Reversible optical transcription of supramolecular chirality into molecular chirality

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Fig. 4. (A) An end view of nanotubes wound onto a square wire former to cover it. **(B)** A wound nanotube covering after infiltration with polyvinyl chloride and removal of the former.
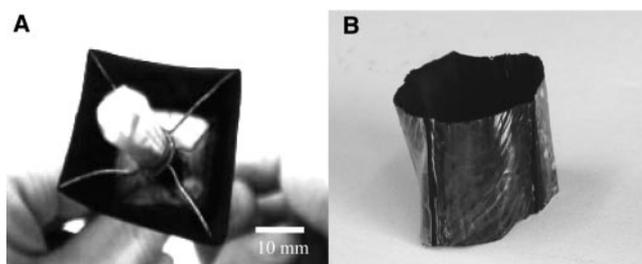
MWNTs in fibers spun at high temperatures was higher (85 to 95 wt % purity) than for material collected from the furnace without spinning (70 to 85 wt % purity). In the latter case, it is possible that iron particles that did not generate nanotubes were effectively caught by the nanotube membrane that formed across the cold end of the furnace. Figure 3, B and C, shows SEM images of a fiber wound up with the offset rod. The alignment of the nanotubes along the fiber axis is apparent in the higher magnification image (Fig. 3C), whereas Fig. 3D shows the fiber's ability to hold a twist imparted after removal from the rod. The best electrical conductivity measured along a fiber was $8.3 \times 10^5 \ \Omega^{-1} \ m^{-1}$, which is slightly higher than the typical value for carbon fibers (*22*). Preliminary mechanical measurements indicate that the fibers have a range of strengths, dependant on process conditions, between 0.05 N/Tex and 0.5 N/Tex (equivalent to 0.10 and 1.0 GPa, assuming a density of 2.0 g/cc, which is within the range of typical carbon fibers). The strain to failure was variable, but could exceed 100% on initial loading. There remains considerable potential to improve properties through process control and postprocess treatments.

Finally, in addition to its ability to spin nanotube fibers, the present process can be extended to the production of nonwoven, macroscopic objects by spin coating differently shaped formers. The alignment of the nanotubes and the thickness of the coatings can be reasonably controlled by the rotation speed and coating time. We demonstrated this process with a hollow frame, rotated normal to the furnace axis, that became covered with an aligned nanotube film (Fig. 4A). An extension of this process is to infiltrate the nanotube covering with a resin, to produce a composite shell from which the former can be removed (Fig. 4B).

This direct spinning process will allow one-step production of nanotube fibers, ribbons, and coatings with potentially excellent properties and wide-range applications. Furthermore, the success of this direct spinning process from the gas phase implies that similar processes could be applied to other fibrous materials that can be synthesized directly from the vapor phase.

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23. We thank S. Cash, M. Jaffe, Q. Li, M. Motta, and P. Smith for their assistance. Supported by Thomas Swan and Co. Ltd.

Reversible Optical Transcription of Supramolecular Chirality into Molecular Chirality

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In nature, key molecular processes such as communication, replication, and enzyme catalysis all rely on a delicate balance between molecular and supramolecular chirality. Here we report the design, synthesis, and operation of a reversible, photoresponsive, self-assembling molecular system in which molecular and supramolecular chirality communicate. It shows exceptional stereoselectivity upon aggregation of the molecules during gel formation with the solvent. This chirality is locked by photochemical switching, a process that is subsequently used to induce an inverted chiral supramolecular assembly as revealed by circular dichroism spectroscopy. The optical switching between different chiral aggregated states and the interplay of molecular and supramolecular chirality offer attractive new prospects for the development of molecular memory systems and smart functional materials.

The challenge of controlling chirality at different hierarchical levels (*1–3*) is particularly evident in the context of molecular self-assembly, protein folding, and the design of memory systems, sensors, and nanostructured materials (*4–6*). Chiral optical molecular switches offer fascinating opportunities, because molecular and supramolecular chirality might be tunable by light in a fully reversible manner. Elegant chiral optical switches, photoresponsive host-guest systems, and receptors have been reported (*7*). However, studies of self-assembling systems (*8–11*) in which the macroscopic properties are affected by light have been limited to switchable organogels (*12*), receptors (*13*), and self-assembling peptide tubes (*14, 15*).

