Fluorous Hydrophobic Fluorescent (*E*)-Stilbene Derivatives for Application on Security Paper

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Abstract

(*E*)-Stilbene hydrophobic fluorophores possessing long perfluorinated or hydrocarbonated chains have been prepared through a stereoselective Wittig-Schlosser reaction. When covalently grafted upon paper, they give rise to a fluorescent-labeled paper upon irradiation with UV light. The hydrophobicity and oleophobicity of the fluorous (*E*)-stilbene derivative furnish self-cleaning properties. Application in the detection of money counterfeiting is envisioned.

1. Introduction

The so-called safety papers need to be protected from any attempts of falsification [1,2]. Official documents such as passports, checks, stamps and other high added value papers, as well as paper money, are some examples. A security document is usually made by using a paper which has specific properties to prevent forgery and allow the user to authenticate the document. Currently, the detection of counterfeited paper money is a severe problem [3]. The means to prevent forgery are based upon special chemical compounds which will show a visible mark. One of the many techniques utilized in safety paper production is the use of luminescence substances [4-6]. Of particular significance is the work of H. El-Saied and coworkers about the use of fluorescent 3-pyridinecarbonitrile containing compounds for dip dyeing process of papers [7,8]. The same authors have reported the preparation of

nanoparticles based on pyridine dicarbonitriles which were sprayed using an automatic atomizer on a paper sheet [9]. Security papers could also be obtained through a covalent link of the chromatic moiety onto the paper surface, thus avoiding the leaching of the fluorophore [10]. As far as we know, very few examples can be found in the literature. One of them is the grafting of photochromic spiropyran ether methacrylate onto the paper surface through atom transfer radical polymerization [4-6].

On the other hand, the interest in highly water and oil repellent materials has grown in recent years, in part due to the promise of creating self-cleaning surfaces [11-17]. Given that cotton fibers almost inevitably undergo a dying process we envisaged that the process of dyeing may also be used to incorporate hydrophobicity. Thus, we designed some reactive dyes possessing long perfluorinated or hydrocarbonated chains that could be covalently link to a cotton surface (Fig. 1). Azo [18] (Fig. 1), anthraquinone [19] and triarylmethane [20] derivatives have been used with success affording new hydrophobic coloured fibers. We got inspired by this previous research to design a reactive molecule that could be used as a fluorescent label to verify the authenticity of high added value paper (Fig. 1). The design structure consists on a (*E*)-stilbene based moiety possessing long perfluorinated or hydrocarbonated tails, responsible of the self-cleaning properties, and a reactive group to covalently link the fluorophore onto paper's surface. (*E*)-stilbene derivatives were selected due to their well known fluorophore properties and the possibility to introduce different substituents in the aromatic positions using cheap starting materials. These fluorescent-labeled papers, which change color upon irradiation with UV light, could be applied for security and authentication purposes.

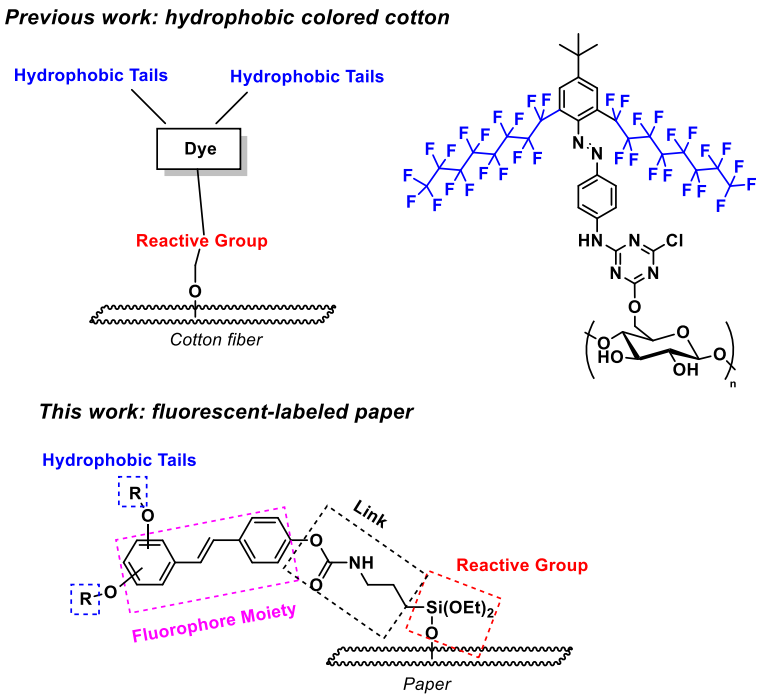


Figure 1. Example of azo based dyes anchored on a cotton surface (previous work) and structure design for fluorescent-labeled paper

2. Materials and methods

2.1. General Information

All starting materials were purchased from Sigma Aldrich or Fluorochem, and used without further purification. All chemical shifts are given in δ (ppm) and coupling constants (J) in Hz. The following abbreviations are used to indicate the multiplicity: s=singlet; d=doublet: t=triplet; q=quartet; m=multiplet. ^{1}H NMR and ^{13}C NMR are refereed with respect to TMS and ^{19}F NMR with respect to CCl_3F. Contact angle measurements: the hydrophobic/oleophobic tests performed were the measurement of the contact angle of a water droplet (4µL), olive oil (4µL) and hexadecane droplet (4µL) deposited on top of each fabric or glass. These experiments were carried out in Institut de Ciència de Materials de Barcelona (ICMAB) installations with a Contact Angle Measuring System DSA 100 from KRÜSS which is located in a physico-chemical laboratory (humidity and temperature control).

2.2. General procedure for the alkylation reactions of 2 (Scheme 1)

To a solution of the corresponding aldehyde **2** (0.28 mmol) in dry DMF (4 mL) were added the corresponding iodide (3 eq) and potassium carbonate (0.11g, 3 eq). The reaction mixture was stirred under argon atmosphere at reflux over 16 hours. The reaction was monitored via TLC. Once the reaction was finished it was quenched with water. The product was extracted with dichloromethane (3x15 mL) and washed with water. The organics were dried under vacuum and the crude was purified by flash chromatography through silica gel using hexane/ethyl acetate (9/1) as eluent yielding compounds **3** (Scheme 1).

2.3. Synthesis of 4-((4,6-bis(dodecylthio)-1,3,5-triazin-2-yl)oxy)benzaldehyde, 3g

A two-neck flask was fitted with a pressure-equalizing addition funnel and charged with 4-hydroxybenzaldehyde (0.23 g, 1.89 mmol) and potassium carbonate (2.5 eq.) in 8 mL of dried DMF. Under inert atmosphere, a solution (2 mL) of the triazine derivative (1 eq.) was added dropwise over 10 min and allowed to stir overnight at 50ºC. The reaction was quenched with water, and the product was extracted with dichloromethane (3 x 20 mL), dried over Na_2SO_4,

and concentrated in vacuo. The product was purified by flash chromatography through silica gel using hexane/ethyl acetate (9/1) to yield a white solid (0.54 g, 0.90 mmol, 92% yield).

2.3. General procedure for the Wittig reactions (Scheme 1)

In a well dried Schlenk methyltriphenylphosphonium bromide salt (0.55 g, 1.56 mmol) was dissolved in THF (4 mL). The mixture was cooled at 0ºC and then *n*-BuLi (2.5 M in hexanes, 2.5 eq) was added dropwise through a syringe. The mixture was stirred for 30 minutes. Once the phosphonium ylide was formed, a solution of the corresponding aldehyde **3** (0.72 mmol, 1 eq.) in 2 mL of THF was added dropwise. The reaction was stirred from 0ºC to room temperature and after 4 hours the reaction poured into methyl-*tert*-buthylether. The solution was filtered through silica gel, and the solvent was evaporated under vacuum, yielding the desired styrene derivative **4** (Scheme 1).

2.4. General procedure for the Heck reactions (Scheme 1)

A solution of the corresponding styrene **4** (350 mg, 1.46 mmol), $Pd(OAc)_2$ (5%), tri(*o*-tolyl)phosphine (7%), and 4-iodophenol (310 mg, 1.42 mmol) in dry NEt_3 (3 mL) was stirred for 1 day at 110 °C. After the reaction was complete, the reaction was poured in water and extraction with CH_2Cl_2 were done. The organics were dried over Na_2SO_4, and the solvent was evaporated. The crude product was purified by column chromatography on silica gel (eluent hexane (9) : ethyl acetate (1)) to obtain a solid which was characterized as the corresponding stilbene **1**.

2.4. General procedure for the Wittig-Schlosser reaction (Scheme 3)

In a dried Schlenk the phosphonium salt **6** (0.13 g, 0.30 mmol) and LiBr (0.04 g, 0.50 mmol) were dissolved in THF (6 mL). The mixture was cooled at 0ºC and then *n*-BuLi (2.5 M in hexanes, 7.5 eq) was added dropwise. The mixture was stirred for 30 minutes. Once the phosphonium ylide was formed a solution of the corresponding alkylated aldehyde **3** (0.15 g, 0.24 mmol) in THF (6 mL) was added dropwise. The reaction was stirred from 0ºC to room temperature and after 4 hours the reaction was quenched with ammonium chloride. The product was extracted with CH_2Cl_2 three times and after evaporation the residue was purified by flash chromatography through silica gel using hexane/ethyl acetate (9/1) as eluent to give the corresponding pure (*E*)-stilbene **1**.

2.5. General procedure for the synthesis of the reactive fluorescent carbamates 7 (Scheme 4)

The corresponding (*E*)-4-hydroxystilbene **1** (0.27 mmol) was dissolved in anhydrous THF (5.5 mL) in a dried Schlenk. To the solution, triethylamine (0.1 mL, 0.3 mmol) and 3-(triethoxysilyl)propylisocyanate (0.17 mL, 0.27 mmol) were added. The reaction was stirred at room temperature over 16 hours. After completion of the reaction, the solvent was removed under vacuum. The crude was purified by chromatography through silica gel using hexane/ethyl acetate (9/1) as eluent to give the final reactive carbamates **7**.

2.6. Characterization of compounds

The description of all the compounds prepared in this manuscript is perfectly described in the suplementary information. ^{1}H (250MHz), ^{13}C (62.5 MHz) and ^{19}F (253.2 MHz) NMR spectra have been registered in a Brucker AC-250 spectrometer. 1H and 13C NMR spectra have also been registered in a 360 MHz and 90 MHz respectively in a Brucker Avance 360 spectrometer or in a 400 MHz and 101 MHz Brucker Avance 400 spectrometer. IR spectra (neat) were performed in a Bruker Tensor 27 using an ATR (Attenuated Total Reflectance) Golden Gate modulus provided with a diamond tip. UV-Vis spectra were performed using a Hewlett-Packard 8453 model with diode array and 1 cm quartz cells. Confocal measurements were analyzed by Confocal TCS SP2 (Leica) equipped with three detectors for fluorescence and AOBS (Acousto-Optical Beam Splitter) system. HR-ESI (High Resolution-ElectroSpray Ionization) experiments were performed using a MicroTof-Q from Bruker daltronics. Melting points were measured in a bloc Kofler apparatus from Reichert or in a B-545 apparatus from Büchi and are uncorrected. Column chromatographies were performed with commercial silica gel (SDS or Fluka) of 35-70 μm grain size.

4-Bis(dodecyloxy)benzaldehyde, **3a**

Colorless oil; Isolated yield: 75% (5.4 mmol, 2.57 g from 1.00 g of starting material); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 10.48 (s, 1H; C*H*O), 7.32 (d, $^{4}J_{H,H}$ = 3.2 Hz, 1H; Ar*H*), 7.10 (dd, $^{4}J_{H,H}$ = 3.2 Hz, $^{3}J_{H,H}$ = 9.1 Hz, 1H; Ar*H*), 6.91 (d, $^{3}J_{H,H}$ = 9.1 Hz, 1H; Ar*H*), 4.02 (t, $^{3}J_{H,H}$ = 6.5 Hz, 2H; C*H*$_2$O), 3.93 (t, $^{3}J_{H,H}$ = 6.5 Hz, 2H; C*H*$_2$O), 1.79 (m, 4H; C*H*$_2$CH$_2$O), 1.79 (m, 4H; CH$_3$C*H*$_2$), 1.28 (broad singlet, 32H; C*H*$_2$), 0.89 (t, $^{3}J_{H,H}$ = 6.6 Hz, 6H; C*H*$_3$); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 190.0 (*C*=O), 156.7 (Ar*C*, $C_{12}H_{25}O$-*C*), 153.4 (Ar*C*, $C_{12}H_{25}O$-*C*), 125.5 (Ar*C*), 124.4 (Ar*C*), 114.7 (Ar*C*), 111.2 (Ar*C*), 69.6 (O*C*H$_2$(CH$_2$)$_{10}$CH$_3$), 69.0 (O*C*H$_2$(CH$_2$)$_{10}$CH$_3$), 32.3 (CH$_3$(*C*H$_2$)$_{11}$O), 30.0 (CH$_3$(*C*H$_2$)$_{11}$O), 29.8 (CH$_3$(*C*H$_2$)$_{11}$O), 29.6 (CH$_3$(*C*H$_2$)$_{11}$O), 26.5 (CH$_3$(*C*H$_2$)$_{11}$O), 26.4 (CH$_3$(*C*H$_2$)$_{11}$O), 23.1 (CH$_3$(*C*H$_2$)$_{11}$O), 14.5

(*C*H$_3$(CH$_2$)$_{11}$O); IR (ATR): $\tilde{\nu}$= 2919, 1678 cm^{-1}; HRMS (ESI): m/z calcd for $C_{31}H_{54}O_3Na$ 497.3965 [*M*+Na$^+$]; found 497.3961.

