

# Silane Meets Click Chemistry: Towards the Functionalization of Wet Bacterial Cellulose Sheets

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The modification of cellulosic materials is of great interest in materials research. Wet bacterial cellulose sheets were modified by an alkoxy silane under mild conditions to make them accessible to click chemistry derivatization. For this purpose (3-azidopropyl)triethoxysilane was grafted covalently onto the cellulosic surface. The silanized bacterial cellulose sheets were characterized comprehensively by attenuated total reflectance FTIR spectroscopy, solid-state NMR spectroscopy, thermogravimetric analysis, SEM with energy-dispersive X-ray spectroscopy,

and elemental analysis. To demonstrate subsequent click chemistry functionalization, a new fluorophore based on fluorescein was synthesized and clicked to the silane-modified bacterial cellulose. The new method renders bacterial cellulose and other never-dried cellulosic materials susceptible to direct and facile functionalization in an aqueous medium without the need to work in water-free organic phases or to employ extensive protecting group chemistry and functional group interconversion.

## Introduction

Materials based on polysaccharides, in particular cellulose, have received wide attention recently because of their natural abundance and their intrinsic properties, such as biodegradability, renewability, and environmental friendliness.<sup>[1]</sup> In addition to plant cellulose used widely, bacterial cellulose (BC) represents a relatively new starting material both for industrial applications and research.

BC is synthesized in large quantities by *Gluconacetobacter xylinum*.<sup>[2]</sup> It has been used for a long time in the food industry as a dessert in Asian cuisine, so-called nata de coco.<sup>[3]</sup> In comparison to plant cellulose, BC (often called microbial cellulose) possesses some very distinct properties: it is highly pure cellulose because hemicelluloses and lignin are absent, it has a very high water retention capacity, high crystallinity, very high degree of polymerization of the exclusively linear polymer, and thus high tensile strength. Moreover, its production is relatively simple and chemical identity with plant cellulose is given.<sup>[2b,4]</sup>

An important application of BC, which is already available commercially, includes wound dressings.<sup>[5]</sup> A commercialized product example is Suprasorb X (Lohmann and Rauscher GmbH, Germany). Further potential areas of application are, for

example, antimicrobial surfaces<sup>[6]</sup> and drug delivery systems.<sup>[3,7]</sup> There have been several approaches to employ BC—which represents a nanostructured cellulosic material—in current biomaterials chemistry. For instance, Montrikittiphant et al. used BC as a reinforcement for polylactide composites,<sup>[8]</sup> and Butchosa et al. prepared antibacterial composite materials that consisted of BC nanofibers and chitin nanocrystals.<sup>[9]</sup> BC has also been used as the starting material for ultra-lightweight cellulosic aerogels.<sup>[10]</sup>

Huisgen's 1,3-dipolar cycloaddition reaction, often called click chemistry,<sup>[11]</sup> is a Cu<sup>I</sup>-catalyzed reaction between organic azides and terminal alkyne functionalities, in which aromatic 1,2,3-triazoles are formed under very mild conditions (e.g., room temperature) in nearly quantitative yield.<sup>[12]</sup> Cu as a catalyst can be used directly as a Cu<sup>I</sup> salt in combination with a base such as Hünig's base<sup>[13]</sup> or as a Cu<sup>II</sup> salt combined with an in situ reducing agent, usually ascorbic acid.<sup>[14]</sup> The major drawback of Cu<sup>I</sup> salts is their susceptibility to oxidation. More recently, catalysts based on less air-sensitive Ru<sup>II</sup> complexes have also been applied for click-chemistry-type reactions.<sup>[15]</sup>

The click chemistry approach to cellulose modification has so far been based primarily on 6-azido-6-deoxycellulose mostly in homogeneous reactions. This can be accomplished by the preactivation of C6-OH as the tosylate, with tosyl chloride in pyridine (heterogeneous reaction) or in caustic aqueous media, followed by nucleophilic tosyl-azide exchange under polar aprotic conditions in DMF at high temperature.<sup>[16]</sup> However, alkyne moieties on cellulose can act also as an immobilization anchor for organic azide derivatives, which represents the reverse of the above method. This can be accomplished by alkynylation of cellulose with propargyl bromide by Williamson etherification.<sup>[17]</sup> The esterification of cellulose using, for example, 5-hexynoic acid has also been reported.<sup>[18]</sup> There have

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been several reports on the click chemistry of nanocellulosic materials other than BC in heterogeneous systems. Illustrative examples are the heterogeneous modification of nanofibrillated cellulose in aqueous suspension with 1-azido-2,3-epoxypropane<sup>[19]</sup> or the homogeneous functionalization of carboxymethyl cellulose (CMC) by Filpponen et al.,<sup>[20]</sup> who coupled 11-azido-3,6,9-trioxaundecan-1-amine and propargylamine to CMC in aqueous suspension by the carbodiimide-mediated formation of amide bonds. Rosilo et al. prepared composite materials by crosslinking CNC in a thiol-ene-type click reaction.<sup>[21]</sup> Another interesting approach is the use of cellulose as a Cu<sup>I</sup> catalyst support for click chemistry reactions: Koga et al. performed the topological loading of Cu<sup>I</sup> onto cellulose nanofibrils oxidized with 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) in aqueous suspension to yield catalytically active aerogels after freeze-drying.<sup>[22]</sup>

If we take into account that, to the best of our knowledge, click chemistry has not been applied in combination with BC sheets as a scaffold material before, we aimed to find a way to functionalize BC and similar nanocellulosics that would tolerate the “problematic conditions” involved mostly, for example, with working in aqueous medium, the presence of an aquogel, heterogeneous reaction conditions, and a nonpowdered, difficult-to-access material. For this purpose an alkoxy silane chemistry approach was selected.

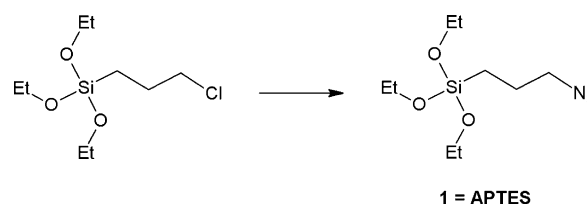
This type of chemical modification has been used previously for the synthesis of antimicrobial, cellulose-based films. For example, Andresen et al. grafted microfibrillated cellulose (MFC) with the quaternary ammonium salt octadecyldimethyl(3-trimethoxysilylpropyl)ammonium chloride (ODDMAC) using simple absorption followed by thermal treatment.<sup>[23]</sup> An alternative reagent used for BC that comprises antimicrobial activity was used by Fernandes et al. (3-Aminopropyl)trimethoxysilane was hydrolyzed in acetone solution by the action of wet BC. Curing resulted in the condensation of aminopropylsilane onto the cellulosic surface, which mimics the antimicrobial properties of chitosan.<sup>[6]</sup> Functionalization of cellulose nanocrystal films was achieved by Huang et al. by combining alkoxy silane chemistry using (3-mercaptopropyl)trimethoxysilane and thiol-ene addition activated photochemically.<sup>[24]</sup>

In the present account, we describe the grafting of azido-alkyl groups onto wet BC using the above-mentioned silane chemistry approach under mild, environmentally friendly conditions. The silylating agent is thus used in a first step to equip the cellulose material with reactive azide groups, which provides a general cellulosic starting material for further click chemistry derivatization, which—through the ease of its preparation—is far superior to comparable products from previous modification approaches. The reactivity of the organic azides was demonstrated in a subsequent Cu<sup>I</sup>-catalyzed Huisgen alkyne-azide cycloaddition, which appended a strongly fluorescent dye based on alkyne-modified fluorescein to the cellulosic substrate.

