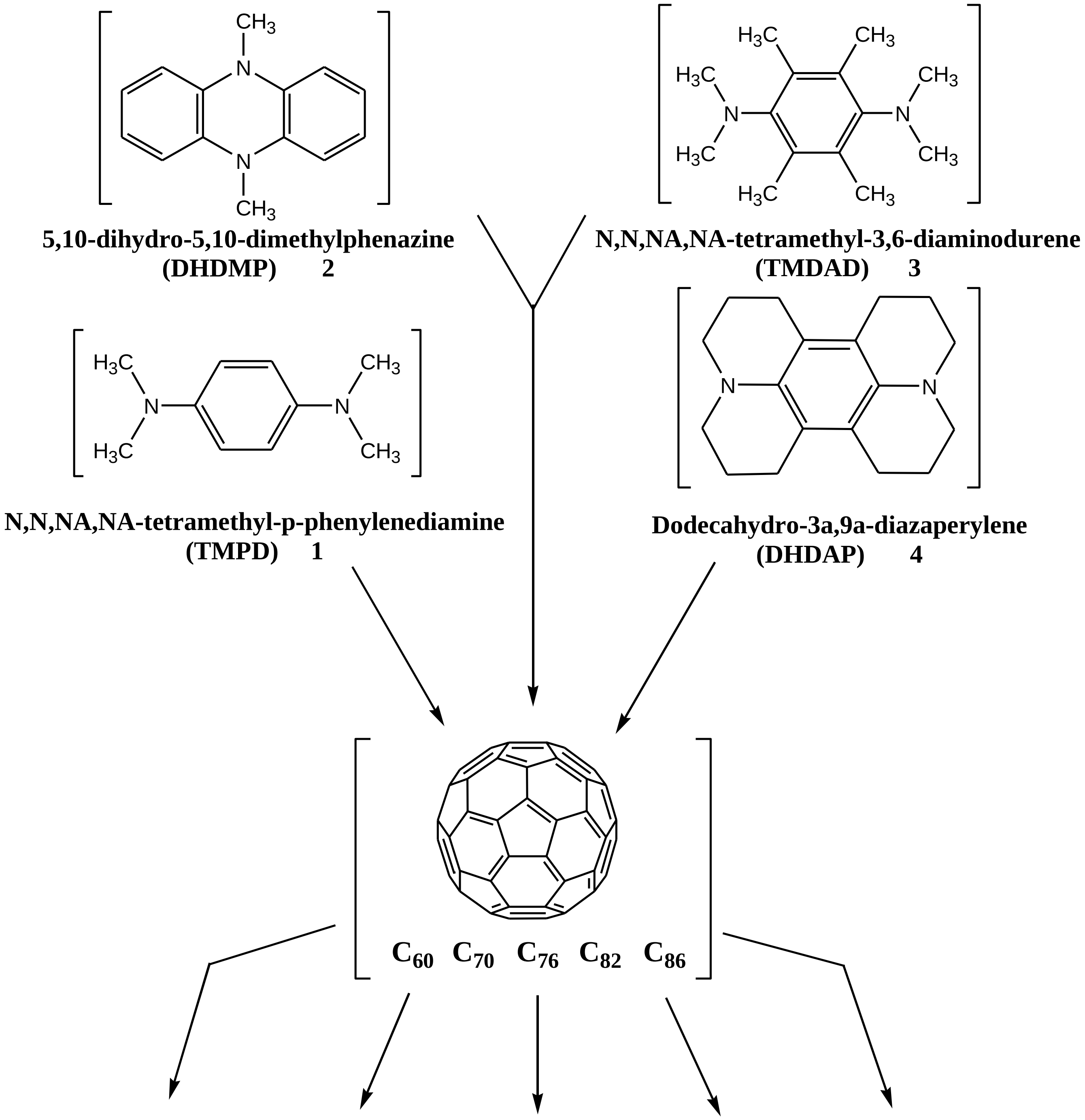
No.	Row	*Formula of [TMDAD].C_n	(ΔG_{et}) in kcal mol^{-1} [TMDAD].C_n			
			$\Delta G_{et(1)}$*	$\Delta G_{et(2)}$*	$\Delta G_{et(3)}$*	$\Delta G_{et(4)}$*
15	C-1	[TMDAD].C_{60}	23.66 (23.57)	32.41 (32.33)	42.86 (42.71)	53.47 (53.31)
16	C-2	[TMDAD].C_{70}	22.31 (22.87)	30.90 (31.87)	39.64(40.86)	49.51 (50.78)
17	C-3	[TMDAD].C_{76}	19.24 (19.42)	27.31 (26.80)	37.47(37.40)	46.76 (46.86)
18	C-4	[TMDAD].C_{82}	14.48 (13.65)	21.68 (21.72)	35.12(34.17)	43.73 (42.48)
19	C-5	[TMDAD].C_{86}	10.37 (11.11)	16.81 (17.34)	33.45(34.64)	41.56 (42.94)
33	C-6	[TMDAD].C_{78}	17.84	25.66	36.70	45.78
34	C-7	[TMDAD].C_{84}	12.52	19.36	34.29	42.66
35	C-8	[TMDAD].C_{96}	-3.20	0.70	28.93	35.57
36	C-9	[TMDAD].C_{120}	-54.96	-60.91	16.05	18.02