1,4-Bis(4,4,4-trifluorobutoxy)benzaldehyde, **3c**

Colorless oil; Isolated yield: 74% (0.95 mmol, 96 mg from 500 mg of starting material); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 10.44 (s, 1H; C*H*O), 7.31 (d, $^3J_{H,H}$ = 2.5 Hz, 1H; Ar*H*),), 7.13 (dd, $^3J_{H,H}$ = 2.5 Hz, $^3J_{H,H}$ = 10.0 Hz, 1H; Ar*H*), 6.93 (d, $^3J_{H,H}$ = 10.0 Hz, 1H, Ar*H*), 4.10 (t, $^3J_{H,H}$ = 6.4 Hz, 2H; C*H*$_2$CF$_3$), 4.00 (t, $^3J_{H,H}$ = 6.3 Hz, 2H, C*H*$_2$CF$_3$), 2.31 (m, 4H; OC*H*$_2$CH$_2$CH$_2$), 2.25 (m, 4H; OCH$_2$C*H*$_2$CH$_2$); ^{19}F NMR (235 MHz, [D]CHCl$_3$): δ = -68.9; ^{13}C NMR (63 MHz, $CDCl_3$): *δ* = 189.3 (*C*=O), 156.1 (Ar*C*), 153.3 (Ar*C*), 127.5 (q, $^1J_{C,F}$ = 245.1 Hz; *C*F$_3$CH$_2$),127.4 (q, $^1J_{C,F}$ = 245.1 Hz; *C*F$_3$), 125.6 (Ar*C*), 124.1 (Ar*C*), 114.6 (Ar*C*), 111.8 (Ar*C*), 67.6 (O*C*H$_2$CH$_2$), 67.0 (O*C*H$_2$*C*H$_2$), 31.0 (q, $^2J_{C,F}$ = 29.1 Hz, CF$_3$*C*H$_2$), 22.5 (t, $^3J_{C,F}$ = 2.54 Hz, OCH$_2$*C*H$_2$); IR (ATR): $\tilde{\nu}$= 2948, 1681 cm^{-1}. HRMS (ESI): m/z calcd for $C_{15}H_{16}F_6O_3Na$ 381.0901[*M*+Na$^+$]; found 381.0905.

1,4-bis((4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)oxy) benzaldehyde, **3d**

Yellowish oil; Isolated yield: 75% (1.36 mmol, 1.48 g from 250 mg of starting material); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 10.47 (s, 1H; C*H*O) 7.31 (d, $^4J_{H,H}$ = 3.2 Hz, 1H; Ar*H*), 7.16 (dd, $^4J_{H,H}$ = 3.2 Hz, $^3J_{H,H}$ = 9.1 Hz, 1H; Ar*H*), 6.96 (d, $^3J_{H,H}$ = 9.1 Hz, 1H; Ar*H*), 4.16 (t, $^3J_{H,H}$ = 5.9 Hz, 2H; C*H*$_2$CF$_3$), 4.06 (t, $^3J_{H,H}$ = 5.9 Hz, 2H; C*H*$_2$CF$_3$), 2.35 (m, 4H; OC*H*$_2$CH$_2$CH$_2$), 2.16 (m, 4H; OCH$_2$C*H*$_2$CH$_2$); ^{19}F NMR (376 MHz, $CDCl_3$): δ = 126.1 (m, 4F). 123.4 (m, 4F), 122.7 (m, 4F), 121.7 (m, 12F), 114.3 (m, 4F), -80.8 (t, $^3J_{C,F}$ = 9.9 Hz, 6F; C*F*$_3$); ^{13}C NMR (91 MHz, [D]CHCl$_3$): *δ* = 189.0 (*C*=O), 155.7 (Ar*C*, *C*-O), 152.9 (Ar*C*, *C*-O), 125.1 (Ar*C*), 123.9 (Ar*C*), 114.2 (Ar*C*), 111.3 (Ar*C*), 67.5 (O*C*H$_2$CH$_2$), 67.0 (O*C*H$_2$CH$_2$), 27.9 (t, $^3J_{C,F}$ = 22.3 Hz; CF$_3$*C*H$_2$), 22.5 (m, OCH$_2$*C*H$_2$); IR (ATR): $\tilde{\nu}$= 2860, 1678 cm^{-1}; HRMS (ESI): m/z calcd for $C_{29}H_{16}F_{34}O_3Na$ 1081.0454 [*M*+Na$^+$]; found 1081.0449.

1-((4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)oxy)-4-methoxy benzaldehyde, **3e**

Yellowish oil; Isolated yield: 89% (2.9 mmol, 1.78 g from 500 mg of starting material); ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 10.45 (s, 1H, CHO), 7.33 (d, $^4J_{H,H}$ = 3.2 Hz, 1H; Ar*H*), 7.12 (dd, $^3J_{H,H}$ = 9.0 Hz, $^4J_{H,H}$ = 3.2 Hz, 1H; Ar*H*), 6.93 (d, $^3J_{H,H}$ = 9.0 Hz, 1H; Ar*H*), 4.12 (t, $^3J_{H,H}$ = 6.0 Hz, 2H; OC*H*$_2$), 3.80 (s, 3H; OC*H*$_3$), 2.34 (m, 2H, OC*H*$_2$CH$_2$CH$_2$), 2.17 (m, 2H,

$OCH_2CH_2CH_2$); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -126.4 (m, 2F), -123.6 (m, 2F), -123.0 (m, 2F), -122.0 (m, 6F), -114.5 (t, $^3J_{F,F}$ = 13.8 Hz, 2F), -81.2 (t, $^3J_{F,F}$ = 9.9 Hz, 3F; CF_3); ^{13}C NMR (101 MHz, [D]$CHCl_3$): δ = 188.8 (*C*=O), 155.4 (Ar*C*, *C*-O), 153.9 (Ar*C*, *C*-O), 125.1 (Ar*C*), 123.2 (Ar*C*), 118.3 (m, CF_2), 114.1 (ArC), 111.0 (m, CF_2), 110.4 (Ar*C*), 67.5 (OCH_2CH_2), 55.6 (OCH_3), 27.8 (t, $^3J_{C,F}$ = 22.5 Hz; CF_3CH_2), 20.5 (t, $^3J_{C,F}$ = 3.6 Hz; OCH_2CH_2); IR (ATR): $\tilde{\nu}$ = 2948, 1681 cm^{-1}. HRMS (ESI): m/z calcd for $C_{19}H_{13}F_{17}O_3Na$ 635.0485 [*M*+Na^+]; found 635.0500.

4-((4,6-bis(dodecylthio)-1,3,5-triazin-2-yl)oxy)benzaldehyde, **3g**

White solid; Isolated yield: 92% (3.8 mmol, 2.26 g from 500 mg of starting material); ^1H NMR (360 MHz, $CDCl_3$): δ = 10.02 (s, 1H; C*H*O), 7.95 (d, $^3J_{(H,H)}$ = 8.5 Hz, 2H; Ar*H*), 7.35 (d, $^3J_{(H,H)}$ = 8.5 Hz, 2H; Ar*H*), 3.00 (t, $^3J_{(H,H)}$ = 6.7 Hz, 4H; $CH_3(CH_2)_{10}CH_2S$), 1.63 (m, 4H; $CH_3CH_2(CH_2)_9CH_2S$), 1.26 (broad singlet, 36H; $CH_3CH_2(CH_2)_9CH_2S$), 0.88 (t, $^3J_{(H,H)}$ = 6.7 Hz, 6H; $CH_3CH_2(CH_2)_9CH_2S$); ^{13}C NMR (91 MHz, [D]$CHCl_3$): δ = 190.7 (*C*HO), 183.6 (Ar*C*, *C*-$SC_{12}H_{25}$), 167.4 (Ar*C*, N=*C*-O), 156.4 (ArC, O-*C*), 134.0 (Ar*C*, *C*-CHO), 131.1 (Ar*C*), 122.5 (Ar*C*), 31.9 ($CH_3(CH_2)_{11}S$),. 30.5 ($CH_3(CH_2)_{11}S$), 29.6 ($CH_3(CH_2)_{11}S$), 29.5 ($CH_3(CH_2)_{11}S$), 29.3 ($CH_3(CH_2)_{11}S$), 29.1 ($CH_3(CH_2)_{11}S$), 28.8 ($CH_3(CH_2)_{11}S$), 22.7 ($CH_3(CH_2)_{11}S$), 14.1 ($CH_3(CH_2)_{11}S$);. HRMS (ESI): m/z calcd for $C_{34}H_{55}N_3O_2S_2Na$ 624.3633 [*M*+Na^+]; found 624.3635.

1,4-Bis(dodecyloxy)-2-vinylbenzene, **4a**

Colorless oil; Isolated yield: 96% (0.40 mmol, 190 mg from 200 mg of starting material); ^1H NMR (250 MHz, $CDCl_3$): δ = 7.37 ppm (s, 1H; ArH), 7.09 (m, 2H; C*H*=CH_2), 6.80 (s, 1H; ArH), 5.78 (d, $^3J_{trans(H,H)}$ = 17.5 Hz, 1H; CH=C*H*$_2$), 5.29 (d, $^3J_{cis(H,H)}$ = 11.1 Hz, 1H; CH=C*H*$_2$), 3.96 (t, $^3J_{(H,H)}$ = 6.7 Hz, 4H; $CH_3CH_2(CH_2)_9CH_2O$), 1.81 (m, 4H; $CH_3CH_2(CH_2)_8CH_2CH_2O$), 1.50 (m, 4H; $CH_3CH_2(CH_2)_9CH_2O$), 1.32 (broad singlet, 32H; $CH_3CH_2(CH_2)_8CH_2CH_2O$), 0.93 (t, $^3J_{(H,H)}$ = 6.7 Hz, 6H; $CH_3CH_2(CH_2)_9CH_2O$); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 153.2 (Ar*C*, $C_{12}H_{25}O$-*C*), 150.7 (Ar*C*, $C_{12}H_{25}O$-*C*), 133.7 (Ar*C*), 131.7 (Ar*C*), 128.7 (Ar*C*), 127.7 (Ar*C*), 114.6 (Ar*C*), 114.3 (Ar*C*), 113.6 (Ar*C*), 112.4 (Ar*C*), 69.3 ($OCH_2(CH_2)_{10}CH_3$), 68.8 ($OCH_2(CH_2)_{10}CH_3$), 31.9 ($CH_3(CH_2)_{11}O$), 29.7 ($CH_3(CH_2)_{11}O$), 29.5 ($CH_3(CH_2)_{11}O$), 29.4 ($CH_3(CH_2)_{11}O$), 26.2 ($CH_3(CH_2)_{11}O$), 26.1 ($CH_3(CH_2)_{11}O$), 22.7 ($CH_3(CH_2)_{11}O$), 14.2 ($CH_3(CH_2)_{11}O$); HRMS (ESI): m/z calcd for $C_{32}H_{56}O_2Na$ 495.4178 [*M*+Na^+]; found 495.4172.

1,3-Bis(dodecyloxy)-5-vinylbenzene, **4b**

Colorless oil; Isolated yield: 96% (0.39 mmol, 180 mg from 200 mg of starting material); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.68 ppm (dd, $^{3}J_{trans(H,H)}$ = 17.5 Hz, $^{3}J_{cis(H,H)}$ = 11.1 Hz, 1H; C*H*=CH_2) 6.60 (d, $^{4}J_{(H,H)}$ = 2.0 Hz, 2H; Ar*H*), 6.43 (s, 1H, Ar*H*), 5.76 (d, $^{3}J_{trans(H,H)}$ = 17.5 Hz, 1H; CH=CH_2), 5.27 (d, $^{3}J_{cis(H,H)}$ = 11.1 Hz, 1H; CH=CH_2), 3.98 (t, $^{3}J_{(H,H)}$ = 6.7 Hz, 4H; $CH_3(CH_2)_9CH_2CH_2O$), 1.82 (m, 4H; $CH_3(CH_2)_9CH_2CH_2O$), 1.50 (m, 4H; ($CH_3(CH_2)_9CH_2CH_2O$), 1.33 (broad singlet, 36H; $CH_3(CH_2)_9CH_2CH_2O$), 0.95 (t, $^{3}J_{(H,H)}$ = 6.7 Hz, 6H; $CH_3CH_2(CH_2)_9CH_2O$); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 160.9 (Ar*C*, *C*-O-$C_{12}H_{25}$), 139.9 (Ar*C*, *C*-CH=CH_2), 137.5 (*C*H=CH_2), 114.4 (CH=*C*H_2), 105.2 (Ar*C*), 101.4 (Ar*C*), 68.4 ($OCH_2(CH_2)_{10}CH_3$), 32.3 ($CH_3(CH_2)_{11}O$), 30.1 ($CH_3(CH_2)_{11}O$), 29.9 ($CH_3(CH_2)_{11}O$), 29.8 ($CH_3(CH_2)_{11}O$), 26.5 ($CH_3(CH_2)_{11}O$), 23.1 ($CH_3(CH_2)_{11}O$), 14.5 ($CH_3(CH_2)_{11}O$); HRMS (ESI): m/z calcd for $C_{32}H_{56}O_2Na$ 495.4178 ; found 495.4172 [*M*+Na^+].

