Functional Molecules for Grafting onto Ionic Surfaces

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Adeline R. Pujol[a, b], Sonia Bataillé[a] and André Gourdon*[a]

Abstract: 2D adsorption of molecules on insulating surfaces is of increasing interest for future devices in emerging technologies like molecular electronics, sensors, single molecule optics, on-surface synthesis. On these substrates, however, most attempts to stabilize molecular structures have been hampered by the weak molecule-surface interactions so that there is a need to develop organic molecules bearing suitable grafting groups. Here we report the syntheses of a series of molecules designed to physisorb on alkali halide crystalline surfaces. They comprise a rigid central benzene or triphenylene core bearing two, respectively six, alkyl ether chains ended by various anchoring groups: cyano, carboxylic, α-aminoacid and 1,2,3 triazole.

Introduction

The adsorption and diffusion of organic molecules on inorganic surfaces has recently appeared as of particular importance for several fields of interest such as molecular electronics, sensors, organic photocatalysts. This exploration has now been rendered possible thanks to the recent rapid development of atomic force microscopy in the non-contact (or frequency modulation) mode,[1] but so far little is known on the detailed adsorption mechanisms, the balance between molecule-substrate and molecule-surface and so on. The main problem in this field remains that the molecules-surfaces interactions are in general weak, often weaker than intermolecular interactions, leading to desorption, or to diffusion and 3D growth instead of 2D supramolecular assembly. In the last few years, many studies have focused on alkali halide surfaces as models for the study of organic-inorganic heteroepitaxy (OIHE)[2] since these surfaces are stable and easy to prepare in ultra-high vacuum conditions (UHV), and despite the fact that the molecules-surfaces interactions are in general very weak. Consequently, there is a general need to investigate these interactions at the atomic scale in order to be able to design criteria and to tailor molecules adsorbing strongly on dielectric surfaces like KBr, KCl or NaCl. One solution we have been exploring in the recent years is to conceive and synthesize molecules comprising aromatic or polyaromatic rigid cores equipped with several flexible chains ending with anchoring groups in local interaction with the surface ions. So far groups possessing a large dipole moment (such as cyano) have been shown to adsorb rather effectively but the number of functions still has to be considerably extended in order to optimize these interactions and master the OIHE on this type of substrates.

We introduce here the preparation of two series of molecules designed for NC-AFM experiments on alkali halide surfaces. The molecules comprise a rigid central benzene or triphenylene core, bearing two, respectively six, alkyl ether chains ended by various anchoring groups: cyano, carboxylic, α–aminoacids and 1,2,3 triazoles (Fig 1)

Results and discussion

Cyano derivatives

The cyano group is so far the grafting group the most used in this type of experiments, for several reasons like the ease of preparation and the thermal stability of molecules comprising this functional group which allows sublimation required for transfer on surfaces in UHV. The exploration of the adsorption and diffusion properties of syn-5,10,15-tris-(cyanophenylmethyl) truxene on KBr(001) nanostructured surface has shown that molecules were diffusing along the monolayer step edges and immobilized at kink sites.[3] An extensive DFT simulation has demonstrated that the control of anchoring and diffusion was depending on the number of anchoring groups acting independently, which requires a flexibility of the anchoring branch to allow the individual groups to bind to specific sites of the surface. The adsorption of rigid mono and dicyano pentahelicenes on Suzuki (001) surface[4] has confirmed that a perfect match between the distances of the substituents and the cations distances was a requirement and that the cyano groups were in in a perpendicular position on top of the surface cations, allowing a compensation of the net dipole. With these parameters in mind, we have designed a series of dicyano/hexacyano functionalized molecules for studies on NaCl(001) and KBr(001) surfaces. The synthesis is a one-step Williamson etherification of hydroquinone/catechol/HHTP and 5-bromovaleronitrile in mild conditions (K_2CO_3 in dry DMF) according to scheme 1 and scheme 2.

The hexacyanopropyloxytriphenylene **2** can also be obtained in low yield by Scholl condensation of **11** by reaction with $MoCl_5$ in cold dichloromethane (Scheme 3).

Although the condensation of 1,2 substituted catechol by oxidative coupling is a standard route to many hexyloxytriphenylene,[5] it is often limited to poorly reactive substituted chains. Several oxidizing groups have been used such as $FeCl_3$,[6],[7] $VOCl_3$,[8] $MoCl_5$.[9],[10] Waldvogel et al. have shown that it was possible to cyclotrimerize 1,3-benzodioxole substituted in 2,2 positions by chains bearing reactive groups such as esters using this later reagent[10],[11],[12] and we have used similar conditions to prepare **2** by this route.

We have studied the adsorption of **2** on KBr(001) surfaces by NC-AFM coupled to Kelvin probe force microscopy (KPFM) in ultra-high vacuum at room temperature.[13] Two types of monolayers were identified, one in which the molecules lies flat on the surface and another in which they stand approximately upright. In the flat lying adsorption geometry, the molecule-surface interaction is dominated by the electrostatic interaction of the cyano group with the K^+ cations leading to total adsorption energy of 1.8 eV. In the vertical geometry, the molecules form π-stacks rows aligned along the polar direction of the surface. Only two of the cyano groups

can interact with the surface cations, contributing to approximately 0.4 eV to the adsorption energy and the stabilization (total adsorption energy ca: 2.5 eV) is gained by this intermolecular interaction.

These results suggest that the dipolar moment of the nitrile group may not be high enough, which prompted us to explore the preparation of the analogous carboxylic derivative **4**.

Carboxylic derivatives

The 2,3,6,7,10,11-hexa(4-(butanoic acid)-oxy)triphenylene **4** can be obtained as a gel by reaction of HHTP with 4-methyl bromobutanoate in basic medium to give the hexamethyl ester **12** in 30% yield, a procedure similar to Bibal et al.[14] for the synthesis of water soluble hosts. **12** is then hydrolysed by aqueous sodium hydroxide in 70% yield. (Scheme 4). Attempts to prepare **4** by condensation of 4,4'-(1,2-phenylenebis(oxy))dibutanoic ester[15] were unsuccessful.

α-Amino acids derivative

A third grafting group that can be envisioned is α–amino alkyl acid. In particular, in their zwitterionic forms, these functions could show high electrostatic interactions with the local partial charges of surfaces of dielectric such as alkali halides, provided that there is commensurability between the local surface charges and the zwitterions local charges. Similar hypotheses have been used by Loppacher et al in the study of the self-organization of the zwitterion 4-methoxy-4'-(3-sulfanatopropyl)stilbazolium on KCl(001).[16] In this compound the sulfonato end-group, which carries a negative charge is linked via an alkyl-chain to the pyridinium ring carrying a positive charge and the distance between the opposite charges in the trans isomer is of ca 1nm. A first rapid evaluation shows that, in α-amino acids, the carboxylate-ammonium distance (ca 2.8 Å) matches the sodium-chloride distance in NaCl(001) (2.82 Å). This observation led us to design the compounds **3** and **7**, bearing 2-aminobutanoic chains.

The hydroquinone/pyrocatechol and HHTP α-amino acids derivatives were obtained by reaction with methyl 2-[(tert-butoxycarbonyl)-amino-4-bromobutanoate in anhydrous DMF in the presence of potassium carbonate. Its preparation requires the synthesis of 2-amino-4-bromobutanoic acid which can be efficiently and rapidly be obtained in quantitative yield by microwave irradiation in HBr/AcOH in 45 mn instead of longer standard heating (4h, 75°C).[17] It must be underlined that this ring opening is reversible in water and we have shown by NMR that half of the 2-amino-4-bromobutanoic acid returned to the lactone after 90 min in D_2O at RT. The amine and carboxylic functions are then protected to give the methyl 2-[(tert-butoxycarbonyl)-amino-4-bromobutanoate by standard procedures.[18],[19]

HHTP-α-aminoacid derivative was obtained similarly by Williamson etherification in DMF to give the protected aminoacid **14**, which is then deprotected in two steps to give **7** as a dark gel in 26% yield (two steps from **14**) (scheme 6).

Attempts to apply Scholl condensation to the catechol derivative according to scheme 7 were unsuccessful leading only to a decomposition of the starting catechol derivative **15**.

1,2,3-Triazole derivatives

The hydroquinone derivatives **5** and **6** where obtained by CuAAC reactions from the true alkynes **16** and **17** respectively as shown in scheme 8.

17 itself was obtained in two steps by condensation of (6-bromohex-1-yn-1-yl)triisopropylsilane with hydroquinone, and then deprotection of the alkyne by TBAF (total yield: 70%).

Similarly, the 1,2,3 triazoles bearing a H atom in position 1 were obtained by reaction of **16** and **17** with methylpivalate azide in standard CuAAC conditions. The pivalate protection is then removed by basic treatment giving **8** and **9** in 90% and 85% yield respectively. Both compounds are very insoluble.

