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RESEARCH ARTICLE

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A Cross-Shaped Monomer as Building Block for Molecular Textiles

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Dedicated to Prof. *Robert Deschenaux* on his retirement

The exploration of new materials is timeless. Especially 2D-materials have gotten much interest in the last decades. This work proposes a new route towards a fascinating class of 2D materials: molecular textiles. The suggested bottom-up approach focuses on the 2D self-assembly of a cross-shaped monomer at the water/air interface. A 3D cross-shaped motive was designed, synthesized, and characterized, which exhibits the required structural features, *i.e.*, static and dynamic control. Analysis of the cross-shaped motive by ^{1}H-NMR spectroscopy, X-ray structure, and chiral stationary phase HPLC proved the rigidity and stability of the system, and thus also its potential for the here suggested new strategy towards molecular textiles. Three variants of a *Schiff*-base precursor pair functionalized monomer were synthesized and characterized by ^{1}H-NMR spectroscopy, ^{13}C-NMR spectroscopy, and mass spectrometry. Finally, the network formation of the monomer is shown to be triggered by deprotonation of its ammonium salt, corroborated with FT-IR analysis.

Keywords: covalent templating, cross-shape, materials science, molecular textiles, *Schiff* bases.

Introduction

Materials consisting of 2D interwoven yarns and threads are an exceptional class of materials due to their flexibility, stability, and shape adaptability.[1] The extraordinary properties of these so-called textiles make them crucial in everyday life and provoke the question on whether we can mimic them on a molecular scale.[2] Fabricating molecular interwoven materials and topologies have gained interest over the last years. However, it has proven challenging due to the scarcity of molecular building blocks resembling the cross-over points of entangled strands.[3] Nevertheless, several successful examples have emerged in the last years based on covalent,[4] metal coordinated,[5–7] and supramolecular[8,9] assemblies. These works show the rise in expertise in synthesizing large-scale molecular weaves effectively. Converting this knowledge gained in 3D molecular weaving to 2D weaving, needed for molecular textiles, gives rise to an additional challenge: the controlled directional interlinking of the molecular building blocks. In recent years, a couple of attempts have succeeded in establishing the 2D-directed assembly. *Wang et al.* used the stepwise assembly of a sandwich-layer surface-mounted molecular organic framework (SURMOF) based on quadritopic organic linkers.[10] Utilizing a size miss-match strategy during the *Glaser* acetylene coupling and subsequent metal removal, they obtained stacked 2D-molecular weaved sheets. Single-layer molecular weaves were reported by *Leigh et al.*,

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which upon crystallization of a *pseudo* interwoven nine-fold coordinated metal complex and subsequent exfoliation, could isolate large mono-layer sheets.[11] Comparison of the mechanical properties of the molecular fabric with its linear polymer analog showed comparable strength while the molecular textile's flexibility increased. The current state-of-the-art fabrication of molecular textiles show promising results but also highlights the synthetic and analytical challenges that accompany them, like the need for highly ordered precursors, the requirement of templating, and the mono-layer scale modification and characterization. Therefore, we are contributing to this fascinating field by exploring new routes towards molecule textiles. Here, we propose a newly designed concept that involves self-assembly at the water surface, proven to be an excellent place for the controlled 2D assembly of various organic networks.[12,13] We report the rational design, synthesis, and characterization of monomer candidates incorporating a newly derived 3D cross-shaped motive.

Results and Discussion

Design and Retrosynthesis

Our bottom-up approach is sketched in *Figure 1*. Here, we visualized that in a textile structure, the infinite number of cross-over points between yarns and threads, could be resembled by a cross-shaped monomer. This monomer, bearing a hydrophilic (blue) and hydrophobic (red) side, is linked together through a covalent template (yellow) that should give rise to the cross-shape. This motive will bring the required static control, *i.e.*, prevent the intra-molecular reaction of the polymerizable groups, hence forcing the inter molecular reaction. Assembling the amphiphilic building block at the water surface would allow us to bring them in close proximity, pre-organize them facing the same orientation, and link them together in a 2D fashion. Here, the direction of all hydrophilic parts towards the water and hydrophobic parts towards the air, forces the monomers to link through alternating top-bottom-top-bottom. Hence, the thereby obtained network consists of covalently interlinked yarns and threads, which after cleavage of the covalent template, would yield an exclusively mechanical interwoven molecular textile.

In order to explore the proposed route, a potential monomer incorporating all criteria mentioned above was designed, synthesized and characterized by some preliminary investigations (*Figure 1*, right). The cross-shape, which should give rise to the required static control, should arise from the center moiety depicted in yellow. DFT optimized geometry calculations (*Supporting Information*, *Figure S1*) indicate that when two biphenyl motives are bridged over two esters in the 2-2′ and 3-3′ positions, respectively, it adopts a cross-