The molecular system presented here is based on a dithienylethene photochromic unit functionalized with (*R*)-1-phenylethylamine–derived amides (Fig. 1) (*16*). The self-assembly behavior of **1**, which arises from the formation of multiple hydrogen bonds between the amide groups, can be influenced by light. The dithienylethene **1** exists as two antiparallel, interconvertible open forms with *P*- and *M*-helicity, which cyclize in a fully reversible manner upon irradiation with ultraviolet (UV) light to two diastereoisomers of ring-closed product **2** (*17*). The light-induced switching between **1** and **2** is attended by changes in both the electronic properties and

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conformational flexibility of the molecules and as a consequence in the aggregation behavior, which phenomenon can, for instance, be recognized by a change in the viscoelastic properties of solutions (18).

Irradiation at 313 nm of a homogenous (non-gelled) toluene solution of **1** (0.35 mM) at 25°C results in photocyclization to **2** with a photostationary state (PSS) (= [2]/([1]+[2]) × 100) of 60%. Subsequent irradiation at wavelengths longer than 420 nm leads exclusively to the open form **1**, as is evident from the UV/visible spectra (Fig. 2, A and B). This photochromic system shows excellent reversibility without fatigue over at least five cycles. The diastereomeric ratio (R,R)-**2**/(S,S)-**2** is 1:1, as determined by ^{1}H nuclear magnetic resonance (NMR) analysis in toluene-d8. Photocyclization of **1** in solution is clearly not stereoselective, despite the presence of two chiral amide groups.

The chirality present in **1** can be expressed in a supramolecular aggregated system. The pronounced self-assembly properties of **1** due to the amide groups lead it to gel at room temperature in organic solvents such as toluene, benzene, and hexane at minimal gelation concentrations of typically 1 to 4 mM. Transmission electron microscopy (TEM) measurements revealed that in toluene and other apolar solvents, a fibrous network is formed, with fibers that are clearly helical, indicative of chiral embedment of the switch molecules in the fibers (3) (Fig. 3).

Toluene was chosen for further investigation, because of the excellent stability of the gel, evidence of supramolecular chirality, and the low critical gelation concentration (19) of 1.6 mM at room temperature. Gels of **1** (1.8 mM in toluene) at −8°C show a strong circular dichroism (CD) band around 320 nm, which is absent in solutions of **1** (Fig. 2C), providing further evidence that the aggregates are chiral. The maximum CD effect appears at a longer wavelength than the UV absorption maximum of the open form. We assign the CD absorption as the negative half of an exciton coupling band (20) resulting from the electronic interactions between molecules of **1** in the chiral arrangement

in the fibers. Upon heating, the intensity of the CD band gradually decreases and is no longer measurable at 50°C, at which point the gel has entirely melted (Fig. 4). Both gelation and the appearance of the CD band at 320 nm are completely reversible upon cooling. Because the solution of the open switch **1** does not show a CD effect, whereas upon aggregation a strong CD absorption is observed, the aggregates apparently exhibit supramolecular chirality owing to locking of the *M*- or *P*-helical conformation of the open form **1** in the aggregate. The molar fraction of monomer in the aggregates and in solution has been measured by ^{1}H NMR at different temperatures (Fig. 4). It is evident that aggregation of **1** and the magnitude of the CD effect are related phenomena that reach a maximum at temperatures below 0°C.

Irradiation at 313 nm of **1** in the gel phase (0°C) resulted in **2**, with an excellent diastereomeric ratio of 98:2 [96% diastereomeric excess (DE)] and a PSS of 40% as determined by ^{1}H NMR. Repetition of this experiment at higher temperatures was accompanied by a gradual decrease of the degree of aggregation of **1** (^{1}H NMR), and the DE decreased from 96 to 0% (Fig. 4). Because in solution the photochemical cyclization is nonselective, the remarkably high diastereoselectivity observed has to originate from switching in the aggregates, and hence confirms that the fibers must consist of **1** in either the *P*- or *M*-helical conformation because of selective aggregation. The intensity of the CD band of the open form **1** correlates excellently with the fraction of **1** in the gel state as well as with the diastereoselectivity in the photochemical formation of **2**. Absolute stereocontrol in cyclizations of diarylethenes in the crystalline state has been described (21, 22), but that is different from the stereoselective photochromic reaction that is fully controlled by supramolecular aggregation in our system.