## Results and Discussion

### Synthetic aspects

The surface grafting agent (3-azidopropyl)triethoxysilane **1** (APTES) was synthesized in a one-step procedure (Scheme 1) following a protocol described in the literature<sup>[25]</sup> with a modified workup. Commercially available (3-chloropropyl)triethoxysilane was used as a starting material. Nucleophilic halide-azide exchange in acetonitrile under the catalytic action of tetra-*n*-butylammonium bromide (TBAB) yielded the corresponding azido derivative of the silane as a transparent oil in 60% yield. Aqueous extraction to remove the remaining salt did not affect the product negatively, which was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

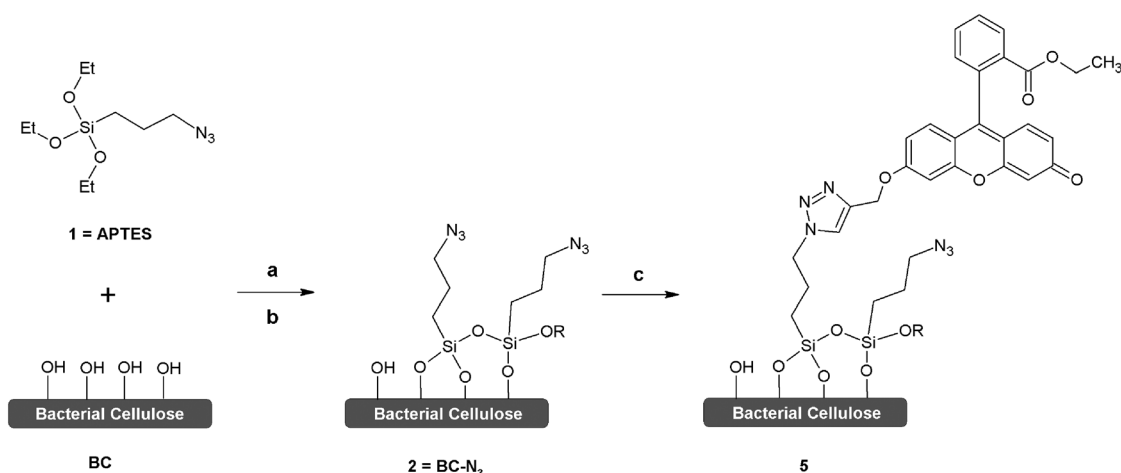


**Scheme 1.** Synthesis of **1** for BC surface preactivation by nucleophilic halide-azide exchange. Conditions: acetonitrile, NaN<sub>3</sub>, TBAB (catalyst), N<sub>2</sub>, reflux, 18 h.

<sup>29</sup>Si NMR spectroscopy was also used to confirm the alkoxy silane structure of the final product after aqueous extraction, which was evident by a single signal at  $\delta = -46.2$  ppm. Further purification of the product by vacuum distillation was, therefore, not necessary. The successful substitution of the terminal chloro group by an azido group was also confirmed by attenuated total reflectance (ATR) FTIR spectroscopy. The significant band at  $\tilde{\nu} = 2094$  cm<sup>-1</sup> was assigned to the vibration of the organic azide. The easy preparation of **1** places a reagent at the disposal of cellulose chemists that allows azide modification in a much easier way than previous approaches that relied on direct azide introduction at C6.

The silylating agent APTES was used in a subsequent step to functionalize BC sheets. In this way the azido moieties were added to the substrate material (Scheme 2), mainly on the surfaces, and were further used for subsequent click chemistry. The azidopropyl group acts as a spacer that increases the accessibility and yield of further derivatization reactions using click chemistry because of the elongated chain and higher spatial flexibility compared to, for example, the azido substitution of C6 of cellulose in 6-azido-6-deoxycellulose.<sup>[16b,26]</sup>

APTES also consists of an alkoxy silane group, which acts as a reactive group anchored to the cellulose surface. This strategy opens up a new possibility in click chemistry for the derivatization of aqueous, wet (bacterial) cellulose and other never-dried celluloses under mild and green conditions. The advantages are evident from a comparison with the conventional method of azido modification of cellulosic materials: drying of cellulose, reaction of the dried cellulose with tosyl

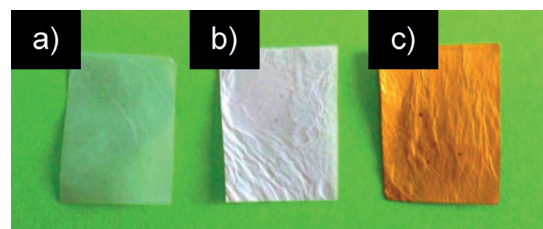


**Scheme 2.** Steps a) and b) chemical surface preactivation of BC sheets towards click chemistry: condensation of **1** with cellulosic hydroxyl groups accompanied by self-condensation to result in the formation of a 3D siloxane and silanol network (R=Si or H) on the surface of the modified BC (**2**). Step c) Cu<sup>I</sup>-catalyzed Huisgen alkyne-azide cycloaddition reaction between preactivated BC-N<sub>3</sub> (**2**) and alkyne-equipped xanthene dye **4** as a representative example for the click reaction. Conditions: a) acetone, H<sub>2</sub>O, RT, 18 h; drying at 40 °C for 3 h; b) curing at 105 °C for 2 h; c) acetonitrile, **4**, Cu<sup>I</sup> (catalyst), DIPEA (Hünig's base), Ar, RT, 72 h, darkness.

chloride in pyridine as a solvent and catalyst, and tosyl-azide exchange in DMF at high temperature.<sup>[16c,27]</sup>

The detailed mechanism of the chemical grafting of (3-azidopropyl)silane onto the cellulose surface normally involves three steps, which is true for all types of alkoxy silane chemical modifications under hydrolytic conditions.<sup>[6,23,28]</sup> In the first step, the alkoxy groups of the silane are hydrolyzed in the presence of water to yield the respective silanols. The silanol groups can interact with the OH-rich surface of BC through multiple hydrogen bonds. The molecules adsorbed physically undergo self-condensation to yield siloxane oligomers and bind covalently to the cellulose surface by condensation. The condensation is effected mostly by thermal treatment, so-called curing. In the present case, curing was performed at 105 °C for 2 h. After curing, opaque, white sheets of surface-modified BC were obtained.

