

Amine charge transfer complexes of perfluoroalkanes and an application to poly(tetrafluoroethylene) surface functionalization

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Abstract

Charge transfer (CT) complexes formed in hexane between substituted amines as donors and perfluoroalkanes as acceptors have CT bands in the range 240–270 nm. The electron affinities of the perfluorocarbons studied were estimated from the data (e.g., perfluorodecalin, 1.3 eV). Photolysis of the CT complexes with *n*-BuNH₂ leads to CF bond breaking but although the reaction was not synthetically useful, it can be used as a method for obtaining robust photomodified surfaces of poly(tetrafluoroethylene) (PTFE) where water contact angles fall from 108° to <60° after 100 min irradiation. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Charge transfer (CT) complexation, established by the work of Benesi and Hildebrand [1] and Mulliken [2], is now recognized as a controlling factor in a variety of reactions [3,4], and as an important molecular recognition element in the assembly of supramolecular complexes and in the formation of crystalline solids [4,5]. Photoexcitation of a CT complex is known [6] to lead to electron transfer (ET) in the excited state, a step which we thought might be useful for functionalization of perfluoroalkanes, a topic of current interest [7–15]. In a recent case, we saw photolytic ET from permethylferrocene to perfluoroalkane, leading to formation of the perfluoroalkene. In the presence of Zn as reductant the reaction became catalytic in ferrocene [16,17]. We tried without success to detect charge transfer (CT) complexation between ferrocenes and perfluoroalkanes, but we find perfluoroarenes do give crystalline molecular complexes with ferrocenes [18,19], such as [Cp*₂Fe·C₁₄F₈] and [Cp₂Fe·C₁₄F₈]₂, but no CT bands could be identified in these systems.

The 1:1 C₆H₆/C₆F₆ molecular complex [20], a solid melting at –3°C, showed no CT bands even for a neat mixture, but CT bands are seen for perfluoroarenes with classical donors [21], such as amines, and for (4, 5, 7, 8)-tetrafluoro[2.2] paracyclophane where π donor and π acceptor rings are covalently constrained to be in close proximity [22].

No case of CT complexation has been reported for a perfluoroalkane, however. In this paper we establish charge transfer complexation for a variety of alkylamine/saturated perfluorocarbon systems and use the phenomenon in the surface modification of polytetrafluoroethylene (PTFE).

2. Results

2.1. Choice of donor and acceptor

At first glance, perfluoroalkanes seem unlikely candidates for participation in CT complexes because of their reputation for inertness. Saturated perfluorocarbons are even extensively used as inert solvents for studies of CT complexation [6]. Photoelectron spectroscopy [23,24] shows that fluorine substituents strongly lower the LUMO energies of hydrocarbon on perfluorination and this lowering is much greater for the C–X σ* orbitals of alkanes (X = H or F) than for the C=C π* orbitals of arenes [23]. Other studies [25–27] show that perfluoroalkanes have surprisingly high electron affinities (EA = 0.8–1.1 eV). Despite the fact that the EA of perfluoromethylcyclohexane (1.06 eV) is higher than that of octafluorotoluene (0.94 eV) [25–27], we know of no report of CT complexation involving saturated perfluorocarbons as acceptors. We chose unhindered amines as donors because their small size minimizes steric effects, and as ‘hard’ [28] bases should be compatible with the ‘hard’ perfluorocarbon

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acceptors. With IPs between 7.5 and 8.7 eV [29], these molecules are also strong Lewis bases and have only high energy UV bands (around 220 nm) which should not obscure any CT transitions. We avoided arylamines because their longer wavelength UV absorptions might obscure the CT bands of any complex. In addition, if the amines had perhydroarene rings, known to give CT complexes with perfluoroarenes, there would be doubt as to which functionality the donor was engaging in complexation.