Although there is no asymmetric induction upon photochemical ring closure of **1** in solution, nearly absolute stereocontrol is obtainable upon self-assembly into a fibrous network (gel). The presence of the chiral amide appendices

and the dynamic chirality of the monomer **1** lead to selection of one of the photoactive open conformations in the hydrogen-bonded aggregation state, as is apparent from the exciton coupling observed by CD. The chirality of the dithienylethene unit is subsequently fixed by photochemical conversion to one of the diastereomers of the closed form of **2**. In accordance with these observations, the enantiomeric (S)-1-phenylethylamine–derived switch **1** showed exactly opposite CD behavior. The gel of **2** (PSS) with 96% DE can be fully converted back to the original gel **1** at −40°C upon irradiation with visible light.

The dramatic selectivity for either the *M*- or *P*-helical conformation in the aggregated state of **1** leads to the expectation that the diastereomeric ratio of **2** at the PSS (**2** PSS) would also influence the aggregation. On cooling of a 3.6 mM toluene solution of **2** (PSS) with 0% DE, a gel forms and CD bands due to exciton coupling appear between 300 and 400 nm (Fig. 2D). The CD effect is qualitatively similar to the CD of a gel of **2** (PSS) with 96% DE formed by photocyclization of **1** in the gel state, and the bisignate CD features point in both cases to the formation of aggregates with *P*-helicity. ^{1}H NMR measurements revealed that in the gel formed from a sample of **2** (PSS) with 0% DE, only one of the two diastereomers of **2** was present, whereas the other diastereomer remained in the solution. There was therefore a pronounced stereoselection during aggregation, also starting from the closed form. Most remarkably, the diastereomer of **2** that aggregated in gels starting from **2** (PSS) with 0% DE was shown (by ^{1}H NMR) to be the opposite of the diastereomer of **2** formed on stereoselective photocyclization of **1** in the gel state, although CD measurements showed that the resulting aggregates both had *P*-helicity.

If a gel of **2** (PSS) with 96% DE is heated to homogeneous solution (100°C) and subsequently cooled to 0°C, a new gel forms that has an inverted (exciton-coupled) CD (Fig. 2D). Because only one diastereomer of **2** with fixed chirality is present as a result of the stereose-

