Writing and Erasing Hidden Optical Information on Covalently

Modified Cellulose Paper Cellulose Paper

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I) Experimental details

1) Material and methods

All commercial solvents and reagents were used as received from Sigma-Aldrich, Fischer Scientific Ltd, Alfa Aesar. Whatman[®] grade 6 filter paper (42.5 mm Ø) was used as cellulose source. ¹H and ¹³C, recorded at 400 MHz, 100 MHz, respectively, were performed on a Bruker Advance 400. Proton chemical shifts were internally referenced to the residual proton resonance in DMSO (2.50 ppm). Carbon chemical shifts were internally referenced to the deuterated solvent signals in DMSO (39.52 ppm). Melting points were recorded on a Stuart Scientific 7SMP3 apparatus. FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer with ATR technic. HRMS in ESI mode were recorded on a LTO-Orbitrap (ThermoFisher Scientific) at the ENV of Nantes. Scanning electron microscopy (SEM) images were recorded with a JEOL 7600 F at the "Centre de microcaractérisation de l'IMN, Université de Nantes". X-Ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-Ray Diffractometer. X-ray photoelectron spectroscopy was performed on a ThermoFisher Scientific K-ALPHA spectrometer was used for disk surface analysis with a monochromatized AlK α source (hv = 1486.6 eV) and a 200 micron spot size. A pressure of 10⁻⁷ Pa was maintained in the chamber during analysis. The full spectra (0-1150eV) were obtained at a constant pass energy of 200eV 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 ThermoFisher Scientific. Thermogravimetric analysis (TGA) profiles were obtained between 25 and 600°C using a Netzsch STA-449 F3 TGA/DSC at a heating rate of 5°C min⁻¹. UV-visible absorption spectra were recorded using a Varian Model Cary 5E spectrophotometer, using an integrating sphere DRA 2500. Photodimerization reaction was performed using a white light source Hg-Xe lamp (Hamamatsu-LC8) equipped with a narrow bandpass filter at 340 nm (12

nm fwmh) and a 6W UV lamp working at 254 nm. QR Code was read with a Samsung Galaxy S5 using QR Code Reader application from Scan,Inc. available for free on Google Play.

2) Preparation of coumarin derivatives

Preparation of ethyl 2-((2-oxo-2H-chromen-7-yl)oxy)acetate (2)¹

7-Hydroxycoumarin (5 g, 27.8 mmol) and potassium carbonate (3.8 g, 27,8 mmol) were placed in a 100 ml round bottom flask containing 25 ml of Acetone. Then ethyl-2-bromoacetate (3.4 ml, 30.5 mmol) was added dropwise. The reaction mixture was refluxed for 16 h under N₂. The reaction mixture was then cooled to room temperature. After salt filtration, acetone was evaporated and the product was recrystallized from ethanol giving pale yellow needles (5.6 g, 81%). mp. 114-116 °C [lit.¹ 113-115 °C].

¹H NMR (400 MHz, DMSO,) δ 7.99 (d, 1H, J = 9.5 Hz), 7.64 (d, 1H, J = 8.4 Hz), 7.0-6.96 (m, 2H), 6.31 (d, 1H, J = 9.5 Hz), 4.92 (s, 1H), 4.19 (q, 2H, J = 7.1 Hz), 1.22 (t, 3H, J = 7.1 Hz); ¹³C NMR (100 MHz, DMSO) δ 168.1, 160.6, 160.1, 155.1, 144.1, 129.5, 112.9 (2C), 112.6, 101.5, 65.0, 60.8, 14.0; IR (ATR) v 3077, 2991, 1708, 1611, 1561, 1509, 1454, 1400, 1376, 1350, 1285, 1264, 1221, 1192, 1157, 1124, 1069, 1017, 981, 897, 861, 840, 811, 755, 725, 689, 630, 617, 588, 477, 460 cm⁻¹; HRMS (ESI) calcd for C₁₃H₁₃O₅ [M+H⁺]: 249.0757, found: 249.0757.

Preparation of 2-((2-oxo-2H-chromen-7-yl)oxy)acetic acid (3)¹

Compound **2** (5 g, 20 mmol) and sodium hydroxide (11.2 g, 280 mmol) were dissolved in 500 mL of water/dioxane (4/6 v/v). The solution was stirred overnight at room temperature, then the solvent was evaporated under reduced pressure. The yellow residue was dissolved in 50 mL of water and acidified with concentrated hydrochloric acid under ice cooling. The white precipitate was collected by filtration, washed with water, recrystallized from ethanol and dried in vacuum at room temperature giving a white solid (3.4 g, 77%). mp. 213-217 °C [lit.¹ 209-213 °C].

¹H NMR (400 MHz, DMSO,) δ 13.09 (bs, 1H), 7.98 (d, 1H, J = 9.5 Hz), 7.64 (m, 1H), 6.97-6.94 (m, 2H), 6.30 (d, 1H, J = 9.5 Hz), 4.82 (s, 1H); ¹³C NMR (100 MHz, DMSO) δ 169.5, 160.8, 160.1, 155.1, 144.2, 129.4, 112.8, 112.7, 112.5, 101.5, 64.8; IR (ATR) v 3079, 2908, 2791, 2591, 1708, 1608, 1561, 1511, 1491, 1459, 1430, 1418, 1403, 1350, 1275, 1250, 1208, 1156, 1123, 1072, 99, 895, 832, 767, 751, 728, 671, 627, 617, 552, 518, 478, 463, 453, 399, 395 cm⁻¹; HRMS (ESI) calcd for C₁₁H₈O₅Na [M+Na⁺]: 243.0269, found: 243.0272.

