Thiacrown Ethers Engaged C$_{60}$ through Charge Transfer: Experimental and Theoretical Study

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ABSTRACT: UV–Vis spectroscopy is used to study the charge transfer complexes of thiacrown ethers 1–6 with fullerene. The size of TCE1–6 and the nature of the heteroatoms (N, O and S) have been systematically changed to examine the effect of these factors on the HOMO/LUMO energy levels, the optical energy gap and the interactions between TCE’s and C$_{60}$. The negative and positive values of ΔS designate the structural forming method and the randomness of the free solvent molecules, respectively. Thermodynamics and stability data show that the complexes have a 1:1 ratio that has been emphasized by density functional theory calculations. Additionally, they show a synergetic interplay of donor–acceptor, π–π, and n–π interactions, which are the basis for the affinity of our novel receptors toward C$_{60}$. The proposed system of enzyme model suggests a development concept in the future design of enzyme model organic photovoltaic systems.

1. INTRODUCTION

There are three crystallographic forms of carbon: diamond, graphite, and fullerene. The spherical shape of fullerene has been the subject of several important properties (such as electron acceptor, charge transfer, a main member in the solar spectrum and photoexcitation, and many other properties). Consequently, it is a hot topic in research and development. Therefore, its chemistry is developed as a powerful system for designing new metal–ligand interactions, π–π stacking, hydrogen bonding, electrostatic interactions, and mechanical bonds.

A great deal of work has been published on the systems in which C$_{60}$ was particularly used as an electron acceptor. As a result, several studies such as complexation between C$_{60}$ and calix[n]arenes and calixarene derivatives and use of other techniques (UV and NMR spectroscopy) to determine the stoichiometry and some thermodynamic parameters have been devoted to the importance of this system and encourage us to study the interaction between C$_{60}$ and different types of electron donors (thiacrown ethers, TCEs).

Since the discovery of π-conjugated organic compounds, which might be acting as semiconductors and could be used in solar cells, organic transistors, and organic light-emitting diodes, the π-conjugated systems emerged as a general and powerful method for organic electronics. Although most of the organic electronics have unique advantages, for instance, lightweight nature, flexibility, low cost, and easy fabrication in comparison to their inorganic counterparts, some other studies have introduced shreds of evidence of the negative aspects along with the large enough commercial applications because of their enormously low efficiency, in addition to the high ruin rate in the presence of air and humidity. That is in fact the scientists acquaint with great endeavors to develop novel materials to conquer the essential issues encountered by organic solar cells.

In connection with our ongoing research toward the synthesis and complexation studies of potential hosts, like crown ethers, calixarene, and their derivatives, we were interested in the design and synthesis of hosts that are capable of binding selectively specific guests. Our design involves changes in dimension, rigidity, and variation of the type of ligating donor atom like sulfur and nitrogen atoms at the periphery of the host. It is a well-known fact that hosts with sulfur or nitrogen atoms have a great affinity toward soft metal ions such as Hg$^{2+}$ and Pd$^{2+}$. Recently, we have reported the synthesis of novel cyclic hosts and that include sulfur and/or nitrogen atoms. Those hosts showed a good tendency toward forming complexes with soft metal ions.

This paper reports the study of the complexation properties of previously synthesized crown ethers (1–6) that contain sulfur or/nitrogen atoms with fullerene (C$_{60}$) via both experimental and theoretical methods.
The schematic diagram of the significant energy levels in organic solar cells where the active layer is a thiacrown ether (TCE1–TCE6) and fullerene (C_{60}) mixture is shown in Figure 1.

