Electronic Supplementary Information

Chemically-Modified Cellulose Paper as Smart Sensor Device for Colorimetric and Optical Detection of Hydrogen Sulfate in Water

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1. Materials

All commercial solvents and reagents were used as received without further purification from Sigma-Aldrich, Fischer Scientific Ltd, Alfa Aesar. Whatman® grade 6 filter paper (42.5 mm Ø) was used as cellulose source.

2. Analytical methods

^{1}H and ^{13}C NMR spectra, recorded at 400 MHz and 100 MHz respectively, were performed on a Bruker Advance 400. Proton chemical shifts were internally referenced to the residual proton resonance in $CDCl_3$ (7.26 ppm). Carbon chemical shifts were internally referenced to the deuterated solvent signals in $CDCl_3$ (77.0 ppm). FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer with ATR technique. Scanning Electron Microscopy (SEM) was performed on a JEOL JSH7600F (field emission gun, accelerating voltage: 5 kV, in lens detector of secondary electrons). X-ray photoelectron spectroscopy (XPS) was performed on a ThermoFisher Scientific K-ALPHA spectrometer for disk surface analysis with a monochromatized AlKα source (hν = 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 (0–1150 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 ThermoFisher Scientific. UV-visible absorption spectra were recorded using a Varian Model Cary 5E spectrophotometer, using an integrating sphere DRA 2500.

3. Synthetic procedures

Compound 2.[8] To a solution of Rhodamine B (**1**) (2.0 g, 4.2 mmol) in ethanol (50 mL) was added dropwise an excess of ethylenediamine (2.20 mL, 33 mmol). The resulting pink mixture was refluxed for 24 hours and became orange. The solvent was removed under reduced pressure, water (35 mL) was added to the residue and the solution was extracted with CH_2Cl_2 (3 x 35 mL). The combined organic phases were washed with water, brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the product was dried under vacuum, affording a pale-orange solid **2** (2.0 g, yield 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.88 (m, 1H), 7.42-7.41 (m, 2H), 7.09-7.06 (m, 1H), 6.43 (s, 1H), 6.41 (s, 1H), 6.37 (s, 2H), 6.28-6.25 (m, 2H), 3.32 (q, J= 7.2 Hz, 8H), 3.18 (t, 2H,

J = 6.8 Hz), 2.40 (t, 2H, J = 6.8 Hz), 1.15 (t, 12H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 153.4, 153.3, 148.8, 132.3, 131.2, 128.6, 128.0, 123.8, 122.7, 108.1, 105.7, 97.7, 64.9, 44.3, 43.9, 40.8, 12.5; FT-IR (ATR) ν 2970, 2926, 2903, 2871, 1686, 1631, 1613, 1545, 1510, 1467, 1447, 1423, 1376, 1352, 1328, 1306, 1261, 1215, 1152, 1115, 1090, 1067, 1017, 816, 784, 756, 700, 535 cm^{-1}; MS (EI) : m/z = 484 (M^+), 454 (M-$CH_2NH_2^+$).

General procedure for the pre-treatment of cellulose paper. Ten pieces of cellulose filter papers (approx. 1.50 g) were immersed in a freshly prepared aqueous solution of 10% NaOH (300 mL). This mixture was shacked overnight on an orbital agitator. The cellulose samples were washed 3 times with 50 mL of EtOH and stored in EtOH.

General procedure for the preparation of paper-grafted benzaldehyde. A pre-treated cellulose filter paper (approx. 145 mg, 0.90 mmol glucose units) washed 2 times with 5 mL of pyridine, was immersed in dry pyridine (25 mL). A catalytically amount of 4-DMAP was added to the reaction media and stirred for 5 minutes. Then, 4-formylbenzoyl chloride[1] (455 mg, 2.7 mmol) dissolved in dry DMF (5 mL) was then added dropwise to the solution. The mixture was stirred for 16 h at 70 °C under N_2 atmosphere. The piece of paper was sequentially washed with EtOH, MeOH, acetone and CH_2Cl_2 under sonication. The sample was dried under vacuum and stored under nitrogen.

General procedure for the paper-grafted rhodamine. Rhodamine **2** (1.53 g, 3.16 mmol), AcOH (two drops) and $MgSO_4$ (100 mg) were added to the paper-grafted benzaldehyde (approx. 170 mg, 1.05 mmol) immersed in dry toluene (30 mL). This heterogeneous mixture was refluxed for 16 hours. After cooling the mixture to room temperature, the cellulose paper was washed with EtOH, acetone and CH_2Cl_2 under sonication and dried under vacuum. To the resulting material immersed in dry MeOH (30 mL), $NaBH_3CN$ (333 mg, 16 mmol) was added portionwise over 3 hours and the resulting mixture was further stirred for 3 h at room temperature. Finally, the piece of paper was sequentially washed with MeOH, acetone and CH_2Cl_2 under sonication, dried under vacuum and stored under nitrogen.

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[1] D. Y. Q. Wong, J. Y. Lau and W. H. Ang, *Dalton Trans.*, 2012, **41**, 6104-6111.