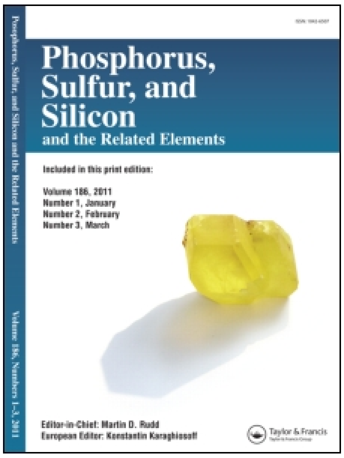

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Structural Relationships and Theoretical Study of Electron Transfer Properties of 1,3,2-Dithiazolyl Radicals with Fullerenes in Nanostructure [1,3,2-DTA(s)]@C_n Supramolecular Complexes

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STRUCTURAL RELATIONSHIPS AND THEORETICAL STUDY OF ELECTRON TRANSFER PROPERTIES OF 1,3,2-DITHIAZOLYL RADICALS WITH FULLERENES IN NANOSTRUCTURE [1,3,2-DTA(s)]@C_n SUPRAMOLECULAR COMPLEXES

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Various empty carbon fullerenes with different carbon atoms have been obtained and investigated. The dithiazolyl radicals have shown important electron-transfer properties. Topological indices are digital values that are assigned based on chemical composition. These values 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 2,3-naphthalene-1,3,2-dithiazolyl (NDTA), 2,3-quinoxaline-1,3,2-dithiazolyl (QDTA), and 1,2,5-thiazolo[3,4-b]-1,3,2-dithiazolo[3,4-b]pyridazin-2-yl (TDP-DTA), radicals, 1–3 as molecular conductor radicals and fullerenes C_n (n = 60, 70, 76, 82, and 86), which create [1,3,2-DTA(s)]@C_n, A-1 to A-5 (NDTA]@C_n), B-1 to B-5 ([QDTA]@C_n), and C-1 to C-5 ([TDP-DTA]@C_n). 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, B1 to B-5, and C-1 to C-5 supramolecular [1,3,2-DTA(s)]@C_n 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-18, B-1 to B-18, and C-1 to C-18 (5–60) for fullerenes C_{60} to C_{300}.

Keywords 1,3,2-Dithiazolyl radicals; electron transfer properties; free energy of electron transfer; fullerenes; molecular conductors; Rehm–Weller equation

INTRODUCTION

1,3,2-Dithiazolyl radicals have important electron-transfer properties. These radicals and their selenium analogues are used as molecular conductors.[1–6] Neutral heterocyclic π-radicals represent versatile building blocks for applications in the field of molecular

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materials.[1–3] Most work has focused on derivatives of the 1,2,3,5-dithiadiazolyl system (DTDA) and their selenium analogues, with the intent of using them as molecular conductors.[145] Their potential as molecular magnets has also been pursued.[1,6] Measurement and comparison of the electrochemical and ESR properties of all three radicals allows an interpretation of their transport properties in terms of the energetic and electronic criteria required for charge transport in a neutral radical conductor.[1]

In contrast to the DTDA system, the solid-state structures and transport properties of derivatives of the 1,3,2-dithiazolyl rings (DTA) have received relatively little attention, although the radicals themselves have been known for well over a decade.[178]

As part of an exploration of the architectural issues behind the diverse structural patterns exhibited by DTA radicals, the solid-state structures and magnetic properties of the 2,3-naphthalene- and quinoxaline-based derivatives NDTA **1** and QDTA **2** were reported.[1,9] As a development of the study on NDTA and QDTA, Barclay et al. have prepared and characterized the ternary heterocyclic radical 1,2,5-thiadiazolo[3,4-*b*]-1,3,2-dithiazolo[3,4-*b*]pyrazin-2-yl, **3** (TDP-DTA).[1] Barclay et al. performed variable temperature magnetic susceptibility measurements on TDP-DTA, and the nature of the observed phase transition near 150 K has been interpreted in the light of the results of single-crystal X-ray structure determinations at 293 and 150 K.[1]

