Theoretical study of electron transfer process between fullerenes and neurotransmitters; acetylcholine, dopamine, serotonin and epinephrine in nanostructures [neurotransmitters]. C_n complexes

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Abstract Neurotransmitters are the compounds which allow the transmission of signals from one neuron to the next across synapses. They are the brain chemicals that communicate information throughout brain and body. 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. Topological indices 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 neurotransmitters (NTs) acetylcholine (AC) 1, dopamine (DP) 2, serotonin (SE) 3, and epinephrine (EP) 4 as the well-known redox systems and fullerenes C_n ($n=60, 70, 76, 82$, and 86) which create [NT]. C_n ; A-1 to A-5 up to D-1 to D-5. The relationship between the number of carbon atoms and the free energy of electron transfer ($\Delta G_{et(n)}$; $n=1-4$) is assessed using the *Rehm-Weller* equation for A-1 to A-5 up to D-1 to D-5 supramolecular [NT]. C_n complexes. The 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 energy values of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) of the supramolecular complexes A-1 to A-8 up to D-1 to D-8 for fullerenes C_{60} to C_{120} . The first to fourth free activation energy values of electron transfer and the maximum wavelength of the electron transfers, $\Delta G_{et(n)}^\ddagger$ and λ_{et} ($n=1-4$), respectively, were also calculated in this study for A-1 to A-8 up to D-1 to D-8 in accordance with the *Marcus* theory.

Keywords Fullerenes · Neurotransmitters · Acetylcholine · Dopamine · Serotonin · Epinephrine · Rehm-Weller equation · Free energy of electron transfer · Electron transfer properties · Activated free energy of electron transfer · Marcus theory · Molecular modeling

Introduction

Neurotransmitters are introduced as very important natural compounds that regulate different physical and emotional processes such as mental performance, emotional states, and pain response. Interactions between neurotransmitters, hormones, and the brain chemicals have a profound influence on overall health. All functions in life are controlled by neurotransmitters (such as acetylcholine, dopamine, serotonin, and epinephrine) as the chemical messengers. Neurotransmitters are released into the synaptic cleft, where they bind to receptors in the membrane on the postsynaptic side of the synapse [1–12] (<http://en.wikipedia.org/wiki/Acetylcholine>, <http://en.wikipedia.org/wiki/Dopamine>, <http://en.wikipedia.org/wiki/Serotonin>, <http://en.wikipedia.org/wiki/Epinephrine>). The acetylcholine (AC) is a neurotransmitter in both the peripheral nervous system and central nervous system in many organisms including humans. Acetylcholine is one of

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many neurotransmitters in the **autonomic nervous system** and the only neurotransmitter used in the motor division of the **somatic nervous system**. Acetylcholine is also the principal neurotransmitter in all **autonomic ganglia**. When acetylcholine neurotransmission is inhibited, the heart rate is decreased [3–7] (<http://en.wikipedia.org/wiki/Acetylcholine>). Dopamine (DA) plays a major role in the brain system that is responsible for reward-driven learning. Every type of reward that has been studied increases the level of dopamine transmission in the brain, and a variety of highly addictive drugs, including **stimulants** such as cocaine and methamphetamine, act directly on the dopamine system. Dopamine is available as one of the intravenous medications acting on the **sympathetic nervous system**, producing effects such as increased **heart rate** and **blood pressure** [3, 8]. Serotonin (SE) is a **monoamine neurotransmitter**. This compound functions as a neurotransmitter in the nervous systems of simple, as well as complex, animals. In accordance with the biochemical aspects, serotonin is derived from **tryptophan**. Serotonin is primarily found in the **gastrointestinal (GI) tract**, **platelets**, and in the **central nervous system (CNS)** of animals including humans. It is thought to be a contributor to feelings of well-being and **happiness** [3, 9]. Epinephrine (EP) or adrenaline is a **hormone** and a **neurotransmitter** [3, 10]. It increases heart rate, constricts blood vessels, dilates air passages, and participates in the **fight-or-flight response** of the **sympathetic nervous system** [10, 12] (<http://en.wikipedia.org/wiki/Epinephrine>). In chemical terms, adrenaline is one of a group of **monoamines** called the **catecholamines**. It is produced in some **neurons** of the central nervous system from the **amino acids phenylalanine** and **tyrosine** [10, 12] (<http://en.wikipedia.org/wiki/Epinephrine>). Up to now, various empty carbon fullerenes with different numbers “n” such as C₆₀, C₇₀, C₇₆, C₈₂, and C₈₆ have been obtained. The chemical, physical, and mechanical properties of empty and endohedral fullerenes have been the subject of many studies [13–43]. 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 [15, 31]. The unique stability of molecular allotropes such as C₆₀ and C₇₀ was demonstrated in 1985 [13–15].