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

Table 4. The data values on the Dodecahydro-3a,9a-diazaperylene (DHDAP) D-1 to D-5 and the values of the 4 free energies of electron transfer (ΔG_{et}), in kcal mol^{-1}, between DHDAP with C_n (as [DHDAP].C_n compounds D-6 to D-9) (forms 20-24 and 37-40) 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 [DHDAP].C_n	(ΔG_{et}) in kcal mol^{-1} [DHDAP].C_n			
			$\Delta G_{et(1)}$*	$\Delta G_{et(2)}$*	$\Delta G_{et(3)}$*	$\Delta G_{et(4)}$*
20	D-1	[DHDAP].C_{60}	12.08 (11.99)	20.83 (20.75)	31.50 (31.13)	42.15 (41.74)
21	D-2	[DHDAP].C_{70}	10.72 (11.30)	19.34 (20.29)	28.38(29.29)	38.28 (39.20)
22	D-3	[DHDAP].C_{76}	7.66 (7.84)	15.74 (15.22)	26.26(25.83)	35.59 (35.28)
23	D-4	[DHDAP].C_{82}	2.90 (2.27)	10.12 (10.15)	23.97(22.60)	32.62 (30.90)
24	D-5	[DHDAP].C_{86}	-1.22 (-1.03)	5.25 (5.76)	22.34(23.06)	30.50 (31.36)
37	D-6	[DHDAP].C_{78}	6.26	14.09	25.52	34.63
38	D-7	[DHDAP].C_{84}	0.93	7.80	23.16	31.57
39	D-8	[DHDAP].C_{96}	-14.79	-10.86	17.91	24.64
40	D-9	[DHDAP].C_{120}	-66.55	-72.45	5.25	7.50

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



A-1: [TMPD]@C_{60}	**A-2:** [TMPD]@C_{70}	**A-3:** [TMPD]@C_{76}	**A-4:** [TMPD]@C_{82}	**A-5:** [TMPD]@C_{86}
B-1: [DHDMP]@C_{60}	**B-2:** [DHDMP]@C_{70}	**B-3:** [DHDMP]@C_{76}	**B-4:** [DHDMP]@C_{82}	**B-5:** [DHDMP]@C_{86}
C-1: [TMDAD]@C_{60}	**C-2:** [TMDAD]@C_{70}	**C-3:** [TMDAD]@C_{76}	**C-4:** [TMDAD]@C_{82}	**C-5:** [TMDAD]@C_{86}
D-1: [DHDAP]@C_{60}	**D-2:** [DHDAP]@C_{70}	**D-3:** [DHDAP]@C_{76}	**D-4:** [DHDAP]@C_{82}	**D-5:** [DHDAP]@C_{86}

Figure 1. The conjectured structures of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD), 5,10-dihydro-5,10-dimethylphenazine (DHDMP), dodecahydro-3a,9a-diazaperylene (DHDAP) and *N,N,N',N'*-tetramethyl-3,6-diaminodurene (TMDAD), 1-4 and fullerenes C_n (n=60, 70, 76, 82 and 86) which create [TMPD].C_n A-1 to A-5, [DHDMP].C_n, B-1 to B-5, [TMDAD].C_n, C-1 to C-5 and [DHDAP].C_n, D-1 to D-5.

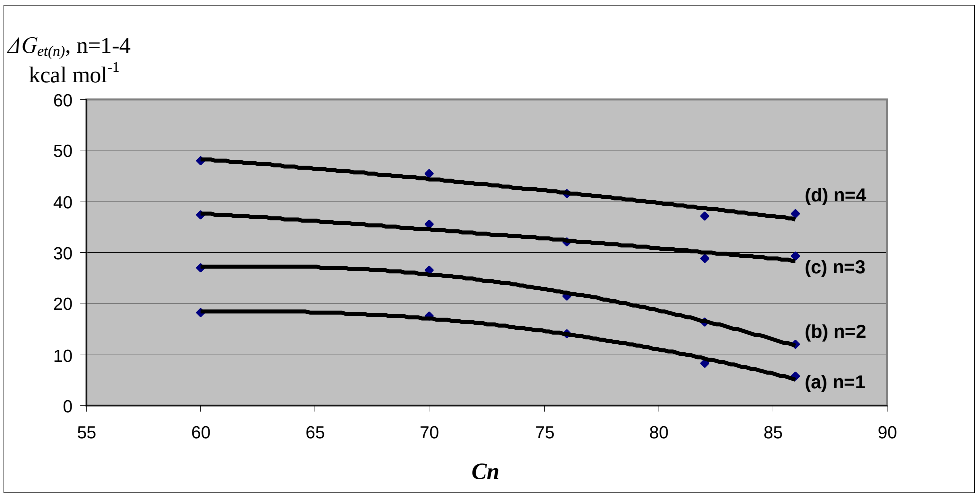


Figure 2. The relationship between the number "n" of carbon atoms in the fullerenes and the first(a), second(b), third(c) and fourth(d) free-energies of electron transfer ($\Delta G_{et(n)}$, n=1-4) of [TMPD].C_n (n = 60, 70, 76, 82 and 86), compounds A-1 to A-5.

- The related curves for [DHDMP].C_n, B-1 to B-5, [TMDAD].C_n, C-1 to C-5 and [DHDAP].C_n, D-1 to D-5 have similar structures to Fig. 2(a-d) [TMPD].C_n A-1 to A-5 .

