Langmuir
Article
pubs.acs.org/Langmuir

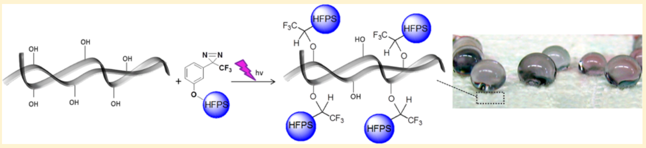
Photoinduced Carbene Generation from Diazirine Modified Task Specific Phosphonium Salts To Prepare Robust Hydrophobic Coatings

Sara Ghiassian, Hossein Ismaili, Brett D. W. Lubbock, Jonathan W. Dube, Paul J. Ragogna,* and Mark S. Workentin*

Department of Chemistry and the Centre of Materials and Biomaterials Research (CAMBR), Western University, London, Ontario, Canada N6A 5B7

Supporting Information

ABSTRACT: 3-Aryl-3-(trifluormethyl)diazirine functionalized highly fluorinated phosphonium salts (HFPS) were synthesized, characterized, and utilized as photoinduced carbene precursors for covalent attachment of the HFPS onto cotton/paper to impart hydrophobicity to these surfaces. Irradiation of cotton and paper, as proof of concept substrates, treated with the diazirine-HFPS leads to robust hydrophobic cotton and paper surfaces with antiwetting properties, whereas the corresponding control samples absorb water readily. The contact angles of water were determined to be 139° and 137° for cotton and paper, respectively. In contrast, water placed on the untreated or the control samples (those treated with the diazirine-HFPS but not irradiated) is simply absorbed into the surface. Additionaly, the chemically grafted hydrophobic coating showed high durability toward wash cycles and sonication in organic solvents. Because of the mode of activation to covalently tether the hydrophobic coating, it is amenable to photopatterning, which was demonstrated macroscopically.



■ INTRODUCTION

There is a host of potential applications of hydrophobic coatings in such things as microfluidic[1] or biomedical devices,[2] self-cleaning and impermeable textiles,[3,4] and in the printing and packaging industries.[5] Recent successful efforts to prepare superhydrophobic surfaces have involved the incorporation of nanoparticles (to provide uniform surface roughness) or using a mechanically roughened rigid surface prior to deposition of the hydrophobic layer.[6,7] The chemical modification of surfaces with low-surface-energy functionalities, especially fluorine-containing hydrocarbons or perfluorosilanes, is an efficient and practical method to fabricate a hydrophobic surface. In addition to the more common use of small fluorinated molecules for preparing coatings, fluorinated silica nanoparticles have also been used to produce rough superhydrophobic surfaces.[8−10] However, in many cases the deposited layer on the surface should have a thickness equal to or higher than the particle diameter, and having such a thick layer of coating can change the intrinsic properties of the substrate and damage its transparency.

Highly fluorinated phosphonium salts (HFPS) have demonstrated promise in a wide variety of fields over the past several years[11] in areas such as surfactants[12] and solvents for phase transfer catalysis,[13] but only more recently have we demonstrated it as an effective medium for imparting hydrophobic properties to various metal surfaces such as Au and Ag.[14,15] The advantage the HFPS systems possess, compared to other strategies, is that the phosphonium salts can be readily modified using selective substitution chemistry on the phosphorus center, which is much more difficult to obtain in related C- or Si-centered and even polymer systems. In this way, using a small number of simple quantitative transformations one can impart specific functionality onto the cation. A drawback of the HFPS we described earlier and indeed other systems mentioned above is that they lack a *universal tether* or they need to have functionality tailored for a specific surface. So, despite the many successes, there remains a need for the development of materials that allow for facile, efficient, and mild approaches to impart hydrophobic character more universally on any surface.

Photolinkers are a versatile method for covalent attachment of molecules onto surfaces. Common highly efficient photolinkers used generally include diaryldiazo,[16−19] azide,[20−22] and diazirine[23−26] molecules that generate highly reactive carbene or nitrene intermediates that then react with functionality native to or deliberately functionalized onto the desired surface. To the best of our knowledge, only diaryldiazo and azide photoactivation have been used to tether hydrophobic substrates onto surfaces. For example, very recently Ling et al. reported the use of azide functionalized silica nanoparticles as a way to impart hydrophobicity to cotton fiber.[27] To date, the diazirine moiety has not been used in this sort of technology. However, it has been suggested that diazirine as a photolinker can be more beneficial because aryl azides can

Received: May 14, 2012
Revised: July 26, 2012
Published: July 27, 2012

generate a singlet nitrene that can undergo a ring expansion and to a much less reactive species, and many diazo compounds suffer from low thermal stability. The use of diazirine, however, combines the high reactivity of a carbene with its inherent high stability. Compounds containing 3-aryl-3-(trifluormethyl)-diazirine moieties are accessible synthetically useful carbene precursors. Their most common application is in photoaffinity labeling, prolific in biological applications.[28−30] The ease of synthesis, excellent thermal and chemical stability of the diazirine, and its nearly quantitative photochemical generation of a reactive carbene, which reacts with a wide range of functionalities (e.g., C═C; X−H bonds),[23,30,31] are the basis of its widespread use in these applications.[32] However, utilizing the diazirene functionality for the modification of substrates in polymer and materials science remains relatively unexplored. Hayes and co-workers in particular have utilized this chemistry creatively, mainly for the modification of polymers.[23,30,33−35] We have recently established the utility of this diazirine moiety as the carbene precursor for the modification of other materials, including CNT, diamond, graphene, and glass surfaces with gold nanoparticles.[24−26] In these studies the photochemistry of 3-aryl-3-(trifluormethyl)diazirine is utilized to generate the carbene to tether the attached gold nanoparticles (AuNPs) via insertion into the native C═C, C−H, or O−H functionality inherent on these substrates. The result is a suite of covalent hybrid materials containing the properties of both the host material and the AuNP. Lawrence et al. have used this protocol recently to append acylferrocene as a redox-active functional group onto CNT.[36,37]

In the present report we extend the applications of the photochemistry of diazirines to new functional materials by incorporating the photoactive diazirine moiety onto the structure of a novel hydrophobic highly fluorinated phosphonium salt (HFPS). The high hydrophobicity imparted by this HFPS especially given the relatively small fluorinated chain length makes this material commercially viable from an environmental perspective, compared to many that use longer fluorinated hydrocarbons. We utilize the high reactivity of the photogenerated carbene to attach the HFPS to form robust hydrophobic coatings on model cotton and paper surfaces simply and efficiently. Because the carbene reacts with virtually any functional group, the approach provides a way to marry the high reactivity of the carbene with the newly discovered use of HFPS to introduce hydrophobicity efficiently and generally to any substrate/surface. The process is photochemically activated and allows for the coverage of macroscale substrates and surface patterning, which has implications for the application of this technology at the micro- and nanoscale. Because the highly fluorinated phosphine used in the synthesis of our novel diazirine highly fluorinated phosphonium salt (HFPS) is available in commercial quantities and can be made in the 100 g to 1 kg scale in our lab and the required diazirine can be prepared in multigram quantities through a series of simple organic transformations, the approach allows for the exploration of potential applications of the proof of concept results described herein.

