Conformational Analysis of the Supramolecular Complexation of Diaryl-Substituted Tetrathiafulvalene Vinylogues with Fullerenes

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ABSTRACT: Tetrathiafulvalene vinylogues (TTFVs) functionalized with diaryl substituents (aryl = 1-naphthyl, 9-anthryl, and 1-pyrrenyl) via click chemistry have been previously synthesized and studied as tweezer-type receptors for binding with C60 and C70 fullerenes. In particular, dianthryl-TTFV exhibits unique selectivity for C70 fullerene, giving rise to effective fluorescence turn-on sensing of C70 in the presence of a large excess of C60 fullerene. This observation indicated that dianthryl-TTFV has a preferential binding affinity for C70 over C60 fullerene, but the reason for such selectivity is unclear. Aiming at addressing this issue, we herein investigated the relative conformational stability of diaryl-substituted TTFVs in complexation with C60 and C70 fullerenes. The dispersion-corrected density functional theory approximation (B3LYP-D3) was employed in our computational analysis to determine binding energies and electronic properties of these supramolecular complexes. It was found that the highest binding energies (and the lowest relative conformational energies) are in pairings when fullerenes are placed around the central TTFV moieties (such as the triazole rings). The results of electronic properties show that the dianthryl-TTFV and dipyrrenyl-TTFV conformers have lower highest occupied molecular orbital–lowest unoccupied molecular orbital gaps relative to the ones obtained for dinaphthyl-TTFV, indicating that dianthryl-TTFV, and to some extend dipyrrenyl-TTFV, could be good candidates for chemical sensing of fullerenes with fluorescence spectroscopy. We also investigated the effect of the solvent on the interactions of the diaryl-TTFVs with fullerenes using the polarizable continuum model. In general, the presence of a solvent decreases the diaryl-TTFV/fullerene binding energies, presumably because of the interactions of the solvent with individual fullerenes and diaryl-TTFVs.

1. INTRODUCTION

Since the discovery of buckminsterfullerene C60 by Kroto, Curl, and Smalley in 1985,1 fullerenes and fullerene-containing materials have stimulated tremendous scientific interest.2−5 The most stable and abundant fullerenes prepared by usual methods such as the Kratschmer−Huffman arc discharge technique are C60 and C70 fullerenes.6 Higher fullerenes are also accessible, including C74, C76, C78, C80, C82, and C84, but their preparation and isolation are more challenging.7 The design and synthesis of selective molecules that have the ability to detect and separate fullerenes have been receiving great attention in the field of supramolecular chemistry.8−14 Efficient separation and purification of different types of fullerenes can be achieved by the host–guest complexation of fullerenes (guests) with proper receptor molecules (hosts).8 In 1994, both Atwood et al.15 and Shinkai et al.16 succeeded in preparing the first two different calixarene-based fullerene receptors to separate C60 from carbon soot with purity of 99.5 and 99.8%, respectively. Since then, much research efforts have been devoted to the host–guest chemistry of fullerenes and organic receptors.9,12,15 Of particular note is the development of tetrathiafulvalene (TTF)-based fullerene receptors, which have been widely reported in the recent literature. TTF is an excellent organic π-electron donor, and its π-extended analogues can show favored binding properties with fullerenes via π-stacking and charge-transfer interactions. Martin and co-workers designed a number of fullerene receptors using π-extended TTFs (ex-TTFs) as the active components to achieve high affinity and selectivity for fullerenes.16−22 In addition to TTF derivatives, other organic π-conjugated systems have been successfully applied in making fullerene receptors. For example, Morin et al. in 2008 developed a rotaxane−porphyrin conjugate to act as a tweezer-type supramolecular host for fullerenes.23 Sanders and co-workers reported chiral naphthalene diimide derivatives as selective receptors for C70 fullerene.24 In 2007, Sygula et al. synthesized a corannulene-based molecular pincer, termed “buckycatcher”, which could form an inclusion complex with C60 fullerene through
concave/convex π−π interactions. The binding and charge-transfer properties of the buckycatcher/C_{60} complex were later examined by several groups using computational analysis.