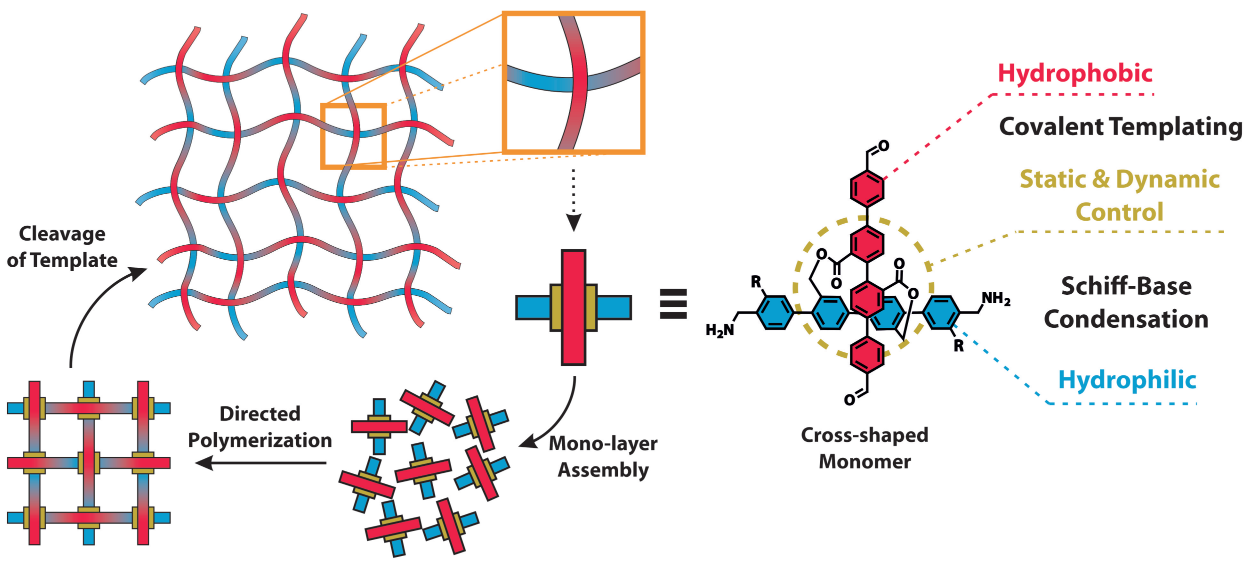


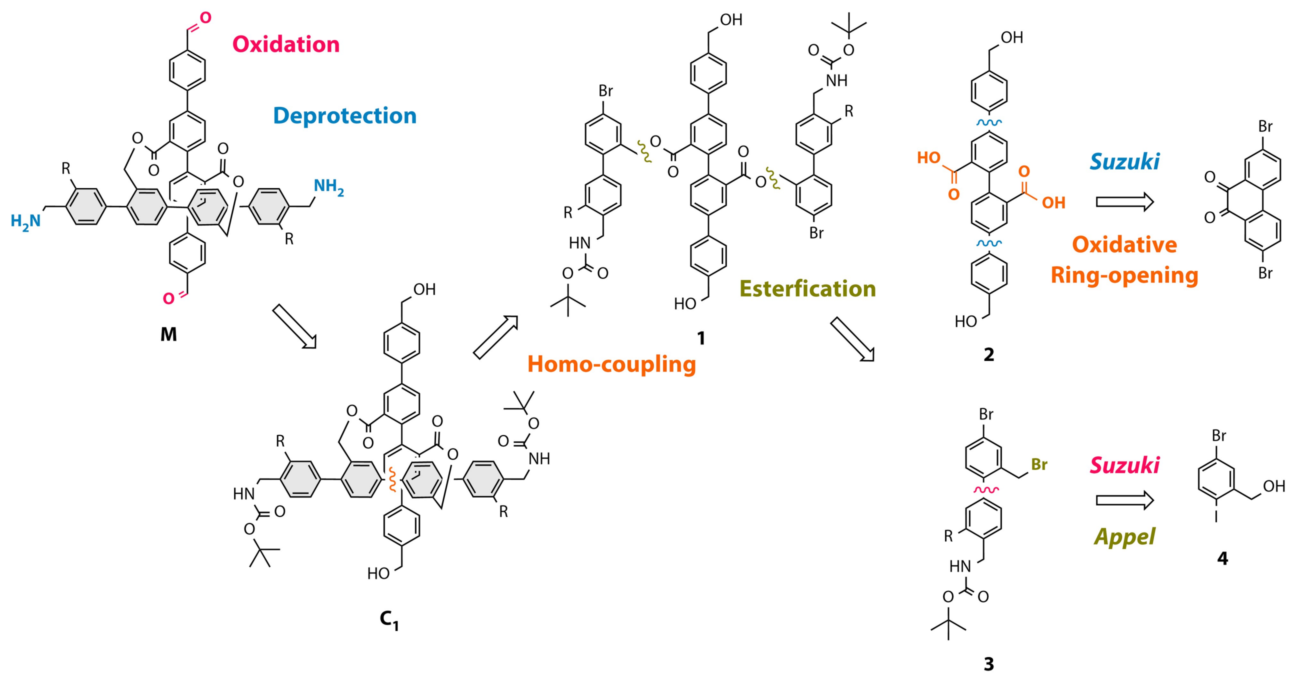
Figure 1. *left)* Schematic illustration of our bottom-up approach, utilizing the assembly of an amphiphilic monomer at the air-water interface to pre-align them into a monolayer. Polymerization by reacting the bottom side of one monomer with the top of neighboring ones and *vice versa*, and finally by cleavage of the template a molecular textile could be obtained. *right)* Molecular design of the cross-shaped monomer.

shaped 3D configuration. A further advantage is that this motive directly incorporates the required dynamic control due to the cleavable nature of ester bonds, *i.e.*, covalent templating.[14,15] In our design, we extended the biphenyls to *p*-tetraphenyl's bearing on one side of the molecule aldehydes and the other amines. This *Schiff*-base formation was chosen as optimal polymerization strategy due to its reversible character and proven ability to form 2D polymers on the water surface.[16–18] Finally, the asymmetric character of both terphenyl subunits should introduce amphiphilicity. The bare protonated amine groups should favor this terphenyl for the water surface, an effect that could be further enhanced by suitable R-groups. Here we considered three candidates with the rationale of simplicity (R=H), introducing hydrophilicity (R=OH), and improved solubility (R=OMe).

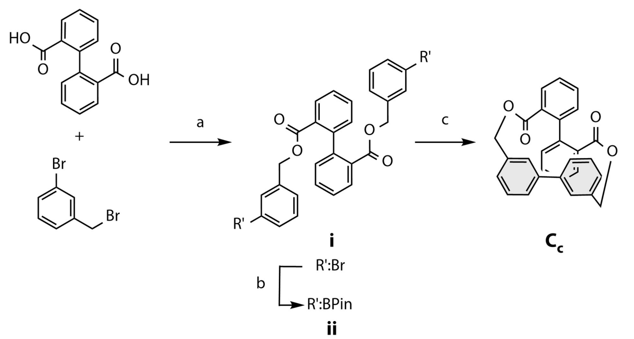
In *Scheme 1*, the retrosynthetic analysis of monomer **M** is shown. Monomer **M** can be obtained in a late stage from intermediate $\mathbf{C_1}$ through oxidation of the alcohols and acidic deprotection of the Boc-protected amines. The critical step of the synthetic strategy would be the assembly of the macro-cycle through an intramolecular homo-coupling reaction of precursor **1**. Here, a pre-organized system was preferred over a bi-molecular reaction because it potentially has more reaction control in terms of unwanted side reactions, *e.g.*, linear polymer formation. Precursor **1** could be formed through the esterification of building blocks **2** and **3**, which could be assembled through a series of well-established synthetic steps including, *Suzuki*, *Appel*, and ring-opening reactions starting from commercially available precursors.

