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Length-dependence of intramolecular electron transfer in σ -bonded rigid molecular rods: an ab initio molecular orbital study

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Abstract

The dependence of electron transfer (ET) coupling element, V_{AB} , on the length of rigid-rod-like systems consisting of bicyclo[1.1.1]pentane (BCP), cubane (CUB), and bicyclo[2.2.2]octane (BCO) monomers, has been investigated with the use of ab initio Hartree–Fock (HF) method employing Marcus–Hush two-state (TS) model. The value of V_{AB} decreases exponentially with increase in the number of the cage units of the σ -bonded molecules. The calculated decay constant, β , shows good agreement with previously reported data. For molecular length $\geq 15 \text{ \AA}$, the value of V_{AB} becomes negligibly small, suggesting complete suppression of the through bond direct tunneling contribution to ET process. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Long distance intramolecular electron transfer (ET) constitutes the basis of many chemical and biological phenomena in nature. For this reason, ET in organic molecules has been the subject of numerous theoretical and experimental studies [1–3]. Recently, there has also been interest in intramolecular ET due to its potential application in molecular electronic/photonic devices [3–6]. An

important property quantifying the electronics application of molecules is the ET rate, which in a two-state (TS) theory [1–3] is related to the ET coupling matrix element, V_{AB} .

The dependence of ET rate and the coupling matrix element, V_{AB} , on the structural features, such as the geometry, stereochemistry, and effective length of the molecule has been the subject of several studies in the past [7–21]. Two recent articles by Newton [3] and Newton and Cave [5] present excellent reviews on the subject. In general, electron transport in molecules follows radically different mechanisms from those known in semiconductor materials and is affected by such factors

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14. ABSTRACT The dependence of electron transfer (ET) coupling element, V_{AB}, on the length of rigid-rod-like systems consisting of bicyclo[1.1.1]pentane (BCP), cubane (CUB), and bicyclo[2.2.2]octane (BCO) monomers, has been investigated with the use of ab initio Hartree-Fock (HF) method employing Marcus-Hush two-state (TS) model. The value of V_{AB} decreases exponentially with increase in the number of the cage units of the sigma-bonded molecules. The calculated decay constant, beta, shows good agreement with previously reported data. For molecular length ≥ 15 AA, the value of V_{AB} becomes negligibly small, suggesting complete suppression of the through bond direct tunneling contribution to ET process.			
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as the symmetry, geometrical arrangement, spatial extension, and the separation between the participating one-electron orbitals. Therefore, a systematic study of the factors affecting intramolecular ET constitutes an essential first-step toward developing the foundation of molecular electronics.

In this Letter, we present the results of our ab initio molecular orbital (MO) study of the length-dependence of ET in σ -bonded rigid-rod molecules. Specifically, the systems studied are oligomeric chains ($\text{CH}_2\text{-cage}_{n=1,2,3}\text{-CH}_2$) involving σ -bonded bicyclo[1.1.1]pentane (BCP), cubane (CUB), and bicyclo[2.2.2]octane (BCO) monomer (cage) units. These molecular rods are of interest in molecular electronic circuits and photo-induced ET reactions [22].

In a recent study [23], the ET properties of the three monomers, BCP, CUB, and BCO were investigated by the ab initio MO method in the premise of the Marcus–Hush TS model [1–3]. The three molecular systems exhibited the same qualitative behavior for ET with respect to the conformation of the donor (D) and acceptor (A) moieties, represented for simplicity by two $-\text{CH}_2$ groups, attached to the two sides of the cage. Specifically, the value of V_{AB} was calculated to be maximum and minimum when the planes of the two $-\text{CH}_2$ groups were, respectively, planar and perpendicular to each other. Based on this study, an operational mechanism for a conformational molecular switch was proposed [23]. Quantitatively, the BCO system was calculated to have the highest ‘molecular resistance’ (lowest magnitude of V_{AB}) among the three systems, followed by CUB and BCP in that order. However, it was not clear if the same trend also holds in the oligomeric forms of the three systems.