Fig. 1. Chiral switch **1**, which contains amide functionalities to induce aggregation by multiple hydrogen bonding, exists in the open form in two helical conformations *P*-**1** and *M*-**1** in rapid equilibrium. These can be transformed by irradiation into closed forms **2**. (R,R)-**2** can only be obtained from *P*-**1**, and (S,S)-**2** is exclusively formed from *M*-**1**. The two 1-phenylethylamine moieties continue to have the *R* configuration in either diastereomer of **2**. VIS, visible light.
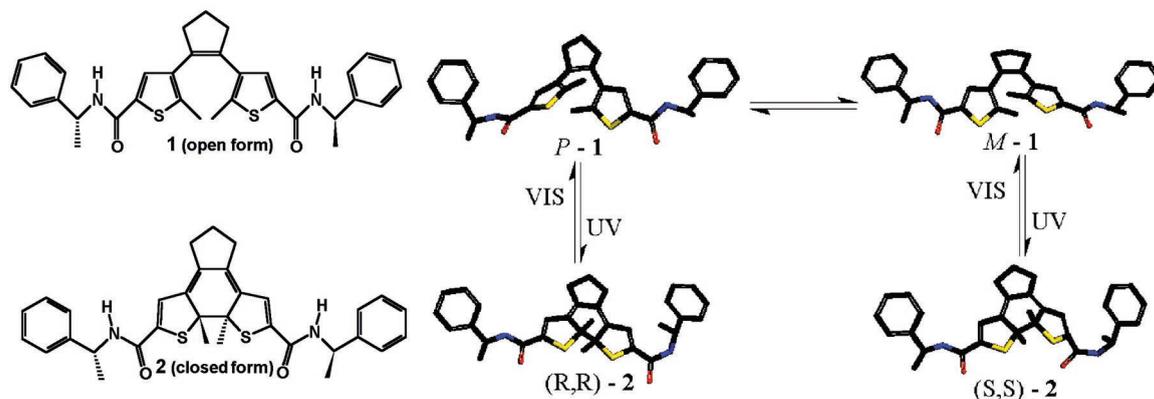
Fig. 2. UV-visible spectra (top panels) and corresponding CD spectra (bottom panels) for **1** (left) and **2** (right). (**A** and **C**) Solution (dashed line) (0.35 mM) and stable gel (solid line) (1.8 mM) of **1** obtained upon cooling of a hot solution solution of **1**, and unstable gel **1** (3.6 mM) (dotted line) formed by photochemical ring-opening of a stable gel of **2**. (**B** and **D**) Photochemical ring-closure of a solution of **1** leads to a gel of **2** with no DE (dash-dotted line). Irradiation of a stable gel of **1** (3.6 mM) leads to an unstable gel **2** (96% DE) (solid line), that transforms to a stable gel of **2** (96% DE) (dotted line) by a heating-cooling cycle involving a solution of **2** (96% DE) (dashed line).
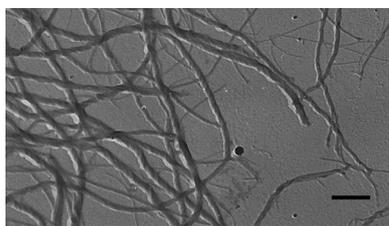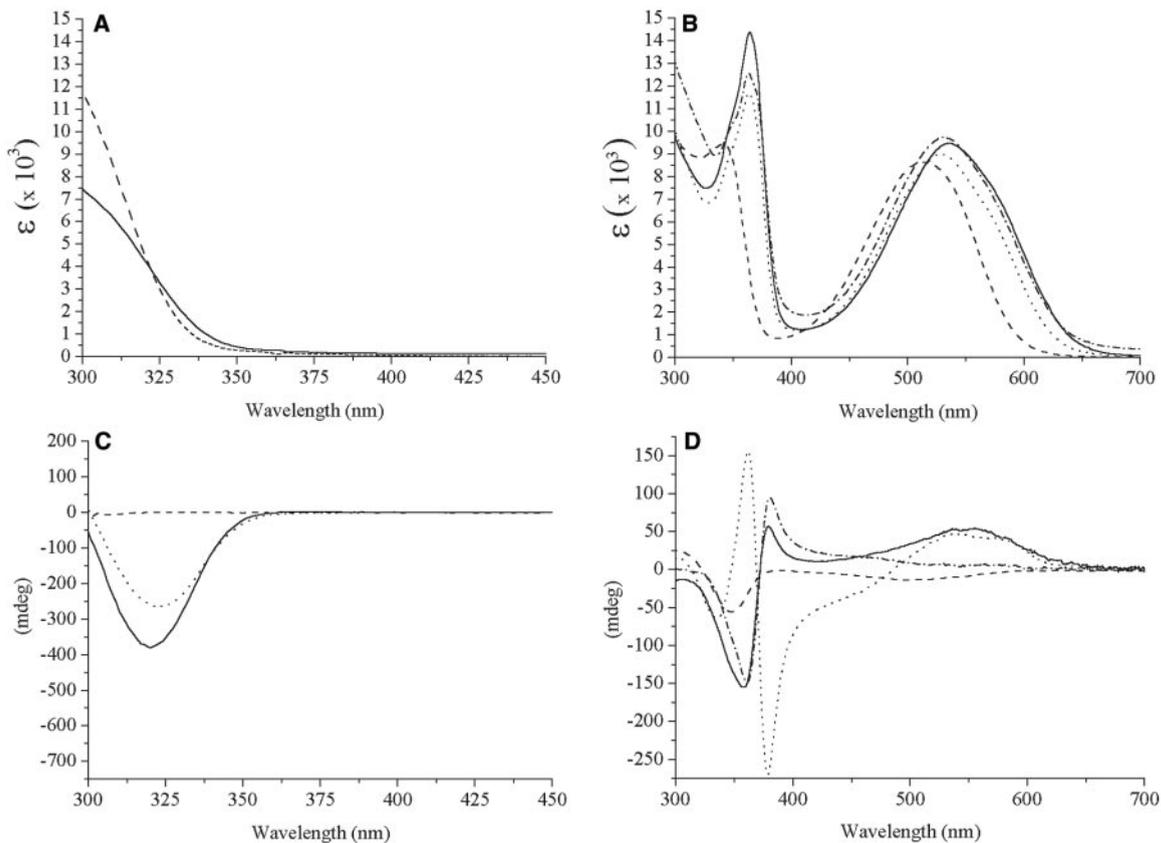

Fig. 3. Electron micrograph (TEM) of toluene gel of **1**; the chiral fibers can be clearly seen (concentration, 1.8 mM; platinum shadow, 45°; scale bar, 500 nm).

