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Single-Molecule Transport of Fullerene-Based Curcuminoids

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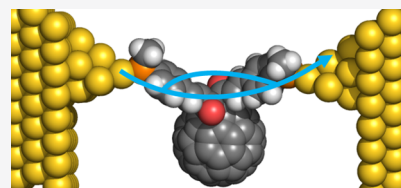
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ABSTRACT: We present experimental and theoretical studies of single-molecule conductance through nonplanar fullerocurcuminoid molecular dyads in ambient conditions using the mechanically controllable break junction technique. We show that molecular dyads with bare fullerenes form configurations with conductance features related to different transport channels within the molecules, as identified with filtering and clustering methods. The primary channel corresponds to charge transport through the methylthio-terminated backbone. Additional low-conductance channels involve one backbone side and the fullerene. In fullerenes with four additional equatorial diethyl malonate groups attached to them, the latter transport pathway is blocked. Density functional theory calculations corroborate the experimental observations. In combination with nonequilibrium green functions, the conductance values of the fullerocurcuminoid backbones are found to be similar to those of a planar curcuminoid molecule without a fullerene attached. In the nonplanar fullerocurcuminoid systems, the highest-conductance peak occurs partly through space, compensating for the charge delocalization loss present in the curcuminoid system.



INTRODUCTION

Because of their unique electronic properties, C_{60} and its derivatives represent ideal candidates for molecular-based devices.^{1,2} Thus far, the synthesis of a wide variety of fullerene derivatives has been reported and their potential applications as electronic, magnetic, catalytic, biological, and optical materials have been investigated.^{3–9} At the single-molecule level, establishing robust electronic functionalities in fullerene derivatives connected to gold electrodes has, however, proven to be a challenging task. Pristine C_{60} has been studied using both scanning tunneling microscope break-junctions¹⁰ and mechanically controllable break junction (MCBJ) techniques.^{11–13} Conductance values around $0.1G_0$ have been reported, where G_0 is the quantum of conductance equaling $2e^2/h = 77.48 \mu S$, where e is the elementary charge and h is Planck's constant, in agreement with theoretical calculations.^{14,15}

Taking advantage of their affinity to metals, various groups have studied “dumbbell” benzene-difullerene derivatives in which C_{60} 's are placed at both ends of the molecule and act as the anchoring groups to the metal leads.^{16–18} A conductance value of around $10^{-4}G_0$ was reported in these cases. The lower conductance value compared to that of pristine C_{60} was attributed to a charge transport limiting barrier created by the nitrogen atoms of the pyrrolidine bridging the benzene backbone to the C_{60} end groups. A more recent study of a dumbbell fullerene derivative shows two different electronic transport configurations, one assigned to transport through the molecular bridge and the second, at higher conductance values, ascribed to a single C_{60} anchoring group trapped between the

two adjacent electrodes.¹⁹ Additional experimental studies of amino²⁰ and diazofluorene²¹ C_{60} -terminated derivatives also show multiple conductance configurations.

Here, we present experimental and theoretical charge transport studies of the single-molecule conductance through fullerocurcuminoid (CCM- C_{70} / C_{60}) molecular dyads (see Figure 1). Me-S-terminated CCMs were chosen because

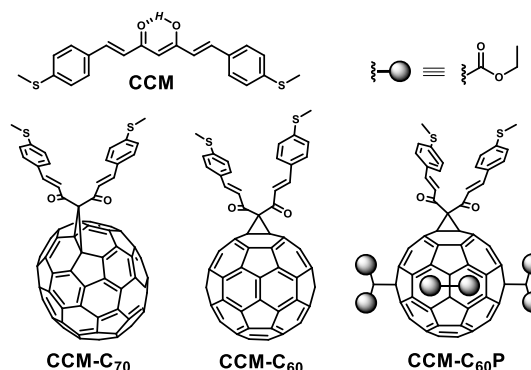


Figure 1. Chemical structures of the CCM derivatives used in this study.

