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The effect of carbon nanotubes on chiral chemical reactions

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ABSTRACT

The intrinsic helicity of carbon nanotubes influences the formation of chiral molecules in chemical reactions. A racemic mixture of ***P*** and ***M*** enantiomers of nanotubes affects the enantiomeric excess of the products of the autocatalytic Soai reaction proportional to the amount of nanotubes added in the reaction mixture. An intermediate complex formed between the nanotube and the organometallic reagent is essential and explains the observed correlation between the enantiomeric distribution of products and the curvature of the carbon nanostructure. This Letter establishes a key mechanism for harnessing the helicity of nanoscale carbon surfaces for preparative organic reactions.

1. Introduction

Carbon nanotubes – extended cylinders of sp^2 hybridised carbon – are becoming rapidly established as nanoscale substrates for a wide range of known preparative reactions [1,2] and platforms for the discovery of new types of chemical processes [3]. While possessing their own rich chemical reactivity [4,5] and supramolecular chemistry [6], their potential for templating the formation of new molecular structures, inaccessible by other means, is becoming increasingly more apparent [3,7,8], but still not entirely relevant to preparative synthesis.

Although the influence of carbon nanotube structural parameters, such as diameter, length, surface morphology and functionality on chemical reactions is currently being investigated, one important aspect of nanotubes – their intrinsic helicity – has yet to be explored. The helicity of carbon nanotubes emerges as a result of 'wrapping' the graphene sheet along any chiral vector $\boldsymbol{C_h}$ which is not parallel to the graphene lattice vectors $\boldsymbol{a_1}$ and $\boldsymbol{a_2}$ (Scheme 1). The length of $\boldsymbol{C_h}$ (which determines the circumference of the nanotube) is defined by indices (n,m), while the handedness of the helical twist, notated as ***P*** (right-handed or plus) and ***M*** (left-handed or minus) and differing from each other only by which side of the graphene is curled inward to form a cylinder, is determined by the $\boldsymbol{C_h}$ direction. Since the separation of ***P*** and ***M*** nanotubes on a scale sufficient for tests in preparative reactions is currently not feasible [9–11], no chemical reactions with enantiomerically pure nanotubes have been carried out to date. Furthermore, caution should be exercised in such experiments as the chiral molecules typically used for extraction of carbon nanotube enantiomers are likely to persist within the final enriched nanotube sample and may lead to false positives when employed in preparative reactions where the effect of the impurity masks the effect of the nanotube surface.

In this Letter, we have chosen the Soai reaction [12] of diisopropyl zinc and 2-substituted pyrimidine-5-carbaldehyde **1** yielding the corresponding *sec*-alcohol **2** (Scheme 2) as it is the only chemical reaction offering the chance to study asymmetric autocatalysis, the process by which a chiral product enantioselectively catalyses its own formation.

This reaction is very sensitive to many parameters including any chiral molecules present in the mixture prior to initiation of the reaction [13], surfaces of inorganic crystals [14–16], circularly polarised light [17] and even isotopic substitution [18], all of which have been shown to initiate the amplification of enantiomeric excess (*ee*) in the Soai reaction. As such, the reaction is an extremely sensitive qualitative sensor for the chirality of macroscopic solids and in this Letter we exploit this phenomenon of asymmetric autocatalysis to probe the influence of carbon nanotube chirality on the formation of chiral molecules in preparative chemical reactions.

2. Experimental

2.1. General experimental

All reagents were purchased from Sigma–Aldrich, UK and used without further purification. Carbon nanotubes (6,5)-SWNT (Lot No. MKBF6413V) and PD30L520 MWNT (Lot No. 71310) were purchased from Sigma–Aldrich, UK and NanoLab Inc., USA, respectively. Water was purified (>18 MΩ cm) using a Barnstead NANOPure II system and toluene was distilled over calcium hydride. All glassware was cleaned with a mixture of hydrochloric and nitric acid (3:1 v/v, 'aqua regia') and rinsed thoroughly with deionised water, cleaned with potassium hydroxide in isopropyl alcohol and finally rinsed thoroughly with deionised water before use to avoid contamination from chiral impurities. ^{1}H and ^{13}C