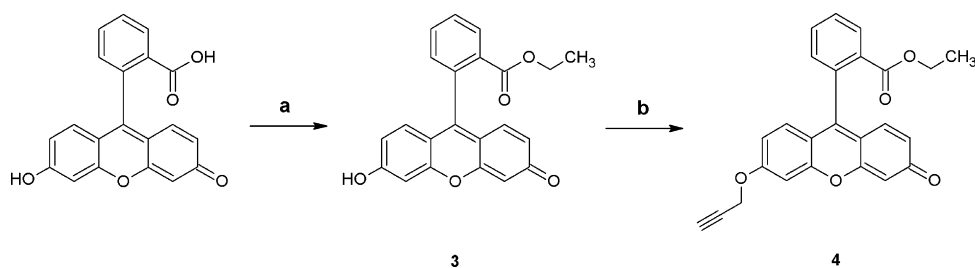
The silane-grafted BC sheet was further subjected to Soxhlet extraction with EtOH (18 h) for the removal of possibly adsorbed, unreacted reagent. However, a comparison of the ATR-FTIR spectra before and after Soxhlet extraction showed that there was no significant change in the material, which indicates that only a little unreacted reagent is present and proves that no cleavage of siloxane occurred. This possible process would have been detected easily by the reduced intensity of the prominent azide band at  $\tilde{\nu} = 2098 \text{ cm}^{-1}$  (data not shown). A mass increase in dry weight of 38% indicated the effectiveness of the BC modification. Furthermore, a change in color of the dried samples from milky and opaque (natural BC) to white was observed (Figure 1). The grafting yield was calculated



**Figure 1.** Photograph of different BC derivatives. a) Dried, milky, and opaque BC; b) BC-N<sub>3</sub> (**2**); c) silanized BC **5** after click reaction with chromophore **4**.

from the N content of the material obtained by elemental analysis, which was determined to be 3.17%. This corresponds to a grafting amount of 75  $\mu\text{mol}$  of azide per 100 mg of material.

To demonstrate the accessibility of premodified BC to the Cu<sup>I</sup>-catalyzed click reaction, a new fluorophore molecule based on the well-known reagent fluorescein was synthesized in two steps by esterification and subsequent etherification (Supporting Information). As the modified cellulose carries an azide moiety, the coreacting fluorophore had to be equipped with an alkyne group. For the synthesis of **4**, fluorescein (free acid) was esterified in a first step with EtOH in the presence of H<sub>2</sub>SO<sub>4</sub> as a catalyst (Scheme 3). This step was required to



**Scheme 3.** Synthesis of chromophore **4** derived from fluorescein (free acid) in two steps. Conditions: a) EtOH, H<sub>2</sub>SO<sub>4</sub>, reflux, 6 h; b) acetone, DMF, propargyl bromide, K<sub>2</sub>CO<sub>3</sub>, 60 °C, 18 h.

ensure the neat reaction of the propargyl anchor and a clean subsequent click process.

The synthesized fluorescein ethyl ester **3** was subsequently etherified with propargyl bromide in the presence of  $K_2CO_3$  (Claisen conditions) to give fluorophore **4**. The workup of this compound was optimized and was relatively simple without the need to use flash column chromatography to obtain a pure product.

The new fluorophore **4** was appended onto azide-preactivated BC sheets by the  $Cu^I$ -catalyzed Huisgen alkyne-azide cycloaddition reaction (CuAAC). This reaction was performed to prove the accessibility and reactivity of the azido groups on the surface of the modified BC. The conditions for this reaction were adapted from a procedure published recently,<sup>[12]</sup> in which silica gel for HPLC was modified by a similar approach. As a result of the photoactivity of the fluorescent dye, the reaction was performed under the exclusion of light. After three days, the resulting orange/yellow BC sheets were allowed to shake successively in solvents and solutions with different polarities and properties (acetonitrile, acetone,  $H_2O$ , aqueous 2% ethylenediaminetetraacetic acid (EDTA) disodium solution, MeOH, and  $CH_2Cl_2$ ) until colorless supernatants were obtained. Extensive washing of the material was necessary to remove any unreacted dye so that only fluorescent dye bound covalently remained. EDTA was used to remove the Cu catalyst by complexation. Notably, the mass yield of the modified sheets is lower than the initial weight of cellulosic material **2** (93%) as some powdered material, most probably derived from mechanical stress during shaking, was lost upon work-up.

### Structural characterization of BC- $N_3$

A typical ATR-FTIR spectrum of BC is shown in Figure 2 together with spectra of **2** (BC- $N_3$ ) and **5**. Besides the typical absorption bands of cellulose at approximately  $\tilde{\nu}=3350$  (OH stretching vibration), 2900 (CH and  $CH_2$  stretching vibrations), and  $1050\text{ cm}^{-1}$  (vibration of C–O–C glycosidic bonds), the spectrum of BC- $N_3$  shows an intense band at  $\tilde{\nu}=2098\text{ cm}^{-1}$ , attributed to the antisymmetric N=N=N stretching vibration. The same band ( $\tilde{\nu}=2094\text{ cm}^{-1}$ ) was observed in the spectrum of **1**.

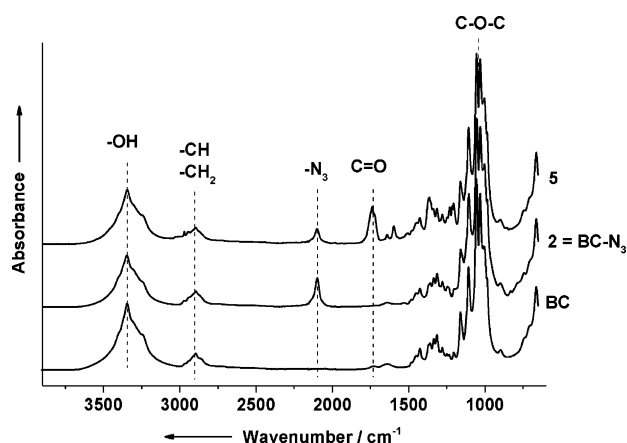


Figure 2. Normalized ( $\tilde{\nu}=1055\text{ cm}^{-1}$ ) ATR-FTIR spectra of BC, **2**, and **5**.

As a result of the intense C–O–C vibration band of cellulose at around  $\tilde{\nu}=1050\text{ cm}^{-1}$ , it is difficult to extract signals that could be attributed to Si–O–Si or Si–O–cellulose bridges ( $\tilde{\nu}=1135$  and  $1150\text{ cm}^{-1}$ , respectively<sup>[6]</sup>) formed by the condensation of the silanol moieties with other silanols to give siloxanes and by condensation with cellulosic hydroxyl groups, respectively.