Fig. 4. Temperature dependency of the CD effect [wavelength (λ) = 320 nm], extent of aggregation (^{1}H NMR), and diastereoselectivity of photochemical formation of **2** in toluene {the molar fraction aggregated is related to the CD effect by [θ (mdeg)$_{obs}$/θ(mdeg)$_{max}$] $\times$ 100}. The excellent correlation clearly indicates that these are related phenomena.

lective photocyclization, the inversion of the CD effect must be due to the transformation of the original *P*-helical aggregates to aggregates with *M*-helicity. Apparently, the initially formed gel state of **2** (PSS) with 96% DE is metastable and can only be reached by photochemical conversion of a gel containing **1** (*23*). The existence of a metastable *P*-helical state of closed form **2** strongly indicates that aggregates of **1** remain intact during photochemical ring closure, and that the original chirality and supramolecular information are preserved during switching. The remarkable inversion of helical chirality in the aggregated state of **2** can now be understood. A heating-cooling cycle is necessary to transform the aggregates of the ring-closed system to the thermodynamically favored state with opposite *M*-helicity, induced now by the chirality in the central photoactive part of the switch rather than by the peripheral
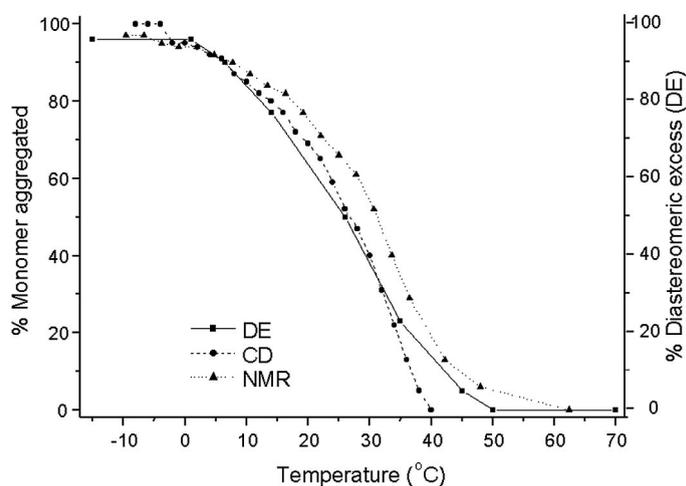
amide groups. The different expression of supramolecular chirality in the thermodynamically favored aggregates of gels of **2** (PSS) with 96% DE and 0% DE is fully consistent with the presence of the two different diastereomers, in which the dithienylcyclopentene moiety has opposite chirality, in the two types of gels. It would be intriguing to see whether photochemical ring-opening of the thermodynamically stable gel **2** also proceeds with retention of the supramolecular organization to give an anticipated metastable gel **1**. Irradiation of stable gel **2** (at 3.6 mM concentration) with visible light at 0°C results indeed in a gel of **1**, with a different CD spectrum than that of the original gel **1** (Fig. 2C).

A crucial observation is that upon irradiation of this metastable gel **1** with UV light at 0°C, it directly reverts into stable gel **2** (Fig. 2D). However, heating of metastable gel **1** and subsequent cooling provide the original stable gel **1** (*23*). Therefore the metastable gel **1** state can only be reached by photochemical conversion of stable gel **2**. These transformations can be repeated several times without photochemical degradation.

From the experimental results presented here, it is clear that the photoactive supramolecular system comprises two different aggregation states, denoted as α and β, which can include either the open **1** or closed **2** form, leading to a total of four different states. The