The HHTP hexa-substituted analogue **21** is obtained by Williamson etherification with (6-bromohex-1-yn-1-yl)triisopropylsilane followed by standard TIPS deprotection by TBAF. This route was preferred to the recently published procedure by Stackhouse and Hird[20] where **21** is obtained by condensation of HHTP with unprotected 6-chlorohex-1-yne in a better yield (66%) but a significantly longer reaction time (9 days).

From **21**, the target compound **10** is obtained in 50% yield following the CuAAC procedure developed for hydroquinone analogues (scheme 10). This compound is very similar to the recently described triazole HHTP derivative prepared by Bhalla et al[21] which shows very interesting gel-to-sol phase transition selectively controlled by interaction with Cd^{2+} ions and can work as an efficient and sensitive fluorescent sensor for nitroaromatic explosives.

Attempts to prepare **10** analogues by a convergent approach following the scheme 11 below has been so far unsuccessful probably due to the fragility of the intermediate **22** towards Lewis acids required for Scholl condensation.

Conclusions

To sum up, a series of molecules designed for experiments on alkali halide surfaces has been synthesized by functionalizing hydroquinone and hexahydroxytriphenylene with alky chains ended with cyano, carboxylic acid, triazole or amino acid groups. Scholl condensations of pyrocatechol derivatives to form the triphenylene core turned out to be unsuccessful.

Figures and schemes

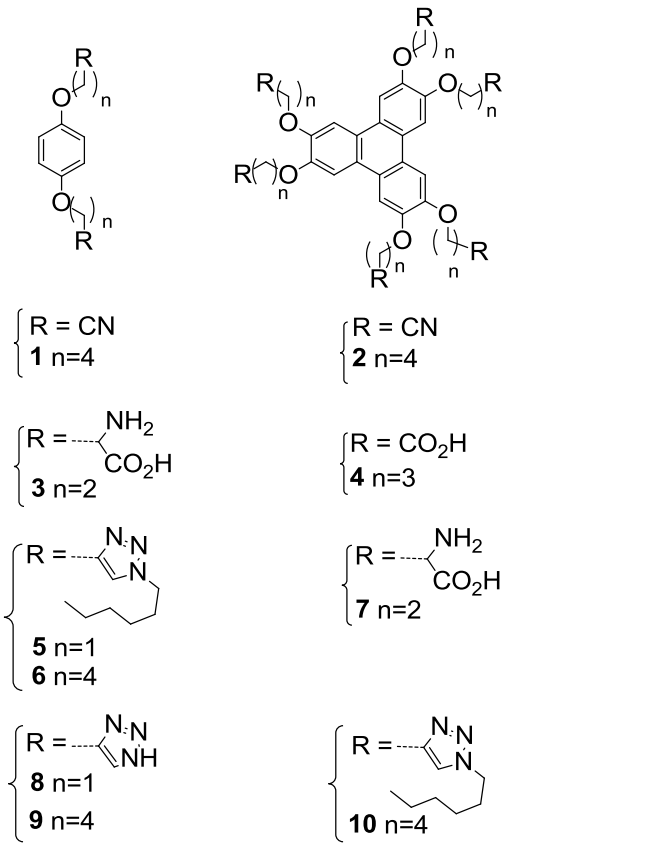
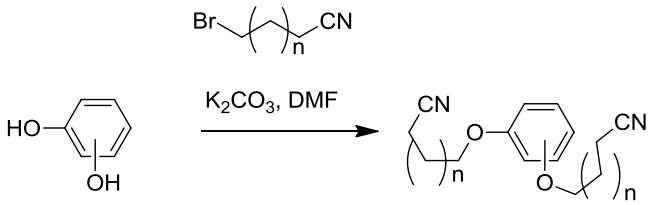
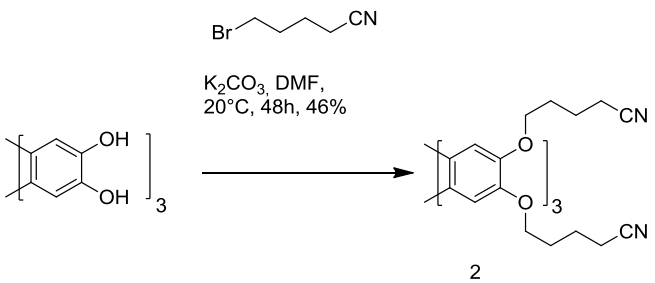


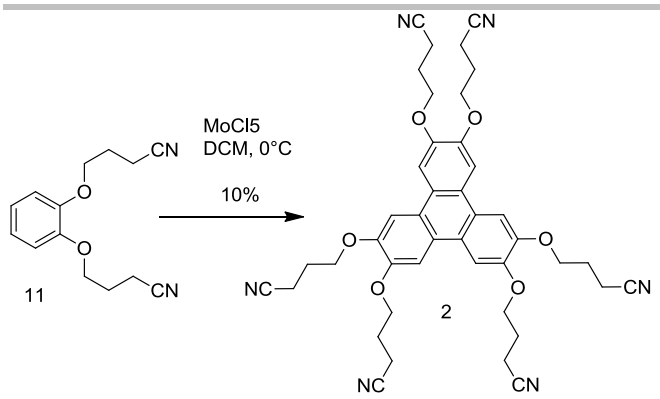
Figure 1. Hydroquinone and hexahydroxytriphenylene derivatives designed for physisorption on alkali halides surfaces.



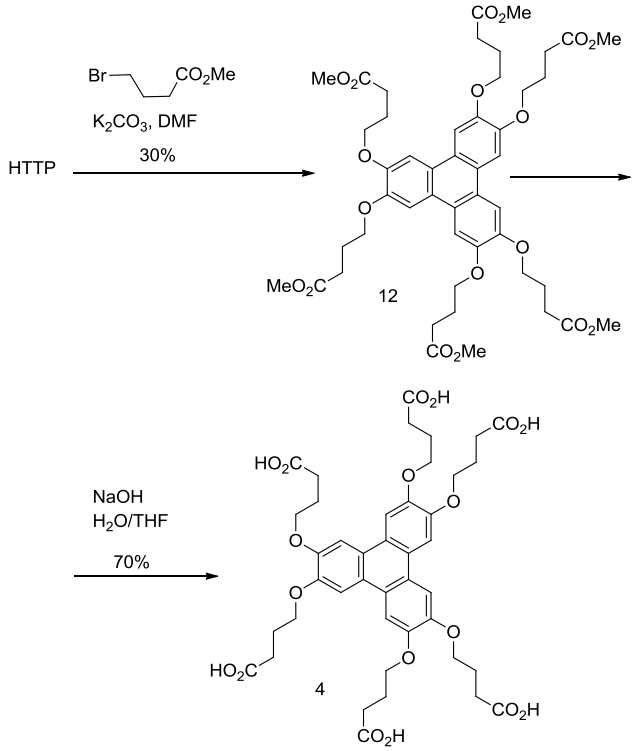
*Scheme 1. Preparation of **1** (isomer 1,4; n=2 - yield 50%) and of **11** (isomer 1,2; n=1 - yield 71%).*



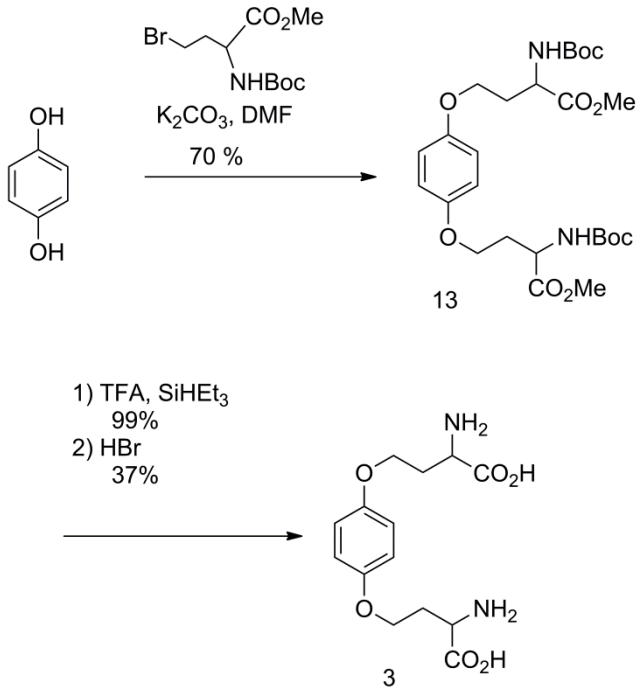
*Scheme 2: Synthesis of **2** from HHTP*