BC- $N_3$  after  $Cu^I$ -catalyzed Huisgen alkyne-azide cycloaddition with **4** is shown in Figure 2 (top). A reduction of the antisymmetric azide stretching vibration band at  $\tilde{\nu}=2100\text{ cm}^{-1}$  indicates the successful covalent bonding with the fluorescent dye. The occurrence of a residual azide band after the click reaction could reflect the impact of steric hindrance on the surface of the modified BC material caused by the binding of bulky fluorescent dye, although the dye was used in excess. This could also originate from the weak out-of-plane vibration of the N atoms in the product triazole that coincides with the symmetric azide vibration band. A longer spacer than the propylsilane unit could, therefore, help to achieve higher surface densities of any clicked functional molecule. The appearance of the broad carbonyl band at approximately  $\tilde{\nu}=1739\text{ cm}^{-1}$  in the spectrum of **5** is indeed a striking feature and in good agreement with the carbonyl band observed for fluorescent dye **4** ( $\tilde{\nu}=1718\text{ cm}^{-1}$ ). Furthermore, the nonappearance of the stretching bands of the alkyne moiety of **4** bound covalently ( $\tilde{\nu}=3198$  and  $2121\text{ cm}^{-1}$ , which corresponds to the stretching vibration of  $C\equiv C-H$  and  $C\equiv C$ ) is evident, which in turn proves the successful chemical bonding by the formation of a heteroaromatic 1,2,3-triazole by CuAAC and the absence of unreacted, adsorbed reagent **4**. Unfortunately the intensity of the IR band of the C=N bond around  $\tilde{\nu}=1650\text{ cm}^{-1}$ <sup>[16c]</sup> is generally weak and, therefore, difficult to use as a proof of a successful reaction.

The solid-state  $^{13}C$  NMR spectrum of BC- $N_3$  is shown in Figure 3. Besides the typical peaks of cellulosic C atoms in the  $\delta=110$ –60 ppm range (anomeric C1  $\delta=\sim 106$  ppm; crystalline region of C4  $\delta=\sim 91$  ppm, amorphous region of C4  $\delta=\sim 85$  ppm; C2, C3, and C5  $\delta=\sim 72$ –78 ppm; and C6  $\delta=\sim 67$  ppm) three new peaks compared to neat BC appeared in the spectrum of BC- $N_3$ . These three peaks ( $\gamma$ - $CH_2$   $\delta=55.5$  ppm,  $\beta$ - $CH_2$   $\delta=24.8$  ppm,  $\alpha$ - $CH_2$   $\delta=12.2$  ppm) were assigned in

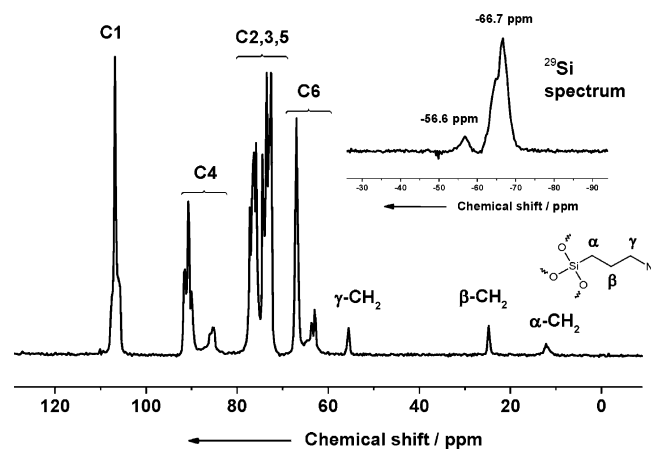


Figure 3. Solid-state  $^{13}C$  and  $^{29}Si$  NMR spectra of BC- $N_3$  (**2**).

agreement with the three resonances of the azidoalkyl chain of modification reagent APTES in  $\text{CDCl}_3$ -solution  $^{13}\text{C}$  NMR spectroscopy (Experimental Section). Notably, the condensation of silanol groups that results in covalent bonds between the reagent and BC does not affect the shifts of the cellulosic C atoms. Although etherification of cellulosic hydroxyl groups (which results in  $\text{C}_{\text{cell}}\text{--O--C}$  bonds) causes significant downfield shifts of the resonances of the etherified C–O unit, the silylation (which results in  $\text{C}_{\text{cell}}\text{--O--Si}$  bonds) apparently does not. A further confirmation for successful hydrolysis and covalent binding of the silane reagent is the absence of the respective  $\text{CH}_2$  and  $\text{CH}_3$  signals of the triethoxy moiety of APTES in the  $^{13}\text{C}$  NMR spectrum of the modified BC.

The corresponding solid-state  $^{29}\text{Si}$  NMR spectrum of  $\text{BC-N}_3$  is displayed in the inset in Figure 3. Two major peaks are observed at  $\delta = -56.6$  and  $-66.7$  ppm. This information is useful to gain more information about the structure of the siloxane network. According to common nomenclature,<sup>[29]</sup> the Si atom of the starting APTES is designated as  $T$ , which corresponds to the three ( $=T$ ) siloxane Si–O bonds present in the molecule in addition to the single Si–C bond. Three alkoxy substituents are attached to the central Si atom in APTES. By hydrolysis and condensation, alkoxy substituents (Si–O–R) are replaced progressively by other silyloxy groups (Si–O–Si). An additional superscript  $i$  represents the number of those silyloxy (Si–O–) groups bound to a respective Si atom, and  $(3-i)$  alkoxy groups remain attached. If we use this nomenclature,  $T^i$  corresponds to  $\text{R}'\text{--Si}(\text{OSi})_i(\text{OR})_{3-i}$ . Integration of the two peaks in the solid-state  $^{29}\text{Si}$  NMR spectrum yielded a silane composition of 7%  $T^2$  structure (linear sequences) and 93%  $T^3$  structure (3D oligomer structures). The chemical shifts are in agreement with values observed by Salon et al. who studied the interaction between silane coupling agents and cellulose fibers.<sup>[29]</sup> According to these results, the homo-polycondensation of silanes was thus favored over simple hydrolysis to yield a 3D network of polysiloxanes.

