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Triarylmethane dyes for artificial repellent cotton fibers

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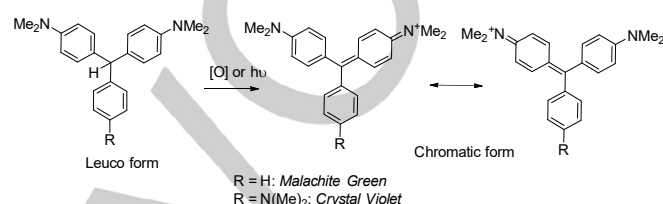
Dedication ((optional))

Abstract: Families of new hydrophobic and/or oleophobic triarylmethane dyes possessing long hydrocarbon or polyfluorinated chains have been prepared. When covalently grafted upon cotton fabric, these dyes give rise to a new type of colored superhydrophobic fibers.

The interest in highly water and oil repellent surfaces has grown in recent years, in part due to the promise of creating self-cleaning surfaces.^[1] A superhydrophobic surface is one that achieves a water contact angle of 150° or greater.^[2] Water coming into contact with a superhydrophobic surface forms spherical bead-like drops, minimizing the solid/liquid contact area. Self-cleaning relies on the spherical droplets rolling off the surface and picking up particulate dirt in their path. Superhydrophobic textiles can be used as high protective clothing textiles and outdoor clothing materials. Furthermore, it can be reduced the number of launderings thanks to the self-cleaning performance. To form a surface with superhydrophobic properties, a low energy surface must be combined with high surface roughness, and different imaginative preparation approaches have been reported.^[3] Textiles such as cotton already have some surface roughness, and different treatments to render them superhydrophobic have been performed.^[4] For example coating the fiber with silica nanoparticles followed by hydrophobization,^[5] with organosilanes-modified silica nanoparticles^[6] with fluoroalkylsilanes^[7] or with fluorocarbon polymers^[8]; or functionalizing the textile with polyalkylsiloxane^[9] or carbon nanotubes.^[10] Given that fibers almost inevitably undergo a dying process, it may be envisaged that the process of *dying might be also used to impart hydrophobicity at the same time*.^[11]

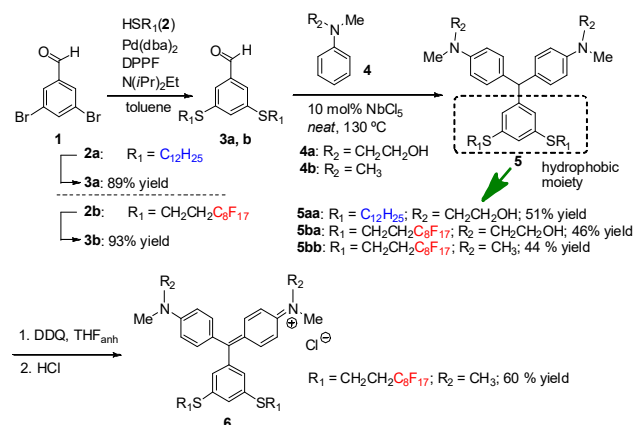
Triarylmethanes and their analogues are an important class of synthetic dyes used to stain silk, wool, jute, leather, cotton and paper.^[12] These dyes are known for their outstanding intensity of color and their brilliant shades of red, blue and green. It has also been reported that they possess diverse biological properties such as antifungal, antiproliferative, antiviral and cytotoxic, phototoxicity toward tumor cells and activity toward the central nervous system.^[13] Important dyes belonging to this class include the well-known Malachite Green and Crystal Violet (Scheme 1).

Triarylmethanes are leuco dyes that through chemical oxidation or photochemical irradiation can be converted to the chromatic form (Scheme 1).^[14]



Scheme 1. Structure of leuco and chromatic triarylmethanes.

