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Ultra-fast and Sustainable Catalyst-Free Chemical Functionalization of Cellulose Paper with Diazo Compounds – Application to Hydrophobic Materials

Samuel Calderoni, Guillaume Bretel, Medy C. Nongbe, Marie Denis, Erwan Le Grogne, François-Xavier Felpin*

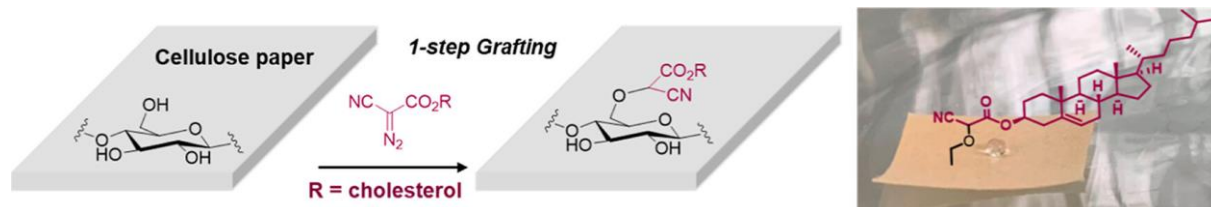
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■ ABSTRACT GRAPHIC



■ ABSTRACT

This work describes an ultra-fast and sustainable approach for the covalent functionalization of cellulose paper using diazo compounds under catalyst free conditions. The methodology requires *ca.* 10 min of reaction to attain a level of grafting in the range of 8 to 17% which allows for significant modification of the physical properties of the cellulosic material without compromising its integrity and strength. As an application, the work emphasizes on the preparation of plastic- and fluorine-free hydrophobic cellulose paper. The grafting of hydrophobic diazo compounds based on cholesterol, an inexpensive, bio-sourced, abundant, and non-toxic compound, resulted in a material with excellent hydrophobicity and strong

oleophobicity, making it suitable for applications in food packaging and textiles as an alternative to plastic and fluorine solutions.

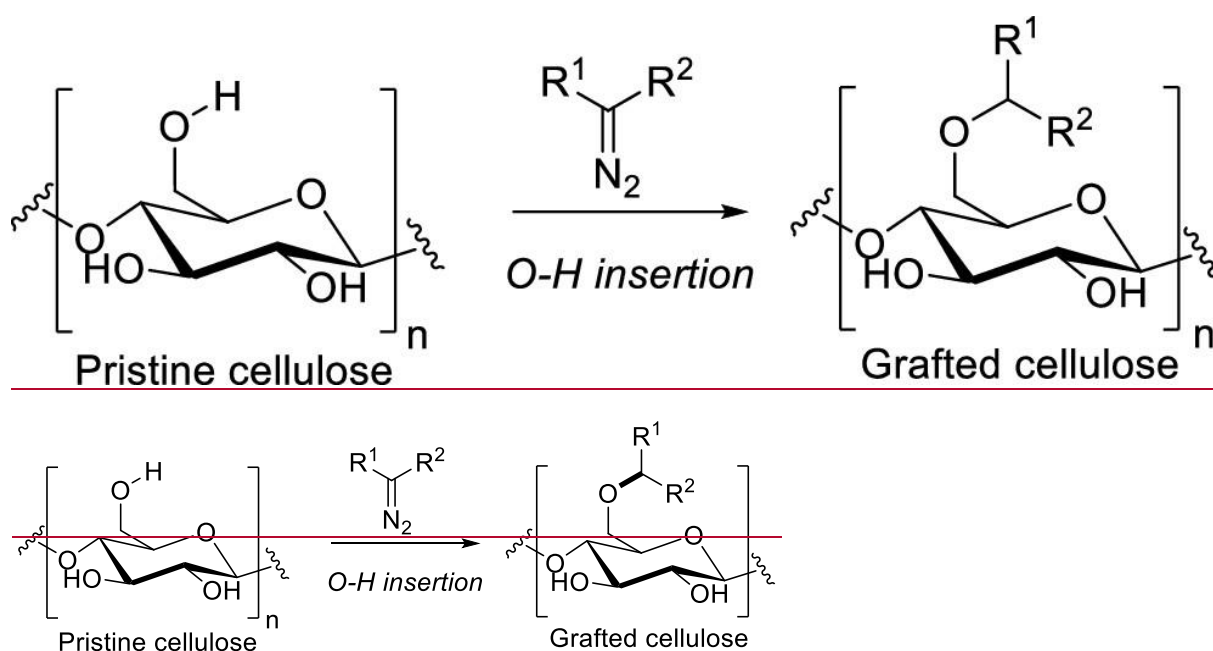
■ INTRODUCTION

Cellulose is a polysaccharide consisting of a supramolecular arrangement of linear chains of β -(1-4)-linked D-glucose units through a dense hydrogen bond network.¹⁻³ Cellulose is a sustainable biomaterial par excellence due to its biocompatibility, low cost, thermal and chemical stability, and worldwide availability with an estimated annual bioproduction by the vegetal kingdom of more than 10^{12} tons.⁴ While fabric and paper are the most important uses in volume, cellulose also enters in the fabrication of high-value materials⁵ with applications in catalysis,⁶⁻⁸ sensing,⁹⁻¹³ remediation,¹⁴⁻¹⁷ self-cleaning materials,¹⁸⁻²¹ medicine²²⁻²⁷ and covalent printing.^{20,28,29}

