were obtained in transmission mode by drying methanolic solutions of the SLICs on precleaned CaF_2 windows. Reflectance absorbance spectra were recorded at an angle of incidence of 85° using p-polarized light. The amide I and II bands were deconvoluted by applying a curve-fitting procedure based on the Levenberg–Marquardt algorithm using a combination of Gaussian and Lorentzian line shapes. Initial guesses for the curve fitting were determined from second-derivative spectra.

IS was done in an electrochemical cell comprising a membrane-covered gold electrode and a counter/reference Ag/AgCl electrode in 0.1M KCl/ 5 mM sodium phosphate buffer, pH 7.4. The surface area of the gold disk electrode was 3.34×10^{-2} cm². No direct current voltage was applied. A sinusoidal potential of 10 mV amplitude (root mean square) was applied to the cell at 199 successive frequencies equally spaced on a logarithmic scale from 1 to 20 KHz. The resulting current was recorded by a phase-sensitive lock-in amplifier to calculate the complex impedance and admittance. Details on the interpretation of IS spectra can be found in the Supporting Information.

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Super-"Amphiphobic" Aligned Carbon Nanotube Films[**]

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Carbon nanotubes (CNTs) are of tremendous interest for both fundamental and applied research[1–6] since they show unique properties. Wettability is an important factor for a material. Ebbesen and co-workers have studied the wettability of CNTs in detail and found they could be wet and filled by different substances.[7] In order to assess the properties of CNTs easily, it is highly desirable to prepare aligned carbon nanotube (ACNT) films in which the nanotubes are perpendicular to the substrate surface and densely packed with a fairly uniform length and diameter. To the best of our knowledge, no attention has been paid to the wettability of ACNT films.

In general, the wettability of solid surfaces is controlled by the chemical composition and the geometrical structures of the surfaces, and it is usually enhanced by surface roughness,[8–12] especially by fractal structures.[12] Recently, super-hydrophobic or super-lipophobic surfaces, that is, those with a contact angle for water or oil, respectively, that is higher than 150°,[8, 12c] have attracted much interest for practical applications. These surfaces have been commonly prepared through the combination of surface roughening and the lowering of the surface energy. However, few reports have concerned super-"amphiphobic" surfaces,[13] which have both super-hydrophobic and super-lipophobic properties. Öner and McCarthy reported that super-hydrophobic surfaces with a micrometer-scale post structure could be prepared by photolithography and made hydrophobic using silanization reagents.[11c] As the structure of ACNT films is similar to that of these super-hydrophobic surfaces, the films are expected to show special wettability features. Here we report that the nanostructured ACNT films show super-"amphiphobic" properties, namely, the contact angles for both water and oil are larger than 160°.

In a previous paper we demonstrated that honeycomblike ACNTs could be prepared by pyrolysis of metal phthalocyanines.[14] The approach used herein for the preparation of ACNT films is similar to that reported previously, namely ACNT films are prepared by pyrolysis of metal phthalo-

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cyanines $FeC_{32}N_8H_{16}/YC_{32}N_8H_{16}$ (abbreviated as FePc/YPc) on quartz glass plates (see Experimental Section). The length of the aligned nanotubes can be varied over a wide range (up to several tens of micrometers) in a controllable fashion by changing the experimental conditions (for example, the pyrolysis time, flow rate). Figure 1a shows a typical scanning electron microscopy (SEM) image of the top view of the ACNT films, where the aligned nanotubes produced are almost free from pyrolytic impurities (for example, carbon particles and other carbonaceous materials). Depending on the experimental conditions, we can prepare ACNTs with different morphologies, such as those with a bent top end or a vertical top end. ACNTs with a bent top end are shown in Figure 1a. Figure 1b shows the cross-sectional image of the ACNT films in which the as-synthesized nanotubes align almost normal to the substrate surface, and the alignments are densely packed with fairly uniform length (ca. 3 μm) and external diameter (ca. 60 nm). The as-grown ACNT films are super-hydrophobic and super-lipophilic. The contact angles (CAs) for water and rapeseed oil are 158.5 ± 1.5 and 0 ± 1.0°, respectively. The shape of a water droplet on the film is shown in Figure 2a. However, the CA for water on a film of carbon nanotubes lying flat on a surface is 136.5 ± 7.0°,[15] which shows that the aligned structure of the ACNT film is responsible for the super-hydrophobic properties.