Since the discovery of fullerenes (C_n), one of the main classes of carbon compounds, the unusual structures and physiochemical properties of these molecules have been discovered, 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 Smith 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.[12d]d reported evidence for the latter interaction to measure 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 ref. [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, Xie et al.[16] cathodically reduced C_{60} in six reversible one-electron steps for −0.97 V 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, Jehoulet et al. [17] first reported on the irreversible electrochemical and structural reorganization of solid fullerenes in acetonitrile. Janda 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 $\sim$100 nm in diameter.[18,19]

Graph theory has been a useful tool in assessing the quantitative structure activity relationship (QSAR) and quantitative structure property relationship (QSPR).[25–36] Numerous studies in different areas have used topological indices (TI).[25–33] 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 2,3-naphthalene-1,3,2-dithiazolyl (NDTA), 2,3-quinoxaline-1,3,2-dithiazolyl (QDTA), and 1,2,5-thiazolo[3,4-b]-1,3,2-dithiazolo[3,4-b]pyridazin-2-yl (TDP-DTA), radicals **1–3** [1,3,2-DTA(s)], 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[47] to create [1,3,2-DTA(s)]@C_n, **A-1** to **A-5** (NDTA]@C_n), **B-1** to **B-5** ([QDTA]@C_n), and **C-1** to **C-5** ([TDP-DTA]@C_n). 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 NDTA, QDTA, and TDP-DTA **1–3** as a class of electron-transfer radicals, with fullerenes C_{60} to C_{300} ([1,3,2-DTA(s)]@C_n, complexes **5–60**). This study calculated the four free energies of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) of **A-1** to **A-18**, **B-1** to **B-18**, and **C-1** to **C-18**. See Equations (1) to (13), Tables I to III, and Figures 1 and 2.

Table I The data values on the NDTA **A-1** to **A-5** and the values of the four free energies of electron transfer (ΔG_{et}), in kcal mol^{-1}, between NDTA radical **1** with C_n (as [NDTA]@C_n compounds **A-6** to **R-6**) (forms **5–9** and **20–32**) supramolecular complexes

No.	Row	*Formula of [NDTA]@C_n	(ΔG_{et}) in kcal mol^{-1} [NDTA]@C_n			
			$\Delta G_{et(1)}$*	$\Delta G_{et(2)}$*	$\Delta G_{et(3)}$*	$\Delta G_{et(4)}$*
5	**A-1**	[NDTA]@C_{60}	31.56 (31.36)	39.95 (40.12)	50.64 (50.5)	61.26 (61.1)
6	**A-2**	[NDTA]@C_{70}	30.75 (30.66)	37.75 (37.81)	47.42 (48.65)	57.3 (58.57)
7	**A-3**	[NDTA]@C_{76}	27.44 (27.21)	34.28 (34.59)	45.25 (45.19)	54.55 (54.65)
8	**A-4**	[NDTA]@C_{82}	22.02 (21.44)	29.20 (29.51)	42.90 (41.96)	51.52 (50.27)
9	**A-5**	[NDTA]@C_{86}	17.22 (17.06)	24.91 (25.13)	41.23 (42.43)	49.34 (50.73)
20	**A-6**	[NDTA]@C_{78}	25.87	32.77	44.49	53.57
21	**A-7**	[NDTA]@C_{84}	19.74	27.14	42.08	50.45
22	**A-8**	[NDTA]@C_{120}	−61.50	−40.44	23.83	25.81
23	**A-9**	[NDTA]@C_{132}	−105.51	−75.87	16.31	15.35
24	**A-10**	[NDTA]@C_{140}	−139.56	−103.08	10.90	7.75
25	**A-11**	[NDTA]@C_{146}	−167.57	−125.37	6.63	1.73
26	**A-12**	[NDTA]@C_{150}	−187.41	−141.12	3.68	−2.44
27	**A-13**	[NDTA]@C_{160}	−241.15	−183.64	−4.03	−13.42
28	**A-14**	[NDTA]@C_{162}	−252.60	−192.68	−5.63	−15.70
29	**A-15**	[NDTA]@C_{240}	−882.68	−685.08	−83.77	−129.32
30	**A-16**	[NDTA]@C_{276}	−1294.15	−1004.27	−130.10	−197.76
31	**A-17**	[NDTA]@C_{288}	−1448.24	−1123.57	−146.98	−222.82
32	**A-18**	[NDTA]@C_{300}	−1610.79	−1249.32	−164.58	−249.12