Cross-Shaped Motive

In order to confirm the cross-shaped motive and establish a synthetic pathway for the macro-cyclization, the simplest form of the 'biphenyl cross', bearing hydrogens on the peripheral 4-4′ positions, was investigated. The preparation of cross $\mathbf{C_C}$ was envisioned as described before: two-fold esterification followed by a homo-coupling as shown in *Scheme 2*. In the first step, **i** was obtained in 76% yield through a two-fold cesium fluoride mediated substitution of 3-bromo benzyl bromide in dry-DMF, modified from a literature-known procedure.[19] This approach was preferred over other suitable and even higher yielding (90%) esterifications, *e.g.*, *Steglich* (*Supporting Information*, page S7), due to the compatibility with the functional groups of the envisioned larger systems. With **i**, initial attempts of homo-coupling were performed through reductive nickel-mediated macrocyclization, which did not result in the expected product but mainly in dehalogenation. A suitable approach was found, based on the work of *Darzi et al.*,



Scheme 1. Retrosynthetic analysis of cross-shaped monomer **M** (R=H, OH, OMe).



Scheme 2. Synthesis of cross $\mathbf{C_C}$. Conditions: a) CsF, DMF, r.t., 20 h, 78 %. b) $PdCl_2$(dppf), KOAc, B_2Pin_2, DMSO, 80 °C, 4 h. c) $PdCl_2(PPh_3)_2$, KF, $B(OH)_3$, HF/H_2O (9 : 1), r.t., 22 h, 48 % over two steps.

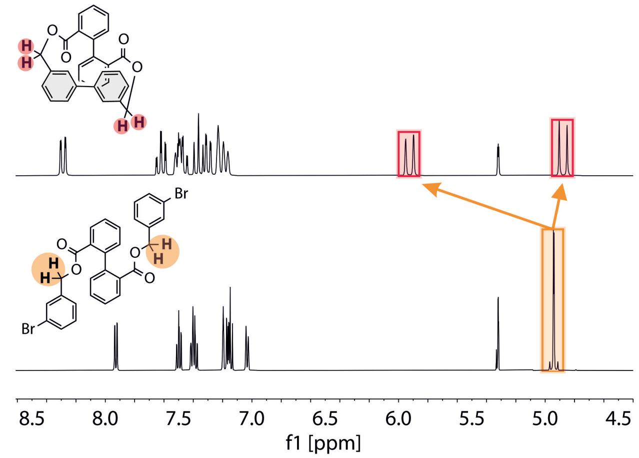


Figure 2. Stacked ^{1}H-NMR spectra of top) cross $\mathbf{C_C}$ and bottom) **i** in CD_2Cl_2; the benzylic protons of **i** (orange) split into two distinct signals upon macro-cyclization to $\mathbf{C_C}$ (red).

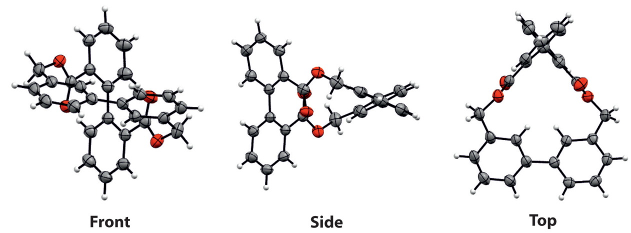


Figure 3. Solid-state structure of cross (*M*)-$\mathbf{C_C}$ plotted as ORTEP plots from different perspectives with 50 % probability.

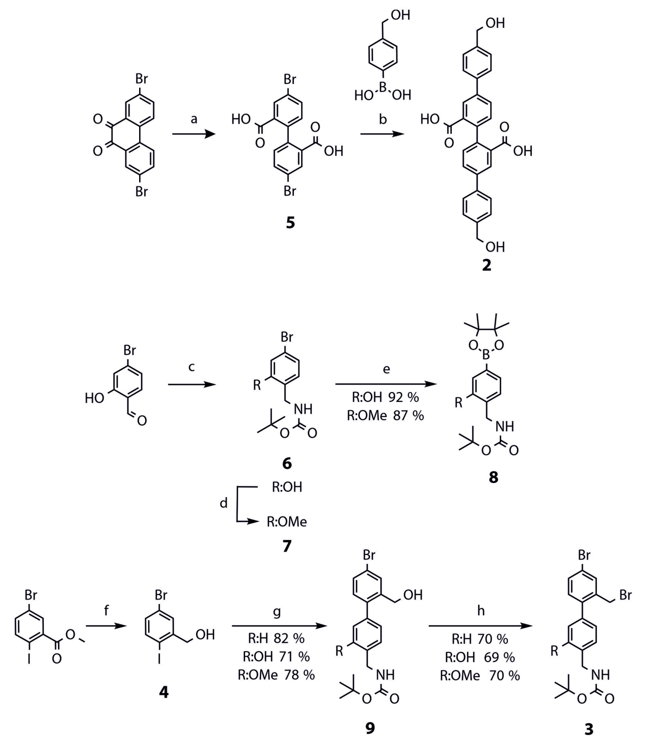
where a Pd-catalyzed homo-coupling of boronic esters could cyclize strained aromatic systems.[20] Dibromide **i** was therefore converted to diboronic ester **ii** through standard *Miyaura*-borylation conditions in DMSO. In the final reaction step, the homo-coupling of the boronic esters seemed to work well. A simple screening of conditions (*Supporting Information*, *Table S1*) proved that employing a high catalyst loading leads to high yields. Thus, performing the reaction with 1 equiv. of $Pd(PPh_3)_2Cl_2$ yielded $\mathbf{C_C}$ in 74 %. Interestingly, the reaction also worked efficiently with impure starting material **ii**, which is why we refrained from its tedious purification. An alternative route was investigated by directly converting **i** to cross $\mathbf{C_C}$ through an *in-situ Miyaura*-borylation followed by *Suzuki* reaction using only 1 equiv. of bis(pinacolato borane) (B_2Pin_2) and potassium carbonate (K_2CO_3) as a strong base. The conditions yielding the best result (43 %) are shown in the *Supporting Information*, page S7. However, due to the lower control over catalyst *vs.* substrate stoichiometry, the oxidative homo-coupling was used as the main macro-cyclization approach in this work.

With cross $\mathbf{C_C}$ in hand, we studied the 3D conformation, which directly indicated the suspected rigid structure through nuclear magnetic resonance (NMR) spectroscopy. Comparison of the ^{1}H-NMR spectra of $\mathbf{C_C}$ with precursor **i** showed that the protons of the benzylic positions next to the esters split in two distinct signals, of which one in a similar range while the other shifts downfield (*Figure 2*). Through 2D-NMR, it was confirmed that the protons are rendered diastereotopic. The cross-shaped structure was proven by X-ray crystallography (*Figure 3*) of a single-crystal obtained through slow vapor diffusion of heptane into a solution of cross $\mathbf{C_C}$ in toluene. The X-ray structure proves that the motive is adapting a 3D cross-shaped structure with the opposing biphenyls almost perpendicular, as seen in the front-view image.

