ChemPubSoc Europe

DOI: 10.1002/ejoc.201501077

EurJOC European Journal of Organic Chemistry

Full Paper

Molecules for Grafting

Functional Molecules for Grafting onto Ionic Surfaces

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

Abstract: The 2D adsorption of molecules onto insulating surfaces is of increasing interest for future devices in emerging technologies such as molecular electronics, sensors, single-molecule optics, and on-surface synthesis. However, most attempts to stabilize molecular structures on these substrates have been hampered by weak molecule–surface interactions and so there is a need to develop organic molecules bearing suitable grafting groups. We report herein the synthesis of a series of molecules designed to be physisorbed onto alkali halide crystalline surfaces. They comprise a rigid central benzene or triphenylene core bearing, respectively, two or six alkyl ether chains terminated by cyano, carboxylic, α-amino acids, or 1,2,3-triazoles as anchoring groups.

Introduction

The adsorption and diffusion of organic molecules onto inorganic surfaces has recently become of particular importance for several fields of interest, such as molecular electronics, sensors, and organic photocatalysis. Investigations in these areas have now been rendered possible by the recent rapid development of atomic force microscopy in the noncontact (or frequency modulation) mode (NC-AFM),[1] but so far little is known, for example, of the detailed adsorption mechanisms and the balance between molecule–substrate and molecule–molecule interactions. The main problem in this field remains the fact that molecule–surface 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 been focused on alkali metal halide surfaces as models for the study of organic/inorganic heteroepitaxy (OIHE)[2] because these surfaces are stable and easy to prepare under ultra-high vacuum conditions (UHV) even though the molecule–surface interactions are in general very weak. Consequently, there is a general need to investigate these interactions on the atomic scale to be able to design and tailor molecules that adsorb strongly on dielectric surfaces such as KBr, KCl, or NaCl. One solution we have been exploring in recent years is the conception and synthesis of molecules comprising aromatic or polyaromatic rigid cores equipped with several flexible chains terminating with anchoring groups that interact locally 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 to optimize these interactions and master the OIHE on this type of substrate.

We describe herein the preparation of two series of molecules designed for NC-AFM experiments on alkali halide surfaces. The molecules comprise a rigid central benzene or tri-

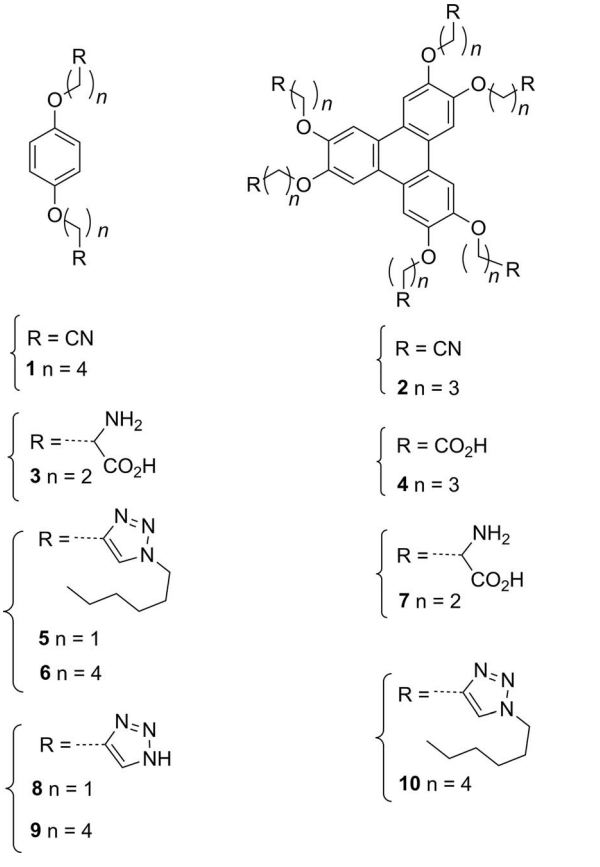


Figure 1. Hydroquinone and hexahydroxytriphenylene derivatives designed for physisorption on alkali metal halide surfaces.

[a] NanoSciences Group, CEMES-CNRS,
29 rue Jeanne Marvig, BP 94347, 31055 Toulouse Cedex 4, France
E-mail: andre.gourdon@cemes.fr
http://www.cemes.fr/GNS
[b] Université de Toulouse, UPS,
118 route de Narbonne, 31062 Toulouse Cedex 9, France

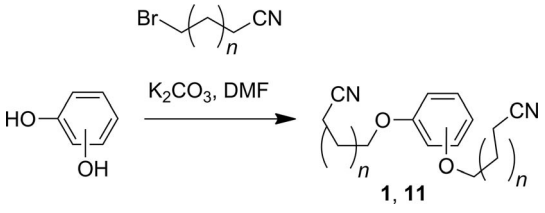
Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/ejoc.201501077.

phenylene core bearing, respectively, two or six alkyl ether chains terminated by cyano, carboxylic, α-amino acids, or 1,2,3-triazoles as anchoring groups (Figure 1).

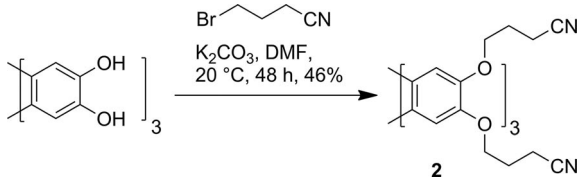
Results and Discussion

Cyano Derivatives

The cyano group is the most used grafting group in this type of experiment for several reasons, namely the ease of preparation and thermal stability of molecules comprising this functional group, which allows the sublimation required for transfer onto surfaces under UHV. An investigation of the adsorption and diffusion properties of *syn*-5,10,15-tris(cyanophenylmethyl)truxene onto a KBr(001) nanostructured surface showed that molecules diffused along the monolayer step edges and were immobilized at kink sites.[3] An extensive DFT simulation demonstrated that the control of anchoring and diffusion was dependent on the number of anchoring groups acting independently; this requires a flexibility of the anchoring branch to allow the individual groups to bind to specific sites on the surface. The adsorption of rigid mono- and dicyanopentahelicenes onto a Suzuki (001) surface[4] confirmed that a perfect match between the distances of the substituents and the cations was required and that the cyano groups were in a perpendicular position on top of the surface cations, allowing compensation of the net dipole. Taking these facts into account, we have designed a series of dicyano/hexacyano-functionalized molecules to study their interactions on NaCl(001) and KBr(001) surfaces. The synthesis involves a one-step Williamson etherification of hydroquinone/catechol/hexahydroxytriphenylene (HHTP) and 5-bromovaleronitrile/5-bromobutyronitrile under mild conditions (K_2CO_3 in dry DMF), as shown in Schemes 1 and 2.