■ EXPERIMENTAL SECTION

Synthesis of 3-(3-(6-Bromohexyloxy)phenyl)-3-(trifluoromethyl)-3*H*-diazirine [1.8]. All steps in preparation and synthesis were performed in accordance with the literature procedure,[38] with the exception that 1,6-dibromohexane was used in place of 1,12-dibromododecane. Details are provided in the Supporting Information.

Synthesis of [1-HFPS][Br]. Under an inert atmosphere (N_2) a solution of the synthesized diazirine derivative [**1.8**] (200 mg, 0.55 mmol) in DMF (1 mL) and $CF_3(C_6H_5)$ (1 mL), was added to $(CH_3)_3CCH_2CH(CH_3)CH_2P((CH_2)_2(CF_2)_2CF_3)_2$ (380 mg, 0.60 mmol). The reaction mixture was stirred for 4 weeks at 45 °C and continually monitored by $^{31}P\ \{^1H\}$ NMR. The precursor fluorinated phosphine ($\delta_P = -30.4$) was converted to a singlet in the region consistent with the target product phosphonium species ($\delta_P = 35.2$), an oxide was also present in the reaction mixture ($\delta_P = 44.0$) but was removed by purification.

Synthesis of [1-HFPS][I]. First [**1.8**] was converted to [**1.9**] using sodium iodide. To prepare [1-HFPS][I], under an inert atmosphere (N_2) a solution of [**1.9**] (225 mg, 0.55 mmol) in DMF (1 mL) and $CF_3(C_6H_5)$ (1 mL) was added to $(CH_3)_3CCH_2CH(CH_3)CH_2P((CH_2)_2(CF_2)_2CF_3)_2$ (380 mg, 0.60 mmol). The reaction mixture was stirred for 2 weeks at 45 °C. The reaction was continually monitored by $^{31}P\ \{^1H\}$ NMR. The fluorinated phosphine ($\delta_P = -30.4$) was converted to a singlet in the region consistent with the target product phosphonium species ($\delta_P = 35.9$), an oxide was also present in the reaction mixture ($\delta_P = 44.1$) but was removed by purification.

Synthesis of [1-PMe$_3$S]. Under an inert atmosphere (N_2), PMe_3 (19 mg, 0.25 mmol, 26 mL) was added to a solution of the diazirine [**1.8**] (109 mg, 0.238 mmol) in DMF (2 mL), and the reaction mixture was stirred for 3 h at 45 °C. The reaction was monitored by $^{31}P\ \{^1H\}$ NMR and was purified upon completion.

Surface Modification of Cotton Fabric and Paper. [1-HFPS][X] (X = Br or I) 1, 2, 5, 10, and 20 mg/mL solutions of [1-HFPS] in THF were prepared. Prior to photocoating, cotton substrate was pretreated by washing with deionized water and detergent three times to remove any surfactants or chemical coatings and subsequently washed with distilled water and then dried in a 60 °C oven. The paper samples were used as obtained with no pretreatment. Both the cotton and paper substrates were treated by submersion into solution of [1-HFPS][X] and were allowed to air-dry until the solvent evaporated. Next, the 1-HFPS-coated substrates were placed in a sealed vessel that was purged with argon. All of the substrates were irradiated with ultraviolet light on both sides, using a medium-pressure mercury lamp (Hanovia S9 PC 451050/805221), which was contained in quartz water jacket, ~10 cm from the samples (ca. 1800 mJ/cm^2). After irradiation, all substrates were thoroughly rinsed with THF and DCM to remove any unbound HFPS and yield the light treated samples.

Patterning Paper. Simple plain white printer paper, 92 Bright, was soaked in a solution of [1-HFPS][I] in THF for 15 min and allowed to air-dry until no solution remained. A photomask made out of cardboard with a circular gap (1 cm in diameter) was placed on top of the HFPS-coated paper substrate, and the backside was covered with a full mask to avoid any light exposure from the backside. Next, it was placed in a sealed vessel that was purged with argon and irradiated with ultraviolet light, using a medium-pressure mercury lamp (Hanovia S9 PC 451050/805221). After irradiation, the treated paper was thoroughly rinsed with THF and DCM to afford the patterned surface.

Simulated Wash Cycles. Two washing methods were used for coated samples. In a typical experiment, a piece of 2 × 2 cm treated cotton fabric was washed in a 50 mL flask that contained 30 mL of aqueous detergent solution and a stir bar. The fabric was stirred at 500 rpm for 15 min. It was then rinsed with distilled water and stirred for another 15 min in a flask containing 30 mL of distilled water to remove any adsorbed detergent. Fabric was then dried for 10 min in a 60 °C oven before it was used for contact angle measurement. In a separate experiment a piece of 2 × 2 cm treated cotton was immersed in three different solvents and sonicated for 5 min periods: EtOH, DCM, THF subsequently. Water contact angles were measured before and after sonication.

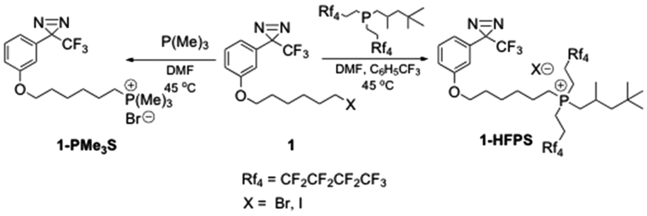
Contact Angle Measurement. Contact angles (CAs) were measured with deionized water using a Kruss DSA 100 goniometer with DSA (drop shape analysis) software, at room temperature (21 °C). All the static water contact angles were determined by averaging values measured for 5 μL droplets at five different spots on each substrate. The Laplace−Young fitting method was used to calculate all the static contact angles. Contact angle hysteresis was determined by placing a 5 μL droplet on the surface, rotating the stage 30°, and measuring the difference between the advancing and receding contact angles.

