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COMMUNICATION

Anthraquinone dyes for superhydrophobic cotton

J. Salabert, R. M. Sebastián* and A. Vallribera*

Water-repellent, self-cleaning and stain resistant textiles are of interest for industry applications. Anthraquinone reactive dyes were covalently grafted on cotton fabric surfaces obtaining bright colors with good wash-fastness properties and giving rise to breathable superhydrophobic textiles with self-cleaning properties.

The interest in highly water-repellent surfaces has grown in recent years due to the desire for self-cleaning surfaces and many other industrial applications such as anti-biofouling paints for boats, antisticking of snow for antennas and windows, anti-corrosion etc.[1] Water coming into contact with a super-hydrophobic surface forms into spherical bead-like drops, minimizing the surface/water contact area. A superhydrophobic surface is one that achieves a water contact angle of 150° or greater.[1a] Self-cleaning relies on the spherical droplets rolling off the surface and picking up particulate dirt in their path. To obtain a surface with superhydrophobic properties, a low energy must be combined with high surface roughness. Superhydrophobic surfaces are observed in nature. The lotus effect describes the self-cleaning action of some leaf surfaces (lotus plant, *Nelumbo nucifera*). Textiles such as cotton already have some surface roughness, so additional chemical treatments to render them superhydrophobic can be performed. Alkyl and fluorinated alkyl groups have a low energy of interaction with water which is strongly repelled, that results in an increase of its contact angle. In recent years, superhydrophobicity surfaces on textiles have been obtained by different approaches. For instance, fibers have been decorated with $-Si(CH_3)_3$ functionalized SiO_2 nanoparticles,[2] textiles have been coated with octadecylthiol-ligand nanocrystals (metals and oxide nanoparticles, such as Fe, Co, Ni, Cu and Ag),[3] diamond-like carbon films have been used as coatings for cotton[4] and fibers coated with chitosan-based hydrophobic nanoparticles that were functionalized through reaction of hydroxyl groups of chitosan with chlorodimethyl-1*H*,1*H*,2*H*,2*H*-perfluorodecylsilane have been obtained.[5] Our approach is completely different and consists in *using the dyeing process of the textile to incorporate the water repellency property*.[6]

One of the most important carbonyl dyes are those based on anthraquinone. The great importance of these dyes is attributable to the fact that long-wavelength absorption bands can be obtained with short conjugated systems. In contrast to electron withdrawing substituents which have little influence on the spectrum of anthraquinone, electron-donating groups cause significant bathochromic and hyperchromic effects, particularly when two of them are linked in the α-positions. Their color is due to a charge transfer band to the oxygen of one of the carbonyl groups involving the electron lone pair of, for instance, an amino group contained in the anthraquinone derivative.
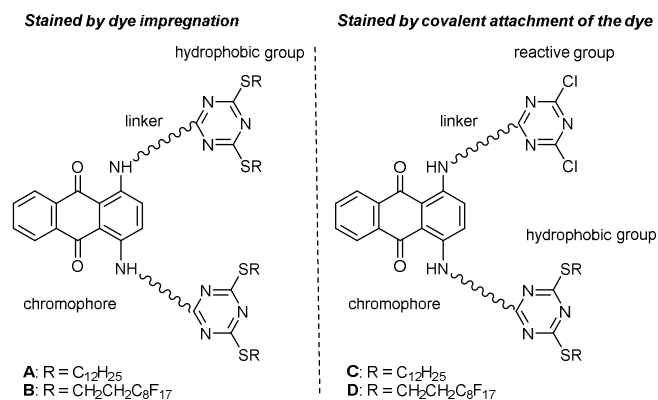
Figure 1. General structures of synthesized anthraquinone derivatives and type of textile stain process.