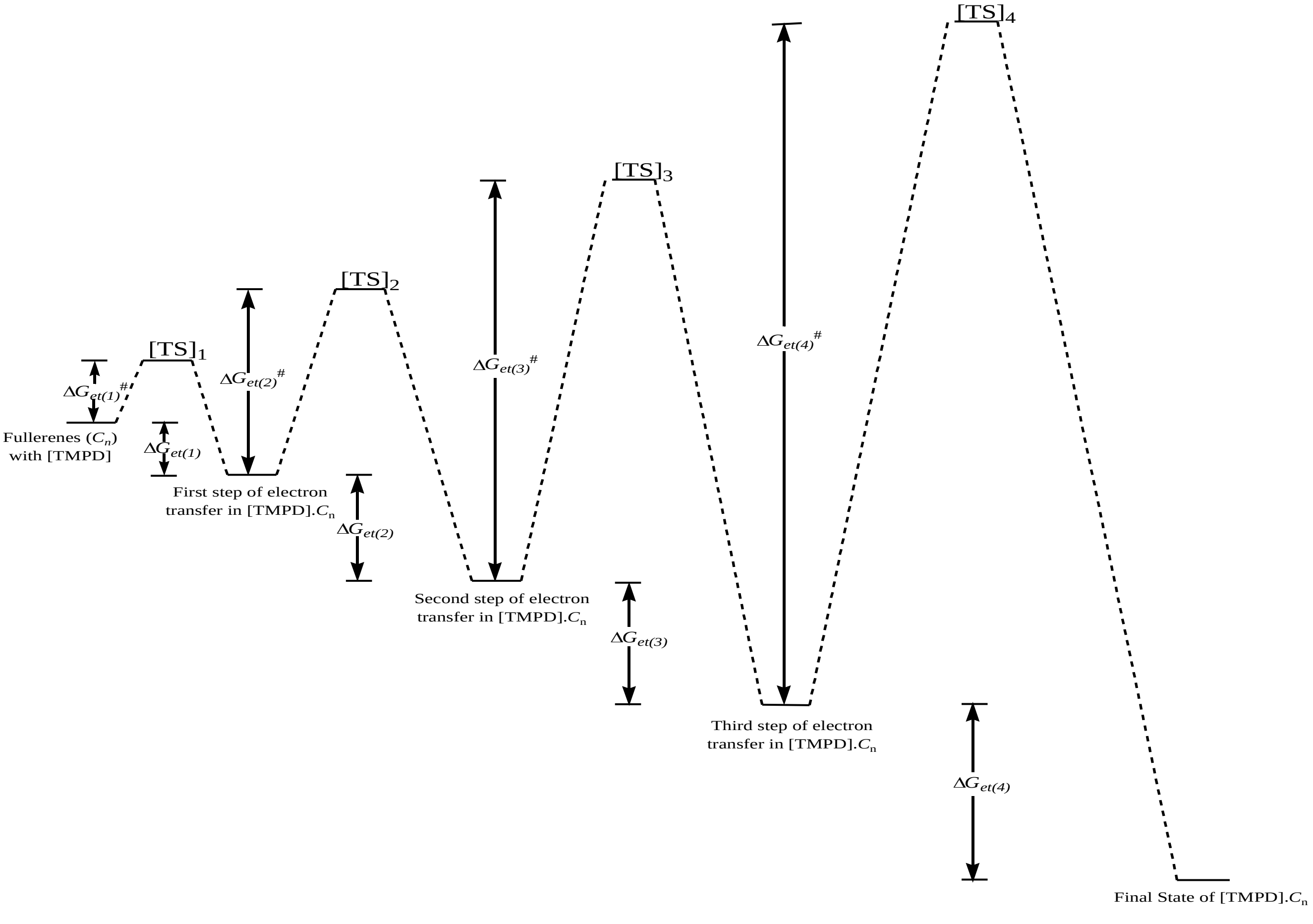


Figure 3. The surfaces of the free energies of electron transfer $\Delta Get_{(n)}$ and $\Delta Get_{(n)}{}^{\#}$ (n=1-4) between 1-4 and fullerenes in 5-40.

Table 5. 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 k_{et} (sec^{-1}, n=1-4), respectively, of [TMPD].C$_n$ supramolecular complexes (5-9 and 25-28) supramolecular complexes.

Id.	**[TMPD].C$_n$***	$\Delta G_{et(1)}^{\#}$	$k_{et(1)}$	$\Delta G_{et(2)}^{\#}$	$k_{et(2)}$	$\Delta G_{et(3)}^{\#}$	$k_{et(3)}$	$\Delta G_{et(4)}^{\#}$	$k_{et(4)}$
		1		2		3		4	
5	[TMPD].C_{60}	20.55	0.0049	35.68	3.91×10^{-14}	59.20	2.22×10^{-31}	89.12	2.48×10^{-53}
6	[TMPD].C_{70}	18.58	0.14	32.77	5.31×10^{-12}	51.32	1.33×10^{-25}	77.24	1.29×10^{-44}
7	[TMPD].C_{76}	14.48	139.00	26.36	2.71×10^{-7}	46.33	6.08×10^{-22}	69.49	6.28×10^{-39}
8	[TMPD].C_{82}	9.13	1.17×10^{6}	17.70	0.61	41.21	3.44×10^{-18}	61.42	5.19×10^{-33}
9	[TMPD].C_{86}	5.50	5.37×10^{8}	11.60	1.81×10^{4}	37.76	1.18×10^{-15}	55.95	5.35×10^{-29}
25	[TMPD].C_{78}	12.78	2.46×10^{3}	23.64	2.65×10^{-5}	44.62	1.09×10^{-20}	66.82	5.65×10^{-37}
26	[TMPD].C_{84}	7.28	2.64×10^{7}	14.63	107.76	39.47	6.46×10^{-17}	58.69	5.22×10^{-31}
27	[TMPD].C_{96}	0.0123	5.68×10^{12}	0.57	2.23×10^{12}	29.17	2.35×10^{-9}	42.17	6.85×10^{-19}
28	[TMPD].C_{120}	70.73	7.66×10^{-40}	88.17	1.25×10^{-52}	10.76	7.45×10^{4}	12.99	1.72×10^{3}

*The data of $\Delta G_{et(n)}^{\#}$ (in kcal mol^{-1}, n=1-4) and k_{et} (sec^{-1}, n=1-4) for [TMPD].C$_n$ supramolecular complexes (5-9 and 25-28).