2.2. Observation of CT bands

A hexane solution of an amine such as NEt_3 and a cyclic perfluoroalkane such as perfluorodecalin showed a new UV band, in this case at 270 nm, that was identified as a CT band diagnostic of CT complexation. The mixtures did not undergo any chemical reaction and remained unchanged under the conditions of our studies and the spectra observed were stable with time. The new CT band was observed in every case in a spectral region in which none of the individual components

Table 1
Observed charge transfer bands for different amine–perfluoroalkane complexes

Amines	IP (eV)	λ_{CT} (nm)	λ_{CT} (nm)	λ_{CT} (nm)	λ_{CT} (nm)
		1 ^a	2 ^b	3 ^c	4 ^d
NEt_3	7.50	270	282	272	268
NBu_3	7.40	269	280	274	270
$\text{NH}(i\text{-Pr})_2$	7.73	257	263	260	260
NHPr_2	7.84	261	264	261	260
BuNH_2	8.71	245	246	241	250
$t\text{-BuNH}_2$	8.64	241	243	243	245

^aPerfluorodecalin (1), 1:1 mixture of *cis* and *trans* isomers.

^bPerfluoroperhydrofluorene (2) mixture of isomers.

^cPerfluoroperhydrophenanthrene (3) mixture of isomers.

^dPerfluoro-1-methyl decalin (4), mixture of isomers.

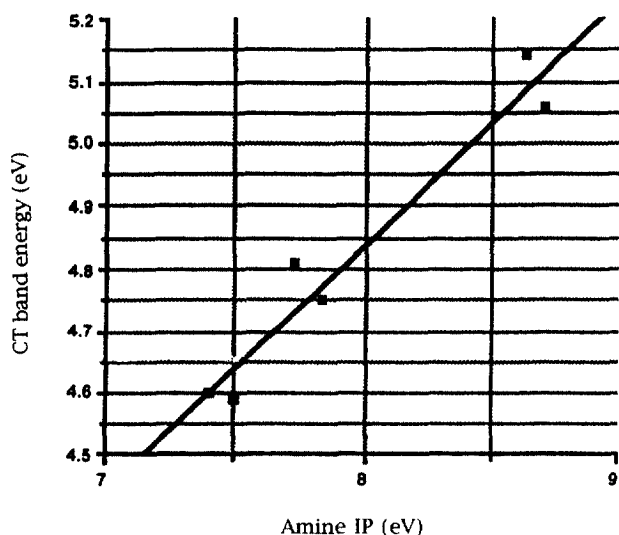
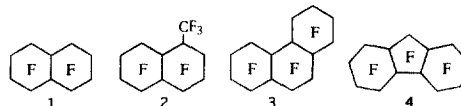


Fig. 1. Linear relationship between the energy of the CT (E_{CT}) band and the ionization potential (IP) of the alkyl amines for CT complexes of 1.

of the solution absorbs. The results of measurements with perfluoroalkanes 1–4 (0.06 M) and the amines listed (1.9 M) can be seen in Table 1, which also shows the IPs of the amines. Since an electron moves from the donor to the acceptor in a charge transfer process, the charge transfer transition energy should be a function both of the IP of the amine and the EA of the perfluoroalkane [30]. As expected, the plot shown in Fig. 1, shows that for a given perfluoroalkane, there is a linear relationship between the energy of the CT band and the known [29] IP of the amine.



To extract [31–35] the perfluoroalkane EA from the data, the relationship [30] of Eq. (1) can be used, where h is Planck's constant and W is the dissociation energy of the CT excited state.

$$h\nu_{\text{CT}} = \text{IP} - \text{EA} - W \quad (1)$$

Knowing the literature [36] EA of C_7F_{14} (1.08 eV), we were able to estimate an average value for the dissociation energy W from Eq. (1) by measuring the CT energies for the series of amines. The results shown in Table 2 suggest that W does not vary very much and so we have adopted an average value of $\langle W \rangle = 1.87$ eV for interpreting the other data, recognizing that this assumption will introduce an uncertainty of ca. 0.01 eV in the results. Using the average value of W , we were able to estimate the EAs of the perfluoroalkanes shown in Table 3. The fact that the EA values for all the fluorocarbons are the same gives us some confidence in the results, since the structures of the perfluoroalkanes are rather similar. Comparison of the estimated EAs of the perfluoroalkanes studied with

Table 2
Observed charge transfer bands for amine– C_7F_{14} complexes

Amine	IP (eV)	λ_{CT} (nm)	$h\nu_{\text{CT}}$ (eV)	W (eV)
NEt_3	7.50	268	4.62	1.82
NBu_3	7.40	270	4.60	1.74
$\text{NH}(i\text{-Pr})_2$	7.73	260	4.76	1.91
NHPr_2	7.84	260	4.76	2.02
				$\langle W \rangle = 1.87$

