Anthraquinone dyes for superhydrophobic cotton

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Contents

| Synthetic procedures 4 Synthesis of compound 2 4 Synthesis of compound 3 4 Synthesis of compound 4 5 Synthesis of compound 5 5 Synthesis of compound 6 6 Synthesis of compound 7 7 Synthesis of compound 7 7 Synthesis of compound 8 7 Synthesis of compound 9 8 Synthesis of compound 10 9 Synthesis of compound 11 9 Synthesis of compound 12 10 Synthesis of compound 13 11 Synthesis of compound 14 11 Synthesis of compound 15 12 Synthesis of compound 16 13 Synthesis of compound 17 14 Synthesis of compound 18 14 Collection of spectra 15 Compound 2 16 Compound 3 18 Compound 5 22 Compound 6 25 |
|--|
| Synthesis of compound 2 |
| Synthesis of compound 3 |
| Synthesis of compound 4 .5 Synthesis of compound 6 .5 Synthesis of compound 7 .7 Synthesis of compound 8 .7 Synthesis of compound 9 .8 Synthesis of compound 10 .9 Synthesis of compound 11 .9 Synthesis of compound 12 .10 Synthesis of compound 13 .11 Synthesis of compound 14 .11 Synthesis of compound 15 .12 Synthesis of compound 16 .13 Synthesis of compound 17 .14 Synthesis of compound 18 .14 Collection of spectra .15 Compound 3 .18 Compound 4 .20 Compound 5 .22 Compound 5 .22 Compound 6 .25 Some and 7 .28 |
| Synthesis of compound 5 |
| Synthesis of compound 6 6 Synthesis of compound 7 7 Synthesis of compound 8 7 Synthesis of compound 9 8 Synthesis of compound 10 9 Synthesis of compound 11 9 Synthesis of compound 12 10 Synthesis of compound 13 11 Synthesis of compound 14 11 Synthesis of compound 15 12 Synthesis of compound 16 13 Synthesis of compound 17 14 Synthesis of compound 18 14 Collection of spectra 15 Compound 3 18 Compound 4 20 Compound 5 22 Compound 6 25 |
| Synthesis of compound 77Synthesis of compound 87Synthesis of compound 98Synthesis of compound 109Synthesis of compound 119Synthesis of compound 1210Synthesis of compound 1311Synthesis of compound 1411Synthesis of compound 1512Synthesis of compound 1613Synthesis of compound 1714Synthesis of compound 1814Collection of spectra15Compound 318Compound 420Compound 522Compound 625Compound 728 |
| Synthesis of compound 8 .7 Synthesis of compound 10 .8 Synthesis of compound 10 .9 Synthesis of compound 11 .9 Synthesis of compound 12 .10 Synthesis of compound 13 .11 Synthesis of compound 14 .11 Synthesis of compound 15 .12 Synthesis of compound 16 .13 Synthesis of compound 17 .14 Synthesis of compound 18 .14 Collection of spectra .15 Compound 2 .16 Compound 3 .18 Compound 5 .22 Compound 6 .25 Compound 7 .28 |
| Synthesis of compound 9 .8 Synthesis of compound 10 .9 Synthesis of compound 11 .9 Synthesis of compound 12 .10 Synthesis of compound 13 .11 Synthesis of compound 14 .11 Synthesis of compound 15 .12 Synthesis of compound 16 .13 Synthesis of compound 16 .13 Synthesis of compound 16 .13 Synthesis of compound 17 .14 Synthesis of compound 18 .14 Collection of spectra .15 Compound 2 .16 Compound 3 .18 Compound 4 .20 Compound 5 .22 Compound 6 .25 Compound 7 .28 |
| Synthesis of compound 109Synthesis of compound 119Synthesis of compound 1210Synthesis of compound 1311Synthesis of compound 1411Synthesis of compound 1512Synthesis of compound 1613Synthesis of compound 1714Synthesis of compound 1814Collection of spectra15Compound 216Compound 318Compound 420Compound 522Compound 625Compound 728 |
| Synthesis of compound 11.9Synthesis of compound 12.10Synthesis of compound 13.11Synthesis of compound 14.11Synthesis of compound 15.12Synthesis of compound 16.13Synthesis of compound 17.14Synthesis of compound 18.14Collection of spectra.15Compound 2.16Compound 4.20Compound 5.22Compound 6.25Compound 7.28 |
| Synthesis of compound 12 10 Synthesis of compound 13 11 Synthesis of compound 14 11 Synthesis of compound 15 12 Synthesis of compound 16 13 Synthesis of compound 17 14 Synthesis of compound 18 14 Collection of spectra 15 Compound 2 16 Compound 3 18 Compound 5 22 Compound 6 25 Compound 7 28 |
| Synthesis of compound 1311Synthesis of compound 1411Synthesis of compound 1512Synthesis of compound 1613Synthesis of compound 1714Synthesis of compound 1814Collection of spectra15Compound 216Compound 318Compound 420Compound 522Compound 625Compound 728 |
| Synthesis of compound 14 11 Synthesis of compound 15 12 Synthesis of compound 16 13 Synthesis of compound 17 14 Synthesis of compound 18 14 Collection of spectra 15 Compound 2 16 Compound 3 18 Compound 4 20 Compound 5 22 Compound 6 25 Compound 7 28 |
| Synthesis of compound 1512Synthesis of compound 1613Synthesis of compound 1714Synthesis of compound 1814Collection of spectra15Compound 216Compound 318Compound 420Compound 522Compound 625Compound 728 |
| Synthesis of compound 1613Synthesis of compound 1714Synthesis of compound 1814Collection of spectra15Compound 216Compound 318Compound 420Compound 522Compound 625Compound 728 |
| Synthesis of compound 1714Synthesis of compound 1814Collection of spectra15Compound 216Compound 318Compound 420Compound 522Compound 625Compound 728 |
| Synthesis of compound 1814Collection of spectra15Compound 216Compound 318Compound 420Compound 522Compound 625Compound 728 |
| Collection of spectra 15 Compound 2 16 Compound 3 18 Compound 4 20 Compound 5 22 Compound 6 25 Compound 7 28 |
| Compound 2 |
| Compound 3 |
| Compound 4 20 Compound 5 22 Compound 6 25 Compound 7 28 |
| Compound 5 22 Compound 6 25 Compound 7 28 |
| Compound 6 |
| Compound 7 28 |
| Compound 7 |
| Compound 8 |
| Compound 9 |
| Compound 10 |
| Compound 11 |
| Compound 12 |
| Compound 13 |
| Compound 14 |
| Compound 15 |

| Compound 16 | 53 |
|---|----------|
| Compound 17 | 56 |
| Staining processes | 59 |
| Measures of contact angles of a drop of water deposited on top of stained | fabric61 |
| Determination of water vapor permeability under static conditions | 62 |
| ISO 105-C06 colour fastness to domestic and commercial laundering | 63 |