Fig. 5. Aggregation and switching processes and relation between different states. **1**, open form; **2**, closed form; UV, $\lambda =$ 313 nm; visible (Vis), $\lambda >$ 460 nm; *, cooling; Δ, heating. Heat is required

to irreversibly transform the unstable aggregates (from the α to the β state and vice versa). Photochemical steps go with the retention of configuration; irradiation converts open form **1** and closed form **2** in a fully reversible manner.
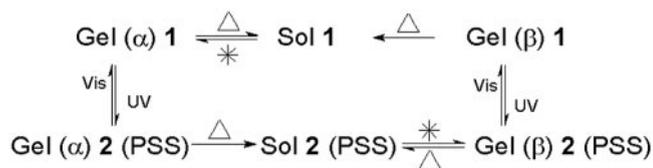
aggregation and switching processes by which these four states can be addressed as described above are summarized in Fig. 5. Starting with an isotropic solution of open form **1**, a stable gel (α) **1** (*P*-helicity) is obtained upon gelation (cooling). Photocyclization results in metastable gel (α) **2** (PSS) (*P*-helicity) with high diastereoselectivity (96% DE), a process that is fully reversible. Heating of gel (α) **2** (PSS) leads to an isotropic solution of **2** [sol **2** (PSS)], which upon cooling results in stable gel (β) **2** (PSS) (*M*-helicity). Irradiation of gel (β) **2** (PSS) with visible light results in metastable gel (β) **1**, which can be reconverted to the stable gel (β) **2** (PSS) by UV irradiation. Finally, a heating-cooling cycle results in the transformation of metastable gel (β) **1** to the original stable gel (α) **1** via an isotropic solution of **1** (sol **1**). In the photochemical steps, the supramolecular chirality is preserved. However, the photochemical ring-opening or ring-closure changes the rigidity and chirality (fixed or dynamic) of the central unit and as a consequence the stability of the chiral aggregate.

This mutual ability to control chirality at different hierarchical levels in a synthetic system has great potential for new approaches in asymmetric synthesis, the understanding of molecular communication processes, and the development of molecular memory systems and smart materials. The sequential processes shown in Fig. 5 complete a full cycle of four addressable chiral aggregated states and together comprise a four-state chiroptical supramolecular switch. Despite the fact that there is no stereoselectivity at all in solution, after aggregation, nearly absolute stereocontrol is exerted at the molecular level. In turn, the molecular chirality obtained governs both the stability and the helicity of the aggregate. Particularly relevant are the discoveries that metastable chiral aggregates can be obtained in a reversible manner and that the aggregation process can be controlled by an external signal. It is interesting to consider the results in the context of the delicate complex balance between molecular chirality and aggregate stability in natural systems; for instance, in actin filaments and processes such as protein folding and enzyme function, which all rely on the subtle interplay of molecular and supramolecular chirality. The presence of a photoactive diarylethene unit in the gelator molecules **1** and **2** offers the distinct advantage that the transformation between sta-

ble and metastable gels can be achieved in a fully reversible manner controlled by light. The formation of such systems, not accessible by common thermal aggregation processes, is particularly attractive for the future development of smart functional materials.

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Controlled Atomic Doping of a Single C_{60} Molecule

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We report a method for controllably attaching an arbitrary number of charge dopant atoms directly to a single, isolated molecule. Charge-donating K atoms adsorbed on a silver surface were reversibly attached to a C_{60} molecule by moving it over K atoms with a scanning tunneling microscope tip. Spectroscopic measurements reveal that each attached K atom donates a constant amount of charge ($\sim$0.6 electron charge) to the C_{60} host, thereby enabling its molecular electronic structure to be precisely and reversibly tuned.

The ability to modify the electronic properties of materials via charge donating or accepting dopant atoms plays a crucial role in semiconductor electronics (*1*). As devices shrink in size, the use of dopants (*2*, *3*) will present new challenges, especially if variations in dopant distributions lead to large changes in interdevice performance. Progress in understanding and overcoming these limitations has been made through the synthesis of new molecular compounds (*4*) and also via electronic gating techniques (*5*), but the idea of placing charged dopant atoms directly onto

individual molecular elements in situ has been less vigorously pursued. Here, we show how it is possible to tune molecular electronic properties by attaching an arbitrary number of charge-donating K atoms onto an isolated fullerene adsorbate. This method is reversible and should be applicable to more complex molecular structures.

The ability of bulk C_{60} to incorporate alkali metals and form fullerides has long been known (*6*, *7*). The basis of our technique for creating molecular fullerides is the molecular manipulation capability of the scanning tunneling microscope (STM) (*8*, *9*). By manipulating a single C_{60} molecule over successive K adsorbates on Ag(001), we formed K_xC_{60} in a completely controllable manner for x ranging from 0 to 4. The electronic structure of a single K_xC_{60} complex could be controllably tuned via the charge transferred

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