Our goal in this work was to fabricate *functional dyes* with structures comprising an antraquinone chromophore system and hydrophobic fragments based on long hydrocarbon or perfluorinated tails (**A** and **B** in Figure 1). The textiles will be stained through an impregnation process of the dye. We also designed some *reactive functional dyes*, for covalent grafting on the textile, replacing one of the hydrophobic fragments by a reactive group derived from cyanuric chloride (**C** and **D** of Figure 1). The dyestuff will be then fixed on cotton in basic conditions.

The initial idea for the synthesis of anthraquinone derivatives was to start from commercial 1,4-diaminoantraquinone, **1**, and carry out a direct S_NAr reaction using 2-chloro-4,6-bis(dodecylthio)-1,3,5-triazine, **2**[7] (Scheme 1). The reaction was studied in the presence of different bases as DIPEA, NaH, Cs_2CO_3, and Bu_4NCl without success. Even with more reactive fluoride as leaving group (**3**, Scheme 1) no reaction could be achieved. Triazine derivative **3** was accomplished in 76% yield through the selective disubstitution of trifluorotriazine with long chain aliphatic thiol, $HSC_{12}H_{25}$, in CH_2Cl_2 at -78ºC using diisopropylethylamine (DIPEA) as a base. The lack of reactivity of compound **1** was probably due to the deactivation of the amino group by the presence of the carbonyl (Scheme 1). At this stage we decided to completely change the strategy through an umpolung of the reactivity of the nucleophilic anthraquinone derivative. We planned to use the 1,4-dinitroanthraquinone, **4**, as starting material. The reactivity would be now based on the much known ability of nitro to act as leaving group in S_NAr.
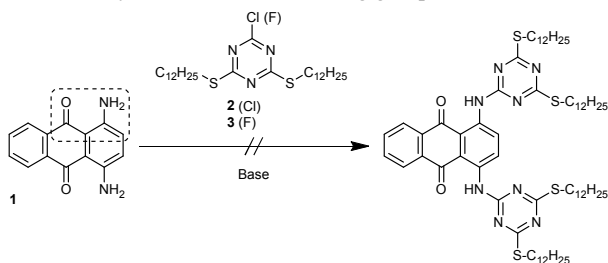
Scheme 1. Lack of reactivity of compound **1**.

In 1990 Krapcho[8] and coworkers described the preparation of 1,4-dinitroanthraquinone, **4**, (84% yield) from the corresponding diamine **1** by oxidation with trifluoroperacetic acid (prepared by mixing trifluoroacetic anhydride with 90% hydrogen peroxide). After some tests to avoid employing 90% H_2O_2 we found that the use of a large excess of trifluoroacetic anhydride and 30% H_2O_2 during 6 days at 40ºC allowed the formation of **4** in a 62% yield (Scheme 2).
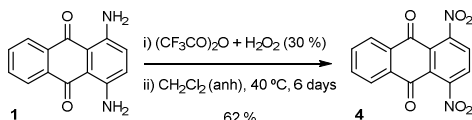
**Scheme 2.** Preparation of 1,4-dinitroanthraquinone, **4**.

Preparation of symmetrically disubstituted 1,4-bis[(aminoalkyl)amino]anthracene-9,10-diones by displacement of nitro substituents of **4** by diamines was then examined (Scheme 3). In the first experiment, we used a large excess of ethylendiamine (16 equiv.) in DMSO at 40ºC giving a complex mixture. We found in the literature that other authors had also observed side reactions using ethylenediamine with this substrate **4**, as for example giving 1,2,3,4-tetrahydroquinoxaline.[8] For this reason, 1,4-diaminobutane was tested (16 equiv., DMSO, 100ºC, 72h) yielding a low 32% of 1,4-bis-(aminobutyl)amino]anthracene-9,10-dione, **6**. After some experimentation we found than a sequential substitution of both nitro groups gave much better results. Thus, first a nitro was displaced using 6 equiv. of 1,4-diaminobutane in dioxane at room temperature during 6 hours to render **5** (85% yield). Afterwards, treatment of **5** with an excess of 1,4-diaminobutane in a more polar solvent as DMSO and higher temperature (100ºC), gave **6** in an excellent 96% yield. At this point, both primary terminal amines of compound **6** (Scheme 3) nicely reacted with triazines **2** and **7**[7] in the presence of DIPEA as a base in a 1:1 mixture of DMSO:THF as solvent at 50ºC. In these conditions dyes **8** (72%) and **9** (74%) were obtained. All