The isolated $\mathbf{C_C}$ is a racemic mixture of two atropisomers arising from the helical twist of the diphenic acid motive (*Supporting Information*, *Figure S2*). The racemic mixture was separated by chiral stationary phase HPLC (heptane/ethyl acetate 6 : 4), and circular dichroism (CD) was measured for the pure enantiomers. The CD spectra indicated that the cotton bands have opposed signs (*Supporting Information*, *Figure S3*). By comparison to DFT calculated spectra, the first eluting isomer was assigned to the (*M*)-isomer and, therefore, the second to the (*P*)-isomer (*Supporting Information*, *Figures S4–S6*). The enantiomeric and thermal stability, *i.e.*, stability of the cross-shape, was investigated by heating a solution of (*P*)-$\mathbf{C_C}$ in isobutyl acetate at 100 °C for 24 h. Analysis by chiral HPLC (*Supporting Information*, *Figure S7*) using 1,1′-biphenyl (**BP**) as an internal standard revealed no decomposition nor racemization. In other words, the diester cross motive $\mathbf{C_C}$ has the enantiomeric stability required for further processing as subunit in the monomer of the textile strategy.

Monomer Synthesis

The synthesis of monomers $\mathbf{M_H}$, $\mathbf{M_{OH}}$, and $\mathbf{M_{OMe}}$ started with the preparation of building blocks **2** and **3** shown in *Scheme 3*. Di-acid **2** was obtained in two steps. First, 4-4′ dibromodiphenic acid **5** was synthesized, in high yield (87 %), through a modified oxidative ring-opening[21] of 2,7-dibromophenanthrene-9,10-dione in the presence of H_2O_2 and NaOH. In the following step, **5** was reacted with [4-(hydroxymethyl)phenyl]boronic acid in a two-fold *Suzuki* cross-coupling reaction using tetrakis(triphenylphosphine)palladium(0) as catalyst and Na_2CO_3 as a base to obtain **2** in excellent yields (93 %). Purification was performed by base extraction, acidification, and subsequent filtration, where the choice of base was found to be crucial for simplifying the

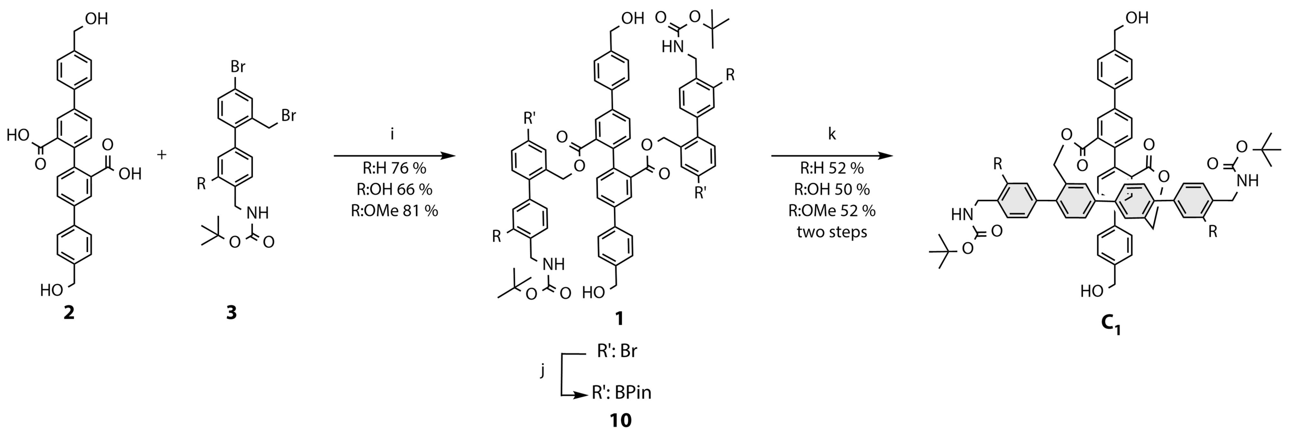


Scheme 3. Synthesis of precursors **2** and **3**. Conditions: a) H_2O_2, NaOH, THF/H_2O (1:1), 0 °C-r.t., 3 h, 87 %. b) $PdCl_2(PPh_3)_2$, Na_2CO_3, dioxane/H_2O (1:1), 95 °C, 16 h, 93 %. c) Boc-NH_2, Et_3SiH, TFA, CH_2Cl_2/acetonitrile, r.t., 22 h, 83 %. d) MeI, K_2CO_3, DMF, r.t., 3 h, 96 %. e) $PdCl_2$(dppf), KOAc, dioxane, 85 °C, 4 h. f) DIBAL-H, CH_2Cl_2/toluene (1:1), 0 °C-r.t., 3 h, quant. g) $PdCl_2$(dppf), Na_2CO_3, THF/H_2O (4:1), 65 °C, 4–16 h. h) CBr_4, PPh_3, CH_2Cl_2, 0 °C-r.t., 5–20 h.

work-up. While K_3PO_4 resulted in salt residues in the product even after several washing steps with water, Na_2CO_3 circumvented this problem.

The synthesis of the three bromides **3** started with the preparation of the hydroxy- and methoxy-functionalized boronic esters $\mathbf{8_{OH}}$ and $\mathbf{8_{OMe}}$, respectively. Starting from 4-bromo-2-hydroxybenzaldehyde, the Boc-protected amine **6** could be obtained on gram scale through an already reported[22] reductive amination with *tert*-butyl carbamate in the presence of trifluoro acetic acid (TFA) and tri-ethylsilane. Next, the methyl group was introduced through a S_N2 reaction with methyl iodide to obtain **7**, which was used as the building block for the methoxy monomer. From here, the synthesis towards both boronic esters was done through *Miyaura* borylation, yielding the desired building blocks $\mathbf{8_{OH}}$ and $\mathbf{8_{OMe}}$ in 92 % and 87 %, respectively. Methyl 5-bromo-2-iodobenzoate was quantitatively reduced to alcohol **4** with DIBAL-H before it was coupled to commercially available 4-(*N*-Boc-aminomethyl)phenylboronic acid pinacol ester, $\mathbf{8_{OH}}$ or $\mathbf{8_{OMe}}$ through a *Suzuki* reaction. The selective cross-coupling on the iodine was found to be best performing using [1,1′-bis(diphenylphosphino)ferrocene] palladium(II) dichloride ($PdCl_2$(dppf)) as the catalyst at 65 °C in a mixture of tetrahydrofuran (THF) and water. After purification by column chromatography, the desired alcohols **9** were obtained in good yields of up to 82 %. Conversion of **9** to **3** was done by applying standard *Appel*-reaction conditions, including triphenylphosphine and CBr_4 in dichloromethane (CH_2Cl_2). By column chromatography, the desired building blocks $\mathbf{3_H}$, $\mathbf{3_{OH}}$, and $\mathbf{3_{OMe}}$ bearing a hydrogen, hydroxy and, methoxy group, respectively, could be obtained in good yields of *ca.* 70 %.