The first goal of the present work was the synthesis of hydrophobic leucotriarylmethane derivatives of type **5** possessing long hydrocarbon or polyfluorinated chains on one of the aryl moieties (indicated in **5**, Scheme 2). We planned to address the synthesis starting from the commercial 3,5-dibromobenzaldehyde, **1**, through a palladium-catalyzed cross-coupling reaction for the formation of C_{sp}²-S bonds. Although frequently conducted under rather strongly basic reaction conditions,^[15] a convenient method for Pd-catalyzed C-S cross-coupling of arylbromides with various thiols was developed by Okauchi and co-workers^[16] using 1,1'-bis(diphenylphosphino)ferrocene (DPPF) as ligand and *N,N*-diisopropylethylamine (DIPEA) as a base; the mild reaction conditions make the process compatible with the aldehyde groups. Thus, when 3,5-dibromobenzaldehyde, **1**, was treated under these conditions with aliphatic and polyfluorinated thiols **2a** and **2b** (2 equiv.) in refluxing anhydrous toluene under nitrogen atmosphere for 12 hours, products **3a** and **3b** were obtained in 89 and 93% yield respectively (Scheme 2). At lower reaction times, mixtures of mono and dithiolated compounds were obtained, that could not be separated by column chromatography.

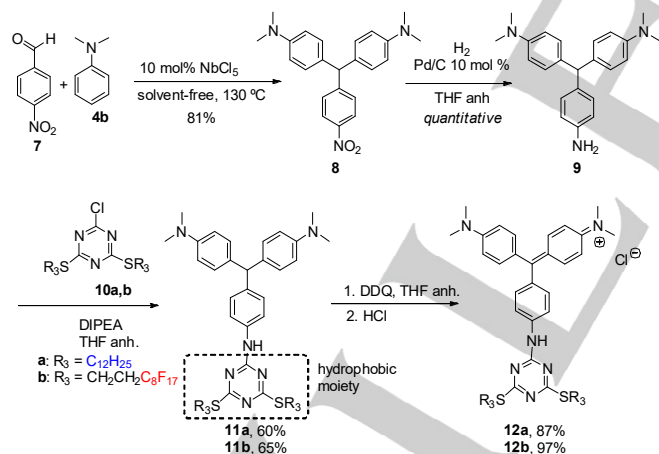


Scheme 2. Synthesis of hydrophobic triarylmethane derivatives **5** and **6**.

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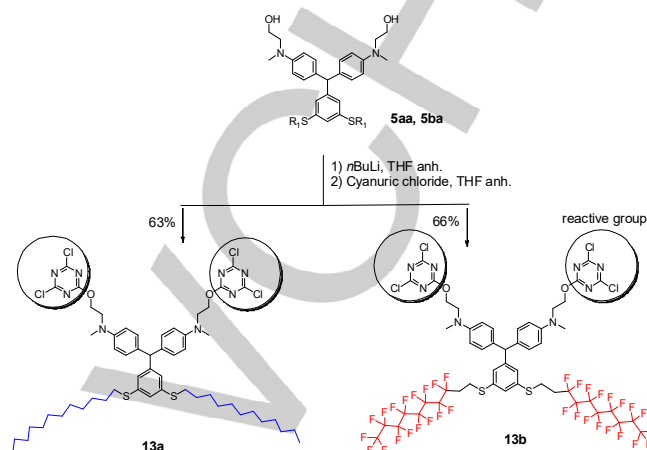
Among the existing methods, the acid-catalyzed Baeyer condensation of aromatic aldehydes and *N,N*-dialkylanilines is one of the most simple and straightforward approaches for the synthesis of diaminotriarylmethanes.^[17] It was recently discovered that NbCl_5 acts as a useful mild Lewis acid catalyst in the Baeyer condensation.^[18] Thus, benzaldehyde **3a** reacted with 2-(methyl(phenyl)amino)ethanol, **4a**, under NbCl_5 catalysis (10 mol%) and solvent-free conditions to give leuco **5aa** in 51% yield (Scheme 2). The same reaction starting with the fluoruous **3b** gave compound **5ba** in 46% yield (Scheme 2). Finally, compound **5bb** was obtained in 44% yield when the reaction was carried out using **3b** and *N,N*-dimethylaniline, **4b** (Scheme 2). The mechanism of this reaction can be attributed to a double regioselective electrophilic aromatic substitution reaction. A qualitative way to establish the formation of triarylmethane derivative is the appearance of blue-green color due to partial photooxidation of compound **5** leuco to its chromatic form **6**. In UV-vis spectrum, the existence of the chromatic form was also confirmed by the presence of a small absorption band (636 nm) in the visible region of the spectrum. The chromatic form **6** was separated from the leuco **5** form by column chromatography, due to the high affinity of the cationic form to silica. The leuco form was confirmed by the appearance of a characteristic "central" benzylic CH proton in ^1H NMR spectra (5.28–5.45 ppm depending on the substituents in the aryl groups). The chromatic blue form **6** could be obtained quantitatively by oxidation of leuco **5bb** with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (Scheme 2). Compounds **5aa** and **5ba** were not oxidized at this stage due to the presence of alcohol function and will be used later. The cationic molecule **6** was difficult to purify and manipulate.