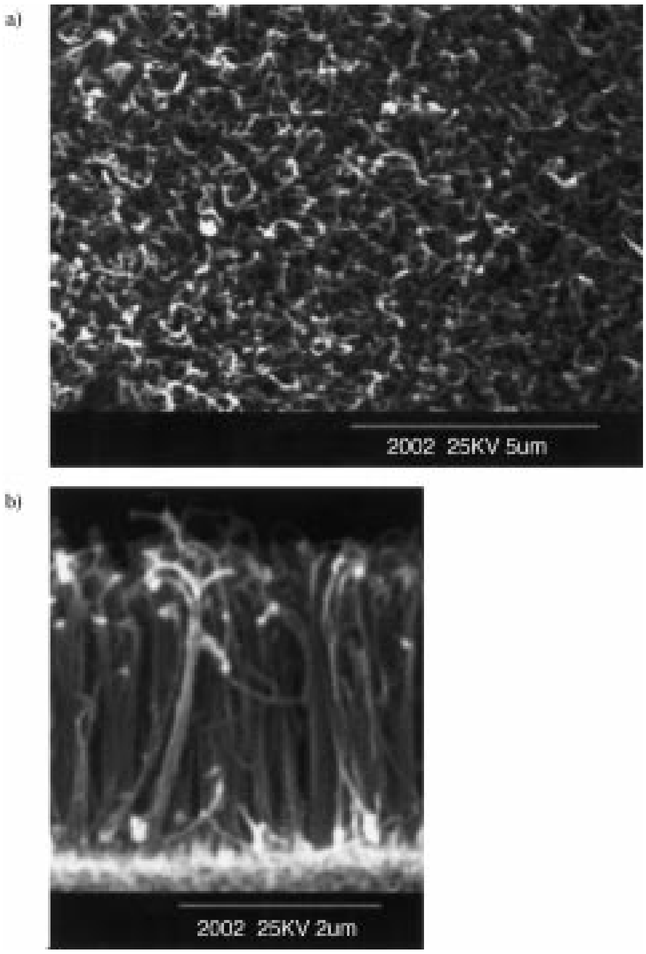

Figure 1. Scanning electron microscopy images of aligned carbon nanotubes peeled off from the quartz substrate. a) Top view of aligned nanotubes obtained by the pyrolysis of metal phthalocyanines. b) Cross-sectional view of aligned nanotubes.