The data of $\Delta G_{et(n)}$ (n = 1–4) were predicted by using Eqs. (2)–(5), and those in parentheses were calculated by the Rehm–Weller equation [Eq. (1)].

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

Table II The data values on the QDTA **B-1** to **B-5** and the values of the four free energies of electron transfer (ΔG_{et}), in kcal mol^{-1}, between QDTA radical **2** with C_n (as [QDTA]@C_n compounds **B-6** to **B-6**) (forms **10–14** and **33–45**) supramolecular complexes

			(ΔG_{et}) in kcal mol^{-1} [QDTA]@C_n			
No.	Row	*Formula of [QDTA]@C_n	$\Delta G_{et(1)}{}^{*}$	$\Delta G_{et(2)}{}^{*}$	$\Delta G_{et(3)}{}^{*}$	$\Delta G_{et(4)}{}^{*}$
10	**B-1**	[QDTA]@C_{60}	39.51 (39.43)	48.21 (48.19)	58.71 (58.57)	69.65 (69.18)
11	**B-2**	[QDTA]@C_{70}	37.91 (38.74)	46.70 (47.73)	55.50 (56.72)	65.67 (66.64)
12	**B-3**	[QDTA]@C_{76}	34.82 (34.82)	43.10 (42.66)	53.33 (53.26)	63.06 (62.72)
13	**B-4**	[QDTA]@C_{82}	30.15 (29.51)	37.47 (37.58)	50.98 (50.04)	60.29 (58.34)
14	**B-5**	[QDTA]@C_{86}	26.15 (26.98)	32.60 (33.20)	49.32 (50.50)	58.34 (59.26)
33	**B-6**	[QDTA]@C_{78}	33.44	41.45	52.27	62.15
34	**B-7**	[QDTA]@C_{84}	28.24	35.15	50.16	59.33
35	**B-8**	[QDTA]@C_{120}	−36.39	−45.14	31.93	38.87
36	**B-9**	[QDTA]@C_{132}	−70.66	−88.09	24.41	30.73
37	**B-10**	[QDTA]@C_{140}	−97.05	−121.22	19.00	24.94
38	**B-11**	[QDTA]@C_{146}	−118.69	−148.42	14.73	20.40
39	**B-12**	[QDTA]@C_{150}	−134.01	−167.69	11.79	17.28
40	**B-13**	[QDTA]@C_{160}	−175.39	−219.78	4.07	9.16
41	**B-14**	[QDTA]@C_{162}	−184.19	−230.87	2.47	7.48
42	**B-15**	[QDTA]@C_{240}	−665.55	−838.82	−75.63	−72.35
43	**B-16**	[QDTA]@C_{276}	−978.41	−1234.73	−121.94	−118.63
44	**B-17**	[QDTA]@C_{288}	−1095.42	−1382.89	−138.82	−135.38
45	**B-18**	[QDTA]@C_{300}	−1218.81	−1539.14	−156.41	−152.80

The data of $\Delta G_{et(n)}$ (n = 1–4) were predicted by using Eqs. (6)–(9), and those in parentheses were calculated by the Rehm–Weller equation [Eq. (1)].

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

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 [1,3,2-DTA(s)]@C_n, **A-1** to **A-5** ([NDTA]@C_n), **B-1** to **B-5** ([QDTA]@C_n), and **C-1** to **C-5** ([TDP-DTA]@C_n) compounds **5–60**.