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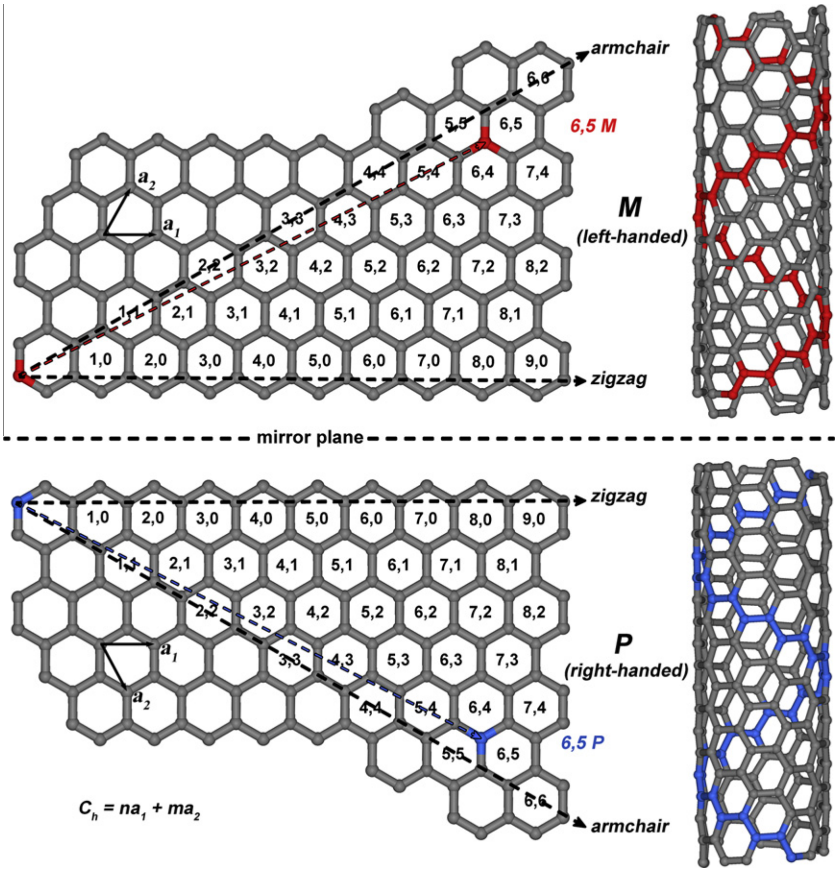
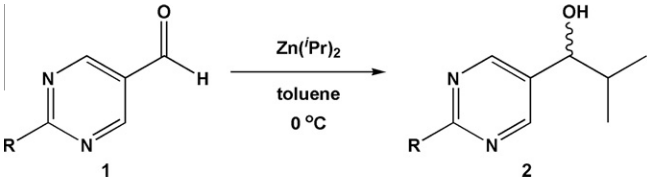


Scheme 1. The helicity of carbon nanotubes are defined by the roll-up vector (*n*,*m*) and yields two enantiomers ***P*** (right-handed) and ***M*** (left-handed).



Scheme 2. The Soai reaction.

NMR spectra were obtained using a Bruker DPX-300 (300.13 and 75.48 MHz, respectively) spectrometer at 298 K using $CDCl_3$ as the solvent. Attenuated total reflectance infra-red spectra were measured using a Nicolet 380 FT-IR spectrometer (spectral resolution = 0.9 cm^{-1}) over the range 4000–600 cm^{-1}. UV–vis spectra were recorded in solution using 1 cm quartz cuvettes using a Perkin–Elmer Lambda 25 UV–vis spectrophotometer at a scan rate of 480 nm min^{-1} over the range 400–900 nm. Mass spectrometry was conducted on a Bruker Apex IV using ESI in positive mode. Specific rotation was determined using by polarimetry on a Bellingham Stanley ADP440 polarimeter at 22 °C. Samples were made up to a concentration of 1 g 100 mL^{-1} in chloroform. Enantiomeric excess was calculated by HPLC analysis on a Shimadzu SPD-M20A using a chiral stationary phase (Chiralcel OD-H: 4 × 250 mm, 254 nm UV detector, eluent is *n*-hexane/2-propanol = 19/1, flow rate is 1.0 mL min^{-1}). Retention times of 8.33, 9.85, 9.40, 10.10, 11.10 and 16.27 min were recorded for *S*-**2a**, *R*-**2a**, *S*-**2b**, *R*-**2b**, *S*-**2c** and *R*-**2c**, respectively. Mean values of specific rotation and enantiomeric excess were obtained from a minimum of two experiments. Thermogravimetric analysis was performed using a TA Instruments SDT Q600 under a flow of air at a rate of 90 mL min^{-1} at a heating rate of 10 °C min^{-1} from room temperature to 1000 °C. Raman spectroscopy was conducted using a HoribaJY LabRAM HR spectrometer (spectral resolution = 1.1 cm^{-1}/pixel) with a laser wavelength of 532 nm. Samples were dropcast from methanolic solutions onto Si(100) wafers and a minimum of five spectra recorded from different areas of the sample. The spectra shown are the most representative of the averaged spectra. Transmission electron microscopy was performed using a JEOL 2100F TEM (field emission gun source, information limit < 0.19 nm) at room temperature. Energy dispersive X-ray analysis was performed using an Oxford Instruments INCA 560 X-ray microanalysis system. Samples were prepared via drop-drying methanolic solutions onto copper grid mounted 'lacey' carbon films. Spectra were recorded both 'locally' (measuring a clean bundle of nanotubes suspended over a hole on the 'lacey' carbon film and therefore avoiding the contribution of the amorphous carbon support film) and 'globally' (measuring a few micron-sized square) from a variety of areas of the sample and therefore permitting more quantitative analysis. The values quoted represent an average of at least three measurements.

2.2. The Soai reaction

A typical experimental procedure was as follows: To **1** (0.025 mmol) and the carbon nanotubes (0–5 mg) at 0 °C was added dropwise over the course of 15 min a solution of diisopropyl zinc (0.1 mL, 1 M in toluene, 0.1 mmol) and the combined mixture was stirred at 0 °C for 1 h, then at room temperature for 23 h. To this was added dropwise a solution of diisopropyl zinc (0.3 mL, 1 M in toluene, 0.3 mmol) and toluene (0.75 mL), followed by the dropwise addition over the course of 15 min of **1** (0.1 mmol) in