In 2013, Zhao et al. synthesized a series of tweezer-shaped molecular hybrids of diphenyl-substituted TTF vinylogues (TTFVs) functionalized with three different planar arene end groups (from now on referred to simply as diaryl-TTFVs) through click chemistry (compounds 1a−c, Figure 1).

![Molecular structure of diaryl-TTFV compound 1a−c and 2a−c.](image)

Figure 1. Molecular structure of diaryl-TTFV compounds 1a−c and 2a−c.

view of their π-electron-donating properties and tweezer-like molecular shapes, these diaryl-TTFVs were designed to act as receptors for C_{60} and C_{70} fullerenes. The supramolecular interactions of 1a−c with C_{60} and C_{70} fullerenes were investigated by UV–vis absorption and fluorescence spectroscopy. In terms of fluorescence responses to fullerenes in chlorobenzene, molecular tweezers 1a−c showed end group-dependent behaviors: (i) dinaphthyl-TTFV 1a did not give significant fluorescence changes upon titration with either C_{60} or C_{70}, (ii) dianthryl-TTFV 1b showed a slight degree of fluorescence enhancement upon titration with C_{60} but a much more significant fluorescence enhancement upon titration with C_{70} and (iii) dipyrenyl-TTFV 1c exhibited prominent fluorescence turn-on responses to both C_{60} and C_{70}. Analysis of binding constants revealed that dianthryl-TTFV 1b has a uniquely high selectivity toward binding C_{70} over C_{60}; however, the reason for this has remained unclear.

In this work, with the help of density functional theory (DFT) calculations, we carried out conformational/structural analysis and investigated the interactions between the three diaryl-TTFVs and fullerenes with the aim of gaining deeper understanding of the previously reported experimental results. In our computational studies, three analogous compounds 2a−c, which bear SMes (for computational expediency) instead of S_{C_{12}}H_{25} as side chains on the 1,3-dithiole moieties, were chosen as models to be examined. It has been shown that noncovalent, intramolecular, and intermolecular interactions must be properly taken into account when analyzing structures and energetics of supramolecular complexes.

Post-Hartree–Fock methods such as MP2 and CCSD(T), which can accurately account for noncovalent interactions, are impractical and computationally too expensive to study our large-sized molecular systems. On the other hand, dispersion-corrected DFT (D-DFT) methods such as B97D, B3LYP-D3, or ωB97XD that also take into account noncovalent interactions, scale well with molecular size and have a good computational performance-to-cost ratio. D-DFTs are therefore the appropriate choice for computational studies on relatively large supramolecular complexes. In our previous works, the B3LYP-D3 method was found to give results consistent with experimental observations and/or trends. This method was hence adopted to perform all computations in this study.

2. COMPUTATIONAL DETAILS

We have performed all electronic structure computations in this work using the Gaussian 16, Revision B.01 software.

Geometries of all isolated molecules and supramolecular pairs of diaryl-TTFVs and fullerenes were optimized at the B3LYP-D3/6-31G(d) level. The B3LYP-D3 method includes the hybrid B3LYP functional plus the D3 dispersion correction term. B3LYP-D3 accounts for van der Waals and intermolecular noncovalent interactions as well as for intramolecular noncovalent interactions. The effect of a solvent (chlorobenzene) on the structures and energetics of isolated molecules and supramolecular (diaryl-TTFV/fullerene) pairs was investigated using the polarizable continuum model (PCM). We have also calculated the basis set superposition error (BSSE) using the counterpoise correction method as proposed by Boys and Bernardi.

We carried out the (B3LYP-D3) conformational analysis of diaryl-TTFVs as well as their 1:1 supramolecular complexes with C_{60} and C_{70} fullerenes, respectively. For the complexes, we have determined the lowest-energy structures by considering strategically important orientations of fullerenes relative to TTFV molecules. In order to assess the relative conformational stability of the complexes, we computed their relative conformational energies defined as the differences between the energies of the lowest-energy structure and of other higher energy structures. The binding energy (E_b) for each supramolecular pair was also computed. E_b is defined as