Both linear (MLR: multiple linear regressions) and nonlinear (ANN: artificial neural network) models were used in this study. Equations (1)–(13) 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]

$$\Delta G^{\circ} = e[E_D^{\circ} - E_A^{\circ}] - \Delta E^{*} + \omega_1 \tag{1}$$

where e is the unit electrical charge, $E_D{}^{\circ}$ and $E_A{}^{\circ}$ 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

Table III The data values on the TDP-DTA radical **C-1** to **C-5** and the values of the four free energies of electron transfer (ΔG_{et}), in kcal mol^{-1}, between TDP-DTA radical **3** with C_n (as [TDP-DTA]@C$_n$ compounds **C-6** to **C-6**) (forms **15–19** and **46–60**) supramolecular complexes

No.	Row	*Formula of [TDP-DTA]@C_n	(ΔG_{et}) in kcal mol^{-1} [TDP-DTA]@C_n			
			$\Delta G_{et(1)}$*	$\Delta G_{et(2)}$*	$\Delta G_{et(3)}$*	$\Delta G_{et(4)}$*
15	**C-1**	[TDP-DTA]@C_{60}	48.27 (48.19)	57.03 (56.95)	67.70 (67.33)	78.35 (77.94)
16	**C-2**	[TDP-DTA]@C_{70}	46.92 (47.50)	55.53 (56.49)	64.57 (65.49)	74.47 (75.40)
17	**C-3**	[TDP-DTA]@C_{76}	43.85 (44.04)	51.94 (51.42)	62.46 (62.03)	71.78 (71.48)
18	**C-4**	[TDP-DTA]@C_{82}	39.09 (38.27)	46.32 (46.35)	60.16 (58.8)	68.82 (67.1)
19	**C-5**	[TDP-DTA]@C_{86}	34.98 (35.74)	41.45 (41.96)	58.53 (59.26)	66.69 (67.56)
46	**C-6**	[TDP-DTA]@C_{78}	42.45	50.29	61.71	70.82
49	**C-7**	[TDP-DTA]@C_{84}	37.13	43.99	59.36	67.77
50	**C-8**	[TDP-DTA]@C_{120}	−30.34	−36.24	41.45	43.69
51	**C-9**	[TDP-DTA]@C_{132}	−66.37	−79.18	34.04	33.48
52	**C-10**	[TDP-DTA]@C_{140}	−94.15	−112.30	28.70	24.06
53	**C-11**	[TDP-DTA]@C_{146}	−116.96	−139.50	24.48	20.17
54	**C-12**	[TDP-DTA]@C_{150}	−133.10	−158.75	21.57	16.11
55	**C-13**	[TDP-DTA]@C_{160}	−176.76	−210.88	13.95	5.39
56	**C-14**	[TDP-DTA]@C_{162}	−186.05	−221.92	12.36	3.15
57	**C-15**	[TDP-DTA]@C_{240}	−695.19	−829.77	−65.04	−107.69
58	**C-16**	[TDP-DTA]@C_{276}	−1006.61	−1201.73	−108.65	−170.48
59	**C-17**	[TDP-DTA]@C_{288}	−1150.63	−1373.78	−127.80	−198.90
60	**C-18**	[TDP-DTA]@C_{300}	−1281.41	−1530.01	−145.29	−224.43

