

Photocatalytic surface patterning of cellulose using diazonium salts and visible light†

Cite this: *Org. Biomol. Chem.*, 2013, **11**, 6510Received 9th May 2013,
Accepted 1st August 2013

DOI: 10.1039/c3ob40990b

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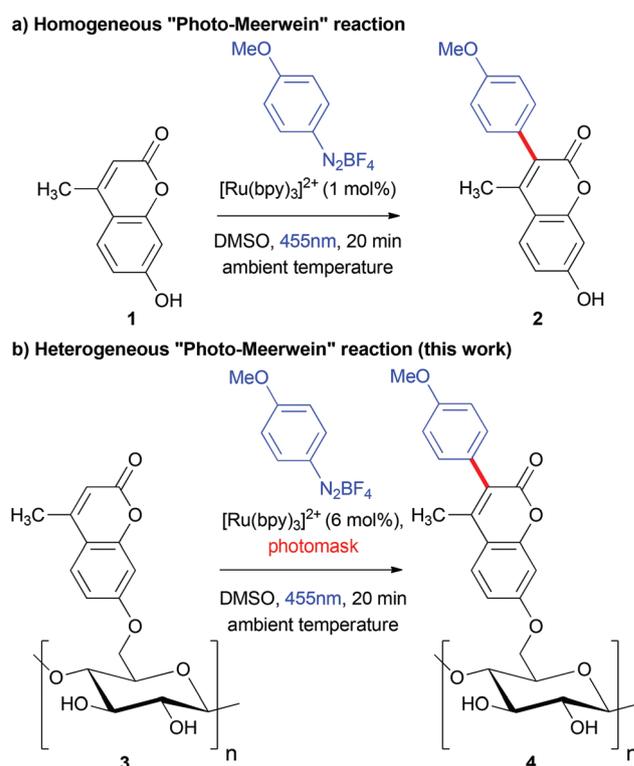
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Coumarin-functionalized cellulose sheets were chemically modified using a visible light catalyzed "Photo-Meerwein" arylation. Use of a photomask to pattern the surface resulted in directly visible images.

The selective functionalization of surfaces is important in many research areas. Creating defined mono- or multilayer structures requires surface patterning techniques with resolutions spanning from macroscopic to sub-nanometer scales.^{1,2} Patterned surfaces allow the development of sensor materials,³ shape-changing materials,⁴ microelectronic devices such as light-emitting displays⁵ and plastic electronics,⁶ as well as the production of photonic crystals,^{7,8} and are important for the study of cells.^{9,10}

The range of patterning techniques is large and can be divided into printing methods,¹¹ direct writing techniques,² and electrochemical^{12–14} and photochemical methods.¹⁵ Printing methods do not require masks and include screen printing,² nanoimprinting,¹⁶ microcontact printing by a stamp that transfers an inked material to the substrate,^{17–19} and ink-jet printing where a jet of a polymer solution breaks up into droplets, which are deposited onto a surface and form a pattern when the solvent evaporates.^{2,11} Direct writing allows a resolution down to the submicrometer range by nanografting:²⁰ the tip of a scanning probe microscope scratches the surface. In photolithography, a monomer- or polymer-coated surface is exposed to photoirradiation in order to trigger photo-polymerization or -decomposition.^{2,15,21}

Modifications have been accomplished on a diverse array of surface materials. Depending on their application, it may be necessary to functionalize conductors, semiconductors, or insulators. Important materials in this respect are metals (gold), glass, carbon, graphene sheets,²² inorganic quantum dots (CdSe,²³ TiO₂), bionanomaterials, and polymers (PVC,



Scheme 1 Homogeneous and heterogeneous "Photo-Meerwein" arylation.