1,4-bis(4,4,4-trifluorobutoxy)-2-vinylbenzene, **4c**

Colorless oil; Isolated yield: 95% yield (0.53 mmol, 0.189 g from 0.20 g of starting material); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.38 ppm (s, 1H, Ar*H*), 7.06 (m, 2H, Ar*H* and C*H*=CH_2), 6.81 (s, 1H, Ar*H*), 5.78 (d, $^{3}J_{trans(H,H)}$ = 17.6 Hz, 1H, CH=CH_2), 5.34 (d, $^{3}J_{cis(H,H)}$ = 11.1 Hz, 1H CH=CH_2), 4.03 (t, $^{3}J_{(H,H)}$ = 6.3 Hz, 4H, OCH_2CH_2), 2.36 (m, 4H, CH_2CF_3), 2.10 (m, 4H, $CH_2CH_2CH_2$); ^{19}F NMR (235 MHz, $CDCl_3$): δ = -66.8 (s, 6F, CF_3); ^{13}C NMR (63 MHz, [D]$CHCl_3$): δ = 153.1 (Ar*C*, $C_{12}H_{25}O$-*C*), 150.3 (Ar*C*, $C_{12}H_{25}O$-*C*), 131.2 (Ar*C*), 127.5 (q, $^{1}J_{(C,F)}$ = 245.1 Hz, *C*F_3), 127.4 (q, $^{1}J_{(C,F)}$ = 245.1 Hz, *C*F_3), 131.1 (Ar*C*), 128.9 (CH=*C*H_2), 127.8 (Ar*C*), 114.5 (*C*H=CH_2), 112.2 (Ar*C*), 67.3 ($OCH_2(CH_2)_2CF_3$), 66.6 ($OCH_2(CH_2)_2CF_3$), 31.5 (m, $OCH_2(CH_2)_2CF_3$), 22.3 (m, $OCH_2(CH_2)_2CF_3$); HRMS (ESI): m/z calcd for $C_{16}H_{18}F_6O_2Na$ 379.1109 [*M*+Na^+]; found 379.1108.

1,4-Bis((4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)oxy)-2-vinylbenzene, **4d**

Colorless oil; Isolated yield: 93% (0.18 mmol, 185 mg from 200 mg of starting material); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.01 (m, 2H, C*H*=CH_2 and Ar*H*), 6.79 (bs, 2H, Ar*H*), 5.74 (d, $^{3}J_{trans(H,H)}$ = 17.1Hz, 1H, CH=CH_2, *trans*), 5.31 (d, $^{3}J_{cis(H,H)}$ = 11.1 Hz, 1H, CH=CH_2, *cis*), 4.03 (t, $^{3}J_{(H,H)}$ = 5.7 Hz, 4H, $OCH_2CH_2CH_2(CF_2)_7CF_3$), 2.33 (m, 2H, -$OCH_2CH_2C\underline{H}_2(CF_2)_7CF_3$) and 2.12 (m, 2H, -$OCH_2C\underline{H}_2$ $CH_2(CF_2)_7CF_3$); ^{19}F NMR (235 MHz, $CDCl_3$): δ = -126.6 (m, 4F), -123.9 (m, 4F), -123.2 (m, 4F), -122.4 (m, 12F), -114.8 (t, $^{3}J_{(F,F)}$ = 13.8 Hz, 4F), -81.3 (t, $^{3}J_{(F,F)}$ = 9.9 Hz, 6F; CF_3); ^{13}C NMR (63 MHz, [D]$CHCl_3$): δ = 153.0 (Ar*C*, *C*-O), 150.2 (Ar*C*,

C-O), 131.0 (Ar*C*), 128.0 (CH=*C*H_2), 114.5 (*C*H=CH_2), 113.6 (Ar*C*), 112.6 (Ar*C*), 111.7 (Ar*C*), 67.7 (O*C*H_2CH_2), 66.9 (O*C*H_2CH_2), 27.9 (m, CF_3CH_2), 20.6 (m, OCH_2CH_2); $C_{30}H_{18}F_{34}O_2Na$ 1079.0662 [*M*+Na^+]; found 1079.0665.

1-((4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundecyl)oxy)-4-metoxy-2-vinylbenzene, **4e**

Colorless oil; Isolated yield: 97% (0.26 mmol, 164 mg from 160 mg of starting material); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.36 (broad singlet, 1H; Ar*H*), 7.06 (m, 2H; Ar*H* and C*H*=CH_2), 6.81 (d, $^4J_{(H,H)}$ = 1.6 Hz, 2H; Ar*H*), 5.78 (d, $^3J_{trans\ (H,H)}$ = 17.7 Hz, 1H; CH=CH_2), 5.33 (d, $^3J_{cis\ (H,H)}$ = 11.1 Hz, 1H; CH=CH_2), 4.03 (t, $^3J_{(H,H)}$ = 6.8 Hz, 2H; OCH_2), 3.82 (s, 3H; OCH_3), 2.36 (m, 2H; OC$H_2CH_2CH_2$), 2.13 (m, 2H; $OCH_2CH_2CH_2$); ^{19}F NMR (235 MHz, $CDCl_3$): δ = -126.6 (m, 2F), -123.9 (m, 2F), -123.2 (m, 2F), -122.4 (m, 6F), -114.8 (t, $^3J_{(F,F)}$ = 13.8 Hz, 2F), -81.3 (t, $^3J_{(F,F)}$ = 9.9 Hz, 3F; CF_3); ^{13}C NMR (63 MHz, [D]$CHCl_3$): δ = 154.1 (Ar*C*, *C*-O), 150.1 (Ar*C*, *C*-O), 131.2 (Ar*C*), 128.0 (CH=*C*H), 114.7 (*C*H=CH), 113.8 (Ar*C*), 113.6 (Ar*C*), 111.7 (Ar*C*), 67.7 (O*C*H_2CH_2), 55.5 (O*C*H_3), 28.0 (t, $^2J_{(C,F)}$ = 22.5 Hz, CF_3CH_2), 22.7 (t, $^3J_{(C,F)}$ = 3.6 Hz, OCH_2CH_2); $C_{20}H_{15}F_{17}O_2Na$ 633.0698 [*M*+Na^+]; found 633.0694. 1,3-Bis(dodecyloxy)-2-vinylbenzene, **4f**

Colorless oil; Isolated yield: 96% (0.30 mmol, 140 mg from 150 mg of starting material); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.85 (t, $^3J_{(H,H)}$ = 8.5 Hz, 1H, Ar*H*). 6.68 (dd, $^3J_{trans(H,H)}$ = 17.5 Hz, $^3J_{cis(H,H)}$ = 11.1 Hz, 1H; C*H*=CH_2), 6.40 (d, $^3J_{(H,H)}$ = 8.5 Hz, 2H, Ar*H*), 5.76 (d, $^3J_{trans(H,H)}$ = 17.5 Hz, 1H, CH=CH_2), 5.27 (d, $^3J_{cis(H,H)}$ = 11.1 Hz, 1H, CH=CH_2), 3.98 (t, $^3J_{(H,H)}$ = 6.7 Hz, 4H, $CH_3CH_2(CH_2)_9CH_2O$), 1.82 (m, 4H, $CH_3CH_2CH_2(CH_2)_8CH_2O$), 1.50 (m, 4H, $CH_3CH_2(CH_2)_9CH_2O$), 1.33 (broad singlet, 36H, $CH_3CH_2(CH_2)_9CH_2O$), 0.95 (t, $^3J_{(H,H)}$ = 6.7 Hz, 6H, $CH_3CH_2(CH_2)_9CH_2O$). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 160.9 (Ar*C*, $C_{12}H_{25}O$-*C*), 139.9 (Ar*C*), 137.5 (CH=*C*H_2), 114.4 (*C*H=CH_2), 105.2 (Ar*C*), 101.4 (Ar*C*), 68.4 (O*C*$H_2(CH_2)_{10}CH_3$), 32.3 ($CH_3(CH_2)_{11}O$), 29.9 ($CH_3(CH_2)_{11}O$), 29.8 ($CH_3(CH_2)_{11}O$), 26.5 ($CH_3(CH_2)_{11}O$), 23.1 ($CH_3(CH_2)_{11}O$), 14.5. (*C*$H_3(CH_2)_{11}O$); HRMS (ESI): m/z calcd for $C_{32}H_{56}O_2Na$ 495.4178 [*M*+Na^+]; found 495.4172.

2,4-Bis(dodecylthio)-6-(4-vinylphenoxy)-1,3,5-triazine, **4g**

Colorless oil; Isolated yield: 97% (0.30 mmol, 140 mg from 200 mg of starting material); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.44 (d, $^3J_{(H,H)}$ = 8.5 Hz, 2H; Ar*H*), 7.13 (d, $^3J_{(H,H)}$ = 8.5 Hz, 2H; Ar*H*), 6.73 (dd, $^3J_{trans\ (H,H)}$ = 17.6 Hz, $^3J_{cis\ (H,H)}$ = 10.9 Hz, 1H; C*H*=CH_2), 5.74 (d, $^3J_{trans\ (H,H)}$ = 17.6 Hz, 1H; CH=CH_2), 5.27 (d, $^3J_{cis\ (H,H)}$ = 10.9 Hz, 1H; CH=CH_2), 3.00 (t, $^3J_{(H,H)}$ = 6.7 Hz,

4H; $CH_3(CH_2)_{10}CH_2S$), 1.62 (m, 4H; $CH_3CH_2(CH_2)_9CH_2S$), 1.27 (broad singlet, 36H; $CH_3(CH_2)_9CH_2CH_2S$), 0.90 (t, $^3J_{(H,H)}$ = 6.7 Hz, 6H; $CH_3(CH_2)_{11}S$); ^{13}C NMR (91 MHz, $CDCl_3$): δ = 183.3 (Triazine*C*-$SC_{12}H_{25}$), 167.9 (Triazine***C***-O), 151.3 (ArC, O-*C*), 135.8 (*C*H=CH_2), 135.3 (Ar*C*, *C*-CH=CH_2), 127.1 (Ar*C*), 121.8 (Ar*C*), 114.0 (CH=CH_2), 31.9 (CH_3(**C**H_2)$_{11}$S), 30.5 (CH_3(*C*H_2)$_{11}$S), 29.6 (CH_3(*C*H_2)$_{11}$S), 29.5 (CH_3(*C*H_2)$_{11}$S), 29.4 (CH_3(*C*H_2)$_{11}$S), 29.2 (CH_3(*C*H_2)$_{11}$S), 28.8 (CH_3(*C*H_2)$_{11}$S), 22.7 (CH_3(*C*H_2)$_{11}$S), 14.1 (*C*H_3(CH$_2$)$_{11}$S); HRMS (ESI): m/z calcd for $C_{35}H_{57}N_3OS_2Na$ 622.3841[*M*+Na^+]; found 622.3844.

(*E*)-4-(2,5-Bis(dodecyloxy)styryl)phenol, **1a**

White solid; Isolated yield: 97% (0.20 mmol, 116 mg from 100 mg of starting material);

m.p.: 135-137ºC; ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.43 ppm (d, $^3J_{(H,H)}$ = 7.9 Hz, 1H; Ar*H*), 7.34 (d, $^3J_{(H,H)}$ = 16.4 Hz, 1H; CH=C*H*), 7.15 (d, $^3J_{(H,H)}$ = 1.9 Hz, 1H; Ar*H*), 7.07 (d, $^3J_{trans(H,H)}$ = 16.4 Hz, 1H; CH=CH), 6.84 (m, 3H; Ar*H*), 6.78 (dd, $^3J_{(H,H)}$ = 8.5 Hz, $^4J_{(H,H)}$ = 1.9 Hz, 1H; Ar*H*), 3.98 (t, $^3J_{(H,H)}$ = 6.7 Hz, 4H; $CH_3CH_2(CH_2)_9CH_2O$), 5.11 (s, 1H; O*H*), 1.83 (m, 4H; $CH_3(CH_2)_9CH_2CH_2O$), 1.49 (m, 4H; $CH_3CH_2(CH_2)_9CH_2O$), 1.30 (broad singlet, 32H; $CH_3CH_2(CH_2)_8CH_2CH_2O$), 0.91 (t, $^3J_{(H,H)}$ = = 6.7 Hz, 6H; $CH_3CH_2(CH_2)_9CH_2O$); ^{13}C NMR (91 MHz, $CDCl_3$): δ = 153.2 (Ar*C*, $C_{12}H_{25}O$-*C*), 153.2 (Ar*C*, $C_{12}H_{25}O$-*C*), 150.7 (Ar*C*, $C_{12}H_{25}O$-*C*), 133.7(Ar*C*), 131.7 (CH=*C*H), 128.7 (Ar*C*), 127.7 (CH=*C*H), 114.6 (Ar*C*), 114.3 (Ar*C*), 113.6 (Ar*C*), 112.4 (Ar*C*), 69.3 (O*C*H_2(CH$_2$)$_{10}$CH$_3$), 68.8 (O*C*H_2(CH$_2$)$_{10}$CH$_3$), 31.9 (CH_3(*C*H_2)$_{11}$O), 29.7 (CH_3(*C*H_2)$_{11}$O), 29.5 (CH_3(*C*H_2)$_{11}$O), 29.4 (CH_3(*C*H_2)$_{11}$O), 26.2 (CH_3(*C*H_2)$_{11}$O), 26.1 (CH_3(*C*H_2)$_{11}$O), 22.7 (CH_3(*C*H_2)$_{11}$O), 14.2 (CH_3(CH$_2$)$_{11}$O); IR (ATR): $\tilde{\nu}$= 3317, 2919, 1231 cm^{-1}; UV/vis (CH_3CN): λ_{max} (ε)= 298 nm (12235 mol^{-1} dm^3 cm^{-1}); fluorescence (CH_3CN): (λ_{em}) = 405 nm; HRMS (ESI): m/z calcd for $C_{38}H_{61}O_3$ 565.4615 [*M*+H^+]; found 565.4615.