$$E_b = (E_{\text{fullerene}} + E_{\text{TTFV}}) - E_{\text{pair}}$$

where E_{\text{fullerene}}, E_{\text{TTFV}} and E_{\text{pair}} are the total electronic energies of either C_{60} or C_{70} fullerene, the diaryl-TTFV, and the diaryl-TTFV/fullerene pair, respectively. We note that relative conformational and relative binding energies give the same information; hence, our discussion will be primarily focused on the analysis of the binding energies. For single TTFVs, we also determined their distortion energies which are defined as the energy differences between the energies of the most (optimized) stable conformers of TTFV and the energies of the structures they adopt in the complexes [obtained using single-point (SP) DFT calculations]. In addition to conformational and binding energies, we also analyzed their electronic structures, in particular, the trends of frontier molecular orbital energy levels [such as highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) eigenvalues] and their (HOMO−LUMO) differences.

As in our previous work, binding energies per atom (E_b per atom) for all (diaryl-TTFV/fullerene) combinations were calculated to normalize their total binding energies. The E_b per atom for each complex is calculated by dividing the respective total E_b by the number of interacting atom pairs with one atom being on a fullerene and the other on a diaryl-TTFV. In each atom pair, the individual atoms must be separated by less than their respective van der Waals distances in order for this pair to be considered as interacting. The van der Waals distances are calculated from the van der Waals radii determined by Bondi in 1964 as 2.90, 3.40, 3.25, and 3.50 Å...
for C–H, C–C, C–N, and C–S pairs, respectively. The intermolecular distances (Δd), between the diaryl-TTFV and the fullerene in each combination, were also computed by determining the minimum distances between atoms of the diaryl-TTFV and atoms of the fullerene. That is, for every atom in the diaryl-TTFV, the minimum distance was found by calculating all of the Euclidean distances between this atom and all of the atoms of a given fullerene (using the coordinates of that atom and coordinates of all atoms of the fullerene) and choosing the smallest distance. Δd was then taken as the average of all of the minimum distances for a given diaryl-TTFV.

3. RESULTS AND DISCUSSION

The diaryl-TTFV compounds investigated in this work (2a–c, Figure 1) contain three different aryl end groups, namely, 1-naphthyl, 9-anthryl, and 1-pyrenyl. They differ from compounds 1a–c, which were previously synthesized and investigated by Zhao and co-workers, only in the sizes of the alkyl chains attached to the 1,3-dithiole units. Compounds 2a–c contain only SMe instead of the much larger SC10H12 groups. The conformational and supramolecular properties of 2a–c should not be much different from those of 1a–c. As aforementioned, the major goal of this work is to theoretically and computationally rationalize the experimental findings of the supramolecular interactions between diaryl-TTFVs 1a–c and fullerenes;11 compounds 2a–c are therefore ideal models to simulate 1a–c with significantly reduced DFT computational costs. For these diaryl-TTFVs, different conformational structures are possible in the solution phase. The single-crystal X-ray structure of dianthryl-TTFV 2b was previously determined by Zhao et al., which provided valuable insight into its molecular shape and conformational properties in the solid state. As shown in Figure 2, the two dithiole units in 2b favor a cis-like orientation and the two anthryl end groups point inwardly to show an edge-to-edge contact.

The B3LYP-D3/6-31G(d) fully geometry optimized structures of 2a–c compounds are shown in Figure 3. Very similar optimized geometries are obtained without and with a solvent (chlorobenzene) for each of the three molecules. As can be seen from Figure 3, the structures of the TTFV moieties are very similar to that observed in the X-ray structure of 2b. One interesting feature of these diaryl-TTFVs is that the aryl end groups do not adopt the conformation similar to that shown in the X-ray structure of 2b. These results are not surprising, considering that intermolecular stacking plays a significant role in the solid-state packing, which in turn affect the molecular conformation, particularly the orientation of the end groups. In our geometry optimization, we only considered individual molecules and the intramolecular π-stacking among the aryl end groups, hence dictates the favored molecular conformation. As an example, the energies required to convert their lowest-state geometries (shown in Figure 3) into their less-stable tweezer-like geometries (shown in Figure 4b) are 0.48 eV (2a), 0.40 eV (2b), and 0.82 eV (2c) without a solvent and 0.42 eV (2a), 0.39 eV (2b), and 0.79 eV (2c) with chlorobenzene when interacting with C60 fullerene (see Table S1 in the Supporting Information). Table S1 shows

Figure 2. ORTEP plots (50% probability) of dianthryl-TTFV tweezer 2b (CCDC 900616). (A) Front view and (B) side view. Hydrogen atoms are omitted for clarity.