Other Techniques. The decomposition temperature for compounds [1-HFPS][I] and [1-PMe$_3$S] were determined using thermal gravimetric analysis (Q600 SDT, TA Instruments). A 0.005−0.010 g sample was heated at a rate of 10 °C/min over a temperature range of 30− 600 °C under a flow of N_2(g) (100 mL/min). X-ray photoelectron spectroscopy (XPS) was carried out using a Kratos Axis Ultra spectrometer using a monochromatic Al Kα source (15 mA, 14 kV). Scanning electron microscopy (SEM) images were recorded on a TM3000 Hitachi scanning electron microscope.

■ RESULTS AND DISCUSSION

The 3-aryl-3-(trifluormethyl)diazirine functionalized perfluorinated phosphonium salts 1-HFPS were prepared by reacting the 3-(3-(6-halohexyloxy)phenyl)3-(trifluoromethyl)-3*H*-diazirine derivatives (halo = Br or I) with a highly fluorinated alkyl phosphine ($RP[(CH_2)_2Rf_4]_2$ (R = 2,4,4-trimethylpentyl, $Rf_4 = (CF_2)_4CF_3$) via a quaternization reaction, with bromide or iodine as the counterion. The reaction involved mixing a solution of the diazirine in dimethylformamide with a solution of $C_8H_{17}P(CH_2Rf_4)_2$ in trifluorotoluene under an inert atmosphere (N_2) (Scheme 1).

Scheme 1. Reaction Pathway toward the Synthesis 1-HFPS and the Model Compound 1-PMe$_3$S



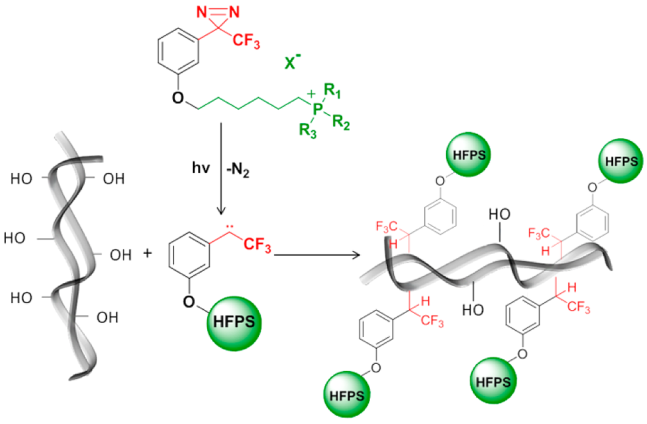
The reaction mixture was stirred at 45 °C and monitored by $^{31}P\ \{^1H\}$ NMR spectroscopy over this period, by following the disappearance of the phosphine ($\delta_p = -30$) and the appearance of the signal from the phosphonium ion. Upon disappearance of the characteristic resonance of the precursor phosphine, the reaction was exposed to air to convert any trace unreacted phosphine to the oxide and then worked up with water. The product was characterized using multinuclear NMR and IR spectroscopy, ESI MS, and TGA. Although both the bromide and iodide salts of 1-HFPS behaved similarly in further chemical tests and exhibited all the specifications that were sought for surface modification of various substrates, the I^- salt is the preferred target: the quaternization reaction is generally slow due to the attenuated nucleophilicity of the fluorinated phosphine and because the reaction is performed at temperatures not exceeding 45 °C to avoid thermal degradation of the diazirine. To achieve a faster and more efficient method for synthesizing the target, the 3-(3-(6-iodohexyloxy)phenyl)3-(trifluoromethyl)-3*H*-diazirine derivative formed by halide exchange from the corresponding bromo derivative is preferred, and using it results in a pure product.[39] The 1-HFPS were viscous liquids, exhibiting single signals in the ^{31}P NMR spectrum (δ_p = 35 ppm), and the expected signals in the ^{19}F NMR spectrum ($\delta_F = -65$ (CF_3 of diazirine) and −81, −114, −124, and −126 (fluorinated alkyl chains). The glass transition temperature ($T_g = -27.2$ °C) and decomposition temperature (T_d = 304.2 °C) were also determined for 1-HFPS[I]. The model compound 1-PMe$_3$S was also prepared in a similar manner using trimethylphosphine; in this case the reaction proceeds much more readily (3 h) because of the more nucleophilic and less sterically encumbered phosphine. Compound 1-PMe$_3$S was used as a model to demonstrate that any modification observed in the surface properties of the substrates is in fact due to grafting the HFPS on the surfaces and not simply due to the diazirine CF_3 or phosphonium ion moieties.

As a proof of principle of using the diazirine moiety as the carbene precursor to insert into the native functionality of the surfaces to act as a molecular tether, the reactivity of the salt 1-HFPS was studied upon exposure to UV light in the presence of methanol as a model O−H containing molecule. The *m*-methoxyphenyl(trifluoromethyl)carbene is known to be a ground state triplet; however, its reactivity generally corresponds to that of the singlet carbene (namely insertion reactions).[40] A solution of [1-HFPS][I] in methanol was purged with argon to remove any oxygen and then irradiated (λ >300 nm) with a medium-pressure Hg lamp. The course of the reaction was monitored with ^{19}F NMR spectroscopy. The starting material peak at $\delta_F = -65$ (CF_3 of diazirine) disappeared, and a new peak at $\delta_F = -77$ known to be that due to the methanol insertion product appeared quantitatively, verifying the reactivity of carbene for insertion into O−H bonds.[38] The details of these model reactions are provided in the Supporting Information.