The chemical functionalization of the hydroxyl groups of the glucose units is an important requirement to prepare original materials with physical properties distinct from pristine cellulose.³⁰⁻³² Functionalizing pristine cellulose through chemical synthesis is not trivial as the dense hydrogen bond network strongly affect both the reactivity of hydroxyl groups and limits the solubility of cellulose in most solvents including water. Cellulose pulp and cellulose powder can be solubilized in tailored media associating a polar solvent (DMF, DMA or DMSO) with a dissolved salt (LiCl or TBAF).³³ Alternatively, the use of ionic liquid have also been described to efficiently dissolve cellulose.^{34,35} The use of these specific solvents allows to partially break the hydrogen bond network, to increase the reactivity of hydroxyl groups and thereby to facilitate chemical functionalization. However, this approach destroys the initial properties of the material and additional steps are required to restore the supramolecular arrangement. Functionalizing cellulose fibers as paper, fabric or powder is even more difficult as the inherent inertness of cellulose is amplified by the bulk nature of these materials due to mass transfer limitations and the use of dissolving media is prohibited, otherwise the physical integrity of the materials would be destroyed. The direct chemical functionalization of bulk cellulose mainly relies on esterification^{18,36-38} and silanization processes of C6-alcohols.^{39,40} While the simplicity of execution and the good degree of substitution (>10%) generally obtained are the main assets of these approaches, they are poorly time efficient and the corresponding ester or siloxane linkage suffer from a modest stability to hydrolytic conditions. This later shortcoming can be addressed through the tosylation of C6-alcohols followed by the displacement of the tosylate

groups with amines or azide anions; this approach allows the creations of stable C-N bonds but requires at least two chemical steps.²¹

The development of strategies compatible with industrial settings remains a great challenge since the chemical functionalization of bulk cellulose has to be i/ fast enough to be compatible with a high production rate, ii/ direct, in one chemical step and iii/ environmentally suitable in the industrial setting. In the current contribution we disclose an uncovered strategy for the fast chemical functionalization of bulk cellulosic materials through the use of diazo compounds, addressing most drawbacks of traditional approaches (Scheme 1).



Scheme 1. General strategy for the covalent grafting of cellulose with diazo compounds

■ MATERIAL AND METHODS

General remarks. All reagents, starting materials and solvents were obtained from commercial suppliers and used as such without further purification, unless otherwise noted. Whatman grade 6 filter paper (42.5 mm Ø) with a grammage of *ca.* 100 g/m² was used as cellulose source. High-field ¹H and ¹³C NMR spectra were recorded at 400 or 300 MHz and 100 or 75 MHz, respectively. ¹H, ¹³C spectra were referenced to the internal deuterated solvent (CDCl₃) at 7.26 and 77.16 ppm, respectively. Coupling constants were measured in Hertz. ¹⁹F spectra were recorded at 400 MHz. All chemical shifts were quoted in ppm, relative to TMS, using the residual solvent peak as a reference standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br =

broad. FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer in the ATR mode. Wavelengths of maximum absorbance (ν_{\max}) are shown in wave numbers (cm^{-1}). High resolution mass spectrometry (HRMS) was recorded on a Xevo G2-XS QTOF spectrometer equipped with either an orthogonal electrospray interface (ESI) or an atmospheric solid analysis probe (ASAP) for the direct analysis of samples by atmospheric pressure ionization (ASAP+ or ASAP-). Reactions were monitored by thin layer chromatography (TLC) with 0.25 mm pre-coated silica gel plates (60 F254), and visualization was accomplished with UV light at 254 nm, or with KMnO_4 as developing agent. Flash column chromatography was performed using silica gel 60 (40–63 μm). Scanning electron microscopy (SEM) images were recorded with a JEOL 7600 F. X-ray photoelectron spectroscopy was performed on a Thermo Fisher Scientific K-ALPHA spectrometer which was used for disk surface analysis with a monochromatized Al $\text{K}\alpha$ source ($h\nu = 1486.6 \text{ eV}$) and a 200 μm spot size. A pressure of 10^{-7} Pa was maintained in the chamber during analysis. The full spectra (0–1150 eV) were obtained at a constant pass energy of 200 eV, and high-resolution spectra at a constant pass energy of 40 eV. Charge neutralization was required for all insulating samples. High resolution spectra were fitted and quantified using the AVANTAGE software provided by Thermo Fisher Scientific. Elemental analyses were performed on a Thermo Fisher Scientific Flash 2000 CHNS organic elemental analyzer.

4-toluenesulfonyl azide. Sodium azide (5.72 g, 88 mmol) was added to a mixture of ethanol/water (6/1, 260 mL). After dissolution of the solid, *p*-toluenesulfonyl chloride (15.25 g, 80 mmol) dissolved in 200 mL of acetone was added to the reaction mixture and the resulting solution was stirred at 25 °C for 16h. After filtration and concentration under reduced pressure, the mixture was diluted with dichloromethane (200 mL), washed with water (3 x 100 mL), dried with MgSO_4 and concentrated under reduced pressure to give 4-toluenesulfonyl azide as a colourless oil (14.98 g, 95 %). IR (ATR) ν 2124, 1597, 1369, 1163, 1086, 815, 744, 658, 588, 533 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.84 (d, 2H, $J = 7,8 \text{ Hz}$), 7.40 (d, 2H, $J = 7,4 \text{ Hz}$), 2.48 (s, 3H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 146.3, 135.6, 130.4 (2C), 127.7 (2C), 21.9 HRMS (ASAP+) m/z $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_7\text{H}_8\text{N}_3\text{O}_2\text{S}$ 198.0337; Found 198.0332.