Figure 3. Optimized geometries of diaryl-TTFVs (2a–c) at the B3LYP-D3/6-31G(d) level of theory. Similar results were obtained using the B3LYP-D3/6-31G(d) level in chlorobenzene.

Figure 4. Optimized geometries for the 15 supramolecular complexes of diaryl-TTFVs and C60 fullerene investigated in this work obtained using the B3LYP-D3/6-31G(d) method: (a) right, (b) middle, (c) left, (d) up, and (e) down (similar results are obtained at the PCM/B3LYP-D3/6-31G(d) level in chlorobenzene).
that the distortion energies are the largest (greater than 0.4 eV) in all cases for the “middle” and “middle-2” configurations that involve opening up of the overlapping planar aryl end groups. These results of distortion energies reveal that tweezer-like structures are the least favorable ones for the diaryl-TTFVs.

On the basis of the conformational analysis of single diaryl-TTFVs as discussed above, five structures for the supramolecular pairs were considered, each of which consisting of a diaryl-TTFV and a fullerene (C_{60} or C_{70}). These combinations differ by the orientation of the fullerene molecule (right, middle, left, up, and down) relative to the diaryl-TTFV molecule. The full conformational analysis should consider numerous (many of them nearly degenerate) configurations of these supramolecular complexes. The sample of five used in this work is deemed as representative configurations because they cover important general locations of the fullerene relative to the TTFV molecule. In total, we have examined 15 different diaryl-TTFV/fullerene pairs for each fullerene. The B3LYP-D3/6-31G(d) optimized geometries of these pairs are shown in Figures 4 and 5 for C_{60} and C_{70} fullerenes, respectively.

In view of the fact that C_{70} fullerene has an oblong nonspherical shape, an additional structure for each of diaryl-TTFV/fullerene pairs was investigated when C_{70} is in the middle of the diaryl-TTFV tweezer. This conformer is designated as “middle-2” (see Figure S1 in the Supporting Information for the optimized geometries of “middle-2” conformers). The “middle” and “middle-2” conformers differ by the relative orientation of C_{70}; in the “middle-2” conformers, the long-axis of C_{70} is pointing vertically upward toward the dithiole rings (see Figure S2 in the Supporting Information), whereas in the “middle” conformers, the long-axis is rotated 90° relative to its “middle-2” orientation and points into the page, as shown on Figure S2. As in the case of single diaryl-TTFV molecules, all chlorobenzene-solvated supramolecular complexes gave optimized geometries very similar to those computed in vacuo.

The relative stability of these diaryl-TTFV/fullerene supramolecular complexes was investigated by computing their binding energies (E_b's). Figure 6 and Table S2 in the Supporting Information show E_b's for the various configurations of diaryl-TTFVs with each of C_{60} and C_{70} fullerenes obtained at the B3LYP-D3/6-31G(d) level: (a) without a solvent, (b) with chlorobenzene, and (c) with BSSE correction (R: right, M: middle, L: left, U: up, and D: down).