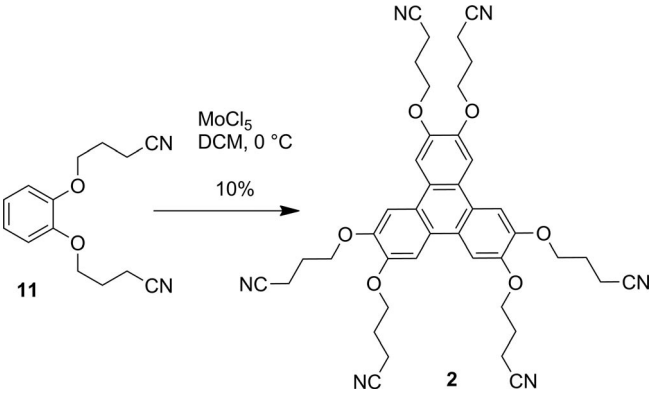


Scheme 1. Preparation of **1** (1,4 isomer, $n = 2$, yield: 50 %) and **11** (1,2 isomer, $n = 1$, yield: 71 %).



Scheme 2. Synthesis of **2** from HHTP.

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



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

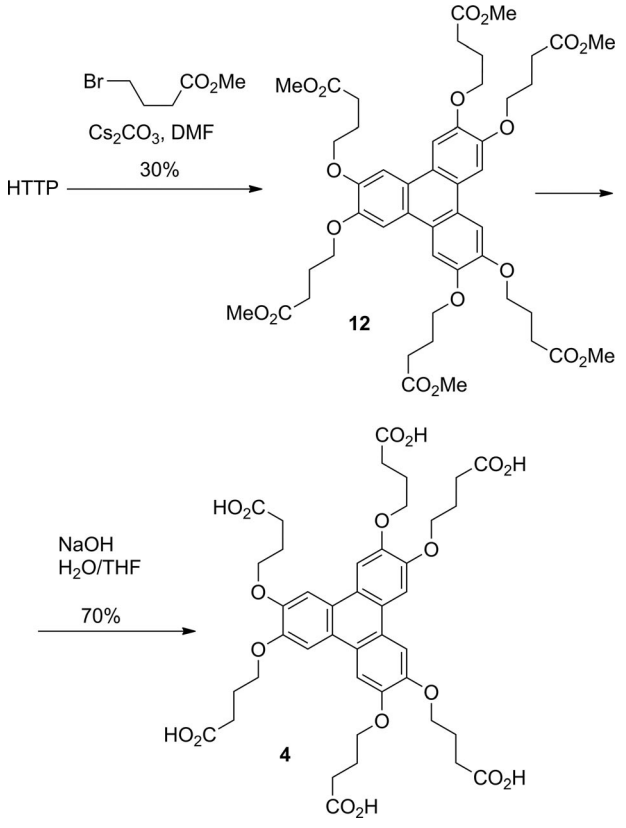
Although the condensation of 1,2-substituted catechol by oxidative coupling is a standard route to many hexyloxytriphenylenes,[5] it is often limited to poorly reactive substituted chains. Several oxidizing groups have been used, such as $FeCl_3$,[6,7] $VOCl_3$,[8] and $MoCl_5$.[9,10] Waldvogel and co-workers showed that it was possible to cyclotrimerize 1,3-benzodioxole disubstituted at the 2-position by chains bearing reactive groups such as esters by using $MoCl_5$,[10–12] and we used similar conditions to prepare **2** by this route.

We studied the adsorption of **2** on KBr(001) surfaces by NC-AFM coupled with Kelvin probe force microscopy (KPFM) under ultra-high vacuum at room temperature.[13] Two types of monolayers were identified, one in which the molecules lie 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 a total adsorption energy of 1.8 eV. In the vertical geometry, the molecules form π-stacked rows aligned along the polar direction of the surface. Only two of the cyano groups interact with the surface cations, contributing approximately 0.4 eV to the adsorption energy; the stabilization (total adsorption energy ca. 2.5 eV) is gained by this intermolecular interaction.

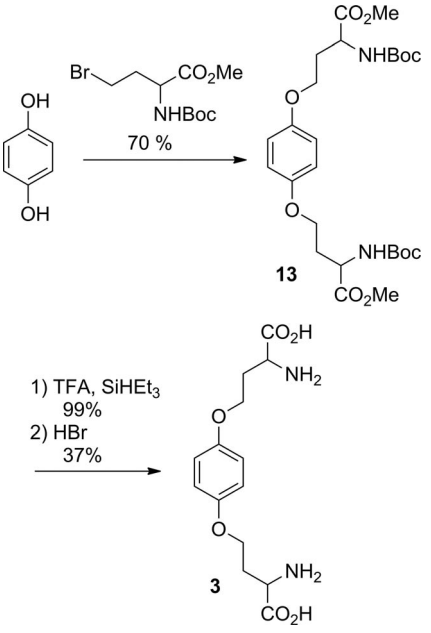
These results suggest that the dipolar moment of the nitrile group may not be high enough for strong adsorption, which prompted us to explore the preparation of the analogous derivative **4** bearing a carboxylic group.

Carboxylic Derivatives

2,3,6,7,10,11-Hexakis(3-carboxypropyloxy)triphenylene (**4**) can be obtained as a gel by the reaction of HHTP with methyl 4-bromobutanoate in a basic medium to give the hexamethyl ester **12** in 30 % yield, a procedure similar to that of Bibal and co-workers.[14] for the synthesis of water-soluble hosts. Compound **12** was then hydrolyzed by aqueous sodium hydroxide to give **4** in 70 % yield (Scheme 4). Attempts to prepare **4** by the condensation of 4,4′-(1,2-phenylenedioxy)dibutanoic ester[15] were unsuccessful.



Scheme 4. Preparation of **4**.