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they form stable and well-defined molecular junctions.^{22,23} Three systems with the CCM skeleton connected to a C₇₀, C₆₀, and C₆₀ fullerene all-equatorial tetramalonate derivative (CCM-C₇₀, CCM-C₆₀, and CCM-C₆₀P, respectively) have been investigated. In the latter, four equatorial diethyl malonate groups were added to the C₆₀. The ethyl esters in these groups are expected to have a high contact resistance and low affinity for gold, thus modifying the interaction between the fullerene moiety and the electrodes in comparison with the nonequatorially modified molecule (CCM-C₆₀). We find that the presence of the fullerenes attached to the CCM backbone lowers the conductance only slightly with respect to the single CCMs without fullerenes attached to them. A priori, the results were unexpected because of the dramatic conformational changes that occur to the CCM backbone in CCM-C₇₀, CCM-C₆₀, and CCM-C₆₀P, where the CCM structure changes from almost planar to the one with a distinct V-shape in the fullerocurcuminoid systems, with a corresponding change in the charge transfer pathway (see Figure 1). In addition, the two unprotected fullerene-based derivatives show multiple junction configurations at lower conductance values, attributed to junction formation between one of the Me-S groups and the respective fullerene moiety; this second charge transport pathway is not found for CCM-C₆₀P, showing that the diethyl malonate groups effectively disrupt the direct interaction of the fullerene to the gold electrodes.

METHODS

CCM-C₇₀ and CCM-C₆₀ were synthesized following a reported procedure.²⁴ CCM-C₆₀P was synthesized in a multistep topologically controlled approach,²⁵ see the Supporting Information for the detailed synthesis. The conductance of the CCM-fullerenes (Figure 2) was measured in air at room temperature using the MCBJ technique explained in more detail elsewhere.^{26,27} Briefly, a narrow gold constriction is fabricated by e-beam lithography on a flexible substrate, under etched, and subsequently mounted in a setup equipped with a three-point bending mechanism. Bending the substrate causes the suspended gold wire to stretch until a single gold atom connects two thicker parts of the gold wire. Further bending results in breaking of the wire, thereby forming two sharp electrodes. The single-gold atom termination can be observed in a conductance versus electrode displacement trace (breaking trace) as a short plateau around 1G₀. A sudden drop in conductance to about 10⁻³G₀ signals the rupture of the gold wire. This point is defined as the zero displacement in a breaking trace. After the initial opening of the junction, the electrodes are moved further apart, and the conductance is recorded until the measured value reaches the noise level. When this sequence has been finished, the electrodes are fused forming a continuous wire again with a conductance of more than 20G₀ and the whole process is repeated in an automated way.

Prior to the deposition of the molecule of interest, each experiment starts by characterizing the bare device. A bias voltage of 0.1 V is applied across the gold wire, and the current passing through it is measured while repeatedly opening and closing the junction. Devices are used for molecule measurements only if they show just vacuum tunneling behavior and a clear sign of single-gold atom contact, that is, a clear 1G₀ plateau. A 30 μM solution with the molecule under investigation is then prepared by dissolving the starting compound in dichloromethane. Two 2 μL droplets of the