Perfluoro-1-butanesulfonyl azide. A suspension of sodium azide (1.08 g, 16.6 mmol) in methanol (25 mL) under argon atmosphere was cooled to 0°C. Perfluoro-1-butanesulfonyl fluoride (2.97 mL, 16.6 mmol) was added in one portion. The reaction mixture was allowed to warm to 25 °C, and stirred for 22h. The mixture was poured onto ice (30 mL) and the solution

obtained was transferred to a test tube. The cloudy organic bottom layer was washed several times with distilled water. The process was repeated until a clear fluoruous layer was obtained. Removal of the aqueous layer with a syringe gave **7**, as a dry colorless oil (3.85 g, 71%). No further purification was needed. Characterization data were in accordance with the literature.⁴¹ ¹⁹F NMR (400 MHz, CDCl₃) δ -81.13 (tt, 3H, $J = 9.8$ Hz, $J = 2.2$ Hz), -109.64 (m, 2H), -121.12 (m, 2H), -126.16 (m, 2H). IR (ATR) ν 2150, 1421, 1186, 1140, 696, 579, 561, 529 cm⁻¹.

Ethyl 2-cyano-2-diazoacetate (1). To a solution of ethyl 2-cyanoacetate (46.096 mg, 0.4075 mmol) in dry dichloromethane (1 mL) was added triethylamine (45.4 mg, 0.062 mL, 0.448 mmol). The reaction mixture was cooled to 0°C and perfluoro-1-butanesulfonyl azide (158.98 mg, 0.489 mmol) was added dropwise, and stirring was maintained for 15 minutes at 25 °C. The reaction mixture was treated with a saturated aqueous sodium bicarbonate solution (3 mL). Then, the organic layer was washed with a saturated aqueous sodium bicarbonate solution (5 x 3 mL), dried over NaSO₄ and concentrated under reduced pressure to give **1** as a yellow oil (34.7 mg, 61 %). IR (ATR) ν 2231, 2130, 1714, 1293, 1246, 1127, 1014, 739 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 4.34 (q, 2H, $J = 7.2$ Hz), 1.33 (t, 3H, $J = 7.2$ Hz). ¹³C NMR (CDCl₃, 75 MHz) δ 161.3, 107.4, 77.36, 63.6, 14.4.

α -Diazo- β -oxobenzeneopropanenitrile (2) To a solution of 3-oxo-3-phenylpropanenitrile (0.946 g, 6.52 mmol) in dry dichloromethane (16 mL) was added triethylamine (0.726 g, 1 mL, 7.17 mmol). The reaction mixture was cooled to 0°C and perfluoro-1-butanesulfonyl azide (2.54 g, 7.82 mmol) was added dropwise, and stirring was maintained for 15 minutes at 25 °C. The reaction mixture was treated with a saturated aqueous sodium bicarbonate solution (20 mL). Then, the organic layer was washed with a saturated aqueous sodium bicarbonate solution (5 x 20 mL), dried over Na₂SO₄ and concentrated under reduced pressure to give **2** as a yellow oil (0.690 g, 62 %). IR (ATR) ν 2140, 1633, 1449, 1279, 1243, 1148, 917, 693 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 7.88 (m, 2H), 7.63 (m, 1H), 7.51 (m, 2H). ¹³C NMR (CDCl₃, 75 MHz) δ 183.0, 134.7, 134.0, 129.0 (2C), 128.2 (2C), 109.3, 77.36.

2-diazo-*N,N*-dimethyl-3-oxobutanamide (3) To a solution of *N,N*-dimethyl-3-oxobutanamide (1.29 g, 10 mmol) in acetonitrile (10 mL) was added triethylamine (1.31 g, 1.81 mL, 13 mmol). The reaction mixture was cooled to 0°C and a solution of 4-toluenesulfonyl azide (2.17 g, 11 mmol) in acetonitrile (10 mL) was added dropwise, and stirring was maintained for 24 h at 25 °C. The reaction mixture was concentrated under reduced pressure

and flushed with nitrogen. Water (20 mL) was added and the aqueous layer was extracted with diethyl ether (2 x 20 mL). The combined organic layers were washed with brine (20 mL), dried over MgSO₄ and concentrated under reduced pressure. Purification by flash chromatography on silica gel (dichloromethane) gave **3** as a yellow solid (1.21 g, 78 %). IR (ATR) ν 2100, 1625, 1494, 1388, 1261, 1046, 892 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 2.99 (s, 6H), 2.33 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz) δ 189.7, 161.5, 73.5, 37.6 (2C), 27.4. HRMS (ES-) *m/z* [M - H]⁻ Calcd for C₆H₉N₃O₂ 154.0617; Found 154.0624.