(*E*)-4-(2,5-bis(4,4,4-trifluorobutoxy)styryl)phenol, **1c**

White solid; Isolated yield: 89% (0.74 mmol, 334 mg from 300 mg of starting material); m.p.: 117-118ºC; ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.43 ppm (d, $^3J_{(H,H)}$= 8.6 Hz, 2H; Ar*H*),. 7.28 (d, $^3J_{(H,H)}$= 16.4 Hz, 1H; C*H*=CH), 7.15 (d, $^3J_{(H,H)}$= 2.9 Hz, 1H; Ar*H*), 7.06 (d, $^3J_{(H,H)}$= 16.4 Hz, 1H; CH=C*H*), 6.86 (d, $^3J_{(H,H)}$= 8.6 Hz, 2H; Ar*H*), 6.83 (d, $^3J_{(H,H)}$= 8.9 Hz, 1H; Ar*H*), 6.77 (dd, $^3J_{(H,H)}$= 8.8 Hz, $^4J_{(H,H)}$= 2.9 Hz, 1H, Ar*H*), 5.01 (s, 1H; O*H*), 4.05 (t, $^3J_{(H,H)}$= 6.3 Hz, 4H; C*H*$_2$CF$_3$), 2.38 (m, 4H; OC*H*$_2$CH$_2$CH$_2$), 2.10 (m, 4H; OCH$_2$CH_2CH$_2$); ^{19}F NMR (376 MHz, [D]$CHCl_3$): δ = -66.3 (s, CF_3); ^{13}C NMR (101 MHz, $CDCl_3$ [D]$CHCl_3$) δ = 153.3 (Ar*C*, *C*-O).

150.0 (Ar*C*, *C*-O), 150.3 (Ar*C*, *C*-O), 130.5 (Ar*C*), 129.2 (*C*H=CH), 127.9 (Ar*C*), 127.5 (q, $^{1}J_{(C,F)}$ = 245.1 Hz, *C*F_3CH_2), 127.4 (q, $^{1}J_{(C,F)}$ = 245.1 Hz, *C*F_3CH_2), 120.7 (Ar*C*), 115.6 (Ar*C*), 115.0 (Ar*C*), 113.9 (CH=*C*H), 113.8 (Ar*C*), 112.2 (Ar*C*), 67.5 (OCH_2CH_2), 66.6 (O*C*H_2CH_2), 30.7 (m, CF_3*C*H_2),22.3 (m, OCH_2*C*H_2); IR (ATR): $\tilde{\nu}$= 3332, 2937 cm^{-1}; UV/vis (CH_3CN): λ_{max} (ε)= 296 nm (20340 mol^{-1} dm^3 cm^{-1}); fluorescence emission (CH_3CN): (λ_{em}) = 405 nm; HRMS (ESI): m/z calcd for $C_{22}H_{22}F_6O_3Na$ 449.155 [*M*+Na^+]; found 449.1546.

(E)-4-(2,5-bis(((4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)oxy)styryl)phenol, **1d**

White solid; Isolated yield: 80% (0.06 mmol, 70 mg from 80 mg of starting material); m.p.: 124-127ºC; ^{1}H NMR (400 MHz, [D_6]CH_3COCH_3): δ = 8.51 (s, 1H, O*H*), 7.43 (d, $^{3}J_{(H,H)}$= 8.5 Hz, 2H; Ar*H*), 7.34 (d, $^{3}J_{trans(H,H)}$= 16.5 Hz, 1H; C*H*=CH), 7.27 (d, $^{4}J_{(H,H)}$= 2.9 Hz, 1H; Ar*H*), 7.20 (d, $^{3}J_{trans(H,H)}$= 16.5 Hz, 1H; CH=C*H*), 6.96 (d, $^{3}J_{(H,H)}$= 8.6 Hz, 1H; ArH), 6.84 (m, 3H; Ar*H*), 4.15 (q, $^{3}J_{(H,H)}$= 5.8 Hz, 4H; OCH_2), 2.51 (m, 4H; $OCH_2CH_2CH_2$), 2.16 (m, 4H; $OCH_2CH_2CH_2$); ^{19}F NMR (376 MHz, [D_6]CH_3COCH_3): δ = -126.7 (m, 4F), -123.9 (m, 4F), -123.2 (m, 4F), -122.3 (m, 12F), -114.7 (t, $^{3}J_{(F,F)}$= 13.8 Hz, 4F), -81.7 (m, 6F; CF_3); ^{13}C NMR (101 MHz, [D_6]CH_3COCH_3): δ = 157.4 (Ar*C*, *C*-OH), 153.3 (Ar*C*, *C*-O),) 150.4 (Ar*C*, *C*-O), 129.4 (Ar*C*), 129.3 (CH=*C*H), 128.0 (Ar*C*), 127.7 (Ar*C*), 119.7 (*C*H=CH), 115.5 (Ar*C*), 114.0 (Ar*C*), 113.9 (Ar*C*), 111.9 (Ar*C*), 67.5 (O*C*H_2CH_2), 66.6 (O*C*H_2CH_2), 27.5 (m, CF_3*C*H_2), 20.5 (m, OCH_2*C*H_2); IR (ATR): $\tilde{\nu}$= 3332, 2937 cm^{-1}; UV/vis (CH_3CN): λ_{max} (ε)= 283 nm (56195 mol^{-1} dm^3 cm^{-1}); fluorescence emission (CH_3CN): (λ_{em}) = 407 nm; HRMS (ESI): m/z calcd for $C_{36}H_{21}F_{34}O_3Na$ 1148.1010 [*M*+Na^+]; found 1148.1021.

(*E*)-4-(2-((4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)oxy)-5-metoxy) styryl)phenol, **1e**

White solid; Isolated yield: 81% (0.13 mmol, 93 mg from 100 mg of starting material); m.p.: 142-145ºC; ^{1}H NMR (400 MHz, [D_6]CH_3COCH_3): δ = 8.51 (s, 1H; O*H*), 7.44 (d, $^{3}J_{(H,H)}$= 8.5 Hz, 2H; Ar*H*), 7.34 (d, $^{3}J_{(H,H)}$= 16.5 Hz, 1H; C*H*=CH), 7.22 (m, 2H; Ar*H* and CH=C*H*), 6.97 (d, $^{3}J_{(H,H)}$= 9.0 Hz, 1H, Ar*H*), 6.86 (d, $^{3}J_{(H,H)}$= 8.5 Hz, 2H; Ar*H*), 6.80 (dd, $^{3}J_{(H,H)}$= 9.0 Hz, $^{2}J_{(H,H)}$= 2.9 Hz, 1H; Ar*H*), 4.17 (t, $^{3}J_{(H,H)}$= 6.0 Hz, 2H; OCH_2), 3.81 (s, 3H; OCH_3), 2.57 (m, 2H; O<u>C</u>$H_2CH_2CH_2$), 2.19 (m, 2H; OCH_2<u>C</u>H_2CH_2); ^{19}F NMR (376 MHz, [D_6]CH_3COCH_3): δ = -126.7 (m, 2F), -123.9 (m, 2F), -123.2 (m, 2F), -122.3 (m, 6F), -114.7 (t, $^{3}J_{(F,F)}$= 13.8 Hz, 2F), -81.6 (t, $^{3}J_{(F,F)}$= 9.9 Hz, 3F; CF_3); ^{13}C NMR (101 MHz, [D_6]CH_3COCH_3) δ = 157.3 (Ar*C*, *C*-O). 154.3 (Ar*C*, *C*-O), 150.1 (Ar*C*, *C*-OH), 129.4 (Ar*C*), 129.2 (CH=*C*H), 127.9 (Ar*C*),

127.6 (Ar*C*), 119.8 (*C*H=CH), 115.4 (Ar*C*), 114.1 (Ar*C*), 113.2 (Ar*C*), 110.9 (Ar*C*), 67.6 (O*C*$H_2$$CH_2$), 54.9 (O*C*$H_3$), 27.5 (t, $^2J_{(C,F)}$ = 21.9 Hz, CF_3*C*H_2), 20.5 (t, $^3J_{(C,F)}$ = 3.6 Hz, OCH$_2$*C*H_2); IR (ATR): $\tilde{\nu}$= 3371, 2945 cm^{-1}; UV/vis (CH_3CN): λ_{max} (ε)= 283 nm (50615 mol^{-1} dm^3 cm^{-1}); fluorescence emission (CH_3CN): (λ_{em}) = 408 nm; HRMS (ESI): m/z calcd for $C_{26}H_{19}F_{17}O_3Na$ 725.0955 [*M*+Na^+]; found 725.0948.

(*E*)-4-(2,6-bis(dodecyloxy)styryl)phenol, **1f**

White solid; Isolated yield: 85% (0.17 mmol, 102 mg from 100 mg of starting material); m.p.: 132-133ºC. ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.43 ppm (t, $^3J_{(H,H)}$ = 7.9 Hz, 1H, Ar*H*), 7.34 (d, $^3J_{(H,H)}$ = 16.4 Hz, 1H, C*H*=CH), 7.15 (d, $^3J_{(H,H)}$ = 7.9 Hz, 2H, ArH), 7.07 (d, $^3J_{(H,H)}$ = 16.4 Hz, 1H, C*H*=CH), 6.84 (m, 3H, Ar*H*), 6.78 (dd, $^3J_{(H,H)}$ = 8.5 Hz, $^4J_{(H,H)}$ = 1.9 Hz, 1H, Ar*H*), 5.11 (s, 1H, O*H*), 3.98 (t, $^3J_{(H,H)}$ = 6.7 Hz, 4H, $CH_3CH_2(CH_2)_9CH_2O$), 1.83 (m, 4H, $CH_3(CH_2)_9CH_2CH_2O$), 1.49 (m, 4H, $CH_3CH_2(CH_2)_9CH_2O$), 1.30 (broad singlet, 32H, $CH_3CH_2(CH_2)_8CH_2CH_2O$), 0.91 (t, $^3J_{(H,H)}$ = 6.7 Hz, 6H, $CH_3CH_2(CH_2)_9CH_2O$). ^{13}C NMR (91 MHz, $CDCl_3$): δ = 155.5 (Ar*C*, $C_{12}H_{25}$O-*C*), 153.2 (Ar*C*, $C_{12}H_{25}$O-*C*), 150.7 (Ar*C*, $C_{12}H_{25}$O-*C*), 133.7(Ar*C*), 131.7 (CH=*C*H), 128.7 (Ar*C*), 127.7 (CH=*C*H), 114.6 (Ar*C*), 114.3 (Ar*C*), 113.6 (Ar*C*), 112.4 (Ar*C*), 69.3 (O*C*$H_2$$(CH_2)_{10}CH_3$), 68.8 (O*C*$H_2$$(CH_2)_{10}CH_3$), 31.9 ($CH_3$(*C*$H_2$)$_{11}$O), 29.7 ($CH_3$(*C*$H_2$)$_{11}$O), 29.4 ($CH_3$(*C*$H_2$)$_{11}$O), 29.3 ($CH_3$(*C*$H_2$)$_{11}$O), 26.2 ($CH_3$(*C*$H_2$)$_{11}$O), 26.1 ($CH_3$(*C*$H_2$)$_{11}$O), 22.7 ($CH_3$(*C*$H_2$)$_{11}$O), 14.2 (C$H_3$$(CH_2)_{11}$O); IR (ATR): $\tilde{\nu}$= 3320, 2919, 1230 cm^{-1}; UV/vis (CH_3CN): λ_{max} (ε)= 297 nm (12235 mol^{-1} dm^3 cm^{-1}); fluorescence (CH_3CN): (λ_{em}) = 406 nm; HRMS (ESI): m/z calcd for $C_{38}H_{61}O_3$ 565.4615 [*M*+H^+]; found 565.4615.