After the discovery of C₆₀ peapods by Luzzi et al. [16–24], the aligned structure of encapsulated molecules, due to the molecule-molecule and/or molecule-single-wall carbon nanotube (SWNT) interactions, has been studied as a new type of hybrid material [21, 22]. Zhang et al. [16] reported evidence for the latter interaction measuring the thermal stability of C₆₀ peapods [16–23].

The electrochemical properties of the C₆₀ fullerene have been studied since the early 1990s, when these materials first became available in macroscopic quantities (for a review, see [21]) [20, 21]. In 1990, Haufler et al. [22] showed that CH₂Cl₂ electrochemically reduces C₆₀ to C₆₀¹⁻ and C₆₀²⁻. In 1992,

Echegoyen et al. [23] cathodically reduced C₆₀ 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 lowest unoccupied molecular orbital (LUMO) of C₆₀ can accept up to six electrons to form C₆₀⁶⁻, but the position of the highest occupied molecular orbital (HOMO) does not allow for hole doping under the usual reported electrochemical conditions. In 1991, Bard et al. [24] first reported on the irreversible electrochemical and structural reorganization of solid fullerenes in acetonitrile. Dunsch et al. [25] improved upon the experimental conditions by investigating highly organized C₆₀ films on highly oriented pyrolytic graphite (HOPG), in an aqueous medium. The reduction of these films induces a morphological change; they restructure into conductive nanoclusters of ~100 nm in diameter [25, 26].

Graph theory has been a useful tool in assessing the quantitative structure-activity relationship (*QSAR*) and quantitative structure-property relationship (*QSPR*). Numerous studies in different areas have used topological indices (TI) [44–54]. Any extrapolation of results from one compound to other compounds must take into account considerations based on a *QSAR* 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 [31–56]. 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 energy values of electron transfer ($\Delta G_{et(n)}$; n=1–4) of fullerenes C_n (n=60, 70, 76, 82, and 86) with neurotransmitters (NTs), AC 1, dopamine (DP) 2, SE 3, and EP 4, on the basis of the four reduction potentials (^{Red}E₁ to ^{Red}E₄) of the fullerenes, as assessed by applying the *Rehm-Weller* equation [57] to create [NT].C_n A-1 to A-5, up to D-1 to D-5. The results were extended to calculate the four free energy values of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) of other complexes of NT 1–4, with fullerenes C₆₀ to C₁₂₀ ([NT].C_n, complexes). In this study, the four free energy values of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) of A-1 to A-8 up to D-1 to D-8 were calculated. It should be noted that the theoretical electron transfer has been performed separately between the NT (1–4) and the fullerenes (as the two chemical parts of the oxidation-reduction process related to this study). The theoretical electron transfer (ET) process between NTs 1–4 and fullerenes has been separately demonstrated in Fig. 1. See Scheme 1; Eq. 1 to 20; Tables 1, 2, 3, 4, 5 and 6; and Figs. 1, 2, and 3.

The study also calculated the first to fourth activate free energy values of electron transfer and the maximum wave length of the electron transfers, $\Delta G_{et(n)}^\ddagger$ and λ_{et} (n=1–4), respectively, as assessed using the *Marcus* theory and the equations on the basis of the first to fourth reduction potentials

Fig. 1 The conjectured structures of NTs 1–4 and fullerenes C_n ($n=60, 70, 76, 82$, and 86) which create [NT]. C_n , A-1 to A-5 up to D-1 to D-5. The theoretical electron transfer has been shown separately between the NT (1–4) and the fullerenes

($^{Red}E_1$ to $^{Red}E_4$) of fullerenes C_n ($n=60, 70, 76, 82$, and 86) for the predicted supramolecular complexes [NT]. C_n ; NT=1–4 (complexes A-1 to A-8 up to D-1 to D-8). See the equations, tables, and Fig. 3.

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**. Photoinduced electron transfer is an **electron transfer** that occurs when certain photoactive

Scheme 1 The concentration on the selected NTs 1–4 and the electron transfer with fullerenes. The imaginary ET process between NTs 1–4 and fullerenes has separately demonstrated in Fig. 1

Table 1 The oxidation potentials (in volts) of the neurotransmitters (NTs) 1–4

$^{\alpha x}E$	$^{\alpha x}E$	Reference ^a
+0.57	+0.57	[76]
+0.124	+0.124	[68, 77]
+0.55	+0.55	[78]
+0.24	+0.24	[67]

^a See the reference list

materials interact with light, including **semiconductors** that can be photoactivated, such as many **solar cells**, biological systems like those used in **photosynthesis**, and small molecules with suitable absorption and redox states [57–66].

It is supposed that the electron transfer process between the NTs with the fullerenes to construct the [NT].C_n complexes makes a disturbance in the transmission of signals from one neuron to the next across synapses. It seems that the discussed electron transfer has also stopped some phenomena related to high transmission of signals from one neuron to the next across synapses in seizure and neurogenic shocks.