(3 β)-Cholest-5-en-3-yl-2-cyanoacetate (5). A suspension of cyanoacetic acid (6.60 g, 77.6 mmol) in dry CH₂Cl₂ (240 mL) under argon atmosphere was cooled to 0 °C. Oxalyl chloride (9.98 mL, 116.4 mmol) was added in portion and dimethylformamide (1.2 mL) was added over 1 min. The reaction mixture was allowed to warm to 25 °C, and stirred for 2 hours until completion of the reaction. The excess of oxalyl chloride was then evaporated under reduced pressure to yield the desired acyl chloride as a brown viscous oil. A solution of cholesterol **4** (3.00 g, 7.8 mmol) in dry CH₂Cl₂ (180 mL) under argon atmosphere was cooled to 0°C. Triethylamine (3.24 mL, 23.3 mmol) was added in one portion, and a solution of the acyl chloride previously obtained in dry CH₂Cl₂ (60 mL) was added over 5 min. The reaction mixture was allowed to warm to 25 °C and stirred for 16h. The reaction mixture was treated with water (600 mL). The aqueous phase was extracted with CH₂Cl₂ (3 × 200 mL). The organic layers were combined, dried over Na₂SO₄ and concentrated under reduced pressure. Purification by flash chromatography on silica gel (cyclohexane/ethyl acetate – 9:1) gave **5** as a white powder (3.33 g, 94%). mp 179-182 °C. IR (ATR) ν 2935, 1735, 1466, 1339, 1206, 1007, 927 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 5.39 (m, 1H), 4.70 (m, 1H), 3.42 (s, 2H), 2.37 (m, 2H), 2.05-1.77 (m, 5H) 1.71-1.43 (m, 7H), 1.42-1.03 (m, 12H), 1.02 (s, 3H), 1.01-0.94 (m, 2H), 0.92 (d, 3H, *J* = 6.5 Hz), 0.87 (d, 3H, *J* = 1.7 Hz), 0.86 (d, 3H, *J* = 1.7 Hz) 0.68 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.4, 139.1, 123.5, 113.2, 77.3, 56.8, 56.3, 50.2, 42.5, 39.9, 39.7, 37.9, 37.0, 36.7, 36.3, 35.9, 32.04, 31.99, 28.4, 28.2, 27.7, 25.2, 24.4, 24.0, 23.0, 22.7, 21.2, 19.4, 18.9, 12.0. HRMS (ASAP) *m/z* [M-H]⁻ Calcd for C₃₀H₄₆NO₂ 452.3529; Found 452.3534.

(3 β)-Cholest-5-en-3-yl-2-cyano-2-diazoacetate (6). A solution of **5** (3.22 g, 7.1 mmol) in dry CH₂Cl₂ (150 mL) under argon atmosphere was cooled to 0°C. Another solution of perfluoro-1-butanefluorobutyl azide (2.77 g, 8.5 mmol) in dry CH₂Cl₂ (80 mL) was added in one portion, and triethylamine (1.09 mL, 7.8 mmol) was added over 1 min. The reaction mixture was allowed to warm to 25 °C, and stirred for 3h until total consumption of starting material.

The reaction mixture was treated with a saturated aqueous sodium bicarbonate solution (80 mL). The organic layer was washed with a saturated aqueous sodium bicarbonate solution (5 × 80 mL), dried over Na₂SO₄, and concentrated under reduced pressure. Purification by flash chromatography on silica gel (cyclohexane/ethyl acetate – 9:1) gave **6** as a pale-yellow solid (3.38 g, 99%). mp 123-126 °C. IR (ATR) ν 2936, 2135, 1717, 1465, 1260, 1139, 735 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 5.40 (m, 1H), 4.77 (m, 1H), 2.39 (m, 2H), 2.05-1.77 (m, 5H) 1.73-1.45 (m, 7H), 1.43-1.04 (m, 12H), 1.03 (s, 3H), 1.01-0.93 (m, 2H), 0.92 (d, 3H, *J* = 6.6 Hz), 0.87 (d, 3H, *J* = 1.8 Hz), 0.86 (d, 3H, *J* = 1.8 Hz) 0.68 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.8, 139.1, 123.6, 107.6, 77.9, 77.4, 56.8, 56.3, 50.2, 42.5, 39.9, 39.7, 38.2, 37.0, 36.7, 36.3, 35.9, 32.05, 31.99, 28.4, 28.2, 27.9, 24.4, 24.0, 23.0, 22.7, 21.2, 19.4, 18.9, 12.0.

Procedure for the pretreatment of cellulose paper. Whatman grade 6 filter papers (14 cm², ca. 146 mg) was immersed in 2M NaOH aqueous solution (100 mL). After being stirred for 24 hours at 25 °C on an orbital agitator at a speed of 100 rpm, the piece of paper was washed 3 times with EtOH (50 mL) and stored in EtOH.

Procedure for the grafting of 6 on cellulose (Cell-4). On a Whatman grade 6 filter paper (1 cm², ca. 10 mg, 0.06 mmol) was deposited a 2M NaOH aqueous solution (20 μ L, 0.05 mmol). After 15 minutes at 25 °C, a solution of **6** in CH₂Cl₂ (1.5 M, 20 μ L, 0.03 mmol) was deposited on the flash-mercerized cellulose paper. After 15 minutes, the piece of paper was sonicated two times with water, then two times with toluene and dried under vacuum to give **Cell-4** (LG = 5%).