(*E*)-4-(4-((4,6-bis(dodecylthio)-1,3,5-triazin-2-yl)oxy)styryl)phenol, **1g**

White solid; Isolated yield: 81% (0.10 mmol, 75 mg from 80 mg of starting material); m.p.: 142-145ºC; ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.51 (d, $^3J_{(H,H)}$= 8.6 Hz, 2H; Ar*H*). 7.42 (d, $^3J_{(H,H)}$= 8.6 Hz, 2H; Ar*H*), 7.14 (d, $^3J_{(H,H)}$= 8.6 Hz, 2H;), 7.04 (d, $^3J_{trans(H,H)}$= 16.3 Hz, 1H; CH=C*H*), 6.96 (d, $^3J_{trans(H,H)}$= 16.3 Hz, 1H; C*H*=CH), 6.85 (d, $^3J_{(H,H)}$= 8.6 Hz, 2H; Ar*H*), 5.02 (s, 1H; O*H*), 3.01 (t, $^3J_{(H,H)}$= 6.7 Hz, 4H; CH_3 $(CH_2)_{10}CH_2S$), 1.64 (m, 4H; $CH_3CH_2(CH_2)_9CH_2S$), 1.25 (broad singlet, 36H; $CH_3(CH_2)_9CH_2CH_2S$), 0.90 (t, $^3J_{(H,H)}$= 6.8 Hz, 6H; C$H_3$$(CH_2)_{11}$S); ^{13}C NMR (91 MHz, $CDCl_3$): δ = 183.3 (Triazine*C*-S$C_{12}H_{25}$) 168.0 (Ar*C*, Triazine*C*-O), 155.5 (Ar*C*, O-*C*), 150.8 (Ar*C*, *C*-OH), 135.4 (*C*-CH=CH), 130.1 (CH=CH-*C*), 128.4 (CH=*C*H), 127.9 (Ar*C*), 127.0 (Ar*C*), 125.5 (*C*H=CH), 121.9 (Ar*C*), 115.7 (Ar*C*), 31.9 (CH_3(*C*H_2)$_{11}$S), 30.5 (CH_3(*C*H_2)$_{11}$S), 29.6 (CH_3(*C*H_2)$_{11}$S), 29.5

($CH_3(CH_2)_{11}S$), 29.4 ($CH_3(CH_2)_{11}S$), 29.2 ($CH_3(CH_2)_{11}S$), 28.8 ($CH_3(CH_2)_{11}S$), 22.7 ($CH_3(CH_2)_{11}S$),14.1 ($CH_3(CH_2)_{11}S$); UV/vis (CH_3CN): λ_{max} (ε)= 285 nm (31220 mol^{-1} dm^3 cm^{-1}); fluorescence emission (CH_3CN): (λ_{em}) = 390 nm; HRMS (ESI): m/z calcd for $C_{41}H_{61}N_3O_2S_2Na$ 714.4103 [M+Na^+]; found 714.4105.

(*E*)-4-(2,5-bis(dodecyloxy)styryl)phenyl (3-(triethoxysilyl) propyl)carbamate, **7a**

White solid; Isolated yield: 92% (0.24 mmol, 199 mg from 150 mg of starting material); m.p.: 117-118ºC; ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.51 ppm (d, $^3J_{(H,H)}$= 8.5 Hz, 2H; Ar*H*); 7.41 (d, $^3J_{trans(H,H)}$= 16.4 Hz, 1H; CH=C*H*), 7.10 (m, 4H; Ar*H* and C*H*=CH), 6.83 (d, $^3J_{(H,H)}$= 8.9 Hz, 1H; Ar*H*), 6.78 (dd, $^3J_{(H,H)}$= 8.5 Hz, $^4J_{(H,H)}$= 1.9 Hz, 1H; Ar*H*), 5.43 (t, $^3J_{(H,H)}$= 6.6 Hz, 1H; N*H*CH_2CH_2), 3.97 (t, $^3J_{(H,H)}$= 6.7 Hz, 4H; $CH_3CH_2(CH_2)_9CH_2O$), 3.87 (q, $^3J_{(H,H)}$= 7.0 Hz, 6H; $Si(OCH_2CH_3)_3$), 3.30 (q, $^3J_{(H,H)}$= 6.6 Hz, 2H; NHCH_2CH_2), 1.78 (m, 6H, $CH_3(CH_2)_9CH_2CH_2O$ and $CH_2CH_2CH_2Si$), 1.50 (m, 4H, $CH_3CH_2(CH_2)_9CH_2O$), 1.27 (m, 41H $CH_3CH_2(CH_2)_8CH_2CH_2O$ and $Si(OCH_2CH_3)_3$), 0.90 (t, $^3J_{(H,H)}$= 6.6 Hz, 6H; $CH_3CH_2(CH_2)_{10}$), 0.71 (t, $^3J_{(H,H)}$= 9.0 Hz, 2H; CH_2Si); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.6 (O=*C*-NH) 153.3 (Ar*C*, *C*-O-C=O), 150.9 (Ar*C*, $C_{12}H_{25}O$-*C*), 150.4 (Ar*C*, $C_{12}H_{25}O$-*C*), 135.1 (Ar*C*), 128.2 (CH=C*H*), 127.5 (Ar*C*), 127.3 (Ar*C*), 123.4 (C*H*=CH), 121.7 (Ar*C*), 114.5 (Ar*C*), 113.8 (Ar*C*), 112.3 (Ar*C*), 69.5 ($OCH_2(CH_2)_{10}CH_3$), 68.6 ($O\mathbf{C}H_2(CH_2)_{10}CH_3$), 68.6 ($OCH_2(CH_2)_{10}CH_3$), 58.5 ($Si(O\mathbf{C}H_2CH_3)_3$), 43.6 ($NHCH_2CH_2$), 31.9 ($CH_3(CH_2)_{11}O$), 29.7 ($CH_3(CH_2)_{11}O$), 29.5 ($CH_3(CH_2)_{11}O$), 29.4 ($CH_3(CH_2)_{11}O$), 26.3 ($CH_3(CH_2)_{11}O$), 26.1 ($CH_3(CH_2)_{11}O$), 23.1 ($CH_2CH_2CH_2Si$), 22.7 ($CH_3(CH_2)_{11}O$), 18.3 ($Si(OCH_2CH_3)_3$), 14.1 ($CH_3(CH_2)_{11}O$), 7.7 ($CH_2Si$); IR (ATR): $\tilde{\nu}$= 3360, 2918, 1752 cm^{-1}; UV/vis (CH_3CN): λ_{max} (ε)= 279 nm (104970 mol^{-1} dm^3 cm^{-1}); fluorescence emission (dte): (λ_{em}) = 408 nm; HRMS (ESI): m/z calcd for $C_{48}H_{81}NO_7SiNa$ 834.5675 [M+Na^+]; found 834.5682.

(*E*)-4-(2,5-bis(((4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)oxy)styryl) phenyl (3-(triethoxysilyl)propyl)carbamate, **7d**

White solid; Isolated yield: 75% (0.08 mmol, 109 mg from 120 mg of starting material); m.p.: 112-114ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.49 (d, $^3J_{(H,H)}$= 8.2 Hz, 2H; Ar*H*). 7.35 (d, $^3J_{trans(H,H)}$= 16.4 Hz, 1H; CH=C*H*), 7.13 (m, 4H; Ar*H* and C*H*=CH), 6.84 (d, $^3J_{(H,H)}$= 8.9 Hz, 1H; Ar*H*), 6.79 (dd, $^3J_{(H,H)}$= 8.8 Hz, $^4J_{(H,H)}$= 2.2 Hz, 1H; Ar*H*), 5.39 (t, $^3J_{(H,H)}$= 5.5 Hz, 1H; N*H*CH_2CH_2), 4.07 (t, $^3J_{(H,H)}$= 5.0 Hz, 4H; $C_8F_{17}(CH_2)_2CH_2O$), 3.87 (t, $^3J_{(H,H)}$= 7.0 Hz, 6H; $O(CH_2CH_3)_3$), 3.31 (q, $^3J_{(H,H)}$= 6.4 Hz, 2H; NHCH_2CH_2), 2.39 (m, 4H; $OCH_2CH_2CH_2$), 2.16 (m, 4H; $OCH_2CH_2CH_2$), 1.74 (m, 2H; $CH_2CH_2CH_2Si$), 1.27 (t, $^3J_{(H,H)}$= 7.0 Hz, 9H;

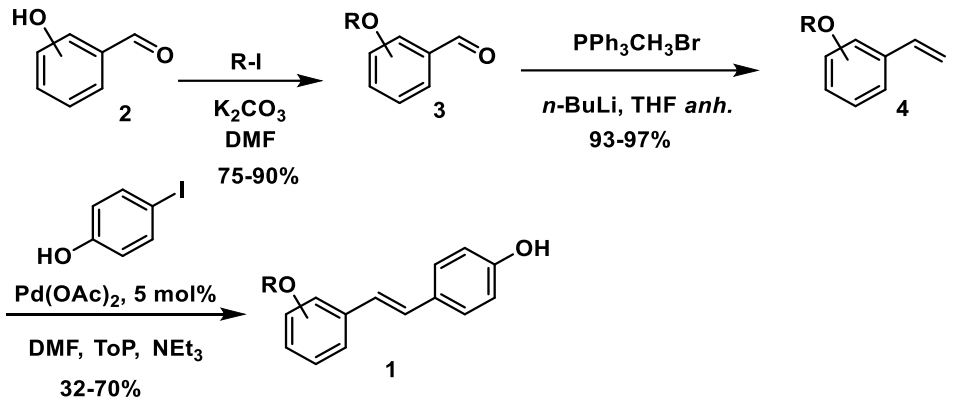
Si(OCH$_2$C*H*$_3$)$_3$), 0.72 (t, $^3J_{(H,H)}$= 8.0 Hz, 2H; C*H*$_2$Si); ^{19}F NMR (376 MHz, CDCl$_3$): δ = -126.7 (m, 2F), -123.9 (m, 2F), -123.2 (m, 2F), -122.3 (m, 6F), -114.7 (t, $^3J_{(F,F)}$= 13.8 Hz, 2F), -81.6 (t, $^3J_{(F,F)}$= 9.9 Hz, 3F; C*F*3); ^{13}C NMR (101 MHz, CDCl$_3$) δ = 154.4 (O=*C*-NH). 152.1 (Ar*C*, *C*-O-C=O), 150.6 (Ar*C*, O-*C*), 150.5 (Ar*C*, O-*C*), 134.6 (Ar*C*), 128.9 (CH=*C*H), 127.8 (Ar*C*), 127.2 (Ar*C*), 122.5 (*C*H=CH), 121.7 (Ar*C*), 114.3 (Ar*C*), 113.8 (Ar*C*), 112.4 (Ar*C*), 67.8 (C$_8$F$_{17}$CH$_2$CH$_2$*C*H$_2$O), 66.9 (C$_8$F$_{17}$CH$_2$CH$_2$*C*H$_2$O), 58.4 (Si(O*C*H$_2$CH$_3$)$_3$), 43.5 (NH*C*H$_2$CH$_2$), 28.0 (t, $^2J_{(C,F)}$ = 22.4 Hz, C$_8$F$_{17}$*C*H$_2$CH$_2$CH$_2$), 28.0 (t, $^2J_{(C,F)}$ = 22.4 Hz, C$_8$F$_{17}$*C*H$_2$CH$_2$CH$_2$), 23.0 (CH$_2$*C*H$_2$CH$_2$Si), 20.7 (m, C$_8$F$_{17}$CH$_2$*C*H$_2$CH$_2$), 20.6 (m, C$_8$F$_{17}$CH$_2$*C*H$_2$CH$_2$), 18.2 (Si(OCH$_2$*C*H$_3$)$_3$), 7.7 (*C*H$_2$Si); IR (ATR): $\tilde{\nu}$= 3336, 2931, 1740 cm^{-1}); UV/vis (CH$_3$CN): λ_{max} (*ε*)= 282 nm (357554 mol^{-1} dm^3 cm^{-1}); fluorescence emission (CH$_3$CN): (λ_{em}) = 412 nm; HRMS (ESI): m/z calcd for C$_{43}$H$_{43}$F$_{34}$NO$_7$SiNa 1418.2158 [*M*+Na$^+$]; found 1418.2156.