PET). Existing polymers can be modified with one of the above-mentioned methods, or polymerization can be initiated on a surface. Aryl radicals can induce polymerization or bind directly to the surface and both processes have been used for surface functionalization.^{24,25}

We have previously described a "Photo-Meerwein" arylation reaction for the homogeneous cross-coupling of an aryl diazonium salt with an unsaturated compound, activated by means of a photocatalyst and visible light (Scheme 1a). The reaction works both inter- and intramolecularly, and is suitable for the arylation of olefins such as styrenes, enones, enol

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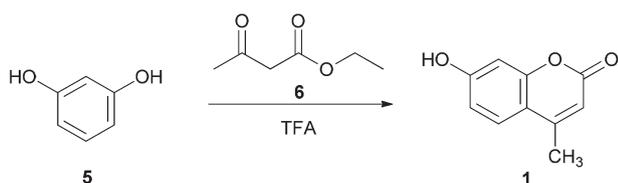
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†Electronic supplementary information (ESI) available: Experimental procedures, characterization data and calculations for all compounds. See DOI: 10.1039/c3ob40990b

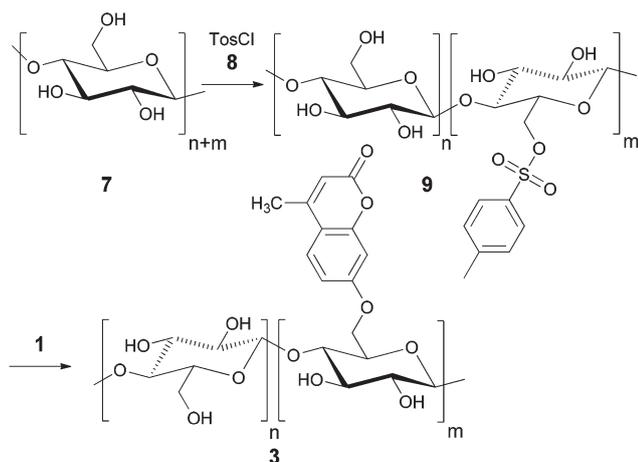
esters, alkynes, and heteroarenes with various functionalized aryl diazonium salts.^{26–29} In contrast to thermal or chemical initiation of the aryl radical formation, light allows spatial control of the reaction on surfaces (Scheme 1b). We describe here the selective patterning of a cellulose surface using a visible light photocatalyzed Meerwein reaction.

A prerequisite for accomplishing spatial resolution is the covalent immobilization of one of the two coupling partners on the surface.³⁰ Suitably modified surfaces can undergo selective coupling in the presence of a solution of the second coupling partner and the photocatalyst, using a photomask to limit the irradiation area. Only irradiated parts of the surface will undergo carbon–carbon bond formation, leading to a patterned arylated surface which can be detected by optical methods.

Coumarins react in a “Photo-Meerwein” arylation²⁶ with diazonium salts in high yields. The absorption and emission of the chromophore are sensitive to the local environment of the molecule,³¹ including perichromic shifts by surface immobilization.³² Although the parent coumarin itself absorbs only ultraviolet light, a suitable polar surface will shift the absorption considerably towards the visible region. The photocatalytic arylation of the coumarin chromophore causes an additional red-shift, easily detectable by the naked eye. We therefore selected coumarins to functionalize a surface for subsequent photo-patterning, as the arylation reaction can be visually monitored by a color change. 7-Hydroxycoumarin **1** was prepared from 1,3-dihydroxybenzene **5** and β -ketoester **6**