Electronic transitions have two types of energies: The first type is the fundamental energy gap ($E_{\text{gap}}$) that represents the difference among LUMO ($E_{\text{LUMO}}$) and HOMO ($E_{\text{HOMO}}$) energies (Figure 1); this $E_{\text{gap}}$ separates the electrons and holes for carrier transport. The second type is called the optical gap ($E_{\text{opt}}$), which represents the first excitation energy. $E_{\text{opt}}$ is the minimum energy required for an electronic transition to arise, producing bound electron–hole pairs referred to as an exciton. Consequently, $E_{\text{gap}}$ is usually larger than $E_{\text{opt}}$ for organic semiconductors and their difference is referred to as the exciton binding energy ($E_B$), which may be calculated by using eq 1

$$E_B = E_{\text{gap}} - E_{\text{opt}}$$

Using density functional theory (DFT), the optical and electronic properties of chemically modified organic solar cell systems turn out to be more understandable and predictable. The DFT computations indicate the theoretical values in good accordance with the experimental results. Thus, the DFT will propose a very valuable vision in predicting the effects of various thiacrown ethers on the modification of the organic solar cell system potency.

Complexation of C_{60} with different types of crown ethers, such as those shown in Figure 2, was also reported. Some of the crown ethers formed 1:1 C_{60}:crown complexes and others formed 1:2 C_{60}:crown complexes.

Two factors that control the stability causing more favored host–guest interactions of the C_{60}:crown complexes: (1) the macrocyclic cavity size where it was found that the stability of the complexes is higher as the cavity size of thiacrown ether matches the C_{60} size and/or (2) the type of the donor atoms at the border of the crown part when oxygen atom(s) is (are) replaced by sulfur or nitrogen atom(s). Therefore, it will be worthwhile to explore the underlying host–guest interaction for a specific guest fullerene (C_{60}) by altering the donor atom(s) and the cavity size of thiacrown ethers (TCEs). Ashram has recently reported the synthesis of the crown ethers 1–6 (TCE1–CE6) as shown in Figure 3. Owing to the cavity sizes and different donor atoms (O, N, and S atoms) to form host–guest complexes, some of these thiacrown ethers have the ability to incubate some transition metals. In addition, Ashram has also measured their stability constants and thermodynamic properties.

In this work, the nature of interactions between TCEs and C_{60} was studied and detected through a series of TCE derivatives that have different cavity sizes and heteroatoms. UV–Vis spectroscopy can discover their complexation with C_{60} and measure some physical properties like stoichiometry, formation constants, and thermodynamic parameters. Moreover, theoretical calculations were carried out using the COSMO continuum solvation model to initiate these studies in order to understand the issues affecting the resulting binding constants. Furthermore, besides the DFT method, time-dependent density functional theory (TD-DFT) calculations were performed to determine the effects on optoelectronic properties of TCE1–TCE6:C_{60} mixtures.

2. RESULTS AND DISCUSSION

2.1. Experimental Study. As an example, Figure 4 shows the electronic absorption spectra of fullerene C_{60} (1.00 × 10^{-4} M) in the presence of an excess thiacrown ether 1 in toluene at 15 °C. As shown, the resulting complexes have an absorption band at about λ = 440 nm.

The absorption of the hosts in this range is negligible. Thus, the existence of this new band must be associated with the formation of donor–acceptor molecular complexes between thiacrown ethers 1–6 and C_{60} in the solution. Mukherjee et al. reported the formation of similar charge transfer absorption bands of the complexes of calix[6] and calix[8]arene derivatives with C_{60}.

The stoichiometry of the molecular complexes determined by Job’s method for all thiacrown ethers 1–6 and C_{60}, is 1:1, as shown in Figure 5. In this figure, χ refers to the mole fraction and ΔA refers to the absorbance change between the measured solution and C_{60} free solution. For more details, see ref 22 and references therein.

Since the concentrations of both thiacrown 1 and C_{60} are very low and comparable, the stability constant $K_c$ can be
calculated using the following modified form of the Benesi–Hildebrand equation (eq 2)

\[
\frac{[C_{60}]}{\Delta A} = \frac{1}{\Delta \varepsilon [\text{thiacrown 1}]} K_c + \frac{1}{\Delta \varepsilon}
\]

where \([C_{60}]_0\) is the initial concentration of \(C_{60}\), \(K_c\) is the formation constant, \(\Delta A\) is the absorbance change at \(\lambda = 440\) nm of \(C_{60}\) solution in toluene upon the successive addition of thiacrown 1, and \(\Delta \varepsilon\) represents the difference in the molar extinction coefficient between the \(C_{60}\)–1 complex and that of uncomplexed \(C_{60}\) at 440 nm. Figure 6a indicates that the \(C_{60}\)–1 complexation process in toluene solution according to eq 2 is linear (\(r^2 = 0.9940\)).