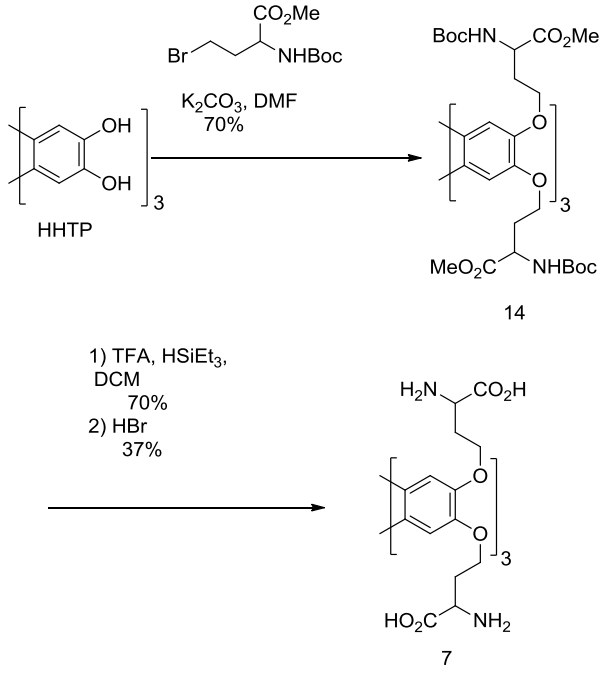
*Scheme 3: Scholl condensation of **11** to give the HHTP derivative **2**.*



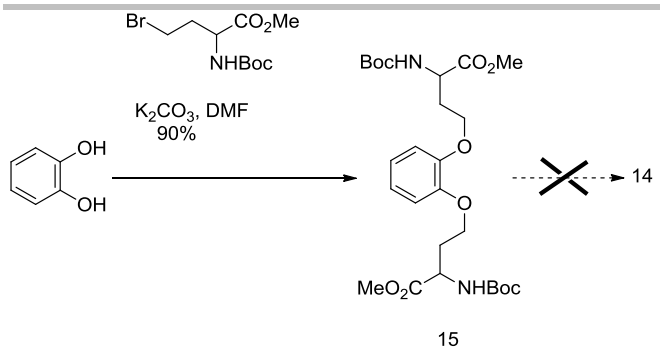
*Scheme 4. Preparation of **4**.*



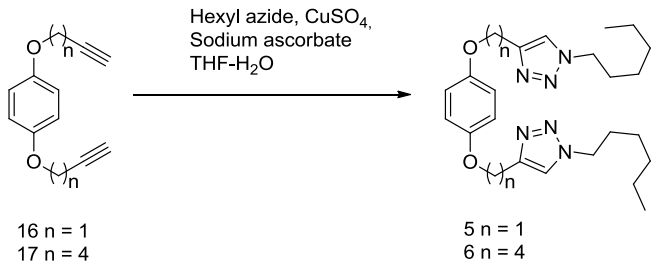
*Scheme 5. Synthesis of **3**.*



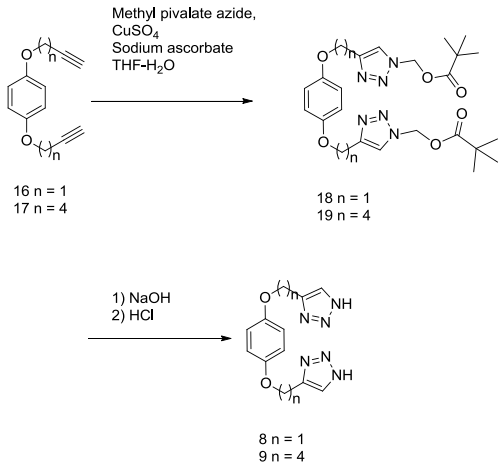
*Scheme 6. Three steps synthesis of **7**.*



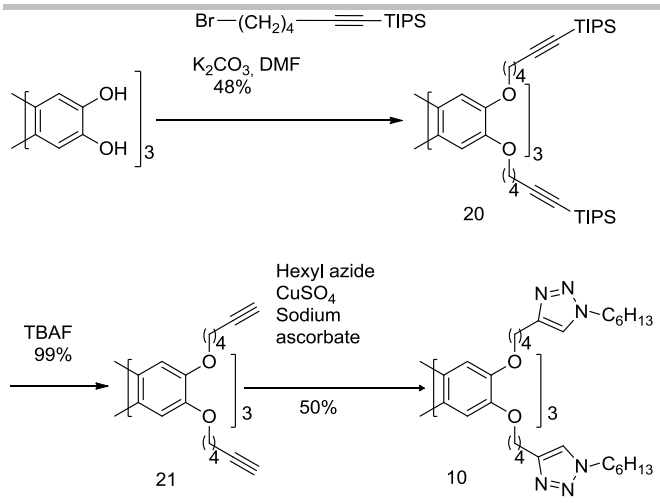
*Scheme 7. Attempted synthesis of **14** by Scholl condensations.*



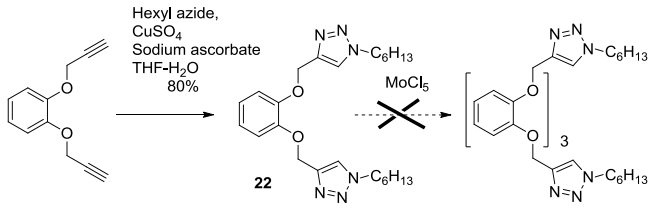
*Scheme 8 Preparation of **5** and **6** from **16** and **17**, respectively.*



*Scheme 9. Preparation of **8** and **9** (total yields, respectively from **16**: 56%, from **17**: 36%*



*Scheme 10. Preparation of **10** from HHTP.*



*Scheme 11. Attempted trimerization via Scholl condensation of **22**.*

Experimental Section

General experimental methods

Dry DMF was from Acros Organics or Sigma Aldrich. THF was distilled on sodium/benzophenone. Other solvents were dried over molecular sieves prior to use. Flash column chromatography was performed by using silica gel (60 Å pore size, 40-63 µm Merck). The reactions were monitored by thin layer chromatography (TLC) on silica gel-coated plates (Merck 60 F_{254}). Detection was performed by using UV light and by charring the plate at ca. 200°C, after dipping it in an ethanolic solution of potassium permanganate. The yields refer to chromatographically and spectroscopically (^{1}H-NMR and ^{13}C-NMR) homogeneous materials, unless otherwise stated. The NMR spectroscopic data were recorded with Bruker Avance 300/400/500 MHz instruments and were calibrated by using the residual undeuterated solvent as an internal reference ($CDCl_3$ at δ_H = 7.26 ppm, δ_C = 77.16 ppm, CD_2Cl_2 at δ_H= 5.33 ppm, δ_C = 53.84 ppm). Chemical shifts are reported in parts per million (ppm) on the δ scale and coupling constants (J) are in Hertz (Hz). The abbreviations used to describe the multiplicities are s= singlet, bs= broad singlet d= doublet, t= triplet= dd= doublet of doublets, q= quintuplet, m= multiplet. Mass spectra were recorded at the Service Commune de Spectrometrie de Masse of University Paul Sabatier (Toulouse 3), Toulouse (France). Elemental analyses were done by the Service d'Analyse de l'ICSN (Paris, France). Microwave heating was carried out in closed vials with a CEM-Discovery monomode microwave apparatus under the specified conditions (power, temperature, time).

1,2-bis(prop-2-ynyloxy)benzene,[22] methyl 2-amino-4-bromobutanoate bromide,[18] methyl 2-[(tert-butoxycarbonyl)-amino-4-bromobutanoate,[19] hexyl azide,[23] methyl pivalate azide, [24] 6-(bromo-hex-1-ynyl)-triisopropylsilane,[25] were obtained according to published procedures. HHTP[26] was obtained from hexamethoxytriphenylene (HMTP) [27], and synthetized by literature procedures. When required, HHTP was purified before use using the following procedure: 198 mg of partially oxidized HHTP are added to 30 mL of warm (75 °C), degassed distilled water. After 5 min stirring under argon, 250 mg of sodium hydrosulfite are added. Then the mixture is filtered under argon as soon as the mixture passes from violet to clear grey. The beige solid is then washed with water, and dried under vacuum at 40°C. Nearly quantitative yield.

Caution should be exercised when using azides. Both organic and inorganic azides can be heat- and shock-sensitive and can explosively decompose.