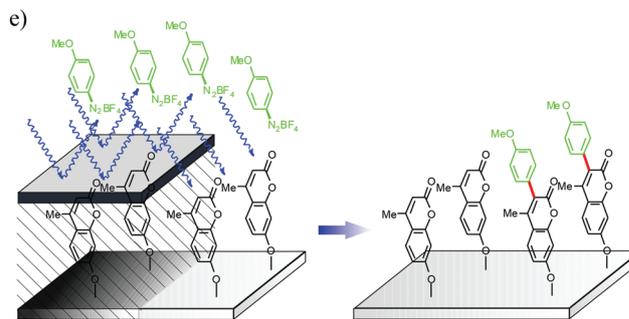
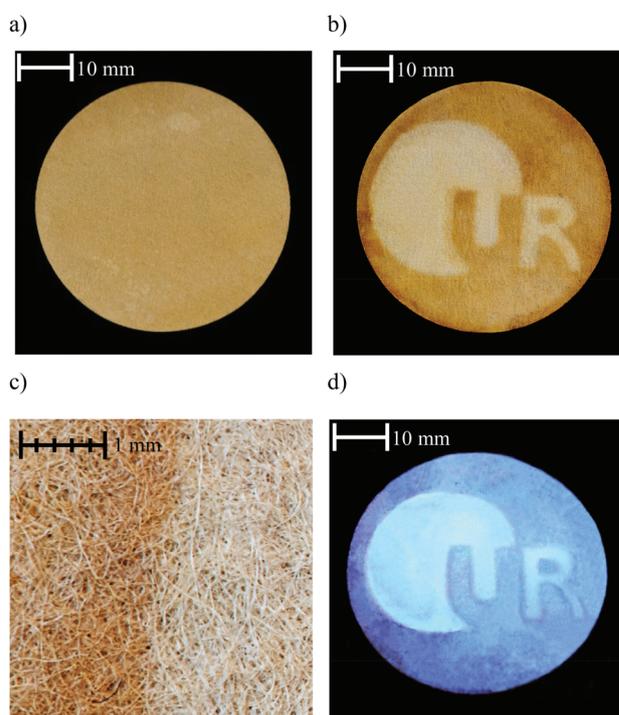
Scheme 2 Synthesis of 7-hydroxycoumarin by the Pechmann reaction.



Scheme 3 Synthesis of functionalized cellulose sheets. Loading of 21% coumarin per glucose monomer unit indicates a ratio of $n : m$ of about 4 : 1.

under acidic conditions by following a reported procedure (Scheme 2).³³

Cellulose contains several hydroxyl moieties able to serve as anchors for the covalent attachment of unsaturated chromophore **1**. The 7-hydroxy group of **1** represents the linker for attachment to the cellulose polymer. From the various hydroxyl groups in the polymer, the 6'-hydroxyl group is the most reactive.³⁴ Attachment of **1** *via* ether formation was achieved by tosylation of the 6'-hydroxyl group of cellulose in the form of filter papers followed by reaction with **1** (Scheme 3). The loading of cellulose with coumarin **1** was determined gravimetrically to be $21\% \pm 3\%$ with respect to the amount of glucose monomers as the average of three independent experiments. The method is suitable for the modification

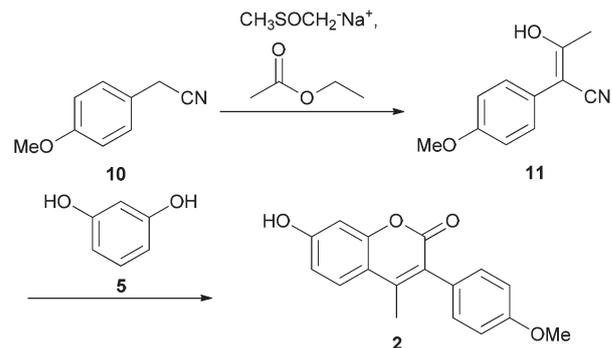


Scheme 4 (a) Photographs of coumarin-functionalized cellulose reacted with an aryl diazonium salt and $[Ru(bpy)_3]^{2+}$ photocatalyst through a mask before and (b) after exposure to visible light; (c) magnified boundary between illuminated and dark cellulose; (d) fluorescence emission at an excitation wavelength of 366 nm; (e) schematic molecular description of contrast formation through a photomask.

of larger cellulose sheets. In our case, standard filter paper 45 mm in diameter proved convenient for modification.

Cellulose filter paper sheets functionalized in this way were then used for photocatalytic experiments. Modified cellulose was soaked with a solution of *p*-methoxyphenyl diazonium tetra-fluoroborate and $[\text{Ru}(\text{bpy})_3]^{2+}$ in DMSO. A photomask covering part of the area was placed on the filter paper, and the setup was irradiated for 20 minutes with a blue high power light emitting diode. The filter paper was rinsed in methanol, water, and acetone, and dried in air. A pattern was immediately visible on the surface, as shown in Scheme 4.

