

## Theoretical and quantitative structural relationships of the electrochemical properties of *Cis*-unsaturated thiocrown ethers and *n*-type material bulk-heterojunction polymer solar cells as supramolecular complexes [X-UT-Y]@R (R = PCBM, *p*-EHO-PCBM, and *p*-EHO-PCBA)

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Since the discovery of fullerenes as a class of nanostructure compounds, many potential applications have been suggested for their unusual structures and properties. The isolated pentagon rule (IPR) states that all pentagonal carbon rings are isolated in the most stable fullerene. Fullerenes  $C_n$  are a class of spherical carbon allotrope group with unique properties. Electron transfer between fullerenes and other molecules is thought to involve the transfer of electrons between the molecules surrounding the fullerene cage. One class of electron transfer molecules is the methanofullerene derivatives ([6,6]-phenyl  $C_{61}$ -butyric acid methyl ester (PCBM), 4-(2-ethylhexyloxy)-[6,6]-phenyl  $C_{61}$ -butyric acid methyl ester (*p*-EHO-PCBM), and 4-(2-ethylhexyloxy)-[6,6]-phenyl  $C_{61}$ -butyric acid (*p*-EHO-PCBA), **10–12**). It has been determined that  $C_{60}$  does not obey IPR. Supramolecular complexes **1–9** and **10–12** are shown to possess a previously unreported host–guest interaction for electron transfer processes. The unsaturated, *cis*-geometry, thiocrown ethers, (**1–9**) (described as [X-UT-Y], where X and Y indicate the numbers of carbon and sulfur atoms, respectively), are a group of crown ethers that display interesting physiochemical properties in the light of their conformational restriction compared with a corresponding saturated system, as well as the sizes of their cavities. Topological indices have been successfully used to construct mathematical methods that relate structural data to various chemical and physical properties. To establish a good relationship between the structures of **1–9** with **10–12**, a new index is introduced,  $\mu_{cs}$ . This index is the ratio of the sum of the number of carbon atoms ( $n_c$ ) and the number of sulfur atoms ( $n_s$ ) to the product of these two numbers for **1–9**. In this study, the relationships between this index and oxidation potential ( $^{ox}E_I$ ) of **1–9**, as well as the first to third free energies of electron transfer ( $\Delta G_{et(n)}$ , for  $n = 1–3$ , which is given by the Rehm–Weller equation) between **1–9** and PCBM, *p*-EHO-PCBM, and *p*-EHO-PCBA (**10–12**) as [X-UT-Y]@R (where R is the adduct PCBM, *p*-EHO-PCBM, and *p*-EHO-PCBA group) (**13–15**) supramolecular complexes are presented and investigated.

**Keywords:** methanofullerenes; Rehm–Weller equation; electron transfer process; unsaturated thiocrown ethers; molecular modeling

### Introduction

The unique stability of molecular allotropic forms such as  $C_{60}$  and  $C_{70}$  was demonstrated in 1985 [1]. This event led to the discovery of a whole new set of carbon-based substances known as fullerenes. One of the simplest compounds in the huge family of fullerenes is  $C_{60}$  [2]. Fullerenes are more reactive than planar aromatics because an important driving force for addition reactions is the reduction of strain, which results from pyramidalization in the  $sp^2$ -carbon network [2,3].

All pentagonal carbon rings are isolated in the most stable fullerenes, in accordance with the isolated pentagon rule (IPR). IPR has been proven valuable in understanding the stability of the cage structures of fullerenes and metallofullerenes [2]. The most abundant fullerenes,  $C_{60}$  and  $C_{70}$ , and all pure-carbon fullerenes larger than  $C_{70}$  follow IPR [4–7]. Non-IPR fullerenes, which contain adjacent

pentagons (APs), have been experimentally stabilized in the cases where it is topologically impossible to isolate all the pentagons fully, in accordance with Euler's theorem [4]. Alcamí et al. have shown that apart from strain, the most important physical property that governs the relative stabilities of fullerenes is the charge distribution within the cage [4]. This charge distribution is controlled by the number and location of APs and pyrene motifs. Alcamí et al. have also shown that when these motifs are uniformly distributed and well separated from one another, stabilization of non-IPR endohedral and exohedral derivatives as well as pure-carbon fullerene anions and cations becomes the rule rather than the exception [4].