Table 6. 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 k_{et} (sec^{-1}, n=1-4), respectively, of [DHDMP].C$_n$ supramolecular complexes (10-14 and 29-32) supramolecular complexes.

Id.	**[DHDMP].C$_n$***	$\Delta G_{et(1)}^{\#}$	$k_{et(1)}$	$\Delta G_{et(2)}^{\#}$	$k_{et(2)}$	$\Delta G_{et(3)}^{\#}$	$k_{et(3)}$	$\Delta G_{et(4)}^{\#}$	$k_{et(4)}$
		1		2		3		4	
10	[DHDMP].C_{60}	21.94	4.67×10^{-4}	37.52	1.77×10^{-15}	61.83	2.58×10^{-33}	92.83	4.76×10^{-56}
11	[DHDMP].C_{70}	19.90	0.015	34.53	2.73×10^{-13}	53.90	1.71×10^{-27}	80.96	2.42×10^{-47}
12	[DHDMP].C_{76}	15.66	19.09	27.92	1.94×10^{-8}	48.85	8.61×10^{-24}	73.19	1.22×10^{-41}
13	[DHDMP].C_{82}	10.07	2.39×10^{5}	19.00	0.068	43.66	5.54×10^{-20}	65.06	1.11×10^{-35}
14	[DHDMP].C_{86}	6.22	1.58×10^{8}	12.65	3.06×10^{3}	40.14	2.10×10^{-17}	59.55	1.22×10^{-31}
29	[DHDMP].C_{78}	13.89	379.79	25.14	2.12×10^{-6}	47.12	1.61×10^{-22}	70.51	1.12×10^{-39}
30	[DHDMP].C_{84}	8.12	6.47×10^{6}	15.81	14.65	41.89	1.09×10^{-18}	62.30	1.17×10^{-33}
31	[DHDMP].C_{96}	0.068	5.17×10^{12}	0.82	1.46×10^{12}	31.36	5.82×10^{-11}	45.59	2.11×10^{-21}
32	[DHDMP].C_{120}	68.24	5.20×10^{-38}	85.35	1.46×10^{-50}	12.23	6.19×10^{3}	15.45	27.11

*The data of $\Delta G_{et(n)}^{\#}$ (in kcal mol^{-1}, n=1-4) and k_{et} (sec^{-1}, n=1-4) for [DHDMP].C$_n$ supramolecular complexes (10-14 and 29-32).

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 k_{et} (sec^{-1}, n=1-4), respectively, of [TMDAD].C$_n$ supramolecular complexes (15-19 and 33-36) supramolecular complexes.

Id.	[TMDAD].C$_n$*	$\Delta G_{et(1)}^{\#}$	$k_{et(1)}$	$\Delta G_{et(2)}^{\#}$	$k_{et(2)}$	$\Delta G_{et(3)}^{\#}$	$k_{et(3)}$	$\Delta G_{et(4)}^{\#}$	$k_{et(4)}$
		1		2		3		4	
15	[TMDAD].C_{60}	29.31	1.85×10^{-9}	46.98	2.02×10^{-22}	73.52	6.88×10^{-42}	106.53	4.26×10^{-66}
16	[TMDAD].C_{70}	26.95	9.91×10^{-8}	43.63	5.75×10^{-20}	64.71	1.99×10^{-35}	93.50	1.54×10^{-56}
17	[TMDAD].C_{76}	21.96	4.55×10^{-4}	36.18	1.70×10^{-14}	59.09	2.64×10^{-31}	84.95	2.88×10^{-50}
18	[TMDAD].C_{82}	15.23	39.26	25.89	6.00×10^{-7}	53.30	4.72×10^{-27}	76.00	1.05×10^{-43}
19	[TMDAD].C_{86}	10.41	1.35×10^{5}	18.37	0.20	49.36	3.65×10^{-24}	69.90	3.13×10^{-39}
33	[TMDAD].C_{78}	19.85	0.016	32.98	3.74×10^{-12}	57.16	6.90×10^{-30}	82.00	4.18×10^{-48}
34	[TMDAD].C_{84}	12.81	2.32×10^{3}	22.15	3.32×10^{-4}	51.32	1.33×10^{-25}	72.96	1.78×10^{-41}
35	[TMDAD].C_{96}	0.98	1.10×10^{12}	2.67	6.39×10^{10}	39.46	6.69×10^{-17}	54.38	7.53×10^{-28}
36	[TMDAD].C_{120}	56.69	1.52×10^{-29}	72.41	4.55×10^{-41}	17.31	1.16	20.12	0.010

*The data of $\Delta G_{et(n)}^{\#}$ (in kcal mol^{-1}, n=1-4) and k_{et} (sec^{-1}, n=1-4) for [TMDAD].C$_n$ supramolecular complexes (15-19 and 33-36).

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 k_{et} (sec^{-1}, n=1-4), respectively, of [DHDAP].C$_n$ supramolecular complexes (20-24 and 37-40) supramolecular complexes.