Materials and Methods

Reagents: All commercially acquired reagents were used as received. Tetrahydrofuran and dichloromethane were dried by passing through a column of activated molecular sieves using a solvent purification system.

Reaction conditions: Reactions requiring inert atmosphere were conducted under nitrogen or argon using standard Schlenk techniques. All other reactions were performed employing standard organic synthesis protocols.

Chromatography: Thin layer chromatography (TLC) was performed using Merck aluminium backed plates of TLC Silica gel 60 F_{254} ; the plates were revealed using UV light. Standard Flash Column chromatography was accomplished using silica gel (60 Å pore size, 230-400 µm mesh size).

NMR: Spectra were recorded using Bruker spectrometers DXP-360 and AVANCE-III 400 (Servei de Ressonància Magnètica Nuclear, UAB, 360 MHz (¹H); 90 MHz (¹³C) and 400 MHz (¹H); 100 MHz (¹³C); 235 MHz (¹⁹F) respectively). ¹H and ¹³C chemical shifts are reported in ppm relative to tetramethylsilane, using residual proton and ¹³C resonances from solvent as internal standards. The ¹⁹F chemical shifts are reported in ppm relative to external CFCl₃.

Other analytical techniques: Infrared spectra were recorded using a Bruker Tensor 27 instrument equipped with an ATR Golden Gate cell and a diamond window. UV-Vis spectra were recorded using a Hewlett-Packard 8453 and quartz cuvette (1 cm). High resolution mass spectra were determined at the *Servei d'Anàlisi Química* of the *Universitat Autònoma de Barcelona* and at the *Universidad de Zaragoza* using a direct inlet system (ESI). Spin-coating depositions were conducted at Nanoquim platform of the ICMAB (CSIC) using a Laurell WS-650SZ-6NPP/LITE spinner; contact angles were determined using a KRÜSS DSA 100, in a controlled humidity atmosphere.

Synthetic procedures

Synthesis of compound 2



In a 250 mL round bottom Schlenk flask equipped with magnetic stir bar cyanuric chloride (5.42 mmol, 1 g, 1 eq.) was added and the atmosphere was replaced for argon. Cyanuric chloride was dissolved in anhydrous THF (50 mL), DIPEA (16.07 mmol, 2.8 mL, 3 eq.) was added and the mixture was cooled at 1-2°C. At this temperature a solution of 1-dodecanethiol (9.17 mmol, 2.2 mL, 1.7 eq.) in anhydrous THF (40 mL) was slowly added, the mixture is allowed to react during 150 min. After this time the solvent was removed and the reasulting white semisolid was purified by flash chromatography (silica gel, Hexane:AcOEt 98:2). Colorless liquid, yield: 2.3 g, 83 %, which is stored at -30°C.

¹H NMR (360 MHz, CDCl₃, 25°C): $\delta = 3.12$ (t, J = 7.5 Hz, 4H), 1.72 (quin, J = 7.5 Hz, 4H), 1.40 (m, 4H), 1.26 (m, 32H), 0.88 (t, J = 6.7 Hz, 6H). ¹³C NMR (90 MHz, CDCl₃, 25°C): $\delta = 183.0$, 167.9, 31.9, 30.7, 29.6, 29.5, 29.4, 29.3, 29.0, 28.7, 22.6, 14.0. (reference 7 in the text)

Synthesis of compound 3



In a 50 mL round bottom Schlenk flask equipped with magnetic stir bar cyanuric fluoride (0.74 mmol, 64 μ L, 1 eq.) was added and the atmosphere was replaced for argon. Cyanuric fluoride was dissolved in anhydrous CH₂Cl₂ (20 mL), DIPEA (8.61 mmol, 1.5 mL, 12 eq.) was added and the mixture was cooled at -78°C. At this temperature a solution of 1-dodecanethiol (1.3 mmol, 0.3 mL, 1.8 eq.) in anhydrous CH₂Cl₂ (16 mL) was slowly added (via cannula), the mixture is allowed to react during 45 min. After this time the solvent was removed and the reasulting white semisolid was dissolved in hexane (20 mL) and extracted with 2 x 10 mL of acetonitrile. Solvent was

removed from the hexane fraction affording a colorless oil (yield: 255 mg, 76 %), which is stored at -30°C.

¹H NMR (360 MHz, CDCl₃, 25°C): δ = 3.13 (t, *J* = 7.2 Hz, 4H), 1.72 (quin, *J* = 7.2 Hz, 4H), 1.43 (quin, *J* = 7.2 Hz, 4H), 1.26 (m, 32H), 0.88 (t, *J* = 7.1 Hz, 6H).). ¹⁹F NMR (235 MHz, CDCl₃, 25°C): δ = -41.7.

Synthesis of 1,4-dinitroanthraquinone 4



A 1 L round bottom flask equipped with magnetic stir bar was charged with trifluoroacetic anhydride (0.57 mol, 80 mL) and H_2O_2 (30 %) (0.65 mol, 20 mL) was slowly dropped during 15 minutes. Then, 800 mL of a solution containing 1 (8.39 mmol, 2 g) in anhydrous CH_2Cl_2 was added and the mixture is allowed to react at 40 °C protected from water with CaCl₂ tube for 6 days. After that, solvent was removed using a rotary evaporator until the volume was constant. The suspension was filtered affording 3 g of pale yellow solid (62 % yield).