Scheme 3. Synthesis of hydrophobic triarylmethane derivatives **11** and **12**.

Our next objective was the synthesis of new hydrophobic triarylmethane derivatives of type **11**, possessing a different hydrophobic moiety (Scheme 3). Bisarylation of *p*-nitrobenzaldehyde **7** was carried out in an excellent 81% yield. The subsequent reduction of the nitro (**8**) to amino group (**9**) took place quantitatively. The aniline **9** reacted smoothly with cyanuric chloride derivatives **10a** and **10b** with 60% and 65% yield

respectively, giving rise to the leuco triarylmethane derivatives **11a** and **11b**. The corresponding chromatic blue forms **12a** and **12b** could be obtained in excellent yields by oxidation with DDQ in THF (Scheme 3).



Scheme 4. Synthesis of bifunctional dyes **13**.

Taking into account that the leaching stability of dyed coating is essential for long-term applications and that wash-fastness is a particular requirement for textiles, we then designed hydrophobic triarylmethane-based reactive dyes by introducing functional groups that can react with natural or synthetic fibers to form covalent bonds. Aiming to ensure a good fixation ability, we envisioned bifunctional dyes containing two reactive groups on the molecule (Scheme 4).

Treatment of dyes **5aa** and **5ba**, both possessing a primary alcohol, with butyllithium allowed the deprotonation of both terminal primary alcohols, which then reacted with an excess of cyanuric chloride through a nucleophilic aromatic substitution. An excess of cyanuric chloride was used in order to avoid di- and tri-substitutions, and/or the formation of undesirable polymeric derivatives. Moreover, light oxidation of leuco to chromatic form takes place along the reaction. During the purification of the reaction crude by column chromatography using silica-gel, separation of leuco and chromatic form is achieved. Compounds leuco **13a** and **13b** were obtained in 63% and 66% yields respectively under these conditions (Scheme 4).

With the synthesis completed, we proceeded to study the hydrophobic and the oleophobic properties of the newly synthesized dyes. These dyes were first deposited on a glass surface using a spin-coating technique (addition of 0.1 mL of a 2.5×10^{-3} M solution in acetone of each compound indicated in Table 1). The test performed was the measurement of the contact angle by the addition of a droplet of water (4 μL) on top of the previously modified glass surface. The highest contact angles correspond to compounds **5bb** (116°, entry 4) and **11b** (140°, entry 6) which is in concordance with the presence of two perfluoroalkyl ponytails chains and dimethylamino groups. In contrast, changing to polar ethanolmethyl amino substituents, **5ba**, the contact angle drops down from 116° to 108°. The results

also indicate that triarylmethane derivatives possessing long hydrocarbon tails (**5aa** (77°), **11a** (108°) and **13a** (106°)) have in general lower contact angles than their fluorinated analogues (**5ba** (108°), **11b** (140°) and **13b** (107°)). Thus, *fluorinated triarylmethane analogues being more hydrophobic than the hydrocarbon ones*.