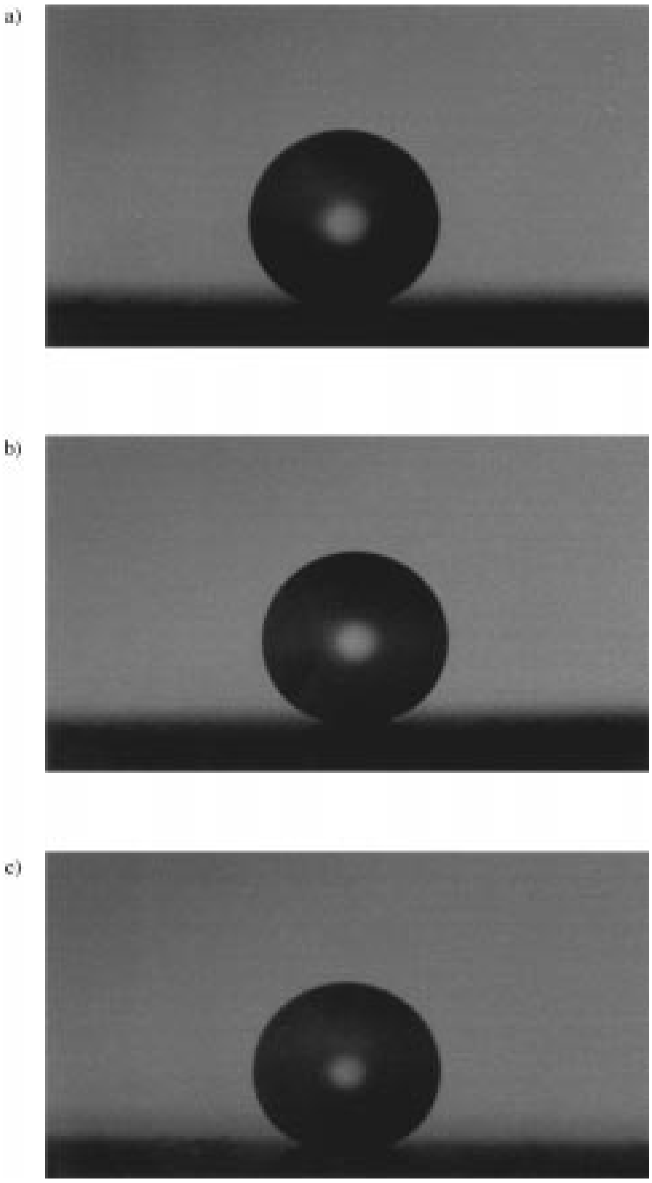

Figure 2. Shapes of water and rapeseed oil droplets (about 1.5 mm diameter) on the aligned carbon nanotube films: a) a water droplet on the untreated film; b) a water droplet on the treated film; c) a rapeseed oil droplet on the treated film.

A low free energy surface is required for a super-lipophobic surface to be obtained, and this can be realized by modifying the ACNT films with fluorinated compounds. Since the surface of ACNTs is rather inert, it is very difficult to modify the surface directly. A hot concentrated mixture of H_2SO_4 and HNO_3 (1:1, v:v) was employed to oxidize the ACNTs for further chemical modification. The contact angle for water on the ACNT film was 128 ± 3.0° after oxidation. It has been reported that some functional groups, such as hydroxyl and carboxyl, can be realized on the surface of CNTs through chemical oxidation treatments.[16] This possibility indicates that the oxidized ACNT film contains these hydrophilic groups, which result in the severe decrease in the contact angles for water. Hence, the oxidized films were modified through immersion in a methanolic solution of hydrolyzed fluoroalkylsilane. After this modification the ACNT film contains fluoroalkylsilane groups, which repel both water and oil. The chemical composition of the treated ACNT film was measured by X-ray photoelectron spectroscopy (XPS). The C, F, Si, O, N, S concentrations are 49.7, 36.2, 1.3, 12.1, 0.2, and 0.5 atom %, respectively. The obtained film mainly consists of carbon and fluorine, and thus indicates that the ACNT film was fluorinated. The CAs for water and rapeseed oil on the film were 171 ± 0.5 and $161 \pm 1.0^\circ$, respectively. Hence the film shows both super-hydrophobic and super-lipophobic properties, namely it is a super-"amphiphobic" surface. The water droplets move spontaneously and do not come to rest, even when there is little or no apparent tilt of the surface ($<1^\circ$), while the rapeseed oil droplets remain pinned in one place. The shapes of the water droplet and rapeseed oil droplet on the treated ACNT film are shown in Figures 2b and 2c, respectively. It is clear by comparing Figures 2a and 2b that the water repellency is improved remarkably through fluorination.