Previous studies have shown that the ET rate between two active centers generally falls off exponentially with the increase in their separation length [14]. This exponential decrease of ET rate is characterised by a decay constant β , whose value depends upon the molecular system. Some representative values for β derived from experimental measurements are: $\leq 0.2\text{--}1.4 \text{ \AA}^{-1}$ for DNA [15], $1.0\text{--}1.4 \text{ \AA}^{-1}$ for proteins [16], $0.8\text{--}1.0 \text{ \AA}^{-1}$ for saturated hydrocarbons [9,17,18], and $0.2\text{--}0.6 \text{ \AA}^{-1}$

[19,20] for unsaturated organic systems such as phenylene, polyene, polyynes and phenylenevinylene. Recent experiments [24] give a somewhat narrow range ($0.8\text{--}1.2 \text{ \AA}^{-1}$) for β in the case of DNA molecule. It is, however, clear from the widely varying range in the value of β that the ET decay rate strongly depends on the chemical nature and electronic structure of the molecules.

The length-dependence of ET in BCP, CUB, and BCO rods has been the subject of a number of previous investigations. Liang and Newton [11] have calculated β for BCP and CUB with the use of ab initio Hartree–Fock (HF) method and Koopman’s theorem (KT) approximation. A semi-empirical calculation of the length-dependence of ET rate in systems involving a BCO spacer has been reported recently by Do Monte [22]. The decay constant, β , and the ET coupling matrix element, V_{AB} , in systems involving CUB and BCO as the spacer have also been reported from rate constant measurements [9,18,21] in organic solvents. However, a number of inconsistencies among the reported results for V_{AB} exist in the literature. For example, a fluorescence measurement study [18] on organic molecules containing BCO oligomers as the spacer shows a monotonic decrease in V_{AB} with length. In contrast, ab initio HF calculations by Liang and Newton [11] using KT approach show a non-monotonic variation of V_{AB} with the increase in the number of BCO cage units in a molecular rod. Furthermore, the value of V_{AB} for CUB monomer derived from experimental rate constant measurements [9] differs from that obtained from ab initio HF calculations [23] by an order of magnitude.

The present study is an attempt to resolve the outstanding inconsistencies in the previously reported data and also to develop a more detailed understanding of the qualitative behavior of the length-dependence of ET in σ -bonded systems from a reliable and uniform theoretical treatment. Results are presented on the dependence of ET on the number of the cage units between D and A moieties, represented, for simplicity, by $-\text{CH}_2$ groups. The effect of the one-electron basis set on the calculated ET coupling is examined. The calculated results are compared with previously reported theoretical and experimental data.

2. Theory and calculations

For the weak coupling between donor and acceptor centers, the ET rate constant is related to ET coupling matrix element V_{AB} as [1–3]

$$K_{\text{et}} = \frac{2\pi}{\hbar} |V_{AB}|^2 \text{FCWD}, \quad (1)$$

where FCWD represents the Franck–Condon-weighted density of states, which reflects the nuclear modes of the system. The electronic coupling element, V_{AB} , represents the strength of interaction between localized states A and B participating in the intramolecular ET. Since FCWD in Eq. (1) only weakly depends on the D – A separation in a molecule [10,18,22], the distance dependence of ET rate is primarily determined by the distance dependence of electronic coupling element, V_{AB} , given as [22]

$$|V_{AB}|^2 = K_0 \exp(-\beta R_{DA}), \quad (2)$$

where K_0 is a kinetic prefactor, R_{DA} is the separation between two active reaction centers, and β is the decay constant, a characteristic of the spacer system, which determines the distance dependence of ET rate.

In the present study, we used the Marcus–Hush TS model [1–3] as formulated by Farazdel and Dupuis [25] to calculate the electronic coupling element, V_{AB} . A brief description of the method has been presented in an earlier publication [23]. In this approach, the V_{AB} is calculated directly from the ab initio self-consistent wavefunctions of the two participating electronic states, A and B. In contrast to the more commonly used and somewhat less expensive KT approach, the present approach offers fully relaxed charge-localized electronic states participating in the ET process and thus includes, to some extent, electron correlation effect in the calculation. Detailed descriptions of and comparison among various theoretical methods used for calculating V_{AB} has been given by Newton [3] in a recent review. The details of the formulation and computational algorithm of the ab initio TS method used here can be found in the original papers by Farazdel et al. [6,25]. Calculations of V_{AB} were performed with the use of the HONDO-8 electronic structure code [26].

In the KT approach, the value of V_{AB} for cationic systems can be simply approximated as the half of the splitting between the highest occupied molecular orbital (HOMO) and the HOMO-1 energy levels in the triplet state of the neutral molecule. Due to this simplicity, the KT approach has been widely used for estimating V_{AB} in complex organic molecular systems [3,5,7,10–13]. In the present work, we have also estimated V_{AB} using the KT approach to compare with our results obtained from a more rigorous self-consistent method [6,25].