1,4-Bis(cyanobutoxy)benzene (1): 500 mg of hydroquinone (4.5 mmol, 1 eq) and 6 equivalents of potassium carbonate (4.53 g, 27.9 mmol) are added to 10 mL of anhydrous DMF. Argon is then bubbled (2mL) and 2 equivalents of 5-bromovaleronitrile (1.12 mL, 9.7 mmol) are added and the mixture is stirred 16 h at 60°C under argon. After cooling to RT, water (20 mL) and DCM (20 mL) are added and the mixture is extracted with 3 x 20 mL of DCM. The grouped organic phases are dried over $MgSO_4$. After distillation of solvents, column chromatography (SiO_2: DCM/AcOEt (0 to 10%)) gave **1** as white crystals in 50% yield. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 6.82 (s, 4H, H_{aro}); 3.94 (t, ^{3}J = 6 Hz, 4H, CH_2—O); 2.43 (t, ^{3}J = 7 Hz, 4H, CH_2—CN); 1.95-1.78 (m, 8H, CH_2). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 153.4 (Cq_{aro}); 120.0 ($Cq_{nitrile}$); 115.7 (CH_{aro}); 67.7 (CH_2—O); 28.7 (CH_2); 22.8 (CH_2); 17.3

($\underline{CH_2}CN$). MS (DCI, NH_3): m/z = 290.2 ($[M+ NH_4]^+$, calcd.: 290.2). HRMS (DCI, CH_4): m/z = 273.1591 ($[M+H]^+$ for $C_{16}H_{21}N_2O_2$, calcd.: 273.1603). Anal. For $C_{16}H_{20}N_2O_2$: calcd.: C 70.56; H 7.40; N 10.29 ; found: C 68.30 ; H 7.41 ; N 9.97.

2,3,6,7,10,11-Hexa(cyanopropoxy)triphenylene (2) from HHTP: In 11 mL of anhydrous DMF are added potassium carbonate (1.93 g, 13.9 mmol, 25 eq) and 4-bromobutyronitrile (0.39 mL, 3.9 mmol, 7 eq) and the mixture is degased by argon bubbling for 2 min., followed by addition of HHTP (180 mg, 0.55 mmol, 1 eq). After stirring at RT under argon for 48h, the mixture is poured in water (110 mL). Neutralization by a 5M solution of sulfuric acid gave a precipitate which is filtered, washed with water and dried. Recrystallization in ethyl acetate gave **2** as a grey powder in 46% yield. Rf = 0.5 (TLC, DCM/AcOEt, 7:3). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.91 (s, 6H, H_d); 4.37 (t, ^{3}J = 6 Hz, 12H, H_c); 2.71 (t, ^{3}J = 7 Hz, 12H, H_a); 2.27 (m, ^{3}J = 7 Hz, 12H, H_b). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 148.9 (Cq_{aro}); 124.2 ($Cq_{nitrile}$); 107.9 (CH_{aro}); 67.6 (CH_2—O); 26.0 (CH_2); 14.7 (CH_2). HRMS (DCI, CH_4): m/z = 727.3275 ($[M+H]^+$ for $C_{42}H_{43}N_6O_6$, calcd. 727.3244).

1,2-Bis(cyanopropoxy)benzene (11): In 20 mL of anhydrous DMF are added 913 mg of catechol (8.3 mmol, 1 eq) and 4.2 equivalents of potassium carbonate (4.762 g, 34.5 mmol). After 2 min of argon bubbling, 1.8 mL of 4-bromobutyronitrile are added and the mixture is stirred under argon at 80°C for 16h. After cooling to RT, water (3 mL) and DCM (30 mL) are added and the organic phase is extracted with DCM (3 x 20 mL), washed with water (20 mL) and dried over $MgSO_4$. Filtration and distillation of solvents lefts a residue which is chromatographed on silica gel using hexane/DCM (80 to 100%) as eluent. **11** is obtained as white crystals in 71% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.93 (s, 4H, H_d); 4.11 (t, ^{3}J = 6 Hz, 4H, H_c); 2.63 (t, ^{3}J = 7 Hz, 4H, H_a); 2.16 (m, 4H, H_b). MS (ESI): m/z = 245.1 ($[M+ H]^+$, calcd.: 245.1).

2,3,6,7,10,11-Hexa(cyanopropoxy)triphenylene (2) from (11): A degassed solution at 0 °C of 270 mg of **11** (1, 11 mmol, 1 eq) in 3.4 mL of anhydrous DCM is rapidly added under argon to a solution of $MoCl_5$ (1.046 g, 3.83 mmol, 3.45 eq) in 34 mL of anhydrous DCM The mixture is stirred under argon at 2 °C for 2 h. Then, 60 mL of saturated aqueous $NaHCO_3$ and 60 mL of AcOEt are added. The organic phase is extracted with ethyl acetate (3 x 20 mL) and dried over $MgSO_4$. After distillation of solvents, the residue is column chromatographed (SiO_2: DCM/AcOEt; 7:3) giving **2** as a gel in 10% yield. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.91 (s, 6H); 4.36 (t, J = 6 Hz, 12H); 2.71 (t, J = 7 Hz, 12H); 2.27 (m, 12H). MS (ESI): m/z = 727.3 ($[M+ H]^+$, calcd.: 727.3).

2,3,6,7,10,11-Hexa(butoxycarbonylmethoxy)triphenylene (12): 2.54 g of cesium carbonate (7.8 mmol, 10 eq) and 0.9 mL of 4-methyl bromobutanoate (7.1 mmol, 9 eq) are added to 8 mL of anhydrous DMF. After 2 min argon bubbling, 253 mg of HHTP (0.8 mmol, 1 eq) are added and the mixture is stirred under argon at RT for 24h. Then 18 mL of water are added to the mixture which is then filtered. The gel is then washed with water and dissolved in DCM. The organic phase is then extracted with DCM (3 x 10 mL), dried over $MgSO_4$ and filtrated. **12** is obtained as a gel in 30% yield. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.91 (s, 6H, H_d); 4.30 (t, ^{3}J = 6 Hz, 12H, H_c); 3.70 (s, 18H, H_e); 2,64 (t, ^{3}J = 7 Hz, 12H, H_a); 2.22 (m, 12H, H_b). ^{13}C NMR (300 MHz, CD_2Cl_2): δ 173.9 (Cq_{ester}); 149.1 (Cq_{aro}); 123.9 (Cq_{aro}); 107.5 (CH_{aro}); 68.6 (CH_2—O); 51.8 (CH_3); 30.7 (CH_2-$_{ester}$); 25.1 (CH_{2int}). MS (DCI, NH_3): m/z = 942.0 ($[M+NH_4]^+$, calcd. 942.4). Anal. For $C_{42}H_{60}O_{18}$: calcd.: C 62.33; H 6.54; found.:C 62.23 ; H 6.50.

2,3,6,7,10,11-Hexa(4-(butanoic acid)-oxy)triphenylene (4): To a solution of **12** (250 mg) in 2 mL of a 3:1 mixture of THF and water THF/H_2O (3:1), is added 2 mL of aqueous sodium hydroxide (C = 1.3 mol.L^{-1}) and the mixture is stirred for 16h at room temperature. Solvents are then evaporated and the residue is dissolved in water (2 mL). Dropwise addition of 1M HCl down to pH=1 gives a precipitate which is filtered and dried under vacuum. **4** is obtained as a white powder with a yield of 70%. ^{1}H NMR (500 MHz, MeOD/H_2O): δ 7.91 (s, 6H, H_d); 4.28 (t, ^{3}J = 6 Hz, 12H, H_c); 2.62 (t, ^{3}J = 7 Hz, 12H, H_a); 2.20 (qt, 12H, H_b). ^{13}C NMR (125 MHz, MeOD/H_2O): δ 178.0 (Cq_{COOH}); 149.9 (Cq_{aro}); 124.9 (Cq_{aro}); 108.1 (CH_{aro}); 69.5 (CH_2—O); 31.9 (CH_2); 26.1 (CH_2). MS (DCI, NH_3): m/z = 839.9 ($[M-H]^+$, calcd. 839.3). Anal. for $C_{42}H_{48}O_{18}$:calcd.: C 59.99; H 5.75; found.: C 57.77 ; H 5.78.

1,4-Bis(4-(methyl-2-(tert-butoxycarbonyl)aminobutanoate)oxy)-benzene (13): 638 mg of potassium carbonate (4.62 mmol, 5.6 eq) and 609 mg of methyl 2-[(tert-butoxycarbonyl)-amino-4-bromobutanoate (2.06 mmol, 2.5 eq) are mixed in 5 mL of anhydrous DMF. The mixture is purged by argon bubbling; then 90 mg of hydroquinone (0.82 mmol, 1 eq) are added to the mixture which is stirred at 60°C for 16h. After cooling to RT, 20 mL of water are added and the organic phase is extracted with 4*20 mL of DCM, washed with brine (15 mL) and water (15 mL). The grouped organic phases are dried over $MgSO_4$. After distillation of solvents under vacuum, the residue is chromatographied (SiO_2 : Hex-AcOEt (0 to 30%). **13** is obtained as a white powder with a yield of 70%. Rf = 0.2 (TLC, Hex – AcOEt, 7 :3). ^{1}H NMR (300 MHz, $CDCl_3$) : δ 6.77 (s, 4H, H_a); 5.32 (m, 2H, H_f); 4.47 (m, 2H, H_d); 3.97 (t, ^{3}J= 6 Hz, 4H, H_b) ; 3.74 (s, 6H, H_e); 2.35-2.11 (m, 4H, H_c); 1.42 (s, 18H, H_g). ^{13}C NMR (75 MHz, $CDCl_3$) : δ 172.8 (Cq_{ester}) ; 155.4 (Cq_{amide}); 153.0 (Cq_{aro}); 115.6 (H_{aro}); 80.1 (Cq_{tBu}); 64.9 (CH_2-O); 52.5 (CH_3); 51.4 (CH); 31.9 (CH_2); 28.4 (CH_3 / tBu). MS (ESI) : m/z = 558.5 ($[M+H]^+$, calcd.558.3). HRMS (DCI, CH_4): m/z = 563.2585 ($[M+Na]^+$ for $C_{26}H_{40}O_{10}N_2Na$, calcd. 563.2581), m/z = 579.2324 ($[M+K]^+$ for $C_{26}H_{40}O_{10}N_2K$, calcd. 579.2320). Anal. for $C_{26}H_{40}O_{10}N_2$: calcd. : C 57.76 ; H 7.46 ; N 5.18 ; found : C 57.65 ; H 7.50 ; N 5.02.