The \(K_c\) values in each case are calculated by dividing the intercept by the slope (determined by linear regression analysis according to van’t Hoff, eq 3). Table 1 lists the stability constant values determined at 25 °C for the charge-transfer complexes formed between \(C_{60}\) and thiacrown ethers 1–6.

The stability constant values are generally considered to be an indication of the stability of the complex between the donor and acceptor, i.e., the strength of acceptor–donor interaction. The larger its value, the higher is the stability of the complex. Many factors influence the stability constants. Such factors include the size of the guest, the identity of the donor atoms, and a macrocyclic effect that involves the dimensional compatibility between the macrocycle and the size of the guest.

As shown in Table 1, the differences in the values of \(\ln K_c\) are insignificant; however, the \(K_c\) values of \(C_{60}\)–thiacrown ethers 1–6 are in the order \(2 > 1 > 3 > 5 > 6 > 4\). These observations lead to the following conclusions: (a) Thiacrown ether 2 has the highest stability constants, while Schiff base crown ether 4 has the lowest one. This could be due to the larger cavity size and the number of sulfur atoms, which are a better-donating base toward neutral acceptors.62,63 (b) The higher flexibility of 2 enables the cavity of these compounds to wrap around \(C_{60}\) and cause stronger interactions. (c) In all cases, the stability constant values increase as the cavity size and the number of donor atoms increase.

To achieve a better understanding of the thermodynamics of thiacrown ether: \(C_{60}\) complexes, it is useful to consider the enthalpic and entropic contributions to these complexation processes. These thermodynamic parameters (\(\Delta H^o\) and \(\Delta S^o\), Table 1) were calculated from the temperature dependence of the stability constants (\(K_c\)) and applying the van’t Hoff equation (eq 3)

\[
\ln K_c = -\frac{\Delta G^o}{RT} = \left(\frac{-\Delta H^o}{RT}\right) + \frac{\Delta S^o}{R}
\]

A plot of \(\ln K_c\) against \(1/T\) gives a straight line with \(-\Delta H^o/R\) as a slope and \(\Delta S^o/R\) as an intercept, as shown in Figure 6b for the \(C_{60}\)–thiacrown 1 complex. All other \(C_{60}\)–thiacrown ether complexes give similar linear plots.

\(\Delta H\) values usually measure the strength of the interaction between the host and the guest, the more negative the value, the stronger the interaction. Results in Table 1 show that \(\Delta H\) values are negative, indicating an exothermic process. Compound 1 has a significantly higher \(\Delta H\) value than the others, indicating the strongest interaction with \(C_{60}\). This could

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**Figure 3.** Thiacrown ethers 1–6 (TCE1–TCE6).

**Figure 4.** Absorption spectra of \(C_{60}\) \((1.00 \times 10^{-4} \text{ mol/L})\) in the presence of 1 in toluene at 15 °C; concentration of 1 (from the bottom to the top): 0.00 to 8.00 \(\times 10^{-3} \text{ mol/L}\).

**Figure 5.** Job’s plot for \(C_{60}\)–1 complex in toluene.

**Figure 6.**
be due to several reasons; among them is the smaller cavity size than those of compounds 2 and 3. A compound with smaller cavity size is less flexible and has fewer preorganization requirements, causing more exposure to C60 and provides a stronger interaction than ligands with larger cavities. However, this cannot explain the large difference as we were unable to specify that at the used level of theory, in addition to the cavity size that may contribute to this as well. Despite the lower \( \Delta H^o \) values for 2, 3, and 5, they have positive \( \Delta S^o \) values that compensate for the lower \( \Delta H^o \) values. These positive values could be attributed to a solvophobic effect that liberates more solvent molecules from the larger cavities and increases the entropy of the system. The data in Table 1 show that the values of \(-\Delta H^o\) are correlated to the values of \(\Delta S^o\); as \(\Delta H^o\) values increase, \(\Delta S^o\) values also increase. This phenomenon is known as “enthalpy–entropy compensation”. A straight line with a good correlation was found when \(T \Delta S^o\) is plotted against \(\Delta H^o\), as shown in Figure 6c. In conclusion, it is found from the Gibbs energy values of the complexations that TCE1–TCE6–C60 is readily formed and stable.