Three basis sets, namely STO-3G, 3-21G and double zeta-plus polarization (DZP) Cartesian Gaussian functions were used in the calculation on the monomer units. For the oligomeric systems ($n > 1$), we could not use the polarized basis set (DZP) due to computational limitation.

Initially, the geometry of neutral rod structures containing 1, 2, and 3 monomer units terminated by $-\text{CH}_3$ groups at the two ends were optimized with the use of STO-3G basis set. Subsequently, the $-\text{CH}_3$ groups at the two ends were replaced by $-\text{CH}_2$ groups to model the molecular interconnect. In all the oligomeric systems ($n > 1$), a staggered conformation of the σ -bonded cage units was found to be the most stable structure. The largest oligomer, with $n = 3$, for each system optimized in this work is shown in Fig. 1. The optimized inter-cage distances for the rods containing BCP, CUB, and BCO are 1.514, 1.511, and 1.590 Å, respectively. The optimized geometrical parameters for the monomer units have been reported in an earlier publication [23] and did not change in the present calculations. The geometry optimization calculations were performed with the use of the GAUSSIAN 94 [27] electronic structure code.

In order to calculate V_{AB} an electron was removed from the neutral system to create an open-shell system with one unpaired electron. The charge-localized structures and wave functions were obtained by varying the C(CH_2)–C(cage) bond distances while keeping the cage structure fixed. The charge-localized wavefunctions were used as the initial guess for the calculation of ET matrix element at an average geometry of the two localized structures.

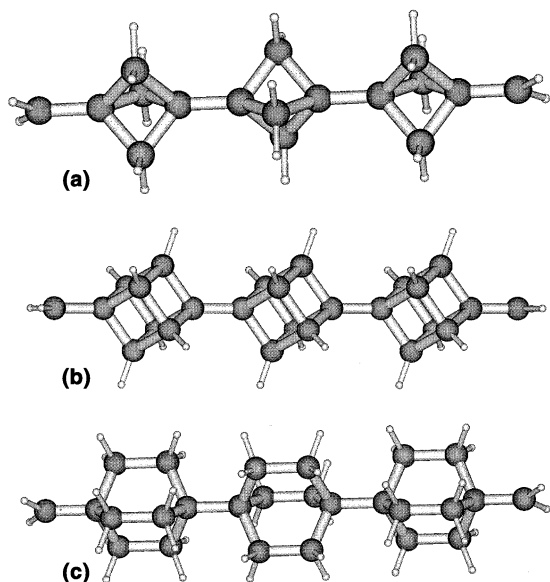


Fig. 1. (a) Optimized $\text{CH}_2-(\text{C}_5\text{H}_6)_{n=3}-\text{CH}_2$ structure; (b) optimized $\text{CH}_2-(\text{C}_8\text{H}_6)_{n=3}-\text{CH}_2$ structure; (c) optimized $\text{CH}_2-(\text{C}_8\text{H}_{12})_{n=3}-\text{CH}_2$ structure. The large (dark) spheres represent C atoms and the small (light) spheres are H atoms.

3. Results and discussion

The calculated results for V_{AB} are presented in Table 1, together with the available theoretical and experimental results reported earlier. The two basis sets (STO-3G and 3-21G) give very similar results although the magnitude of the V_{AB} is larger for the latter. For the CUB system, improvement of the basis set appears to have no noticeable effect on V_{AB} . The KT method also shows a similar effect with respect to basis set. The only exception is BCO system, in which the TS self-consistent approach shows an increase, while the KT method shows a decrease in the value of V_{AB} with the improvement of the basis set. For the BCP and CUB rods, the results obtained for V_{AB} from the TS and the KT approaches reasonably agree with each other. In the case of the BCO rod, the TS approach shows a monotonic decrease in the ET coupling with increase in the number (n) of the cage units. In contrast, the KT approach shows an increase in the value of V_{AB} in going from $n = 1$ to 2 and then a decrease from $n = 2$ to 3 in the BCO rod. A similar trend in the change in ET coupling

with increase in the number of the BCO cage unit was also noted in the KT calculations by Liang and Newton [11]. Experimental measurements [18] on the rate constant, however, suggested a monotonic decrease in ET coupling with increase in rod length of the BCO system. A closer examination of the results in Table 1 suggests that for molecular rod with $n = 2$ and 3, the KT approach tends to overestimate the value of V_{AB} . To the best of our knowledge, no experimental data on the length-dependence of V_{AB} in BCP rods is available in the literature for comparison.