1,4-Bis(4-(methyl-2-amino-butanoate)oxy)benzene*:* 290 mg of **13** (537 mmol, 1 eq) are dissolved in a mixture of triethylsilane (150 µL) and of DCM (1.35 mL). The solution is cooled to 0°C and 1.5 mL of TFA are added. The stirring is maintained at 0°C for 15 min, then at RT for 1h. After distillation of solvents, the residue is recrystallized in EtOH-Et_2O. 1,4-bis(4-(methyl-2-amino-butanoate)oxy)benzene is obtained as a white solid (yield: 99%). ^{1}H NMR (300 MHz, MeOD) : δ 6.90 (s, 4H, H_{aro}); 4.27 (t, *J*= 6 Hz ,2H); 4.12 (m, 4H) ; 3.84 (s, 6H, CH_3); 2.43-2.34 (m, 4H). ^{13}C NMR (75 MHz, MeOD) : δ 170.8 (Cq_{ester}) ; 154.2 (Cq_{aro}); 116.6 (H_{aro}) ; 65.2 (CH_2-O); 53.7 (CH_3); 51.9 (CH); 31.3 (CH_2). MS (ESI) : m/z = 341.0 ($[M+H]^+$, calcd. 341.2). HRMS (DCI, CH_4): m/z = 341.1707 ($[M+H]^+$ for $C_{16}H_{25}O_6N_2$, calcd. 341.1713). Anal. for $C_{16}H_{24}O_6N_2.2(C_2HF_3O_2)$: calcd. : C, 42.26; H, 4.61; N, 4.93 ; found : C 42.14 ; H 4.58 ; N 4.58.

1,4-Bis(3-amino(4-butanoic acid)oxy)benzene (3): 1,4-bis(4-(methyl-2-amino-butanoate)oxy)benzene (345 mg, 0.61 mmol) is dissolved in 2 mL an aqueous solution of HBr (48%) and the mixture is refluxed for 4h. After cooling to RT, the solvents are evaporated and the residue is recrystallized in water. **3** is obtained as a white solid with a yield of 37%. ^{1}H NMR (500 MHz, D_2O/MeOD) : δ 6.97 (s, 4H, H_{aro}); 4.21 (m, 6H); 2.49-2.35 (m, 4H). ^{13}C NMR (125 MHz, D_2O/MeOD) : δ 172.9 (Cq_{acid}) ; 153.5 (Cq_{aro}); 116.8 (H_{aro}) ; 65.8 (CH_2-O); 52.5 (CH); 30.5 (CH_2). MS (ESI) : m/z = 313.4 ($[M+H]^+$, calcd. 313.1). HRMS (DCI, CH_4): m/z = 313.1400 ($[M+H]^+$ for $C_{14}H_{21}O_6N_2$, calcd. 313.1400). Anal. for $C_{14}H_{20}O_6N_2$. $2(C_2HF_3O_2)$: calcd. : C, 40.01; H, 4.10; N, 5.18 ; found : C 40.73 ; H 5.56 ; N 6.46.

1,2-Bis(4-(methyl-2-(tert-butoxycarbonyl)amino-butanoate)oxy)-benzene (15): 578 mg of potassium carbonate (4.12 mmol, 5 eq) and 718 mg of **3** (2.43 mmol, 2.9 eq) are mixed in 8.5 mL of anhydrous DMF. The mixture is purged by argon bubbling for 2 min. Then catechol (92 mg, 0.84 mmol, 1 eq) is added to the mixture which is stirred at 60°C for 16h.After cooling to RT, water is added (15 mL) and the organic phase is extracted with 3*15 mL of DCM and washed with water (2*10 mL). The organic phases are dried over $MgSO_4$. After distillation of solvents, the residue is purified by column

chromatography (SiO_2 : Hex-AcOEt (0 to 30%) giving **15** as a colorless oil (yield: 90%). Rf = 0.2 (TLC, Hex – AcOEt, 7 :3). ^{1}H NMR (300 MHz, CD_2Cl_2) : δ 6.90 (s, 4H, H_a); 6.10-5.60 (large, 2H); 4.56-4.28 (large, 2H); 4.20-3.98 (m, 4H, H_b) ; 3.71 (s, 6H, H_d); 2.44-2.12 (m, 4H, H_c); 1.42 (2*s, 18H, H_e). ^{13}C NMR (75 MHz, CD_2Cl_2) : δ 173.0 (Cq_{ester}) ; 155.8 (Cq); 148.8 (Cq); 121.8 (H_{aro}); 114.2 (H_{aro}); 79.9 (Cq_{tBu}); 66.3 (CH_2-O); 66.1 (CH_2-O); 52.5 (CH_3); 52.0 (CH); 31.9 (CH_2); 28.4 (CH_3). MS (DCI, NH_3) : m/z = 541.0 ($[M+H]^+$, calcd. 541.3). HRMS (DCI, CH_4): m/z = 563.2582 ($[M+Na]^+$ for $C_{26}H_{40}O_{10}N_2Na$, calcd. 563.2581); m/z = 579.2316 ($[M+K]^+$ for $C_{26}H_{40}O_{10}N_2K$, calcd. 579.2320). Anal. for $C_{26}H_{40}O_{10}N_2$: calcd. : C 57.76 ; H 7.46 ; N 5.18 ; found : C 55.69 ; H 7.06 ; N 4.72.

2,3,6,7,10,11-Hexa(4-(methyl-2-(tert-butoxycarbonyl)aminobutanoate)oxy)-triphenylene (14): A large excess of potassium carbonate (1.816 g, 13.3 mmol, 21 eq) and of methyl 2-[(tert-butoxycarbonyl)-amino-4-bromobutanoate (1.240 g, 4.20 mmol, 6.7 eq) are mixed in 10 mL of anhydrous DMF. The mixture is degassed by argon purging for 2 mn, and then 204 mg of HHTP (0.63 mmol, 1 eq) are added, and the mixture is stirred under argon at 60°C for 42 h. After cooling to RT, 30 mL of water are added and the organic phase is extracted with DCM (3x30 mL) and washed with water (2 x 15 mL). The grouped organic phases are the dried over $MgSO_4$. After solvent removal, the raw product is purified by silica gel chromatography using DCM/AcOEt (0 to 30%) as eluent. **14** is obtained as a white solid (yield: 70%). Rf = 0.5-0.6 (CCM, DCM/AcOEt, 7 :3). ^{1}H NMR (300 MHz, CD_2Cl_2) : δ 7.88 (s, 6H, H_a); 6.26-5.70 (large, 6H); 4.60 (m, 6H); 4.50-4.26 (m, 12H, H_b) ; 3.74 (s, 18H, H_d); 2.58-2.28 (m, 12H, H_c); 1.42 (2*s, 54H, H_e). ^{13}C NMR (75 MHz, CD_2Cl_2) : δ 173.1 (Cq_{ester}) ; 155.9 (Cq); 148.8 (Cq); 124.0 (Cq); 107.4 (H_{aro}); 80.0 (Cq_{tBu}); 66.5 (CH_2-O); 52.3 (CH_3); 52.1 (CH); 32.0 (CH_2); 28.4 (CH_3). MS (ESI) : m/z = 1637.8 ($[M+Na]^+$, Calcd 1637.7). HRMS (DCI, CH_4): m/z = 1637.7524 ($[M+Na]^+$ for $C_{78}H_{114}N_6O_{30}Na$, Calcd 1637.7477). Anal. for $C_{78}H_{114}N_6O_{30}$: Calcd : C 57.98; H 7.11; N 5.20 ; Found : C 55.79 ; H 6.86 ; N 5.09 .

