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Docking of Chiral Molecules on Twisted and Helical Nanotubes: Nanomechanical Control of Catalysis

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ABSTRACT

We theoretically demonstrate the possibility of *dynamically controlling* catalysis by nanomechanical means. This novel methodology is based on switching the configuration (activity) of catalysts docked on nanoscale surfaces that are reversibly deformed. We test the approach by molecular dynamics simulations of an organic chiral catalyst that is docked by van der Waals coupling on twisted carbon nanotubes. Our results show that its catalytic activity is sharply correlated with the direction and amount of the nanotube twist. We also observe a small selectivity in docking of chiral molecules on straight helical nanotubes.

Introduction

In the last decades, catalysis has become indispensable in most branches of chemistry.[1,2] Catalytic reactions make technological processes more efficient, facilitate the synthesis of novel materials with rich potential applications, and could open new energy resources. Homogeneous catalysis, usually realized under well-controlled conditions in solutions, allows the production of many unique chemicals.[3] Heterogeneous catalysis, used in the preparation of a wide range of chemicals, was recently often realized with the intriguing assistance of nanoparticles,[4] whose roles are yet to be elucidated.

Although many catalytic reactions are not yet well understood, their rates can often be tuned by structural variations of the catalysts. Some catalysts, besides being able to reduce the reaction barriers, can also function as *auxiliaries* that imprint their structures into the products and prepare them in specific configurations.[5] For example, asymmetric catalysts assist in the preparation of chiral molecules in one (left or right) enantiomeric form[6,7] and can be also substituted by optical fields.[8]

In this work, we theoretically investigate the possibility of *dynamically controlling* the chemical activity of catalysts attached to "deformable" nanoscale surfaces. Such "tunable auxiliaries" in close contact with the catalyst could provide quick and reversible means of controlling its configuration and activity. Carbon nanotubes that withstand large and reproducible deformations of their structures[9,10] could be excellent candidates for this job. When a single-wall carbon nanotube (SWNT) is reasonably twisted, its structure flattens and develops chiral "pockets" aligned along its symmetry axis,[11] even if its original structure is not chiral. Chiral molecules might selectively dock in these tunable pockets by $\pi - \pi$ stacking interactions and be controlled by the SWNT twist.

We first briefly analyze how chiral molecules could dock by van der Waals coupling on the twisted armchair (n,n) SWNTs, with $n = 4-10$ and twist angles $\varphi_t \approx 5°$ per cell. Our molecular dynamics (MD) simulations, performed here without solvation,[12−16] reveal that the docked molecules should be large enough to recognize the nanotube twist; i.e., their chirality should be extended over a molecular region that fills a significant part of the formed chiral pocket. As a result, molecules such as tryptophane and cholesterol, docked in energetically favorable ways on the twisted SWNTs, can change their binding energies by 10−20% and *rotate* their axes by tens of degrees for opposite twists of the tubes. We have also observed that left and right enantiomers of chiral molecules can bind differently to straight helical SWNTs $((m, n), m \neq n)$, but the difference in binding energies is $<5\%$.

The idea is to use the configuration change of chiral catalysts docked on differently twisted SWNTs as a control tool of their chemical activity. Among the many available asymmetric catalysts, those equipped with the aromatic binaphthyl skeleton,[17,18] such as BINOL[19] (1,1-binaphthol, $C_{20}H_{14}O_2$) and its numerous derivatives, could be particularly

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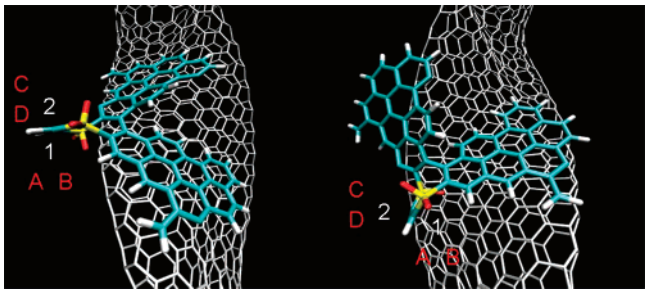

Figure 1. Visualization of the two configurations acquired by the modified 1,2-(1,1′-binaphthalene-2,2′-diyldisulfonyl)ethylene on the chiral surfaces of the oppositely twisted (8,8) SWNT. The twist is −5.83° per cell, "free catalyst" (left), and 5.83° per cell, "blocked catalyst" (right). Sides 1 and 2 associated with the A, B and C, D reaction modes are denoted, respectively.