Fullerenes violating IPR are obtained only in derivatized form since the [5,5] bond carbons readily react to release bond strain. Non-IPR fullerenes, however, still have unsaturated  $sp^2$  carbons at the [5,5] bond junctions, which

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allow their chemical properties to be probed [4–7]. It is concluded that although the fused-pentagon sites are very reactive toward carbene, the carbons forming the [5,5] junctions are less reactive than the adjacent ones; this confirms that these carbons interact strongly with the encaged metals and are stabilized by them [7]. For  $C_{60}$  and  $C_{72}$ , only one IPR structure is consistent with their symmetry. Theoretical studies on  $C_{60}$  and  $C_{72}$  have shown that the non-IPR-satisfying structures are more stable than the IPR-satisfying structure mentioned above [4–11].

The electrochemical properties of  $C_{60}$  have been studied since the early 1990s, when these materials became available in macroscopic quantities (for a review, see reference [12]). In 1990, Hauffler et al. [13] showed that  $C_{60}$  is electrochemically reducible in  $CH_2Cl_2$  to  $C_{60}^-$  and  $C_{60}^{2-}$ . In 1992, Echegoyen et al. [14] reported a cathodic reduction of  $C_{60}$  in six reversible, one-electron steps at a potential of  $-0.97$  V, vs. a ferrocene/ferrocenium standard couple [14]. This fact, along with the absence of anodic electrochemistry of fullerenes, is consistent with the electronic structure of fullerenes; the lowest unoccupied molecular orbital (LUMO) of  $C_{60}$  can accept up to six electrons to form  $C_{60}^{6-}$ , but the highest occupied molecular orbital (HOMO) energy gap does not allow for hole doping under the usual electrochemical conditions [14,15]. In 1991, Bard et al. [15] first reported the irreversible electrochemical and structural reorganization of solid fullerenes in acetonitrile. Dunsch et al. [16] extended these experimental conditions by investigating highly organized  $C_{60}$  films on highly ordered pyrolytic graphite in an aqueous medium [16,17].

One promising application of  $C_{60}$  research is in forming mixtures with  $\pi$ -conjugated polymers, to mimic photosynthesis for solar-energy conversion [18–22]. The possibility of replacing silicon wafers with new organic semiconductor materials in the fabrication of photovoltaic cells offers the prospects of lowering the manufacturing costs (printing and coating technologies using solution-processable materials) and forming lightweight solar modules for flexible, large-area applications [18,19]. In 2008, the syntheses and electrochemical properties of  $C_{60}$ -methanofullerene derivatives with [6,6]-phenyl  $C_{61}$ -butyric acid methyl ester (PCBM), 4-(2-ethylhexyloxy)-[6,6]-phenyl  $C_{61}$ -butyric acid methyl ester (*p*-EHO-PCBM), and 4-(2-ethylhexyloxy)-[6,6]-phenyl  $C_{61}$ -butyric acid (*p*-EHO-PCBA) were presented by Wudl et al. for usage in organic solar cells and field-effect transistors [18]. The results demonstrated how the addition of an electron-donating substituent in  $C_{60}$ -methanofullerene derivatives allowed them to be used as n-type materials for organic solar cells and organic field-effect transistor applications [18]. One of the widely used configurations in devices contains an active layer consisting of a blend of electron-donating materials (such as p-type conjugated polymers) and an electron-accepting material (such as the n-type, (6,6)-phenyl  $C_{61}$ -butyric acid methyl ester, PCBM) [18]. It was noted that placing electron-donating

substituents on the phenyl ring of PCBM can raise the LUMO energy, which will allow further optimization of the open-circuit voltage ( $V_{oc}$ ) of polymer/ $C_{60}$  fullerene organic solar cells [18,23]. The polymer solar cells had a layered structure of glass/PEDOT:PSS/P3HT/ $C_{60}$ -methanofullerene derivatives (PCBM, *p*-EHO-PCBM, and *p*-EHO-PCBA) blend/Al. P3HT and PEDOT:PSS denote poly(3-hexylthiophene) and poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate layers, respectively [18]. The  $C_{60}$ -methanofullerene derivatives with *p*-EHO-PCBM and *p*-EHO-PCBA were synthesized using the Wudl–Hummelen approach [18,24].