The slope \(\alpha\) is defined as a quantitative measure of the extent of the entropic cancelling effect, which is attributed to a strong or weak binding that results from the enthalpy changes due to C60–crown ether interaction. The intercept \(T \Delta S^o = 0\) is defined as the intrinsic entropy gain upon complexation for each crown ether, mainly attributed to the desolvation of the complex with C60.

The entropic change thus consists of two components: The first component, \(T \Delta S^o = 0\), is independent of the enthalpy change and the second component is proportional to the enthalpy of complexation, \(\Delta H^o\). The proportionality factor, \(\alpha\) (value), is a quantitative measure of enthalpy–entropy compensation.

2.2. Computational Studies. The TCE 1–6 complexes with fullerene (C60) were explored at the B3LYP-D3/QZVP level of theory. The 1:1 stoichiometric ratio is computed.
according to the experimental evidence; however, 1:2 stoichiometric ratios are also carried out for comparison reasons. Figure 7 shows the minimum energy-optimized structure calculated for TCE2-C$_{60}$ and TCE2-C$_{60}$\textsuperscript{TCE} as representative examples.

The host–guest arrangements show that none of the TCEs fold themselves away from C$_{60}$ to assess the stabilization due to the embracing movement. B3LYP-D3/QZVP predicts binding energies of $-43.67$, $-55.46$, $-42.33$, $-22.89$, $-40.70$, and $-35.88$ kcal mol$^{-1}$ for the complexation of TCE1-C$_{60}$, TCE2-C$_{60}$, TCE3-C$_{60}$, TCE4-C$_{60}$, TCE5-C$_{60}$, and TCE6-C$_{60}$ respectively, as shown in Table 2. The calculations therefore suggest that the embraced drive is favored by an increase in the size of the TCE and the strength of the nucleophilicity of the corresponding atoms in TCE (S > N > O atoms).\textsuperscript{64–66} For (TCE)$_2$C$_{60}$ two TCE2 stabilize the complex by the amount of energy of $-12.28$ kcal mol$^{-1}$, as revealed in Table 2, while TCE1 stabilizes the complex (TCE)$_2$C$_{60}$ by $-23.97$ kcal mol$^{-1}$ due to the smaller size of the TCE that produces an extra interaction, whereas the second TCE3 leads to a significantly lower stabilization of $-10.65$ kcal mol$^{-1}$ due to the steric hindrance between the two crown ethers.

The following question remains to be answered: why the 2:1 ratio is less favored than the 1:1 ratio (Table 2)? This can be explained in light of one of the factors that affect the binding ability between the host and guest. These factors are the size-matching effect between the host and guest, charge density, conformation of the ligands (TCEs), and polarity of the solvent.\textsuperscript{67–69} The size-matching effect usually plays a primary role in the neutral systems and our system (TCEs and C$_{60}$). One pendent TCE ligand can encapsulate C$_{60}$ whose size is a bit smaller (the diameter is 7.02 Å, Figure 7) than TCEs’ cavities (the diameter range is 8.3–10.2 Å) and thus forms a 1:1 ratio. TCE1 and TCE4 have diameters of 8.8 and 8.3 Å, respectively, which have a greater affinity for C$_{60}$ with a relatively larger diameter of $\sim$10 Å. Consequently, this factor affects the complexation ability and the result of the values of the binding Gibbs energies (Table 2).

The B3LYP-D3/QZVP-optimized geometries reveal intermolecular contacts of different natures along with the host–guest interface. Table 3 summarizes the shortest distances computed for the intermolecular contacts, which determine the stabilization of the complexes between TCE1–TCE6 and C$_{60}$. The natural bond orbital analysis (NBO) indicates the binding energy (which is calculated from eq 4) of $-55.46$ kcal mol$^{-1}$ for TCE2 (Table 2) due to the two extra interactions originating from the presence of $\pi-\pi$ interactions between the lateral benzene rings of TCE2 and the benzene rings of C$_{60}$ centroid–centroid distances of 3.40 Å and $n-\pi$ interactions due to the short S(host)/C(guest) intermolecular distances of 2.757 Å, as shown in Table 3.