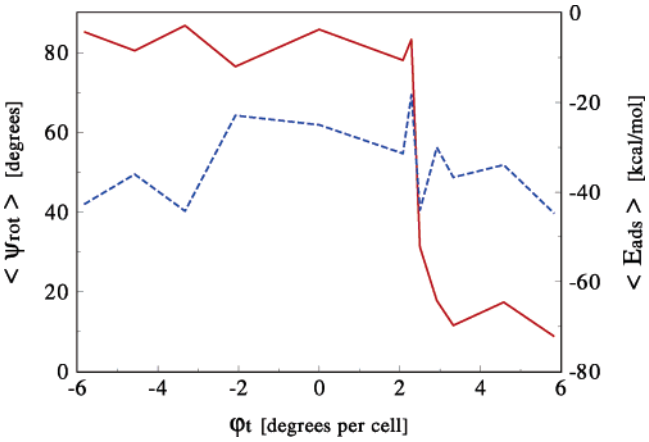

Figure 2. The average rotation angle $\langle\psi_{rot}\rangle$ between the symmetry axis of the catalyst and the tube, plotted as a function of the SWNT twist angle φ_t (solid line). The average adsorption energy $\langle E_{ads}\rangle$ of the catalyst to the tube is also shown (dashed line).

convenient, since their chirality is extended through the whole molecule. As a prototypic example, we consider the 1,2-(1,1-binaphthalene-2,2′-diyldisulfonyl)ethylene, which catalyzes the *Diels−Alder reaction*.[20] We extend its "aromatic wings" in such a way that they attach well to the twisted SWNTs and study its docking in the dichloromethane solvent.[12]

In Figure 1, we present the equilibrated catalyst docked on the (8,8) SWNT, twisted in two opposite directions, without showing the solvent molecules. The tube has 24 elementary cells, and the last elementary cells at its two ends are rotated (without deformation) in opposite directions by the $\varphi_t/2$ angle, giving for $\varphi_t = 140°$ an average twist of 5.83° per cell. For simplicity, the tube length is not varied during its deformation. Our simulations reveal that the catalyst can be found in two typical equilibrium configurations, shown in Figure 1, obtained for opposite twists of the SWNT.

To analyze this behavior in more detail, we show in Figure 2 the dependence of the average rotation angle $\langle\psi_{rot}\rangle$ of the catalyst, given by the angle between its C_2-symmetry axis and the axis of the tube, as a function of the tube twist angle φ_t.[21] We can see that the catalyst sharply *switches* between the two distinct configurations, depicted in Figure 1, at $\varphi_t \approx 2.5°$ per cell, where it rotates by about $\Delta\langle\psi_{rot}\rangle \approx 70°$. At this φ_t, the variance associated with the $\langle\psi_{rot}\rangle$-angle fluctuations is $\sigma_{\psi_{rot}} \approx 7.1°$, signaling the presence of a "configuration transition". The variance is also large, $\sigma_{\psi_{rot}} = 6.5°$, at $\varphi_t \approx -2.08°$ per cell, where a small change in the configuration takes part, while everywhere else it is $\sigma_{\psi_{rot}} \approx 2-5°$.

It is also interesting to find the average adsorption energy, $\langle E_{ads}\rangle$, of the catalyst to the twisted SWNT. It is equal to the difference between the average total energy of the equilibrated system when the catalyst is on the surface in the solvent, $\langle E_{surf,in}\rangle$, and that when the catalyst is away from the surface in the solvent, $\langle E_{solv,in}\rangle$

$$\begin{aligned}\langle E_{ads}\rangle &= \langle E_{surf,in}\rangle - \langle E_{solv,in}\rangle \\ &= \langle E_{surf,in} - E_{surf,out}\rangle - \langle E_{solv,in} - E_{solv,out}\rangle \\ &\quad + \langle E_{surf,out} - E_{solv,out}\rangle \quad (1)\end{aligned}$$