¹H NMR (360 MHz, [D₆]DMSO, 25°C): δ = 8.48 (s, 2H), 8.13 (dd, *J* = 5.5, 3.2 Hz, 2H), 7.96 (dd, *J* = 5.5, 3.2 Hz, 2H). ¹³C NMR (90 MHz, [D₆]DMSO, 25°C): δ = 179.0, 149.0, 135.6, 132.9, 129.7, 127.3, 126.2. (reference 8 in the text)

Synthesis of compound 5



In a 250 mL round bottom flask equipped with magnetic stir bar 4 (10.1 mmol, 3 g, 1 eq.) was dissolved in 1,4-dioxane (118 mL). Then, 1,4-diaminobutane (60.4 mmol, 6.1 mL, 6 eq.) was added and the mixture was protected from water with CaCl₂ tube and allowed to react during 16 h. After that time the reaction crude was poured into a mixture of 700 mL of CH₂Cl₂ and 150 mL of methanol. The organic layer was extracted

with 2 x 250 mL of brine, dried with anhydrous Na_2SO_4 and the solvent was removed without heating affording red solid which was purified by flash chromatography (silica gel, CHCl₃:MeOH 95:5 to 90:10). Red solid, yield: 2.9 g, 85 %.

¹H NMR (400 MHz, CDCl₃+[D₄]MeOH, 25°C): $\delta = 7.92$ (m, 1H), 7.83 (m, 1H), 7.54 (m, 2H), 7.34 (d, J = 9.1 Hz, 1H), 6.83 (d, J = 9.1 Hz, 1H), 3.16 (t, J = 6.7 Hz, 2H), 2.61 (t, J = 7.4 Hz, 2H), 1.60 (m, 2H), 1.49 (m, 2H). ¹³C NMR (100 MHz, CDCl₃+[D₄]MeOH, 25°C): $\delta = 188.4$, 185.5, 156.1, 142.9, 138.4, 137.6, 137.5, 136.4, 133.8, 131.7, 130.5, 130.4, 120.6, 115.5, 46.4, 44.4, 32.5, 29.8. HRMS (ESI) m/z calcd for C₁₈H₁₇N₃O₄ [M+H]⁺ 340.1292, found 340.1288. IR (ATR) v (cm⁻¹) 3365, 3269, 2931, 2868, 1627, 1629, 1593, 1514, 1471, 1440, 1359, 1299, 1259, 1170, 1149, 1047, 1012, 823, 796, 725, 698, 638. UV-Vis (CHCl₃) λ_{max} : 501 nm ($\varepsilon = 4464$ M⁻¹·cm⁻¹).

Synthesis of compound 6



In a 250 mL round bottom flask equipped with magnetic stir bar **5** (2.94 mmol, 1.0 g, 1 eq.) was dissolved in DMSO (150 mL) and was heated at 100 °C. When set temperature was reached 1,4-diaminobutane (23.5 mmol, 1.8 mL, 8 eq.) was added and the mixture was protected from water with CaCl₂ tube and allowed to react during 36 h. After that time the reaction crude was poured over 1000 mL of CH₂Cl₂, the organic layer was extracted with 4 x 500 mL of water, dried with anhydrous Na₂SO₄ and the solvent was removed, affording **6**. Blue solid, yield: 1.1 g, 96 %.

¹H NMR (400 MHz, CDCl₃ + [D₂]HFIP, 25°C): $\delta = 10.78$ (t, J = 5.3 Hz, 2H), 8.30 (dd, J = 5.8, 3.2 Hz, 2H), 7.66 (dd, J = 5.8, 3.2 Hz, 2H), 7.17 (s, 2H), 3.38 (q, J = 7.0 Hz, 4H), 2.77 (t, J = 7.0 Hz, 8H), 1.78 (m, 4H), 1.64 (m, 4H). ¹³C NMR (100 MHz, CDCl₃ + [D₂]HFIP, 25°C): $\delta = 182.2$, 146.0, 134.4, 131.9, 125.9, 123.4, 109.7, 42.6, 41.6, 30.8, 27.0. HRMS (ESI) m/z calcd for C₂₂H₂₈N₄O₂ [M+H]⁺ 381.2285, found 381.2265. IR (ATR) v (cm⁻¹) 2923, 2852, 1643, 1569, 1554, 1519, 1467, 1390, 1257, 1162, 1049, 1014, 798, 725, 665, 651. UV-Vis (CHCl₃) λ_{max} : 601 nm ($\varepsilon = 7765$ M⁻¹·cm⁻¹); 650 nm ($\varepsilon = 8620$ M⁻¹·cm⁻¹).

Synthesis of compound 7



A 1 L round bottom Schlenk flask equipped with magnetic stir bar was charged with cyanuric chloride (21.6 mmol, 4.0 g, 1 eq.) and the atmosphere was replaced for argon. Cyanuric chloride was dissolved with anhydrous THF (300 mL), DIPEA (68.8 mmol, 12 mL, 3.2 eq.) was added and the mixture was placed into ice/brine cooling bath. When the temperature reached 1-2 °C 400 mL of a solution of 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (34.6 mmol, 10 mL, 1.6 eq.) in anhydrous THF was slowly added via cannula under inert atmosphere during 2.5 h. After that time solvent was removed, affording a white solid which was dissolved with 100 mL of absolute ethanol and the suspension was filtered. The solid was discarded and the solution's solvent was removed, affording 7. Viscous colourless liquid, yield: 19.9 g, 91 %. Store at -30 °C.

¹H NMR (250 MHz, CDCl₃, 25°C): $\delta = 3.72$ (q, J = 6.9 Hz, 4H), 2.57 (m, 4H). (reference 7 in the text)

Synthesis of compound 8



A 100 mL round bottom flask equipped with magnetic stir bar was charged with **6** (0.26 mmol, 100 mg) and DMSO (26 mL, anhydrous). The solution was allowed to stir some minutes and then a solution of **2** (0.78 mmol, 403 mg) in THF (26 mL, anhydrous) and DIPEA (0.93 mmol, 160 μ L) were added at the same time. The mixture was heated at 50 °C protected from water with CaCl₂ tube for 16 h. The crude was poured into CH₂Cl₂ (300 mL) and the organic layer was extracted with brine (150 mL) and water

(150 mL, twice). The organic layer was dried using Na_2SO_4 (anh), the solvent was removed and the product **8** was purified by column chromatography (silica gel, CH₂Cl₂:MeOH 98:2). Blue solid, yield: 250 mg, 72 %.