Liquids have very large contact angles on ACNT films, and the films are sufficiently rough that the liquid may trap air so as to give a composite surface effect. In this case, a roughness factor r, which is defined as the ratio of the actual surface area of a rough surface to the projected area, may be introduced into the Cassie and Baxter equation. The relationship between the contact angle of the flat surface θ and that of the suitably rough surface θ_r is expressed by Equation (1),[9]

$$\cos\theta_r = rf_1\cos\theta - f_2 \tag{1}$$

in which f_1 and f_2 are the fractions of the nanotubes and air on the ACNT films, respectively. Equation (1) indicates that the contact angle θ_r increases with an increasing fraction of air (f_2). We can roughly estimate f_1 and f_2 from known contact angles. Carbon nanotubes can be thought of as graphite sheets with a hexagonal lattice that have been wrapped up into seamless cylinders.[17] The contact angle θ for water on a flat graphite surface is 86°,[18] and the contact angle θ_r for water on ACNT films is $158.5 \pm 1.5^\circ$. In contrast, the water contact angle θ_r on an ACNT film after fluoroalkylsilane modification was $171 \pm 0.5^\circ$ and the contact angle θ on fluoroalkylsilane-coated plane glass was 108°.[10a] By using these values f_1 and f_2 are calculated to be 0.06 and 0.94, respectively. These values reveal that the very large fraction of air and the very small fraction of carbon nanotubes on the treated ACNT films cause super-"amphiphobic" properties. Tadanaga et al.[10b] previously reported that the CA for water on super-water-repellent Al_2O_3-coated films was 165° and the f_2 value was 0.92. It is clear that the fraction of air on the treated ACNT films is larger than that on Al_2O_3-coated films. We further predict, from fractal theory,[12] that the CA will be close to 180° on the surface of single-walled ACNT films after fluoroalkylsilane treatment.

In conclusion, the aligned structure of ACNT films and the very large fraction of air on the films determine the super-hydrophobic properties, while ACNT films with a fluoroalkylsilane coating show super-"amphiphobic" properties. From the view-point of practical applications, carbon nanotubes can be prepared on patterned surfaces,[5, 19] and this further increases the fluidity of liquids on the surfaces. On the other hand, the anisotropic dewetting properties might be realized by the substrate structure if ACNT films could be prepared on micrometer-size striped surfaces.[20] This would allow the controlled manipulation of the behavior of surfaces and the design of a new type of microfluidic device (for example, DNA chips),[21] nonwetting liquid transfer, liquid microchannels, and liquid microtracks.[20] These kinds of devices are different from normal microfluidic devices which are based on a single hydrophilic or hydrophobic property. Also further study of this issue might open up new perspectives in the study of fundamental problems of interfacial science and in the design of physical systems with prescribed properties.

Experimental Section

ACNT films were prepared by pyrolysis of metal phthalocyanines FePc/YPc containing both the metal catalyst and carbon source required for the nanotube growth. The pyrolysis of FePc/YPc was performed under Ar/H_2 at 600–900°C on quartz glass plates in a flow reactor consisting of a quartz glass tube and a furnace fitted with independent temperature controllers. The resulting ACNT films appeared on the quartz glass plates as a black layer. After drying the ACNT films in vacuum, they were treated with a hot concentrated mixture of H_2SO_4 and HNO_3 (1:1, v:v) for 2 h to generate functional groups, such as hydroxyl and carboxyl, on the surface of the carbon nanotubes. The treated samples were then rinsed with pure water and dried in a vacuum again. The ACNT films were then treated with a methanolic solution of hydrolyzed heptadecafluorodecyltrimethoxysilane ($CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$; 1.0 wt %) for 3 h and subsequently heated at 140°C for 1 h.

Contact angles were measured with an optical contact angle meter at ambient temperature. Water droplets or oil droplets (1–2 mm diameter) were dropped carefully onto the ACNT films and the average value of five measurements made at different positions of the same sample was adopted as the contact angle. The ACNT samples were examined by SEM (Hitachi s-530) to characterize their morphology. XPS analyses of the samples were performed on a VG ESCALAB 220-IXL spectrometer using an $Al_{K\alpha}$ X-ray source (1486.6 eV). The energy scale was internally calibrated by referencing to the binding energy (E_b) of the C_{1s} peak of a carbon contaminant at 284.6 eV.