We calculate $\langle E_{ads}\rangle$ by resolving it in the three terms shown in eq 1. The first term represents the coupling energy of the catalyst to the cavity formed in the solvent at the SWNT surface, the second term gives this binding energy inside the solvent alone, and the third term is the difference of the cavitation energies for the catalyst in the solvent at the SWNT surface and away from it.[22]

The $E_{surf,in} - E_{surf,out}$ term can be calculated as the difference in the total energy of the system (for the given φ_t and chosen frame), when the catalyst is taken out of the SWNT surface and the solvent, while all the other molecules are kept intact. The $E_{solv,in} - E_{solv,out}$ term can be found in the same way, when the catalyst is away from the surface. We find that the first term (averaged over 20 frames) is $\langle E_{surf,in} - E_{surf,out}\rangle \approx -70$ to -90 kcal/mol, while the second term is $\langle E_{solv,in} - E_{solv,out}\rangle \approx -41.4$ kcal/mol.

To evaluate the last $\langle E_{surf,out} - E_{solv,out}\rangle$ term, we assume that the cavities at the surface and in the pure solvent have approximately the same surface S, and the cavitation energies are proportional to the surface tension coefficients $\Gamma_{surf,solv}$ and $\Gamma_{solv,solv}$ at the hybrid SWNT surface−solvent interface and in the pure solvent,[22] respectively

$$\langle E_{surf,out} - E_{solv,out}\rangle \approx S\,\Gamma_{surf,solv} - S\,\Gamma_{solv,solv} \quad (2)$$

To estimate the surface tension coefficients, we assume that these are associated with the breaking of intermolecular interactions between molecules at the particular interfaces and neglect the curvature of the formed cavities.[23] We have found that the interaction energy between two equilibrated layers of the solvent molecules, divided by the area of both of them, is $\Gamma_{solv,solv} \approx 0.022$ N/m, which is close to the value, $\Gamma_{solv,solv} = 0.027$ N/m, known for dichloromethane.[24] Analogously, we obtain that the interaction energy between an equilibrated layer of the solvent molecules and a graphene sheet, divided by the area of both of them, is $\Gamma_{surf,solv} \approx 0.11$ N/m. This value is large due to the strong van der Waals binding of the solvent to the graphene layer with conjugated C−C bonds. By assuming that the surface of the cavities is $S \approx 100$ Å^2, we find that $\langle E_{surf,out} - E_{solv,out}\rangle \approx 8$ kcal/mol.

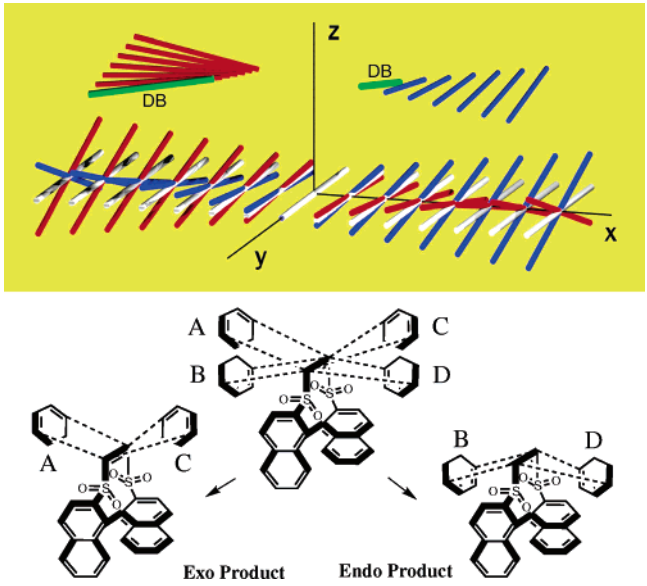

Figure 3. (top) Geometrical model of the configuration control of the catalyst. For one twist of the SWNT stripe, the catalyst stripe is oriented in one way. When the SWNT stripe is twisted in the opposite direction, the catalyst stripe rotates by 90°. (bottom) The exo and endo products formed in the Diels−Alder reaction.