Table 3
Electron affinities of some perfluoroalkanes

Name	EA (eV)	Reference
Perfluoromethylcyclohexane (C_7F_{14})	1.0	[36]
Perfluorodecalin (1)	1.3	This work
Perfluoroperhydrofluorene (2)	1.3	This work
Perfluoroperhydrophenanthrene (3)	1.3	This work
Perfluoro-1-methyl decalin (4)	1.3	This work

those [37,38] of other compounds known to form CT complexes, such as I_2 (EA = 1.75 eV) or O_2 (EA = 0.5 eV), suggests that these perfluoroalkanes indeed do have comparable EAs and would indeed be expected to form CT complexes with suitable electron donors.

2.3. Equilibrium constants (K) and extinction coefficients (ϵ)

The standard method [1] used to analyze the results of such spectrophotometric studies involves the Benesi–Hildebrand equation (Eq. (2)).

$$\frac{[A]_i}{A} = \frac{1}{\epsilon_{DA}} + \frac{1}{K \cdot \epsilon_{DA}} \left(\frac{1}{[D]_i} \right) \quad (2)$$

In Eq. (2), A is the absorbance of the CT band and $[D]_i$ and $[A]_i$ are the initial concentrations of the donor and acceptor, for which the condition $[D]_i \gg [A]_i$ must hold for successful application of the method; a cell pathlength of 1 cm is also assumed. A plot of the $[A]_i/A$ vs. $1/[D]_i$ for solutions of 1:1 complexes is expected to give a straight line from which K can be obtained from the slope, and ϵ_{DA} from the intercept.

Use of this treatment gave the data shown in Table 4, which confirms that weak charge transfer complexation is present. Both K and ϵ are rather small relative to the better known classes of CT complex. For example, TCNE– C_6H_6 has $\epsilon = 3600$ [6], but the closer example of PhNMe₂– C_6F_6 has $\epsilon = 730$ [21]. In contrast with previous CT complexes with π donors or π^* acceptors, the present case involves a C–F σ^* orbital as acceptor and an amine lone pair as donor. The overlap expected from these two highly directional orbitals is expected to be smaller than in prior cases and so smaller ϵ values are not surprising. As K increases, ϵ decreases, consistent with standard contact charge transfer complexation [39] as is often found for weak CT complexation.

2.4. Temperature dependence

By measuring K values at different temperatures in the range 0–50°C, we were able to estimate values for ΔS° , ΔH° and ΔG° for some of the CT complexes. Table 5 compares the data obtained with that for I_2 –benzene [1]. Both the ΔH° and ΔS° values are small and negative as expected. These CT interactions are therefore comparable in strength (ΔH°) with familiar interactions such as aromatic stacking and weak hydrogen bonding and they should therefore also be important in deciding the packing of crystals of fluoroorganic species, a topic which we hope to examine in future.

2.5. Linear vs. cyclic perfluoroalkanes

A weak band, observed at 270 nm for the case of a linear alkane, n - C_9F_{20} and n -BuNH₂, was tentatively identified as the CT band. This system is less strongly associated and less well defined than those for the cyclic alkanes because

Table 4
Equilibrium constants K and extinction coefficients ϵ of some CT complexes by the Benesi–Hildebrand treatment

Acceptor	Donor	K^a	ϵ^b
1	NEt ₃	0.95	55.5
	NH(<i>i</i> -Pr) ₂	2.75	15.5
2	NEt ₃	0.94	62.5
3	NEt ₃	0.58	143.0
4	NEt ₃	0.23	330.0

^aIn mol⁻¹ dm³.

^bIn dm³ mol⁻¹ cm⁻¹.

Table 5
Thermodynamic functions for some CT complexes

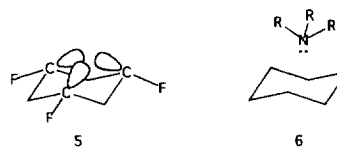
Acceptor	Donor	ΔH° ^a	ΔS° ^b	ΔG° ^a
1	NEt ₃	-3.66	-12.63	0.10
2	NEt ₃	-2.66	-9.23	0.09
3	NEt ₃	-1.51	-6.23	0.34
4	NEt ₃	-0.57	-4.94	0.84
I_2	C_6H_6	-1.32	-3.6	-0.26

^aIn kcal mol⁻¹.