Scheme 4 shows how the previously prepared building blocks were assembled into di-esters $\mathbf{1_H}$, $\mathbf{1_{OH}}$, $\mathbf{1_{OMe}}$ by using CsF in DMF, as mentioned in the synthesis of cross $\mathbf{C_C}$. Here, the hydroxy functionalized ester was obtained in slightly lower yields compared to the others, probably caused by the slight acidic phenol proton interfering with the base. The bromines were converted to boronic esters through *Miyaura*-borylation using B_2Pin_2 in the presence of $PdCl_2$(dppf) as catalyst and potassium acetate (KOAc) as the base. After work-up, crude **10** was collected and directly used in the previously established oxidative homo-coupling reaction with bis(triphenylphosphine)palladium chloride, potassium fluoride, and boric acid. Crosses $\mathbf{C_{1,H}}$, $\mathbf{C_{1,OH}}$, and $\mathbf{C_{1,OMe}}$ could be isolated in comparable yields (*ca.* 52 %) over two steps, by column chromatography and a subsequent washing



Scheme 4. Synthesis of crosses $\mathbf{C_{1,H}}$, $\mathbf{C_{1,OH}}$ and $\mathbf{C_{1,OMe}}$. Conditions: i) CsF, DMF, r.t., 24 h. j) $PdCl_2(dppf)$, KOAc, DMSO or dioxane, 80–85 °C, 4 h. k) $PdCl_2(PPh_3)_2$, KF, $B(OH)_3$, THF/H_2O (9:1), r.t., 24 h.

step with cold-MeOH for $\mathbf{C_{1,H}}$ and $\mathbf{C_{1,OH}}$ or size exclusion chromatography for $\mathbf{C_{1,OMe}}$, to remove the co-eluting triphenyl-phosphine oxide (PPh_3O). The presence of PPh_3O restricted the use of higher catalyst loadings to prevent purification issues. The ^{1}H-NMR of all crosses (*Supporting Information*, Pages S56, S94 and S131) shows the expected splitting of the benzylic ester protons, confirming the successful assembly of the center moiety.

Slow vapor diffusion of heptane into a solution of $\mathbf{C_{1,H}}$ in chlorobenzene provided single crystals suitable for x-ray diffraction analysis. The solid-state structure of $\mathbf{C_{1,H}}$ (*Figure 4*) confirms both, the similar cross-shaped conformation as cross $\mathbf{C_C}$ and the presence of

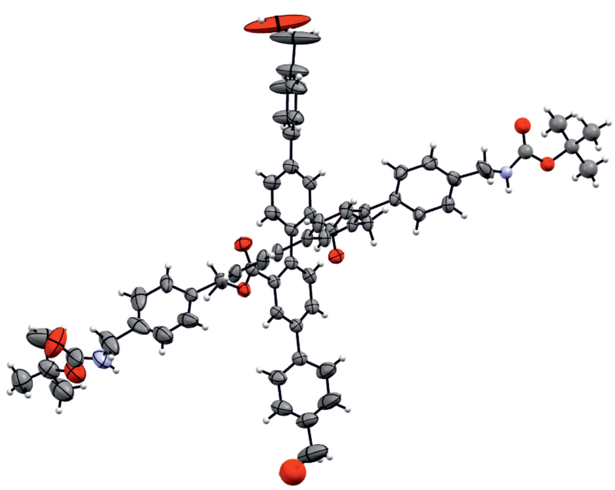
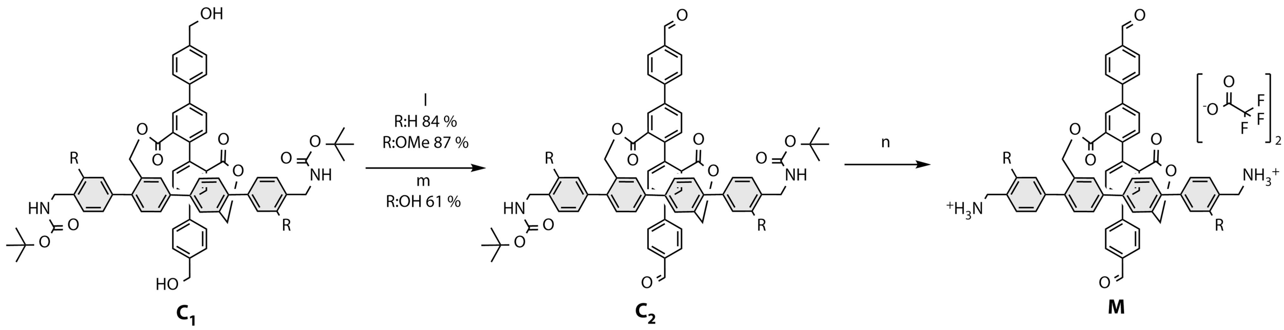


Figure 4. Solid-state structure of cross (*P*)-$\mathbf{C_{1,H}}$, plotted as ORTEP plots with 50% probability. Plotted as single enantiomer and without solvent for clarity.

two atropisomers (*Supporting Information*, *Figure S9*). However, a slight difference can be observed in the angle between the phenyl backbones.

While $\mathbf{C_C}$ approached an almost 90° angle between both biphenyl subunits, the solid structure of $\mathbf{C_{1,H}}$ indicates a smaller angle (*ca.* 85° *vs.* 70°), which probably arises due to the steric hindrance of the phenyl groups in the 4-4′ position with respect to the central moiety and the benzylic protons.