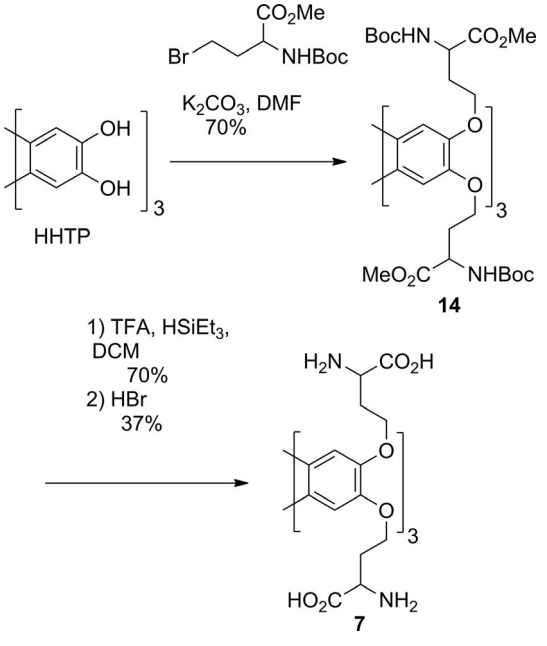
Scheme 5. Synthesis of **3**.

α-Amino Acid Derivatives

A third grafting group that can be envisioned is the α-amino acid. In particular, in their zwitterionic forms, these functions could show strong electrostatic interactions with the local partial charges of dielectric surfaces such as alkali halides provided that there is commensurability between the local surface charges and zwitterionic charges. Similar hypotheses have been used by Loppacher and co-workers 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 by an alkyl chain to the pyridinium ring carrying a positive charge, and the distance between the opposite charges in the *trans* isomer is around 1 nm. A first rapid evaluation shows that the carboxylate–ammonium distance in α-amino acids (ca. 2.8 Å) matches the sodium–chloride distance in NaCl(001) (2.82 Å). This observation led us to design compounds **3** and **7** bearing 2-aminobutanoic chains (Scheme 5).

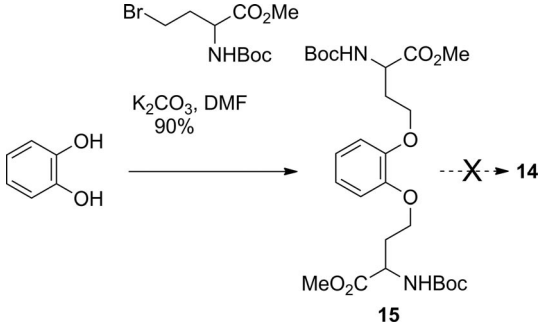
The hydroquinone/catechol and HHTP α-amino acid derivatives were obtained by their reactions with methyl 4-bromo-2-(*tert*-butoxycarbonylamino)butanoate in anhydrous DMF in the presence of potassium carbonate. Its preparation requires the synthesis of 2-amino-4-bromobutanoic acid, which can be efficiently and rapidly obtained in quantitative yield by microwave irradiation in HBr/AcOH in 45 min (compared with 4 h by standard heating at 75 °C).[17] It must be underlined that this ring-opening is reversible in water and we have shown by NMR analysis that half of the 2-amino-4-bromobutanoic acid returned to the lactone after 90 min in D_2O at room temperature. The amine and carboxylic functions were then protected by standard procedures to give methyl 4-bromo-2-(*tert*-butoxycarbonylamino)butanoate (Scheme 5).[18,19]

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



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

Attempts to apply the Scholl condensation to the catechol derivative according to Scheme 7 were unsuccessful, leading only to the decomposition of the catechol derivative **15**.

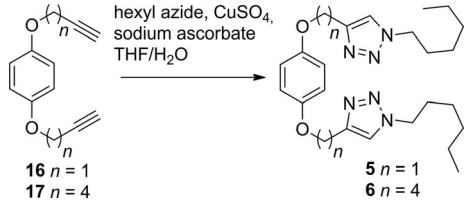


Scheme 7. Attempted synthesis of **14** by the Scholl condensation reaction.

1,2,3-Triazole Derivatives

A fourth grafting group potentially suitable for strong electrostatic interactions with alkali halide surfaces is 1,2,3-triazole. Indeed, the local dipole moment of 1,2,3-triazole is 4.23 D, similar to that of carboxylic acid (4.25 D), whereas it is 4.38 D for 1-hexyl-1,2,3-triazole.

The hydroquinone derivatives **5** and **6** were obtained by CuAAC reactions starting from the dialkynes **16** and **17**, respectively, as shown in Scheme 8.

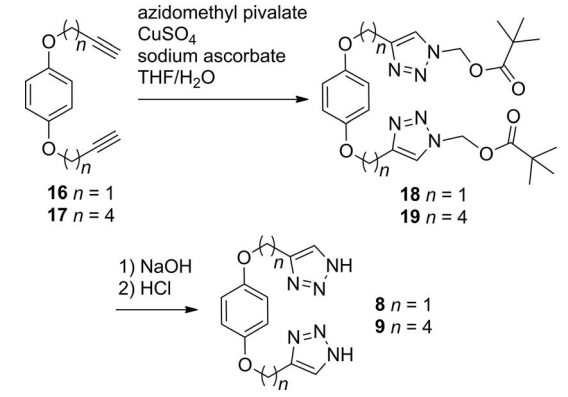


Scheme 8. Preparation of **5** and **6** from **16** and **17**, respectively.

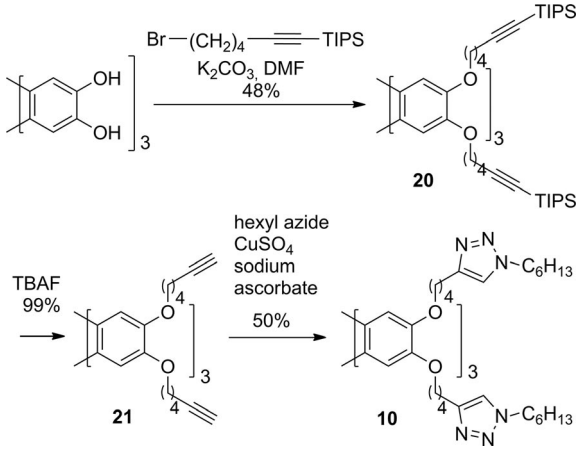
Dialkyne **17** itself was obtained in two steps by the condensation of (6-bromohex-1-yn-1-yl)triisopropylsilane with hydroquinone, followed by the deprotection of the alkyne by tetrabutylammonium fluoride (TBAF; total yield: 70 %).