anthraquinone derivatives possessing two electron-donating groups have a bright blue color (**6**, **8** and **9**), whereas compound **5** with still one NO_2 substituent in the anthraquinone core is red (Scheme 3). Both red and blue colours were extremely intense and bright.
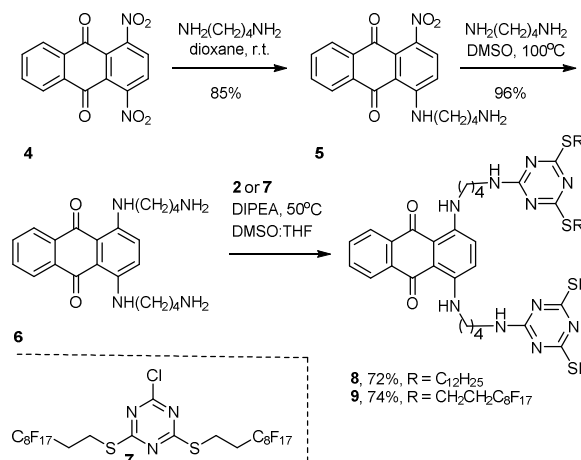
Scheme 3. Synthesis of functional dyes **8** and **9**.

As mentioned, compound **5** has been obtained in a good 85% yield (Scheme 3). In the same reaction conditions, which are pretty different from the ones previously assayed in disubstitution reaction, ethylenediamine was successfully used. The corresponding compound **10** was afforded in 83% yield (Scheme 4). Then, alkylation of the primary terminal amine of **5** and **10** with the hydrophobic triazines **2** and **7** was carried out using DIPEA as a base in THF to afford dyes **11-14** in excellent yields (82-99%). As expected all were bright red solids.
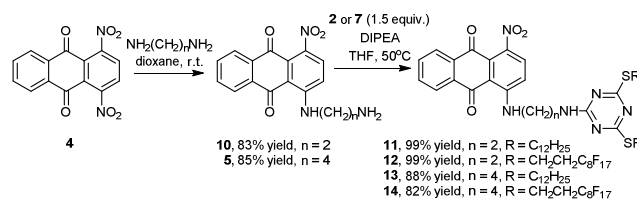
Scheme 4. Synthesis of functional dyes **11-14**.

Once those blue and red dyes were obtained their optical properties were evaluated as well as their hydrophobicity (Table 1). Two bands were observed in the visible spectrum of all blue anthraquinone derivatives (**6**, **8** and **9**), whereas only one band was observed for the red ones (**5**, **10-14**). A remarkable increase of the molar extinction coefficient was obtained when the triazine hydrophobic group is present (compare values for **6** with values for **8** and **9**; compare values for **5** with values for **11-14**, Table 1). For instance, the molar extinction coefficient of compound **8** ($\varepsilon = 14.034$ $M^{-1}cm^{-1}$) is almost twice than of compound **6** ($\varepsilon = 7.765$ $M^{-1}cm^{-1}$). The same effect is observed comparing **5** ($\varepsilon = 4464$ $M^{-1}cm^{-1}$) with **13** ($\varepsilon = 7.100$ $M^{-1}cm^{-1}$) and **14** ($\varepsilon = 6.160$ $M^{-1}cm^{-1}$). The presence of long hydrocarbon or perfluoroalkyl ponytails makes dyes **8**, **9**, **11-14** highly hydrophobic as shown by the contact angle of a droplet of water added on top of previously treated glass surface through the deposition of the anthraquinone dyes using the spin-coating technique (Table 1). The larger contact angles were observed for dyes containing two polyfluoroalkyl hydrophobic long chains (dye **12** (124º) and dye **14** (117º)).
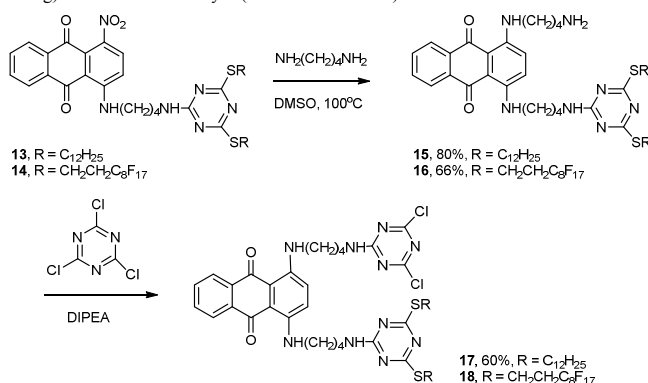
Then we focused our attention on the surface modification of a cotton fabric with the idea of obtaining a permanently colored