Preparation of 2-((2-oxo-2H-chromen-7-yl)oxy)acetyl chloride (4)²

Carboxylic acid **3** (880 mg, 4 mmol) and a catalytic amount of DMF were suspended in chloroform (30 ml). Then, thionyl chloride (2.8 ml, 38 mmol) was added dropwise. The reaction mixture was refluxed for 2 h under N_2 . Then the solution was evaporated under reduce pressure and dry toluene was added to remove remaining thionyl chloride. Acyl chloride **4** was obtained as a white solid and was used directly without further purification.

3) Preparation of cellulosic material

General procedure for the pre-treatment of cellulose paper³

Five piece of cellulose filter paper (approx. 750 mg) were dispersed in 250 ml of 10% NaOH. This mixture is then shacked for 24 h on a shacking device. The cellulose samples were then washed 6 times with 50 ml of EtOH and stored in EtOH.

General procedure for the preparation of paper-grafted coumarins⁴

After being washed 2 times with 10 ml pyridine, a piece of pretreated cellulose paper (approx. 145 mg, 0.9 mmol) was immersed in 25 ml of dry pyridine. A catalytic amount of DMAP was

added to the reaction media and stirred for 5 minutes. Acyl chloride 4 (476 mg, 2 mmol) dissolved in 5 ml of dry DMF was then added dropwise to the solution. The mixture is then stirred for 20 h at 60 °C under N_2 . The piece of paper was then sonicated in DMF, EtOH, Acetone and DCM before being dried under vacuum. The sample was kept in dark with an aluminum foil during all the preparation and storage.

General procedure for the photodimerization of coumarin modified cellulose paper

A piece of coumarin modified cellulose paper was fixed on a glass microscope slide. This piece of paper was then irradiated with both 340 and 254 nm light sources.

4) Computational details

We have carried out our theoretical simulations using Density Functional Theory (for groundstate) and Time-Dependent Density Functional Theory (for the excited-states). More precisely, we have selected the PBE0 hybrid functional⁵ to perform our calculations, as this functional was previously reported to be adequate to determine the spectral properties of coumarin derivatives,⁶ and the 6-31G(d) atomic basis set. In addition, we have added dispersion correction that are potentially necessary to accurately describe the interactions between coumarins as well as the interactions between cellulose and the dyes. The dispersion corrections were added using the D3-BJ empirical scheme.⁷ To perform our calculations, we have extracted a segment of 6 D-glucose units from an experimentally available X-Ray structure,⁸ and added the coumarins and their grafting moiety. In other words, primary hydroxyl groups of glucose units were functionalized with 7-hydroxycoumarin through an acetate linker. Several relative positions of the coumarins have been tested (attached to the third and fourth or to the third and fifth glucose - more distant arrangements making dimerization clearly very unlikely) and for each case, several starting conformations have been considered. We nevertheless underline that our goal was not to provide a complete investigation of all possible isomers and conformers of coumarin grafted on cellulose, but rather to confirm the viability of the proposed strategy. Optimization, considering a frozen structure for the cellulose (and unconstrained structures for coumarins and their arms) were then carried out *via* a standard force minimization process until the *rms* force was smaller than 10⁻⁵ a.u., corresponding to the so-called *tight* threshold. Several structures were obtained, but only the lowest energy ones are discussed in the main text. The excited-state calculations have been performed at the TD-PBE0/6-31G(d) level, considering the vertical approximation and the most stable systems obtained at the optimization step, so to provide indications of the influence of the dimerization on the optical spectra of grafted coumarins. Calculations (same level of theory) have also been performed on the 7-OMe-coumarin and the corresponding dimer for comparison purposes. All calculations were performed with the Gaussian09.D01 program.⁹

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¹³C NMR (DMSO, 100MHz) of ethyl 2-((2-oxo-2H-chromen-7-yl)oxy)acetate (2)



¹H NMR (DMSO, 400MHz) of 2-((2-oxo-2H-chromen-7-yl)oxy)acetic acid (3)



¹³C NMR (DMSO, 100MHz) of 2-((2-oxo-2H-chromen-7-yl)oxy)acetic acid (3)





Fig. S1 UV-Visible spectrum of paper-grafted coumarins



Fig. S2 FT-IR spectra of (a) pristine paper, (b) functionalized paper with (4), (c) paper stirred with coumarin (3)



Fig. S3 SEM images of (a) pristine paper, (b) paper-grafted coumarins with the corresponding photograph as inset.



Fig. S4 Survey scan spectra of (a) pristine paper, (b) paper-grafted coumarins. High resolution C1s spectra of (c) pristine paper and (d) paper-grafted coumarins



Fig. S5 Fatigue test resistance of the patterned paper upon alternate irradiation at 340 (decrease in absorbance) and 254 nm (increase in absorbance)



Fig. S6 XRD pattern of the paper-grafted coumarins



Fig. S7 Thermogravimetric analysis of pristine cellulose paper (blue) and paper-grafted coumarins (red)