The binding free energies ($\Delta G_{\text{binding}}$ from eq 4) as a function of stabilization energy ($E_2$, NBO analysis) for 1:1 and 1:2 complexes are plotted in Figure 8. The stabilization energies $E_2$ from NBO analysis of two types of interactions, $\pi-\pi$ and $n-\pi$ interactions, are reported in Figure 8. A comparison of $\Delta G_{\text{binding}}$ and $E_2$ of the 1:1 complex, in general, provides a good analysis of the influence of the $\pi-\pi$ interactions on the structures and the ratio of complexes.

| complex     | $\Delta G_{\text{binding}}$ (kcal mol$^{-1}$) | $\Delta G_{\text{binding}}$ (debye) | complex     | $\Delta G_{\text{binding}}$ (kcal mol$^{-1}$) | $\Delta G_{\text{binding}}$ (debye) |
|-------------|--------------------------------------------|-------------------------------------|-------------|--------------------------------------------|-------------------------------------|
| TCE1-C$_{60}$ | $-43.67$                                   | 2.210                               | TCE2-C$_{60}$ | $-35.88$                                   | 1.816                               |
| TCE2-C$_{60}$ | $-55.46$                                   | 2.807                               | TCE3-C$_{60}$ | $-12.28$                                   | 0.626                               |
| TCE3-C$_{60}$ | $-42.33$                                   | 2.142                               | TCE4-C$_{60}$ | $-10.65$                                   | 0.543                               |
| TCE4-C$_{60}$ | $-22.89$                                   | 1.158                               | TCE5-C$_{60}$ | $-17.34$                                   | 0.884                               |
| TCE5-C$_{60}$ | $-40.70$                                   | 2.060                               | TCE6-C$_{60}$ | $-8.80$                                    | 0.449                               |
| TCE6-C$_{60}$ | $-35.88$                                   | 1.816                               |             |                                            |                                     |

\textsuperscript{4}All the binding Gibbs energies in kcal mol$^{-1}$.\textsuperscript{b}$\mu$ denotes the dipole moment in debye.

Figure 7. (a, b) Intermolecular distances in Å, calculated at the B3LYP-D3/QZVP.
This comparison suggests that the 1:1 complex favors greater \( E_2 \). Figure 8 shows that the stabilization energy \( E_2 \) increases with \( \Delta G_{\text{binding}} \) for both 1:1 and 1:2 ratios and proposes that the \( \pi-\pi \) interactions are greater than the \( n-\pi \) interactions. For example, the \( E_2 \) values of TCE2-C\(_{60} \) complexes to C\(_{60} \) are 201 and 50 kcal/mol, respectively, for the \( \pi-\pi \) and \( n-\pi \) interactions (Figure 8). Furthermore, the value of the dipole moment suggests that the 1:1 ratio has very high polarity and would interact better than the 1:2 ratio (Table 2). In the last point, a comparison of stabilization energies for different complexes (1:1 or 1:2 ratio) will also guide us to a similar conclusion that \( \pi-\pi \) interactions are stronger than \( n-\pi \) interactions and this system prefers the 1:1 ratio (Figure 8).