Table 1. Obtained contact angles of a droplet of different solvents on a modified glass surface (previously coated with the indicated compounds).

Entry	Compound ^[a]	Water	Olive oil	Hexadecane
1	Glass	41	35	15
2	5aa	77	38	17
3	5ba	108	104	105
4	5bb	116	85	78
5	11a	108	42	19
6	11b ^[b]	140	-	-
7	13a	106	45	15
8	13b	107	89	77

[a] 2.5×10^{-3} M solution in acetone. [b] Due to solubility problems, CHCl_3 was used.

Regarding to the oleophobicity measurements (Table 1), droplets of olive oil and hexadecane were added on top of the treated glass surface through the deposition of the triarylmethane derivatives (addition of 0.1 mL of a 2.5×10^{-3} M solution of the dye in acetone). Fluorinated **5ba**, possessing a polar hydroxyl functional group, gave the best results (entry 5). In the case of olive oil, comparing both **5ba** (fluorinated chains) and **5aa** (alkyl chains) the results indicate a difference of 66° in the contact angle, the fluorinated compound being more oleophobic. Comparing compounds **13a** and **13b**, practically a double contact angle is obtained for the fluorinated **13b** (entries 7 and 8). In the experiments with hexadecane the differences in the same direction are even more accused. Again, *fluorinated analogues being more oleophobic than the hydrocarbon ones*. Compound **5ba** possessing a polar hydroxyl functional group and a fluorinated chain presented the best amphiphobic properties to both water and oil fluids.^[19]

Then, we took some pieces of commercial cotton fabric from a 100% cotton (knitted) T-shirt which were firstly washed with liquid soap, rinsed with distilled water and dried at 105° for three days. Subsequently, the activation of the cotton pieces was carried out by sinking them in a 0.1 M of NaOH aqueous solution for 30 minutes and then rinsing with acetone (4x5mL). Afterwards, the staining process was carried out in a screw-top 60 mL tube, by soaking of swatches of the activated cotton fabrics (1x3 cm) in a solution of 7×10^{-3} g of dyes **13a** and **13b** (0.23% weight) in 4.5 mL of THF. After 3 days, DDQ (2 mg, 7.9×10^{-6} mol) and 3 drops of HCl were introduced into the reactor. For practical reasons, we decided to carry out the oxidation as the last step once the dye was covalently

anchored on the cotton fabric. Afterwards, the stained fabrics were rinsed with THF and acetone. The obtained organic solvents were colorless despite the high solubility of dyes **13a** and **13b** in acetone and THF, proving stability of the dye through the covalent link to the cotton surface.

The surface morphologies of the original and modified cotton fabric **B** were compared by SEM. No substantial differences were found, which means that the surface feature is preserved despite the dye grafting. Analysis by energy-dispersive X-Ray spectroscopy (EDS) established the presence of fluorine, sulfur and chlorine atoms at the surface, which is indicative of the presence of dye **13b** (Figure 2).

Figure 1. Schematic representation of stained fiber **B** (dye **13b**). Photograph of a droplet of water deposited on fiber **B** with a contact angle of 152° (average of three measures, max. deviation $\pm 4^\circ$).

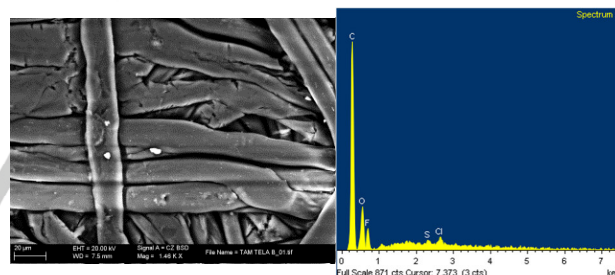


Figure 2. Left image: Scanning electron microscope (SEM) image of stained cotton fabric **B** (dye **13b**). Right image: Energy dispersive analysis (EDS) graph of the treated cotton fabric **B**.