Id.	[DHDAP].C$_n$*	$\Delta G_{et(1)}^{\#}$	$k_{et(1)}$	$\Delta G_{et(2)}^{\#}$	$k_{et(2)}$	$\Delta G_{et(3)}^{\#}$	$k_{et(3)}$	$\Delta G_{et(4)}^{\#}$	$k_{et(4)}$
		1		2		3		4	
20	[DHDAP].C_{60}	12.30	5.51×10^{3}	24.48	6.43×10^{-6}	44.95	6.24×10^{-21}	71.53	1.98×10^{-40}
21	[DHDAP].C_{70}	10.78	7.18×10^{4}	22.11	3.50×10^{-4}	38.33	4.50×10^{-16}	61.16	8.02×10^{-33}
22	[DHDAP].C_{76}	7.73	1.25×10^{7}	16.89	2.37	34.13	5.42×10^{-13}	54.43	6.93×10^{-28}
23	[DHDAP].C_{82}	3.98	6.94×10^{9}	10.14	2.11×10^{5}	29.86	7.25×10^{-10}	47.46	9.06×10^{-23}
24	[DHDAP].C_{86}	1.74	3.09×10^{11}	5.68	3.97×10^{8}	27.00	9.09×10^{-8}	42.77	2.48×10^{-19}
37	[DHDAP].C_{78}	6.50	9.94×10^{7}	14.73	90.87	32.72	5.85×10^{-12}	52.12	3.41×10^{-26}
38	[DHDAP].C_{84}	2.79	5.17×10^{10}	7.86	1.01×10^{7}	28.42	8.24×10^{-9}	45.10	4.81×10^{-21}
39	[DHDAP].C_{96}	0.84	1.41×10^{12}	0.073	5.13×10^{12}	19.96	0.013	31.08	9.27×10^{-11}
40	[DHDAP].C_{120}	89.07	2.73×10^{-53}	108.35	1.98×10^{-67}	5.68	3.97×10^{8}	7.58	1.60×10^{7}

*The data of $\Delta G_{et(n)}^{\#}$ (in kcal mol^{-1}, n=1-4) and k_{et} (sec^{-1}, n=1-4) for [DHDAP].C$_n$ supramolecular complexes (20-24 and 37-40).

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*, as well as the *Gibbs* free energy. The reorganization energy is defined as the energy required reorganizing the system structure from initial to final coordinates, without changing the electronic state.

2. GRAPHING AND MATHEMATICAL METHOD

All graphs were generated using the *Microsoft Office Excel 2003* program. Using the number of carbon atoms contained within the C_n fullerenes, several valuable properties of the fullerenes can be calculated. The values were used to calculate the four free energies of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$), according to the Rehm-Weller equation for [TMPD].C_n; 5-9 & 25-28, [DHDMP].C_n; 10-14 & 29-32, [TMDAD].C_n; 15-19 & 33-36 and [DHDAP].C_n; 20-24 & 37-40 (supramlecular complexes 5-40).

Both linear (MLR:Multiple Linear Regressions) and nonlinear (ANN:Artificial Neural Network) models were used in this study. Equations 1 and 4-19 were utilized to calculate the remaining values of $\Delta G_{et(1)}$ to $\Delta G_{et(4)}$ for complexes that have yet to be 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 [37]

$$\Delta G^{o} = e[E_D^{o} - E_A^{o}] - \Delta E^{*} + \omega_1 \qquad \text{(Eq.-1)}$$

where e is the unit electrical charge, E_D^{o} and E_A^{o} are the reduction potentials of the electron donor and acceptor, respectively, ΔE^{*} is the energy of the singlet or triplet excited state, and ω_1 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]

Marcus theory of electron transfer implies rather weak (<0.05eV) 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 rate constant k_{et} is controlled by the activation free energy $\Delta G_{et}^{\#}$, which is a function of the reorganization energy (l/4) and electron transfer driving force ΔG_{et}:

$$\Delta G_{et}^{\#} = (l/4)(1+\Delta G_{et}/l)^2 \qquad \text{(Eq.-2)}$$

$$k_{et} = k_0 \exp(-\Delta G_{et}^{\#}/RT) \qquad \text{(Eq.-3)}$$

For organic molecules, the reorganization energy was found to be in the range 0.1-0.3eV. In this study, the minimum amount of reorganization energy was used. [43a-h]

3. DISCUSSION

The anion-cation pair systems were found to show the thermo- and solvatochromism. This is an important step to developing the materials useful for optical and magnetic applications.[1,38] The photo-induced electron transfer from *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine (TMPD) to the triplet form of C_{60} in nitrobenzene had reported by Foote et al.[38,39]. It was reported that the electron-transfer from TMPD (1) to La@C_{82} occurs, which leads to the $[TMPD]^{\cdot +}$ radical cation [40] and the $[La@C_{82}]^{-}$ anion.[38,40] The reported results of vis-NIR absorptions of the La@C_{82}/TMPD and the $[La@C_{82}]^{-}/[TMPD]^{\cdot +}$ pair were different. This result reveals a solvatochromism.[38,41] The spin-site exchange process between La@C_{82} and 1 in nitrobenzene was confirmed by EPR measurement.[38] The results demonstrated that the intensity of EPR signals of La@C_{82} was diminished in the presence of TMPD (1) and the signals of $[TMPD]^{\cdot +}$ was appeared.[38,42] EPR measurements in variable temperature from 320 to 240K in *o*-dichlorobenzene/benzonitrile showed that the equilibrium shifted to the formation of the ion pair at low temperatures.[38] The repeated temperature change denoted that La@C_{82} and TMPD were in equilibrium with $[La@C_{82}]^{-}/[TMPD]^{\cdot +}$ in solution.[38] Reversible intermolecular spin-site exchange systems at complete equilibrium in solution were accomplished by utilizing paramagnetic La@C_{82} and organic donor molecules, which form stable diamagnetic anion and radical cations, respectively.[38] In the reports of Leventis *et al.* has reported that all redox data for 1, 3 and 4 were determined by cyclic voltammetry in CH_3CN (0.1M) and *n*-$Bu_4N^+ClO_4^-$ (applying 80% compensation for the solution resistance), and are reported *versus* ferrocene. For 2 (DHDMP) Akasaka *et al.* reported that the electrochemical results were obtained by CV.[38] The conditions were *n*-$Bu_4N^+PF_6^-$ (0.1 M) in nitrobenzene, versus Fc/Fc^+.[1] The oxidation potentials of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD), 5,10-dihydro-5,10-dimethylphenazine (DHDMP), dodecahydro-3a,9a-diazaperylene (DHDAP) and *N,N,N',N'*-tetramethyl-3,6-diaminodurene (TMDAD) 1-4 are: –0.281 [1], –0.260 [38], –0.573 [1] and –0.068 [1] Volt, respectively.[1,38]