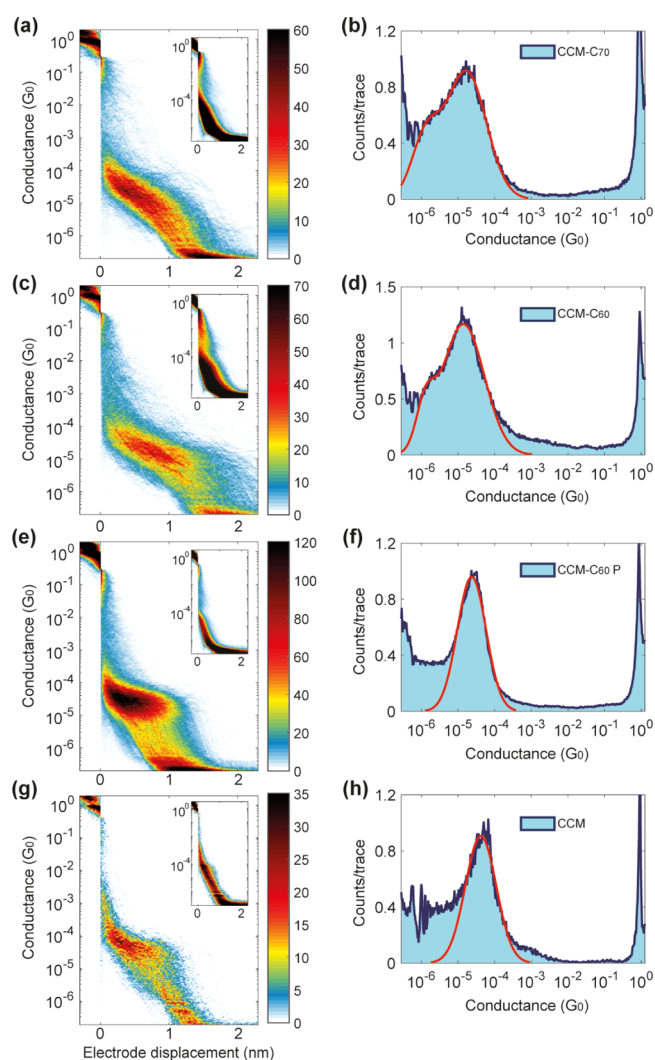


Figure 2. (a,c,e,g) Two-dimensional conductance histograms built from filtration of 10 000, 10 000, 10 000, and 2000 consecutive breaking traces recorded after drop-casting a solution containing CCM-C₇₀, CCM-C₆₀, CCM-C₆₀P, and CCM, respectively. For the selection of the traces, method I was used. The insets show all the traces that were excluded in the filtering procedure. The applied bias voltage was 100 mV, and the measurement speed was 6.0 nm/s for molecules CCM-C₇₀, CCM-C₆₀, and CCM-C₆₀P and 4.8 nm/s for molecule CCM. (b,d,f,h) Normalized one-dimensional histograms obtained by integrating the breaking traces along the displacement axis of the filtered data in the corresponding 2D histograms (light blue areas) of CCM-C₇₀, CCM-C₆₀, CCM-C₆₀P, and CCM, in this order. The red lines correspond to log-normal fits, which define the most probable conductance values listed in Table 1.

solution are drop-casted and dried on the freshly characterized device; subsequently, thousands of consecutive breaking traces are measured in an automated way.

COMPUTATIONAL DETAILS

Fully consistent nonequilibrium green function (NEGF) calculations^{28,29} were performed using the ATK program (2016.3 version).³⁰ The PBE exchange–correlation functional³¹ was used together with the numerical wave function of double- ζ quality with polarization for all the atoms except the gold atoms using a single- ζ quality with polarization. To calculate the conductance values assuming a linear regime, the

experimental bias value used in the break-junction measurements was 0.10 V. We have thus corroborated the linear regime between the current and bias, and therefore, the conductance can be easily obtained as one calculated value for a nonzero bias. The electrode structure employed in the calculations was a 2D 4×4 gold superlattice including a tip of 10 gold atoms on each electrode, while a 4×8 superlattice was employed for the fullerene systems (see Figure S16). A total number of 138 k -points was used to calculate the energy and wave function properties, while a 23×15 2D grid was used for transport properties. The distances between the anchoring S atoms and the gold atom of the tip were fixed to a value of 2.49 Å for all the molecules. The molecules were optimized with the Gaussian09 code³² using the B3LYP functional³³ with a 6-311G* basis set. The position of the methyl of the anchoring group is coplanar for geometry optimization of the isolated molecules, but to reduce the repulsion with the gold electrodes, a perpendicular disposition to the molecular plane was adopted. To confirm the role of the frontier orbitals in the transport (because GGA functionals show limitations to calculate highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energies), we performed nonperiodic calculations using hybrid density functionals. The transmission function was obtained in a postprocessing routine through the Artaios^{34,35} program. Hamiltonian and overlap matrices needed for the calculation of the transmission function were obtained using ORCA 4.0.1³⁶ (B3LYP functional/def2-SVP basis set).^{37–39} This transport code allows calculations with more accurate hybrid functionals improving the orbital energies but using nonperiodic models with a rather simpler wide-band limit approximation.⁴⁰ The fullerene-electrode contacts for the sliding process were optimized by using the tight-binding approach proposed by Grimme et al.⁴¹