With the crosses $\mathbf{C_{1,H}}$, $\mathbf{C_{1,OH}}$ and, $\mathbf{C_{1,OMe}}$ in hand, two steps remained, as displayed in *Scheme 5*. First, the oxidation of the alcohols to the aldehydes was performed. For $\mathbf{C_{1,H}}$ and $\mathbf{C_{1,OMe}}$ this was achieved in high yields (84% and 87%) with *Dess–Martin* periodane (DMP), using either dichloromethane or a mixture of THF and CH_2Cl_2 depending on the solubility. However, for $\mathbf{C_{1,OH}}$ this path resulted in enormous side product formation and a severe drop in yield (20%). Most likely the phenol subunits were partially oxidized to their quinone form under these reaction conditions. This hypothesis was further supported by *Magdziak et al.*, who reported the oxidation of phenols with 2-iodoxybenzoic acid,[23] which is the degradation product of DMP. As alternative the milder oxidant manganese(IV)oxide in DMSO was considered and resulted in the successful synthesis of $\mathbf{C_{2,OH}}$ in moderate yields (61%). The corresponding aldehydes $\mathbf{C_{2,H}}$, $\mathbf{C_{2,OH}}$, $\mathbf{C_{2,OMe}}$ were treated with TFA in dichloromethane, obtaining monomers $\mathbf{M_H}$, $\mathbf{M_{OH}}$, and $\mathbf{M_{OMe}}$ as the ammonium TFA salt after solvent evaporation in quantitative yields. Important to note is that throughout the final reaction steps, the diester interlinkage responsible for the cross-shape remains untouched, as indicated by the characteristic splitting of its benzylic



Scheme 5. Synthesis of monomers $\mathbf{M_H}$, $\mathbf{M_{OH}}$ and $\mathbf{M_{OMe}}$. Conditions: l) DMP, THF/CH_2Cl_2 (4:1) (R:H), CH_2Cl_2 (R:OMe); 0 °C-r.t., 1.5 h. m) MnO_2, DMSO, r.t., 48 h. n) TFA, CH_2Cl_2, r.t., quant.

protons, shown in the ^{1}H-NMR spectra (*Supporting Information*) of compounds $\mathbf{C_{2,H}}$, $\mathbf{C_{2,OH}}$, $\mathbf{C_{2,OMe}}$, $\mathbf{M_H}$, $\mathbf{M_{OH}}$, and $\mathbf{M_{OMe}}$.

Schiff-Base Condensation

The cross-shaped monomers $\mathbf{M_H}$, $\mathbf{M_{OH}}$, and $\mathbf{M_{OMe}}$ were developed to investigate their potential as precursors of molecular textiles. However, the investigation and optimization of their self-orientation, self-assembly, oligo- and polymerization properties at the water surface will take at least another year. As fundamental prerequisite for the textile approach, the ability of the monomer to polymerize by *Schiff*-base condensation was investigated in solution. As preliminary assessment the polymerization behavior of the cross-shaped motive was analyzed using the monomer $\mathbf{M_H}$.

A saturated sodium hydrogen carbonate solution was added to the solution of $\mathbf{M_H}$ in dichloromethane/TFA from the final N-Boc-deprotection step. The immediate formation of a white precipitate was detected, as expected for the monomer exposing four polymerizable groups. After collection, the white solid showed to be insoluble in a variety of solvents, *e.g.*, CH_2Cl_2, THF, DMSO, DMF, which suggested the formation of a densely cross-linked network. Evidence was found in a comparison of the *Fourier*-transform infrared (FT-IR)-spectra of precursor $\mathbf{C_{2,H}}$, monomer $\mathbf{M_H}$ and the suspected polymer, shown in *Figure 5*. Upon deprotection of $\mathbf{C_{2,H}}$ the N–H stretch signal originating from the N-Boc group vanishes. At the same time, a typical ammonium band appears, while the carbonyl (C=O) at 1697 cm^{-1} and C–H in the 2600–2800 cm^{-1} region signals of the aldehyde remain. Then, considering the precipitate's IR spectrum, all of these characteristics disappear while there is a clear appearance of a peak at 1645 cm^{-1}, originating from the C=N vibration, *i.e.*, imine bond formation. The analysis of the IR spectra thus corroborates the interlinking of the monomers by *Schiff*-base condensation in the insoluble polymer, and thus the polymerization of the monomer $\mathbf{M_H}$ upon deprotonation of the ammonium group.

Conclusions and Outlook

A new strategy for fabricating molecular textiles is proposed based on the self-assembly of cross-shaped monomers at the water surface. The design and synthesis of a new 3D cross-shaped motive are reported based on the two-fold ester linkage of two biphenyl units in the 2-2′ and 3-3′ positions, respectively. The absolute configuration and required structural features of the racemic mixture were confirmed by X-ray structure analysis, while chiral stationary phase HPLC experiments proved the thermal stability of the enantiomers. A set of three potential monomer candidates were synthesized with, the oxidative Pd mediated homo-coupling as a key-step. All three monomers were acquired as their TFA-salt, proven by NMR and FT-IR spectroscopy.

As preliminary interlinking test, $\mathbf{M_H}$ showed successful polymerization upon deprotonation of the terminal ammonium groups, indicated by the appearance of the characteristic imine signal in the FT-IR spectra.

The deprotonation-triggered *Schiff*-base condensation initiation shows the potential of these building blocks as monomers on the water surface, which is the step we are currently working on.