### Morphology of $\text{BC-N}_3$

The surface morphology of BC, silane-grafted  $\text{BC-N}_3$  **2**, and the click product **5** was studied by SEM (Figure 4). The typical 3D

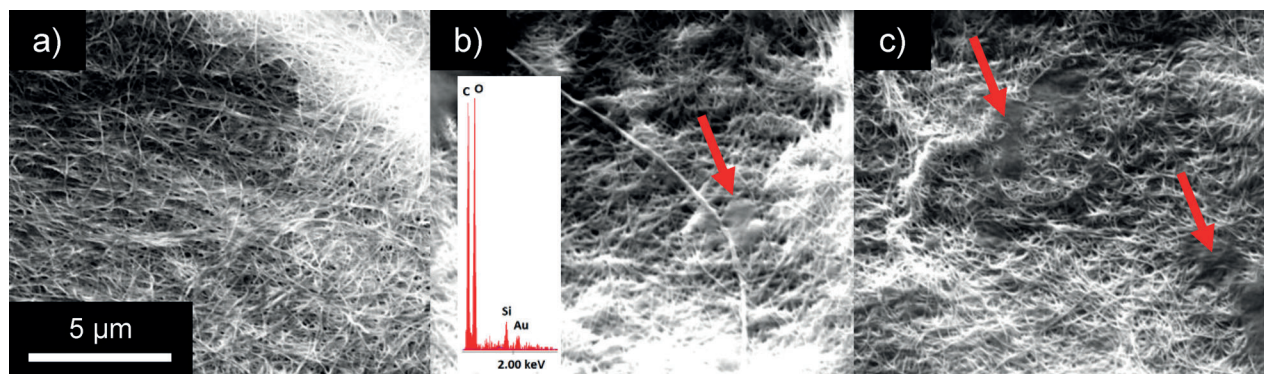
network of cellulosic fibers of BC is shown in Figure 4a (left) at a magnification of 20k.  $\text{BC-N}_3$  is shown in the middle (Figure 4b), and **5** is shown in Figure 4c (right), both at the same magnification. The successful modification is evident from the micrographs: in both images the fibrils are covered by the siloxane network (increase in thickness) and 3D siloxane “islands” are formed on the surface of the grafted BC as a result of self-condensation of the hydrolyzed azidoalkyl silane. These islands are indicated by arrows. Energy-dispersive X-ray (EDX) spectroscopy further confirmed the presence of Si in the modified BC sheets **2** and **5** (data shown in the inset of Figure 4b for  $\text{BC-N}_3$ ).

### Thermal properties of $\text{BC-N}_3$

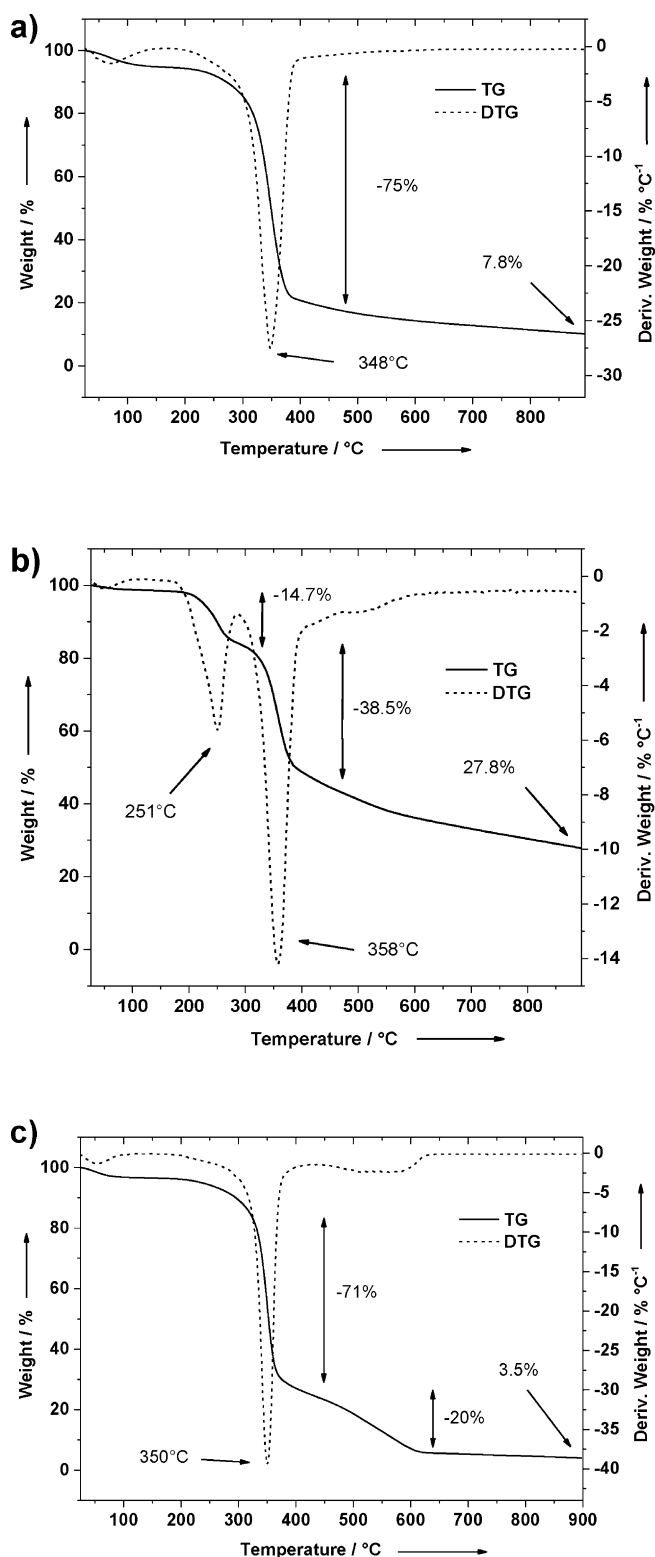
The thermal properties of  $\text{BC-N}_3$  as well as its thermal degradation profile were studied by thermogravimetric (TG) analysis (Figure 5) in a  $\text{N}_2$  atmosphere. A typical TG thermogram of BC is shown in Figure 5a. The loss of water was observed at  $\sim 100^\circ\text{C}$ . A maximum decomposition at  $348^\circ\text{C}$  in combination with a mass decrease of 75% and approximately 10% residual mass in a  $\text{N}_2$  atmosphere match experimental data published elsewhere.<sup>[6]</sup> In contrast, the BC sheets grafted with APTES exhibited weight loss profiles with two major steps at  $251^\circ\text{C}$  (weight loss of  $\approx 15\%$ ) and  $358^\circ\text{C}$  (weight loss of 39%). The first step results from the degradation of the azido moiety,<sup>[30]</sup> which supports the structural characterization provided by NMR and FTIR spectroscopy. The significant increase in residual mass (28 vs. 10% residual mass in the case of BC) is attributable to siloxy moieties and further contributes to this conclusion.

### Conclusions

In this study, a new approach towards the azide functionalization of wet cellulose was presented. The azide was required for further modification by click chemistry reactions with alkynes. In the present work, bacterial cellulose gels were used, but in principle, the methodology can be applied analogously to all never-dried and wet celluloses, such as pulps or fibers, and is thus quite versatile. It is distinguished from previous azide



**Figure 4.** SEM images of the surface of different BC derivatives (magnification 20 k). a) lyophilized BC as a reference; b)  $\text{BC-N}_3$  (**2**; inset = EDX spectrum), 3D siloxane islands indicated by arrows; c) compound **5**.