(*E*)-4-(2-(((4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)oxy)-5-methoxystyryl)phenyl (3-(triethoxysilyl)propyl)carbamate, **7e**

White solid; Isolated yield: 84% (0.17 mmol, 159 mg from 140 mg of starting material); m.p.: 125-128ºC; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.49 (d, $^3J_{(H,H)}$= 8.5 Hz, 2H; Ar*H*), 7.36 (d, $^3J_{trans(H,H)}$= 16.4 Hz, 1H; CH=C*H*), 7.13 (m, 4H; Ar*H* and C*H*=CH), 6.84 (d, $^3J_{(H,H)}$= 8.9 Hz, 1H; Ar*H*), 6.79 (dd, $^3J_{(H,H)}$= 8.9 Hz, $^4J_{(H,H)}$= 2.8 Hz, 1H; Ar*H*), 5.46 (t, $^3J_{(H,H)}$= 6.6 Hz, 1H; N*H*CH$_2$CH$_2$), 4.06 (t, $^3J_{(H,H)}$= 5.9 Hz, 2H; C$_8$F$_{17}$(CH$_2$)$_2$C*H*$_2$O), 3.87 (m, 9H; OC*H*$_3$ and Si(OC*H*$_2$CH$_3$)$_3$), 3.31 (q, $^3J_{(H,H)}$= 6.6 Hz, 2H; NHC*H*$_2$CH$_2$), 2.39 (m, 2H; OCH$_2$CH$_2$C*H*$_2$), 2.17 (m, 2H; OCH$_2$C*H*$_2$CH$_2$), 1.74 (m, 2H; CH$_2$C*H*$_2$CH$_2$Si), 1.27 (t, $^3J_{(H,H)}$= 7.1 Hz, 9H; Si(OCH$_2$C*H*$_3$)$_3$), 0.72 (t, $^3J_{(H,H)}$= 8.0 Hz, 2H; C*H*$_2$Si); ^{19}F NMR (376 MHz, [D$_6$]CH$_3$COCH$_3$): δ = -126.7 (m, 4F). -123.3 (m, 4F), -122.9 (m, 4F), -121.9 (m, 12F), -114.3 (t, $^3J_{(F,F)}$= 13.8 Hz, 4F), -80.7 (t, 3J (F,F) = 9.9 Hz, 6F); ^{13}C NMR (101 MHz, CDCl$_3$) δ =154.5 (O=*C*-NH), 154.1 (Ar*C*, *C*-O-C=O), 150.6 (Ar*C*, O-*C*),150.2 (Ar*C*, O-*C*), 134.6 (Ar*C*), 128.7 (CH=C*H*), 127.7 (Ar*C*), 127.2 (Ar*C*), 122.7 (C*H*=CH), 121.7 (Ar*C*), 113.9 (Ar*C*), 113.7 (Ar**C**), 111.5 (Ar*C*), 67.8 (C$_8$F$_{17}$CH$_2$CH$_2$*C*H$_2$O), 58.4 (Si(O*C*H$_2$CH$_3$)$_3$), 55.6 (O*C*H$_3$), 43.5 (NH*C*H$_2$CH$_2$), 28.0 (t, $^2J_{(C,F)}$ = 22.4 Hz, C$_8$F$_{17}$*C*H$_2$CH$_2$CH$_2$), 23.0 (CH$_2$*C*H$_2$CH$_2$Si), 20.7 (t, $^3J_{(C,F)}$= 3.5 Hz, C$_8$F$_{17}$CH$_2$*C*H$_2$CH$_2$), 18.2 (Si(OCH$_2$*C*H$_3$)$_3$), 7.7 (*C*H$_2$Si); IR (ATR): $\tilde{\nu}$= 3320, 2978, 1714 cm^{-1}); UV/vis (CH$_3$CN): λ_{max} (*ε*)= 285 nm (50615 mol^{-1} dm^3 cm^{-1}); fluorescence emission (CH$_3$CN): (λ_{em}) = 410 nm; HRMS (ESI): m/z calcd for C$_{36}$H$_{40}$F$_{17}$NO$_7$SiNa 972.2195 [*M*+Na$^+$]; found 972.2180.

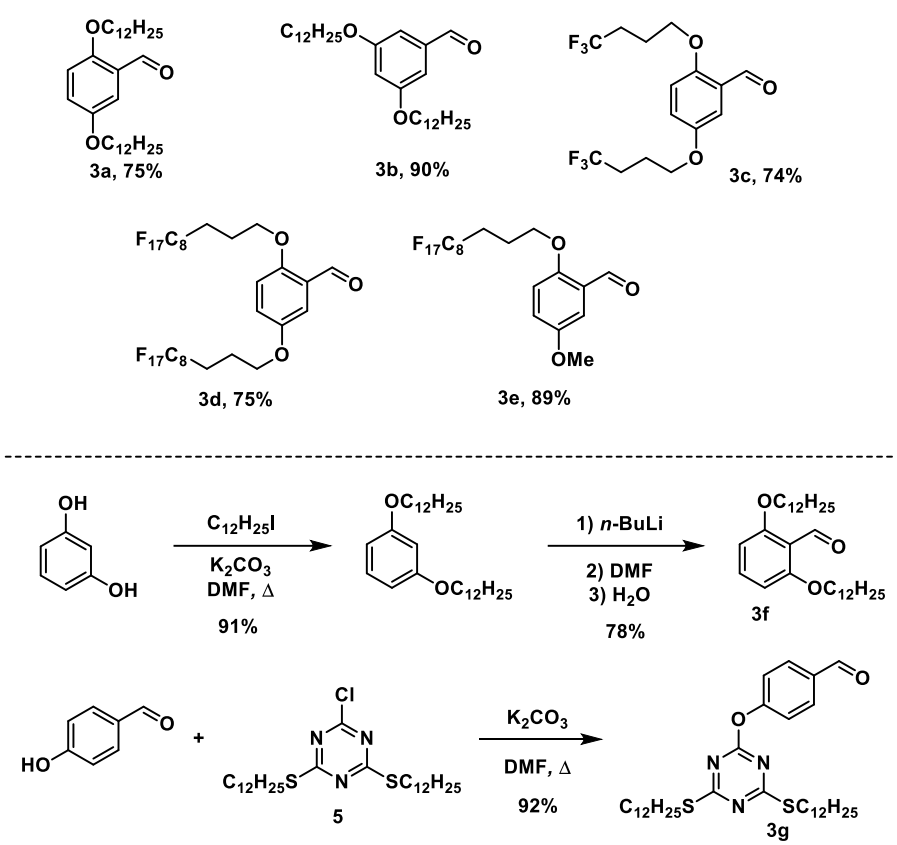
Results and discussion

Our first goal was the synthesis of highly conjugated (*E*)-stilbene derivatives of type **1** possessing fluorinated or hydrocarbonated chains in their structure. At first it seemed that the (*E*)-configuration was a requirement since the Z stereoisomer can photoisomerize as a competitive process under UV light irradiation [21], although there are several reports in which *E* isomer has also been found to photoisomerize [22] Moreover, in the initial design, we took into account that most intensive fluorescence would be obtained with electron donating groups on the aromatic moiety. Thus, O-electron-donor substituents were integrated with the expectation of achieving energetically lower-lying emissive states. We addressed the synthesis [23] from commercial phenolic aldehydes **2** through a first alkylation process, followed by Wittig and Heck reactions (Scheme 1).



Scheme 1. Preparation of target compounds **(*E*)-1**.

First, we selected some commercial phenolic aldehydes **2** (Scheme 1). Alkylation of **2** with different alkyl iodides (3 equiv.) using K_2CO_3 (3 equiv.) as a base in DMF, afforded compounds **3a-d** (Scheme 2) in excellent yields (75-90%). For compound **3e** (89% yield), we added 1.5 equivalents of the alkyl halide. Additionally, **3f** was obtained by the dialkylation of resorcinol followed by a Bouvealt aldehyde synthesis (two steps: 70% yield, Scheme 2). Compound **3d** (Scheme 2) was synthesized though a nucleophilic aromatic substitution of 4-hydroxybenzaldehyde. Another approach to introduce long hydrocarbonated chains on the stilbene moiety was to use 1,3,5-triazine derivative **5** that was prepared as previously described in the group [24].



Scheme 2. Hydroxy-substituted phenolic benzaldehydes **3**.

Secondly, we followed the synthetic route through the Wittig olefination (Scheme 1) [25]. The corresponding hydroxy-substituted phenolic aldehydes **3**, were added to the previous formed methyltriphenylphosphonium ylide [26], yielding the desired styrene derivatives **4** (93-97% yield, Table 1, Fig. 2). At this point, the target stilbene compounds **1** were accomplished by a Heck reaction (Scheme 1) [27, 28]. The hydroxy-substituted styrenes **4** were mixed with 4-iodophenol, $Pd(OAc)_2$ as catalyst (5 mol%) in the presence of tri-o-tolylphosphine, and triethylamine as base in DMF [29]. The consumption of the starting material was complete in all cases, with high yields, but the reaction was not completely steroselective to the (*E*)-stereoisomer (Table 1), giving Z/E mixtures. In most of the cases, stereoisomer (*E*) was isolated though a silica gel column chromatography, affording the pure (*E*)-stilbene derivatives in moderate to good yields (32-70%, Table 1). Nevertheless, the **(*E*)-1f** could not be successfully isolated (Table 1, entry 6). The main reason for the non-(*E*)-selectivity is attributed to a C-C bond rotation previous to the *syn*-elimination step.

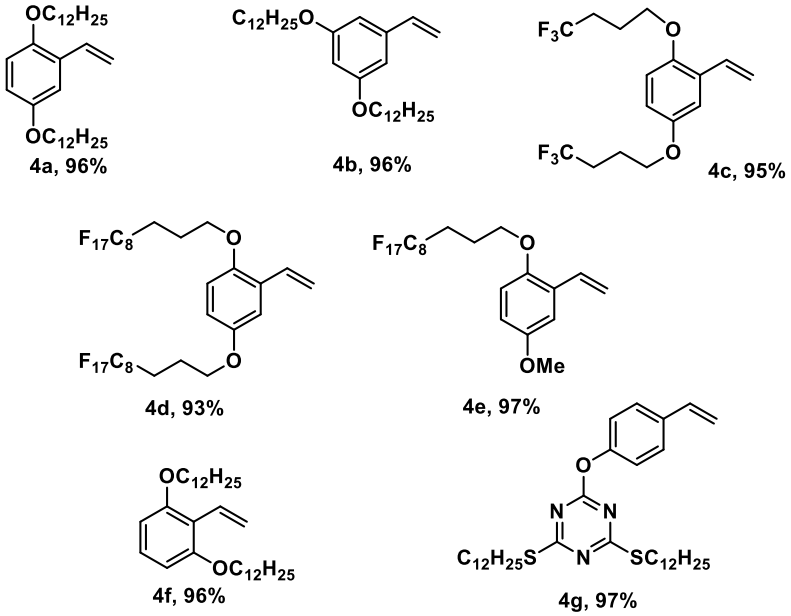


Figure 2. Structures of compounds **4**.

Table 1. Results of reactions of Scheme 1and fluorescent properties of stilbene derivatives **(*E*)-1**

Entry	Wittig Step yield %	Heck Step *Z/E*	Heck Step **(*E*)-1** yield %	Emission[a] **(*E*)-1** λ_{max} (nm)	ϕ^{b} **(*E*)-1**
1	**4a** 96%	35/65	**1a** 60%	405	0.36
2	**4b** 96%	38/62	**1b** 61%	392	0.29
3	**4c** 95%	25/75	**1c** 70%	405	0.15
4	**4d** 93%	30/70	**1d** Mixture	407	0.38
5	**4e** 97%	30/70	**1e** 32%	408	0.12

6	**4f** 96%	31/69	**1f** 42%	406	0.22
7	**4g** 97%	40/60	**1g** 57%	390	0.25

[a]Fluorescence maximum measured in acetonitrile under 280 nm wavelength irradiation. [b]Fluorescent quantum yields were measured relative to ϕ = 0.023 for *trans*-stilbene in acetonitrile (Roberts and Pincock 2006).

The fluorescence properties of the prepared (*E*)-stilbene derivatives **1a-g** were determined in acetonitrile, since this solvent does not absorb in the studied range. Solutions of concentrations of the order of 10^{-8} M in acetonitrile were used. The fluorimetry spectra of compounds **1** are shown in Fig. 3. The fluorimetry experiments of all isolated **(*Z*)-1** isomers (except **1d**, see Table 1) were performed presenting no fluorescence in the visible area. According to the results, (*E*)-stilbenes **1b** and **1g** (entry 2 and 7 of Table 1) do not emit fluorescence in the visible range. If we compare the structure of these two with the set of stilbenes, it seems necessary the presence of a donor alkoxide group in *ortho* position with respect to the double bond. However, placing two alkoxides in the *ortho* positions does not cause the fluorescence emission to take place at a longer wavelength (**3f**, entry 6). Different alkoxides (**1a**, **1c** and **1d**) do not provide significant differences in terms of the maximum emission of fluorescence (Table 1, Fig. 3) which is in consonance with a basically resonance effect. The fluorescent quantum yields (Table 1) of **(*E*)-1a** (ϕ = 0.36) and **(*E*)-1d** (ϕ = 0.38) in acetonitrile were the biggest in the series and larger than that of *trans*-stilbene (ϕ = 0.023) [30]. This is excellent for our purposes, mainly because both compounds possess long hydrophobic chains.