2,3,6,7,10,11-Hexa(4-(methyl-2-amino-butanoate)oxy)triphenylene: *(***14)** (286 mg, 0.18 mmol, 1 eq) is dissolved in a mixture of triethylsilane (200 µL) and DCM (3.90 mL). The mixture is then cooled down to 0°C and 1.95 mL of TFA are added. After 15 min stirring at 0°C, and then 1h at RT, solvents are evaporated. The solid residue is then recrystallized in a mixture EtOH-Et_2O to give 2,3,6,7,10,11-hexa(4-(methyl-2-amino-butanoate)oxy)triphenylene as a gel (yield: 70%). ^{1}H NMR (300 MHz, MeOD) : δ 8.09 (s, 6H, H_{aro}); 4.93 (large ,12H); 4.58 (m, 12H) ; 4.49 (t, ^{3}J = 6 Hz, 6H) ; 3.87 (s, 9H, CH_3); 3.85 (s, 9H, CH_3); 2.71-2.51 (m, 12H, CH_2). ^{13}C NMR (75 MHz, MeOD) : δ 170,8 (Cq_{ester}) ; 163.1 (q, $^2J_{C-F}$ = 30 Hz); 149.0 (Cq_{aro}); 125.3 (Cq_{aro}) ; 118.2 (q, $^1J_{C-F}$ = 300 Hz); 107.9 (H_{aro}) ; 66.5 (CH_2-O); 53.9 (CH_3); 52.4 (CH); 31.1 (CH_2). NMR ^{19}F (MeOD) : detection d'un signal. MS (ESI) : m/z = 1015.3 ($[M+H]^+$, Calcd 1015.5). Anal. for $C_{60}H_{72}F_{18}N_6O_{30}$: Calcd : C 42.41; H 4.27; N 4.95; Found : C 41.14 ; H 4.21 ; N 4.73.

2,3,6,7,10,11-Hexa(3-amino(4-butanoic acid)oxy)triphenylene (7): 2,3,6,7,10,11-hexa(4-(methyl-2-amino-butanoate)oxy)triphenylene (108 mg, 0.064 mmol) is dissolved in 2 mL a 48% aqueous solution of HBr. The mixture is refluxed for 4h. After cooling and evaporation of solvents, **7** is obtained as a black gel with a 37% yield. Purification by HPLC. ^{1}H NMR (300 MHz, D_2O) : δ 7.37 (s, 6H, H_{aro}); 4.37-4.13 (m, 18H); 2.59-2.40 (m, 12H). ^{13}C NMR (125 MHz, D_2O/MeOD) : δ 173.8 (Cq_{acid}) ; 147.8 (Cq_{aro}); 123.9 (Cq_{aro}) ; 106.5 (H_{aro}) ; 66.4 (CH_2-O); 53.1 (CH); 30.5 (CH_2). MS (ESI) : m/z = 931.5 ($[M+H]^+$, Calcd 931.4).

1,4-Bis[6-(triisopropylsilyl)-hex-5-ynyloxy]-benzene*:* Argon is bubbled for 2 min in a mixture of potassium carbonate (608 mg, 4.4 mmol, 6.8 eq) and 442 mg of (6-bromohex-1-yn-1-yl)triisopropylsilane (1.4 mmol, 2.2 eq) in 5 mL of anhydrous DMF. Then 71 mg of hydroquinone (0.65 mmol, 1 eq) are added and the mixture is stirred at 60°C for 16 h under argon. After cooling to RT, 15 mL of water and 15 mL of DCM are added and the organic phase is extracted with DCM (2 x 20 mL) and washed with water (20 mL). The grouped organic phases are then dried over $MgSO_4$. After distillation of solvents, the residue is chromatographed on SiO_2, with a mixture hexane/AcOEt (0 to 5%) as eluent, yielding 1,4-bis[6-(triisopropylsilyl)-hex-5-ynyloxy]-benzene as a white powder in 70% yield. Rf = 0.5 (TLC, Hex – AcOEt, 95:5). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 6.81 (s, 4H, H_e); 3.93 (t, ^{3}J = 6 Hz, 4H, H_d); 2.33 (t, ^{3}J = 7 Hz, 4H, H_a); 1.89 (m, 4H, H_c); 1.70 (m, 4H, H_b); 1.07 (m, 42H, H_f). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 153.6 (Cq_{aro}); 115.7 (CH_{aro}); 109.2 (Cq); 80.8 (Cq); 68.4 (CH_2-O); 28.9 (CH_2); 26.0 (CH_2); 20.0 (CH_2); 18.9 ($CH_{3\ TIPS}$); 11.7 (CH_{TIPS}). MS (DCI, NH_3): m/z = 600.3 ($[M+NH_4]^+$, calcd. 600.5). Anal. for $C_{36}H_{62}O_2Si_2$: calcd.: C 74.16; H 10.72; found: C 73.02 ; H 10.87.

1,4-Bis(hex-5-ynyloxy)benzene (17): 0.6 ml of TBAF (2.07 mmol, 11 eq) are added to a solution of 1,4-bis[6-(triisopropylsilyl)-hex-5-ynyloxy]-benzene (106 mg, 0.18 mmol, 1 eq) in 4 mL anhydrous THF. The mixture is stirred at RT for 4h, and then a saturated NH_4Cl (4 mL) aqueous solution is added. The organic phase is extracted with DCM (3 x 4 mL), washed with water (4 mL) and the grouped organic phases are dried over $MgSO_4$. After distillation of solvents, the residue is purified by column chromatography on silica gel using hexane/AcOEt (95:5) as eluent to give **17** as a white powder (yield: 99%). Rf = 0.3 (TLC, Hexane/AcOEt, 95:5). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 6.81 (s, 4H, H_e); 3.92 (t, ^3J=7 Hz, 4H, H_d); 2.27 (dt, ^{3}J = 7 Hz and ^4J=3 Hz, 4H, H_a) ; 2.00 (t, ^4J= 3 Hz, 2H, H_f); 1.85 (m, 4H, H_c); 1.69 (m, 4H, H_b). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 153.5 (Cq_{aro}); 115.6 (CH_{aro}); 84.5 (Cq); 68.7 (CH); 68.3 (CH_2-O); 28.8 (CH_2); 25.5 (CH_2); 18.5 (CH_2). MS (DCI, NH_3): m/z = 288.2 ($[M+NH_4]^+$, calcd. 288.2). Anal. for $C_{18}H_{22}O_2$: calcd.: C 79.96; H 8.20; found: C 78.80 ; H 8.40.

2,3,6,7,10,11-Hexa[6-(triisopropylsilyl)-hex-5-ynyloxy]-triphenylene (20): 1.746 g of potassium carbonate (12.6 mmol, 21 eq) and 1.205 g of (6-bromohex-1-yn-1-yl)triisopropylsilane (3.81 mmol, 6.4 eq) are added to 10 mL of dry DMF under argon. After 2 min of argon bubbling, 194 mg of HHTP (0.60 mmol, 1 eq) are added and the mixture is stirred at 60°C for 16 h under argon. After cooling to RT, 60 mL of water are added and the organic phase is extracted with DCM (3 x 30 mL), and washed with water (30 mL). The grouped organic phases are then dried under $MgSO_4$, and the solvents are rotoevaporated. The compound is purified by column chromatography over SiO_2, using hexane/DCM (5:5) as eluent). **20** is obtained as white powder in 48% yield. Rf = 0.5 (TLC, hexane/DCM, 1:1). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.86 (s, 6H, H_e); 4.28 (t, ^3J=6 Hz, 12H. H_d); 2.44 (t, ^3J=7 Hz, 12H, H_a); 2.08 (m, 12H, H_c); 1.85 (m, 12H, H_b) ; 1,11-0.88 (m, 126H, H_f). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 149.4 (Cq_{aro}); 123.9 (Cq_{aro});109.2 (CH_{aro});107.5 (CH_{aro}); 80.7 (Cq); 69.3 (CH_2); 28.9 (CH_2); 26.0 (CH_2); 20.0 (CH_2); 18.8 (CH); 11,7 (CH_3).. MS (DCI, CH_4): m/z = 1742.2 ($[M+H]^+$, calcd. 1442.2).

2,3,6,7,10,11-Hexa(hex-5-ynyloxy)triphenylene (21)[20]: To a solution of 20 (250 mg, 0,14 mmol, 1 eq) in 15 mL of anhydrous THF is added a 1M solution of TBAF in THF (1.2 mL, 1.2 mmol, 30 eq). The mixture is stirred 4h at RT and then the reaction is quenched by addition of a saturated ammonium chloride aqueous solution (20 mL). The organic phase is extracted with DCM (25 mL), and washed with brine (20 mL). The grouped organic phases are dried over $MgSO_4$. After distillation of solvents, the product is purified by chromatography over SiO_2 (hexane/DCM (50 to 100%) giving **21** as a white powder in 99% yield; Rf = 0.6 (TLC, DCM); ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.85 (s, 6H, H_d); 4.26 (t, ^3J=6 Hz, 12H, H_c); 2.37 (dt, ^3J=7 Hz, ^{4}J = 3Hz, 12H, H_b); 2.10-1.99 (m, 18H, H_a and CH_2); 1.83 (m, 12H, CH_2). MS (DCI, NH_3): m/z = 803.1 ($[M-H]^+$, calcd. 803.4); Anal. for $C_{54}H_{60}O_6$: calcd.: C 80.56; H 7.51; found: C 79.43 ; H 7.58.