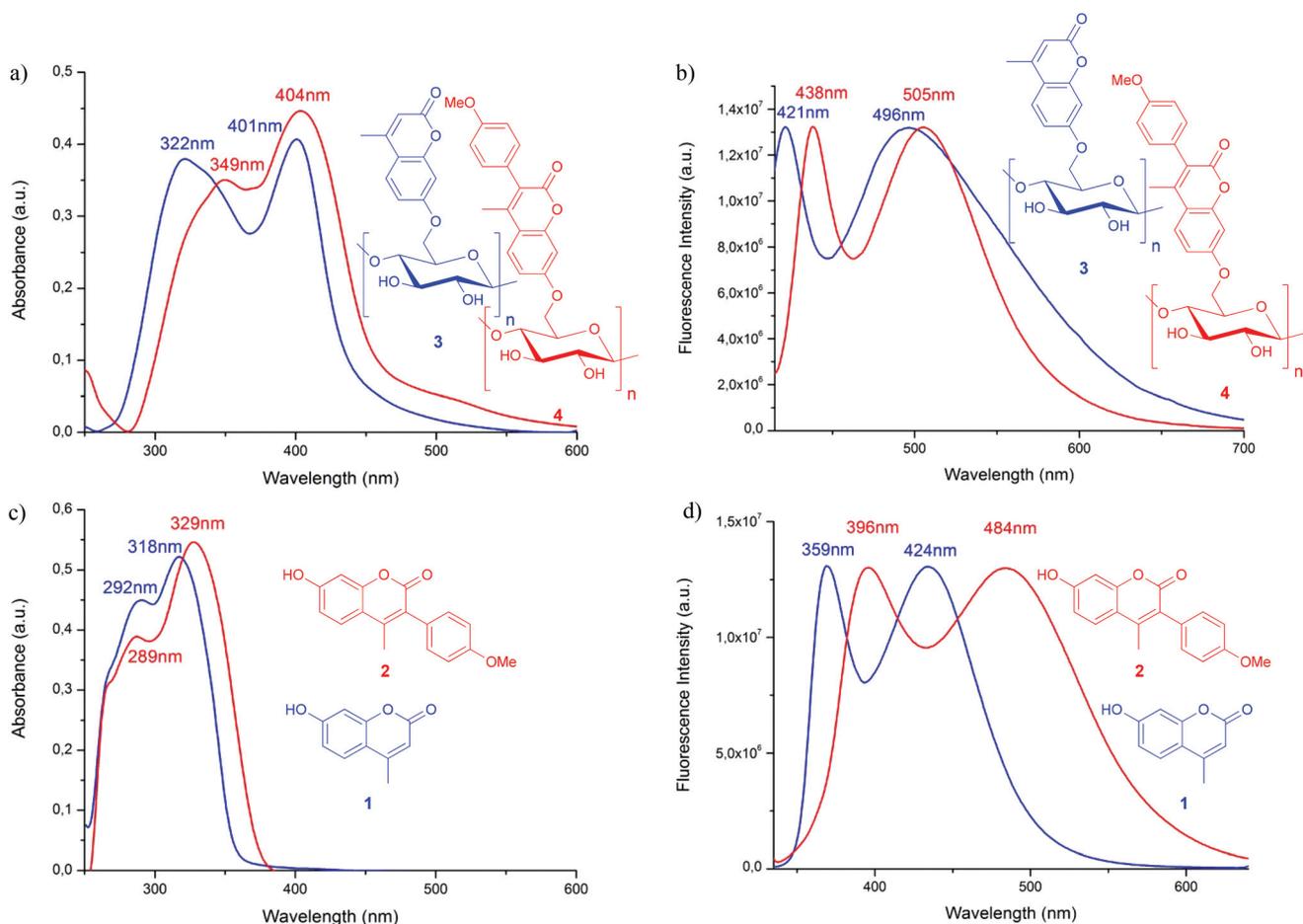
We attribute the absorption property changes to the photocatalytic arylation reaction that proceeded in irradiated areas, but not in surface areas of the cellulose sheet that were covered by the photomask. The reaction proceeds equally well with eosin Y as a metal-free photocatalyst, but the contrast of the image is lower in this case because removal of the dye eosin Y is less effective. A schematic description of the image formation is given in the following scheme. It is noteworthy that the 4-methyl group in 7-hydroxy-4-methyl-2*H*-chromen-2-one **3** has little effect on the molecule's absorption