**Figure 6.** Binding energies (E_b in eV) for the supramolecular complexes of diaryl-TTFVs with each of C_{60} and C_{70} fullerenes obtained at the B3LYP-D3/6-31G(d) level: (a) without a solvent, (b) with chlorobenzene, and (c) with BSSE correction (R: right, M: middle, L: left, U: up, and D: down).
their energies differ by less than 0.14, 0.01, and 0.37 eV with C₆₀ and less than 0.12, 0.06, and 0.25 eV with C₇₀ for dianthryl-2a, diantithrlyl-2b, and dipyrenyl-TTFV 2c, respectively. With C₇₀, the most stable pair is the “right” structure followed by “middle” and then “left” structures for each of the three diaryl-TTFVs, with diantithrlyl-TTFV 2b being nearly degenerate for these three configurations. It was found that the “middle–2” structures are less stable than “middle” structures by 0.12, 0.13, and 0.07 eV without a solvent and 0.11, 0.12, and 0.06 eV with chlorobenzene for dianthryl-2a, diantithrlyl-2b, and dipyrenyl-TTFV 2c, respectively (see Table S3 in the Supporting Information). The three pairs of C₆₀ and diaryl-TTFVs have somewhat different stability orders: (“right” > “left” > “middle”), (“middle” = “left” ≃ “right”), and (“right” > “middle” ≃ “left”) for dianthryl-2a, diantithrlyl-2b, and dipyrenyl-TTFV 2c, respectively. Again, the smallest energy difference was observed for diantithrlyl-TTFV structures 2b. In most cases, the total binding energy for the supramolecular pairs is larger for C₇₀ than that for C₆₀. The main conclusion of this energy analysis is that the “right”, “middle”, and “left” orientations of diaryl-TTFVs with C₆₀ and C₇₀ fullerenes have very similar values of binding energies that are higher than those for the “up” and “down” orientations, indicating that they are considerably more stable than the “up” and “down” configurations.

More general, these findings indicate that in order to form stable diaryl-TTFV/fullerene complexes, the fullerene molecule should be placed somewhere along the line connecting the “right” and “left” orientations (including the “middle” one). The “right” pairs (in which the fullerene molecules are placed facing away from the nitrogen atoms of triazole rings of diaryl-TTFVs, see Figure S4 in the Supporting Information) are somewhat more stable and have higher binding energies than the “left” pairs (in which the fullerenes are facing toward the nitrogen atoms of triazole rings as shown in Figure S4) for all pairs except the pair of diantithrlyl-TTFV 2b with C₆₀. In general, the most stable conformational pairs, their order of the stability is as follows: “right” > “middle” > “left”. Similar trends with slightly lower binding and relative conformational energies can be seen in Figures 6 and S3 and Table S3 for the PCM/chlorobenzene results of all diaryl-TTFV structures. The presence of the solvent (chlorobenzene) reduces total binding energies by an average of 0.05 eV for most of the structures compared to those obtained without a solvent (see Figure 6 and Table S2), indicating that the solvent reduces the interaction between diaryl-TTFVs and fullerenes.

The BSSE-corrected ΔEᵢ’s for all diaryl-TTFV/fullerene complexes are shown in Figure 6 and Table S2 in the Supporting Information. The BSSE corrections lowered the ΔEᵢ values by 0.13–0.26, 0.37–0.56, and 0.48–0.60 eV for “up and down”, “right and left”, and “middle and middle–2” conformers, respectively. With the BSSE corrections, the relative order of the low-energy states is changed. The ΔEᵢ’s for the “middle” conformers become lower than those for “right” and “left” conformers in all cases as shown in Figure 6, indicating that the “middle” ones can no longer be considered as the low-energy conformations. This is consistent with the distortion energy data (see Table S1 in the Supporting Information), which showed that relatively large energies are required to convert the geometries of the diaryl-TTFV molecules from their lowest-state configurations to the tweezer-like configurations of their “middle” conformers. The BSSE analysis indicates that the increased overlap between diaryl-TTFVs and fullerenes in their “middle” conformations also leads to the largest BSSE correction and hence changes the relative conformational stability order. This result points to the fact that during the interactions of a fullerene with a diaryl-TTFV molecule, the entry of fullerene into the middle of diaryl-TTFV is not an easy process. Rather, the preferred binding motif is to place the fullerene outside the diaryl-TTFV around its mid-section.

In order to assess if BSSE corrections penalize to a larger extent the more compact “middle” structures, thus favoring even more the formation of complexes outside of TTFVs, we have also carried out SP B3LYP-D3 calculations with a higher triple-zeta basis set (see Table S4 in the Supporting Information). As can be seen from these data, the binding energies for these three structures are similar in all cases, once again showing that there is no strong preference for the “middle” tweezer-like structure. Hence, we point out that with or without the BSSE corrections, our conclusions are pretty much the same, there are a number of stable structures of the complexes, with the “middle” structure being one of them (rather than being the only one).