Graphing and mathematical method

All mathematical and graphing operations were performed using *MATLAB-7.4.0(R2007a)* and *Microsoft Office Excel-2003* programs. Using the number of carbon atoms contained

Table 2 Second-order polynomial Eq. 5–20 that indicate the relationship between the “C_n” index of the fullerenes and the first to fourth free energy values of electron transfer ($\Delta G_{et(n)}$, $n=1-4$) between neurotransmitters (NT) acetylcholine (AC) 1, dopamine (DP) 2, serotonin (SE) 3, and epinephrine (EP) 4 with fullerenes (C₆₀, C₇₀, C₇₆, C₈₂, and C₈₆) in the structures [NT].C_n; NT=1–4

[NT].C _n		$\Delta G_{et(n)}$	Equations	R^2 value	$\Delta G_{et(n)}=a(n)^2+b(n)+c$		
n					a	b	c
[AC].C _n	1	Eq. 5	0.987	–0.0235	2.9196	–52.2080	
[AC].C _n	2	Eq. 6	0.992	–0.0281	3.5028	–61.8920	
[AC].C _n	3	Eq. 7	0.938	–0.0025	0.0081	66.1910	
[AC].C _n	4	Eq. 8	0.947	–0.0039	0.1112	75.5480	
[DA].C _n	1	Eq. 9	0.987	–0.0235	2.9201	–62.520	
[DA].C _n	2	Eq. 10	0.992	–0.0280	3.4983	–72.0130	
[DA].C _n	3	Eq. 11	0.938	–0.0025	0.0125	55.7510	
[DA].C _n	4	Eq. 12	0.947	–0.0039	0.1108	65.2900	
[SE].C _n	1	Eq. 13	0.987	–0.0235	2.9196	–52.6680	
[SE].C _n	2	Eq. 14	0.992	–0.0281	3.5028	–62.352	
[SE].C _n	3	Eq. 15	0.938	–0.0026	0.0183	65.3190	
[SE].C _n	4	Eq. 16	0.947	–0.0087	0.8292	49.5360	
[EP].C _n	1	Eq. 17	0.987	–0.0234	2.9064	–59.3661	
[EP].C _n	2	Eq. 18	0.992	–0.0278	3.4580	–67.9050	
[EP].C _n	3	Eq. 19	0.938	–0.0025	0.0081	58.5810	
[EP].C _n	4	Eq. 20	0.947	–0.0038	0.1064	68.1290	

Table 3 The data values on the acetylcholine

Row	Formula of [acetylcholine].C _n ^a	[Acetylcholine].C _n $\Delta G_{et(n)}^{\#}$				[Acetylcholine].C _n $\lambda_{et(n)}$			
		$\Delta G_{et(1)}$	$\Delta G_{et(2)}$	$\Delta G_{et(3)}$	$\Delta G_{et(4)}$	$\lambda_{et(1)}$	$\lambda_{et(2)}$	$\lambda_{et(3)}$	$\lambda_{et(4)}$
A-1	C ₆₀	38.44 (38.28)	47.23 (47.04)	57.72 (57.42)	68.35 (68.02)	61.57	86.38	121.46	163.10
A-2	C ₇₀	37.12 (37.59)	45.77 (46.58)	54.57 (55.57)	64.45 (65.49)	58.21	81.97	100.30	1147.11
A-3	C ₇₆	34.07 (34.13)	42.20 (41.51)	52.50 (52.12)	61.74 (61.57)	50.80	71.67	103.26	136.49
A-4	C ₈₂	29.33 (28.36)	36.61 (36.43)	50.13 (48.89)	58.76 (57.19)	40.29	56.94	95.48	125.27
A-5	C ₈₆	25.23 (25.83)	31.76 (32.05)	48.49 (49.35)	56.61 (57.65)	32.17	45.52	90.28	117.47
A-6	C ₇₈	32.68	40.56	51.69	60.78	47.59	67.17	100.57	132.82
A-7	C ₈₄	27.37	34.30	49.32	57.70	36.29	51.34	92.89	121.39
A-8	C ₁₂₀	–39.95	–45.72	31.34	33.41	25.59	36.10	44.60	49.26

C_n A-1 to A-5 and the values of the four energy types of $\Delta G_{et(n)}$, $\Delta G_{et(n)}^{\#}$ in kilocalorie per mole, and the $\lambda_{et(n)}$ ($n=1-4$), between acetylcholine (1) with C_n (as [acetylcholine].C_n compounds A-6 to A-8) supramolecular complexes. The data of $\Delta G_{et(n)}$ ($n=1-4$) were predicted by using Eq. 5 to 8, and those in parentheses were calculated by the Rehm-Weller equation (Eq. 1)

^aThe of the free energy of electron transfer $\Delta G_{et(n)}$, $\Delta G_{et(n)}^{\#}$, and $\lambda_{et(n)}$ ($n=1-4$) for [acetylcholine].C_n compounds had not been previously reported