■ RESULTS AND DISCUSSIONS

Methodology development. Diazo compounds are a class of highly reactive compounds with the general formula of R¹R²C=N₂. They are considered as carbene or metal carbenoids equivalents after the release of N₂.⁴² With the exception of diazomethane, aliphatic diazo compounds (R¹, R² = alkyl groups) are rarely exploited in synthesis because they are generally too unstable and potentially explosive.⁴³ By contrast, stabilized diazo compounds by electron-withdrawing substituents (R¹, R² = ketones, esters, nitriles, sulfones, phosphonates and aromatic rings) can be safely handled and even purified by chromatography.⁴⁴ Stable diazo compounds are very appealing and popular reagents because they display a large spectrum of reactivities and, as carbene equivalents, they are prone to insert into C-H or X-H bonds (X =

Si, N, S, O).^{45–50} We reasoned that the insertion of diazo compounds into the O-H bonds of the hydroxyl groups of the glucose units could offer a fast and direct access to functionalized cellulosic materials. In addition, the use of diazo compounds offers a number of benefits in the context of green chemistry. Indeed, transformations using diazo compounds are often associated with simple experimental conditions, requiring no additives such as base or ligand and N₂ is the only released by-product.

The chemical functionalization of pristine cellulose paper with diazo compound **1** was selected as benchmark surface functionalization to optimize the level of grafting (LG) through the variation of experimental conditions. Prior to any chemical modification, a pre-activation step of the pristine cellulose paper was required to increase the reactivity of hydroxyl groups. This activation, called mercerization, involves breaking the hydrogen bond network with aqueous NaOH solution, thereby exposing the more ordered regions to chemical functionalization. The activated paper sheets can be stored in EtOH within an inert atmosphere for several days before being employed in the functionalization process.

In the initial standard grafting procedure, a piece of paper (10 mg, *ca.* 1 cm²) immersed in a solution of Rh₂(OAc)₄ (1 mol%) was treated with a solution of ethyl 2-cyano-2-diazoacetate **1** (3 equivalents per glucose unit). After the required time for grafting, the piece of paper was thoroughly washed to remove unreacted diazo **1** and residual rhodium species. The level of grafting was assessed by elemental analysis. A screening of different solvents was initially carried out for 1 hour of grafting time at room temperature in the presence of Rh₂(OAc)₄ as catalyst and 3 equivalents of diazo **1** (Entries 1-5). From the set of 5 solvents selected for their compatibility with diazo compounds, we did not observed much differences as the calculated LG was in the range of 6 to 9%. An increase of the temperature allowed the reduction of the grafting time to only 10 minutes (Entry 6). During control experiments, we were surprised to see that the grafting also occurred in toluene at a similar level without rhodium catalyst (Entries 7-8). This unexpected result is still unclear at this stage but we observed a similar behavior with diazonium salts which spontaneously released nitrogen when deposited on the surface of cellulose paper (unpublished work). The possibility to graft diazo compound on cellulose paper under catalyst-free conditions is a formidable opportunity to develop a sustainable and affordable surface functionalization. Following this perspective, we evaluated the possibility to functionalize cellulose paper without any catalyst and with the minimum amount of solvent. In this frame, a piece of mercerized cellulose paper was impregnated (instead of immersed) with a solution of diazo compound **1** (1 M, 0.5 equivalent) allowing the reduction by > 97% of the volume of solvent used. Gratifyingly, in these sustainable conditions, the grafting occurred with

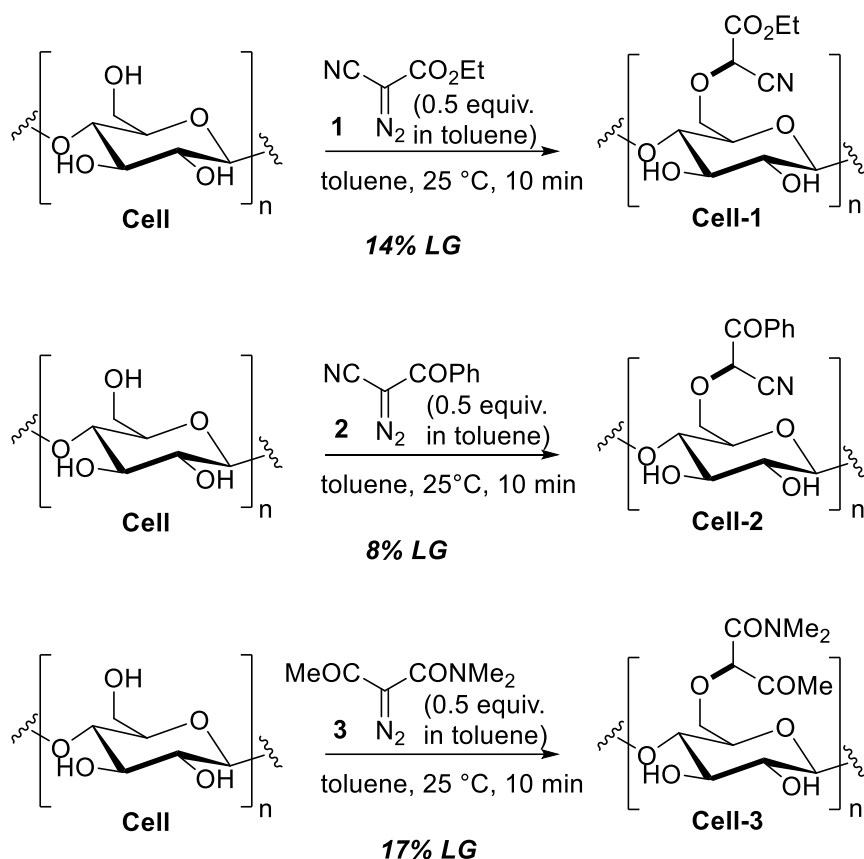
an increased level (14%) in only 10 minutes at 25 °C (Entry 9). A level of grafting of 14% means that an average of 1.4 alcohol functions were grafted every 10 glucose units.