One notes (Table 1) a difference of an order of magnitude between the value of V_{AB} for the CUB monomer calculated in the present study by the TS self-consistent method and the experimental value estimated from rate constant measurements in solution [9]. The TS results show a decrease in the value of V_{AB} by an order magnitude as the number of the cage unit increases from 1 to 2. The corresponding change in the measured value is much smaller by only a factor of 2. However, in a CUB rod, for $n = 2$ and 3, the calculated TS results for V_{AB} show excellent agreement with the corresponding experimental values estimated from rate constant measurements. This could very well be accidental since the calculations have been performed on isolated systems while experiments were performed in solution.

The optimized distance between the two C atoms of the $-\text{CH}_2$ end groups, where the charge localization occurs, was taken as the effective tunneling length, L , for ET. The calculated value of L in the systems investigated in the present study is listed in the second column of Table 1. The decay constant β was estimated from an exponential fit of V_{AB} with L . A plot of $\ln(|V_{\text{AB}}|)$ as a function of L for BCP, CUB, and BCO rod is shown in Figs. 2–4, respectively. The plotted curves for BCP (Fig. 2) and CUB (Fig. 3) exhibit an exponential decrease in the value of V_{AB} with increase in L . The same is not true for BCO, where the plots deviate from a straight line, suggesting a somewhat non-exponential, but monotonic decrease (Table 1) in decay rate with increase in the value of L .

The values of β estimated from the calculated slope of the best-fit straight line for the three sys-

Table 1
ET coupling, $|V_{AB}|$ (kJ/mol), as a function of the distance (L) between the donor and acceptor groups in molecular rods ($\text{CH}_2\text{--}[\text{cage}]_{n=1-3}\text{--CH}_2^+$) involving BCP, CUB and BCO monomer units

(Cage) _{<i>n</i>}	L^a (Å)	Present work (TS)			Present work (KT)			Previous results	
		STO-3G	3-21G	DZP	STO-3G	3-21G	DZP	Theory	Experimental
(BCP) ₁	4.84	36.16	47.98	52.00	44.38	58.77	58.85	54.08 ^b	
(BCP) ₂	8.26	5.04	9.64		11.34	16.63		17.12 ^b	
(BCP) ₃	11.67	0.65	1.77		2.80	4.83		5.62 ^b	
(CUB) ₁	5.64	25.65	25.50	25.25	36.66	39.48	34.73		2.51 ^c
(CUB) ₂	9.88	1.49	0.80		9.36	7.68			0.49 ^c
(CUB) ₃	14.11	0.07	0.06		2.49	1.64			0.05 ^c
(BCO) ₁	5.62	2.29	4.78	6.83	11.58	2.69	1.93	(3.15 ± 3.93) ^b , 0.79 ^d , 2.12 ^e	1.67 ^c
(BCO) ₂	9.96	0.97	1.23		5.80	5.73		5.54 ^b	
(BCO) ₃	14.26	0.08	0.14		1.23	1.29		1.63 ^b	

^a Distance between the C atoms of the two end --CH_2 groups.

^b Ref. [11], obtained using KT approach and super exchange analysis.

^c Ref. [9], estimated from PR rate constant measurements in solution.

^d Ref. [13], obtained using KT approach.

^e Ref. [7]. The theoretical results were obtained using KT approach and the experimental results were obtained from pulse radiolysis (PR) rate constant measurements in solution.

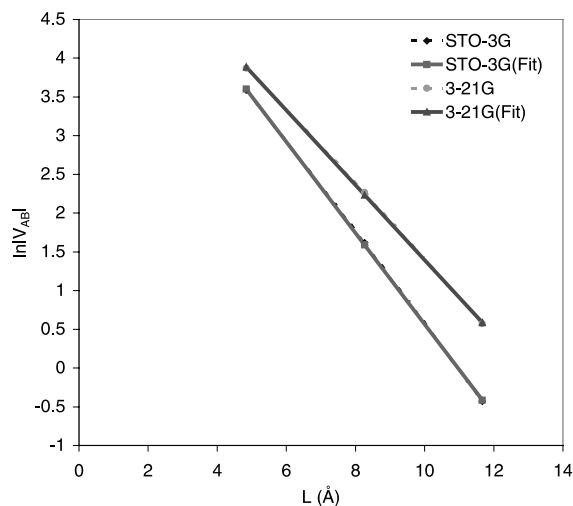


Fig. 2. Electronic coupling matrix element, V_{AB} (kJ/mol), in natural logarithmic scale, as a function of the effective length (\AA) of the BCP-rod.