The unsaturated, *cis*-geometry thiocrown ethers (**1–9**) comprise a group with interesting physicochemical properties in the light of their conformational restrictions compared with the corresponding saturated systems and the sizes of their cavities. The *cis*-unsaturated thiocrown ethers (described as [X-UT-Y], where X and Y indicate the numbers of carbon and sulfur atoms, respectively), **1–9**, were synthesized, and their structures were confirmed [25–34]. 1,4-dithiin is the smallest member of compounds **1–9** that has been widely studied [35–45]. In 2001, the structures of [X-UT-Y] (X = 6, 9, 12, 15, 18, 21, 24, and 27 and Y = 2–9) **1–9** were reported by Tsuchiya et al. [25]. In that report, the  $^1H$  and  $^{13}C$ -NMR spectra, X-ray crystallographic data, Oak Ridge Thermal Ellipsoid Plot (ORTEP) drawings, cavity size, and UV spectra of [X-UT-Y] **1–9** were carefully considered [25]. The X-ray crystal structures and ORTEP drawings for some members of **1–9** [X-UT-Y], namely X = 15, 18, 21, 24, and 27 and Y = 5–9, show the presence of cavities and a nearly coplanar arrangement of sulfur atoms [25]. The average radii of the cavities for **4–8** were found to be 1.76, 2.34, 3.48, 4.43, and 5.36 Å, respectively [25]. The previously reported  $^{13}C$  and  $^1H$ -NMR spectra in  $CDCl_3$  showed that compound **4** has the highest chemical shifts. The electron densities of the C=C bonds increase with the increasing ring size from **4** to **9**, and decrease from **4** to **1** with the decreasing ring size [25,26]. In 2006, the oxidation potential ( $^{ox}E_1$ ), cyclic voltammograms (Fc/Fc $^+$ ), and free energies of electron transfer ( $\Delta G_{et}$ ) of the supramolecular complexes of [X-UT-Y] [ $C_{60}$ ] with *cis*-unsaturated thiocrown ethers **1–9** were considered by Tsuchiya et al. [26]. The endohedral metallofullerenes and their complexes with the thiocrown ethers have shown interesting properties for applications and basic research studies.

The wide variety of useful applications of the graph theory shows that this branch of discrete mathematics can benefit various science fields. The graph theory has been found to be an effective tool in quantitative structure-activity relationship (QSAR) and quantitative structure-property relationship (QSPR) [46–51]. A graph is a topological concept rather than a geometric concept, and hence, Euclidean metric lengths, angles, and three-dimensional spatial configurations have no meaning. Numerous studies have related these fields using topological indices (TIs) [51]. One group of TI was founded by Randić, who introduced the

molecular-branching index [52]. In 1975, Randić proposed a topological index that has become one of the most widely used in both QSAR and QSPR studies. The TIs are based on Randić's original idea of molecular branching but have been extended to account for contributions coming from path clusters, clusters, and chains of different lengths [53–60]. A burst in the research on TIs began in the 1990s and is marked by an increase in the number of studies and applications of TIs in chemistry [61,62]. Among the successful TIs in these applications, it is worth noting the molecular-connectivity indices [61,63] (including the Randić index [52]), the Randić index [52,56–60,64,65], the Kier indices [66,67], the electrotopological-state indices [68], the Balaban index [68], and the Wiener index [69]. Trinajstić et al. reported that 39 topological indices are presently available in the literature [65,70]. Estrada has performed important studies of generalized TIs with several topological indices in the graph invariant [64]. In 1993 and 1997, the Wiener and Harary indices were applied to studies on fullerenes [65,71,72]. The use of effective mathematical methods in establishing strong correlations between chemical properties and the indices have been reported [65,71,72], which is an important area of development. The ratio of the sum of the number of carbon atoms ( $n_c$ ) and the number of sulfur atoms ( $n_s$ ) to the product of these two numbers ( $\mu_{cs}$ ) was a useful numerical and structural value in the studies reported herein on unsaturated thiocrown ethers **1–9**.

QSAR studies of the  $\mu_{cs}$  index with respect to the oxidation potentials ( ${}^{\text{ox}}E_1$ ) of thiocrown ethers **1–9** as well as the free energies of electron transfer ( $\Delta G_{et}$ ) between **1–9** with La@C<sub>82</sub>, Sc<sub>2</sub>@C<sub>84</sub>, Er<sub>2</sub>@C<sub>82</sub>, and La@C<sub>72</sub>(C<sub>6</sub>H<sub>3</sub>Cl<sub>2</sub>; isomers: '2,4-', '2,5-', and '3,4-dichloro') were previously reported [71–73].

In this work, the reported electrochemical behavior [18] of series **10–12** was utilized to calculate the first to third free energies of electron transfer ( $\Delta G_{et(n)}$ , for  $n = 1, 2$ , which is given by the Rehm–Weller equation) between **1–9** and methanofullerene derivatives (PCBM, *p*-EHO-PCBM, and *p*-EHO-PCBA) **10–12**, and their supramolecular complexes derivatives as [X-UT-Y]@R (where 'R' is the adduct PCBM, *p*-EHO-PCBM, and *p*-EHO-PCBA group) (**13–15**) are presented and investigated (see Figure 1).