Table 4 The data values on the dopamine

Row	Formula of [dopamine].C _n ^a	[Dopamine].C _n ΔG _{et(n)} ^a				[Dopamine].C _n ΔG _{et(n)} ^a				[Dopamine].C _n λ _{et(n)}			
		ΔG _{et(1)}	ΔG _{et(2)}	ΔG _{et(3)}	ΔG _{et(4)}	ΔG _{et(1)}	ΔG _{et(2)}	ΔG _{et(3)}	ΔG _{et(4)}	λ _{et(1)}	λ _{et(2)}	λ _{et(3)}	λ _{et(4)}
B-1	C ₆₀	28.15 (27.99)	36.96 (36.76)	47.43 (47.13)	58.07 (57.74)	37.86	65.56	86.99	122.74	754	435	328	232
B-2	C ₇₀	26.83 (27.30)	35.49 (36.30)	44.28 (45.29)	54.17 (55.21)	35.23	54.19	77.59	108.92	811	527	368	262
B-3	C ₇₆	23.78 (23.84)	31.92 (31.22)	42.15 (41.83)	51.46 (51.29)	29.52	45.88	71.53	99.81	967	632	399	286
B-4	C ₈₂	19.04 (18.08)	26.34 (26.15)	39.84 (38.60)	48.47 (46.90)	21.65	34.28	65.24	90.21	1319	833	437	316
B-5	C ₈₆	14.94 (15.54)	21.49 (21.77)	38.20 (39.06)	46.33 (47.37)	15.82	25.57	60.96	83.65	1086	1117	468	341
B-6	C ₇₈	22.39	30.28	41.40	50.50	27.09	42.30	69.46	96.68	1054	675	411	295
B-7	C ₈₄	17.09	24.02	39.03	47.42	18.77	29.95	63.11	86.96	1522	953	452	328
B-8	C ₁₂₀	-50.23	-55.93	20.98	23.12	45.57	59.12	24.72	28.35	1626	1283	1155	1007

C_n B-1 to B-5 and the values of the four energy types of ΔG_{et(n)}, ΔG_{et(n)} in kilocalorie per mole, and the λ_{et(n)} (n=1–4), between dopamine (2) with C_n (as [dopamine].C_n compounds B-6 to B-8) supramolecular complexes. The data of ΔG_{et(n)} (n=1–4) were predicted by using Eq. 9 to 12, and those in parentheses were calculated by the Rehm-Weller equation (Eq. 1)

^aThe free energy of the electron transfer ΔG_{et(n)}, ΔG_{et(n)}, and λ_{et(n)} (n=1–4) for [dopamine].C_n compounds had not been previously reported

Table 5 The data values on the serotonin

Row	Formula of [serotonin].C _n ^a	[Serotonin].C _n ΔG _{et(n)} ^a				[Serotonin].C _n ΔG _{et(n)} ^a				[Serotonin].C _n λ _{et(n)}			
		ΔG _{et(1)}	ΔG _{et(2)}	ΔG _{et(3)}	ΔG _{et(4)}	ΔG _{et(1)}	ΔG _{et(2)}	ΔG _{et(3)}	ΔG _{et(4)}	λ _{et(1)}	λ _{et(2)}	λ _{et(3)}	λ _{et(4)}
C-1	C ₆₀	37.98 (37.82)	46.78 (46.58)	57.23 (56.93)	67.96 (67.57)	60.39	85.01	119.69	161.46	473	336	238	176
C-2	C ₇₀	36.66 (37.13)	45.32 (46.12)	54.10 (55.11)	64.94 (65.03)	57.06	80.63	108.69	149.07	500	354	262	191
C-3	C ₇₆	33.61 (33.67)	41.75 (41.05)	51.98 (51.65)	62.29 (61.11)	49.73	69.93	101.53	138.61	574	408	281	206
C-4	C ₈₂	28.87 (27.90)	36.16 (35.97)	49.87 (48.43)	59.01 (58.37)	39.33	55.82	94.65	126.19	426	511	301	226
C-5	C ₈₆	24.77 (25.37)	31.31 (31.59)	48.03 (48.89)	56.48 (57.19)	31.32	44.53	88.84	117.00	912	641	321	244
C-6	C ₇₈	32.22	40.11	51.23	61.27	46.55	65.96	99.05	134.69	613	433	288	212
C-7	C ₈₄	26.91	33.85	48.86	57.78	35.39	50.29	91.44	121.68	807	568	312	234
C-8	C ₁₂₀	-40.41	-46.17	30.79	23.73	26.36	36.10	43.39	29.43	1083	971	856	790

C_n C-1 to C-5 and the values of the four energy types of ΔG_{et(n)}, ΔG_{et(n)} in kilocalorie per mole, and the λ_{et(n)} (n=1–4), between serotonin (3) with C_n (as [serotonin].C_n compounds C-6 to C-8) supramolecular complexes. The data of ΔG_{et(n)} (n=1–4) were predicted by using Eq. 13 to 16, and those in parentheses were calculated by the Rehm-Weller equation (Eq. 1)