Here, was calculated four free energies of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) of other supramolecular complexes of this class of electron-transfer radicals, i.e. *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD), 5,10-dihydro-5,10-dimethylphenazine (DHDMP), *N,N,N',N'*-tetramethyl-3,6-diaminodurene (TMDAD) and dodecahydro-3a,9a-diazaperylene (DHDAP), 1-4 as the most well-known redox systems and fullerenes C_n (n=60, 70, 76, 82 and 86), which create [TMPD].C_n; 5-9 & 25-28, [DHDMP].C_n; 10-14 & 29-32, [TMDAD].C_n; 15-19 & 33-36 and [DHDAP].C_n; 20-24 & 37-40 (supramlecular complexes 5-40).

The four reported reduction potentials (${}^{Red.}E_1$ to ${}^{Red.}E_4$) of fullerenes C_n are as follows: for C_{60} are, -1.12, -1.50, -1.95 and -2.41V, respectively. [42] The ${}^{Red}E_n$(Volt, n=1-4) for C_{70} are -1.09, -1.48, -1.87 and -2.30V, respectively. [42] The values of ${}^{Red}E_n$(Volt, n=1-4) for C_{76} are -0.94, -1.26, -1.72 and -2.13V, respectively. [42] Four values of ${}^{Red}E_n$(Volt, n=1-4) for C_{82} are -0.69, -1.04, -1.58 and -1.94V, respectively. [42] The ${}^{Red}E_n$(Volt, n=1-4) for C_{86} are -0.58, -0.85, -1.60 and -1.96V, respectively.[42] C_{180} and C_{240} have not been prepared or isolated among the fullerenes which they have listed in Tables 1-4.

Tables 1-4 contain a summary of the data. They show the 300 calculated values for 5-40 of the four electron transfer free energies ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$, in kcal mol^{-1}) between *p*-phenylenediamine derivatives 1-4 and fullerenes C_n (n = 60, 70, 76, 82 and 86) as [*p*-phenylenediamine derivatives].C_n complexes. These values were calculated using the Rehm-Weller equation (Eq.-1). The selected *p*-phenylenediamine derivatives (1-4) were used to model the structural relationship between the number of carbon atoms in the fullerenes and $\Delta G_{et(n)}$(n=1-4). The data of compounds A-1 to A-9, B-1 to B-9, C-1 to C-9 and D-1 to D-9 (complexes 5-40) are reported in the appropriate tables. Figure-1 depicts the structures of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD), 5,10-dihydro-5,10-dimethylphenazine (DHDMP), *N,N,N',N'*-tetramethyl-3,6-diaminodurene (TMDAD) and dodecahydro-3a,9a-diazaperylene (DHDAP), 1-4 as the most well-known redox systems and fullerenes C_n (n=60, 70, 76, 82 and 86), which create [TMPD].C_n, A-1 to A-5, [DHDMP].C_n, B-1 to B-5, [TMDAD].C_n, C-1 to C-5 and [DHDAP].C_n, D-1 to D-5.

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 ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) of [TMPD].C_n (n = 60, 70, 76, 82 and 86). Equations 4-7 correspond to Fig.-2 (graphs *a*-*d*). This data was regressed with a second-order polynomial. The R-squared values (R^2) for these graphs are 0.9876, 0.9924, 0.9382 and 0.9476, respectively.

$$\Delta G_{et(1)} = -0.0235\,(n)^2 + 2.9197(n) - 72.2690 \qquad \text{(Eq.-4)}$$

$$\Delta G_{et(2)} = -0.0281\,(n)^2 + 3.5028(n) - 81.9520 \qquad \text{(Eq.-5)}$$

$$\Delta G_{et(3)} = -0.0025\,(n)^2 + 0.0032(n) + 46.3130 \qquad \text{(Eq.-6)}$$

$$\Delta G_{et(4)} = -0.0039\,(n)^2 + 0.1112(n) + 55.4880 \qquad \text{(Eq.-7)}$$

By using Equations 4-7, it is possible to calculate the values of $\Delta G_{et(1)}$ to $\Delta G_{et(4)}$ of [TMPD].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 *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) 1 and C_n (as [TMPD].C_n compounds A-1 to A-5) 5-9 supramolecular complexes. The $\Delta G_{et(n)}$ (n=1-4) for [TMPD].C_n (C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}, C_{84}, C_{96}, C_{120}, C_{132}, C_{140}, C_{146}, C_{150}, C_{160}, C_{162}, C_{240}, C_{276}, C_{288} and C_{300}) 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 [DHDMP].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, 0.9924, 0.9387 and 0.9478, respectively.