¹H NMR (360 MHz, CDCl₃, 25°C): $\delta = 10.79$ (t, J = 5.2 Hz, 2H), 8.33 (dd, J = 6.1, 3.2 Hz, 2H), 7.68 (dd, J = 6.1, 3.2 Hz, 2H), 7.20 (s, 2H), 5.40 (t, J = 5.7 Hz, 2H), 3.50 (m, 4H), 3.44 (m, 4H), 3.03 (m, 8H), 1.81 (m, 8H),1.67 (m, 8H), 1.39 (m, 8H) 1.25 (m, 64H), 0.87 (t, J = 6.7 Hz, 12H). ¹³C NMR (90 MHz, CDCl₃, 25°C): $\delta = 182.4$, 180.2, 179.4, 162.8, 146.0, 134.4, 132.0, 126.0, 123.4, 109.9, 42.3, 40.3, 31.9, 30.1, 30.0, 29.6, 29.6, 29.4, 29.3, 29.2, 29.2, 29.0, 28.8, 27.1, 26.8, 22.6, 14.1. HRMS (ESI) m/z calcd for C₇₆H₁₂₆N₁₀O₂S₄ [M+Na]⁺ 1361.8840, found 1361.8838. IR (ATR, cm⁻¹): 3259, 2920, 2850, 1568, 1487, 1299, 1263, 1242, 1164, 1016, 850, 796, 721. UV-Vis (CHCl₃) λ_{max} : 601 nm ($\varepsilon = 14034$ M⁻¹·cm⁻¹); 649 nm ($\varepsilon = 14083$ M⁻¹·cm⁻¹).

Synthesis of compound 9



A 250 mL round bottom flask equipped with magnetic stir bar was charged with 6 (0.47 mmol, 180 mg, 1 eq.), 40 mL of anhydrous DMSO under N₂ atmosphere. Then, DIPEA (1.40 mmol, 240 μ L, 1.5 eq.) and 7 (0.93 mmol, 1.0 g, 1 eq.) in 80 mL of anhydrous THF were added at the same time. The mixture was heated at 50 °C and allowed to react for 16 hours. After that, the solvent was partially removed (until volume remains constant) and the solution was poured into 500 mL of water. The precipitate was filtered and washed with 4 x 50 mL of water. 9 can be separated from 6 putting them in CH₃CN, solvent in which 9 floats and 6 doesn't. Blue solid, yield: 0.85 g, 74 %.

¹H NMR (400 MHz, CDCl₃ + [D₂]HFIP, 25°C): $\delta = 8.23$ (dd, J = 6.0, 3.2 Hz, 2H), 7.73 (dd, J = 6.0, 3.2 Hz, 2H), 7.28 (s, 2H), 3.48 (m, 8H), 3.26 (m, 8H), 2.52 (m, 8H), 1.79 (br s, 8H). ¹³C NMR (100 MHz, CDCl₃ + [D₂]HFIP, 25°C): $\delta = 181.7, 179.4, 177.8, 161.9, 147.5, 133.9, 132.6, 125.7, 124.7, 42.1, 40.3, 31.3, 26.4, 26.3, 21.0. MS (MALDI⁺) (Ditranol/NaTFA) m/z calcd for C₆₈H₄₂F₆₈N₁₀O₂S₄ [M+H]⁺ 2451.1,$

[M+Na⁺] 2473.1 found 2451.4, 2473.4 . IR (ATR) v (cm⁻¹) 3239, 2929, 2856, 1676, 1573, 1523, 1197, 1143, 1020, 954, 848, 798, 727, 705, 651. UV-Vis (CHCl₃) λ_{max} : 598 nm ($\varepsilon = 12026 \text{ M}^{-1} \cdot \text{cm}^{-1}$); 649 nm ($\varepsilon = 12772 \text{ M}^{-1} \cdot \text{cm}^{-1}$).

Synthesis of compound 10



A 25 mL round bottom flask equipped with magnetic stir bar was charged with 4 (0.33 mmol, 100 mg, 1 eq.), 1,4-dioxane (4 mL) and ethylenediamine (2 mmol, 135 μ L, 6 eq.). The mixture was protected from water with CaCl₂ tube and allowed to react at r.t. for 5 h. After that time, solvent was removed without heating, affording **10**. The product was purified by column chromatography (silica gel, CHCl₃:MeOH 95:5). Red solid, yield: 86 mg, 83 %.

¹H NMR (360 MHz, CDCl₃, 25°C): $\delta = 10.24$ (br s, 1H), 8.23 (d, J = 7.3 Hz, 1H), 8.13 (d, J = 7.3 Hz, 1H), 7.76 (m, 2H), 7.56 (d, J = 9.6 Hz, 1H), 7.02 (d, J = 9.6 Hz, 1H), 3.43 (q, J = 5.5 Hz, 2H), 3.12 (t, J = 5.5 Hz, 2H), 1.48 (br s, 2H). ¹³C NMR (90 MHz, CDCl₃, 25°C): $\delta = 184.8$, 181.5, 152.5, 139.2, 134.5, 133.8, 133.7, 132.7, 129.9, 128.2, 126.9, 116.5, 112.0, 45.7, 40.7. IR (ATR) v (cm⁻¹) 1677, 1581, 1540, 1419, 1369, 1319, 1282, 1161, 1008, 881, 856, 808, 800, 727, 711. UV-Vis (CHCl₃) λ_{max} : 492 nm ($\varepsilon = 1917$ M⁻¹·cm⁻¹).