**Figure 5.** TG and differential thermogravimetric (DTG) analysis of a) dried BC, b) BC-N<sub>3</sub> (2), and c) compound 5.

modifications for cellulose as it is a simple, mild, and green procedure. (3-Azidopropyl)triethoxysilane was attached covalently to the cellulosic surface by the condensation of hydrolyzed alkoxy silane and cellulosic hydroxyl groups. The fibrillar structure of the cellulosic starting material was preserved;

moreover, the fibrils were covered by siloxanes and additional 3D polysiloxane networks on the surface of the bacterial cellulose mats. To demonstrate the accessibility and reactivity of the attached azide functional groups in Cu<sup>I</sup>-catalyzed Huisgen alkyne-azide 1,3-dipolar cycloaddition, a new alkyne derivative of the well-known chromophore fluorescein was synthesized and its fluorescence properties were determined comprehensively (Supporting Information). The clicking of this compound to the azide-equipped cellulose proceeded neatly. The introduction of azidoalkyl groups onto wet (bacterial) celluloses using the current silane grafting approach represents a general and promising way to introduce different functional molecules to cellulose surfaces with opportunities that reach far beyond the plain fluorophore example presented. With regard to the increasing awareness of green chemical procedures, the mild and environmentally friendly conditions used in the approach are an additional bonus.

## Experimental Section

### Materials and methods

Solution NMR spectra were recorded by using a Bruker Avance II 400 instrument (Rheinstetten, Germany) with a <sup>1</sup>H resonance frequency at 400.13 MHz, <sup>13</sup>C at 100.61 MHz, and <sup>29</sup>Si at 79.53 MHz. Samples were dissolved in CDCl<sub>3</sub> (99.8% D, Euriso-top, Saint-Aubin, France) and recorded at RT with standard Bruker pulse programs. Data processing was performed by using ACD/NMR Processor Academic Edition. The signals were assigned using attached proton test (APT) and 2D NMR techniques (COSY, HSQC, and HMBC). Chemical shifts are given in δ [ppm] relative to tetramethylsilane (TMS) as an internal standard. Coupling constants are given in Hz. Solid-state <sup>13</sup>C cross polarization (CP)/total suppression of spinning sidebands (TOSS) and <sup>29</sup>Si CP NMR spectra were recorded by using a Bruker Avance III HD instrument (Rheinstetten, Germany) with a resonance frequency of <sup>13</sup>C at 100.68 MHz and <sup>29</sup>Si at 79.53 MHz.

A PerkinElmer Frontier IR Single-Range spectrometer (Waltham, Massachusetts, USA) was used in ATR mode for FTIR measurements. UV/Vis absorption experiments were performed by using a PerkinElmer Lambda 35 UV/Vis and a HP-8452 diode array spectrophotometer. Fluorescence spectra were recorded by using a temperature-controlled FluoroLog 2 (model F-111) spectrofluorimeter (Horiba Jobin Yvon, Rome, Italy).

Melting points were determined by using an IA9300 digital melting point apparatus from Thermo Scientific (Loughborough, UK). Elemental analysis was performed by using a EURO EA 3000 CHNS-O instrument from HEKAtech (Wegberg, Germany). SEM and EDX experiments were performed by using an FEI INSPECT S50 instrument (Hillsboro, Oregon, USA). Samples were sputtered with Au (layer thickness 4 nm) by using a Leica EM SCD005 sputter coater. For TG analysis, a NETZSCH TG 209 F1 instrument (Selb, Germany) was used with a temperature gradient starting from 25 °C and a heating rate of 20 °C min<sup>-1</sup> until 900 °C. All experiments were performed under the exclusion of O<sub>2</sub> in an inert N<sub>2</sub> atmosphere.

TLC was performed by using Silica gel 60 F<sub>254</sub> precoated glass plates (Merck). Synthesis-grade solvents were purchased from ROTH, Sigma-Aldrich, and VWR and used as received. Granular 3 Å molecular sieves were purchased from Carl Roth (Graz, Austria). Reagents for synthesis were obtained from Sigma-Aldrich, Fluka, and TCI. Wet BC sheets (processed with 100 ppm H<sub>2</sub>O<sub>2</sub> and 850 ppm

chlorhexidine for preservation,  $M_w \approx 972 \text{ kDa mol}^{-1}$ ) were kindly provided by Lohmann & Rauscher (Neuwied, Germany).

## Synthesis

### (3-Azidopropyl)triethoxysilane (1)

A suspension of TBAB (3.20 g, 9.9 mmol) and  $\text{NaN}_3$  (10.0 g, 153.8 mmol) in anhydrous acetonitrile was prepared and stirred under  $\text{N}_2$ . (3-Chloropropyl)triethoxysilane (10 mL, 41.5 mmol) was added with constant flushing with  $\text{N}_2$ , and the reaction mixture was allowed to stir for 18 h under reflux conditions. The reaction mixture was filtered to remove the bulk of the salt. After evaporation of the solvent, the product was dissolved in dichloromethane (50 mL), filtered through Celite<sup>®</sup>, and washed with water and brine (2 × 20 mL each). The organic phase was dried carefully over  $\text{Na}_2\text{SO}_4$  and evaporated. The remaining colorless oil (which contained a small portion of oily yellowish drops) was allowed to stand overnight at RT for complete separation of the phases. The yellowish phase was discarded and the product was dried under high vacuum at RT for 5 h. Yield: 6.15 g (24.9 mmol, 60%) of colorless oil.  $^1\text{H NMR}$  (400.13 MHz,  $\text{CDCl}_3$ ):  $\delta = 3.84$  (q,  $^3J(\text{H,H}) = 7 \text{ Hz}$ , 6H;  $\text{CH}_2$ ), 3.28 (t,  $^3J(\text{H,H}) = 7 \text{ Hz}$ , 2H;  $\gamma\text{-CH}_2$ ), 1.73 (m, 2H;  $\beta\text{-CH}_2$ ), 1.24 (t,  $^3J(\text{H,H}) = 7 \text{ Hz}$ , 9H;  $\text{CH}_3$ ), 0.69 ppm (m, 2H;  $\alpha\text{-CH}_2$ );  $^{13}\text{C NMR}$  (100.61 MHz,  $\text{CDCl}_3$ ):  $\delta = 58.4$  ( $\text{CH}_2$ ), 53.8 ( $\gamma\text{-CH}_2$ ), 22.7 ( $\beta\text{-CH}_2$ ), 18.3 ( $\text{CH}_3$ ), 7.6 ppm ( $\alpha\text{-CH}_2$ );  $^{29}\text{Si NMR}$  (79.49 MHz,  $\text{CDCl}_3$ ):  $\delta = -46.2$  ppm; FTIR:  $\tilde{\nu} = 2973$  (C–H), 2929 (C–H), 2879 (C–H), 2094 ( $\text{N}_3$ ), 1444, 1390, 1242, 1166, 1101, 1074, 954, 775  $\text{cm}^{-1}$ .