Similarly, the 1,2,3-triazoles **8** and **9** bearing a hydrogen atom at the 1-position were obtained by the reaction of **16** and **17** with azidomethyl pivalate under standard CuAAC conditions. The pivalate protecting group was then removed by basic treatment followed by acidification to give **8** and **9** in yields of 90 and 85 %, respectively. Both compounds are very insoluble (Scheme 9).

The HHTP hexasubstituted analogue **21** was obtained by Williamson etherification with (6-bromohex-1-yn-1-yl)triisopropylsilane, followed by standard TIPS deprotection by TBAF (Scheme 10). This route was preferred to the recently published procedure by Stackhouse and Hird[20] in which **21** was obtained by the condensation of HHTP with unprotected 6-chlorohex-1-yne in a better yield (66 %) but with a significantly longer reaction time (9 d).



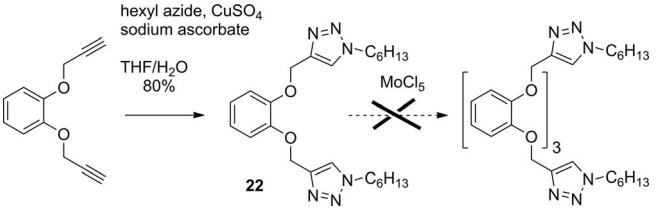
Scheme 9. Preparation of **8** and **9** (total yield from **16**: 56 %; from **17**: 36 %).



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

From **21**, the target compound **10** was obtained in 50 % yield following the CuAAC procedure developed for hydroquinone analogues (Scheme 10). Compound **10** is very similar to the recently described triazole HHTP derivative prepared by Bhalla et al.,[21] which shows a 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 analogues of **10** by a convergent approach according to Scheme 11 have so far been unsuccessful, probably due to the fragility of the intermediate **22** towards the Lewis acids required for the Scholl condensation.



Scheme 11. Attempted trimerization of **22** by the Scholl condensation reaction.

Conclusions

A series of molecules designed for experiments on alkali halide surfaces have been synthesized by functionalizing hydroquinone and hexahydroxytriphenylene with alkyl chains terminated with cyano, carboxylic acid, triazole, or amino acid groups. Scholl condensations of catechol derivatives to form the triphenylene core turned out to be unsuccessful.

Experimental Section

General Methods: Dry DMF was from Acros Organics or Sigma Aldrich. THF was distilled over sodium/benzophenone. Other solvents were dried with molecular sieves prior to use. Flash column chromatography was performed on silica gel (60 Å pore size, 40–63 μm Merck). Reactions were monitored by TLC on plates coated with silica gel (Merck 60 F_{254}). Detection was achieved by using UV light and by charring the plate at around 200 °C after dipping it in an ethanolic solution of potassium permanganate. The yields refer to chromatographically and spectroscopically (^{1}H and ^{13}C NMR) homogeneous materials unless otherwise stated. NMR spectra were recorded with Bruker Avance 300, 400, and 500 MHz spectrometers and were calibrated by using residual undeuteriated solvent as the 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 ppm on the δ scale and coupling constants are in Hz. The abbreviations used to describe the multiplicities are as follows: s = singlet, br. s = 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 the University Paul Sabatier (Toulouse 3, France). Elemental analyses were performed by the Service d'Analyse de l'ICSN (Paris, France). Microwave heating was carried out in sealed 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,[18] methyl 4-bromo-2-(*tert*-butoxycarbonylamino)butanoate,[19] hexyl azide,[23] azidomethyl pivalate,[24] and (6-bromohex-1-ynyl)triisopropylsilane[25] were obtained according to the published procedures. HHTP[26] was obtained from hexamethoxytriphenylene (HMTP)[27] according to literature procedure. When required, HHTP was purified before use according to the following procedure: partially oxidized HHTP (198 mg) was added to warm (75 °C), degassed distilled water (30 mL). After stirring for 5 min under argon, sodium hydrosulfite (250 mg) was added. The mixture was filtered under argon as soon as the mixture changed from violet to clear grey. The beige solid was then washed with water and dried under vacuum at 40 °C to give pure HHTP in nearly quantitative yield.

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

1,4-Bis(cyanobutoxy)benzene (1): Hydroquinone (500 mg, 4.5 mmol, 1 equiv.) and potassium carbonate (6 equiv., 4.53 g, 27.9 mmol) were added to anhydrous DMF (10 mL). Argon was then bubbled (2 min) through the solution, 5-bromovaleronitrile (2 equiv., 1.12 mL, 9.7 mmol) was added and the mixture stirred for 16 h at 60 °C under argon. After cooling to room temp., water (20 mL) and DCM (20 mL) were added and the mixture extracted with DCM (3 × 20 mL). The combined organic phases were dried with $MgSO_4$. After distillation of the 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, 4 H, $H_{ar.}$), 3.94 (t, ^3J = 6 Hz, 4 H, CH_2-O), 2.43 (t, ^3J = 7 Hz, 4 H, CH_2-CN), 1.95–1.78 (m, 8 H, CH_2) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 153.4 ($C_{q,ar.}$), 120.0 ($C_{q,nitrile}$), 115.7 ($CH_{ar.}$), 67.7 (CH_2-O), 28.7 (CH_2), 22.8 (CH_2), 17.3 (CH_2CN) ppm. MS (DCI, NH_3): calcd. for $[M + NH_4]^+$ 290.2; found 290.2. HRMS (DCI, CH_4): calcd. for $C_{16}H_{21}N_2O_2$ 273.1603 $[M + H]^+$; found 273.1591. $C_{16}H_{20}N_2O_2$ (272.15): 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-Hexakis(cyanopropoxy)triphenylene (2) from HHTP: Potassium carbonate (1.93 g, 13.9 mmol, 25 equiv.) and 4-bromobutyronitrile (0.39 mL, 3.9 mmol, 7 equiv.) were added to anhydrous DMF (11 mL) and the mixture was degassed by argon bubbling for 2 min, followed by the addition of HHTP (180 mg, 0.55 mmol, 1 equiv.). After stirring at room temp. under argon for 48 h, the mixture was poured into water (110 mL). Neutralization with a 5 M solution of sulfuric acid gave a precipitate that was filtered, washed with water, and dried. Recrystallization from ethyl acetate gave **2** as a grey powder in 46 % yield. R_f = 0.5 (TLC, DCM/AcOEt, 7:3). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.91 (s, 6 H, H_d), 4.37 (t, ^3J = 6 Hz, 12 H, H_c), 2.71 (t, ^3J = 7 Hz, 12 H, H_a), 2.27 (m, ^3J = 7 Hz, 12 H, H_b) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 148.9 ($C_{q,ar.}$), 124.2 ($C_{q,nitrile}$), 107.9 ($CH_{ar.}$), 67.6 (CH_2-O), 26.0 (CH_2), 14.7 (CH_2) ppm. HRMS (DCI, CH_4): calcd. for $C_{42}H_{43}N_6O_6$ 727.3244 $[M + H]^+$; found 727.3275.