hydrophobic cotton surface. As the leaching stability of the dye is essential for long-term applications, the covalent grafting of the dye on the cotton fibre is essential.[9] Thus, we designed new anthraquinone dyes possessing a reactive group to covalently anchor the dye on the textile surface (Scheme 5). Displacement of nitro group from 13 was achieved in a 80% yield using an excess of 1,4-diaminobutane in DMSO at 100ºC. In the same conditions fluorous 14 gave a complicated reaction mixture and after some experimentations we noticed that best results were obtained using a mixture of 1,4-diaminobutane/DMSO (1:1) at 100ºC during 1 hour (66% yield). Reaction of compound 15 with 1 equiv. of cyanuric chloride was carried out in the presence of DIPEA (1 equiv.) in THF at 0ºC under argon atmosphere to give 17 in 60% yield. In these conditions compound 16 resulted unreactive. However in a mixture of THF/CH_2Cl_2 (1:1), and using 2.5 equiv. of cyanuric chloride and 5 equiv. of DIPEA during 2.5 hours under argon atmosphere, we obtained a 100% conversion. Compound 18 could not be perfectly purified.

Table 1. UV-Vis description and contact angle measurements of dyes.

| Dye	λ_{max} (nm)[a]	ε ($M^{-1}cm^{-1}$)[a]	Colour	Contact angle[b]
6	601,650	7765, 8620	blue	-
8	601,649	14034,14083	blue	106
9	598,649	12026,12772	blue	111
10	492	1917	red	54
5	501	4464	red	-
11	494	5811	red	103
12	488	6068	red	124
13	500	7100	red	91
14	498	6160	red	117

[a] Maximum absorbance (λ_{max}) and molar extinction coefficient (ε) in $CHCl_3$. [b] Contact angle of a droplet of water deposited on a modified glass surface (by spin coating) with the indicated dyes (max. deviation ± 2º).

13, R = $C_{12}H_{25}$
14, R = $CH_2CH_2C_8F_{17}$

15, 80%, R = $C_{12}H_{25}$
16, 66%, R = $CH_2CH_2C_8F_{17}$

17, 60%, R = $C_{12}H_{25}$
18, R = $CH_2CH_2C_8F_{17}$

Scheme 5. Synthesis of reactive functional dyes 17 and 18.

Then, we took some pieces of commercial 100% white cotton fabric (10x5 cm) which were submitted to a scouring process, first washed with liquid soap (1 mL) in a hot solution (70ºC) of 400 mL of water and K_2CO_3 (20 g) during one hour, rinsed with distilled water and dried in an oven at 100ºC during 1 hour (cotton fabrics **A**).