Synthesis of compound 11



A 100 mL round bottom flask equipped with magnetic stir bar was charged with **10** (1.28 mmol, 400 mg, 1 eq.), the solid was dissolved in anhydrous THF (45 mL) under N₂ atmosphere. Then, DIPEA (1.95 mmol, 333 μ L, 1.5 eq.) and **2** (1.95 mmol, 996 mg, 1.5 eq.) in anhydrous THF (2 mL) were added at the same time. The mixture was heated

at 50 °C and was allowed to react during 16 hours. After that the solvent was removed and the product **11** was purified by column chromatography (silica gel, CHCl₃). Red solid, yield: 1.0 g, quantitative.

¹H NMR (400 MHz, CDCl₃, 25°C): $\delta = 10.20$ (br s, 1H), 8.16 (dd, J = 7.5, 1.5 Hz, 2H), 7.76 (dquin, J = 7.5, 1.5 Hz, 2H), 7.61 (d, J = 9.5 Hz, 1H), 7.37 (d, J = 9.5 Hz, 1H), 6.30 (t, J = 5.8 Hz, 1H), 3.71 (m, 2H), 3.65 (m, 2H), 2.99 (m, 4H), 1.66 (quin, J = 7.3 Hz, 4H), 1.39 (m, 4H), 1.23 (m, 32H), 0.88 (t, J = 7.3 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, 25°C): $\delta = 184.8$, 181.3, 180.5, 179.7, 162.8, 152.5, 139.6, 134.4, 133.8, 133.6, 132.8, 129.9, 128.0, 127.0, 126.7, 117.1, 112.3, 42.1, 39.4, 31.9, 30.2, 30.1, 29.6, 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 29.2, 29.0, 28.9, 22.6, 14.1. HRMS (ESI) m/z calcd for C₄₃H₆₂N₆O₄S₂ [M+Na]⁺ 813.4166, found 813.4163. IR (ATR) v (cm⁻¹) 3375, 3257, 3072, 2860, 1666, 1633, 1569, 1512, 1346, 1267, 1010, 908, 871, 800, 786, 727, 636. UV-Vis (CHCl₃) λ_{max} : 494 nm ($\varepsilon = 5811$ M⁻¹·cm⁻¹).

Synthesis of compound 12



A 100 mL round bottom flask equipped with magnetic stir bar was charged with **10** (0.48 mmol, 150 mg, 1 eq.), the solid was dissolved in anhydrous THF (15 mL) under N₂ atmosphere. Then, DIPEA (0.72 mmol, 135 μ L, 1.5 eq.) and **7** (0.72 mmol, 732 mg, 1.5 eq.) in anhydrous THF (5 mL) were added at the same time. The mixture was heated at 50 °C and was allowed to react during 16 hours. After that the product **12** was forced to precipitate by adding 20 mL of hexane to the reaction crude. The suspension was filtered and the solid was washed with 4 x 20 mL of methanol. Red solid, yield: 631 mg, quantitative.

¹H NMR (250 MHz, CDCl₃ + [D₂]HFIP, 25°C): $\delta = 8.17$ (d, J = 7.3 Hz, 1H), 8.06 (d, J = 7.3 Hz, 1H), 7.81 (quin, J = 6.4 Hz, 2H), 7.62 (d, J = 9.5 Hz, 1H), 7.22 (d, J = 9.5 Hz, 1H), 3.82 (m, 2H), 3.64 (m, 2H), 3.30 (m, 4H), 2.53 (m, 4H). ¹³C NMR (60 MHz, CDCl₃ + [D₂]HFIP, 25°C): $\delta = 185.7$, 183.5, 180.4, 178.9, 162.8, 153.0, 139.4, 135.7, 134.8, 133.8, 132.6, 130.5, 128.9, 127.3, 127.2, 117.4, 112.9, 42.4, 39.6, 31.6 (t, J = 22.1, 6.1 Hz), 21.5 (br). HRMS (ESI) m/z calcd for C₃₉H₂₀F₃₄N₆O₄S₂ [M+Na]⁺ 1369.0337, found 1369.0328. IR (ATR) v (cm⁻¹) 3350, 1677, 1639, 1585, 1513, 1440, 1402, 1371, 1197, 1143, 1087, 1008, 954, 833, 798, 727, 707, 651. UV-Vis (CHCl₃) λ_{max} : 488 nm ($\varepsilon = 6068$ M⁻¹·cm⁻¹).



A 100 mL round bottom flask equipped with magnetic stir bar was charged with **5** (1.77 mmol, 600 mg, 1 eq.), the solid was dissolved in anhydrous THF (70 mL) under N₂ atmosphere. Then, DIPEA (2.64 mmol, 460 μ L, 1.5 eq.) and **2** (2.63 mmol, 1360 mg, 1.5 eq.) in anhydrous THF (5 mL) were added at the same time. The mixture was heated at 50 °C and was allowed to react during 16 hours. After that the solvent was removed and the product **13** was purified by column chromatography (silica gel, CHCl₃). Red solid, yield: 1.3 g, 88 %.

¹H NMR (400 MHz, CDCl₃, 25°C): δ = 10.04 (t, *J* = 4.9 Hz, 1H), 8.22 (dd, *J* = 7.5, 1.3 Hz, 1H), 8.14 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.77 (m, 2H), 7.57 (d, *J* = 9.3 Hz, 1H), 6.99 (d, *J* = 9.3 Hz, 1H), 5.40 (t, *J* = 6.1 Hz, 1H), 3.52 (q, *J* = 6.5 Hz, 2H), 3.40 (q, *J* = 6.5 Hz, 2H), 3.04 (m, 4H), 1.82 (m, 4H), 1.68 (m, 4H), 1.39 (m, 4H), 1.25 (m, 32H), 0.87 (t, *J* = 6.9 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, 25°C): δ = 184.8, 181.4, 180.2, 179.4, 162.8, 152.2, 139.2, 134.4, 133.7, 133.6, 132.7, 129.9, 128.1, 126.9, 126.7, 116.3, 111.9, 42.6, 40.1, 31.8, 30.1, 29.9, 29.6, 29.5, 29.5, 29.3, 29.2, 29.2, 29.1, 28.9, 28.8, 27.0, 25.9, 22.6, 14.0. HRMS (ESI) m/z calcd for C₄₅H₆₆N₆O₄S₂ [M+Na]⁺ 841.4479, found 841.4476. IR (ATR) *v* (cm⁻¹) 3375, 3255, 2918, 2850, 1672, 1629, 1589, 1523, 1396, 1369, 1359, 1292, 1261, 1014, 796, 719, 638. UV-Vis (CHCl₃) λ_{max} : 500 nm (ε = 7100 M⁻¹·cm⁻¹).