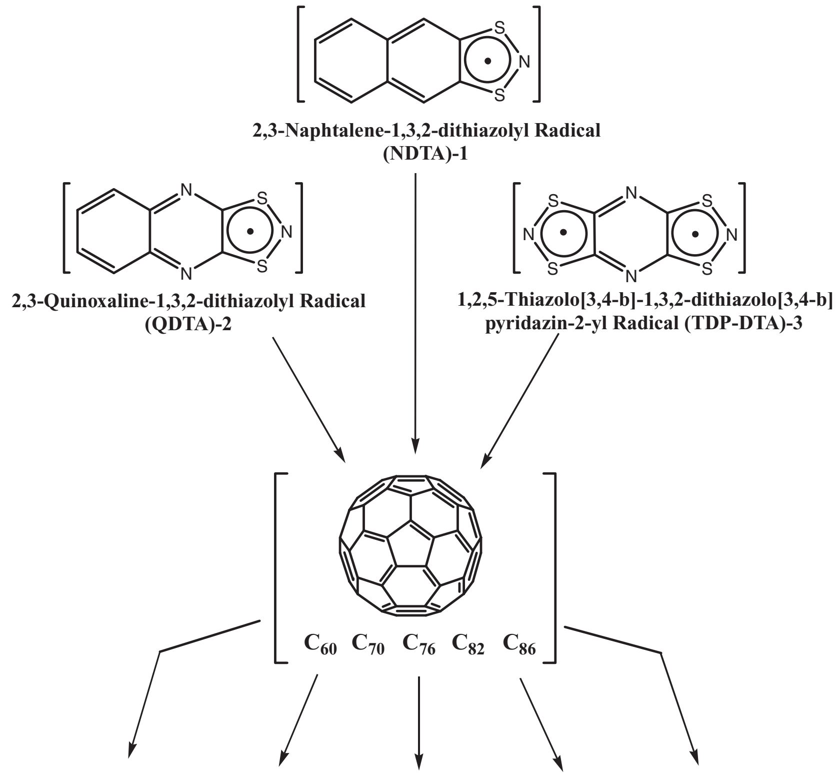
The data of $\Delta G_{et(\mathrm{n})}$ (n = 1–4) were predicted by using Eqs. (6)–(9), and those in parentheses were calculated by the Rehm–Weller equation [Eq. (1)].

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

(ET) distance. If an electrostatic complex forms before the electron transfer, the work term in this expression is zero.[37]

DISCUSSION

The derivatives of 1,2,3,5-dithiadiazolyl system were utilized as molecular conductors. A variety of preparative routes to dithiazolyl radicals has been developed, and, as Heckmann et al. have pointed out,[1,38] there is no single method that serves for all systems. Most methods, indeed, have relatively restricted applicability. The reduction of dithiazolylium salts was one of the first approaches developed.[1] The addition of the NS_2^+ cation to alkynes provides an effective route to the necessary dithiazolylium cations,[1,39] while the condensation of *ortho*-bis(sulfenyl chlorides) with trimethylsilyl azide allows access to aromatic derivatives such as NDTA, QDTA, and TDP-DTA as a class of electron-transfer molecules.[1,40–42] The compound is prepared by treatment of 5,6-dithiolo-1,2,5-thiadiazolo[3,4-*b*]pyrazine with $S_3N_3Cl_3$ and purified by fractional sublimation in vacuo. In the course of this reaction, the chloride salt of the binary cation $S_4N_3^+$ is produced as a side product, along with the neutral form of TDP-DTA. Under excess chlorine gas conditions, TDP-DTA can be oxidized to what was presumed is a chloride salt of the corresponding dithiazolylium cation, but this material readily was reverted to the neutral material upon heating it to 60 °C.[1] The preparation of QDTA, by the treatment of the corresponding benzenesulfonamide with ammonia, had been described by previous research.[1,43]



A-1: [NDTA]@C_{60}	**A-2:** [NDTA]@C_{70}	**A-3:** [NDTA]@C_{76}	**A-4:** [NDTA]@C_{82}	**A-5:** [NDTA]@C_{86}
B-1: [QDTA]@C_{60}	**B-2:** [QDTA]@C_{70}	**B-3:** [QDTA]@C_{76}	**B-4:** [QDTA@C_{82}	**B-5:** [QDTA]@C_{86}
C-1: [TDB-DTA]@C_{60}	**C-2:** [TDB-DTA]@C_{70}	**C-3:** [TDB-DTA]@C_{76}	**C-4:** [TDB-DTA]@C_{82}	**C-5:** [TDB-DTA]@C_{86}