Table 1. Optimization of the covalent grafting of cellulose fabric with diazo compound **1**

Entry	Solvent	Temp. (°C)	Time (min)	Diazo 1 (equiv.)	LG (%) ^a
1	CH ₂ Cl ₂	25	60	3	9
2	CH ₃ CN	25	60	3	6
3	EtOAc	25	60	3	8
4	C ₆ H ₆	25	60	3	8
5	C ₆ H ₅ -CH ₃	25	60	3	9
6	C ₆ H ₅ -CH ₃	100	10	3	10
7	C ₆ H ₅ -CH ₃	100	10	3	10 ^b
8	C ₆ H ₅ -CH ₃	25	10	1	11 ^b
9	C ₆ H ₅ -CH ₃	25	10	0.5	14 ^{b,c}

^a LG: Level of grafting. ^b no catalyst. ^c Solution of diazo deposited on the paper

Having optimized the experimental conditions with diazo **1**, we next focused on the grafting of a selection of diazo compounds on the cellulose backbone (Scheme 2).



Scheme 2. Covalent grafting of paper with diazo compounds

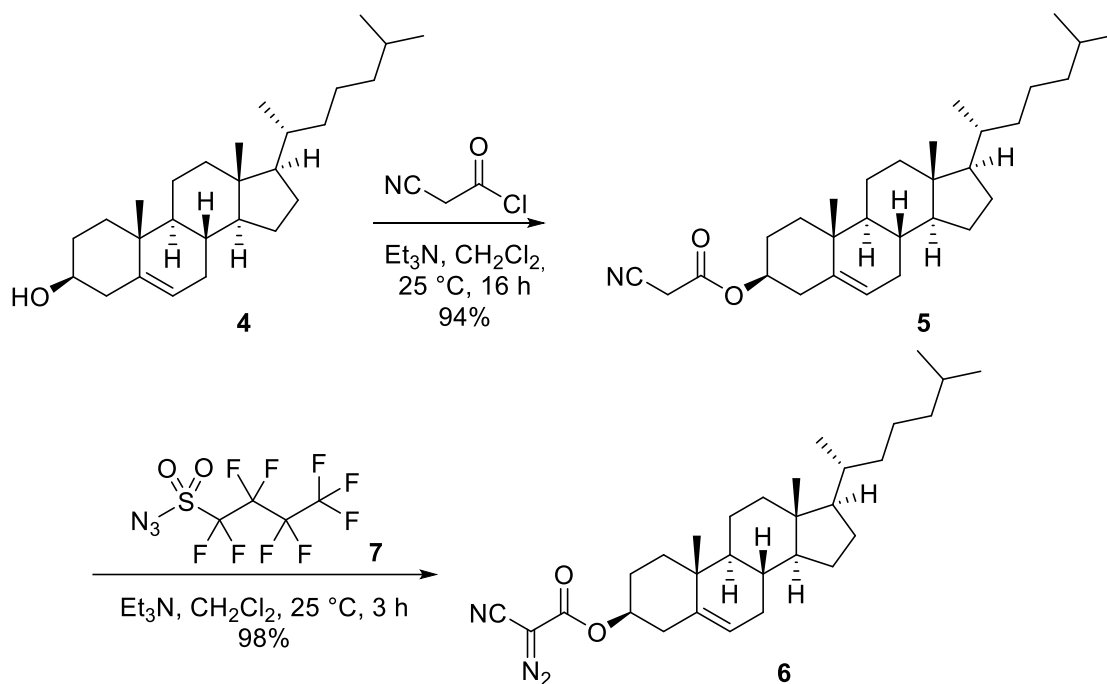
The results depicted in scheme 2 reveal a number of interesting features. First, whatever the diazo compound used, good levels of grafting are obtained, in the range of 8 to 17%. These values are in the ideal range to introduce a significant modification of the physical properties of the cellulosic material without compromising its physical integrity and strength. We previously showed that a level of grafting exceeding significant extent, weaken the cellulosic material due to a loss of cohesion of fibers, ultimately leading to a solubilization of cellulose in organic solvents.²¹ Second, several functional groups such as ketone, nitrile, ester and amide are well tolerated and allow further functionalization.

The grafting of diazo compounds **1-3** onto cellulose paper was monitored through FTIR spectroscopy, showing the appearance of carbonyl bands between 1630 and 1750 cm^{-1} (Figure S1). Additionally, the surface chemical modifications of the cellulose paper were followed using X-ray photoelectron spectroscopy (XPS). The survey scan spectra of **cell-1-3** show new peaks at ca. 397-400 eV assigned to the nitrogen atoms of the installed ether groups, confirming the successful grafting (Figure S2). The high resolution C1s spectra show a significant increase of the component corresponding to C=O bonds at 288.9-289.0 eV (Figure S3). Interestingly,

the grafting did not alter the fiber network; the average diameter of fibers was maintained in the range of 5-35 μm as determined by scanning electron microscopy (SEM), (Figure S4).

Preparation of hydrophobic cellulose paper. Hydrophobized cellulose recently emerged as a promising material for replacing plastic- and perfluorinated-based materials in food packing. Pristine cellulose being highly hydrophilic by nature, chemists invented several chemical approaches to reduce water adsorption.