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

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

2,3,6,7,10,11-Hexakis[3-(methoxycarbonyl)propyloxy]triphenylene (12): Cesium carbonate (2.54 g, 7.8 mmol, 10 equiv.) and methyl 4-bromobutanoate (0.9 mL, 7.1 mmol, 9 equiv.) were added to anhydrous DMF (8 mL). After 2 min argon bubbling, HHTP (253 mg, 0.8 mmol, 1 equiv.) was added and the mixture was stirred under argon at room temp. for 24 h. Then water (18 mL) was added to the mixture, which was then filtered. The gel was then washed with water and dissolved in DCM. The organic phase was then extracted with DCM (3 × 10 mL), dried with $MgSO_4$, and filtered. Compound **12** was obtained as a gel in 30 % yield. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.91 (s, 6 H, H_d), 4.30 (t, ^3J = 6 Hz, 12 H, H_c), 3.70 (s, 18

H, H_e), 2,64 (t, ^3J = 7 Hz, 12 H, H_a), 2.22 (m, 12 H, H_b) ppm. ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 173.9 ($C_{q,ester}$), 149.1 ($C_{q,ar.}$), 123.9 ($C_{q,ar.}$), 107.5 ($CH_{ar.}$), 68.6 (CH_2-O), 51.8 (CH_3), 30.7 ($CH_{2,ester}$), 25.1 (CH_{2int}) ppm. MS (DCI, NH_3): calcd. for $[M + NH_4]^+$ 942.4; found 942.0. $C_{42}H_{60}O_{18}$: calcd. C 62.33, H 6.54; found C 62.23, H 6.50.

2,3,6,7,10,11-Hexakis(4-carboxypropyloxy)triphenylene (4): Aqueous sodium hydroxide (1.3 M, 2 mL) was added to a solution of **12** (250 mg) in THF/H_2O (3:1, 2 mL) and the mixture was stirred for 16 h at room temperature. The solvents were then evaporated and the residue dissolved in water (2 mL). Dropwise addition of 1 M HCl to pH 1 gave a precipitate that was filtered and dried under vacuum. Compound **4** was obtained as a white powder in a yield of 70 %. ^1H NMR (500 MHz, MeOD/H_2O): δ = 7.91 (s, 6 H, H_d), 4.28 (t, ^3J = 6 Hz, 12 H, H_c), 2.62 (t, ^3J = 7 Hz, 12 H, H_a), 2.20 (qt, 12 H, H_b) ppm. ^{13}C NMR (125 MHz, MeOD/H_2O): δ = 178.0 ($C_{q,COOH}$), 149.9 ($C_{q,ar.}$), 124.9 ($C_{q,ar.}$), 108.1 ($CH_{ar.}$), 69.5 (CH_2-O), 31.9 (CH_2), 26.1 (CH_2) ppm. MS (DCI, NH_3): calcd. for $[M - H]^+$ 839.3; found 839.9. $C_{42}H_{48}O_{18}$ (820.28): calcd. C 59.99, H 5.75; found C 57.77, H 5.78.

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

1,4-Bis[3-amino-3-(methoxycarbonyl)propyloxy]benzene: Compound **13** (290 mg, 537 mmol, 1 equiv.) was dissolved in a mixture of triethylsilane (150 µL) and DCM (1.35 mL). The solution was cooled to 0 °C and TFA (1.5 mL) was added. The mixture was stirred at 0 °C for 15 min, and then at room temp. for 1 h. After distillation of the solvents, the residue was recrystallized from EtOH/Et_2O. 1,4-Bis[3-amino-3-(methoxycarbonyl)propyloxy]benzene was obtained as a white solid (yield: 99 %). ^1H NMR (300 MHz, MeOD): δ = 6.90 (s, 4 H, $H_{ar.}$), 4.27 (t, ^3J = 6 Hz, 2 H), 4.12 (m, 4 H), 3.84 (s, 6 H, CH_3), 2.43–2.34 (m, 4 H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 170.8 ($C_{q,ester}$), 154.2 ($C_{q,ar.}$), 116.6 ($CH_{ar.}$), 65.2 (CH_2-O), 53.7 (CH_3), 51.9 (CH), 31.3 (CH_2) ppm. MS (ESI): calcd. for $[M + H]^+$ 341.2; found 341.0. HRMS (DCI, CH_4): calcd. for $C_{16}H_{25}O_6N_2$ 341.1713 $[M + H]^+$; found 341.1707. $C_{16}H_{24}O_6N_2 \cdot 2(C_2HF_3O_2)$: 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-3-carboxypropyloxy)benzene (3): 1,4-Bis[3-amino-3-(methoxycarbonyl)propyloxy]benzene (345 mg, 0.61 mmol) was dissolved in an aqueous solution of HBr (48 %, 2 mL) and the mixture was heated at reflux for 4 h. After cooling to room temp., the solvents were evaporated and the residue was recrystallized from water. Compound **3** was obtained as a white solid in a yield of 37 %. ^1H NMR (500 MHz, D_2O/MeOD): δ = 6.97 (s, 4 H, $H_{ar.}$), 4.21 (m, 6 H), 2.49–2.35 (m, 4 H) ppm. ^{13}C NMR (125 MHz, D_2O/MeOD): δ = 172.9 ($C_{q,acid}$), 153.5 ($C_{q,ar.}$), 116.8 ($CH_{ar.}$), 65.8 (CH_2-O), 52.5 (CH), 30.5 (CH_2) ppm. MS (ESI): calcd. for $[M + H]^+$ 313.1; found 313.4. HRMS (DCI, CH_4): calcd. for $C_{14}H_{21}O_6N_2$ 313.1400 $[M + H]^+$; found 313.1400. $C_{14}H_{20}O_6N_2 \cdot 2(C_2HF_3O_2)$: calcd. C 40.01, H 4.10, N 5.18; found C 40.73, H 5.56, N 6.46.