Figure 2 shows the average adsorption energy, $\langle E_{ads} \rangle$, of the catalyst to the twisted SWNT, calculated by summing the above three terms in eq 1. We can see that $\langle E_{ads} \rangle$ correlates well with $\langle \psi_{rot} \rangle$, and it is larger for larger φ_t. Therefore, the best recognition of the chiral catalyst by the twisted SWNT could be achieved when the surface is relatively largely distorted. This good recognition ability in the two configurations, shown in Figure 1, implies that the catalyst configuration might be controlled in a robust way.

Let us now try to clarify the switching behavior of the chiral catalyst in a simple geometrical model, where the catalyst and the twisted SWNT are substituted by two "saddle-like" surfaces positioned on the top of each other. The saddle-like surface of the twisted SWNT can be modeled like a twisted stripe, formed by straight lines, which extends along the *x*-axis (symmetry axis of the nanotube), as shown in Figure 3 (top). In the absence of deformation, the straight lines are oriented along the *y* direction. Once we start to twist each end of the stripe around the *x*-axis, the straight lines become deflected in the $y-z$ plane and the deflection angle is proportional to their distance from the $x = 0$ plane. The points on the *x*-axis ($y = z = 0$) and on the *y*-axis ($x = z = 0$) are not moved when the stripe is twisted. Therefore, the stripe surface can be approximately described by the function

$$z(x,y) = cxy, \qquad c = f(\varphi t) \tag{3}$$

which gives the zero shift ($z = 0$) for the points on the *x*- and *y*-axis. The $(x,y) = (0,0)$ point on this surface has a *hyperbolic character*, due to the two opposite main curvatures there, going along the $x = y$ and $x = -y$ directions.

Analogously, we can model the saddle-like surface of the chiral catalyst by a short piece of such a twisted stripe. We can identify the symmetry axis of its two wings and the perpendicular axis to it with the *x*- and *y*-axis, respectively. The double bond (catalytic site) is located at one of the ends of this short stripe, and denoted as DB in Figure 3 (top).

The catalyst stripe docks on the nanotube stripe in such a way that the *two normal directions*, associated with the extremal curvatures of the same signs, from both saddles are aligned along each other (see Figure 3 (top)). The normal coordinate system of the curvature tensor for the surface in eq 3 can be obtained by rotating the $x-y$ coordinates around the *z*-axis ($x = x' \cos(\theta) - y' \sin(\theta)$, $y = x' \sin(\theta) + y' \cos(\theta)$) and finding the angle θ for which the mixed "$x'y'$" term in eq 3 disappears in the $x'-y'$ coordinates, i.e., only the "$(x')^2$" and "$(y')^2$" terms remain nonzero. We can easily realize that the normal coordinate system is rotated with respect to the $x-y$ coordinate system by $\theta = \pm 45°$, where the sign of *c* in eq 3 determines which of these two options occurs.

This means that when we change the direction of the SWNT twist, i.e., when we change the sign of *c*, the normal coordinate system of the nanotube stripe rotates by 90°. Therefore, the catalyst stripe docked on it should rotate by 90° too, so that the two saddles fit each other. In one case, the double bond of the catalyst points in the *x* direction of the original system, and in the other case, it points in the *y* direction, as shown in Figure 3 (top). This is exactly what we observe in the simulations, presented in Figure 2, except that the flipping with $\Delta\langle \psi_{rot} \rangle \approx 70°$ occurs at $\varphi_t \approx 2.5°$ per cell. Since the catalyst is not C_2-symmetric around the *z*-axis, as we assume in this simple analysis, its flipping angle $\Delta\langle \psi_{rot} \rangle$ is slightly different from 90° and occurs at a nonzero twist angle φ_t.

We now briefly describe the Diels−Alder reaction[20] to find out how its rate could be varied by this configuration switching of the catalyst, without altering the character of the reaction. In the course of the reaction, the diene, such as cyclohexadiene (CHD), shown in Figure 3 (bottom), approaches the catalyst and reacts with the dienophile, which is the C−C double bond in the catalyst that binds to the two sulfonyl groups. The sulfonyl groups activate the dienophile by electron-withdrawing mechanisms, allowing facile removal of the chiral auxiliary and reactivation of its functionality. In the absence of the SWNT, the reaction can proceed in four modes, A, B, C and D, where CHD attacks the double bond from either side, to form two new σ bonds (see Figure 3). In all four modes, the diene and dienophile bind one to another in face to face configurations.[25] Due to the C_2 symmetry of the catalyst along the *x*-axis, the A and C modes are equivalent one to another and lead to the same "endo" product, while the equivalent B and D modes lead to the same "exo" product. The reaction conditions for these four modes could largely be altered on the SWNT surface, when the catalyst's configuration is changed.