Methods for the hydrophobization of cellulose paper rely on two main approaches.⁵¹ The first one is based on non-covalent coating mainly through inkjet printing,⁵²⁻⁵⁵ dip coating^{39,56-62} or spray coating,^{61,63,64} atomic layer deposition,⁶⁵ adsorption on cellulose pulp⁶⁶ and other coating processes.⁶⁷⁻⁶⁹ In most of these methods, the compounds used to afford hydrophobic cellulose are either wax, modified silica particles, alkyl ketene dimers (AKD), polystyrene (PS), polytetrafluoroethylene (PTFE) or other fluorinated products. With these approaches the physisorbed hydrophobic compounds frequently lack of stability upon intensive uses and most of the methods require two or more chemical steps, sometimes with drastic conditions involving supercritical CO_2 or plasma treatment. On the other hand, the covalent linkage of hydrophobic compounds on cellulose paper increase the robustness of the hydrophobic material. Most described methods are based on polymerization processes,⁷⁰ including atom transfer radical polymerization (ATRP),^{36,71} ring opening polymerization (ROP),^{37,72,73} or free radical polymerization (FRP)^{70,74,75} and reversible addition-fragmentation transfer (RAFT).⁷⁰ Other approaches affording covalent linkage of hydrophobic compounds on cellulose paper also involve click thiol-ene grafting⁷⁶⁻⁷⁸ or hybrid approaches based on nanocellulose functionalization followed by dip coating of cellulose fibers.^{18,79} Pre-functionalization of cellulose paper is needed in most of these current grafting methods, thus requiring at least two chemical steps. In addition, the use of metal catalyst or light irradiation is often mandatory. In this frame, capitalizing on our results related to the ultra-fast functionalization of cellulose paper, we delved into the hydrophobization of cellulose paper without pre-functionalization step, metal catalyst or light irradiation, through the use of diazo compounds, addressing most drawbacks of the existing methods. The objective was to create a hydrophobic material devoid of plastics or fluorine atoms.

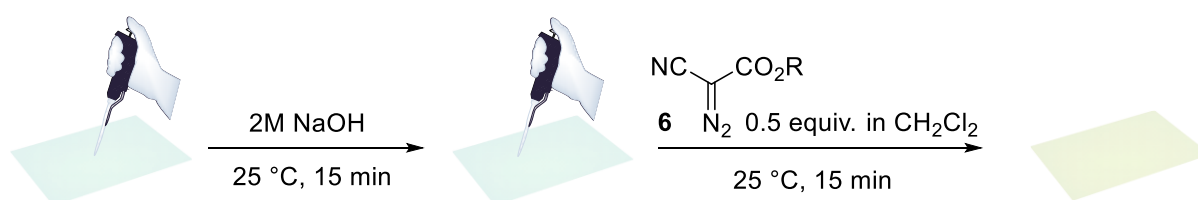


Scheme 3. Synthesis of cholesteryl 2-cyano-2-diazoacetate **6**.

In the search of a bio-sourced, abundant, inexpensive and non-toxic hydrophobic compound that could be grafted through our diazo approach we identified cholesterol **4** as an inexpensive by-product from the wool industry. The diazo derivative **6** was prepared in two steps from cholesterol **4** (Scheme 3). Cholesterol **4** was esterified using 2-cyanoacetyl chloride to afford cholesteryl 2-cyanoacetate **5**. Installation of the diazo moiety with perfluorobutanesulfonyl azide on cyanoacetate **5** provided cholesteryl 2-cyano-2-diazoacetate **6** in excellent yield over two steps (92%). The preparation of cholesteryl 2-cyano-2-diazoacetate **6** exhibited excellent repeatability and was run on a multi-gram scale without any safety concern since the differential scanning calorimetry (DSC) analysis showed that the diazo compound obtained was stable up to 120°C (Figure S5).

In our initial experiments, depicted in Table 1, the mercerization was performed by immersing the pieces of pristine cellulose paper in a 2M NaOH aqueous solution for 24 hours, followed by thorough washing with ethanol. However, we later developed a more convenient and faster procedure, while still maintaining a similar level of grafting (Scheme 4 and Figure 1A). This flash and unprecedented procedure involves a 15-minutes mercerization by deposition of a 2M NaOH aqueous solution on the surface of cellulose paper (20 $\mu\text{L}/\text{cm}^2$) followed by the addition of the diazo compound **6** (20 $\mu\text{L}/\text{cm}^2$). This procedure is not only faster, but it also significantly reduces the volume of solvent at the mercerization step by a

factor of 250 and avoids copious washing with EtOH (*ca.* 10 mL/cm²) after the mercerization step.



Scheme 4. General hydrophobic compound grafting strategy using a micropipette for surface functionalization

The grafting of cholesterol units on cellulose paper was confirmed by X-ray photoelectron spectroscopy (XPS). The survey scan spectra of **Cell-4** showed new peaks at *ca.* 398-399 eV assigned to the nitrogen atoms of the installed ether groups (Figure S6). The high resolution C1s spectrum shows a significant increase of the component corresponding to C-C bonds at 284.6 eV (Figure 1B *vs* 1D). As previously observed with the previous diazo compounds **1-3**, the grafting did not alter the fiber network; the average diameter of fibers was maintained in the range of 5-40 μm as determined by scanning electron microscopy, (Figure 1B *vs* 1D). The hydrophobicity was also characterized through the measurement of the contact angle with water. **Cell-4** displays an excellent hydrophobicity with a contact angle of 133° (Figure 1C), close to the super hydrophobicity level. Remarkably, **Cell-4** also displayed a strong oleophobicity with a contact angle of 115° with diiodomethane (Figure 1C). It should be noted that the same procedure applied to pristine cellulose paper resulted in an instantaneous absorption of both water and diiodomethane, leading to a contact angle of 0°. The fact that **Cell-4** is both hydrophobic and oleophobic means that it can be considered for applications in the field of food packaging and textiles where the search for hydrophobic and self-cleaning bio-sourced materials is crucial as an alternative to plastic solutions.