### Graphing and mathematical method

All graphing operations were performed using the Microsoft Office Excel 2003 program. The ratio of the sum of the number of carbon atoms ( $n_c$ ) and the number of sulfur atoms ( $n_s$ ) to the product of these two numbers ( $\mu_{cs}$ ) is a useful numerical and structural value for the investigated unsaturated thiocrown ethers **1–9** [68,74].

$$\mu_{cs} = n_s + n_c / (n_s \cdot n_c) \quad (1)$$

If  $n_c = 2n_s$ , the coefficient of  $\mu_{cs}$  is given by

$$\mu_{cs} = 3 / (2n_s). \quad (2)$$

For modeling, both linear (MLR) and nonlinear (ANN) models were used. Equations (1) and (2) were used to calculate the previously unreported values. Some other indices were examined, but the best results and equations for evaluating the physicochemical data were chosen.

The Rehm–Weller equation (Rehm and Weller, 1970) estimates that the free-energy change between an electron donor (D) and an acceptor (A) is given by

$$\Delta G^o = e[E_D^o - E_A^o] - \Delta E^* + \omega_1, \quad (3)$$

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,  $\Delta E^*$  is the energy of the singlet or triplet excited state, and  $\omega$  is the work required to bring the donor and acceptor within the ET distance. The work term in this expression can be considered to be 0 inasmuch as there exists an electrostatic complex before electron transfer [75].

### Discussion

The C<sub>60</sub>-methanofullerene derivatives (PCBM, *p*-EHO-PCBM, and *p*-EHO-PCBA) were synthesized by Wudel et al. in 2008 [18], with two principal improvements. The first goal was to introduce an alkoxy side chain as an electron donor on PCBM (*p*-EHO-PCBM). This derivative potentially increases the open-circuit voltage ( $V_{oc}$ ) and solubility in appropriate processes. The second goal was to add a carboxylic-acid group in *p*-EHO-PCBM to provide important functionality in the form of potential interactions with oxides [18]. Wudel et al. has reported the electrochemical properties of *p*-EHO-PCBM and *p*-EHO-PCBA via cyclic voltammetry at room temperature in *o*-DCB (*o*-dichlorobenzene) solution [18]. The experiments were carried out using tetra-*n*-butylammonium perchlorate (Bu<sub>4</sub>NClO<sub>4</sub>) as the supporting electrolyte, a platinum working electrode, a platinum wire as the counter electrode, and Fc/Fc<sup>+</sup> as the internal reference [18]. In the case of *p*-EHO-PCBM and *p*-EHO-PCBA, the reduction values are slightly more negative than those of PCBM. This can be attributed to the inductive effect of the alkoxy group [18]. The first to third ( ${}^{\text{red}}E_n$ ) reduction potentials of PCBM, *p*-EHO-PCBM, and *p*-EHO-PCBA, as reported by Wudel et al., are reproduced in Table 1 [18].

The assignment of formal charges to the fullerene cage suggests that the fullerene derivatives (PCBM, *p*-EHO-PCBM, and *p*-EHO-PCBA) have related molecular orbital structures [18–22]. The predicted complex structures of thio-unsaturated crown ethers (**1–9**) with

Table 1. Reduction potentials  ${}^{\text{red}}E_n$  ( $n = 1–3$  in volt) of **10–12**<sup>a</sup>.

Compound	${}^{\text{red}}E_1$	${}^{\text{red}}E_2$	${}^{\text{red}}E_3$
PCBM	−1.163	−1.538	−2.040
<i>p</i> -EHO-PCBM	−1.171	−1.544	−2.048
<i>p</i> -EHO-PCBA	−1.181	−1.565	−2.087

<sup>a</sup>See Ref. [18].

Table 2. Structural coefficients of unsaturated thiocrown ethers [X-UT-Y] **1–9** and the values of the free energies of electron transfer ( $\Delta G_{et(n)}$ ,  $n = 1–3$ ), in kcal mol<sup>-1</sup>, between unsaturated thiocrown ethers **1–9**, with PCBM, *p*-EHO-PCBM, and *p*-EHO-PCBA in supramolecular complexes **13–15** [18].