Synthesis of compound 14



A 100 mL round bottom flask equipped with magnetic stir bar was charged with 5 (0.74 mmol, 250 mg, 1 eq.), the solid was dissolved in anhydrous THF (30 mL) under N₂ atmosphere. Then, DIPEA (1.11 mmol, 190 μ L, 1.5 eq.) and 7 (1.11 mmol, 1185 mg, 1.5 eq.) in anhydrous THF (5 mL) were added at the same time. The mixture was heated

at 50 °C and was allowed to react during 16 hours. After that the solvent was removed and the product 14 was washed with 3 x 25 mL of CHCl₃. Red solid, yield: 828 mg, 82 %.

¹H NMR (400 MHz, CDCl₃ + [D₂]HFIP, 25°C): $\delta = 8.20$ (dd, J = 7.5, 1.0 Hz, 1H), 8.05 (dd, J = 7.5, 1.0 Hz, 1H), 7.85 (dt, J = 7.5, 1.0 Hz, 1H), 7.79 (dt, J = 7.5, 1.0 Hz, 1H), 7.60 (d, J = 9.5 Hz, 1H), 7.06 (d, J = 9.5 Hz, 1H), 3.56 (m, 2H), 3.43 (m, 2H), 3.33 (m, 4H), 2.55 (m, 4H), 1.84 (br s, 4H). ¹³C NMR (100 MHz, CDCl₃ + [D₂]HFIP, 25°C): $\delta = 216.1$, 185.5, 183.7, 179.5, 177.8, 161.9, 152.7, 138.4, 135.3, 134.3, 133.4, 132.2, 130.1, 128.8, 126.7, 126.6, 111.7, 42.3, 40.3, 29.1 (quin, J = 19.6 Hz), 26.4, 25.4, 20.9. HRMS (ESI) m/z calcd for C₄₁H₂₄F₃₄N₆O₄S₂ [M+Na]⁺ 1397.0650, found 1397.0656. IR (ATR) v (cm⁻¹) 3359, 3207, 3082, 3043, 1579, 1523, 1394, 1307, 1197, 1145, 954, 798, 727, 705, 649. UV-Vis (CHCl₃) λ_{max} : 498 nm ($\varepsilon = 6160$ M⁻¹·cm⁻¹).

Synthesis of compound 15



A 100 mL round bottom flask equipped with magnetic stir bar was charged with **13** (1.42 mmol, 1.16 g, 1 eq.), the solid was dissolved in DMSO (175 mL) and the solution was heated at 100 °C. Then, 1,4-diaminobutane (13.9 mmol, 1.4 mL, 10 eq.) was added and the mixture was allowed to react during 16 hours, protected from water with CaCl₂ tube. The reaction was stopped pouring the reaction crude into 1500 mL of CH₂Cl₂, the organic layer was extracted with brine (3 x 1000 mL), dried with Na₂SO₄ (anh) and the solvent was removed. **15** was purified by column chromatography (silica gel, CHCl₃ to CHCl₃:MeOH 90:10). Blue solid, yield: 696 mg, 60 %.

¹H NMR (400 MHz, CDCl₃+[D₄]MeOH, 25°C): $\delta = 8.13$ (m, 1H), 8.10 (m, 1H), 7.54 (m, 2H), 7.11 (s, 2H), 3.33 (m, 6H), 2.85 (m, 6H), 1.70 (m, 4H), 1.65 (m, 4H), 1.50 (m, 4H), 1.22 (m, 4H), 1.06 (m, 32H), 0.68 (q, J = 6.7 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃+[D₄]MeOH, 25°C): $\delta = 182.2$, 182.0, 180.0, 179.0, 162.4, 146.3, 146.1, 134.3, 134.1, 132.1, 132.0, 125.9, 125.6, 124.0, 123.7, 109.5, 109.2, 42.1, 41.8, 40.1, 39.3, 31.7, 30.0, 29.8, 29.5, 29.4, 29.4, 29.3, 29.2, 29.1, 29.1, 29.0, 28.8, 28.7, 26.7, 26.6, 26.3, 25.0, 22.5, 13.8. HRMS (ESI) m/z calcd for C₄₉H₇₇N₇O₂S₂ [M+H]⁺ 860.5667, found 860.5667. IR (ATR) v (cm⁻¹) 3419, 2918, 2848, 1573, 1517, 1257, 1240, 1176,

1164, 1016, 723, 632. UV-Vis (CHCl₃) λ_{max} : 598 nm (ε = 3557 M⁻¹·cm⁻¹); 649 nm (ε = 4122 M⁻¹·cm⁻¹).

Synthesis of compound 16



A 50 mL round bottom flask equipped with magnetic stir bar was charged with 14 (0.73 mmol, 1.0 g, 1 eq.), the solid was dissolved in DMSO (8 mL) and the solution was heated at 100 °C. Then, 1,4-diaminobutane (8 mL, excess) was added and the mixture was allowed to react during 1 hour, protected from water with CaCl₂ tube. The reaction was stopped pouring the reaction crude into 800 mL of CH₂Cl₂, the organic layer was extracted with water (3 x 500 mL), dried with Na₂SO₄ (anh) and the solvent was filtered and the resulting solid was washed with 50 mL of methanol, the mixture was filtered and the resulting solid was washed with 50 mL of methanol and discarded. The solvent was removed affording 16. Blue solid, yield: 680 mg, 66 %.