RESULTS

To facilitate the identification of molecular traces, we applied two types of statistical analyses: a filtering method (method I), based on conductance plateau recognition, and an unsupervised clustering⁴² method (method II), both described in the Supporting Information. Figure 2 displays filtered (method I) two- (Figure 2a,c,e,g) and one-dimensional (Figure 2b,d,f,h) conductance histograms for CCM-C₇₀, CCM-C₆₀, CCM-C₆₀P, and CCM, respectively. Data sets are composed of breaking traces from individual junctions recorded with the same settings. Insets of Figure 2a,c,e,g represent 2D histograms constructed from the traces that were excluded in the filtering procedure, displaying the empty junctions. The sum of the two histograms, thus, constitutes the complete data sets, which can be found in Figure S7.

The 2D histograms in Figure 2a,c,e,g show high-count regions between 10^{-4} and $10^{-5}G_0$, which extend up to lengths of 1–1.5 nm. For CCM-C₇₀, the counts are mostly concentrated around two values and the log-normal fit to its one-dimensional histogram (Figure 2b) indicates that the corresponding most probable conductance values (using method I, see Table 1) are 1.7×10^{-5} and $1.3 \times 10^{-6}G_0$. Log-normal fits of the one-dimensional histogram of CCM-C₆₀ (Figure 2d) result in two similar values for the most probable conductances: 1.4×10^{-5} and $1.3 \times 10^{-6}G_0$. In contrast, for CCM-C₆₀P, the 1D histogram of Figure 2f only shows one clear peak, with a conductance value of $2.4 \times 10^{-5}G_0$. The analysis of conductance histograms shows that the most

Table 1. Conductance Values Using Method I (See Figure 2)

molecule	conductance peak 1 [G_0]	conductance peak 2 [G_0]
CCM-C ₇₀	1.7×10^{-5}	1.3×10^{-6}
CCM-C ₆₀	1.4×10^{-5}	1.3×10^{-6}
CCM-C ₆₀ P	2.4×10^{-5}	
CCM	3.9×10^{-5}	

prominent and highest conductance peak found for all three molecular junctions is the one close to $2 \times 10^{-5}G_0$. We attribute this value to the conductance through the Me–S-terminated flat CCM backbone which equals $3.9 \times 10^{-5}G_0$ (Figure 2h).²²

DISCUSSION

Initially, the close resemblance of the conductance values to the original CCM, without fullerene substituents, was unexpected considering the different conformations of the fullerene-based CCM skeleton (see Figure 1 and optimized structures in Figure S16). Specifically, in the CCM flat molecule with an enol structure, the two oxygen atoms are close because of the intramolecular hydrogen bonding (Figure 1, top). Instead, the CCM-C₆₀ system presents a diketone moiety (same for CCM-C₇₀ and CCM-C₆₀P) displaying a V-shape. The central carbon of this CCM skeleton is the apex, and in the opposite direction, the two remaining halves of the molecule contain a keto group each (Figures 1 and S16). It is also worth to note that the central carbon of the isolated CCM is involved in a delocalized π bond, while it has sp^3 hybridization in the fullerocurcuminoid systems. Analysis of conductance traces (Figure S12) corresponding to the fullerocurcuminoid systems is slightly shorter than those of the CCM molecule, in agreement with their modified V-shape structures. The additional lower-conductance peaks in CCM-C₇₀ and CCM-C₆₀ are longer and more slanted; therefore, they may be attributed to molecular junctions formed between one side of the Me–S backbone and the fullerene moieties. CCM-C₆₀P traces, on the other hand, show more straight plateaus (see Figure S12).