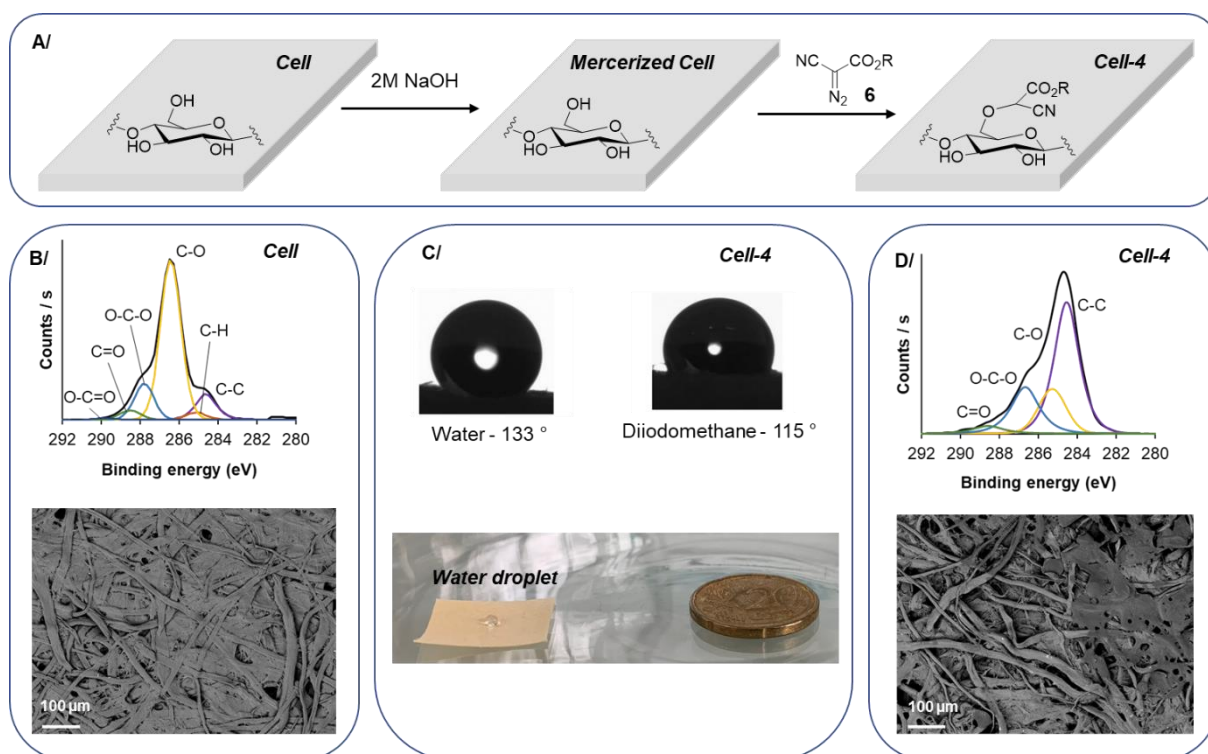


Figure 1. A/ General strategy for the hydrophobic patterning of **Cell**. B/ High resolution C1s spectrum and SEM image of **Cell**. C/ Hydrophobicity evaluation with images of water and diiodomethane droplets. D/ High resolution C1s spectrum and SEM image of **Cell-4**.

■ CONCLUSION

The catalyst-free chemical functionalization of bulk cellulose with diazo compounds is a promising strategy for the fast and environmentally friendly functionalization of cellulosic materials. Good levels of grafting can be achieved, leading to significant modifications of the physical properties of the cellulosic material without compromising its integrity and strength. The use of diazo compounds addresses the drawbacks of traditional approaches as it allows for the direct, one-step functionalization of cellulose without the need for pre-functionalization step, metal catalyst, or light irradiation. The successful grafting of a cholesterol-based diazo compound afforded hydrophobic and oleophobic cellulosic material without the use of any perfluorinated products or plastic membranes, demonstrating the powerfulness of this approach. Overall, our results suggest that this diazo-based grafting method has the potential to be a sustainable, affordable and versatile surface functionalization strategy for cellulosic materials.

■ ASSOCIATED CONTENT

The Supporting Information is available free of charge at https://pubs.acs.org/doi/suppl/10.1021/acsapm.4c01221/suppl_file/ap4c01221_si_001.pdf FTIR, XPS, SEM and DSC analyses. ^1H , ^{19}F and ^{13}C NMR spectra (PDF)

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Author contributions

FXF conceived the project, coordinated the efforts of the research team and secured the funding. SC and GB conducted chemical experiments FXF and ELG supervised chemical experiments. FXF and SC wrote the paper with input from all authors.

Notes

The authors declare no competing financial interest.

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