In Table 1, we list the number of atoms in a given fullerene interacting with the diaryl-TTFV molecules (which are within

| conformer          | dinaphthyl-TTFV | diantithrlyl-TTFV | dipyrenyl-TTFV |
|--------------------|----------------|-------------------|---------------|
| C₆₀ ΔEᵢ (a) | 13 (4) | 12 (7) | 12 (6) | 12 (9) | 17 (7) | 16 (8) |
| C₇₀ ΔEᵢ (a) | 16 (16) | 14 (14) | 16 (16) | 17 (17) | 15 (15) | 13 (13) |
| C₆₀ ΔEᵢ (b) | 14 (7) | 12 (4) | 18 (10) | 17 (8) | 16 (6) | 11 (3) |
| C₇₀ ΔEᵢ (b) | 5 (3) | 2 (2) | 7 (5) | 2 (2) | 5 (5) | 3 (2) |
| C₆₀ ΔEᵢ (c) | 9 (3) | 10 (4) | 8 (5) | 8 (3) | 8 (0) | 7 (0) |
| C₇₀ ΔEᵢ (c) | 2.94 | 3.09 | 2.98 | 3.14 | 3.27 | 3.29 |
| C₆₀ ΔEᵢ (c) | 3.31 | 3.30 | 3.29 | 3.30 | 2.99 | 3.04 |
| C₇₀ ΔEᵢ (c) | 3.01 | 2.96 | 3.12 | 3.03 | 2.96 | 2.83 |
| C₆₀ ΔEᵢ (c) | 3.07 | 3.32 | 3.20 | 3.43 | 3.32 | 3.23 |
| C₇₀ ΔEᵢ (c) | 2.94 | 2.80 | 3.05 | 2.90 | 2.80 | 2.74 |
| C₆₀ ΔEᵢ (d) | 0.09 | 0.11 | 0.13 | 0.13 | 0.08 | 0.09 |
| C₇₀ ΔEᵢ (d) | 0.07 | 0.10 | 0.08 | 0.09 | 0.08 | 0.08 |
| C₆₀ ΔEᵢ (d) | 0.08 | 0.11 | 0.08 | 0.09 | 0.07 | 0.10 |
| C₇₀ ΔEᵢ (d) | 0.17 | 0.40 | 0.11 | 0.40 | 0.15 | 0.25 |
| C₆₀ ΔEᵢ (d) | 0.07 | 0.07 | 0.10 | 0.11 | 0.06 | 0.06 |
| C₇₀ ΔEᵢ (d) | 2.94 | 3.09 | 2.98 | 3.14 | 3.27 | 3.29 |
| C₆₀ ΔEᵢ (d) | 3.31 | 3.30 | 3.29 | 3.30 | 2.99 | 3.04 |
| C₇₀ ΔEᵢ (d) | 3.01 | 2.96 | 3.12 | 3.03 | 2.96 | 2.83 |
| C₆₀ ΔEᵢ (d) | 3.07 | 3.32 | 3.20 | 3.43 | 3.32 | 3.23 |
| C₇₀ ΔEᵢ (d) | 2.94 | 2.80 | 3.05 | 2.90 | 2.80 | 2.74 |
the average (minimal) distances between diaryl-TTFVs and fullerenes; in the case of “right” and “left” structures, these distances are of the order 3.0 Å, whereas for the “middle” structures, these distances are close to 3.3 Å. Given that the C−H van der Waals contact is 2.9 Å, these distances support our conclusion that “right” and “left” structures involve hydrogen atom bonding (in addition to heavy atom bonding), whereas “middle” does not involve hydrogen atom bonding. “Up” structures involve noncovalent bonding between C and S in addition to C−C and possibly C−H noncovalent interactions. This finding illustrates that even though the total binding energy of “up” structures is not as high as that of the “right”, “left”, and “middle” structures, the $E_b$/atom is the highest for “up” structure, indicating that the interaction between C and S is much stronger than that between C and C, or C and N, or C and H atoms. The “down” structures involve predominantly hydrogen atom bondings in most cases. This, combined with the fact the number of atoms involved in these bonding is relatively small, results in this orientation being either the least stable or of similar stability as the “up” configuration. The distance and $E_b$/atom analyses show that, even though in some cases their relative conformational energies and binding energies are nearly the same (e.g., for “right”, “left”, and “middle” structures of dianthryl-TTFV/fullerene complexes), different noncovalent bonding forces may be involved in stabilizing the various structures of diaryl-TTFV/fullerene complexes.