^aThe of the free energy of electron transfer ΔG_{et(n)}, ΔG_{et(n)}, and λ_{et(n)} (n=1–4) for [serotonin].C_n compounds had not been previously reported

Table 6 The data values on the epinephrine

Row	Formula of [epinephrine].C _n ^a	[Epinephrine].C _n ΔG _{et(n)} ^a				[Epinephrine].C _n ΔG _{et(n)} [#]				[Epinephrine].C _n λ _{et(n)}			
		ΔG _{et(1)}	ΔG _{et(2)}	ΔG _{et(3)}	ΔG _{et(4)}	ΔG _{et(1)} [#]	ΔG _{et(2)} [#]	ΔG _{et(3)} [#]	ΔG _{et(4)} [#]	λ _{et(1)}	λ _{et(2)}	λ _{et(3)}	λ _{et(4)}
D-1	C ₆₀	30.83 (30.67)	39.63 (39.43)	(49.81) 50.11	(60.42) 60.75	43.48	64.69	95.42	132.71	657	441	299	215
D-2	C ₇₀	29.49 (29.95)	38.12 (38.97)	(47.96) 46.96	(57.88) 56.84	40.62	60.75	85.55	118.29	703	470	333	241
D-3	C ₇₆	26.44 (26.52)	34.55 (33.80)	(44.51) 44.83	(53.96) 54.13	34.47	51.93	79.19	108.78	828	550	360	262
D-4	C ₈₂	21.71 (20.75)	28.98 (28.82)	(41.28) 42.52	(49.58) 51.15	25.93	39.56	72.57	98.79	1101	722	393	289
D-5	C ₈₆	17.62 (18.22)	24.16 (24.44)	(41.74) 40.88	(50.04) 49.00	19.53	30.21	68.04	91.88	1462	945	419	311
D-6	C ₇₈	25.05	32.92	44.08	53.17	31.84	48.14	77.01	105.51	897	593	371	270
D-7	C ₈₄	19.76	26.68	41.71	50.09	22.77	34.94	70.31	95.35	1254	817	406	299
D-8	C ₁₂₀	-47.35	-52.70	23.73	25.85	39.40	51.23	29.43	33.34	1425	1157	970	856

C_n D-1 to D-5 and the values of the four energy values of ΔG_{et(n)}, ΔG_{et(n)}[#] in kilocalorie per mole, and the λ_{et(n)} (n=1–4), between epinephrine (4) with C_n (as [epinephrine].C_n compounds D-6 to D-8) supramolecular complexes. The data of ΔG_{et(n)} (n=1–4) were predicted by using Eq. 17 to 20, and those in parentheses were calculated by the Rehm-Weller equation (Eq. 1)

^aThe free energy of the electron transfer ΔG_{et(n)}, ΔG_{et(n)}[#] and λ_{et(n)} (n=1–4) for [epinephrine].C_n compounds had not been previously reported

within the C_n fullerenes, several valuable properties of the fullerenes can be calculated. The values were used to calculate the four free energy values of electron transfer (ΔG_{et(n)}; n=1–4), according to the *Rehm-Weller* equation for A-1 to A-8 up to D-1 to D-8 (complexes [NT].C_n; NT=1–4).

Equations 1 and 5–20 were utilized to calculate the remaining values of ΔG_{et(1)} to ΔG_{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 [48–54, 56].

The *Rehm-Weller* equation estimates the free energy change between an electron donor (D) and an acceptor (A) as [57]

$$\Delta G^\circ = e[E_D^\circ - E_A^\circ] - \Delta E^* + \omega_1 \quad (1)$$

where *e* is the unit electrical charge, *E_D*[°] and *E_A*[°] are the reduction potentials of the electron donor and acceptor, respectively, Δ*E*^{*} is the energy of the singlet or triplet excited state, and ω₁ is the work required to bring the donor and acceptor within the ET distance. If an electrostatic complex forms before the ET process, the work term in this expression is zero [57].

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

$$\Delta G_{et}^\# = \left(l/4 \right) \left(1 + \Delta G_{et} / l \right)^2 \quad (2)$$

$$k_{et} = k_0 \exp \left(-\Delta G_{et}^\# / RT \right) \quad (3)$$

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 [58–65].

To calculate the maximum wavelengths (λ_(n); n=1–2) of the electromagnetic photon for the electron transfer process in the nanostructure supramolecular complexes, we used *Planck's* formula:

$$\Delta G_{et}^\# = \Delta E = h.c / \lambda_{(n)} \quad (4)$$

In this study, this formula was also used to calculate the activation free energy of the electron transfer process [58–66].