^bIn cal mol⁻¹.

attempts at carrying out the analysis described above did not give a good fit.

One interesting point emerges from this comparison: the cyclic perfluoroalkanes studied are clearly better CT acceptors than the linear case. Two possible explanations were considered. All the cyclic cases contained tertiary C–F bonds which might be expected to have a lower CF σ^* energy. Because the σ^* orbitals of CF bonds are polarized towards the C end of the bond, the equatorial C–F bonds of cyclic alkanes are oriented in such a way (see diagram 5) that they would be expected to overlap in the regions above and below the ring, giving enhanced acceptor properties. This argument also suggests that the structures of the complexes could be as shown in diagram 6, where the donor and acceptor orbitals are expected to have maximum overlap.



2.6. Surface functionalization of PTFE

Photolysis at the wavelength of the CT band is expected to cause ET which could in turn lead to subsequent cleavage of the CF bond. Photolysis of butylamine–perfluoroalkane mixtures indeed led to chemical reaction with the formation of a precipitate of BuNH₃F, identified by comparison (NMR, IR) with an authentic sample, as a product. The fluorocarbon products proved to be a mixture of fluoroimines and so the

method was not preparatively useful, but it did lead us to develop a useful procedure, described elsewhere [16,17], involving the nonnucleophilic electron donor, permethylferrocene. In all these cases, care was taken to see that the starting material was pure perfluoroalkane, or if not that the material was purified before use; this procedure is also described elsewhere [16,17].

As an example of such a reaction, photolysis of an *n*-BuNH₂-*n*-C₉F₂₀ mixture in a quartz tube using a medium pressure Hg lamp gave a yellow oil and a white precipitate. The white precipitate, which was separated by filtration and washed with CH₂Cl₂, proved to be *n*-BuNH₃F as determined by comparison with an authentic sample (¹H NMR and ¹⁹F NMR spectroscopy). TLC analysis suggested that the yellow oil was a complex mixture of products. The ¹⁹F NMR spectra of the yellow oil showed an intense but broad resonance at -81.0 ppm indicating the presence of a variety of -CF₃ groups. Resonances in the region -122 to -128 ppm were assigned to -CF₂-groups. IR spectroscopy of the neat oil showed bands at 2959, 2931 and 2871 cm⁻¹ suggesting the presence of C-H bonds. Other IR absorption bands at 1138, 1663, 3314 cm⁻¹ were assigned to C-F, C=N and N-H bond stretching vibrations, respectively. All attempts to separate and purify this mixture were unsuccessful but we tentatively suggest that the products may contain fluoroimines having *n*-BuN=C groups attached to the main alkane chain. Later work [40,41] led to the development of a mercury photosensitized version of the reaction with NH₃ as electron donor. This gives isolable products, such as imines, from cyclic perfluoroalkanes. The proposed mechanism based on a full mechanistic investigation involves electron transfer/F⁻ ion back transfer from the ammonia exciplex of the mercury triplet excited state. This is considered to lead to the perfluoroalkene, which was in turn shown to give the same final products by nucleophilic attack on the C=C double bond by ammonia. The mechanism suggested [41] for the Hg photosensitized work may be analogous to the one that operates in the present case but we have no mechanistic information at present.

In spite of the formation of mixtures of fluoroorganic products in the present case, the reactivity shown by *n*-C₉F₂₀ suggested that we could still use the reaction for the surface modification of PTFE films. The thermal and chemical stability [42], as well as the low surface energy that makes PTFE useful in many applications is a problem when adhesion of PTFE to other materials is desired [43], in which case the surface of PTFE has to be chemically modified. Many methods are available, including strong reducing agents such as Li in liquid ammonia or benzoin dianion in DMSO [44–46]. Photochemical modification of PTFE surfaces using a variety of electron donors, such as thiolate salts in DMF, have also been reported [47]. The chemical changes that occur can easily be monitored by measuring the water contact angle with the surface.