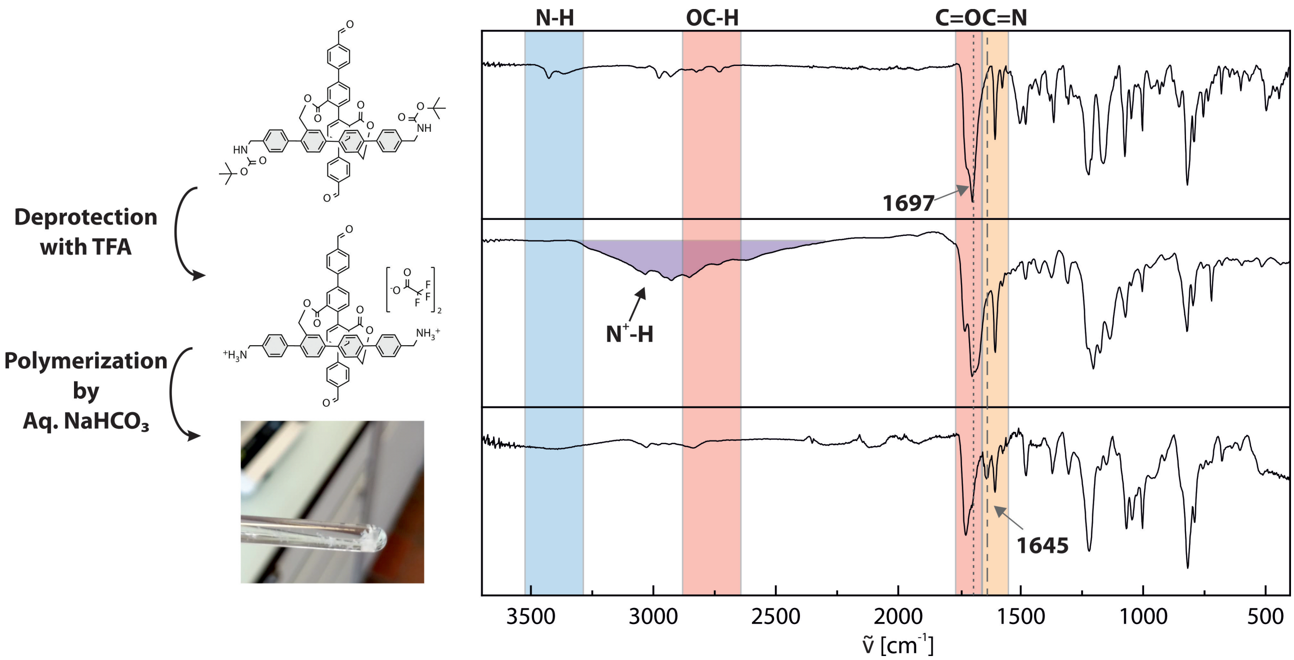


Figure 5. IR-spectra of: Top) cross $\mathbf{C_{2,H}}$, Middle) monomer $\mathbf{M_H}$, Bottom) Polymer. Deprotection of the precursor results in the transformation of N-Boc (blue) to RN^+H_3 (purple) while the aldehyde RCOH and C=O (1697 cm^{-1}) (red) signal remain. Treatment of monomer $\mathbf{M_H}$ with a base initiates polymerization indicated by benzylic imine C=N (orange) signal at 1645 cm^{-1}, while the ammonium and aldehyde signals are gone.

Experimental Section

General

All chemicals and solvents were purchased from *Sigma–Aldrich, Acros, Apollo Scientific, Alfa Aesar and Fluorochem* and used as received. NMR Solvents were obtained from *CIL Cambridge Isotope Laboratories, Inc., Acros, Sigma–Aldrich*, or *Apollo Scientific*. Dry solvents were used as crown capped and purchased from *Acros* and *Sigma–Aldrich*. Column chromatography was performed manually or on a *Biotage Isolera* using *SilicaFlashR P60* from *Silicycle* with particle size of 40–63 μm (230–400 mesh) as stationary phase. TLC was performed with silica gel *60 F254* glass plates purchased from *Merck*. NMR Experiments were performed on *Bruker Avance III* NMR spectrometers operating at 250, 400 or 500 MHz proton frequencies. The instruments were equipped with a direct-observe 5 mm *BBFO* smart probe (250, 400 MHz), or an indirect-detection 5 mm *BBI* probe (500 MHz). All probes were equipped with actively shielded z-gradients (10 A). The chemical shifts are reported in ppm relative to TMS or referenced to residual solvent peak and the J values are given in Hz. Infrared spectra were recorded neat with an ATR equipped *Shimadzu IRTacer-100*. Monomers $\mathbf{M_H}$, $\mathbf{M_{OH}}$, and $\mathbf{M_{OMe}}$ were recorded with a *Bruker Alpha II* as a pellet mixed and pressed with anhydrous KBr. High-resolution mass spectra (HR-MS) were measured with a *Bruker Maxis 4G* ESI-TOF instrument. CD Measurements were performed on a *JASCO J-1500 CD* Spectrophotometer in a 1 cm quartz glass cuvette. For analytical HPLC, a *Shimadzu LC-20AT* HPLC was used, equipped with a diode-array UV/Vis detector (*SPD-M20A* VP from Shimadzu, λ=200–600 nm) and a column oven *Shimadzu CTO-20AC*. For preparative HPLC, a *Shimadzu LC-20AP* HPLC was used equipped with a diode-array UV/Vis detector (*SPD-M20A* VP from *Shimadzu*, λ=200–600 nm). The used column for analytical separation on chiral stationary phase was a *Chiralpak IG*, 5 μm, 4.6×250 mm, *Daicel Chemical Industries Ltd* and for preparative separation, *Chiralpak IG*, 5 μm, 30×250 mm, *Daicel Chemical Industries Ltd.*

Synthesis of Cross $\mathbf{C_C}$

Bis[(3-bromophenyl)methyl] [1,1′-biphenyl]-2,2′-dicarboxylate (**i**). Diphenic acid (1.10 g, 1 equiv.), 3-bromobenzylbromide (3.35 g, 2.9 equiv.) and cesium fluoride (2.00 g, 2.9 equiv.) were added to a 50 mL round-bottom flask and put under inert atmosphere. 20 mL dry DMF was added, and the mixture was allowed to stir for 24 h at room temperature before being poured on ice cold water. The aqueous phase was extracted with CH_2Cl_2 three times to obtain the crude which was purified by silica column chromatography (cyclohexane/AcOEt 10:0 to 8:2 *v/v*) obtaining the product **i** in the third band as a colorless oil (2.03 g, 76 % yield). R_f (SiO_2, cyclohexane/AcOEt 9:1) 0.47. ^{1}H-NMR (500 MHz, CD_2Cl_2): 7.93 (*dd*, J=7.8, 1.4, 2H), 7.50 (*td*, J=7.5, 1.4, 2H), 7.45–7.34 (*m*, 4H), 7.25–7.10 (*m*, 6H), 7.03 (*dt*, J=7.7, 1.4, 2H), 4.94 (*d*, J=2.4, 4H). ^{13}C-NMR (126 MHz, CD_2Cl_2): 166.98, 143.43, 138.39, 131.96, 131.46, 131.43, 130.71, 130.35, 129.71, 127.65, 127.22, 122.62, 65.98. HR-ESI-MS (pos): 600.9609 ($C_{28}H_{20}Br_2NaO_4^+$, $[M+Na]^+$; calc. 600.9621). ATR-FT-IR: 3068*m*, 2924*m*, 2850*m*, 1707*s*, 1597*m*, 1570*m*, 1443*m*, 1369*w*, 1289*s*, 1257*s*, 1127*s*, 1112*m*, 1049 *m*, 985*w*, 880*w*, 834*w*, 774*m*, 753*s*, 707*w*, 678*m*, 566*m*, 526*w*, 424*m*.