1,2-Bis[3-(methoxycarbonyl)-3-(*tert*-butoxycarbonylamino)-propyloxy]benzene (15): Potassium carbonate (578 mg, 4.12 mmol, 5 equiv.) and methyl 4-bromo-2-(*tert*-butoxycarbonylamino)butanoate (718 mg, 2.43 mmol, 2.9 equiv.) were mixed in anhydrous DMF (8.5 mL). The mixture was purged by argon bubbling for 2 min. Then catechol (92 mg, 0.84 mmol, 1 equiv.) was added to the mixture, which was stirred at 60 °C for 16 h. After cooling to room temp., water was added (15 mL) and the organic phase was extracted with DCM (3 × 15 mL) and washed with water (2 × 10 mL). The combined organic phases were dried with $MgSO_4$. After distillation of the solvents, the residue was purified by column chromatography (SiO_2: Hex/AcOEt, 0 to 30 %) to give **15** as a colorless oil (yield: 90 %). R_f = 0.2 (TLC, Hex/AcOEt, 7:3). ^1H NMR (300 MHz, CD_2Cl_2): δ = 6.90 (s, 4 H, H_a), 6.10–5.60 (br., 2 H), 4.56–4.28 (br., 2 H), 4.20–3.98 (m, 4 H, H_b), 3.71 (s, 6 H, H_d), 2.44–2.12 (m, 4 H, H_c), 1.42 (2 s, 18 H, H_e) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 173.0 ($C_{q,ester}$), 155.8 (C_q), 148.8 (C_q), 121.8 ($CH_{ar.}$), 114.2 ($CH_{ar.}$), 79.9 ($C_{q,tBu}$), 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) ppm. MS (DCI, NH_3): calcd. for $[M + H]^+$ 541.3; found 541.0. HRMS (DCI, CH_4): calcd. for $C_{26}H_{40}O_{10}N_2Na$ 563.2581 $[M + Na]^+$; found 563.2582; calcd. for $C_{26}H_{40}O_{10}N_2K$ 579.2320 $[M + K]^+$; found 579.2316. $C_{26}H_{40}O_{10}N_2$: 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-Hexakis[3-(methoxycarbonyl)-3-(*tert*-butoxycarbonylamino)propyloxy]triphenylene (14): A large excess of potassium carbonate (1.816 g, 13.3 mmol, 21 equiv.) and methyl 4-bromo-2-(*tert*-butoxycarbonylamino)butanoate (1.240 g, 4.20 mmol, 6.7 equiv.) were mixed in anhydrous DMF (10 mL). The mixture was degassed by argon purging for 2 min. Then HHTP (204 mg, 0.63 mmol, 1 equiv.) was added and the mixture was stirred under argon at 60 °C for 42 h. After cooling to room temp., water (30 mL) was added and the organic phase was extracted with DCM (3 × 30 mL) and washed with water (2 × 15 mL). The combined organic phases were the dried with $MgSO_4$. After removal of the solvent, the raw product was purified by silica gel chromatography using DCM/AcOEt (0 to 30 %) as eluent. Compound **14** was obtained as a white solid (yield: 70 %). R_f = 0.5–0.6 (CCM, DCM/AcOEt, 7:3). ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.88 (s, 6 H, H_a), 6.26–5.70 (br., 6 H), 4.60 (m, 6 H), 4.50–4.26 (m, 12 H, H_b), 3.74 (s, 18 H, H_d), 2.58–2.28 (m, 12 H, H_c), 1.42 (2 s, 54 H, H_e) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 173.1 ($C_{q,ester}$), 155.9 (C_q), 148.8 (C_q), 124.0 (C_q), 107.4 ($CH_{ar.}$), 80.0 ($C_{q,tBu}$), 66.5 (CH_2-O), 52.3 (CH_3), 52.1 (CH), 32.0 (CH_2), 28.4 (CH_3) ppm. MS (ESI): calcd. for $[M + Na]^+$ 1637.7; found 1637.8. HRMS (DCI, CH_4): calcd. for $C_{78}H_{114}N_6O_{30}Na$ 1637.7477 $[M + Na]^+$; found 1637.7524. $C_{78}H_{114}N_6O_{30}$: 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-Hexakis(3-methoxycarbonyl-3-aminopropyloxy)triphenylene: Compound **14** (286 mg, 0.18 mmol, 1 equiv.) was dissolved in a mixture of triethylsilane (200 µL) and DCM (3.90 mL). The mixture was then cooled to 0 °C and TFA was added (1.95 mL). After stirring for 15 min at 0 °C and then for 1 h at room temp., the solvents were evaporated. The solid residue was then recrystallized from EtOH/Et_2O to give 2,3,6,7,10,11-hexakis(3-methoxycarbonyl-3-aminopropyloxy)triphenylene as a gel (yield: 70 %). ^1H NMR (300 MHz, MeOD): δ = 8.09 (s, 6 H, $H_{ar.}$), 4.93 (br., 12 H),

4.58 (m, 12 H), 4.49 (t, ^3J = 6 Hz, 6 H), 3.87 (s, 9 H, CH_3), 3.85 (s, 9 H, CH_3), 2.71–2.51 (m, 12 H, CH_2) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 170,8 ($C_{q,ester}$), 163.1 (q, $^2J_{C-F}$ = 30 Hz), 149.0 ($C_{q,ar.}$), 125.3 ($C_{q,ar.}$), 118.2 (q, $^1J_{C-F}$ = 300 Hz), 107.9 ($CH_{ar.}$), 66.5 (CH_2-O), 53.9 (CH_3), 52.4 (CH), 31.1 (CH_2) ppm. MS (ESI): calcd. for 1015.5 $[M + H]^+$; found 1015.3. $C_{60}H_{72}F_{18}N_6O_{30}$: 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-Hexakis(3-amino-3-carboxypropyl)triphenylene (7): 2,3,6,7,10,11-Hexakis(3-methoxycarbonyl-3-aminopropyloxy)triphenylene (108 mg, 0.064 mmol) was dissolved in a 48 % aqueous solution of HBr (2 mL). The mixture was heated at reflux for 4 h. After cooling and evaporation of the solvents, **7** was obtained as a black gel in 37 % yield. The product was purified by HPLC. ^1H NMR (300 MHz, D_2O): δ = 7.37 (s, 6 H, $H_{ar.}$), 4.37–4.13 (m, 18 H), 2.59–2.40 (m, 12 H) ppm. ^{13}C NMR (125 MHz, D_2O/MeOD): δ = 173.8 ($C_{q,acid}$), 147.8 ($C_{q,ar.}$), 123.9 ($C_{q,ar.}$), 106.5 ($CH_{ar.}$), 66.4 (CH_2-O), 53.1 (CH), 30.5 (CH_2) ppm. MS (ESI): calcd. for $[M + H]^+$ 931.4; found 931.5.