Figure 1 The conjectured structures of 2,3-naphthalene-1,3,2-dithiazolyl (NDTA), 2,3-quinoxaline-1,3,2-dithiazolyl (QDTA), and 1,2,5-thiazolo[3,4-b]-1,3,2-dithiazolo[3,4-b]pyridazin-2-yl (TDP-DTA), radicals **1–3**, and fullerenes C_n (n = 60, 70, 76, 82, and 86), which create [1,3,2-DTA(s)]@C_n, **A-1** to **A-5** (NDTA]@C_n), **B-1** to **B-5** ([QDTA]@C_n), and **C-1** to **C-5** ([TDP-DTA]@C_n).

The results of cyclic voltammetry (CV) and ESR analysis of TDP-DTA and related heterocyclic dithiazolyls indicate that the spin distributions and donor/acceptor properties of these radicals are extremely sensitive to the nature of the 4,5-substituents.[1]

Here, we 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., NDTA, QDTA, and TDP-DTA, radicals **1–3**, with fullerenes C_{60} to C_{300} ([1,3,2-DTA(s)]@C_n, complexes **5–60**). The oxidation potentials ($^{ox.}E_1$) of NDTA, QDTA, and TDP-DTA, radicals **1–3** are: 0.27, 0.62, and 1.00 V, respectively.

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 −2.41 V, respectively.[44] The $^{Red}E_n$(Volt, n = 1–4) for C_{70} are −1.09, −1.48, −1.87, and −2.30 V, respectively.[44] The values of $^{Red}E_n$(Volt, n = 1–4) for C_{76} are −0.94, −1.26, −1.72, and −2.13 V, respectively.[44] Four values of $^{Red}E_n$(Volt, n = 1–4) for C_{82} are −0.69, −1.04, −1.58, and −1.94 V, respectively.[44] The $^{Red}E_n$(Volt, n = 1–4) for C_{86} are −0.58, −0.85, −1.60, and −1.96 V, respectively.[44] C_{180}

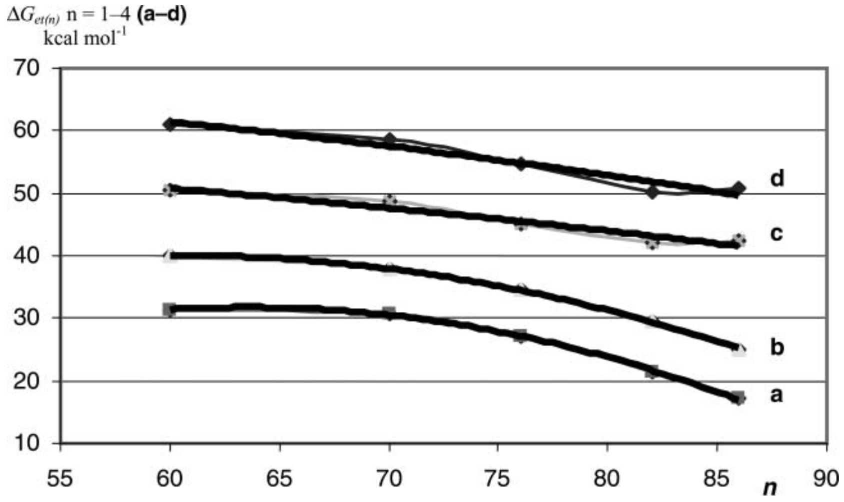


Figure 2 The relationship between the number "n" of carbon atoms in the fullerenes and the (a) first, (b) second, (c) third, and (d) fourth free-energies of electron transfer ($\Delta G_{et(4)}$) of [NDTA]@C_n (n = 60, 70, 76, 82, and 86), compounds **A-1** to **A-5**.

and C_{240} have not been prepared or isolated among the fullerenes, which are listed in Tables I–III.