To demonstrate the utility of 1-HFPS as a photoprecursor to a reactive carbene that can be used to graft the hydrophobic properties of the HFPS, we chose cotton fabric and paper as proof of concept materials. Both of these substrates are known to be rich in O−H and C−H bonds on the surface, which can react with the photogenerated carbene via insertion reactions. The 100% cotton fabric was purchased and cleaned by washing with detergent and deionized water three times and then dried in a 60 °C oven. The paper substrate (simple plain white printer paper, 92 Bright) was used as obtained with no pretreatment. For photocoating, cotton or paper substrate was immersed into a solution of the prepared 1-HFPS in THF for 10 min and allowed to dry in the dark. This process was repeated up to three times to ensure a film of the 1-HFPS was on the surface of each substrate. Next, the coated sample was placed in a sealed Pyrex vessel, which was purged with argon gas for 30 min and then irradiated with UV light (λ > 300 nm) on both sides using a medium-pressure Hg lamp. Upon irradiation, the diazirine loses N_2 and generates a carbene reactive intermediate that inserts into X−H bonds.[30,38] The general photochemical reaction that was utilized for grafting the salts 1-HFPS and 1-PMe$_3$S onto the surfaces of cotton and paper is illustrated in Scheme 2. After irradiation, to remove any unbound, physisorbed 1-HFPS from the surface, the HFPS-photocoated sample was washed repeatedly with THF and dichloromethane and then allowed to air-dry. In parallel, dark control samples consisting of cotton/paper samples that were similarly prepared with the 1-HFPS were left in the dark for 24 h (not exposed to UV irradiation) and then washed using the same protocol as used for the light-treated samples.

To demonstrate the influence of the 1-HFPS solution concentration on the resulting wetting behavior, we prepared [1-HFPS]-coated surfaces on cotton and paper using the same protocol explained above, with *c* = 1, 2, 5, 7, 10, and 20 mg/mL of [1-HFPS][I] in THF and irradiated them for 1 h. Figure 1 shows the dependency of the water contact angle on the

Scheme 2. Illustration of Photochemical Reaction Used for Surface Modification of Cotton and Paper: 1-HFPS and 1-PMe$_3$S



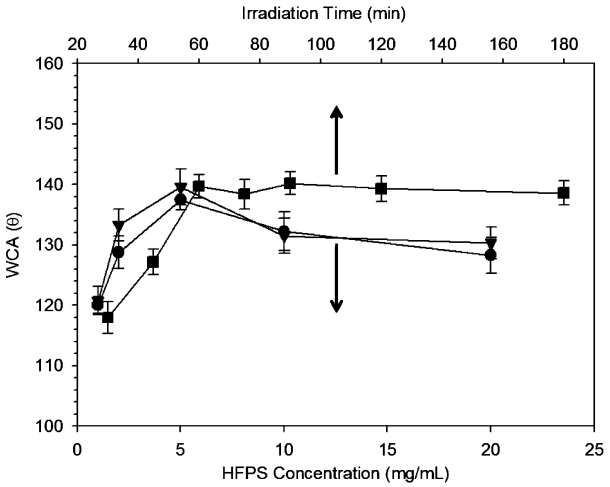


Figure 1. Variation in water contact angles as a function of irradiation time of 5 mg/mL samples (square, top scale) and as a function of the [1-HFPS][I] concentration on both cotton (inverted triangle, bottom scale) and paper (circle, bottom scale).

concentration of the solution used for coating. Even surfaces coated with very dilute solution (1 mg/mL) exhibit high contact angles after the irradiation and washing protocol. Although there is an increase in the water repellency when using more concentrated solutions, we observed that with concentrations higher than 10 mg/mL we not only damage the transparency of the substrate but also decrease the contact angle. We believe that when too concentrated a solution is used, the density of the diazirine molecules on the surface increases. When exposed to UV light, this high density can lead to dimerization of the reactive carbene species at the expense of reactions of the carbene reacting with the OH groups present on the surface. These dimers would simply be rinsed away in the washing protocol.

Using the optimized coating concentration (5 mg/mL solution of [1-HFPS][I] in THF), we then performed experiments to monitor the effect of irradiation time on the resulting hydrophobicity of the light-treated substrates while all the other factors were kept constant. Figure 1 also shows the change in the water contact angles on cotton with time under our irradiation conditions. There are two important observations. The first is that even after very short irradiation times the samples show a high hydrophobicity (antiwetting). The second is that while there is an increase in contact angle with the increase in UV exposure no significant change was observed over 60 min of irradiation under our conditions. Using more lamps (increased intensity) will lead to shorter irradiation times, but for consistency, especially when treating the small analytical samples in this study, we used 60 min of irradiation under our conditions to prepare the hydrophobic substrates for further testing.

We investigated the surface characteristics of treated samples and compared with those of the untreated samples visually and analytically using SEM, XPS, and contact angle measurements. The surface morphology of treated and untreated cotton/paper was examined using SEM (see Supporting Information Figure S1). In this study we used the optimized concentrations of the HFPS, which leads to a very thin layer on the surface. SEM micrographs of the modified samples and their unmodified counterparts did not show any obvious change in diameter or structure of the fibers. There were likewise no other visible changes in color or bulk morphology to the irradiated samples under the conditions of the irradiation. The fact that no obvious change was observed after treating/irradiating substrates supports the thinness of the coatings. As a result, we did not damage the transparency or color of the cotton or paper. The surface of modified samples was also smooth, and no destruction of cotton/cellulose fibers was indicated. More dramatic was the change in the surface wetting properties of the samples, which were evaluated visually and by measuring water contact angles (Figure 2).

The stability of the water droplets on treated cotton/paper was in complete contrast with the untreated ones. It is well-known that both cotton and paper are rich in hydroxyl groups and are therefore very hydrophilic. After chemically grafting the surface with HFPS all the light-treated samples were found to be highly hydrophobic as illustrated by the photographs in Figure 2, while the water droplet soaked into the untreated and dark surfaces immediately after deposition (Figures 2A,E and 2B,F, respectively). In Figure 2, the water droplets were colored for more easily visualization. Also included in Figure 2 are images showing the hydrophobic nature from contact angle measurements using water placed on the irradiated cotton and paper substrates (Figure 2D,H). The water contact angles were measured 30 s after a 5 μL water droplet was placed on the surface. It is worth noting that those fibers protruding out from the cotton surface made the contact angle measurement somewhat difficult. Because of the inherent roughness of the cotton fabric, determining the baseline is less straightforward, and this can lead to possible underestimation of the contact angle data. For each specimen, the contact angle reported is the average of at least five different readings on different spots on the surface. The irradiated cotton and paper surfaces treated with 1-HFPS exhibited average water contact angles (θ) as high as 139.5° and 137.4°, respectively. The lack of hydrophobicity of the dark samples demonstrates that the phototreatment is necessary and suggests that it is the formation of the carbene and subsequent covalent bonding to the substrate via carbene insertion reactions that leads to the robust hydrophobic coating. The magnitudes of the observed contact angles are approaching those of surfaces that have a micro/nanoscale roughness and are ultimately superhydrophobic ($\theta \geq 150°$).[8−10] The effect is dramatic especially when one considers that the surfaces that did not undergo irradiation prior to washing