Hydrophobicity measurements of the stained cotton fabrics **A** (for **13a**) and **B** (Figure 1, for **13b**) were carried out by the measure of the contact angle of a droplet of water on the surface of the cellulose (130° for fabric **A** and 152° for fabric **B**). These results indicate that stained cotton fabric **B** is a superhydrophobic surface. In fact, when placed in a beaker of water, while swatches of the “untreated” cotton and of the dyed cotton fabric **A** sank to the bottom, the dyed cotton fabric **B** remained floating on the surface, indicating higher hydrophobicity when the fluorinated dye **13b** was used (Figure 3). In addition, a piece of (3cmx1cm) of dyed fabric **B** was placed in a tube under mechanical stirring with 5mL of a washing bath at 30°C for 30 min. After the washing the fabric was rinsed with water and the process was repeated three consecutive times.

Another piece of dyed fabric **B** was submitted to six consecutive washings following the same protocol. We evaluated again the contact angle; after three washings dyed fabric suffered a slight decline of 10° (max. deviation $\pm 6^\circ$) whereas after six washings the decline was 11° (max. deviation $\pm 2^\circ$). Thus, dyed fabric **B** maintains the hydrophobic properties after repeatable laundry processes, which is in concordance with its excellent colorfastness properties and confirming the stability and covalent link of the dye to the cellulose.



Figure 3. 1. Untreated cotton; 2. Stained cotton fabric **B**; 3. Stained cotton fabric **A**. Only cotton fabric **B** keeps floating in water.

Finally, we carried out some color fastness tests. The colorimetric measurements were made on a reflectance spectrophotometer. The results indicate excellent color stability after two months of the dyeing process which is really important for industrial applications (as it can be observed in Figure 4 for a stained cotton fabric **B**).

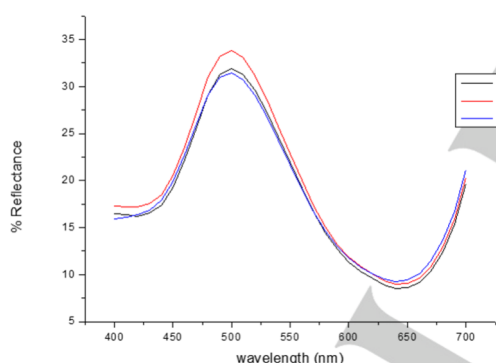


Figure 4. Fastness test of stained cotton fabric **B** along time.

In summary, new triarylmethane dyes have been prepared. The covalent link of reactive dyes to cotton fabrics has resulted in new hydrophobic colored fibers, when dye **13b** was used superhydrophobicity was achieved. This cotton modified fibers have potential applications in sportswear and outdoor textiles with water or oil repellent properties and excellent color fastness. Fluorous dyes being in general more hydrophobic and oleophobic than their hydrocarbon analogues.

Acknowledgements

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Keywords: superhydrophobicity • triarylmethane dyes • cotton fabric • surface modification • oleophobicity

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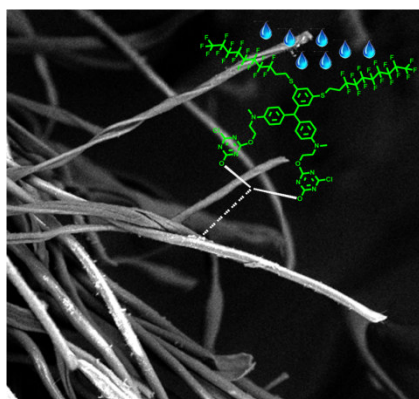
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Layout 1:

COMMUNICATION

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