Upon going from TCE2-C\(_{60} \) to TCE4-C\(_{60} \), TCE5-C\(_{60} \) and TCE6-C\(_{60} \) new \( n-\pi \) interactions with intermolecular distances of 3.409, 3.062, and 3.267 Å (averaged values) over all the N/ C\(_{60} \) longer than the S/ C\(_{60} \) provide to the stabilization of the complex attributable to the presence of the thiacrown ethers in the host system (Table 3). The computations expect that the binding energies of the complexes increase as the size of the crown ether increases, passing from \(-22.89 \text{ kcal mol}^{-1} \) for TCE4-C\(_{60} \) to \(-40.70 \) and \(-34.88 \text{ kcal mol}^{-1} \), respectively, for TCE5-C\(_{60} \) and TCE6-C\(_{60} \) (Table 2). This tendency is in accordance with the increase in the \( \ln K_c \) value predicted experimentally (Table 1). It has to be credited to increasing contributions from the \( n-\pi \) interactions, which are associated with the increasing size of the crown ethers when going from TCE4-C\(_{60} \) to TCE5-C\(_{60} \) and TCE6-C\(_{60} \). The larger size of TCE5 and TCE6 wraps C\(_{60} \) and leads to more compact complexes, in which the benzene ring moiety is closer (by 0.12 and 0.65 Å) to C\(_{60} \) as compared, for example, with TCE4-C\(_{60} \) and TCE5-C\(_{60} \) (distances 1 and 6 in Table 3).

Figure 9 displays the energy levels of the HOMO and LUMO orbitals for TCE1–TCE6 and C\(_{60} \). The results show...
that TCE4–TCE6 has a larger $E_{gap}$ compared with TCE1–TCE3. TCE4–TCE6 have N atoms in the thiacrown ether ring and, as a result, more stabilized $E_{HOMO}$ and destabilized $E_{LUMO}$ causing a larger $E_{gap}$. However, TCE1–TCE3 have smaller $E_{gap}$ which can be attributed to the larger size of the cavity and the presence of S atom. TCE2 and TCE3, compared with the first group (TCE4–TCE6), give good overlap between molecular orbitals and have closer energy between S atomic orbitals and aromatic structures. Although TCE1 has a smaller ring size than TCE2 and TCE3 and has no N atoms in the thiacrown ether ring, similar $E_{gap}$ is found in comparison with the $E_{gap}$ for TCE2 and TCE3.

Table 4 shows the calculated first exciton energy $E_{exc}$, the exciton binding energy $E_{bb}$, the open-circuit voltage $V_{OC}$, and the ionization potential IP. Table 4 demonstrates that the trends are similar to the trends for $E_{gap}$ where TCE1–TCE3 produced smaller $E_{gap}$ than TCE4–TCE6. The calculated $E_{bb}$ gives a good indication of the better exciton dissociation at the junction of the donor–acceptor material and how the improvement of solar cell characteristics is. The explanation for such a result can be credited to the size of atoms (N atom is of smaller size) that have a localized structure, hence hindering the transfer of excitons.

A compromise always exists between providing a sufficient HOMO and LUMO interface offset for efficient exciton dissociation and minimizing the $\Delta E$ ($|E_{HOMO}^{TCE} - E_{LUMO}^{C_{60}}|$) of the heterojunction. In the case of TCE1–TCE3:C$_{60}$, the calculated range of $\Delta E$ is 0.86–1.16 eV, which is significantly smaller and has more efficient exciton dissociation than the 1.34–2.01 eV for TCE4–TCE6:C$_{60}$ (Figure 9). In the larger size of cavity, the presence of sulfur atoms (TCE2 and TCE3) has the effect of lowering the energy levels compared to nitrogen atoms (TCE5 and TCE6), generating a HOMO interface offset, $\Delta E_{HOMO}$ and a consequential decrease in $V_{OC}$ in combination with the C$_{60}$ acceptor (Table 4 and Figure 9).

The open-circuit voltage $V_{OC}$ values for TCE2, TCE3, TCE5, and TCE6 are 0.56, 0.59, 1.43, and 1.04 eV, respectively. The increase in $V_{OC}$ may possibly translate to an increase in photovoltaics of the solar cell, while the increase in the ionization potential IP will lead to an increase in the oxidation stability. However, the higher the number of N atoms in the crown ether cavity, the larger the increase in $E_{gap}$ which would lead to a great increase in light absorption and lower photocurrent density. Therefore, based on the improvement in the intrinsic material properties of TCE1–TCE3, which have larger binding energy to C$_{60}$ (Table 2), compared to TCE4–TCE6, these may be good candidates as an enzyme model for organic solar cells.