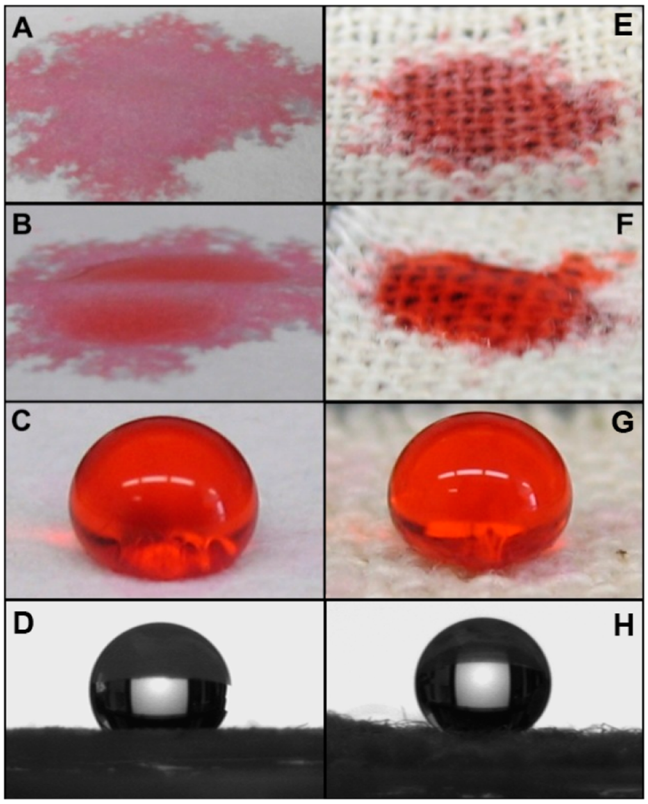


Figure 2. Pictures of colored water droplets (colored to aid visualization) placed on standard printer paper samples (left column) and cotton (right column): (A, E) untreated, (B, F) 1-HFPS treated dark control (no irradiation), and (C, G) 1-HFPS treated and irradiated. Panels D (paper) and H (cotton) are representative pictures of water contact angle measurements.

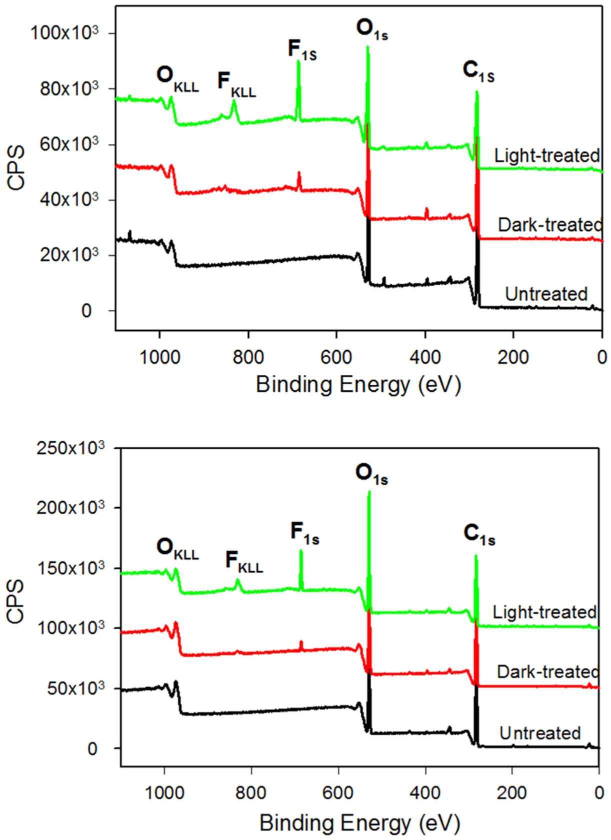


Figure 3. XPS spectra of treated, treated with no light (dark treated), and untreated cotton (top) and paper (bottom) with [1-HFPS].

simply absorb the water due to the abundance of the hydroxyl groups in the structure.

On the light-treated surfaces (Figure 2C,G) the water droplet remained on the surface indefinitely while maintaining their shape and high contact angles, only disappearing through evaporation. These droplets could be simply removed by picking up the substrate and shaking them off or wicking using a Kimwipe or pipet (see Figure S3). Interestingly, even though the surface was coated with a low surface energy compound and exhibited large water contact angles, while measuring contact angle hysteresis we observed the "petal effect" on all the treated surfaces.[41,42] For all the paper/cotton fabric surfaces contact angle hysteresis was relatively high (>10°). The small water droplets stuck to the surface when the sample was tilted vertically (90°) or even turned upside down (180°) (see Figure S4). This indicates that there is a strong adhesion between the water droplet and the modified surfaces. Such surfaces are expected to have many potential applications, such as sticky tapes,[43] for liquid transportation in microfluidic devices[44] or two-dimensional lab on paper devices.[45] Larger water droplets, like those from a Pasteur pipet bead, roll off of the substrates. This is shown for cotton in a movie supplied in the Supporting Information.

To obtain further evidence of coating of the HFPS on the surface of cotton and paper, XPS analysis was performed on substrate treated light and dark control samples and also on untreated samples. Analysis of the spectra (Figure 3) indicates that there is a relatively large peak related to fluorine (10.3%) in the light-treated cotton spectrum that is not observed in XPS of the native sample. This proves that they are in fact coated with a film of HFPS. Although the fluorine peak is also present in XPS of the dark sample, the relative intensity is significantly smaller (1.9%) by comparison to the C and O signals. With the paper sample the results are 7.4% and 1.4%, respectively. Contact angle measurements confirm that the much lower fluorine incorporation in the dark control sample (likely due to some physical absorption or thermal carbene activation) is not enough for the sample to exhibit hydrophobicity.