We have therefore irradiated a film of PTFE in a quartz tube and in the presence of a primary amine using a medium pressure Hg lamp. The observed decrease in the contact angle

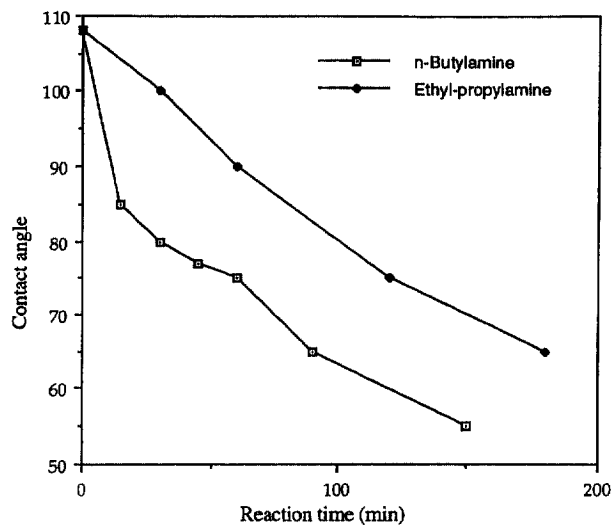


Fig. 2. The change in the water contact angle (°) on progressive photomodification of a PTFE surface with *n*-BuNH₂ (squares) or *i*-PrNH₂ (diamonds).

(Fig. 2) of a 10 μl droplet of water after the photolysis times indicated, shows the expected increase in the hydrophilicity of the surface. Examination of the IR spectra of the progressively more photomodified PTFE for the *n*-BuNH₂ case shows (Fig. 3) that the absorption in the C-H region becomes more intense as the exposure time increases.

Furthermore, at long exposure times (150 min), a new absorption band at 1647 cm⁻¹ was also observed, suggesting the presence of C=N bonds [16,17,40,41]. These observations are consistent with the increase in the polarity of the PTFE surface being due to the presence of *n*-BuN=C groups on the surface. The photomodified surfaces are stable and retain their properties over extended periods. Et₂CHNH₂ also gave similar but smaller changes in contact angle on irradiation with PTFE but this case was not studied in any further detail.

3. Conclusions

Cyclic perfluoroalkanes form CT complexes with a variety of amines in hexane solution, as shown by the appearance of CT bands in the UV spectrum of the mixtures and the successful analysis of these bands by the Benesi-Hildebrand treatment. The EAs of the perfluoroalkanes studied was estimated from the position of the CT band and from the intensity variations with changes in component concentrations, we were also able to extract estimates of the equilibrium constants for complex formation, and the ϵ for the complex itself.

The photolysis of the *n*-BuNH₂ complexes leads to chemical reaction to give *n*-BuNH₃F, but the fluoroorganic products are an intractable mixture so the procedure is not preparatively useful. Spectroscopic data suggests that *n*-BuN=C groups may be present in these products. The photolysis procedure can be successfully applied to PTFE in