Overall, this study is supportive of the prediction proffered herein, namely, the probability of binding enhancement between the TCE and C$_{60}$ and consequently decreasing the oxidation stability and $V_{OC}$ solely by increasing the size of atoms in the cavity of crown ether ring. To the best of our knowledge, the enzyme model, TCE:C$_{60}$ as an organic solar cell system has not been discussed in the literature before.

3. CONCLUSIONS

In this work, we show that it is possible to use the UV–Vis spectroscopy to study the complexation between TCE1–TCE6 and C$_{60}$ to form a 1:1 complex in the toluene solution. It is demonstrated that several factors affect the stability of the complex formation such as the cavity size, the type and number of donor atoms, and the flexibility of the cavity. The formation of constant values increases with flexibility and cavity size. Hence, the order of the stability constants is $2 > 1 > 3 > 5 > 6 > 4$. The negative entropy values increase due to the structural forming method, while the positive entropy values increase due to the randomness of the free solvent molecules. The phenomenon that describes the correlation between the increases in the negative values of $\Delta H$ with the values of $\Delta S$ is called enthalpy–entropy compensation. Computations of binding energy values using DFT methods and continuum solvation models have provided critical insights into each of the interactions in the studied system. Furthermore, the calculated orbital interactions, $\pi\pi$ and $n\pi$ interactions, through NBO analysis show that the stabilization energies depend on the size and nature of thiacrown ethers.

The optoelectronic properties of the studied systems are computed using DFT and TDDFT. These calculations have allowed a comprehensive understanding of the electronic structure, absorption spectra, and solar cell properties of the TCE1–TCE6:C$_{60}$ complexes. The complexes were divided into two groups: TCE1–TCE3 and TCE4–TCE6. It could be deduced that TCE1–TCE3 have better overall solar cell properties than TCE4–TCE6 according to the results that were obtained from the calculations of photocurrent density, open-circuit voltage, and oxidation stability. Thus, we can introduce a new type of solar cell system that can be called an enzyme model of organic photovoltaics.

4. EXPERIMENTAL AND THEORETICAL PARTS

4.1. Experimental Part. Thiacrown ethers 1–6 were prepared according to the published procedures.58,59 Toluene (HPLC grade, GCC, assay 99.8%) and [60]fullerene (99.5%, Aldrich) were used without any further purification. Spectrophotometric measurements were carried out using a UV spectrophotometer (SHIMADZU, model UV-2450) equipped with a thermostat cell holder. The temperature controller was provided with a cooling facility and used to control the cell temperature in the range of 0.00–80.00 °C with an accuracy of ±0.1 °C.

The total concentration of [60]fullerene in each solution was 1.00 × 10$^{-4}$ M, and the concentrations of thiacrown ethers 1–6 were changed from 0.00 to 8.00 × 10$^{-3}$ M. Three runs were made for the calculation of certain K values, Job’s method was applied to confirm the 1:1 stoichiometry of the complexes. The detailed procedure is reported elsewhere. It is important to mention that C$_{60}$ and the complex are the absorbing species here.73 The stability constants were evaluated at various temperatures (15, 20, 25, 30, and 35 °C) by using the Benesi–Hildebrand equation70 and the van’t Hoff equation was applied to determine the thermodynamic parameters.

| Table 4. Parameters Obtained from Several TCE1–TCE6 and C$_{60}$a |
|-------------------|-----|-------|-----|-----|
| TCE               | $E_{gap}$ (eV) | $E_{bb}$ (eV) | $V_{OC}$ (eV) | IP (eV) |
| TCE1              | 1.84 | 0.25  | 0.86 | −6.67 |
| TCE2              | 1.88 | 0.31  | 0.56 | −4.37 |
| TCE3              | 1.86 | 0.39  | 0.59 | −4.40 |
| TCE4              | 3.13 | 0.51  | 1.71 | −5.52 |
| TCE5              | 2.9  | 0.67  | 1.43 | −5.24 |
| TCE6              | 2.91 | 0.46  | 1.04 | −4.85 |