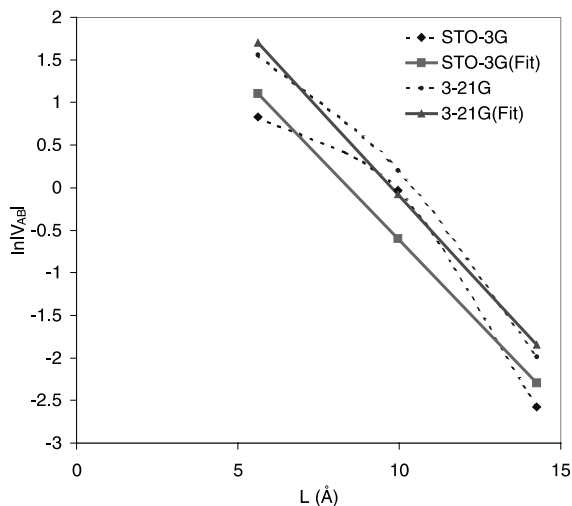


Fig. 4. Electronic coupling matrix element, V_{AB} (kJ/mol), in natural logarithmic scale, as a function of the effective length (\AA) of the BCO-rod.

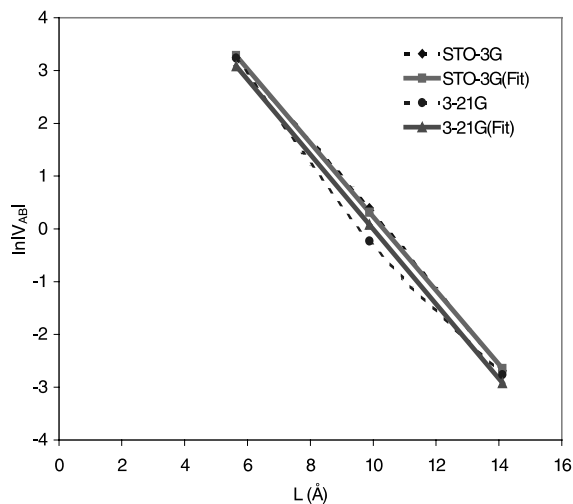


Fig. 3. Electronic coupling matrix element, V_{AB} (kJ/mol), in natural logarithmic scale, as a function of the effective length (\AA) of the CUB-rod.

tems are listed in Table 2. Also listed in the table are the available literature values of β for the three systems. The two basis sets, namely STO-3G and 3-21G, used for the calculation on the oligomeric systems ($n > 1$), give very similar values for β . For the CUB system, the calculated β is found to be somewhat insensitive to the basis set. A compari-

son of the present TS self-consistent results of β for BCP and BCO with the corresponding value obtained with the use of the KT approach [11] suggests that the latter approach gives a somewhat smaller decay rate than the former. Our calculated values of β are, however, in good agreement with the available experimental results, with the latter being somewhat smaller in magnitude. A small quantitative difference between the value of β for CUB obtained in the present study (TS self-consistent approach) and that derived from the ET rate measurements [9] reflects the difference in the chemical and electronic environments around the spacer systems in the two studies. For example, the experiments were performed in a solution in which the intermolecular interaction between the solvent and the solute molecules (the species under investigation) may influence the measured ET rate. In contrast, the present calculations have been performed on an isolated molecule. Furthermore, the experiments were performed on a CUB system with biphenyl and naphthyl groups attached at the two ends, whereas in our calculations, the rigid-rod systems were terminated by $-\text{CH}_2$ end groups. It is also worth noting that a fair degree of uncertainty exists in the experimental value of V_{AB} for the monomer estimated from rate constant mea-

Table 2

Calculated and measured values of the ET decay constant, β (\AA^{-1}), for BCP, CUB, and BCO rods

System	Present work		Previous results	
	STO-3G	3-21G	Theory ^a	Experimental
BCP-rod	1.18	0.97	0.66	
CUB-rod	1.40	1.42		0.90 ^b
BCO-rod	0.79	0.82	0.57	$\geq 0.70^c$

^a Ref. [11], obtained from V_{AB} values estimated using KT method.^b Ref. [9], obtained from pulse radiolysis measurements.^c Ref. [18], obtained from picosecond fluorescence measurements.

surement [9]. In view of the noted differences in the chemical and electronic environments around the CUB rod and uncertainties in the experimental result, the proximity between our calculated value for β and that derived from experiment is quite encouraging and lends confidence to the calculated results obtained in this study. The calculated values of β for the three systems suggest that the ET decay rate is much stronger in CUB rod than those in the BCP and BCO rods.