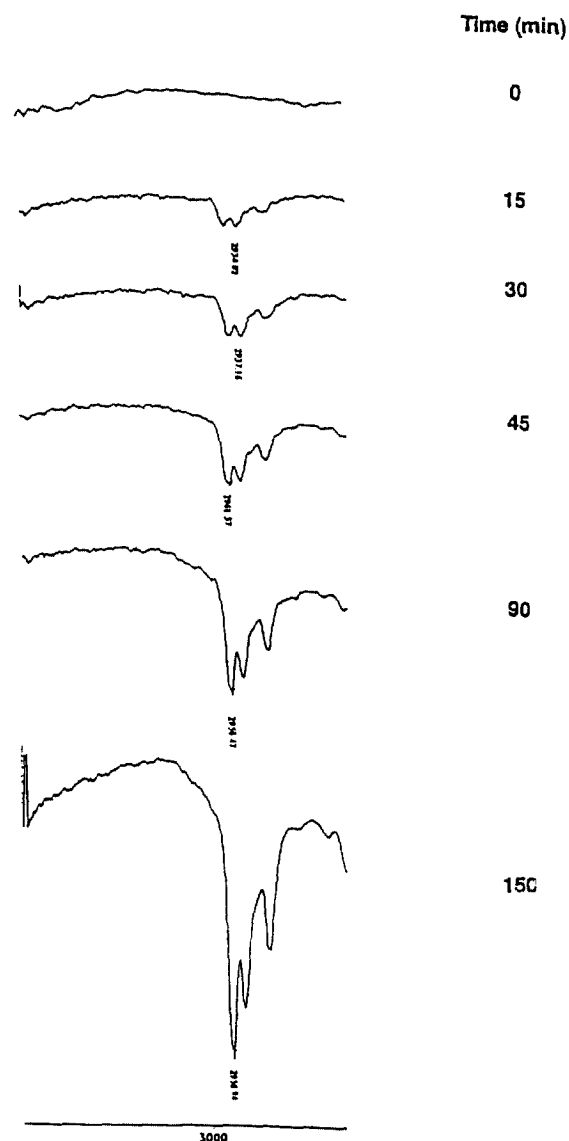


Fig. 3. Progressive changes in the C–H stretching region (cm^{-1}) of the infrared spectra of a PTFE film photomodified with $n\text{-BuNH}_2$.

which case a robust chemically modified surface is obtained, presumably consisting of surface-bound $n\text{-BuN}=\text{C}$ groups.

A photolytic pathway may need to be considered for slow reactions involving nucleophiles and perfluoroalkanes [15], previously thought to be thermal in nature, because normal laboratory light could be enough to promote reactions of this type.

4. Experimental section

4.1. General procedures

UV–Vis spectroscopy was performed on a Varian CARY 3E spectrophotometer with a CARY temperature controller. Infrared spectroscopy was performed on a Nicolet MIDAC GRAMS/386 FTIR spectrometer. Magnetic susceptibilities

were measured using a Cahn electrobalance. Gas Chromatography was performed on a Varian 3300 GC, and GCMS on an HP 5890 Gas Chromatograph (29 m; 0.25 i.d.; capillary column coated with a 0.25 mm film of SE 30). ^{19}F NMR was determined on a Bruker Y-490 MHz with CCl_3F as an external standard. Irradiation was carried out in quartz tubes with a medium pressure Hg lamp (Hanovia, 100 W).

4.2. Reagents

All chemicals were of reagent grade and were used without purification unless noted. Materials were purchased from Aldrich Chemical, except $i\text{-Pr}_2\text{NH}$ (Pfaltz and Bauer) perfluoro-1-methyldecalin (Alfa Chemical) perfluoromethylcyclohexane (PCR) and spectrophotometric grade hexane (Baker) and pentane (Acros). THF was distilled under nitrogen from Na/benzophenone radical anion. Fluorocarbons were purified by procedures previously described [16,17,40,41].

4.3. Charge transfer bands and electron affinities

Measurements of the wavelength of the CT bands for perfluoroalkanes (0.06 M) and amines (1.9 M) were carried out in hexane solutions (Tables 1 and 2).

4.4. Equilibrium constants and extinction coefficients ϵ

The Benesi–Hildebrand method [1] was used to determine the extinction coefficients ϵ and equilibrium constants K of the complexes at 20° . The measurement of absorbances were carried out in hexane solutions of amine:perfluoroalkane with a 10:1 molar ratio; concentrations are in mol l^{-1} . The primary data obtained is provided in the form of supplementary data.

4.5. Temperature dependence

The Benesi–Hildebrand method was used to measure the equilibrium constant K at different temperatures in the range $0\text{--}40^\circ\text{C}$ using the thermostatted cell incorporated in the instrument.

4.6. Photolysis results

A 1:1 molar ratio mixture of $n\text{-BuNH}_2$ and $n\text{-C}_9\text{F}_{20}$ (5 ml) was irradiated for 18 h to give a white precipitate (500 mg) separated by filtration and a yellow oil (3 g) which was chromatographed by TLC (CH_2Cl_2 –hexane) to give a material with the spectral characteristics reported in Section 2.

A strip of PTFE, washed with THF (3×2 ml) and dried under a stream of N_2 , was suspended in a quartz tube and 3 ml of amine added. The amine was heated to reflux so that the entire PTFE surface became wet with amine, and the strip was then irradiated with a medium pressure mercury lamp for up to 150 min. PTFE samples treated for various times were washed with THF (3×2 ml) and CH_2Cl_2 (3×2 ml)

and dried under a stream of N₂ before their contact angle and/or IR spectrum was measured. The PTFE samples for FTIR were prepared from granular PTFE (Aldrich) using a standard pellet press. The samples were then hung in the IR beam of the spectrometer. Contact angle analysis was performed with a 10 µl drop of water using a goniometer.

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