$$\Delta G_{et(1)} = -0.0235(n)^2 + 2.9196(n) - 71.3480 \qquad \text{(Eq.-8)}$$

$$\Delta G_{et(2)} = -0.0281(n)^2 + 3.5028(n) - 81.0320 \qquad \text{(Eq.-9)}$$

$$\Delta G_{et(3)} = -0.0025(n)^2 + 0.0081(n) + 47.0510 \qquad \text{(Eq.-10)}$$

$$\Delta G_{et(4)} = -0.0038(n)^2 + 0.1064(n) + 56.5990 \qquad \text{(Eq.-11)}$$

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 [DHDMP].C_n. Table 2 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 5,10-dihydro-5,10-dimethylphenazine

(DHDMP) 2 and the C_n (as [DHDMP].C_n compounds B-1 to B-5) 10-14 supramolecular complexes. The $\Delta G_{et(n)}$ (n=1-4) for [DHDMP].C_n (C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}, C_{84}, C_{96}, C_{120}, C_{132}, C_{140}, C_{146}, C_{150}, C_{160}, C_{162}, C_{240}, C_{276}, C_{288} and C_{300}) 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 *N,N,N',N'*-tetramethyl-3,6-diaminodurene (TMDAD) 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 [TMDAD].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 0.9876, 0.9924, 0.9382 and 0.9476, respectively.

$$\Delta G_{et(1)} = -0.0235(n)^2 + 2.9197(n) - 66.9190 \qquad \text{(Eq.-12)}$$

$$\Delta G_{et(2)} = -0.0281(n)^2 + 3.5028(n) - 76.6020 \qquad \text{(Eq.-13)}$$

$$\Delta G_{et(3)} = -0.0025(n)^2 + 0.0032(n) + 51.6630 \qquad \text{(Eq.-14)}$$

$$\Delta G_{et(4)} = -0.0039(n)^2 + 0.1112(n) + 60.8380 \qquad \text{(Eq.-15)}$$

By using Equations 12-15, it is possible to calculate the values of $\Delta G_{et(1)}$ to $\Delta G_{et(4)}$ of [TMDAD].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 *N,N,N',N'*-tetramethyl-3,6-diaminodurene (TMDAD) 3 and C_n (as [TMDAD].C_n C-1 to C-5) 15-19 supramolecular complexes. The $\Delta G_{et(n)}$ (n=1-4) for [TMDAD].C_n (C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}, C_{84}, C_{96}, C_{120}, C_{132}, C_{140}, C_{146}, C_{150}, C_{160}, C_{162}, C_{240}, C_{276}, C_{288} and C_{300}) 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 [DHDAP].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, 0.9924, 0.9384 and 0.9478, respectively.

$$\Delta G_{et(1)} = -0.0235(n)^2 + 2.9196(n) - 78.4980 \qquad \text{(Eq.-16)}$$

$$\Delta G_{et(2)} = -0.0281(n)^2 + 3.5033(n) - 88.2040 \qquad \text{(Eq.-17)}$$

$$\Delta G_{et(3)} = -0.0025(n)^2 + 0.0125(n) + 39.7510 \qquad \text{(Eq.-18)}$$

$$\Delta G_{et(4)} = -0.0038(n)^2 + 0.1064(n) + 49.4490 \qquad \text{(Eq.-19)}$$

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 [DHDAP].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 dodecahydro-3a,9a-diazaperylene

(DHDAP) 4 and the C_n (as [DHDAP].C_n, compounds D-1 to D-5) 20-24 supramolecular complexes. The $\Delta G_{et(n)}$ (n=1-4) for [DHDAP].C_n (C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}, C_{84}, C_{96}, C_{120}, C_{132}, C_{140}, C_{146}, C_{150}, C_{160}, C_{162}, C_{240}, C_{276}, C_{288} and C_{300}) are predicted by using equations 16-19 and the Rehm-Weller equation (see Table-4).

By utilizing these results (Eq. 4-19) 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 *p*-phenylenediamine derivatives 1-4 with fullerenes (C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}, C_{84}, C_{96}, C_{120}, C_{132}, C_{140}, C_{146}, C_{150}, C_{160}, C_{162}, C_{240}, C_{276}, C_{288} and C_{300}) were approximated (Tables 1 to 4). The calculated values of the free electron transfer energies of $\Delta G_{et(n)}$ (n=1-4) for selected [*p*-phenylenediamine derivatives].C_n (n = 60, 70, 76, 82 and 86, compounds 5 to 40) in the Rehm-Weller equation and Eq. 4-19, are compared in Tables 1-4. 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 increases as the electron population in the C_n structures increases. See Tables 1-4. It seems that these results are related to the HOMO and LUMO gap of the fullerenees. The Tables also shows that some of the free electron transfer energies $\Delta G_{et(n)}$ (n=1-4) values of [TMPD].C_n, [DHDMP].C_n, [TMDAD].C_n and [DHDAP].C_n are negative.