Control over interfacial adhesion is particularly important when integrating the material into a device design. In our case, the photogenerated carbene can be used to impart well-defined surface functionality with water-repellent properties. The chemical stability and overall robustness of this coating are dictated by the molecular interaction between the coating and the substrate. As a result, in order to remove the chemically grafted HFPS coating from the substrate, covalent bonds must be broken. To find out how strongly the hydrophobic layer is attached to the surface, we subjected the treated samples to two washing protocols. Hydrophobic substrates were immersed in sonication baths of three different solvents that wet the surface completely (EtOH, THF, and DCM), for 5 min periods each time. Water contact angle measurements reveal that even after repeated sonication there is no significant change in the wetting properties of these surfaces. For a representative piece of treated cotton, water contact angles were measured to be 138.7 ± 2.4° and 136.8 ± 3.7° before and after the sonication process, respectively. We also subjected the 1-HFPS treated and irradiated cotton samples to simulated wash cycles where the samples were washed in water containing detergent for 15 min and then rinsed in water for 15 min. After each wash cycle the substrates were dried before measuring the contact angle. Illustrated in Figure S4 is a measure of the WCA as a function of wash cycle; no significant change was observed in the water contact angles even after 10 of these wash cycles. These results support the claim of robustness of our coating that originates from covalent bond between the HFPS and the surface.

Having demonstrated that the 1-HFPS can modify the wetting behavior of the cellulose fiber material surfaces and produce hydrophobic surfaces, we also carried out additional sets of control experiments. Samples of cotton and paper were treated with the nonfluorinated salt 1-PMe$_3$S, according to the previously explained procedure. Hydrophobicity tests performed on these treated surfaces after irradiation and washing cycles showed no hydrophobic properties, with the water absorbing promptly after deposition. This suggests that it is the highly fluorinated phosphonium moiety that imparts the (majority of) hydrophobicity and that the CF$_3$ of the diazirine is not sufficient. Of course, the alkylphosphonium salt (no fluorinated chains) would be expected to make the sample hydrophilic and mask any potential hydrophobicity imparted by the CF$_3$ of the diazirine or the appended alkyl chain. Cotton/paper samples treated with either 3-(3-methoxyphenyl)3-trifluoromethyl)-3*H*-diazirine or 3-(3-(6-iodohexyloxy)phenyl)-3-(trifluoromethyl)-3*H*-diazirine at the same concentrations used for 1-HFPS and subjected to identical irradiation conditions were similarly found to be nonhydrophobic.

By taking advantage of the photosensivity of the diazirine in 1-HFPS, patterning can be achieved on the surfaces using a crude photomask. This is a simple and inexpensive method that enables us to develop any hydrophobic pattern on various surfaces even in the microscale that can be utilized in biochemical assay devices.[46−48] As a proof of concept, to produce a simple patterned hydrophobic surface, a paper substrate coated with 1-HFPS was covered with a shadow mask with only a circular gap allowing the substrate to be exposed to the light in that area. After irradiation followed by rinsing the paper with THF, the surface wetting properties were tested. The circular area exposed to light (indicate by a dark circle drawn with pencil to aid in visualization) exhibited the high hydrophobicity while water soaked into the other masked areas (see Figure 4). With such a simple method for patterning one can create well-defined hydrophobic and hydrophilic channels. This method is compatible with small pieces of paper as well as large. By using the patterning method, we will have control over the hydrophobicity of the paper surface. Therefore, these surfaces can serve as paper-based lab-on-a-chip devices (lab-on-paper) that allow the transport, mixing, or sampling of the liquid droplets all on the paper surfaces.[45]

■ CONCLUSIONS

We have demonstrated for the first time a powerful, new efficient and easy photochemical approach utilizing the photochemistry of diazirine-modified HFPS to imposing highly effective water barrier coatings on two model substrates: cotton and paper. Evidence presented here suggests that the photosensitive salt was covalently grafted onto the cotton and paper surfaces via the generated carbene intermediate by insertion into one of the surface-active groups (likely O−H). This work represents a new class of materials for forming hydrophobic coatings that marry the recently demonstrated hydrophobic character of the HFPS to a diazirine moiety as a photoactivated tethering agent.[49] Like the more ubiquitous diazo and azide substrates used in materials chemistry, this work further demonstrates that the diazirine as an emerging new platform for material modification. The diazirine-HFPS was prepared in a convergent synthesis, bringing the two task specific moieties together in the final step. The materials are easy to prepare and can be made in large quantities. The phosphine precursor can be prepared in our laboratory in the 100 g−1 kg scale but is made commercially in tanker car quantities. The synthesis of the diazirine, while requiring several steps to prepare, is routine and can be made in multigram quantities.[50] While the applications of robust hydrophobic coatings on cotton and other fabrics (water-proofing) and paper (document protection) are fairly obvious, because of the high reactivity of the carbene intermediate, this protocol can be used to form robust hydrophobic coatings on a host of materials including glass, CNT, graphene, diamond, hair, and other fabrics, to name a few. These studies along with a systematic examination of altering the ligands of the HFPS and demonstration of the photopatterning allowed by this method are currently being examined.

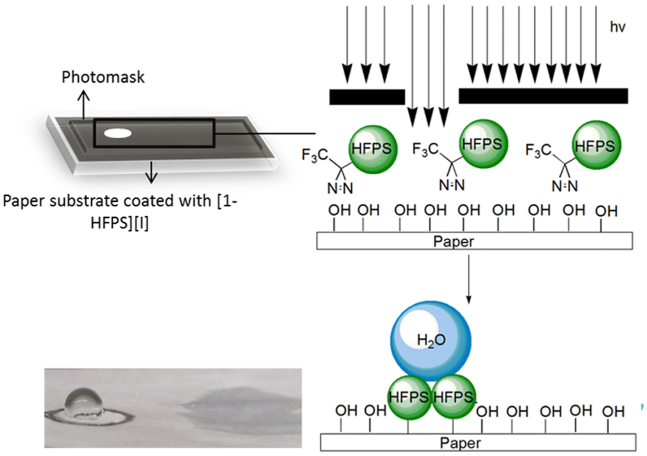


Figure 4. Cartoon of the macropatterning and a photograph of the paper surface after patterning. The spot on the left, indicated by the penciled circle, is where the mask let light through. The spot on the right is where the mask was dark.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full experimental details and characterization of compounds 1-HFPS and 1-PMe$_3$S, control reaction products, SEM of treated and untreated paper and cotton samples, WCA measures on cotton and paper samples, also as a function of washing cycle, and a movie showing the water beading effect. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: mworkent@uwo.ca (M.S.W.); pragogna@uwo.ca (P.J.R.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) and The University of Western Ontario, WorldDiscoveries@Western.