1,4-Bis(1-hexane-1,2,3-triazol-4-ylmethoxy)benzene (5): To 6 mL of a 1:1 mixture of THF and water are added 149 mg of 16 (800 µmol, 1 eq) and 2.1 equivalents of hexyl azide (212 mg, 1.67 mmol). Then 63 mg of copper sulfate (330 µmol, 0.4 eq) and 70 mg sodium ascorbate (690 µmol, 0.9 eq)

are added. The mixture is kept at RT under vigorous stirring for 16h. After addition of 15 mL of AcOEt and 5 mL of water, the organic phase is extracted with DCM (2 x 10 mL), washed with water (2 x 10 mL), and dried (Na_2SO_4). After distillation of solvents and chromatography (SiO_2; DCM/AcOEt (0 to 20%)), **5** is obtained as a white powder in 85% yield. Rf = 0.6 (TLC, DCM/AcOEt, 8:2). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.61 (s, 2H, H_a); 6.93 (s, 4H, H_c); 5.11 (s, 4H, H_b); 4.33 (t, ^{3}J = 7 Hz, 4H, H_d); 1.88 (m, J = 7 Hz, 4H); 1.31 (m, 12H); 0.88 (t, J = 7 Hz, 6H, H_e). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 153.2 (Cq_{aro}); 144.2 ($Cq_{triazole}$); 123.0 (=CH); 116.1 (CH_{aro}); 62.9 (CH_2); 50.7 (CH_2); 31.5 (CH_2); 30.6 (CH_2); 26.5 (CH_2); 22.8 (CH_2); 14.1 (CH_3). MS (DCI, NH_3): m/z = 441.3 ($[M+H]^+$, calcd. 441.3). Anal. for $C_{24}H_{36}O_2N_6$: calcd.: C 65.43; H 8.24; N 19.07; found: C 65.29 ; H 8.47; N 18.72.

1,4-Bis(1-hexane-1,2,3-triazol-4-ylpropoxy)benzene (6): To a 1:1 mixture of THF and water (10 mL) are added 40 mg of 17 (148 µmol, 1 eq) and 2.3 equivalents of hexyl azide (44 mg, 346 µmol), followed by 17 mg of copper sulfate (90 µmol, 0.6 eq) and 22 mg of sodium ascorbate (220 µmol, 1.5 eq). The mixture is vigorously stirred at RT for 16h. Then 15 mL of ethyl acetate and 5 mL of water are added. The organic phase is extracted with 2 x 5 mL of AcOEt, and the grouped organic phases are washed with water (2 x 4 mL) and brine (4 mL) and washed over Na_2SO_4. After distillation of solvents, chromatography of the residue (SiO_2; DCM/AcOEt (0 to 100%) gave **6** as a white powder (yield: 90%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.30 (s, 2H, H_a); 6.80 (s, 4H, H_e); 4.28 (t, ^3J=7 Hz, 4H, H_b); 3.92 (m, ^3J=6 Hz, 4H, H_d); 2.75 (m, ^{3}J = 7Hz, 4H, CH_2) ; 1.82 (m, 12H, CH_2); 1.31 (m, 12H, CH_2); 0.88 (t, ^{3}J = 7Hz, 6H, H_c). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 153.5 (Cq); 147.6 ($Cq_{triazole}$); 120.9 (=CH);115.6 (CH_{aro}); 68.5 (CH_2-O); 50.5 (CH_2-N); 31.5 (CH_2); 30.6 (CH_2); 29.3 (CH_2); 26.5 (CH_2); 26.4 (v); 25.7 (CH_2); 22.8 (CH_2); 14.1 (CH_3). MS (DCI, NH_3): m/z = 525.3 ($[M+H]^+$, calcd. 525.4). Anal. for $C_{30}H_{48}O_2N_6$: calcd.: C 68.67; H 9.22; N 16.02; found: C 68.38 ; H 9.21; N 15.99.

(4,4'-((1,4-Phenylenebis(oxy))bis(methylene))bis(1H-1,2,3-triazole-4,1-diyl))bis(methylene)bis(2,2-dimethylpropanoate) (18): 106 mg of 16 (570 µmol, 1 eq) and 197 mg methyl pivalate azide (1.25 mmol, 2.2 eq) are added to 2L of a 1:1 mixture of THF and water, followed by 72 mg of copper sulfate (380 µmol, 0.7 eq) and 81 mg sodium ascorbate (800 µmol, 1.4 eq) and the mixture is vigorously stirred at RT for 16h. The organic phase is extracted with DCM (3 x 4 mL), washed with water (2 x 4 mL), and dried over Na_2SO_4. After distillation of solvents, the residue is dissolved in ethyl acetate (5 mL) and filtered on celite to give **18** as a white powder in 70% yield. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.87 (s, 2H, H_a); 6.92 (m, 4H, H_c); 6.22 (s, 4H, H_d) ; 5.13 (s, 4H, H_b); 1.17 (s, 18H, H_e). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 177.9 (Cq_{ester}); 153.1 (Cq); 145.0 (Cq); 124.6 (=CH); 116.2 (CH_{aro}); 70.1 (CH_2); 62.7 (CH_2); 39.0 (Cq_{tBu}); 26.9 (CH_3). MS (DCI, NH_3): m/z = 501.3 ($[M+H]^+$, calcd. 501.2). Anal. for $C_{24}H_{32}O_6N_6$: calcd.: C 57.59; H 6.44; N 16.79; found: C 57.37 ; H 6.62; N 16.32.

(4,4'-((1,4-Phenylenebis(oxy))bis(butane-4,1-diyl))bis(1H-1,2,3-triazole-4,1-diyl))bis(methylene)bis(2,2-dimethylpropanoate) (19): In a 1:1 mixture of water and THF (4 mL) are added 110 mg of 17 (407 µmol, 1 eq), 2.5 equivalents of methyl pivalate azide (158 mg, 1.006 mmol), 53 mg of copper sulfate (278 µmol, 0.7 eq) and 60 mg of sodium ascorbate (593 µmol, 1.5 eq). The mixture is vigorously stirred at RT for 16h. The after addition of 5 mL of AcOEt and 5 mL of water, the organic phase is extracted by DCM (2 x 4 mL), washed with ammonium chloride (6 mL) and distilled (6 mL) and dried over Na_2SO_4. After distillation of solvents, **19** is purified by chromatography over silica gel using DCM/AcOEt (0 to 30%) . White powder (yield: 56%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.57 (s, 2H, H_a); 6.80 (s, 4H, H_d); 6.18 (s, 4H, H_e); 3.92 (t, ^3J=6 Hz, 4H, H_c); 2.77 (t, ^3J=7 Hz, 4H, H_b); 1.81 (m, 8H); 1.17 (s, 18H, H_f). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 177.9 (Cq_{ester}); 153.5 (Cq_{aro}); 148.7 ($Cq_{triazole}$); 122.4 (=CH); 115.6 (CH_{aro}); 70.0 (N-CH_2-O); 68.4 (CH_2-O); 39.0 (Cq_{tBu}); 29.2 (CH_2); 26.9 (CH_3); 26.2 (CH_2); 25.5 (CH_2). MS (DCI, NH_3): m/z = 585.4 ($[M+H]^+$, calcd. 585.3).

1,4-Bis((1H-1,2,3-triazol-4-yl)methoxy)benzene (8): To 7 mL of THF and 7 mL of a 1M aqueous solution of sodium hydroxide, 140 mg of 18 (280 µmol, 1 eq) are added , and the mixture is stirred at 50°C for 16h. Then the mixture is diluted with water (3 mL) and hydrochloric acid (37%) is added up to neutral pH. **8** precipitates, is filtered and dried under vacuum (white powder, 80% yield). ^{1}H NMR (500 MHz, DMSO): δ 7.94 (s, 2H, H_b); 6,96 (s, 4H, H_d); 5.11 (s, 4H, H_c) ; 3.34 (large, 2H, NH_a). ^{13}C NMR could not be recorded because of low solubility **8**. MS (FAB): m/z = 273.1 ($[M+H]^+$, calcd. 273.1.