No.	Formula <sup>a</sup> of [X-UT-Y]	$n_s$	$n_c$	$\mu_{cs}$	${}^{\alpha}E_1$ (Volt) 1–9	[X-UT-Y]@[PCBM]-A			[X-UT-Y]@[ <i>p</i> -EHO-PCBM]-B			[X-UT-Y]@[ <i>p</i> -EHO-PCBA]-C		
						$\Delta G_{et(1)}$	$\Delta G_{et(2)}$	$\Delta G_{et(3)}$	$\Delta G_{et(1)}$	$\Delta G_{et(2)}$	$\Delta G_{et(3)}$	$\Delta G_{et(1)}$	$\Delta G_{et(2)}$	$\Delta G_{et(3)}$
1	6-UT-2(1,4-dithiin)	2	4	0.7500	1.02	49.83	58.43	70.06	50.06	58.92	70.96	49.65	58.30	69.87
2	9-UT-3	3	6	0.5000	0.97	48.68	57.28	68.90	48.91	57.77	68.90	48.50	57.14	68.72
3	12-UT-4	4	8	0.3750	0.89	46.83	55.44	67.06	47.07	55.92	67.06	46.65	55.30	66.87
4	15-UT-5	5	10	0.3000	0.82	45.22	53.82	65.44	45.45	54.31	65.44	45.04	53.68	65.26
5	18-UT-6	6	12	0.2500	0.79	44.53	53.13	64.75	44.76	53.61	64.75	44.34	52.99	64.57
6	21-UT-7	7	14	0.2143	0.73	43.15	51.75	63.37	43.38	52.23	63.37	42.96	51.61	63.18
7	24-UT-8	8	16	0.1875	0.69	42.22	50.82	62.45	42.45	51.31	62.45	42.04	50.69	62.26
8	27-UT-9	9	18	0.1667	0.66	41.53	50.13	61.75	41.76	50.62	61.75	41.35	49.99	61.57
9	30-UT-10	10	20	0.1500	0.63	40.84	49.44	60.06	41.07	49.92	61.06	40.65	49.30	60.88

<sup>a</sup>The data for the compounds and their complexes have not been previously reported. Supramolecular complexes **13–15** have not been synthesized nor previously reported.

Table 3. Second-order polynomials (Equations (4–12)) that indicate the relationship between index  $\mu_{cs}$  and the first to third free energies of electron transfer ( $\Delta G_{et}$ ) between unsaturated thiocrown ethers **1–9** with **10–12** in structures **13–15**.

Equations	$\Delta G_{et(n)}$	Complexes [X-UT-Y]@R	R <sup>2</sup> values	$\Delta G_{et(n)} = a(\mu_{cs})^2 + b(\mu_{cs}) + c$		
				a	b	c
4	$n = 1$	<b>13</b>	0.9959	-30.732	42.201	35.232
5	$n = 2$	<b>13</b>	0.9958	-30.683	42.158	43.886
6	$n = 3$	<b>13</b>	0.9958	-30.707	42.172	55.460
7	$n = 1$	<b>14</b>	0.9958	-30.705	42.166	35.423
8	$n = 2$	<b>14</b>	0.9958	-30.751	42.208	44.017
9	$n = 3$	<b>14</b>	0.9958	-30.683	42.158	55.646
10	$n = 1$	<b>15</b>	0.9942	-33.537	44.756	35.277
11	$n = 2$	<b>15</b>	0.9959	-30.732	42.201	44.502
12	$n = 3$	<b>15</b>	0.9949	-25.972	39.285	56.022

**10–12** are indicated herein as [X-UT-Y]@R, where R is PCBM, *p*-EHO-PCBM, and *p*-EHO-PCBA in **13–15** and indicates the adduct-functionalized methanofullerenes as *n*-type materials. The potential difference between oxidation and reduction in these structures is related to the band gap of HOMO–LUMO orbitals [18–22].

The oxidation potentials of **1–9** shown in Table 2 demonstrate that the  $\mu_{cs}$  index decreases with increasing molecular size. In Table 1, the related values for the supramolecular complexes of [X-UT-Y] **1–9** with PCBM, *p*-EHO-PCBM, and *p*-EHO-PCBA (**10–12**) are also shown. Table 2 shows the calculated values of oxidation potential ( ${}^{\alpha}E_1$ ) as well as the first, second, and third free energies of electron transfer ( $\Delta G_{et(n)}$ ,  $n = 1–3$ ) between [X-UT-Y] and complexes **10–12** for the supramolecular **13–15** complexes. The  ${}^{red}E_n$  data for **10**, **11**, and **12** are presented in Table 1 [18].

Oxidation potentials ( ${}^{\alpha}E_1$ ) of **4–7** were found to be 0.82, 0.79, 0.73, and 0.69 V, respectively [25,26,71–73,75,76]. The free energies of electron transfer ( $\Delta G_{et(n)}$ ,  $n = 1–3$ ) between **1–9** and **10–12** for making [X-UT-Y]@R (where R is PCBM, *p*-EHO-PCBM, and *p*-EHO-PCBA in complexes **13–15**) were calculated using the Rehm–Weller equation [71–73,75–81].