### Preparation of preactivated BC- $\text{N}_3$ (2)

A mixture of **1** (4.0 mL, 16.2 mmol) in acetone (32 mL) and  $\text{H}_2\text{O}$  (4 mL) was prepared in a wide Petri dish. A wet BC sheet ( $\varnothing = 13 \text{ cm}$ ,  $\approx 505 \text{ mg}$  of dry cellulose,  $\approx 3.1 \text{ mmol}$  anhydroglucose unit (AGU)) was put into the mixture, and it was allowed to shake at RT for 18 h. Oily drops were formed during solvent exchange. The BC sheet was washed with acetone to remove nonadsorbed reagent on the surface and then predried at  $40^\circ\text{C}$  for 3 h. The predried sheet was subsequently cured at  $105^\circ\text{C}$  for 2 h. To remove the noncondensed reagent, the silane-grafted sheet was subjected to Soxhlet extraction with EtOH for 18 h followed by drying at  $105^\circ\text{C}$  for 1 h. Yield: 699 mg of a white BC sheet.  $^{13}\text{C NMR}$  (100.68 MHz, CP/TOSS, swollen in  $\text{H}_2\text{O}$ ):  $\delta = 108.3\text{--}105.0$  (AGU-C1), 92.6–88.9 (AGU-C4), 79.5–71.3 (AGU-C2+C3+C5), 68.2–65.5 (AGU-C6), 56.8–54.2 ( $\gamma\text{-CH}_2$ ), 25.7–23.0 ( $\beta\text{-CH}_2$ ), 14.2–9.8 ppm ( $\alpha\text{-CH}_2$ );  $^{29}\text{Si NMR}$  (79.53 MHz CP/TOSS, swollen in  $\text{H}_2\text{O}$ ):  $\delta = -54.0$  to  $-59.3$ ,  $-61.1$  to  $-71.5$  ppm; FTIR:  $\tilde{\nu} = 3346$  (OH), 2895 (C–H), 2098 ( $\text{N}_3$ ), 1428, 1314, 1160, 1107, 1054, 1031, 1003, 664  $\text{cm}^{-1}$ ; elemental analysis (%) found C 42.54, H 6.32, N 3.17, S < 0.05, O 41.71; grafting amount of  $-\text{N}_3$  calculated from the N content: 755  $\mu\text{mol g}^{-1}$ .

### Ethyl 2-(6-hydroxy-3-oxo-3H-xanthen-9-yl)benzoate (3)

Fluorescein (free acid, 7.46 g, 22.5 mmol) was suspended in EtOH (50 mL) and concentrated  $\text{H}_2\text{SO}_4$  (2 mL) as the catalyst was added slowly with stirring at RT. The suspension was heated to reflux for 6 h. An additional funnel packed with 3 Å molecular sieves (60 mL) was located between the round-bottomed flask and the condenser to dry the condensed ethanol continuously. After cooling, the reaction mixture was concentrated on a rotary evaporator, water (50 mL) was added, and the suspension was extracted with  $\text{CH}_2\text{Cl}_2$  (3 × 50 mL). The organic phases were combined, washed carefully with saturated  $\text{NaHCO}_3$  solution and water until neutral, and

washed with saturated brine (50 mL). After drying with anhydrous  $\text{Na}_2\text{SO}_4$ , the solvent was evaporated under reduced pressure, and the product was allowed to dry under high vacuum overnight. The intermediate was used without further purification. Yield: 3.20 g (8.9 mmol, 40%) of a dark red solid.  $^1\text{H NMR}$  (400.13 MHz,  $\text{CDCl}_3$ ):  $\delta = 9.62$  (s, br, 1H;  $\text{C}_{\text{ar}}\text{-OH}$ ), 8.23 (d,  $^3J(\text{H,H}) = 7 \text{ Hz}$ , 1H;  $\text{C}_{\text{ar}}\text{H}$ ), 7.71 (t,  $^3J(\text{H,H}) = 7 \text{ Hz}$ , 1H;  $\text{C}_{\text{ar}}\text{H}$ ), 7.65 (t,  $^3J(\text{H,H}) = 7 \text{ Hz}$ , 1H;  $\text{C}_{\text{ar}}\text{H}$ ), 7.28 (d,  $^3J(\text{H,H}) = 7 \text{ Hz}$ , 1H;  $\text{C}_{\text{ar}}\text{H}$ ), 6.96 (d,  $^3J(\text{H,H}) = 7 \text{ Hz}$ , 2H;  $\text{C}_{\text{ar}}\text{H}$ ), 6.87 (s, 2H;  $\text{C}_{\text{ar}}\text{H}$ ), 6.79 (d,  $^3J(\text{H,H}) = 7 \text{ Hz}$ , 2H;  $\text{C}_{\text{ar}}\text{H}$ ), 3.97 (q,  $^3J(\text{H,H}) = 7 \text{ Hz}$ , 2H;  $\text{CH}_2$ ), 0.89 ppm (t,  $^3J(\text{H,H}) = 7.0 \text{ Hz}$ , 3H;  $\text{CH}_3$ );  $^{13}\text{C NMR}$  (100.61 MHz,  $\text{CDCl}_3$ ):  $\delta = 175.6$  (C=O), 165.2 (C=O), 157.9 ( $\text{C}_{\text{ar}}\text{-O}$ ), 156.2 ( $\text{C}_{\text{q}}$ ), 134.1 ( $\text{C}_{\text{q}}$ ), 132.5 ( $\text{C}_{\text{ar}}\text{H}$ ), 131.2 ( $\text{C}_{\text{ar}}\text{H}$ ), 130.6 ( $\text{C}_{\text{ar}}\text{H}$ ), 130.2 ( $\text{C}_{\text{ar}}\text{H}$ ), 129.8 ( $\text{C}_{\text{ar}}\text{H}$ ), 122.1 ( $\text{C}_{\text{ar}}\text{H}$ ), 114.9 ( $\text{C}_{\text{q}}$ ), 103.7 ( $\text{C}_{\text{ar}}\text{H}$ ), 61.4 ( $\text{CH}_2$ ), 13.6 ppm ( $\text{CH}_3$ ); FTIR:  $\tilde{\nu} = 2980$  (C–H), 1715 (C=O), 1639, 1567, 1452, 1381, 1247, 1202, 1103, 1076, 912, 845  $\text{cm}^{-1}$ ; UV/Vis (MeOH):  $\lambda_{\text{max}} = 502 \text{ nm}$ ; TLC (acetone):  $R_f = 0.91$ ; m.p. 129–130  $^\circ\text{C}$  ( $\text{CH}_2\text{Cl}_2$ ).