HOMO and LUMO eigenvalues for the interacting dinaphthyl- (2a), dianthryl- (2b), and dipyrenyl-TTFVs (2c) and their supramolecular pairs with either C$_{60}$ or C$_{70}$ fullerene are displayed in Figures 7–9, respectively (also see Tables S5–S8 in the Supporting Information). We refer to interacting diaryl-TTFVs as molecules which have the same geometries as the ones obtained from the optimization process of diaryl-TTFV/fullerene combinations. The electronic structures (HOMO, LUMO energies, etc.) of interacting diaryl-TTFVs...
are then obtained (after the fullerenes are removed from the combinations) from SP DFT calculations. As can be seen from Figures 7−9, the HOMO eigenvalues are of the ranges of $-5.02$ to $-4.73$ eV without a solvent and $-5.17$ to $-4.74$ eV with chlorobenzene for both the (single) interacting diaryl-TTFVs and the supramolecular pairs. Hence, the presence of either C$_{60}$ or C$_{70}$ fullerene does not affect the HOMO eigenvalues of both the interacting diaryl-TTFVs and the respective combinations. In the presence of C$_{60}$ or C$_{70}$ ranges of LUMO eigenvalues (absolute values) of the interacting diaryl-TTFVs are changed from $1.30$ to $1.61$ to $2.99$−$3.38$, from $2.01$−$2.31$ to $2.96$−$3.34$, and from $1.66$−$1.81$ to $2.83$−$3.46$ eV without a solvent and from $1.30$−$1.46$ to $3.02$−$3.26$, from $2.00$−$2.17$ to $3.04$−$3.25$, and from $1.63$−$1.78$ to $2.96$−$3.27$ eV with chlorobenzene for dinaphthyl- (2a), dianthryl- (2b), and dipryrenyl-TTFV (2c), respectively.

The energy differences between HOMO and LUMO eigenvalues ($E_g$) for the (single) interacting diaryl-TTFVs...
and their supramolecular pairs with each of C\textsubscript{60} and C\textsubscript{70} fullerenes were also determined (see Figure 10). The interacting dianthryl-TTFVs (2b) give the lowest \( E_f \) values in a range of 2.40–2.79 eV without a solvent and 2.82–3.06 eV with chlorobenzene followed by 3.06–3.16 eV without a solvent and 3.30–3.44 eV with chlorobenzene for interacting diphenyl-TTFVs (2c) and 3.20–3.50 eV without a solvent and 3.61–3.81 eV with chlorobenzene for interacting dinaphthyl-TTFVs (2a). These \( E_f \) ranges are lowered significantly by the presence of either C\textsubscript{60} or C\textsubscript{70} fullerene to 1.31–2.02 eV without a solvent and 1.71–2.08 eV with chlorobenzene for all of the diaryl-TTFV/fullerene supramolecular complexes. Experimental results showed that the diaryl-TTFVs give relatively weak fluorescence in solution.\(^{46}\) It is also known that increased \( \pi \)-conjugation in organic molecules typically reduces their HOMO–LUMO gaps and in turn enhances their fluorescence efficiency. On the basis of their \( E_f \) values, individual dinaphthyl-TTFV(2a) possesses a lower degree of \( \pi \)-conjugation than dianthryl-TTFV (2b) and it should therefore exhibit relatively weak fluorescence. This result agrees with the experimental findings of diaryl-TTFV molecules. In combinations of diaryl-TTFVs with fullerenes, the HOMO–LUMO gaps are relatively small and become nearly the same (see Figure 10) for the diaryl-TTFV/fullerene complexes.