Cytec is thanked for the preparation of initial supplies of the phosphine.

REFERENCES

(1) Li, X.; Tian, J.; Garnier, G.; Shen, W. Fabrication of Paper-Based Microfluidic Sensors by Printing. *Colloids Surf., B* **2010**, *76*, 564−570.

(2) Ma, M.; Hill, R. M. Superhydrophobic Surfaces. *Curr. Opin. Colloid Interface Sci.* **2006**, *11*, 193−202.

(3) Blossey, R. Self-Cleaning Surfaces- Virtual Realities. *Nat. Mater.* **2003**, *2*, 301−306.

(4) Bahners, T.; Textor, T.; Opwis, K.; Schollmeyer, E. Recent Approaches to Highly Hydrophobic Textile Surfaces. *J. Adhes. Sci. Technol.* **2008**, *22*, 285−309.

(5) Samyn, P.; Schoukens, G.; Vonck, L.; Stanssens, D.; Abbeele, H. V. D. How thermal curing of an organic paper coating changes topography, Chemistry and Wettability. *Langmuir* **2011**, *27*, 8509−8521.

(6) Latthe, S. S.; Gurav, A. B.; Maruti, S. C.; Vhatkar, R. S. Recent Progress in Preparation of Superhydrophobic Surfaces: A Review. *JSEMAT* **2012**, *2*, 76−94.

(7) Li, X.-M.; Reinhoudt, D.; Crego-Calama, M. What Do We Need for a Superhydrophobic Surface? A Review on the Recent Progress in the Preparation of Superhydrophobic Surfaces. *Chem. Soc. Rev* **2007**, *36*, 1350−1368.

(8) Wang, H.; Fang, J.; Cheng, T.; Ding, J.; Qu, L.; Dai, L.; Wang, X.; Lin, T. One-Step Coating of Fluoro-Containing Silica Nanoparticles for Universal Generation of Surface Superhydrophobicity. *Chem. Commun.* **2008**, 877−879.

(9) Yu, M.; Gu, G. T.; Meng, W. D.; Qing, F. L. Superhydrophobic Cotton Fabric Coating Based on a Complex Layer of Silica Nanoparticles and Perfluorooctylated Quaternary Ammonium Silane Coupling Agent. *Appl. Surf. Sci.* **2007**, *253*, 3669−3673.

(10) Vilčnik, A.; Jerman, I.; Vuk, A. S.; Koželj, M.; Orel, B.; Tomšič, B.; Simončič, B.; Kovač, J. Structural Properties and Antibacterial Effects of Hydrophobic and Oleophobic Sol-Gel Coatings for Cotton Fabrics. *Langmuir* **2009**, *25*, 5869−5880.

(11) Plechkova, N. V.; Seddon, K. R. Applications of Ionic Liquids in the Chemical Industry. *Chem. Soc. Rev.* **2008**, *37*, 123−150.

(12) Merrigan, T. L.; Bates, E. D.; Dorman, S. C.; Davis, J. H., Jr. New Fluorous Ionic Liquids Function as Surfactants in Conventional Room-Temprature Ionic Liquids. *Chem. Commun.* **2000**, 2051−2052.

(13) Emnet, C.; Weber, K. M.; Vidal, J. A.; Consorti, C. S.; Stuart, A. M.; Gladysza, J. A. Synthesis and Properties of Fluorous Quaternary Phosphonium Salts that Bear Four Ponytails; New Candidates for Phase Transfer Catalysts and Ionic Liquids. *Adv. Synth. Catal.* **2006**, *348*, 1625−1634.

(14) Tindale, J. J.; Ragogna, P. J. Highly Fluorinated Phosphonium Ionic Liquids: Novel Media for the Generation of Superhydrophobic Coatings. *Chem. Commun.* **2009**, *14*, 1831−1833.

(15) Tindale, J. J.; Mouland, K. L.; Ragogna, P. J. Thiol Appended, Fluorinated Phosphonium Ionic Liquids as Covalent Superhydrophobic Coatings. *J. Mol. Liq.* **2010**, *152*, 14−18.

(16) Griffiths, J.-P.; Moloney, M. G. Surface functionalization using arylcarbene reactive intermediates. PCT/GB2006/000139.

(17) Moloney, M. G. Functionalized Polymers by Chemical Surface Modification. *J. Phys. D: Appl. Phys.* **2008**, *41*, 174006−174014.

(18) Leonard, D.; Moloney, M. G.; Thompson, C. Chemical modification of materials by reaction with diaryl diazomethanes. *Tetrahedron Lett.* **2009**, *50*, 3499−3502.

(19) Griffiths, J.-P.; Maliha, B.; Moloney, M. G.; Thompson, A. L.; Hussain, I. Surface Functional Polymers by Post-Polymerization Modification using Diarylcarbenes: Introduction, Release and Regeneration of Hydrogen Peroxide and Bactericidal Activity. *Langmuir* **2010**, *26*, 14142−14153.

(20) Ito, Y. Photoimmobilization for Microarrays. *Biotechnol. Prog.* **2006**, *22*, 924−932.

(21) Yan, M.; Ren, J. Covalent Immobilization of Polypropylene Thin Films. *J. Mater. Chem.* **2005**, *15*, 523−527.

(22) Liu, L. H.; Yan, M. Simple Method for the Covalent Immobilization of Graphene. *Nano Lett.* **2009**, *9*, 3375−3378.

(23) Blencowe, A.; Cosstick, K.; Hayes, W. Surface Modification of Nylon 6,6 Using a Carbene Insertion Approach. *New J. Chem.* **2006**, *30*, 53−58.

(24) Ismaili, H.; Lagugne-Labarthet, F.; Workentin, M. S. Covalently Assembled Gold Nanoparticle-Carbon Nanotube Hybrids via a Photoinitiated Carbene Addition Reaction. *Chem. Mater.* **2011**, *23*, 1519−1525.

(25) Ismaili, H.; Workentin, M. S. Covalent Diamond-Gold Nanojewel Hybrids via Photochemically Generated Carbenes. Kantzas, T.; Workentin, M. S. *Chem. Commun.* **2011**, *47*, 7788−7790.