Discussion

It is well known that electrochemical oxidation of phenolic compounds generally produces unstable phenoxy radicals that

Fig. 2 The relationship between the number of carbon atoms in the fullerenes (C_n) and the first (a), second (b), third (c), and fourth (d) free energy of the ET process ($\Delta G_{et(n)}$, $n=1-4$) of [NT]. C_n ($n=60, 70, 76, 82$, and 86), compounds A-1 to A-5. See Tables 2 and 3 (Eq. 5–8). The related curves for the other [NT]. C_n (NT=1–4) complexes have similar structures to a, b, c, and d, [NT]. C_n A-1 to A-5

readily polymerize to passivate the surface of platinum electrodes [67–75] because the phenoxy radicals can interact with each other or with another phenol monomer to give rise to a strongly adherent insulating film with a thickness of 100–1000 Å [70–72] and with irregular pores [67, 68, 74, 75]. In 2006, the oxidation potential of acetylcholine was measured by the use of nano-nickel oxide/nickel incorporated nickel composite coating by Shibli et al. [76]. The electrochemical sensor was developed by electroplating nano-nickel oxide-

reinforced nickel on graphite substrate [76]. In 2010, the electrochemical oxidation of dopamine had been studied in room temperature and ionic liquids by Barnes et al. [77]. They reported that dopamine showed two-electron oxidation in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([C₂mim][NTf₂]). Dopamine showed two irreversible oxidative waves for oxidation to the semi-quinone and the protonated quinone and a further oxidation wave for the amine group to a radical cation [77]. In 2006, the electrochemical

Fig. 3 The surfaces of the free energy of electron transfer $\Delta G_{et(n)}$ and $\Delta G_{et(n)}^{\ddagger}$ ($n=1-4$) between neurotransmitters (NTs) acetylcholine (AC) 1, dopamine (DP) 2, serotonin (SE) 3, and epinephrine (EP) 4 and fullerenes

behavior at a mercury electrode of DA in the presence of citrate was investigated in aqueous solution, using cyclic voltammetry and alternating current polarography by Rath et al. [68]. In 2001, an electrochemical sensor for the determination of serotonin in urine was prepared using Ni(II)-phthalocyanine and Nafion to modify the surface of carbon fiber micro-electrode. The electrochemical activity for the electrocatalytic oxidation of serotonin was investigated by Barrio et al. [78]. In 2007, a novel poly-rutin (Ru) modified glassy carbon-electrode-modified paraffin-impregnated graphite electrode was fabricated with an electrochemical method by Jin et al. [67]. The modified electrode had shown good electrocatalytic activity for the oxidation of EP for better separation of oxidation peaks of EP, with good stability, sensitivity, and selectivity [67].

The published data of ${}^{\text{ox}}E$ for the selected NTs 1–4 have shown that they could be an electron donor to C_{60} and other fullerenes with respect to their reduction potentials (${}^{\text{Red}}E_1$ to ${}^{\text{Red}}E_4$) [67, 68, 76–78]. The reduction potentials of the selected fullerenes are shown (with their references) in Table 1. The results have shown that the electron transfer increases as the electron population in the C_n structures increases. The results were discussed on the basis of the Rehm-Weller equation and Marcus theory that they need to use the reduction and oxidation potentials of the two parts in the ET process. In this theoretical study, the possibilities of the ET process between NTs 1–4 and the selected fullerenes were investigated. The four reported reduction potentials (${}^{\text{Red}}E_1$ to ${}^{\text{Red}}E_4$) of fullerenes C_n are as follows: for C_{60} are -1.12 , -1.50 , -1.95 , and -2.41 V, respectively [79]. The ${}^{\text{Red}}E_n$ values (volts, $n=1-4$) for C_{70} are -1.09 , -1.48 , -1.87 , and -2.30 , respectively [79]. The values of ${}^{\text{Red}}E_n$ (volts, $n=1-4$) for C_{76} are -0.94 , -1.26 , -1.72 , and -2.13 , respectively [79]. Four values of ${}^{\text{Red}}E_n$ (volts, $n=1-4$) for C_{82} are -0.69 , -1.04 , -1.58 , and -1.94 , respectively [79]. The ${}^{\text{Red}}E_n$ (volts, $n=1-4$) for C_{86} are -0.58 , -0.85 , -1.60 , and -1.96 , respectively [79]. C_{180} and C_{240} have not been prepared or isolated among the fullerenes which they have listed in Tables 1, 2, 3, 4, 5, and 6.

Tables 2, 3, 4, 5, and 6 contain the summaries of the data. They show the calculated values for the complexes [NT]. C_n of the four electron transfer free energy values ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$, in kcal mol^{-1}) between NTs 1–4 and fullerenes C_n ($n=60, 70, 76, 82$, and 86) as [NT]. C_n complexes. These values were calculated using the Rehm-Weller equation (Eq. 1). The selected NTs 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-8 and D-1 to D-8 are reported in the appropriate tables. Scheme 1 has depicted the concentration on the selected NTs 1–4. Figure 1 depicts the structures of NTs 1–4 as the redox systems and fullerenes C_n ($n=60, 70, 76, 82$, and 86), which create [NT]. C_n A-1 to A-5 up to D-1 to D-5.