Functional dyes were stained through an impregnation process of the textile whereas reactive bifunctional dyes were covalently grafted on cotton in basic conditions (Figure 2). The dyeing process for functional dyes 11 and 12 was carried out through immersion of a piece of cotton fabric **A** in a THF solution (35 mL) containing the dye (3 mg•mL^{-1}) and 200 mg of sodium chloride during 48h at 70ºC. The red dyed cotton fabrics (cotton fabric **B** (stained with 11) and cotton fabric **C** (stained with 12) were then removed and dried in an oven (100ºC, 4h). Then rinsed with water and dried again (100ºC, 4h). In the case of reactive functional dyes 17 and 18 the process of covalently attachment of the dye to the fabric was different.[10] The cotton fabric **A** was immersed in a solution of dye 17 (125 mg, 0.004 M), NaCl (200 mg) and DIPEA (1 mL) in THF (35 mL) during 24 hours at 70ºC. The blue dyed cotton **D** was removed, dried in an oven (100ºC, 1h) and then rinsed successively with water and THF. As fluorous dye 18 could not be isolated pure the process was slightly different. The cotton fabric **A** was directly sunk in the reaction crude containing 18 (0.004 M), and NaCl (200 mg) and DIPEA (1 mL) were added. Further processing of the fabric was the same (cotton fabric **E**).
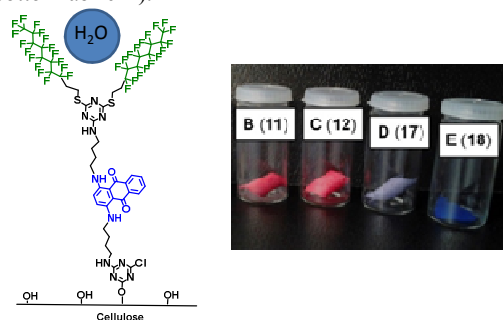

Figure 2. Schematic representation of cotton fabric **E** and photographs of the stained cotton fabrics.

After that, we carried out colorfastness tests (ISO 105-C06) to domestic and commercial laundering washing. The dyed fabrics were sewn on a multi-fibre white fabric (acetate, cotton, nylon, polyester, acrylics and wool) to control the level of staining of these fibbers in case leaching of dye is produced during washing. Each test compound (the sample and the multi-fibre) is placed in a stainless steel tube with 150 ml volume of washing bath and 10 steel balls for mechanical action on tissues and stirred at 40ºC for 30 min. Colorfastness of red dyed fabrics **B** and **C** was determined as fair (3 on 5 scale) whereas, the blue ones (**D** and **E**) (Figure 2) gave a good rating of 4 on 5 scale. Staining results of multi-fibre were excellent (5 on scale 5; only in the case of nylon the rating 4-5), which means there was no color transfer. Moreover, fluorous dye 18 show higher fibber affinities than dye 17 if colour brightness of stained fibbers **D** and **E** are compared (Figure 2).

Subsequently, we performed the measurement of the contact angle of a droplet of water deposited on top of stained fabrics (Figure 3) and also the time taken by this drop to get absorbed by the material. White cotton fabric absorbed the drop of water in less than 5 seconds, whereas the drop was maintained on dyed fabrics until it evaporates. When the surface of a stained fabric was treated with a strong jet of water no wetting was observed mimicking the lotus effect described in the leaves of the lotus flower. As shown in Figure 3 by the photographs, a droplet of water (4 µL) deposited on dyed cotton surfaces gave high contacts angles (148-153º) indicating highly hydrophobic and water-repellent textile surfaces. Dynamic contact angles measurements were performed,[11,12] however receding contact angles could not be determined due to the impossibility of