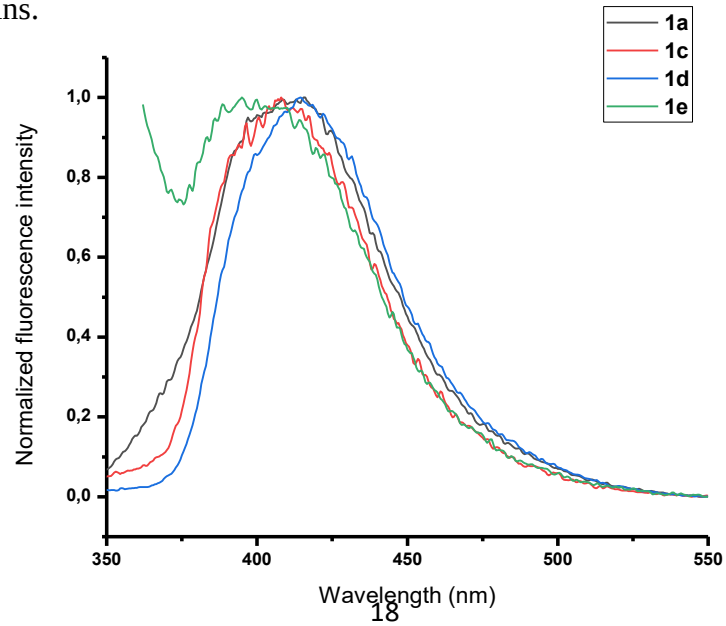
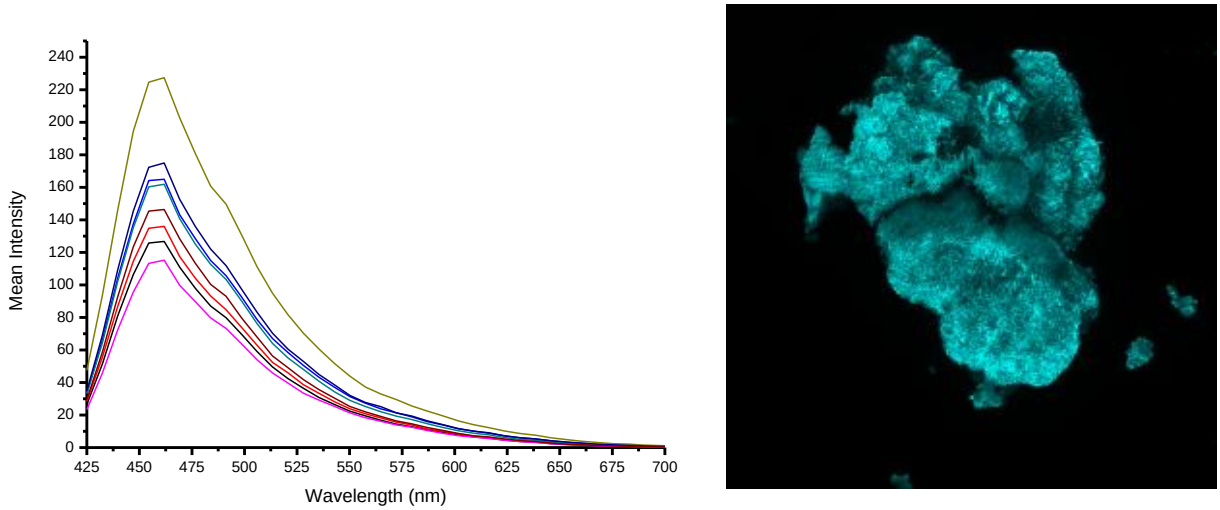


Figure 3. Fluorescence emission spectra of **(*E*)-1** (10^{-8} M in acetonitrile) under 280 nm wavelength irradiation.

For our final application in security papers, compounds **1** should emit fluorescence in solid state. Thus, a confocal fluorescence microscopy was used to obtain a true 3D optical resolution image of the stilbene **(*E*)-1** derivatives in solid state. We selected **1a** and **1d** as representative of the series. The excitation of the fluorophores caused a detectable fluorescence as shown in images of Fig. 4. The fluorescence emission graphics show the uniformity of both samples (**1a** and **1d**).



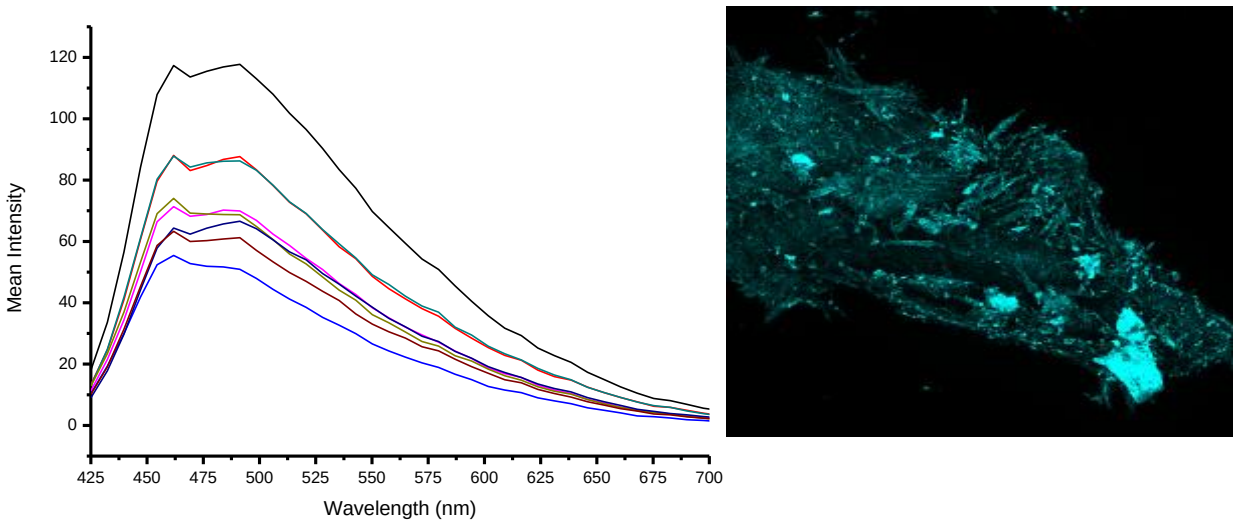
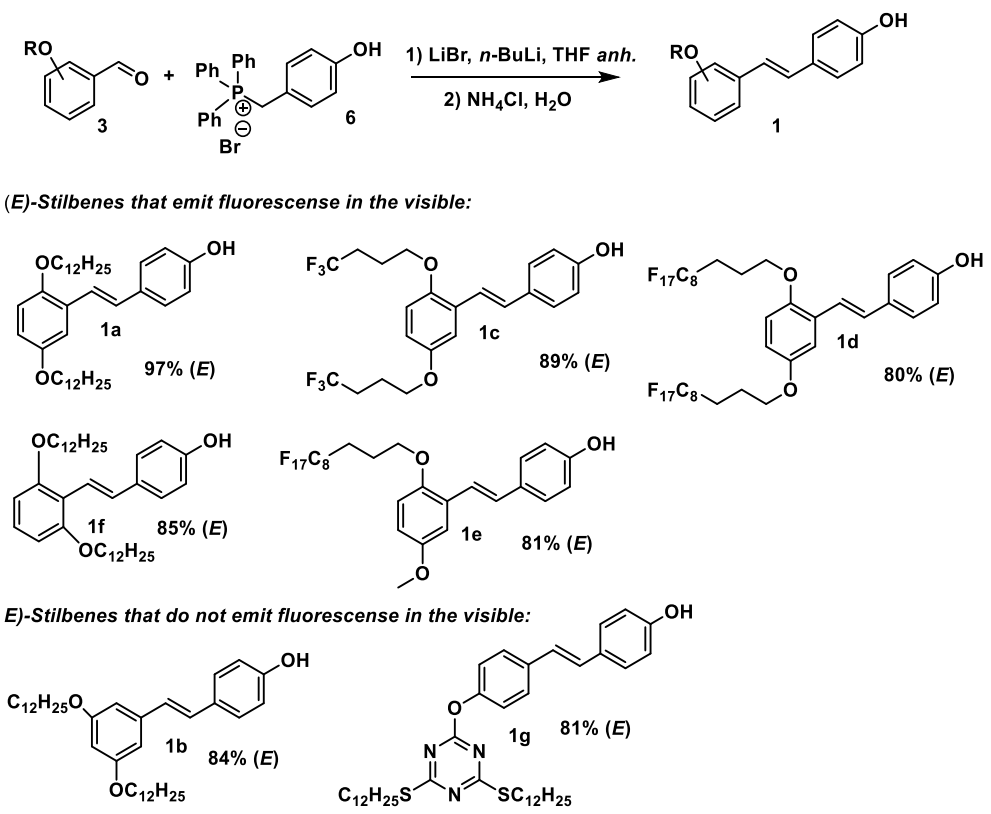


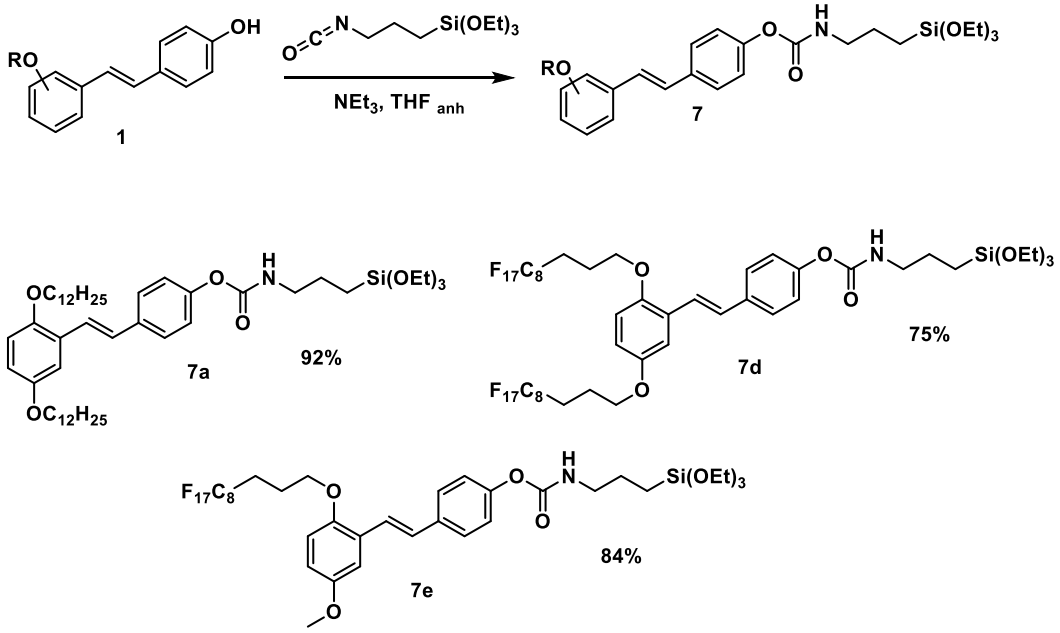
Figure 4. Confocal fluorescence microscopy images and fluorescence emission spectra of solid **1a** (top row) and solid **1d** (bottom row). Note each color on the graph corresponds to the excitation of a different area of the solid.

In view of the results, we decided to address the improvement of the synthesis of pure **(*E*)-1** derivatives. The alternative selected was a Wittig-Schlosser olefination reaction [31-33] following previously reported conditions by the group of Denmark [34]. The substituted aldehydes **3** reacted with the phosphonium salt **6** in the presence of LiBr (2 equiv.) and a large excess of *n*-BuLi (10 equiv.). Nucleophilic addition reaction of triphenylphosphine hydrobromide and 4-hydroxybenzyl alcohol in acetonitrile (18h) accomplished **6** in quantitative yield. Using an excess of lithium bromide and an alkyl litiated base, an equilibration of the lithiobetaines intermediates is obtained, resulting in all the studied cases (**1a-g**) in the exclusive formation of (*E*)-stereoisomer. Other Wittig-type reactions using milder conditions in water have already been reported [35, 36] however, these protocols were not effective due low solubility of compounds **3** in water medium. Therefore, the Schlosser modification of the Wittig reaction has permitted to stereoselectively afford (*E*)-stilbenes **1a-g** in excellent yields (80-98%) and in a really straightforward manner. Only (*E*)-stilbenes that emit fluorescence in the visible range **1a**, **1c**, **1d**, **1f** and **1e** were useful for our purposes. Compounds belonging to the stilbene family have indeed gained remarkable significance in pharmaceutical as well as material science, thus the synthetic approach described in this work can be extremely useful for the stereoselective synthesis of (*E*)-stilbene scaffold and related structures.



Scheme 3. Wittig-Schlosser reaction conditions applied to the selective synthesis of **(*E*)-1a,g**.

Next, we selected –Si(OEt)$_3$ as the reactive group to covalently anchor the label molecule to the paper.[7] Compounds ***(E)-1*** showing best fluorescent properties were selected to be anchored. The addition of the reactive group onto the 4-hydroxy-(*E*)-stilbenes, **1**, was carried out using 3-(triethoxysilyl)propyl isocyanate in anhydrous THF and in the presence of dry triethylamine as a base. The reactive carbamates **7** were achieved successfully in excellent yields (75-92%, Scheme 4).



Scheme 4. Synthesis of the reactive fluorescent carbamates **7a**, **7d** and **7e.**

Afterwards, we proceeded to study the hydrophobic and the oleophobic properties of compounds **7**. Firstly, they were deposited on a glass surface using the spin-coating technique (addition of 0.15 mL of a 1,9 10^{-3} M solution in THF, Table 2). Measurement of the contact angle was performed by the addition of a drop of water on the previous modified surfaces. In all the studied cases (**7a**, **7d** and **7e**) the contact angle was approximately the same (115-119º) indicating high hydrophobicity. Compound **7d**, possessing two long perfluorinated chains, is the only one that has oleophobic capacity. Thus, a drop of hexadecane deposited on the surface of a glass previously impregnated by a solution of **7d**, presents a contact angle of 95º. In consequence, we assume that fluorophore **7d** is the best candidate to obtain durable self-cleaning print on safety paper.