In Table 2, the second-order polynomial Eq. 5–20 that indicate the relationship between the “ C_n ” descriptor of the

fullerenes and the first to fourth free energy values of electron transfer ($\Delta G_{et(n)}$, $n=1-4$) between NTs AC 1, DP 2, SE 3, and EP 4 with the fullerenes (C_{60} , C_{70} , C_{76} , C_{82} , and C_{86}) in the structures [NT]. C_n , NT=1–4, were demonstrated.

Figure 2 (a, b, c, d) demonstrates 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 [AC]. C_n ($n=60, 70, 76, 82$, and 86) A-1 to A-8. Equations 5–8 correspond to Fig. 2 a, b, c, d. These data were regressed with a second-order polynomial. The R -squared values (R^2) for these graphs are 0.987, 0.992, 0.938, and 0.947, respectively.

By using Eq. 5–8, it is possible to calculate the values of $\Delta G_{et(n)}$, $n=1-4$, of [AC]. C_n . Table 3 contains the calculated values of the free energy values of electron transfer ($\Delta G_{et(n)}$, $n=1-4$, in kcal mol^{-1}) between the selected AC 1 and fullerenes C_n in the complexes. The $\Delta G_{et(n)}$ values ($n=1-4$) for [AC]. C_n (C_{60} , C_{70} , C_{76} , C_{82} , C_{86} , C_{78} , C_{84} , and C_{120}) are predicted by using Eq. 5–8 and the Rehm-Weller equation (see Table 3).

Equations 9–12 demonstrate the relationships between the number “ n ” of carbon atoms in the fullerenes and the first, second, third, and fourth free energy values of electron transfers ($\Delta G_{et(n)}$) of the complexes [DA]. C_n ($n=60, 70, 76, 82$, and 86). These data were regressed with the second-order polynomial equations. The R -squared values (R^2) for the equations are 0.987, 0.992, 0.938, and 0.947, respectively.

By using Eq. 1 and 9–12, it is possible to calculate the values of $\Delta G_{et(1)}$ to $\Delta G_{et(4)}$ of the complexes [DA]. C_n (C_{60} , C_{70} , C_{76} , C_{82} , C_{86} , C_{78} , C_{84} , and C_{120}) B-1 to B-8. The $\Delta G_{et(n)}$ ($n=1-4$) values for [DA]. C_n (C_{60} , C_{70} , C_{76} , C_{82} , C_{86} , C_{78} , C_{84} , and C_{120}) are predicted by using Eq. 9–12 and the Rehm-Weller equation (see Table 4).

By utilizing these results (Eq. 13–16) and the Rehm-Weller equation (Eq. 1), the electron transfer energy values of $\Delta G_{et(n)}$ ($n=1-4$) of the complexes between SE 3 and fullerenes (C_{60} , C_{70} , C_{76} , C_{82} , C_{86} , C_{78} , C_{84} , and C_{120}) were approximated (Table 5). The calculated values of the free electron transfer energy of $\Delta G_{et(n)}$ ($n=1-4$) for selected [SE]. C_n ($n=60, 70, 76, 82$, and 86 , compounds C-1 to C-5) in the Rehm-Weller equation and Eq. 13–16 are compared in Table 5.

Equations 17–20 were regressed with a second-order polynomial. The R -squared values (R^2) for these graphs are 0.987, 0.992, 0.938, and 0.947, respectively. By using Eq. 17–20, it is possible to calculate the values of $\Delta G_{et(n)}$; $n=1-4$ of [EP]. C_n (EP = epinephrine). Table 5 contains the calculated values of the free energy of electron transfer ($\Delta G_{et(n)}$, $n=1-4$, in kcal mol^{-1}) between the selected EP 4 and fullerenes C_n in the complexes. The $\Delta G_{et(n)}$ ($n=1-4$) values for [EP]. C_n (C_{60} , C_{70} , C_{76} , C_{82} , C_{86} , C_{78} , C_{84} , and C_{120}) are predicted by using Eq. 17–20 and the Rehm-Weller equation (see Table 5).

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 3, 4, 5, and 6. It seems that these results are related to the HOMO and LUMO gap of the fullerenes.

The Marcus theory is currently the dominant theory of electron transfer in chemistry. The 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 [48].

ET is one of the most important chemical processes in nature, playing a central role in many biological, physical, and chemical (both organic and inorganic) systems. Solid-state electronics depends on 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 in 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 [48].

The free energy of electron transfer ΔG_{et} is the difference between the reactants on the left and the products on the right, and $\Delta G_{et}^\ddagger$ is the activation energy. The reorganization energy is the energy that 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 [48].