reducing the volume of water in a progressive way, thus a fast and complete absorption of the drop of water by the microsyringe took place, probably due to the high repulsion of the surface. After the washings tests performed the surface contact angles were evaluated again. Dyed fabrics **B** and **C** suffered a decline in the contact angle (9-18º) while **D** and **E** maintained the hydrophobic properties (1-4º), which is in concordance with their excellent colorfastness properties, confirming the importance of the covalent bond of dyes to the cellulose. Both fabrics **D** and **E** show excellent similar properties, however the wettability is clearly different whereas fabric **D** sinks in water, fluorous **E** keeps floating. This fabric avoids contact and penetration of water, being impressively waterproof.
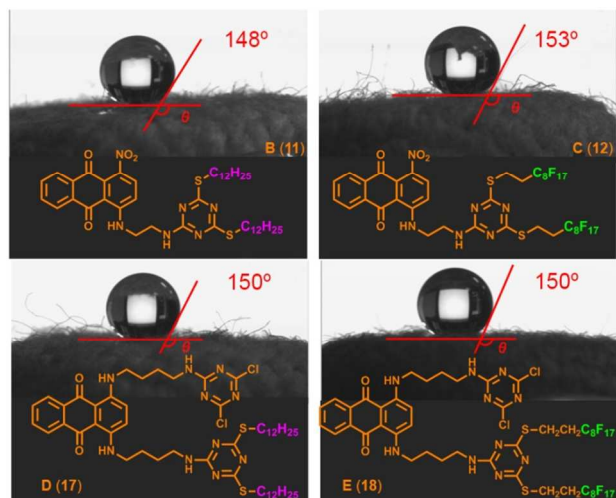
Figure 3. Values of contact angle (3 measurementes with a maximum deviation of 3º) of a droplet of water on top of hydrophobic dyed cotton fabric **B** (dye **11**), **C** (dye **12**), **D** (dye **17**) and **E** (dye **18**).

Being aware that one of the important features in sports fabrics is their breathability (perspiration is essential for applications in sport wear) we have performed the determination of water vapour permeability under static conditions of stained fabric **E** (following standard method FNM 817), obtaining a value of 186.9 water m^2/h using a 37^oC bath temperature. This means that dyed fabric **E**; although being water proof, keeps good breathability. Additionally, when drops of coffee were poured on the fabric surface **E** (Figure 4) we observed that the textile was easily washed with water which is consistent with the superhydrophobicity and self-cleaning properties.

In summary, new superhydrophobic anthraquinone dyes have been prepared from 1,4-dinitroanthraquinone, which was synthesized using optimized practical conditions. Staining of textiles by impregnation (dyes **11** and **12**) or by the formation of a covalent bond between dyes (**17** and **18**) and the surface functional group resulted in new bright red and blue superhydrophobic fabrics. This new textiles have potential applications for sportive clothes or in the household commodity sector possessing important colorfastness, self-cleaning, breathability and control of surface wettability properties. Better performance has been observed for fabrics stained with polyfluorinated reactive dyes.
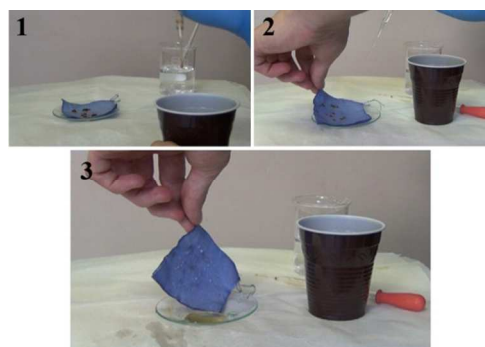
Figure 4. Self-cleaning properties of cotton fabric **E**: the surface is sprayed with a water jet and the textile is easy washed.

Acknowledgements

Notes and references

[a] Dr. J. Salabert, Prof. Dr. R. M. Sebastián, Prof. Dr. A. Vallribera
Department of Chemistry and Centro de Innovación en Química Avanzada (ORFEO-CINQA). Universitat Autònoma de Barcelona, Bellaterra (Spain). E-mail: adelina.vallribera@uab.cat

Electronic Supplementary Information (ESI) available: [Synthesis and collection spectra of compounds **2-18**]. See DOI: 10.1039/c000000x/

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