1,4-Bis[6-(triisopropylsilyl)hex-5-ynyloxy]benzene: Argon was bubbled for 2 min through a mixture of potassium carbonate (608 mg, 4.4 mmol, 6.8 equiv.) and (6-bromohex-1-yn-1-yl)triisopropylsilane (442 mg, 1.4 mmol, 2.2 equiv.) in anhydrous DMF (5 mL). Then hydroquinone (71 mg, 0.65 mmol, 1 equiv.) was added and the mixture was stirred at 60 °C for 16 h under argon. After cooling to room temp., water (15 mL) and DCM (15 mL) were added and the organic phase was extracted with DCM (2 × 20 mL) and washed with water (20 mL). The combined organic phases were then dried with $MgSO_4$. After distillation of the solvents, the residue was purified by chromatography on SiO_2 with a mixture hexane/AcOEt (0 to 5 %) as eluent to yield 1,4-bis[6-(triisopropylsilyl)hex-5-ynyloxy]benzene as a white powder in 70 % yield. R_f = 0.5 (TLC, Hex/AcOEt, 95:5). ^1H NMR (300 MHz, CD_2Cl_2): δ = 6.81 (s, 4 H, H_e), 3.93 (t, ^3J = 6 Hz, 4 H, H_d), 2.33 (t, ^3J = 7 Hz, 4 H, H_a), 1.89 (m, 4 H, H_c), 1.70 (m, 4 H, H_b), 1.07 (m, 42 H, H_f) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 153.6 ($C_{q,ar.}$), 115.7 ($CH_{ar.}$), 109.2 (C_q), 80.8 (C_q), 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}) ppm. MS (DCI, NH_3): calcd. for $[M + NH_4]^+$ 600.5; found 600.3. $C_{36}H_{62}O_2Si_2$: calcd. C 74.16, H 10.72; found C 73.02, H 10.87.

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

1,4-Bis(1-hexyl-1,2,3-triazol-4-ylmethoxy)benzene (5): Dialkyne **16** (149 mg, 800 µmol, 1 equiv.) and hexyl azide (2.1 equiv., 212 mg, 1.67 mmol) were added to THF/water (1:1, 6 mL). Then copper sulfate (63 mg, 330 µmol, 0.4 equiv.) and sodium ascorbate (70 mg 690 µmol, 0.9 equiv.) were added. The mixture was kept at room temp. under vigorous stirring for 16 h. After addition of AcOEt (15 mL) and water (5 mL), the organic phase was extracted with DCM (2 × 10 mL), washed with water (2 × 10 mL), and dried (Na_2SO_4). After distillation of solvents and chromatography (SiO_2: DCM/AcOEt, 0 to 20 %), compound **5** was obtained as a white powder in 85 % yield. R_f = 0.6 (TLC, DCM/AcOEt, 8:2). ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.61 (s, 2 H, H_a), 6.93 (s, 4 H, H_c), 5.11 (s, 4 H, H_b), 4.33 (t, ^3J = 7 Hz, 4 H, H_d), 1.88 (m, J = 7 Hz, 4 H), 1.31 (m, 12 H), 0.88 (t, ^3J = 7 Hz, 6 H, H_e) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 153.2 ($C_{q,ar.}$), 144.2 ($C_{q,triazole}$), 123.0 (=CH), 116.1 ($CH_{ar.}$), 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) ppm. MS (DCI, NH_3): calcd. for $[M + H]^+$ 441.3; found 441.3. $C_{24}H_{36}O_2N_6$: calcd. C 65.43, H 8.24, N 19.07; found C 65.29, H 8.47, N 18.72.

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

1,4-Phenylenebis[4-(oxymethyl)-1*H*-1,2,3-triazol-1-ylmethyl] Bis(2,2-dimethylpropanoate) (18): Dialkyne **16** (106 mg, 570 µmol, 1 equiv.) and azidomethyl pivalate (197 mg 1.25 mmol, 2.2 equiv.) were added to THF/water (1:1, 2 mL), followed by copper sulfate (72 mg, 380 µmol, 0.7 equiv.) and sodium ascorbate (81 mg, 800 µmol, 1.4 equiv.), and the mixture was vigorously stirred at room temp. for 16 h. The organic phase was extracted with DCM (3 × 4 mL), washed with water (2 × 4 mL), and dried with Na_2SO_4. After distillation of the solvents, the residue was dissolved in ethyl acetate (5 mL) and filtered through Celite to give **18** as a white powder in 70 % yield. ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.87 (s, 2 H, H_a), 6.92 (m, 4 H, H_c), 6.22 (s, 4 H, H_d), 5.13 (s, 4 H, H_b), 1.17 (s, 18 H, H_e) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 177.9 ($C_{q,ester}$), 153.1 (C_q), 145.0 (C_q), 124.6 (=CH), 116.2 ($CH_{ar.}$), 70.1 (CH_2), 62.7 (CH_2), 39.0 ($C_{q,tBu}$), 26.9 (CH_3) ppm. MS (DCI, NH_3): calcd. for $[M + H]^+$ 501.2; found 501.3. $C_{24}H_{32}O_6N_6$: calcd. C 57.59, H 6.44, N 16.79; found C 57.37, H 6.62, N 16.32.