¹H NMR (400 MHz, CDCl₃ + [D₂]HFIP, 25°C): $\delta = 8.21$ (m, 2H), 7.74 (m, 2H), 7.33 (d, J = 10.1 Hz, 1H), 7.31 (d, J = 10.1 Hz, 1H), 3.50 (m, 4H), 3.36 (m, 2H), 3.25 (t, J = 7.4 Hz, 2H), 2.90 (t, J = 7.4 Hz, 2H), 2.85 (m, 2H), 2.55 (m, 2H), 1.76 (m, 8H), 1.58 (br s, 4H). ¹³C NMR (100 MHz, CDCl₃ + [D₂]HFIP, 25°C): $\delta = 181.4$, 181.3, 178.2, 163.5, 162.8, 148.0, 133.9, 133.8, 132.7, 132.6, 125.7, 125.6, 125.3, 124.9, 108.6, 108.4, 76.9, 42.1, 41.8, 40.2, 40.1, 39.6, 31.6 (t, J = 21.8 Hz), 26.9, 26.3, 26.0, 20.9. HRMS (ESI) m/z calcd for C₄₅H₃₅F₃₄N₇O₂S₂ [M+H]⁺ 1416.1824, found 1416.1852. IR (ATR) *v* (cm⁻¹) 3363, 3261, 2931, 2856, 1554, 1197, 1143, 1012, 952, 804, 725, 705, 649. UV-Vis (CHCl₃) λ_{max} : 601 nm ($\varepsilon = 15514$ M⁻¹·cm⁻¹); 649 nm ($\varepsilon = 17572$ M⁻¹·cm⁻¹).

Synthesis of compound **17**



A 25 mL round bottom flask equipped with magnetic stir bar was charged with **15** (0.029 mmol, 20 mg, 1 eq.) under N₂ atmosphere. The solid was dissolved in anhydrous THF (10 mL) and the solution was cooled using an ice/brine bath. Then, 1 mL of a solution of cyanuric chloride (0.029 mmol, 5.3 mg, 1 eq.) in THF (anh) was added. After 2 hours, DIPEA (0.029 mmol, 5 μ L, 1 eq.) was added and the mixture was allowed to react during 12 hours at r.t. After this time the reaction crude was quickly filtered through silica gel using CHCl₃ as eluent and the solvent was removed without heating. The resulting solid **17** was purified by column chromatography (silica gel, CHCl₃). Blue solid, yield: 18 mg, 60 %.

¹H NMR (400 MHz, CDCl₃, 25°C): $\delta = 10.78$ (t, J = 3.7 Hz, 2H), 8.33 (dd, J = 5.7, 3.2 Hz, 2H), 7.69 (dd, J = 5.7, 3.2 Hz, 2H), 7.20 (s, 2H), 6.28 (t, J = 5.8 Hz, 1H), 5.51 (t, J = 5.8 Hz, 1H), 3.58 (m, 2H), 3.49 (m, 6H), 3.02 (m, 4H), 1.82 (m, 8H), 1.67 (m, 4H), 1.40 (m, 4H), 1.25 (m, 32H), 0.87 (t, J = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, 25°C): $\delta = 182.6$, 182.5, 180.3, 179.3, 170.9, 169.8, 165.9, 162.8, 145.9, 145.8, 134.4, 134.3, 132.1, 132.1, 126.1, 126.0, 123.4, 123.3, 110.1, 110.0, 42.3, 42.1, 41.0, 40.2, 31.9, 30.1, 30.0, 29.6, 29.3, 29.0, 28.8, 26.9, 26.6, 26.5, 26.4, 22.6, 14.1. HRMS (ESI) m/z calcd for C₅₂H₇₆Cl₂N₁₀O₂S₂ [M+Na]⁺ 1029.4863, found 1029.4864. IR (ATR, cm⁻¹): 3265, 2920, 2850, 1554, 1517, 1404, 1234, 1166, 1112, 1016, 972, 844, 798, 729, 636. UV-Vis (CHCl₃) λ_{max} : 600 nm ($\varepsilon = 13884$ M⁻¹·cm⁻¹); 648 nm ($\varepsilon = 16143$ M⁻¹·cm⁻¹).

Synthesis of compound 18



A 250 mL round bottom flask equipped with magnetic stir bar was charged with 16 (0.23 mmol, 330 mg, 1 eq.) under N₂ atmosphere. The solid was dissolved in anhydrous CH_2Cl_2 (45 mL) and anhydrous THF (20 mL). Then, 20 mL of a solution of cyanuric

chloride (0.28 mmol, 52 mg, 1.2 eq.) in THF (anh) and DIPEA (1.06 mmol, 100 μ L, 5 eq.) were added at the same time. After 2 hours, 5 mL of a solution of cyanuric chloride (0.28 mmol, 52 mg, 1.2 eq.) in THF (anh.) was also added and the mixture was allowed to react for 30 min. Then, the reaction crude was quickly filtered through silica gel using CHCl₃ as eluent and the solvent was removed affording 330 mg of blue solid identified as **18**. Unfortunately, **18** couldn't be perfectly purified by standard procedures.

Collection of spectra











-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 Chemical Shift (ppm)



L2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 Chemical Shift (ppm)







L2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0

Compound 7

Compound 8

Compound 9

¹H NMR (400 MHz, CDCl₃ + [D₂] HFIP)

8.24 8.23 8.23 8.22 8.22 7.73 7.73 7.73

Compound 11

Compound 13

Compound 15

Compound 16

Compound 17

Staining processes

Scouring

Four 100 % white cotton fabrics (10x5 cm, 1.5 g aprox.) were putted into a 400 mL of 20 g Na_2CO_3 and 1 mL liquid soap aquous solution, at 70 °C for one hour. After this times fabrics were washed by immersion in water and were dried in the oven a 100 °C for 4 hours.

Dyeing by impregnation (11 and 12)

In a 50 mL Schleck type tube, 100 mg of the corresponding dye were dissolved in 35 mL of THF (anh). 200 mg of NaCl were added and the mixture was heated at 70 °C. The fabric was sunk in the solution and the tube was protected with Ar. After 48 h the fabric was removed from the solution and dried in the oven a 100 °C for 4 hours. Then the fabric was washed with water and was dried again at 100 °C for 1 hour.