An additional insight from the conductance histograms can be obtained by performing a clustering analysis on the breaking-trace data sets (method II, see Table S1). For the three cases, the highest yield class (class 1) for each molecule corresponds to the conductance values close to those extracted using method I in the region of $1–4 \times 10^{-5}G_0$. It is worth noting that the highest yield class, considering the three systems, is class 1 of CCM-C₆₀P, probably helped by the noncoordinative nature of the bulky substituent, leading to a higher number of measurements with the electrodes anchored to the two Me–S groups. In CCM-C₆₀ (Figure S10c), the traces identified in the class 3 exhibit a broad distribution with conductance traces that decrease in value upon stretching (see Figure S13, e.g., breaking traces). Together with the small displacement involved and the relatively high conductance, this may indicate that the junction forms configurations mainly via the fullerene cage, mostly involving its sliding along the gold electrode. For CCM-C₇₀, similar high conductance features are found, albeit at a lower yield. Interestingly, the clustering does not show an additional low conductance feature as found in the filtering with method I. Further clustering of class one may be needed, but for the analysis presented, however, we have restricted the analysis to a maximum of four classes. The most

important observation is the absence of clear low- or high-conductance features for the CCM-C₆₀P derivative, thereby reinforcing the hypothesis that the pathway through the fullerene moieties is obstructed.

Density functional theory (DFT) and NEGF calculations (see the [Computational Details](#) section) were performed to understand why the highest conductance values of the CCM-fullerene family are similar to that of the CCM system. [Table S2](#) shows the calculated conductance values for the CCM-C₇₀, CCM-C₆₀, and CCM systems. A well-known drawback of the used PBE functional is that it provides small HOMO–LUMO energies, resulting in an overestimation of the conductance values, but giving reliable trends. The calculated conductance values for the most stable conformation in the junction through the two methylthio groups of the CCM for the CCM-C₇₀, CCM-C₆₀, and CCM systems show similar values, being slightly larger for the single CCM, in agreement with the experimental data. A V-shaped CCM without the fullerene was also calculated, giving the same conductance value as the complete structure. This result corroborates the fact that the fullerene only plays a structural role distorting the planar CCM moiety, while its contribution to the current is negligible. The perpendicular orientation of the methyl groups at the ends of the CCM species in all cases is the most stable structure when the molecules are coordinated to the electrode (see [Figures S15 and S16](#)), while the coplanar orientation is the most favorable conformation for the isolated molecules.

[Figure 3](#) displays the transmission curves and transmission eigenfunctions showing that the transport is mainly due to the LUMO channel. Transmission eigenfunctions with a defined transmission ($0 \leq T \leq 1$) are obtained from the diagonalization of the transmission matrix. The total transmission is the sum of the eigenvalues of all transmission eigenfunctions.⁴³ As expected, the calculated transmission curves using nonperiodic models and the hybrid B3LYP functional (see [Figure 3](#)) show a larger HOMO–LUMO gap; however, the LUMO is still mainly responsible for the transport properties. The position of the LUMO orbital with respect to the Fermi level for all the systems is relatively similar ([Figure 3](#)), and consequently, they lead to comparable conductance values (see [Table S2](#) and details in the [Supporting Information](#)). In the case of the CCM molecule, the analysis of the transmission eigenfunctions corresponding to the LUMO shows a delocalized π distribution along the whole molecule. For the CCM-fullerene systems, delocalization is interrupted by the central sp³ carbon. The transmission eigenfunction appears delocalized along the whole backbone consistent with the conductance values found for such types of organic systems.

In addition, a detailed analysis of the calculated conductance values in [Table S2](#) reveals two noticeable features: (i) there is an important influence of the relative orientation of the terminal methyl groups for the transport properties (see transmission curves calculated with the PBE functional for both conformers, coplanar and perpendicular for CCM-C₇₀, CCM-C₆₀, and CCM, [Figure S17](#)). Basically, there is a shift to low energies of all the levels corresponding to the perpendicular conformer. Thus, the LUMO level is closer to the Fermi level for the perpendicular orientations leading to an increase in the conductance when compared with the coplanar case. In this regard, we have already shown that the orientation of the methyl groups of the anchoring Me–S ligands plays a key role in some systems.²² (ii) In the CCM system, the