Table 3 shows the relationship between the  $\mu_{cs}$  index and the first, second, and third free energies of electron transfer

( $\Delta G_{et(n)}$ ,  $n = 1–3$ ) between **1–9** with the first (Equations (4), (7), and (9)), second (Equations (5), (8), and (11)), and third (Equations (6), (9), and (12)) reduction potentials ( ${}^{red}E_n$ ) of PCBM (**10**), *p*-EHO-PCBM (**11**), and *p*-EHO-PCBA (**12**), for the production of [X-UT-Y]@R (**13–15**), respectively.

Figure 2(a–c) shows the relationship between  $\mu_{cs}$  and the three free energies for electron transfer between **1–9** with the first, second, and third reduction potentials of PCBM (**10**) in [X-UT-Y]@PCBM(**13**). The calculated values of the three free energies of the electron transfer (obtained using the Rehm–Weller equation [62]) of complexes **13–15** are shown in Table 2.

Equations (4–6) describe Figure 2(a–c) and show a quadratic relationship between  $\Delta G_{et(n)}$  and  $\mu_{cs}$  for [X-UT-Y]@PCBM (**13**). By using Equations (4–12), it is possible to obtain good approximations for  $\Delta G_{et(n)}$  of supramolecular complexes **13–15** in the first to third reduction potential states of [X-UT-Y]@R (where R is PCBM, *p*-EHO-PCBM, and *p*-EHO-PCBA) in complexes **13–15**. In [X-UT-Y]@PCBM (**13**), the R<sup>2</sup> values for the graphs (Figure 2(a–c)) are 0.9959, 0.9958, and 0.9958, respectively, and the appropriate equations are given in Table 3. The coefficient of determination R<sup>2</sup> is used in the context of statistical models whose main purpose is the prediction