1,4-Phenylenebis[4-(4-oxybutyl)-1*H*-1,2,3-triazol-1-ylmethyl] Bis(2,2-dimethylpropanoate) (19): Dialkyne **17** (110 mg, 407 µmol, 1 equiv.), azidomethyl pivalate (2.5 equiv., 158 mg, 1.006 mmol), copper sulfate (53 mg, 278 µmol, 0.7 equiv.), and sodium ascorbate (60 mg, 593 µmol, 1.5 equiv.) were added to THF/water (1:1, 4 mL). The mixture was vigorously stirred at room temp. for 16 h. Then AcOEt (5 mL) and water (5 mL) were added, the organic phase was extracted with DCM (2 × 4 mL), washed with ammonium chloride (6 mL), distilled water (6 mL), and dried with Na_2SO_4. After distillation of the solvents, **19** was purified by chromatography over silica gel using DCM/AcOEt (0 to 30 %) as eluent to give the product as a white powder (yield: 56 %). ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.57 (s, 2 H, H_a), 6.80 (s, 4 H, H_d), 6.18 (s, 4 H, H_e), 3.92 (t, ^3J = 6 Hz, 4 H, H_c), 2.77 (t, ^3J = 7 Hz, 4 H, H_b), 1.81 (m, 8 H), 1.17 (s, 18 H, H_f) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 177.9 ($C_{q,ester}$),

153.5 ($C_{q,ar.}$), 148.7 ($C_{q,triazole}$), 122.4 (=CH), 115.6 ($CH_{ar.}$), 70.0 (N-CH_2-O), 68.4 (CH_2-O), 39.0 ($C_{q,tBu}$), 29.2 (CH_2), 26.9 (CH_3), 26.2 (CH_2), 25.5 (CH_2) ppm. MS (DCI, NH_3): calcd. for $[M + H]^+$ 585.3; found 585.4.

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

1,4-Bis[4-(1*H*-1,2,3-triazol-4-yl)butoxy]benzene (9): Compound **19** (93 mg, 159 μmol, 1 equiv.) was added to a mixture of THF (7 mL) and a 1 M aqueous solution of sodium hydroxide (7 mL), and the mixture was stirred for 16 h at 50 °C. Then water (2.5 mL) was added and a 37 % solution of hydrochloric acid was added to neutral pH. A white precipitates formed, which was filtered and dried in an oven. Compound **9** was obtained as a white powder in a yield of 65 %. ^{1}H NMR (300 MHz, DMSO): δ = 7.60 (s, 2 H, H_b), 6.82 (s, 4 H, H_e), 3.90 (t, ^3J = 7 Hz, 4 H, H_d), 3.34 (br., 2 H, NH_a), 2.69 (t, ^3J = 7 Hz, 4 H, H_c), 1.72 (m, 8 H, CH_2) ppm. The ^{13}C NMR spectrum could not be recorded because of the low solubility **9**.

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

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

2,3,6,7,10,11-Hexakis(1-hexyl-1,2,3-triazol-4-ylbutoxy)triphenylene (10): Compound **21** (42 mg, 52 μmol, 1 equiv.) and hexyl azide (50 mg, 393 μmol, 7.5 equiv.) were added to THF/water (1:1, 6 mL), followed by copper sulfate (18 mg, 95 μmol, 1.8 equiv.) and sodium ascorbate (24 mg, 237 μmol, 4.5 equiv.). After 16 h of vigorous stirring at room temp., AcOEt (15 mL) and water (5 mL) were added and the organic phase was extracted with AcOEt (2 × 5 mL), washed with aqueous NH_4Cl (2 × 10 mL), brine (10 mL), and water (10 mL), and dried with Na_2SO_4. After distillation of the solvents, the residue was purified by chromatography (SiO_2: AcOEt/MeOH, 98:2) to give **10** as a white powder in a yield of 50 %. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.84 (s, 6 H, H_d), 7.35 (s, 6 H, H_a), 4.26 (m, ^3J = 7 Hz, 24 H, H_c, H_e), 2.82 (t, ^3J = 7 Hz, 12 H, H_b), 1.96 (m, 24 H), 1.83 (m, 12 H), 1.28 (m, 36 H), 0.86 (m, 18 H, H_f) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 149.3 ($C_{q,ar.}$), 148.0 ($C_{q,triazole}$), 123.7 ($C_{q,ar.}$), 121.0 (=CH), 107.2 ($CH_{ar.}$), 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) ppm. MS (DCI, CH_4): calcd. for $[M + H]^+$ 1569.1; found 1569.3.

1,2-Bis[(1-hexyl-1*H*-1,2,3-triazol-4-yl)methoxy]benzene (22): 1,2-Bis(prop-2-ynyloxy)benzene (251 mg, 1.35 mmol, 1 equiv.) and hexyl azide (379 mg, 2.98 mmol, 2,2 equiv.) was added to THF/water (1:1, 4 mL), followed by copper sulfate (152 mg, 0.80 mmol, 0.6 equiv.) and sodium ascorbate (177 mg, 1.75 mmol, 1.3 equiv.). The mixture was vigorously stirred at room temp. for 24 h. The organic phase was extracted with ethyl acetate (3 × 4 mL), washed with water (2 × 10 mL), and dried with Na_2SO_4. After distillation of the solvents, column chromatography (SiO_2: DCM/AcOEt, 0 to 20 %) gave **22** as a white powder in 86 % yield. R_f = 0.6 (TLC, DCM/AcOEt, 8:2). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.68 (s, 2 H, H_a), 7.09–6.89 (m, 4 H, H_c), 5.19 (s, 4 H, H_b), 4.32 (t, ^3J = 7 Hz, 4 H, H_d), 1.88 (m, ^3J = 7 Hz, 4 H), 1.31 (m, 12 H), 0.88 (t, ^3J = 7 Hz, 6 H, H_e) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 148.9 ($C_{q,ar.}$), 144.0 ($C_{q,triazole}$), 123.4 (=CH), 122.2 ($CH_{ar.}$), 115.5 ($CH_{ar.}$), 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) ppm. MS (DCI, NH_3): calcd. for $[M + H]^+$ 441.3; found 441.3.

Acknowledgments

The Agence Nationale de la Recherche (ANR) MOLSIC is gratefully acknowledged for funding. A. P. thanks the French Ministère de l'Enseignement Supérieur et de la Recherche for a Ph. D. grant.

Keywords: Synthesis design · Surface chemistry · Grafting · Ion–molecule interactions · Amino acids · Nitrogen heterocycles

[1] S. Morita, F. J. Giessibl, E. Meyer, R. Wiesendanger (Eds.), *Noncontact Atomic Force Microscopy*, Springer International Publishing, Cham, Germany, **2015**.
[2] R. 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**, 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 Trans. 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**, 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.

Received: August 19, 2015
Published Online: November 30, 2015