The reason why the HOMO–LUMO gaps of the diaryl-TTFV/fullerene complexes are similar in value is that these gaps are effectively formed from the eigenvalues of LUMOs of fullerenes (which reside over the whole of the fullerene) and eigenvalues of HOMOs of diaryl-TTFVs (which reside near the dithiole rings, near the top of the TTFV molecule, and not close to the functional aryl groups). Similar findings have been observed in other donor/fullerene systems (e.g., see ref 47). As an example, the HOMOs and LUMOs of the “right” conformers of the diaryl-TTFV/fullerene combinations are shown in Figure 11. These gaps are nearly equal to the energy differences between the LUMO energies of the acceptor (isolated C\textsubscript{60} and C\textsubscript{70} fullerenes) and the HOMO energies of the donors (isolated diaryl-TTFVs in their interacting geometries), \( \Delta \epsilon_{\text{LA-HD}} = \epsilon_{\text{LUMO(acceptor)}} - \epsilon_{\text{HOMO(donor)}} \). The values of \( \Delta \epsilon_{\text{LA-HD}} \) are typically indicative of the strength of interactions (the lower the value, the stronger the interaction). \( \Delta \epsilon_{\text{LA-HD}} \) values for all supramolecular pairs are shown in Figure S5 in the Supporting Information. This figure shows that the \( \Delta \epsilon_{\text{LA-HD}} \) values are in the range from 1.47 to 1.72 eV for all pairs, which is very close to the 1.4–2.0 eV values for the HOMO–LUMO gaps of the diaryl-TTFV/fullerene complexes. This finding indicates that in supramolecular complexes, the interaction strength between diaryl-TTFVs and fullerenes is of similar order of magnitude for the three types of arene functional groups. Figure S5 also shows that these intermolecular interactions decrease (because their \( \Delta \epsilon_{\text{LA-HD}} \)‘s increase) in the presence of a solvent.

4. CONCLUSIONS

In this work, we employed the B3LYP-D3 method to study the relative conformational stability and electronic structure of diaryl-substituted TTFVs in complexation with C\textsubscript{70} and C\textsubscript{60} fullerenes (both with and without the solvent). We found that for single (isolated) diaryl-TTFV molecules, the most stable conformations have the planar aryl end groups turned inward and consequently do not form open tweezer-like structures. In fact, the distortion energies are relatively large (greater than 0.4 eV) when converting a diaryl-TTFV molecule from its most stable conformer to the open structure. This has consequences for the diaryl-TTFV/fullerene complexation. For the diaryl-TTFV/fullerene supramolecular complexes, we found that the highest binding energies (and the lowest relative conformational energies) were obtained when fullerenes were placed around the central region of the TTFV moieties. The electronic structure analysis showed that the dianthryl-TTFV (2b) and diphenyl-TTFV (2c) conformers have lower HOMO–LUMO gaps relative to the ones obtained for dinaphthyl-TTFV (2a), indicating that dianthryl-TTFV (2b), and to some extend diphenyl-TTFV (2c), could be good candidates for chemical sensing of fullerenes by means of fluorescence responsiveness. When diaryl-TTFVs are in combinations with fullerenes, the HOMO–LUMO gaps of the resulting pairs become nearly the same because they are formed by the HOMOs of the diaryl-TTFVs and LUMOs of the fullerenes in all cases. The presence of a solvent (chlorobenzene) decreases the diaryl-TTFV/fullerene binding energies, presumably because of the interactions of the solvent with individual fullerenes and diaryl-TTFVs. It is our belief that we must look more closely at the excitation spectra of diaryl-TTFV/fullerene complexes, for example, by time-dependent DFT analysis, in order to resolve the mystery as
to why dianthryl-TTFV exhibits unique fluorescence selectivity for C70 fullerene in the presence of a large excess of C60 fullerene. With this study, we can only conclude that the interactions of diaryl-TTFVs with fullerenes result in lowering of HOMO–LUMO gaps. Such changes in electronic structures may be the major reason for the experimentally observed fluorescence enhancement when diaryl-TTFVs were in complexation with fullerenes.

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**Notes**

The authors declare no competing financial interest.

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