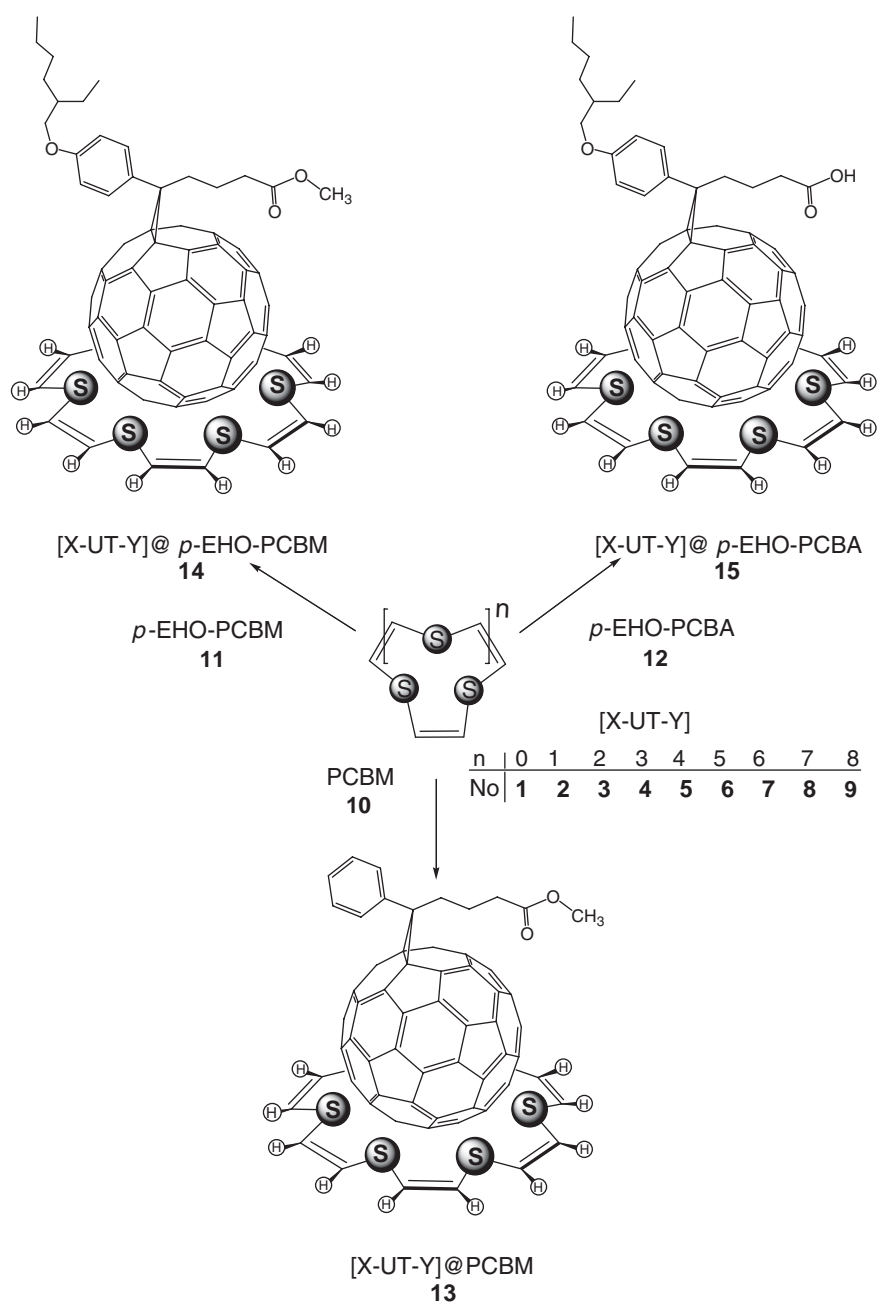


Figure 1. Structures of unsaturated thiocrown ethers **1–9** with PCBM (**10**), *p*-EHO-PCBM (**11**), and *p*-EHO-PCBA (**12**) for the production of supramolecular complexes [X-UT-Y]@R (**13–15**).

of future outcomes based on other related information. In a general form,  $R^2$  can be seen to be related to the unexplained variance because the second term compares the unexplained variance with the total variance (of the data). The  $R^2$  values are near 1.00 and show good correlations between  $\mu_{cs}$  and  $\Delta G_{et(n)}$  in the supramolecular complexes. In the light of the good correlations between  $\mu_{cs}$  and the free energies of electron transfer, it is possible to use  $\mu_{cs}$  to calculate  $\Delta G_{et(n)}$  of [X-UT-Y]@R (where R is PCBM, *p*-EHO-PCBM, and *p*-EHO-PCBA) in complexes **13–15**. The values of  $\Delta G_{et}$  decrease with increasing group

size (**1–9**) and decreasing  $\mu_{cs}$  indices, as indicated in Table 2.

The values of the first to third free energies of electron transfer between unsaturated thiocrown ethers **1–9** and the reduction potential of *p*-EHO-PCBM (**11**) as [X-UT-Y]@*p*-EHO-PCBM (**14**) complexes are shown in Table 2. The predicted values of  $\Delta G_{et(2)}$  for complex **14** were calculated using the Rehm–Weller equation. The relationship between the values of  $\mu_{cs}$  and the free energies of electron transfer  $\Delta G_{et(n)}$  of complex **14** is shown in Table 3. Equations (6–9) show quadratic polynomial structures. The  $R^2$  values that

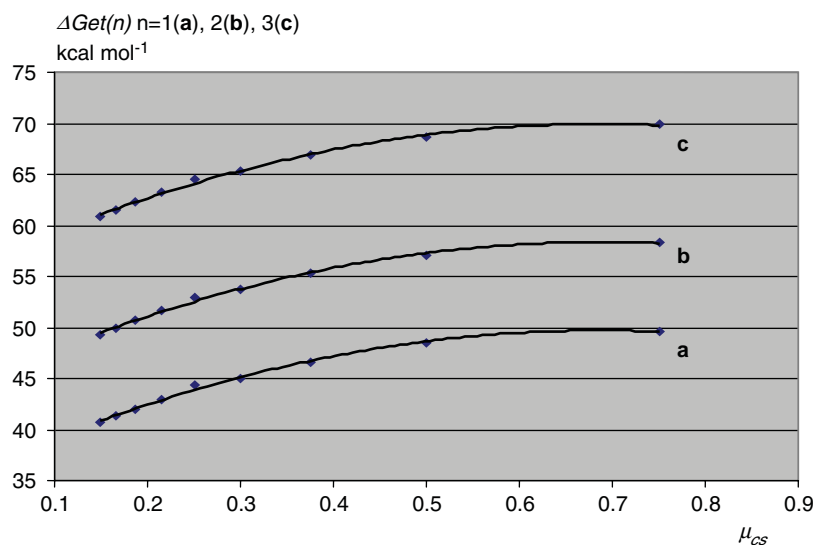


Figure 2. Plots of the relationship between the  $\mu_{cs}$  index vs. the first to third free energies of electron transfer ( $\Delta G_{et(n)}$  ( $n = 1$  (a), 2 (b), and 3 (c)), kcal mol<sup>-1</sup>) between **1–9** with supramolecular PCBM (**10**), for the production of [X-UT-Y]@PCBM in supramolecular complex **13**\*.

\*The structures of the related curves for [X-UT-Y]@R (where R is *p*-EHO-PCBM and *p*-EHO-PCBA) **14** and **15** are similar to those in Figure 2(a–c).

indicate the correlations between  $\mu_{cs}$  and the free energies of electron transfer of complex **14** (in the  ${}^{red}E_n$  ( $n = 1–3$ ) state of complex **11**) are all equal to 0.9958. These good correlations between  $\mu_{cs}$  and the free energies of electron transfer suggest that it is possible to use  $\mu_{cs}$  to calculate  $\Delta G_{et(n)}$  for [X-UT-Y]@*p*-EHO-PCBM (**14**). This case was found to be similar to complex **13**, in which the values of  $\Delta G_{et(n)}$  decrease with increasing size (**1–9**) and decreasing  $\mu_{cs}$  indices (see Table 2).