Tables I–III contain a summary of the data. They show the 216 calculated values for **5–63** of the four electron transfer free energies ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$, in kcal mol^{-1}) between 1,3,2-dithiazolyl electron-transfer radicals **1–3** and fullerenes C_n (n = 60, 70, 76, 82, and 86) as [1,3,2-DTA(s)]@C_n complexes. These values were calculated using the Rehm–Weller equation [Eq. (1)]. The selected 1,3,2-dithiazolyl radicals (**1–3**) 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-18**, **B-1** to **B-18**, **C-1** to **C-18**, and **D-1** to **D-18** (complexes **5–60**) are reported in the appropriate tables. Figure 1 depicts the structures of NDTA, QDTA, and TDP-DTA, radicals **1–3**, and fullerenes C_n (n = 60, 70, 76, 82, and 86), which create [1,3,2-DTA(s)]@$C_{n,}$ **A-1** to **A-5** ([NDTA]@C_n), **B-1** to **B-5** ([QDTA]@C_n), and **C-1** to **C-5** ([TDP-DTA]@C_n).

Figure 2 (graphs *a–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 [NDTA]@C_n (n = 60, 70, 76, 82 and 86). Equations (2)–(5) correspond to Figure 2 (graphs *a–d*). These data were regressed with a second-order polynomial. The R-squared values (R^2) for these graphs are 0.9992, 0.9998, 0.9382, and 0.9476, respectively.

$$\Delta G_{et(1)} = -0.029(\mathrm{n})^2 + 3.7408(\mathrm{n}) - 87.039 \tag{2}$$

$$\Delta G_{et(2)} = -0.224(\mathrm{n})^2 + 2.692(\mathrm{n}) - 40.924 \tag{3}$$

$$\Delta G_{et(3)} = -0.0025(\mathrm{n})^2 + 0.0032(\mathrm{n}) + 59.453 \tag{4}$$

$$\Delta G_{et(4)} = -0.0039(n)^2 + 0.1112(\mathrm{n}) + 68.628 \tag{5}$$

By using Equations (1)–(5), it is possible to calculate the values of $\Delta G_{et(1)}$ to $\Delta G_{et(4)}$ of [NDTA]@C_n. Table I contains the calculated values of the free energies of electron transfer ($\Delta G_{et(\mathrm{n})}$, n = 1–4, in kcal mol^{-1}) between the selected NDTA **1** and C_n (as [NDTA]@C_n compounds **A-1** to **A-5**) **5–9** supramolecular complexes. The $\Delta G_{et(\mathrm{n})}$ (n = 1–4) for [NDTA]@C_n (C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}, C_{84}, 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 (2)–(5) and the Rehm–Weller equation (see Table I).

Equations (6)–(9) 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 [QDTA]@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 0.9868, 0.9924, 0.9386, and 0.9339, respectively.

$$\Delta G_{et(1)} = -0.022(\mathrm{n})^2 + 2.713(\mathrm{n}) - 43.7100 \tag{6}$$

$$\Delta G_{et(2)} = -0.0281(\mathrm{n})^2 + 3.5028(\mathrm{n}) - 60.742 \tag{7}$$

$$\Delta G_{et(3)} = -0.0025(\mathrm{n})^2 + 0.0036(\mathrm{n}) + 67.501 \tag{8}$$

$$\Delta G_{et(4)} = -0.0023(\mathrm{n})^2 + 0.0989(\mathrm{n}) + 83.866 \tag{9}$$

By using Equations (1) and (6)–(9), it is possible to calculate the values of $\Delta G_{et(1)}$ to $\Delta G_{et(4)}$ of [QDTA]@C_n. Table II contains the 72 calculated values of the free energies of electron transfer ($\Delta G_{et(\mathrm{n})}$, n = 1–4, in kcal mol^{-1}) between the selected NDTA, QDTA radical **2**, and the C_n (as [QDTA]@C_n compounds **B-1** to **B-5**) **10–14** supramolecular complexes. The $\Delta G_{et(\mathrm{n})}$ (n = 1–4) for [QDTA]@C_n (C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}, C_{84}, 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 (6)–(9) and the Rehm–Weller equation (see Table II).