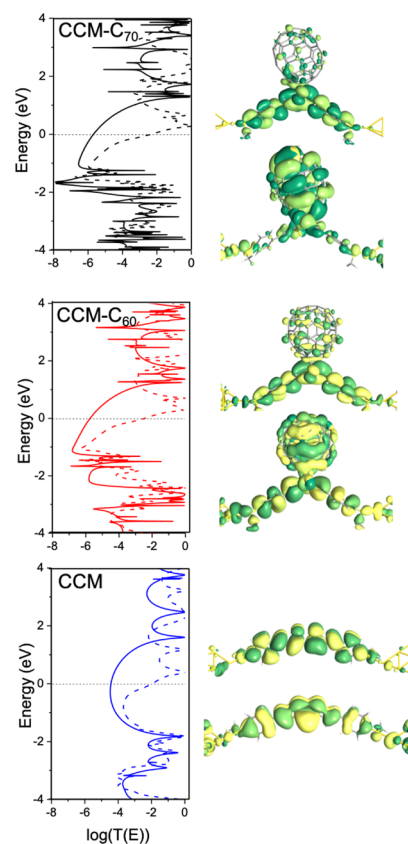


Figure 3. Transmission curves for CCM-C₇₀, CCM-C₆₀, and CCM derivatives calculated with the Artaios code using a nonperiodic model with a wide band limit approach and B3LYP functional (continuous line) and with the ATK code using periodic models with the NEGF approach and PBE functional (dashed line). Transmission eigenfunctions of the PBE results were plotted for the frontier orbitals. The transmission eigenfunctions are obtained by diagonalizing the transmission matrix, and the corresponding eigenvalues indicate the importance of each eigenstate in the transport. As it is a complex wave function, the color map indicates the phase of the function, represented from 0 to 2π by dark green to yellow colors. The isovalue employed for the isosurface was 0.3.

central keto–enol unit favors π -delocalized systems with an odd number of atoms in the backbone showing π delocalization over the whole molecule because of the central keto–enol (C₃O₂H) moiety.

We have also analyzed the transmission pathways ([Figure 4](#)) to gain insight into the transport mechanism considering the structural differences observed among the systems. Transmission pathways are calculated by the projection of the total transmission in pair contributions between atoms employing localized orbitals. This decomposition can be represented in real space by arrows indicating forward and backward current flow.⁴⁴ We find that the transport mechanisms are different for the flat CCM in comparison to the nonplanar fullerocurcuminoid systems. In the CCM system, transport is directly through the neighboring carbon atoms but with some loss of current because of the two oxygens coordinated to the carbon backbone (destructive interference). However, in the fullerocurcuminoid systems, transport through each keto unit is maintained as in the flat molecules, but with a direct tunneling pathway in the central region between the two external carbons of the C₃O₂ diketo unit ([Figure 4](#)). This pathway, assisted by the shorter S...S distance because of the bending of the CCM