(26) Ismaili, H.; Geng, D.; Kantzas, T. T.; Sun, X.; Workentin, M. S. Light activated covalent formation of gold nanoparticle(AuNP)-graphene and AuNP-glass composites. *Langmuir* **2011**, *27*, 13261−13268.

(27) Zhao, Y.; Zhiguang, X.; Wang, X.; Lin, T. Photoreactive Azido-Containing Silica Nanoparticle/Polycation Multilayers: Durable Superhydrophobic Coating on Cotton Fabrics. *Langmuir* **2012**, *28*, 6328−6335.

(28) Brunner, J.; Senn, H.; Richards, F. M. 3-Trifluoromethyl-3-phenyldiazirine: A New Carbene Generating Group for Photolabeling Reagents. *J. Biol. Chem.* **1980**, *255*, 3313−3318.

(29) Hashimoto, M.; Hatanaka, Y. Recent Progress in Diazirine-Based Photoaffinity Labeling. *Eur. J. Org. Chem.* **2008**, 2513−2523.

(30) Blencowe, A.; Hayes, W. Development and Application of Diazirines in Biological and Synthetic Macromolecular Systems. *Soft Matter.* **2005**, *1*, 178−205.

(31) Admasu, A.; Gudmundsdóttir, A. D.; Platz, M. S.; Watt, D. S.; Kwiatkowski, S.; Crocker, P. J. A Laser Flash Photolysis of P-tolyl(trifluoromethyl)carbene. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1093−1099.

(32) Das, J. Aliphatic Diazirines as Photoaffinity Probes for Proteins: Recent Developments. *Chem. Rev.* **2011**, *1111*, 4405−4417.

(33) Blencowe, A.; Blencowe, C.; Cosstick, K.; Hayes, W. A Carbene Insertion Approach To Functionalised Poly(ethylene oxide)-based Gels. *React. Funct. Polym.* **2008**, *68*, 868−875.

(34) Blencowe, A.; Caiulo, N.; Cosstick, K.; Fagour, W.; Heath, P.; Hayes, W. Synthesis of Hyperbranched Poly(aryl ether)s via Carbene Insertion Processes. *Macromolecules* **2007**, *40*, 939−949.

(35) Blencowe, A.; Fagour, W.; Blencowe, C.; Cosstick, K.; Hayes, W. Synthesis of Hyperbranched Poly(aryl amine)s via a Carbene Insertion Approach. *Org. Biomol. Chem.* **2008**, *6*, 2327−2333.

(36) Lawrence, E. J.; Wildgoose, G. G.; Aldous, L.; Wu, Y. A.; Warner, J. H.; Compton, R. G.; McNaughter, P. D. 3-Aryl-3-(trifluoromethyl)diazirine as Versetile Photoactivated "Linker" Molecules for the Improved Covalent Modification of Graphitic and Carbon Nanotube Surfaces. *Chem. Mater.* **2011**, *23*, 3740−3751.

(37) Wildgoose, G. G.; Lawrence, E. J.; Bear, J. C.; McNaughter, P. D. Enabling Electrochemical Studies of Chemically-Modified Carbon Nanotubes in Non-Aqueos Electrolysis Using Supermagnetic Nanoparticle-Nanotube Composites Co-Modified by diazirine Molecular Tethers. *Electrochem. Commun.* **2011**, *13*, 1139−1142.

(38) Ismaili, H.; Lee, S.; Workentin, M. S. Diazirine-Modified Gold Nanoparticle: Template for Efficient Photoinduced Interfacial Carbene Insertion Reactions. *Langmuir* **2010**, *26*, 14958−14964.

(39) The reaction of the bromo derivative takes several weeks longer and subsequently results in some impurities due to the slow degradation of the diazirine under the conditions of the coupling reaction.

(40) Song, M.-G.; Sheridan, R. S. Regiochemical Substituent Switching of Spin States in Aryl(trifluoromethyl)carbenes. *J. Am. Chem. Soc.* **2011**, *133*, 19688−19690.

(41) Guo, Z.-G. Sticky Superhydrophobic Surface. *Appl. Phys. Lett.* **2007**, *90*, 223111-1−223111-3.

(42) Feng, L.; Zhang, Y.; Xi, J.; Zhu, Y.; Wang, N.; Xia, F.; Jiang, L. Petal Effect: A Superhydrophobic State with High Adhesive Force. *Langmuir* **2008**, *24*, 4114−4119.

(43) Geim, A. K.; Dubonos, S. V.; Grigorieva, I. V.; Novoselov, K. S.; Zhukov, A. A.; Shapoval, S. YU. Microfabricated Adhesive Mimicking Gecko Foot-Hair. *Nat. Mater.* **2003**, *2*, 461−463.

(44) Martinez, A. W.; Phillips, S. T.; Whitesides, G. M. Three-Dimensional Microfluidic Devices Fabricated in Layered Paper and Tape. *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105*, 19606−19611.

(45) Balu, B.; Berry, A. D.; Hess, D. W.; Breedveld, V. Patterning of Superhydrophobic Paper to Control the Mobility of Microlitre Drops for Two-Dimensional Lab-on-Paper Applications. *Lab Chip* **2009**, *9*, 3066.

(46) Martinez, A. W.; Phillips, S. T.; Butte, M. J.; Whitesides, G. M. Patterned Paper as a Platform for Inexpensive, Low-Volume, Portable Bioassays. *Angew. Chem., Int. Ed.* **2007**, *46*, 1318−1320.

(47) Martinez, A. W.; Phillips, S. T.; Wiley, B. J.; Gupta, M.; Whitesides, G. M. FLASH: A rapid method for prototyping paper-based microfluidic devices. *Lab Chip* **2008**, *8*, 2146−2150.

(48) Yager, P.; Edwards, T.; Fu, E.; Helton, K.; Nelson, K.; Tam, M. R.; Weigl, B. H. Microfluidic diagnostic technologies for global public health. *Nature* **2006**, *442*, 412−418.

(49) Lubbock, B. W.; Ismaili, H.; Dube, J. W.; Ragogna, P. J.; Workentin, M. S. US Provisional Patent 61/592,418, Jan 2012.

(50) Bentz, E. L.; Gibson, H.; Hudson, C.; Moloney, M. G.; Seldon, D. A.; Wearmouth, E. S. Aryldiazirine-Modified Pyroglutamates: Photoaffinity Lables for Glutamate. *Synlett* **2006**, 0247−0250.