The oxidation potential ($^{ox.}E_1$) of TDP-DTA) radical **3** is equal to 1.00 V. The results of the Rehm–Weller equation show the free energies of electron transfer ($\Delta G_{et(\mathrm{n})}$, n = 1–4, in kcal mol^{-1}) between **3** and C_n. Equations (10)–(13) 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 [TDP-DTA]@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.

$$\Delta G_{et(1)} = -0.0235(\mathrm{n})^2 + 2.9196(\mathrm{n}) - 42.298 \tag{10}$$

$$\Delta G_{et(2)} = -0.0281(\mathrm{n})^2 + 3.5033(n) - 52.004 \tag{11}$$

$$\Delta G_{et(3)} = -0.0025(\mathrm{n})^2 + 0.0125(\mathrm{n}) + 75.951 \tag{12}$$

$$\Delta G_{et(4)} = -0.0038(\mathrm{n})^2 + 0.1064(\mathrm{n}) + 85.649 \tag{13}$$

By using Equations (10)–(13), it is possible to calculate the values of $\Delta G_{et(1)}$ to $\Delta G_{et(4)}$ of [[TDP-DTA]@C_n. Table III contains the 72 calculated values of the free energies of electron transfer ($\Delta G_{et(\mathrm{n})}$, n = 1–4, in kcal mol^{-1}) between the selected TDP-DTA radical **3** and C_n (as [TDP-DTA]@C_n **C-1** to **C-5** **15–19** supramolecular complexes. The $\Delta G_{et(\mathrm{n})}$ (n = 1–4) for [TDP-DTA]@C_n (C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}, C_{84}, 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 (10)–(13) and the Rehm–Weller equation (see Table III).

By utilizing these results [Equations (2)–(13)] and the Rehm–Weller equation, the electron transfer energies of $\Delta G_{et(\mathrm{n})}$ (n = 1–4) of the complexes between the selected class of electron-transfer radicals **1–3** with fullerenes (C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}, C_{84},

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 I–III). The calculated values of the free electron transfer energies of $\Delta G_{et(\mathrm{n})}$ (n = 1–4) for selected [1,3,2-DTA(s)]@C_n (n = 60, 70, 76, 82, and 86, compounds **5** to **60**) in the Rehm–Weller equation and Equations (2)–(13) are compared in Tables I–III. 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 $\Delta G_{et(\mathrm{n})}$ (n = 1–4) were decreased. It seems that electron transfer rate increases as the electron population in the C_n structures increases. Tables I–III indicate that these results are related to the HOMO and LUMO gap of the fullerenes. The tables also show that some of the free electron transfer energies $\Delta G_{et(\mathrm{n})}$ (n = 1–4) values of [NDTA]@C_n, [QDTA]@C_n, and [TDP-DTA]@C_n are negative. The supramolecular complex structures that were discussed here, and the calculated values of $\Delta G_{et(\mathrm{n})}$ (n = 1–4) corresponding to these supramolecular complexes, were neither synthesized nor reported before.

CONCLUSION

1,3,2-Dithiazolyl radicals **1–3** and fullerenes have important electron-transfer properties as molecular conductors. The electrochemical data of selected 1,3,2-dithiazolyl radicals **1–3**, i.e., [NDTA]@C_n, [QDTA]@C_n, and [TDP-DTA]@C_n, were reported in this article. These include the four free-energies of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$), calculated using the Rehm–Weller equation, for **A-1** to **A-5**, **B1** to **B-5**, and **C-1** to **C-5** supramolecular complexes. 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. By using the equations of this model, a good approximation was calculated for $\Delta G_{et(1)}$ to $\Delta G_{et(4)}$ for 1,3,2-dithiazolyl radicals **1–3**, as [NDTA]@C_n, [QDTA]@C_n, and [TDP-DTA]@C_n supramolecular complexes (**A-1** to **A-18**, **B-1** to **B-18**, and **C-1** to **C-18** of the fullerenes C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}, C_{84}, 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.

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