The values of the first to third free energies of electron transfer,  $\Delta G_{et}$ , are shown in Table 2. Equations (10–12) demonstrate the relationships between the free energies of electron transfer with a reduction potential of *p*-EHO-PCBA (**12**) of the [X-UT-Y]@*p*-EHO-PCBA (**15**) complexes with the  $\mu_{cs}$  indices for unsaturated thiocrown ethers **1–9**. These data were fit using regression with a second-order polynomial. The  $R^2$  values for these graphs are 0.9942, 0.9958, and 0.9349. Using Equations (1) and (10–12), it is possible to calculate the values of  $\Delta G_{et(1)}$  to  $\Delta G_{et(3)}$  of the [X-UT-Y]@*p*-EHO-PCBA (**15**) complexes. Similar to complexes **13** and **14**, the values of  $\Delta G_{et(n)}$  in supramolecular complex **15** decrease with the increasing size of **1–9** and the decreasing  $\mu_{cs}$  indices, as shown in Table 2. These data are reported herein for the first time.

The compounds [X-UT-Y]@R (where R is PCBM, *p*-EHO-PCBM, and *p*-EHO-PCBA) (**13–15**) were neither synthesized nor previously reported.

The ratio of the sum of the number of carbon atoms ( $n_c$ ) and the number of sulfur atoms ( $n_s$ ) to the product of these two numbers, given by index  $\mu_{cs}$ , shows a good relationship with the structural values of unsaturated thiocrown ethers **1–9**. These results show the calculated values of the free

energies of electron transfer ( $\Delta G_{et}$ ) based on the first to third reduction potentials ( ${}^{red}E_1$  to  ${}^{red}E_3$  states) of [X-UT-Y]@R (where R is PCBM, *p*-EHO-PCBM, and *p*-EHO-PCBA) in supramolecular complexes **13–15**. Compounds **10–12** have been utilized in solar cells as functionalized C<sub>60</sub>-methanofullerene derivatives. These data and their complexes have not been previously reported. In fact, compounds **13–15** have neither been synthesized nor previously reported.

## Conclusion

The supramolecular PCBM, *p*-EHO-PCBM, and *p*-EHO-PCBA compounds **10–12** were utilized as n-type materials, functionalized C<sub>60</sub>-methanofullerene derivatives in bulk-heterojunction polymers solar cells, and field-effect transistors. Theoretical studies on C<sub>60</sub> demonstrated that non-IPR-satisfying cage structures are more stable than the IPR-satisfying structure. For PCBM, *p*-EHO-PCBM, and *p*-EHO-PCBA (**10–12**), three reduction potential ( ${}^{red}E_1$  to  ${}^{red}E_3$ ) states have been reported. *Cis*-unsaturated thiocrown ethers **1–9** have important physicochemical properties. Electrochemical data of [X-UT-Y] **1–9**, such as the oxidation potential ( ${}^{ox}E_1$ ) and the first, second, and third free energies of electron transfer  $\Delta G_{et(n)}$  ( $n = 1–3$ ) based on the first to third reduction potential ( ${}^{red}E_1$  to  ${}^{red}E_3$ ) of [X-UT-Y]@R (where R is PCBM, *p*-EHO-PCBM and *p*-EHO-PCBA) in the **13–15** supramolecular complex groups, are reported herein. The predicted values of  $\Delta G_{et}$  for the **13–15** supramolecular complex groups were calculated using the Rehm–Weller equation. Using the ratio of the sum of the number of carbon atoms ( $n_c$ ) and the number of sulfur atoms

( $n_s$ ) to the product of these two numbers,  $\mu_{cs}$ , equations were derived, which yield good structural relationships with the aforementioned physicochemical data. These equations allow one to calculate the free energies of electron transfer ( $\Delta G_{et(n)}$  ( $n = 1-3$ )) based on the first to third reduction potentials ( ${}^{red}E_1$  to  ${}^{red}E_3$ ) of PCBM, *p*-EHO-PCBM, and *p*-EHO-PCBA (10–12) for the 13–15 supramolecular complex groups. The group of supramolecular complexes [X-UT-Y]@R (where R is PCBM, *p*-EHO-PCBM, and *p*-EHO-PCBA) (13–15) were neither synthesized nor previously reported.

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