In Tables 3, 4, 5, and 6, the calculated values of the first to fourth free activation energy of electron transfer and kinetic rate constants of the electron transfers are shown, $\Delta G_{et(n)}^\ddagger$ and $\lambda_{et(n)}$ ($n=1-4$) by utilizing Eq. 2 and 3. Using Eq. 2 and 3, it is possible to calculate the first to fourth activated free energy values of electron transfer and kinetic rate constants of the electron transfers, $\Delta G_{et(n)}^\ddagger$ and $\lambda_{et(n)}$ ($n=1, 4$), respectively, for [NT]. C_n A-1 to A-8 up to D-1 to D-8 in accordance with the Marcus theory. Figure 3 shows the surfaces of the free energy values of electron transfer $\Delta G_{et(n)}$ and $\Delta G_{et(n)}^\ddagger$ ($n=1-4$) between the selected NTs 1–4 and fullerenes C_n ($n=60, 70, 76, 82$, and 86), which create the predicted complexes [NT]. C_n A-1 to A-8 up to D-1 to D-8. The values of the first to fourth activated free energy values of electron transfer, $\Delta G_{et(n)}^\ddagger$ ($n=1-4$) for A-1 to A-8 up to D-1 to D-8, 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 $\lambda_{et(n)}$ ($n=1-4$) decrease with increasing $\Delta G_{et(n)}$ and $\Delta G_{et(n)}^\ddagger$ ($n=1-4$) for [NT]. C_n A-1 to A-8 up to D-1 to D-8. The zero values mean that there was not any electron transfer

process between the parts of the predicted complexes. See Tables 3, 4, 5, and 6 and Fig. 3.

By using Eq. 1 (Rehm-Weller equation), Eq. 2 and 3 (Marcus theory), and Eq. 5–20, the values of $\Delta G_{et(n)}$ ($n=1-4$), $\Delta G_{et(n)}^\ddagger$, and $\lambda_{et(n)}$ ($n=1-4$) were calculated for [NT]. C_n A-1 to A-8 up to D-1 to D-8 complexes. The values of the number of carbon atoms (n) show a good relationship with the values of the free energy of electron transfer $\Delta G_{et(n)}$ ($n=1-4$), $\Delta G_{et(n)}^\ddagger$, and $k_{et(n)}$ ($n=1-4$) in [NT]. C_n A-1 to A-8 up to D-1 to D-8 complexes. Figure 3 shows the surfaces of the free energy of electron transfer $\Delta G_{et(n)}$ and $\Delta G_{et(n)}^\ddagger$ ($n=1-4$) between 1 and 15 and fullerenes (C_{60} , C_{70} , C_{76} , C_{82} , C_{86} , C_{78} , C_{84} , and C_{120}) in the structures of A-1 to A-8 up to D-1 to D-8, calculated by Eq. 1–20 and shown in Tables 2, 3, 4, 5, and 6. With the appropriate equations, it is possible to calculate the first to fourth free energy values of electron transfer (ΔG_{et} in kcal mol⁻¹), the first to fourth activated free energy of electron transfer, and kinetic rate constants of the electron transfers, $\Delta G_{et(n)}^\ddagger$ and $\lambda_{et(n)}$ ($n=1-4$), respectively, for [NT]. C_n A-1 to A-8 up to D-1 to D-8 complexes, in close accordance with the results of the Marcus theory.

The complex structures which were discussed here and the calculated values of $\Delta G_{et(n)}$ ($n=1-4$), $\Delta G_{et(n)}^\ddagger$, and $\lambda_{et(n)}$ ($n=1-4$) corresponding to these complexes were neither synthesized nor reported before. It is supposed that the electron transfer process between the NTs and the fullerenes to construct the [NT]. C_n complexes makes a disturbance in the transmission of signals from one neuron to the next across synapses.

Conclusion

The selected NTs AC 1, DP 2, SE 3, and EP 4 and fullerenes have shown important electron transfer properties as the redox systems and molecular conductors. The electrochemical data of selected NT 1–4, i.e., [NT]. C_n A-1 to A-8 up to D-1 to D-8 supramolecular complexes, were reported here. These include the four free energy values of electron transfer ($\Delta G_{et(n)}$), calculated using the Rehm-Weller equation, and $\Delta G_{et(n)}^\ddagger$ as well as $\lambda_{et(n)}$ ($n=1-4$) using equations of the Marcus theory for the complexes A-1 to A-8 up to D-1 to D-8. 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 $\Delta G_{et(n)}$ ($n=1-4$), $\Delta G_{et(n)}^\ddagger$, and $\lambda_{et(n)}$ ($n=1-4$) for NTs 1–4, as nanocomplexes [NT]. C_n , A-1 to A-8 up to D-1 to D-8 of the fullerenes (C_{60} , C_{70} , C_{76} , C_{82} , C_{86} , C_{78} , C_{84} , and C_{120}). It seems that the discussed electron transfer could stop some of the phenomena related to high transmission of signals from one neuron to the next across synapses in neurogenic shocks. The novel complexes discussed have neither been synthesized nor reported previously.

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