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Specific Binding and Separation of Dinucleotides by Ferrocene-Modified Artificial Receptors

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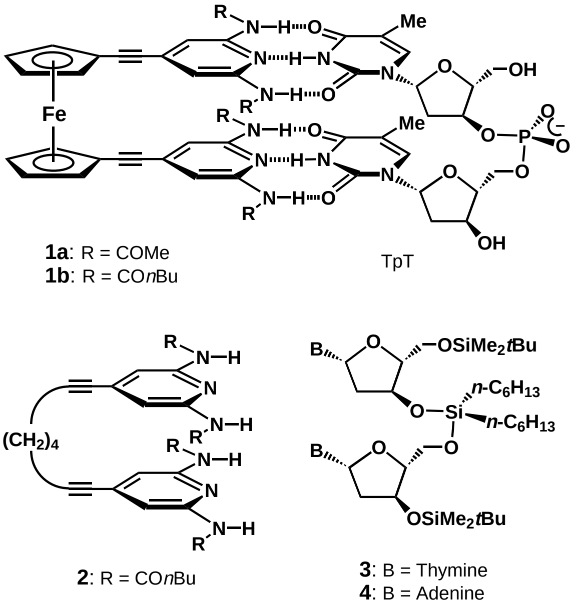
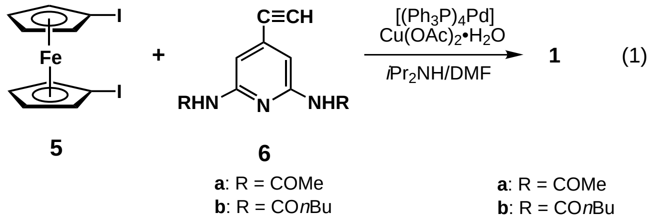
Short oligonucleotides and their derivatives have significant biological activities; for example, they act as antitumor and antiviral agents.[1] Hence, efficient syntheses and simple purification methods of such oligomers on a mg-scale are important.[2, 3] Although many artificial receptors for nucleobase and nucleoside derivatives have been reported,[4] the selective recognition of native oligonucleotides by these receptors remains to be developed.[5] Herein we show the strong binding of designed ferrocene-modified artificial receptors for dinucleotides and demonstrate the highly selective extraction of the dinucleotides into nonpolar solvents by using the receptors.

As a starting point for this project, we chose thymidylyl(3′→5′)thymidine (TpT) as a target dinucleotide because the synthetic recognition site for thymine was already developed and successfully tethered to a ferrocene skeleton.[6] The molecular design of the dinucleotide receptors **1** (Scheme 1) for TpT was based on the inter-ring spacing between two cyclopentadienyl (Cp) rings in ferrocene (0.33 nm),[7] which is almost the same as the distance between stacked base pairs in DNA.[8] Thus, when two diamidopyridine moieties (a hydrogen-bonding site for thymine)[9] are connected to the Cp rings of ferrocene through linear ethynediyl spacers, the entropic disadvantages of the receptors during the complexation must be limited to the restricted free rotation of the Cp rings and of the diamidopyridine side chains. This might play a role in the increasing affinities of **1** for TpT. The dinucleotide receptors **1** were synthesized by the Sonogashira reaction between 1,1′-diiodoferrocene (**5**) and 2,6-diamido-4-ethynylpyridines **6** [Eq. (1)].



Scheme 1. A multipoint hydrogen-bonded complex between dinucleotide receptor **1** and TpT. Analogues **2**, **3**, and **4** were also investigated.



The recognition abilities of the artificial receptors **1** were first investigated in homogeneous solutions by the use of lipophilic TpT analogue **3** (Scheme 1),[10] to obtain detailed information of the complexation. Receptor **1a** (5.0×10^{-4} M)

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