Table 2. Measured contact angles of a drop of different solvents (4 µL) on a modified glass surface previously coated with **7** (addition of 0.15 mL of a 1,9.10^{-3} M solution in THF). Maximum fluorescence emission and quantum yields of **7**.

Entry	Compound	Water[a]	Hexadecane[a]	Emission λmax (nm)	ϕ
1	**7a**	120	0	408	0.34
2	**7d**	115	95	410	0.42
3	**7e**	119	0	412	0.18

[a]Average of three measurements. [b]Fluorescence maximum measured in acetonitrile under 280 nm wavelength irradiation. [c]Fluorescent quantum yields were measured relative to ϕ = 0.023 for *trans*-stilbene (Niembro et al. 2008).

Additionally, we studied the fluorescence properties of carbamates **7**. The fluorimetry spectra showed λmax emissions over 400 nm in the visible area (Table 2). Interestingly enough, **7a** and **7d** possessing long hydrophobic chains had larger fluorescent quantum yields than **7e** (Table 2) and in consequence were selected to be anchored on paper. Fluorous **7d** presented the largest value (Table 2, ϕ = 0.42). The fluorescence of this modified dyes **7a** and **7d** was also studied in the solid state using the confocal microscopy. The measurements evidenced well fluorescence homogeneity in both fluorophores structure. The maximun fluorescence emision was at 450 nm in case of **7a** and 455 nm in case of **7d** (Fig. 5).

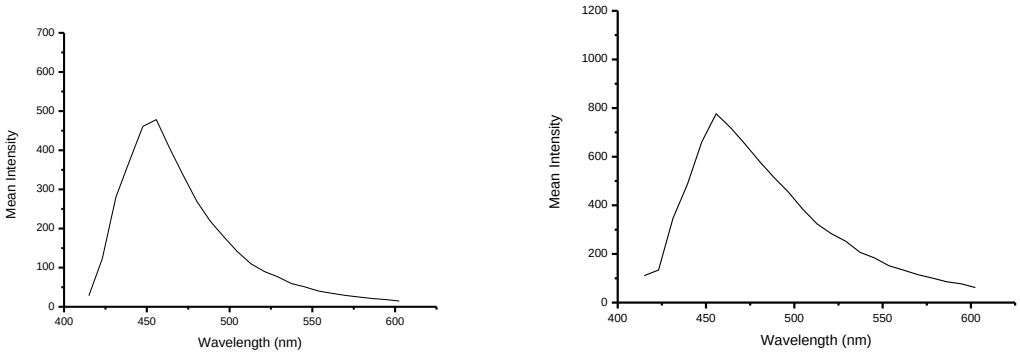


Figure 5. Fluorescence emission spectra of solid **7a** (left graphic) and solid **7d** (right graphic).

Then, we took pieces of commercial WhatmanTM Grade 1 filter paper. The anchoring of compounds **7** on the paper was carried out in a screw-top sealed tube, by shacking vigorously a piece of round filter paper (diameter of 2.5 cm) in a solution of 23 mg of the corresponding (*E*)-stilbene based reactive carbamate (**7a** or **7d**) in anhydrous THF and triethylamine. After three days the reaction was over, and the modified paper was washed with further THF and ethanol. Afterwards, the modified paper (Fig. 6) was well dried in a vacuum oven overnight. Scanning electron microscope (SEM, see SI) was used to evaluate the anchorage of the reactive molecules **7** onto the paper surface. The most important difference observed was that the unmodified paper presented thinner fibers than the modified. Furthermore, the energy dispersive analysis (EDS, see SI) and the X-ray photoelectron spectroscopy (XPS, Fig. 7) studies of modified paper **7d**, confirmed the presence of this highly fluorinated dye (34 F atoms) onto the paper surface due to the presence of fluorine atoms in the performed analysis. The XPS spectrum shows not only the binding energy of F1s state for an organic fluorine (688 eV) but also the binding energy of C1s corresponding to the CF_2 chemical state (292 eV). Hydrophobic and oleophobic properties of modified papers could not be evaluated due to their intrinsic absorption properties. Finally, the final proof that the (*E*)-stilbene based reactive carbamates **7a** and **7d** were anchorage to the paper surfaces, as schematically shown in Fig. 6, was that upon simple UV irradiation both papers exhibited an intense bluish coloration.

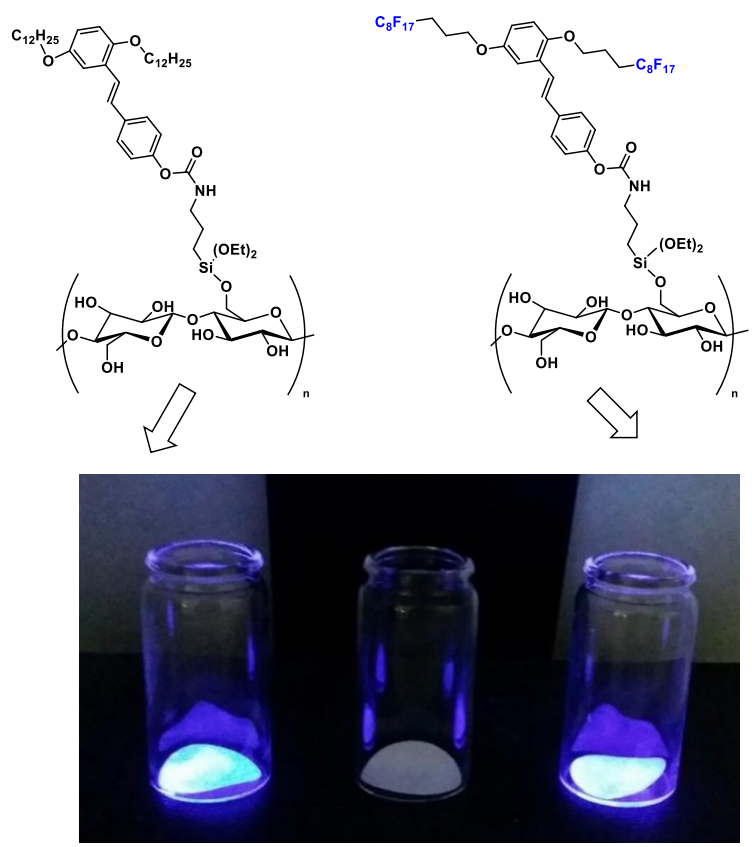


Figure 6. Schematic representation of covalently modified paper with carbamates **7a** (left image) and **7d** (right image). Photograph: UV irradiation of modified and unmodified filter papers images. Left: paper modified with **7a**. Center: unmodified paper. Right: paper modified with **7d**.

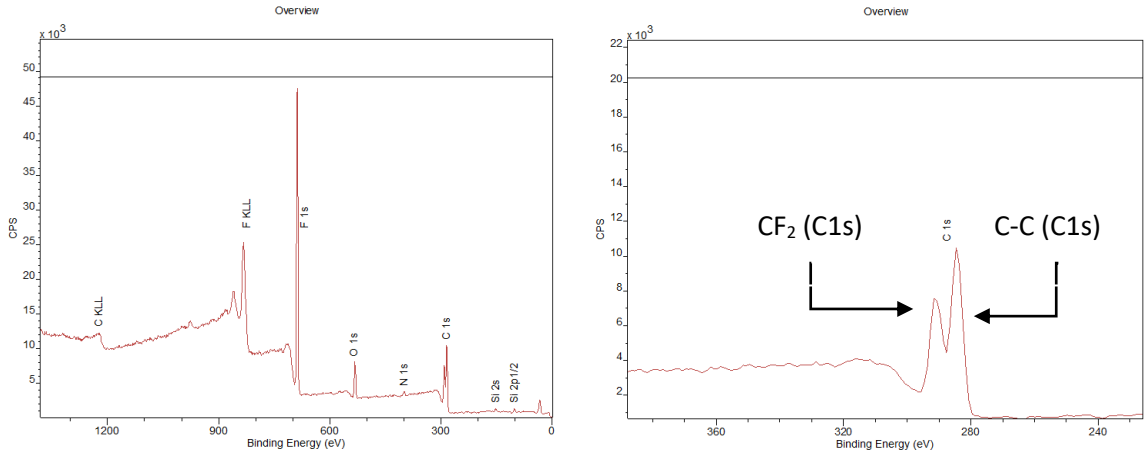


Figure 7. X-ray photoelectron spectroscopy (XPS) spectra of modified paper **7d**

The fluorescence spectroscopy in the modified papers was measured in confocal microscopy. In both modified papers the fluorescence emission was evidenced, observing a maximum at

480 nm (see SI) indicating the possibility for the application to security paper. Moreover, the stability of the fluorescent unit-linker was studied by an immersion test of the modified paper with 7f in water. No leaching of the fluorophore was observed after 5 minutes (control by GCS, see SI) and the fluorescent emission rested identical (Fig. 8). Furthermore, the color-fastness of the modified paper with **7d** was tested measuring the fluorescence in confocal microscopy after eight months of the dyeing process without any special protection; the results indicate excellent color stability which is important for industrial applications (see SI). We appreciate the same wavelength maximum, the same shape of the wave and only a slight loss of intensity (3%)".

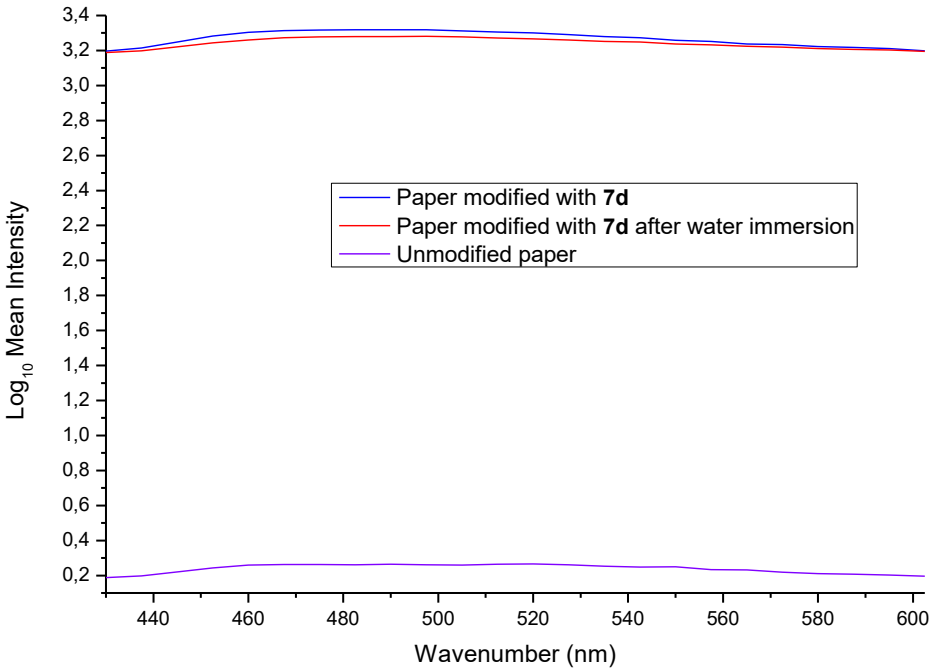


Figure 8. Fluorescence emission spectra of paper and modified papers with **7d** prior and after water immersion.

3. Conclusions

In summary, new fluorescent hydrophobic (*E*)-stilbene derivatives have been prepared through a stereoselective and highly effective Wittig–Schlosser reaction as a key step. The

covalent link of these reactive fluorescent compounds has resulted in new labeled papers with potential applications in the so-called safety papers. Fluorous **7d** was the best in terms of fluorescent quantum yield value and self-cleaning properties. After an immersion test no leaching of the fluorophore was observed and the fluorescent emission of the modified paper with **7d** rested identical.

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Captions

Figure 1. Example of azo based dyes anchored on a cotton surface (previous work) and structure design for fluorescent-labeled paper.

Scheme 1. Preparation of target compounds **(*E*)-1**.

Scheme 2. Hydroxy-substituted phenolic benzaldehydes **3**.

Figure 2. Structures of compounds **4**.

Figure 3. Fluorescence emission spectra of **(*E*)-1** (10^{-8} M in acetonitrile) under 280 nm wavelength irradiation.

Figure 4. Confocal fluorescence microscopy images and fluorescence emission spectra of solid **1a** (top row) and solid **1d** (bottom row). Note each color on the graph corresponds to the excitation of a different area of the solid.

Scheme 3. Wittig-Schlosser reaction conditions applied to the selective synthesis of **(*E*)-1a,g**.

Scheme 4. Synthesis of the reactive fluorescent carbamates **7a**, **7d** and **7e.**

Figure 5. Fluorescence emission spectra of solid **7a** (left graphic) and solid **7d** (right graphic).

Figure 6. Schematic representation of covalently modified paper with carbamates **7a** (left image) and **7d** (right image). Photograph: UV irradiation of modified and unmodified filter papers images. Left: paper modified with **7a**. Center: unmodified paper. Right: paper modified with **7d**.

Figure 7. XPS spectrum of modified paper **7d** (left image). Expansion of C1s zone (right image).

Figure 8. Fluorescence emission spectra of paper and modified papers with **7d** prior and after water immersion.