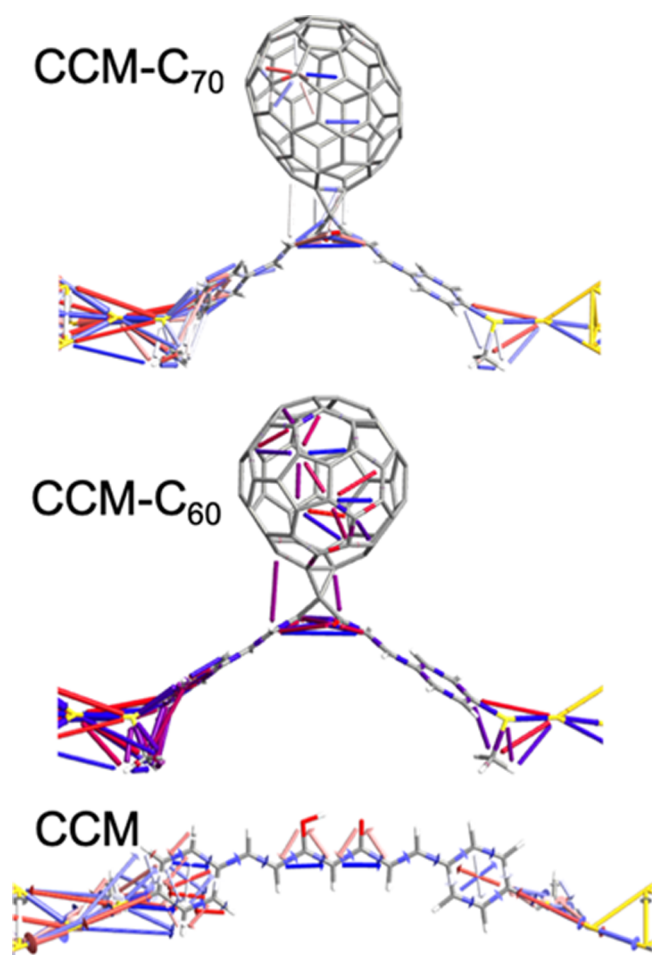


Figure 4. Transmission pathways for the systems based on CCM- C_{70} , CCM- C_{60} , and CCM. The color of the arrows (in CCM) indicates the angle of the direction of the transport, blue (0° , forward) and red (180° , backward), respectively, and intermediate colors (0 – 180°). The width of the arrow is proportional to the magnitude of the transport. A threshold value of 0.0005 was employed.

system, compensates for the nonflat structure of the CCM and results in a similar conductance value to that of the flat CCM system. Furthermore, the calculations indicate the same conductance for systems with the fullerene or two hydrogen atoms replacing carbon atoms of the cyclopropane ring (Table S2). This observation indicates that there is neither significant transport through this ring nor (destructive) quantum interference effects as can also be concluded from the inspection of the transmission pathways in Figure 4. In short, in the conjugated regions, the electrons are traveling through the bonds, but in the nonconjugated parts of the molecule, that is, the central carbon of the fullerocurcuminoid, the electrons are flowing around the bonds.⁴⁵

Finally, the lowest conductance region has been explored by analyzing the sliding process of the gold electrode on the fullerene surface. For that, a total of three optimized structures, taking into account the displacement of electrodes with respect to the molecule, have been calculated (see Figure S18). The decrease found in the calculated conductance values reproduces the experimental trend for CCM- C_{70} and CCM- C_{60} ; such values decrease while the electrode-molecule distance increases, with the fullerene and one of the branches of the V-shaped CCM attached to the gold electrodes (Figure

S18). Logically, the sliding process is not found in the CCM- C_{60} P system as it is blocked by the malonate addends in agreement with the presence of horizontal plateaus in the experimental breaking traces plotted in Figure S12.

CONCLUSIONS

In conclusion, we demonstrated that fullerocurcuminoid molecular dyads can form multiple stable molecular junction configurations with well-defined conductance values and that equatorial diethyl malonate groups attached to the fullerene can block the transport pathway through it. A surprising finding is that both, C_{70} and C_{60} , distort the planarity of the Me-S-terminated CCM molecule drastically; however, the conductance values through the dyads are very similar to the conductance of the planar CCM (around $10^{-5}G_0$); our theoretical findings are in agreement with this observation. On the one hand, CCM is planar and conjugated but there is a loss of current because of the two oxygens coordinated to the carbon backbone, which leads to destructive interference. On the other hand, in the CCM-fullerene systems, there is a direct pathway between the two external carbons of the C_3O_2 diketo unit, assisted by the shorter S...S distance because of the bending of the CCM system, which compensates for the nonflat structure of the CCM. The stability of the MCBJ technique in combination with the filtering and clustering methods applied have been a key in unraveling these features connecting the structure with transport pathways.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.9b10166>.

Detailed synthesis and characterization of the molecules, details of computational-filtering methods, and additional theoretical analysis (PDF)

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

CCM-C₇₀/C₆₀, fullerocurcuminoid molecular dyads; CCM/C₆₀P, all-equatorial tetramalonate C₆₀ fullerocurcuminoid molecular dyad; Me-S, methylthio; DFT, density functional theory; NEGFs, nonequilibrium green functions; MCBJ, mechanically controllable break junction

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