It is useful to establish a quantitative relationship between ET and the effective length of the molecular rods. An examination of the results of Table 1 reveals that the ET matrix element in all three cases nearly vanishes as the effective length increases to ~ 14 \AA . In other words, in the three σ -bonded systems studied here, there appears to be practically no ET beyond a length of ~ 14 \AA . This observation has important implications for the ET mechanism in non-conjugated systems. Since the present theory of ET is based on the direct overlap of many-electron wavefunctions, it provides information on direct ‘through-bond’ electron transport. Our calculated results of V_{AB} suggest that in the σ -bonded systems, the direct through-bond tunneling of electrons is totally suppressed at a length ≥ 15 \AA . It is interesting to note that this number is remarkably close to a value of ~ 20 \AA for the maximum effective distance for direct tunneling current measured for self-assembled monolayers (SAM) of alkane chains [28]. This property of the rigid molecular rods can be usefully exploited for the design and fabrication of molecular capacitors (MC) and molecular field-effect transistors (MFET). Rigid-rod anchors consisting of BCP, CUB, and BCO with

lengths ≥ 15 \AA can be used as ‘insulators’ to completely suppress direct tunneling current between two active reaction centers in a molecular circuit.

4. Summary and conclusion

We have performed ab initio calculations on the length-dependence of the ET coupling matrix element, V_{AB} , in σ -bonded rigid molecular rod structures consisting of BCP, CUB, and BCO monomer units. We have estimated the ET decay constant, β , from the calculated length-dependence of V_{AB} . Calculations on systems containing a single cage unit were performed with three one-electron basis sets, namely STO-3G, 3-21G, and DZP. For oligomeric systems, the calculations were limited to the two small basis sets due to the restrictions imposed by the computational requirements. For the systems consisting of BCP and BCO, the calculated value of V_{AB} exhibits strong sensitivity to the basis set. In contrast, the value of V_{AB} in the case of CUB system appears to be less sensitive to the quality of the basis set. However, both STO-3G and 3-21G basis sets give a similar trend for the distance dependence of V_{AB} , lending confidence to our calculated values of β .

A number of useful findings concerning ET in σ -bonded rigid molecular rods have emerged from the present study. Our calculations reveal that the ability of a σ -bonded rigid molecular rod to act as an insulator in molecular circuits depends upon its electronic and geometrical features. For the monomeric units, the magnitude of V_{AB} is calculated to have the order, BCP > CUB > BCO,

suggesting the BCO to be the best candidate among the three for application as a molecular insulator. However, with the increasing number of the monomer units in the rod, the order in the calculated magnitude of V_{AB} changes to $BCP > BCO > CUB$.

The calculated values of V_{AB} decrease exponentially with an increase in the effective length of the molecule, which is consistent with previously reported theoretical and experimental results in organic systems. The value of the ET rate decay constant, β , estimated from the length-dependence of V_{AB} has the largest magnitude in the case of CUB followed by BCP and BCO in that order. This suggests that among the three molecular rods investigated in the present study, the one consisting of CUB cages is more efficient in controlling the ET rate and hence the tunneling current than those consisting of BCP and BCO monomer units. The β values obtained from our calculations ($0.8\text{--}1.4 \text{ \AA}^{-1}$) is consistent with the experimental observation ($0.8\text{--}1.0 \text{ \AA}^{-1}$) in σ -bonded systems. Furthermore, the present study also lends support to the experimental observation relating the maximum effective length of SAM of alkane chains exhibiting electronic conduction. The present calculations reveal that the direct through-bond ET in molecular rods consisting of BCP, CUB, and BCO units is completely suppressed for an effective molecular length $\geq 15 \text{ \AA}$. This value can be used as a guide in designing MFETs, where the σ -bonded rods in the molecular circuit can be used to suppress leakage current from the gate end.

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