Dyeing by reaction

Dye 17

In a 50 mL Schleck type tube, 125 mg (0.15 mmol, 1 eq.) of **15** were dissolved in 30 mL of THF (anh) and cooled at 0 °C. Then, 27 mg (0.15 mmol, 1 eq.) of cyanuric chloride in 5 mL of THF (anh) were dropped. After 2 hours, 25 μ L (0.15 mmol, 1 eq) of DIPEA were added. One hour later, the cooling bath was removed and the mixture was allowed to react for 12 hours. After this time, 200 mg of NaCl, 1 mL of DIPEA and the fabric were added, the mixture was heated to 70 °C and was allowed to react for 24 h. Finally, the fabric was dried in the oven at 100 °C for 1 hour.

Dye 18

In a 50 mL Schleck type tube, 125 mg (0.09 mmol, 1 eq.) of **16** were dissolved in 14 mL of CH_2Cl_2 (anh) and 8 mL of THF (anh). Then, 20 mg (0.11 mmol, 1.2 eq.) of cyanuric chloride in 8 mL of THF (anh) and 38 μ L (0.45 mmol, 5 eq) of DIPEA were dropped. After 2 hours, 20 mg (0.11 mmol, 1.2 eq.) of cyanuric chloride in 2 mL of THF (anh) were added. One hour later, 20 mg (0.11 mmol, 1.2 eq.) of cyanuric chloride in 2 mL of the fabric were added and the mixture was heated at reflux and was allowed to react overnight. Finally, the fabric was dried in the oven at 100 °C for 1 hour.

How much dye was stained on the fabric was also studied. The pieces of cotton were weighted before and after the dyeing process.

| Dye | Before (g) | After (g) | Difference (g) | Gain | (mg | Dye/g |
|-----|------------|-----------|----------------|---------|-----|-------|
| | | | | fabric) | | |

| 11 | 0.0995 | 0.0999 | +0.0004 | 4 |
|----|--------|--------|---------|----|
| 12 | 0.1133 | 0.1180 | +0.0007 | 6 |
| 17 | 0.1008 | 0.1010 | +0.0002 | 2 |
| 18 | 0.0863 | 0.0872 | +0.0009 | 10 |

As a result of dyeing, only a few amount of dye was incorporated by the fabric: 2-10 mg of dye per gram of fabric. That fact has important economical and safety concerns.

Measures of contact angles of a drop of water deposited on top of stained fabric

| Stained | Three independent contact | Arithmetic | Maximal | Contact angle after washing | |
|---------|---------------------------|-----------------|------------------|-----------------------------|--|
| fabric | angle measures | average contact | contact angle | procedure (average of three | |
| launc | | angle | $\theta_{\rm A}$ | measures) | |
| В | 149.7/ 149.6/ 145.5 | 148 | 143 | 130 | |
| | | | | | |
| C | 157.0/ 152.0/ 149.5 | 153 | 153 | 144 | |
| D | 149.1/ 147.5/ 152.5 | 150 | 148 | 146 | |
| Е | 150.3/ 148.5/ 149.2 | 149 | 154 | 151 | |
| | | | _ | | |

The experiments were performed in a Clean Room ISO 7 class 10.000, with controlled humidity atmosphere.

Determination of water vapor permeability under static conditions (LEITAT Technological Center (Terrassa, Barcelona).

The pattern used to evaluate the permeability is silica gel, and the measure is the increase in weight after 6 h in an humid atmosphere at 37°C. Test conditions correspond to the standard method FNM 817):

Specimen size: 12.56 cm²

Bath temperature: $37^{\circ} \pm 1^{\circ}C$

Test atmosphere: $22^{\circ} \pm 2^{\circ}C$

Dry silica gel: 15 g

Exposure time: 6 h

Results obtained: 186,9 g water m²/h

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DETERMINATION OF WATER VAPOR PERMEABILITY UNDER STATIC CONDITIONS

Standard method FNM 817

Scope: This test is intended to determine the water vapor resistance from perspiration.

Equipment used: PVAM, Thermostatic bath, Balance, Thermometer.

Test conditions:

| N° of specimens: | 1 (according to the costumer) |
|-------------------|-------------------------------|
| Specimen size: | 12,56 cm ² |
| Bath temperature: | 37°±1°C |
| Test atmosphere: | 22±2°C |
| Dry silica gel: | 15g |
| Exposure time: | 6 h |

Results obtained:

| | Water vapour permeability |
|-------|---|
| Value | 186,9 g. water m²/h (4485,62 g. water m²/24 h) |
| Value | 100,3 g. water in /ii (4403,02 g. water in /24 ii) |

ISO 105-C06 colour fastness to domestic and commercial laundering (Institute of Textile Research and Industrial Cooperation of Terrassa, Polytechnic University of Barcelona).

The washings were carried as follows:

We have studied the stained fabrics B, C, D and E and moreover a 10x4cm sample of each fabric was sewn on a piece of fabric Multi-Fibre. Each test compound (the sample and the Multi-Fibre) is placed in a stainless steel tube with 150 ml volum of washing bath and 10 steel balls for mechanical action on tissues. These tubes were assembled to a special mechanical equipment to do the washing for 30 minutes (comprises a water bath, which regulates temperature and a rotor attached to a shaft where you radially place the tubes).

RESULTS

ISO 105-C06 Colour fastness to domestic and comercial laundering (A1S)

Multifibre adjacent fabrics: DW

| Sample | Change in | Change in Staining | | | | | |
|--------------|-----------|--------------------|--------|-------|-----------|---------|------|
| Sample | colour | Acetate | Cotton | Nylon | Polyester | Acrylic | Wool |
| Sample 1: 70 | 3-4 | 5 | 5 | 4-5 | 5 | 5 | 5 |
| Sample 2: 72 | 2-3 | 5 | 5 | 4-5 | 5 | 5 | 5 |
| Sample 3: 80 | 4 | 5 | 5 | 4 | 5 | 5 | 5 |
| Sample 4: 81 | 4 | 5 | 5 | 4 | 5 | 5 | 5 |

Nomenclature for colorfastness ratings (Gray Scale): 5.- Excellent 4.- Good 3.- Fair 2.- Poor 1.- Very poor

Sample 1 corresponds to B(11) in the text.

Sample 2 corresponds to C(12) in the text.

Sample 3 corresponds to D(17) in the text.

Sample 4 corresponds to E(18) in the text.