The *Marcus* theory is currently the dominant theory of electron transfer in chemistry. Marcus theory is so widely accepted because it makes surprising predictions about electron transfer rates that have been nonetheless 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. [43a-h]

Electron transfer (ET) is one of the most important chemical processes in nature, plays as a central role in many biological, physical and chemical (both organic and inorganic) systems. Solid state electronics depends on the control of the ET in semiconductors, and the new area of molecular electronics depends critically on the understanding and the control of the transfer of electrons in/and between molecules and nanostructures. The other reason to study electron transfer is that it is a very simple kind of chemical reaction and understanding it, one can gain insight into other kinds of chemistry and biochemistry. After all, what is important is the chemistry of the transfer of electrons from one place to another. [43a-h]

The free energy of electron transfer ΔG_{et} is the difference 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 the electron transfer. If the entropy changes are ignored, the free energy becomes energy or potential energy. [43a-h]

In Tables 5-8 were shown the calculated values of the first to forth free activation energies of electron transfer and kinetic rate constants of the electron transfers, $\Delta G_{et(n)}^{\#}$ ($\Delta G_{et(1)}^{\#}$ to $\Delta G_{et(4)}^{\#}$) and k_{et} (n=1-4) by utilizing equations 2 and 3. Using Equations 2 and 3, it is possible to calculate the first to fourth activate free energies of electron transfer and kinetic rate constants of the electron transfers, $\Delta G_{et(n)}^{\#}$ and $k_{et(n)}$ (n=1-4), respectively, for 5-40 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 *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD), 5,10-dihydro-5,10-dimethylphenazine (DHDMP), *N,N,N',N'*-tetramethyl-3,6-diaminodurene (TMDAD) and dodecahydro-3a,9a-diazaperylene (DHDAP), 1-4 and fullerenes C_n (n=60, 70, 76, 82 and 86), which create [TMPD].C_n, [DHDMP].C_n, [TMDAD].C_n and [DHDAP].C_n 5-40. The values of the first to fourth activated free energies of electron transfer, $\Delta G_{et(n)}^{\#}$ (n=1-4) for 5-40, increase with increasing the $\Delta G_{et(n)}$ and the number of carbon atoms in the complexes, while the kinetic rate constants of the electron transfers $k_{et(n)}$ (n=1-4), decrease with increasing $\Delta G_{et(n)}$ and $\Delta G_{et(n)}^{\#}$ (n=1-4) for 5-40. The zero values mean that there was not any electron transfer process between the parts of the predicted complexes. See Tables 5-8 and Figure 3.

By using equation 1 (*Rehm-Weller* equation), equeations 2 and 3 (*Marcus* theory) and Equations 4-19, the values of $\Delta G_{et(n)}$ (n=1-4), $\Delta G_{et(n)}^{\#}$ and $k_{et(n)}$ (n=1-4) were calculated for 5-40. The values of the number of carbon atoms (n) show a good relationship with the values of the free energies of electron transfer $\Delta G_{et(n)}$ (n=1-4), $\Delta G_{et(n)}^{\#}$ and $k_{et(n)}$ (n=1-4) in [TMPD].C_n; 5-9 & 25-28, [DHDMP].C_n; 10-14 & 29-32, [TMDAD].C_n; 15-19 & 33-36 and [DHDAP].C_n; 20-24 & 37-40 (supramlecular complexes 5-40). 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 1-4 and fullerenes (C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}, C_{84}, C_{96}, C_{120}, C_{132}, C_{140}, C_{146}, C_{150}, C_{160}, C_{162}, C_{240}, C_{276}, C_{288} and C_{300}) in the structures of 5-80, calculated by Equations 1-19 and shown in Tables 1-8. With the appropriate equations, it is possible to calculate the first to fourth free energies of electron transfer (ΔG_{et} in kcal.mol^{-1}), the first to fourth activated free energies of electron transfer and kinetic rate constants of the electron transfers, $\Delta G_{et(n)}^{\#}$ and $k_{et(n)}$ (n=1-4), respectively, for [TMPD].C_n; 5-9 & 25-28, [DHDMP].C_n; 10-14 & 29-32, [TMDAD].C_n; 15-19 & 33-36 and [DHDAP].C_n; 20-24 & 37-40 (supramlecular complexes 5-40), in close accordance with the results of *Marcus* theory.

The supramolecular complex structures which were discussed here, and the calculated values of $\Delta G_{et(n)}$ (n=1-4), $\Delta G_{et(n)}^{\#}$ and $k_{et(n)}$ (n=1-4) corresponding to these supramolecular complexes were neither synthesized nor reported before.

4. CONCLUSION

N,N,N',N'-tetramethyl-*p*-phenylenediamine (TMPD), 5,10-dihydro-5,10-dimethylphenazine (DHDMP), *N,N,N',N'*-tetramethyl-3,6-diaminodurene (TMDAD) and dodecahydro-3a,9a-diazaperylene (DHDAP), 1-4 and fullerenes have important electron-transfer properties as the most well-known redox systems and molecular conductors. The electrochemical data of selected *p*-phenylenediamine derivatives 1-4, i.e. [TMPD].C_n; 5-9 & 25-28, [DHDMP].C_n; 10-14 & 29-32, [TMDAD].C_n; 15-19 & 33-36 and [DHDAP].C_n; 20-24 & 37-40 (supramlecular complexes 5-40) 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 $k_{et(n)}$ (n=1-4) using equations of the *Marcus* theory for the supramolecular complexes 5-40. 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 $k_{et(n)}$ (n=1-4) for *p*-phenylenediamine derivatives 1-4, as [TMPD].C_n; 5-9 & 25-28, [DHDMP].C_n; 10-14 & 29-32, [TMDAD].C_n; 15-19 & 33-36 and [DHDAP].C_n; 20-24 & 37-40 (supramlecular complexes 5-40) of the fullerenes (C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}, C_{84}, C_{96}, C_{120}, C_{132}, C_{140}, C_{146}, C_{150}, C_{160}, C_{162}, C_{240}, C_{276}, C_{288} and C_{300}). The novel supramolecular complexes discussed have neither been synthesized nor reported previously.

ACKNOWLEDGMENTS
The author gratefully acknowledges colleagues in the Chemistry Department of The University of Queensland-Australia for their useful suggestions.

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