Scheme 5 Synthetic route towards 3-aryl-2*H*-chromen-2-one.

maximum, but blocks the 4-position for arylation leading to the selective formation of a single product.

Control experiments using an identical setup without either photocatalyst, aryl diazonium salt, or light showed no pattern formation on the surface, indicating that all three reagents are indispensable for successful photoreaction. Absorption and emission spectra of the functionalized cellulose have been



Scheme 6 Absorption (left) and emission spectra (right) of cellulose-immobilized coumarins **3** and **4** (top) and compounds **1** and **2** obtained from "Photo-Meerwein" arylation in a homogeneous solution (bottom). Absorption and emission spectra (excitation wavelength 318 nm) in a homogeneous solution were measured in DMSO at $c = 4 \times 10^{-5} \text{ mol L}^{-1}$.

measured before and after the reaction. Diffuse UV/Vis reflectance spectra of the paper samples were recorded and converted into absorption spectra by applying the Kubelka–Munk transformation. Coumarin-functionalized cellulose **3** showed two absorption bands at 322 and 401 nm. After arylation, the bands of **4** were red-shifted to 349 and 404 nm, respectively. Fluorescence measurements of the cellulose paper samples (excitation wavelength 404 nm) showed two emission maxima at 421 and 496 nm before and at 438 and 505 nm after the photoreaction (Scheme 6).

For comparison, an analogous arylation reaction was performed in a homogeneous DMSO solution (Scheme 1a). 7-Hydroxy-4-methyl-2H-chromen-2-one **1** and the corresponding arylated photoproduct **2** showed absorption bands in DMSO at 292 and 318 nm before and 289 and 329 nm after the photoreaction. The absorption bands can be assigned to a π - π^* transition.³⁵ The large bathochromic shift of about 80 nm in a heterogeneous solution compared to the smaller changes in the homogeneous case is rationalized by the polar environment of the cellulose surface. The emission spectrum in DMSO (excitation wavelength 318 nm) of the photoproduct **2** shows two maxima at 396 and 484 nm, while the corresponding peaks of reactant **1** are at 359 and 424 nm.

As an additional proof of the formation of the 3-arylated photoproduct on cellulose, the arylated coumarin **2** was attached to cellulose for comparison. 7-Hydroxy-3-(4-methoxyphenyl)-4-methyl-2H-chromen-2-one **2** (Scheme 5) was immobilized in the same manner as that described in Scheme 3. Absorption spectra of this sample were recorded and showed, within the error of the measurement, identical absorption maxima as the material of the heterogeneous photoreaction, confirming the proposed formation of the arylated photoproduct.

Conclusions

Aryl radicals have previously been used for the direct modification of metal surfaces and polymer grafting on surfaces. We have extended the scope of such surface modifications to the arylation of coumarin-functionalized cellulose sheets using a Photo-Meerwein arylation reaction. The catalytic process generates aryl radicals from diazonium salts in the presence of the photocatalyst $[\text{Ru}(\text{bpy})_3]^{2+}$ upon irradiation with visible light. Such arylation of the coumarin alters the photophysical properties of the chromophore, leading to an image observable with the naked eye. The application of this spatially-controlled surface arylation protocol to diverse surface media bearing alkene or alkyne groups and a large variety of diazonium salts as aryl radical precursors can be readily envisaged.

The authors gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (Germany, DFG GRK 1626 – Chemical Photocatalysis), the Evonik Foundation (Germany, stipend for P.S.), and the NIH Dynamic Aspects of Chemical Biology Training Grant (USA, support for C.F.).

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