From the two distinct configurations of the catalyst, shown in Figure 1, a lot of free space seems to be available for the accommodation of CHD in the A and B modes for the −5.83° per cell twist, while for the opposite twist the space available for the A and B modes appears to be invaded by

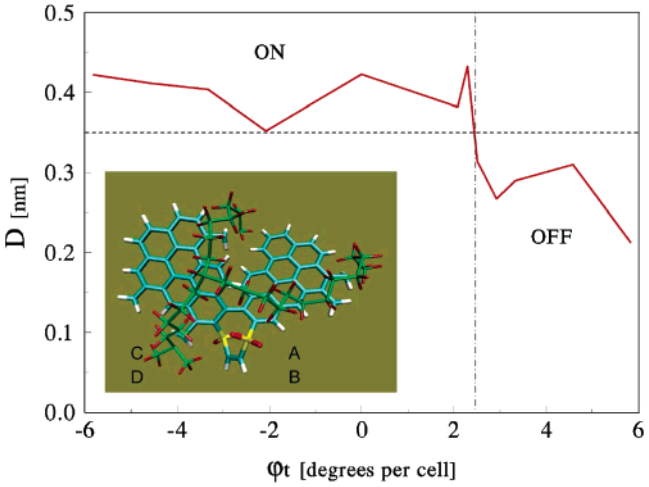

Figure 4. The average distance between the two "imaginary" atoms of the reactant and the nanotube, plotted as a function of the nanotube twist angle. (inset) The modified catalyst, where the C and D modes are blocked by the molecular shield.

the SWNT. We can check the space available for the reactants in the A and B modes by making a simple estimation based on typical equilibrium van der Waals distances between atoms of the reactant and the nanotube. We first introduce two "imaginary" C atoms of the reactant that are in the binding positions to the double bond (dienophile) of the catalyst when the reaction takes part in a free space. Their positions are located along two lines orthogonal to the plane of the double bond at a distance of 3.5 Å from the double bond. Then we calculate the averaged *nearest distance* between these two imaginary atoms and all the C atoms of the nanotube, when the catalyst is docked on the tube.

Figure 4 shows the average distance obtained in this way from our simulations. We can see that the distance varies largely with the twist angle: it is ≈4.2 Å under −5.83° per cell twist, while it becomes ≈2.1 Å under 5.83° per cell twist. Since the typical van der Waals distance is 3.5 Å, we can conclude that the reaction in modes A and B is "turned on" from −5.83° per cell to about 2.30° per cell twists ("free catalyst"), and it is "turned off" from 2.30° per cell to 5.83° per cell twists ("blocked catalyst"). In the last case, the A and B modes are most likely *not* able to accommodate CHD, because of its large van der Waals repulsion from the SWNT surface.

To complete the dynamical control of the catalyst, the C and D modes should be permanently blocked. We solve this problem by "dressing" the catalyst with a *molecular shield*, which occupies the upper space of the catalyst, as shown in the inset of Figure 4. They are formed by three alkyl chains, where one of them is coupled to two methyl groups that block the side of the dienophile plane hosting the C and D modes. At the same time, the chains do not have $\pi-\pi$ stacking interactions with the surface, so the catalyst cannot dock in a stable way on "its back" and expose the A and B modes. In this way, we can complete the dynamical control over the catalysis.

The presented results show that catalytic processes could efficiently be controlled by nanomechanical means in the nanosecond time scale. This methodology might even be used to form a switch for individual catalytic events. The use of deformable nanoscale surfaces could also foster numerous potential applications related to chiral recognition and general switching of molecular functionality. For example, chiral molecules that bind differently to different helical nanotubes might in principle be used in the nanotube separation. Some of these possibilities will certainly be exploited experimentally in the near future.

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