1,4-Bis(4-(1H-1,2,3-triazol-4-yl)butoxy)benzene (9): 93 mg of **19** (159 µmol, 1 eq) are added to a mixture of 7 mL of THF and of 7 mL of 1 M aqueous sodium hydroxide and the mixture is stirred 16h at 50°C. Then 2.5 mL of water are added and a 37% solution of hydrochloric acid are added down to neutral pH. A white precipitates appears, is filtered and dried in oven. **9** is obtained as a white powder with a yield of 65%. ^{1}H NMR (300 MHz, DMSO): δ 7.60 (s, 2H, H_b); 6.82 (s, 4H, H_e); 3.90 (t, ^3J= 7 Hz, 4H, H_d); 3.34 (large, 2H, NH_a) ; 2.69 (t, ^3J= 7 Hz, 4H, H_c); 1.72 (m, 8H, CH_2). Not soluble enough for ^{13}C NMR.

2,3,6,7,10,11-Hexa(1-hexane-1,2,3-triazol-4-ylpropoxy)triphenylene (10): 42 mg of 21 (52 µmol, 1 eq) and 50 mg of hexyl azide (393 µmol, 7.5 eq) are added to a 1:1 mixture of THF and water (6mL), followed by 18 mg of copper sulfate (95 µmol, 1.8 eq) and 24 mg of sodium ascorbate (237 µmol, 4.5 eq). After 16h of vigorous stirring at RT, 15 mL of AcOEt and 5 mL of water are added and the organic phase is extracted with 2 x 5 mL of AcOEt, washed with 2 x 10 mL of aqueous NH_4Cl, 10 mL of brine and 10 mL of water and dried over Na_2SO_4. After distillation of solvents, the residue is chromatographed (SiO_2: AcOEt/MeOH (98:2)) giving **10** as a white powder with a yield of 50%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.84 (s, 6H, H_d); 7.35 (s, 6H, H_a); 4.26 (m, ^3J= 7 Hz, 24H, H_c and H_e); 2.82 (t, ^3J= 7 Hz, 12H, H_b); 1.96 (m, 24H); 1.83 (m, 12H); 1.28 (m, 36H); 0.86 (m, 18H, H_f). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 149.3 (Cq_{aro}); 148.0 ($Cq_{triazole}$); 123.7 (Cq_{aro}); 121.0 (=CH); 107.2 (CH_{aro}); 69.5 (CH_2); 50.4 (CH_2); 31.5 (CH_2); 30.6 (CH_2); 26.5 (CH_2); 25.8 (CH_2); 22.8 (CH_2). MS (DCI, CH_4): m/z = 1569.3 ($[M+H]^+$, calcd. 1569.1).

1,2-Bis(1-hexane-1,2,3-triazol-4-ylmethoxy)benzene (22): 251 mg of 1,2-bis(prop-2-ynyloxy)benzene (1.35 mmol, 1 eq) and 379 mg of hexyl azide (2.98 mmol, 2,2 eq) are added to 4 mL of a 1:1 mixture of THF and water, followed by 152 mg of copper sulfate (0.80 mmol, 0.6 eq) and 177 mg of sodium ascorbate (1.75 mmol, 1.3 eq). The mixture is vigorously stirred at RT for 24h. The organic phase is extracted with ethyl acetate (3 x 4 mL), washed with water (2 x 10 mL), and dried over Na_2SO_4. After distillation of solvents, column chromatography (SiO_2: DCM/AcOEt (0 to 20%) gave **22** as a white powder in 86% yield. Rf = 0.6 (TLC, DCM/AcOEt, 8:2). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.68 (s, 2H, H_a); 7.09-6.89 (m, 4H, H_c); 5.19 (s, 4H, H_b) ; 4.32 (t, ^{3}J = 7 Hz, 4H, H_d); 1.88 (m, ^{3}J = 7 Hz, 4H); 1.31 (m, 12H); 0.88 (t, J = 7 Hz, 6H, H_e). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 148.9 (Cq_{aro}); 144.0 (Cq triazole); 123.4 (=CH); 122.2 (CH_{aro}); 115.5 (CH_{aro}); 63.4 (CH_2-O); 50.7 (CH_2-N); 31.5 (CH_2); 30.5 (CH_2); 26.5 (CH_2); 22.8 (CH_2); 14.1 (CH_3). MS (DCI, NH_3): m/z = 441.3 ($[M+H]^+$, calcd. 441.3).

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Acknowledgements

The ANR MOLSIC is gratefully acknowledged for funding. AP thanks the French “Ministère de l’Enseignement Supérieur et de la Recherche” for a PhD grant.

Keywords: Triphenylene • Hydroquinone • α–aminoacid • 1,2,3 triazoles • Grafting groups

References

[1] S. Morita, F. J. Giessibl, E. Meyer, R. Wiesendanger, Eds. , *Noncontact Atomic Force Microscopy*, Springer International Publishing, Cham, **2015**.
[2] Roland Bennewitz, *J. Phys. Condens. Matter* **2006**, *18*, R417.
[3] B. Such, T. Trevethan, T. Glatzel, S. Kawai, L. Zimmerli, E. Meyer, A. L. Shluger, C. H. M. Amijs, P. de Mendoza, A. M. Echavarren, *ACS Nano* **2010**, *4*, 3429–3439.
[4] B. Hoff, M. Gingras, R. Peresutti, C. R. Henry, A. S. Foster, C. Barth, *J. Phys. Chem. C* **2014**, *118*, 14569–14578.
[5] D. Perez, E. Guitian, *Chem. Soc. Rev.* **2004**, *33*, 274–283.
[6] S. Kumar, B. Lakshmi, *Tetrahedron Lett.* **2005**, *46*, 2603–2605.
[7] G. Cooke, V. Sage, T. Richomme, *Synth. Commun.* **1999**, *29*, 1767–1771.
[8] S. Kumar, S. K. Varshney, *Liq. Cryst.* **1999**, *26*, 1841–1843.
[9] S. Kumar, M. Manickam, *Chem. Commun.* **1997**, 1615–1666.
[10] S. R. Waldvogel, A. R. Wartini, P. H. Rasmussen, J. Rebek Jr., *Tetrahedron Lett.* **1999**, *40*, 3515–3518.
[11] N. M. Boshta, M. Bomkamp, G. Schnakenburg, S. R. Waldvogel, *Chem. – Eur. J.* **2010**, *16*, 3459–3466.
[12] N. M. Boshta, M. Bomkamp, G. Schnakenburg, S. R. Waldvogel, *Eur. J. Org. Chem.* **2011**, *2011*, 1985–1992.
[13] A. Hinaut, A. Pujol, F. Chaumeton, D. Martrou, A. Gourdon, S. Gauthier, *Beilstein J. Nanotechnol.* **2012**, *3*, 221–229.
[14] C. Givelet, T. Buffeteau, F. Arnaud-Neu, V. Hubscher-Bruder, B. Bibal, *J. Org. Chem.* **2009**, *74*, 5059–5062.
[15] J. H. P. Tyman, J. Grundy, G. R. Brown, *J. Chem. Soc. [Perkin 1]* **1981**, 336–343.
[16] L. Nony, F. Bocquet, F. Para, F. Chérioux, E. Duverger, F. Palmino, V. Luzet, C. Loppacher, *Beilstein J. Nanotechnol.* **2012**, *3*, 285–293.
[17] M.-C. Wang, Q.-J. Zhang, W.-X. Zhao, X.-D. Wang, X. Ding, T.-T. Jing, M.-P. Song, *J. Org. Chem.* **2007**, *73*, 168–176.
[18] Y. Xiao, K. Lee, P. Liu, *Org. Lett.* **2008**, *10*, 5521–5524.
[19] M. McLaughlin, R. M. Mohareb, H. Rapoport, *J. Org. Chem.* **2002**, *68*, 50–54.
[20] P. J. Stackhouse, M. Hird, *Liq. Cryst.* **2009**, *36*, 953–965.
[21] V. Bhalla, H. Singh, M. Kumar, S. K. Prasad, *Langmuir* **2011**, *27*, 15275–15281.
[22] B. Li, S.-Q. Zang, R. Liang, Y.-J. Wu, T. C. W. Mak, *Organometallics* **2011**, *30*, 1710–1718.
[23] J. Sinha, R. Sahoo, A. Kumar, *Macromolecules* **2009**, *42*, 2015–2022.
[24] J. C. Loren, A. Krasiński, V. V. Fokin, K. B. Sharpless, *Synlett* **2005**, *2005*, 2847–2850.
[25] S. E. Schaus, J. Brånalt, E. N. Jacobsen, *J. Org. Chem.* **1998**, *63*, 4876–4877.
[26] E. Voisin, V. E. Williams, *Macromolecules* **2008**, *41*, 2994–2997.
[27] R. Zniber, R. Achour, M. Z. Cherkaoui, B. Donnio, L. Gehringer, D. Guillon, *J. Mater. Chem.* **2002**, *12*, 2208–2213.