a$E_{HOMO}$ and $E_{LUMO}$ of C$_{60}$ are −6.11 and −3.51 eV, respectively.
4.2. Theoretical Details. The electronic interaction energy in the gas phase $\Delta E$ was computed for equilibrium structures. The molecules of interest (host, guest, and complex) were optimized in the gas phase on a reasonable level including a dispersion correction, e.g., the B3LYP hybrid-GGA density functional\(^{71,72}\) together with the quadruple-$\zeta$ basis set QZVP\(^{73}\) and the D3 dispersion correction with Becke–Johnson damping (D3(BJ)).\(^{74,75}\) The gas-phase association energy $\Delta E$ was calculated in the supramolecular approach according to eq 4

$$\Delta E = E(\text{complex}) - E(\text{host}) - E(\text{guest}) \quad (4)$$

where $E$ is the total electronic energy of the species involved. At a QZ basis set level, basis set superposition errors (BSSE) are typically less than 2% of $\Delta E$ and can be ignored\(^{76}\) for (hybrid) GGA functionals. The three-body dispersion contribution to $\Delta E$ was found to be always positive and contribute significantly with 2–3 kcal mol\(^{-1}\) for typical supramolecular systems.\(^{77}\) We decided to use the efficient D3 method for its computation without any empirical adjustments. The total electronic interaction energy $\Delta E$ thus contains the pure electronic DFT energy $\Delta E_{\text{el}}^{\text{DFT}}$, two-body $\Delta E_{\text{disp}}^{(2)}$ and three-body dispersion energy $\Delta E_{\text{disp}}^{(3)}$ as shown in eq 5.

$$\Delta E = \Delta E_{\text{el}}^{\text{DFT}} + \Delta E_{\text{disp}}^{(2)} + \Delta E_{\text{disp}}^{(3)} \quad (5)$$

The open-circuit voltage was calculated using eq 6.\(^{43}\)

$$V_{\text{OC}} = \frac{1}{e} [|E_{\text{HOMO}}^{C(\text{TCE})}| - |E_{\text{LUMO}}^{C(\text{TCE})}| - 0.3 \text{ eV}] \quad (6)$$

where $e$ is the elementary charge and 0.3 eV is an empirical factor, a quantity related to the quasi-Fermi energies of electrons and holes of the acceptor and donor materials.\(^{53}\) The ionization potential (IP) was estimated using the negative of the $E_{\text{HOMO}}^{\text{C}}$ based on Koopman’s theorem.\(^{78}\)

A continuum solvation model like COSMO\(^{79,80}\) is used in a black-box manner to calculate the solvation Gibbs energy $\Delta G_{\text{solv}}^{\circ,\circ}(\text{toluene})$ of each gas-phase species at the temperature $T = 25^\circ\text{C}$ in toluene. The resulting values implicitly contained the conversion to standard state conditions. The first singlet excited states ($S_1$ to $S_4$ vertical transition energies) and the exciton binding energy ($E_{\text{ex}}$) values ($n = 10$) were determined using the TD-B3LYP/QZVP level. All DFT, TD-DFT (single-point step), and solvation calculations (single-point step) were performed using the NWChem 6.4 program package.\(^{81}\)

To analyze the intermolecular interactions between the filled donor and empty acceptor in the systems, the second-order perturbation theory analysis of the Fock matrix in the natural bond orbital (NBO)\(^{82}\) analysis is performed on the optimized electronic densities using the NBO program, as implemented in the Gaussian 16 package.\(^{83}\) Intermolecular interactions such as lone pair (LP) or $\pi$-bond $\rightarrow$ antibonding (*$\pi$*) orbital mixtures are representative of donor–acceptor bonding. This overlap allows charge transfer from the former to the latter. For each donor NBO($i$) and acceptor NBO($j$), the stabilization energy $E_{\text{s}}$ associated with electronic delocalization between the donor and acceptor is estimated as

$$E_{\text{s}} = q \frac{(F_{i,j})^2}{e_i - e_j} \quad (7)$$

where $q$ is the orbital occupancy, $e_i$ and $e_j$ are the diagonal elements, and $F_{i,j}$ is the off-diagonal NBO Fock matrix element.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01877.

Excel files for UV absorption for compounds 1–6 at 15, 20, 25, 30, and 35 °C (ZIP)

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Notes

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