### Ethyl 2-[3-oxo-6-(prop-2-yn-1-yloxy)-3H-xanthen-9-yl]benzoate (4)

DMF was added to a suspension of **3** (3.20 g, 8.9 mmol) in acetone (50 mL) until complete dissolution of the reagent. Finely ground  $\text{K}_2\text{CO}_3$  (1.85 g, 13.4 mmol) was added followed by the addition of propargyl bromide solution (80 wt% in toluene, 1.50 mL, 13.4 mmol) at RT. The suspension was allowed to stir at  $60^\circ\text{C}$  for 18 h. The reaction mixture was poured into cold distilled water (300 mL), and the voluminous orange precipitate was collected by filtration. The raw product was washed with water until the initially brownish filtrate became colorless, followed by careful washing with cold acetone (20 mL). After a final washing step with water (20 mL), the product was recrystallized from acetone to remove traces of remaining reagent impurities. The obtained crystals were washed with cold acetone and dried under high vacuum at RT overnight. The crystallization procedure was repeated successively with the mother liquor. Yield: 3.05 g (7.6 mmol, 86% combined yield) of an orange solid.  $^1\text{H NMR}$  (400.13 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.23$  (d,  $^3J(\text{H,H}) = 7 \text{ Hz}$ , 1H;  $\text{C}_{\text{ar}}\text{H}$ ), 7.71 (t,  $^3J(\text{H,H}) = 7 \text{ Hz}$ , 1H;  $\text{C}_{\text{ar}}\text{H}$ ), 7.65 (t,  $^3J(\text{H,H}) = 7 \text{ Hz}$ , 1H;  $\text{C}_{\text{ar}}\text{H}$ ), 7.28 (d,  $^3J(\text{H,H}) = 7 \text{ Hz}$ , 1H;  $\text{C}_{\text{ar}}\text{H}$ ), 7.05 (d,  $^4J(\text{H,H}) = 2 \text{ Hz}$ , 1H;  $\text{C}_{\text{ar}}\text{H}$ ), 6.91 (d,  $^3J(\text{H,H}) = 9 \text{ Hz}$ , 1H;  $\text{C}_{\text{ar}}\text{H}$ ), 6.85 (d,  $^3J(\text{H,H}) = 10 \text{ Hz}$ , 1H; =CH), 6.79 (dd,  $^3J(\text{H,H}) = 9 \text{ Hz}$ ,  $^4J(\text{H,H}) = 2 \text{ Hz}$ , 1H;  $\text{C}_{\text{ar}}\text{H}$ ), 6.54 (d,  $^3J(\text{H,H}) = 10 \text{ Hz}$ , 1H; =CH), 6.48 (s, 1H; =CH), 4.78 (d,  $^4J(\text{H,H}) = 2 \text{ Hz}$ , 2H;  $\text{CH}_2$ ), 4.01 (m, 2H;  $\text{CH}_2$ ), 2.59 (t,  $^4J(\text{H,H}) = 2 \text{ Hz}$ , 1H; =CH), 0.95 ppm (t,  $^3J(\text{H,H}) = 7 \text{ Hz}$ , 3H;  $\text{CH}_3$ );  $^{13}\text{C NMR}$  (100.61 MHz,  $\text{CDCl}_3$ ):  $\delta = 185.5$  (C=O), 165.3 (C=O), 161.8 ( $\text{C}_{\text{ar}}\text{-O}$ ), 158.8 ( $\text{C}_{\text{q}}\text{-O}$ ), 154.0 ( $\text{C}_{\text{ar}}\text{-O}$ ), 150.2 ( $\text{C}_{\text{q}}$ ), 134.1 ( $\text{C}_{\text{q}}$ ), 132.5 ( $\text{C}_{\text{ar}}\text{H}$ ), 131.2 ( $\text{C}_{\text{ar}}\text{H}$ ), 130.8 ( $\text{C}_{\text{q}}$ ), 130.4 ( $\text{C}_{\text{ar}}\text{H}$ ), 130.3 (=CH), 129.9 (=CH), 129.7 ( $\text{C}_{\text{ar}}\text{H}$ ), 129.0 ( $\text{C}_{\text{ar}}\text{H}$ ), 118.1 ( $\text{C}_{\text{q}}$ ), 115.6 ( $\text{C}_{\text{q}}$ ), 113.7 ( $\text{C}_{\text{ar}}\text{H}$ ), 105.8 (=CH), 101.6 ( $\text{C}_{\text{ar}}\text{H}$ ), 77.1 (=C–), 76.8 (≡CH), 61.4 ( $\text{CH}_2$ ), 56.4 ( $\text{CH}_2$ ), 13.6 ppm ( $\text{CH}_3$ ); FTIR:  $\tilde{\nu} = 3198$  (≡CH), 2121 (C≡C), 1718 (C=O), 1591, 1509, 1480, 1441, 1247, 1210, 1107, 856  $\text{cm}^{-1}$ ; UV/Vis (MeOH):  $\lambda_{\text{max}} = 456 \text{ nm}$ ; TLC (acetone):  $R_f = 0.73$ ; m.p. 222–224  $^\circ\text{C}$  (acetone).

### Click reaction of BC- $\text{N}_3$ and **4** to yield fluorescein-modified BC (5)

Azide-modified BC **2** (107 mg) was cut into pieces of approximately 1.5 × 1.5 cm and suspended in ACN (10 mL) in a resealable glass bottle. Alkyne-modified fluorescein derivative **4** (10.3 mg, 25.9  $\mu\text{mol}$ ) and *N,N*-diisopropylethylamine (100  $\mu\text{L}$ , 1.02 mmol) were added. The reaction mixture was degassed by flushing with Ar for 5 min, CuI (7 mg, 37  $\mu\text{mol}$ ) was added as a catalyst and the bottle was capped and sealed tightly with Parafilm. After the glass bottle was covered with aluminum foil to protect against light, the

mixture was shaken at RT for 72 h by using an overhead shaker. The modified BC sheets were then washed carefully by shaking in acetonitrile, acetone, H<sub>2</sub>O, aqueous 2% EDTA disodium solution, H<sub>2</sub>O, MeOH, CH<sub>2</sub>Cl<sub>2</sub>, and acetone (each until a colorless supernatant was obtained). The cellulosic sheets were allowed to dry for 15 min at RT and 15 min at 80 °C. Yield: 99 mg (93 wt%) of an orange/yellow solid. FTIR:  $\tilde{\nu}$  = 3345 (OH), 2895 (C–H), 2100 (N<sub>3</sub>), 1739 (C=O); 1598, 1428, 1366, 1108, 1055, 1032, 664 cm<sup>-1</sup>; elemental analysis calcd (%) found C 42.74, H 5.95, N 1.92, S < 0.05, O 45.84.

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**Keywords:** azides · biomass · click chemistry · green chemistry · silanes

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**Silane Meets Click Chemistry: Towards the Functionalization of Wet Bacterial Cellulose Sheets** 