Bis{[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]methyl} [1,1′-biphenyl]-2,2′-dicarboxylate (**ii**). Dibromide **i** (1.06 g, 1.83 mmol, 1 equiv.), B_2Pin_2 (0.96 g, 3.73 mmol, 2.2 equiv.) and KOAc (1.08 g, 11.1 mmol, 6 equiv.) were loaded into a 100 mL flame-dried *Schlenk* tube and cycled between vacuum and argon three times. Dry DMSO (50 mL) was added, and the mixture was degassed with argon for 15 min. $PdCl_2$(dppf) (0.15 g, 0.19 mmol, 0.1 equiv.) was added, and the mixture was heated to 80 °C. The reaction was tracked through LC/MS, and after full consumption (4 h) of the starting material, the mixture was cooled down to room temperature, diluted with toluene, and washed three times with water. The organic phase was collected, dried with Na_2SO_4 and concentrated under reduced pressure obtaining the crude mixture which was used in the next step without further purification.

11*H*,22*H*-16,12:21,17-Di(metheno)dibenzo[*c*,*e*]-[1,8]dioxacycloicosine-9,24-dione (**C_C**). Crude diboronic ester **ii** (300 mg, 0.445 mmol, 1 equiv.) was added to a 1 L round-bottom flask and dissolved in 420 mL THF. $PdCl_2(PPh_3)_2$ (19 mg, 6 mol-%) and boric acid (152 mg, 2.46 mmol, 5.5 equiv.) were added and the mixture was stirred vigorously for 15 min. KF (29 mg, 0.5 mmol, 1.1 equiv.) was added followed by the addition of water (42 mL) and the mixture was stirred for 16 h at room temperature open to the air. THF was removed under reduced pressure and the remaining aqueous phase was extracted with CH_2Cl_2 three times. The organic fractions were combined, dried over Na_2SO_4 and concentrated in vacuum. The crude was subjected to SiO_2 column chromatography (cyclohexane/CH_2Cl_2 (8:2→1:1 *v/v*)) to obtain the product as a white solid (90 mg, 48 %) over two steps. R_f (SiO_2, cyclohexane/CH_2Cl_2 1:1) 0.44. ^{1}H-NMR (500 MHz, DMSO-d$_6$): 8.22 (*dd*, J=8.1, 1.4, 2H), 7.67 (*td*, J=7.5, 1.4, 2H), 7.58 (*dt*, J=7.8, 1.4, 2H), 7.52 (*td*, J=7.7, 1.4, 2H), 7.42 (*t*, J=7.6, 2H), 7.28 (*td*, J=7.7, 1.5, 4H), 7.06 (*d*, J=1.9, 2H), 5.77 (*d*, J=13.9, 2H), 5.04 (*d*, J=13.9, 2H). ^{13}C-NMR (126 MHz, DMSO-d$_6$): 164.99, 145.32, 139.59, 137.49, 132.35, 131.14, 130.38, 128.90, 127.33, 125.83, 124.96, 124.47, 64.32. HR-ESI-MS (pos): 443.1253 ($C_{28}H_{20}NaO_4^+$, $[M+Na]^+$; calc. 443.1254). ATR-FT-IR: 3058*m*, 3031*m*, 2936*m*, 2849*m*, 1724*s*, 1596*m*, 1572*m*, 1474*w*, 1428*m*, 1367*w*, 1277*m*, 1241*s*, 1136*m*, 1090 *m*, 1071 *s*, 1052 *m*, 1004*w*, 882*w*, 811*w*, 763*s*, 704*m*, 663*m*, 605*w*, 562*m*, 507*w*, 433*w*.

Synthesis of Monomer M_H

4,4′-Dibromo[1,1′-biphenyl]-2,2′-dicarboxylic Acid (**5**). To a 250 mL round bottom flask 2,7-dibromophenanthrene-9,10-dione (7.13 g, 19.5 mmol, 1 equiv.), THF (35 mL) and 10 % NaOH solution (16.5 mL, 41 mmol, 2.1 equiv.) were added and cooled down to 0 °C. A 30 % H_2O_2 solution (4.8 mL, 42.3 mmol, 2.1 equiv.) was added dropwise to the orange suspension and allowed to react at r.t. for 3 h. The resulting solution was quenched with sat. $NaHSO_3$, basified with sat. $NaHCO_3$ and washed with *tert*-butyl methyl ether. The aqueous phase was acidified with conc. HCl until pH < 2 and the formed solids were filtered off obtaining the product after washing with water and drying in vacuum oven overnight as an off-white solid (6.8 g, 87 %). ^{1}H-NMR (500 MHz, DMSO-d$_6$): 12.91 (br. s, 2H), 8.00 (*d*, J=2.2, 2H), 7.76 (*dd*, J=8.2, 2.2, 2H), 7.14 (*d*, J=8.2, 2H). ^{13}C-NMR (126 MHz, DMSO-d$_6$): 166.19, 141.08, 133.97, 132.32, 132.16, 131.96, 120.21. HR-ESI-MS (pos): 420.8678 ($C_{14}H_8Br_2O_4Na^+$, $[M+Na]^+$; calc. 420.8682).

1^4,4^4-Bis(hydroxymethyl)[1^1,2^1:2^4,3^1:3^4,4^1-quaterphenyl]-2^3,3^2-dicarboxylic Acid (**2**). A 100 mL *Schlenk* tube was charged with diacid **5** (1004 mg, 2.51 mmol, 1 equiv.), 4-(hydroxymethyl)phenylboronic acid (948 mg, 6.24 mmol, 2.5 equiv.) and Na_2CO_3 (2660 mg, 25.1 mmol, 10 equiv.) and cycled between argon and vacuum three times. 50 mL dioxane/H_20 1:1 mixture was added and argon was bubbled through for 15 min before $PdCl_2(PPh_3)_2$ (180 mg, 0.26 mmol, 0.1 equiv.) was added. The mixture was heated to reflux for 18 h, before cooled down, diluted in AcOEt, extracted three times with sat. $NaHCO_3$. The combined aqueous phases were acidified with conc.

HCl and the formed white precipitate was filtered off, washed thoroughly with water, subsequently with ice-cold EtOH and dried in a vacuum oven overnight obtaining the product as a white powder (1060 mg, 93 %). ^{1}H-NMR (500 MHz, DMSO-d$_6$): 12.62 (*s*, 2H), 8.15 (*d*, *J*=2.1, 2H), 7.87 (*dd*, *J*=8.0, 2.1, 2H), 7.75–7.69 (*m*, 4H), 7.49–7.43 (*m*, 4H), 7.31 (*d*, *J*=8.0, 2H), 5.25 (*s*, 2H), 4.57 (*s*, 4H). ^{13}C-NMR (126 MHz, DMSO-d$_6$): 167.79, 142.27, 141.53, 138.61, 137.31, 131.20, 128.96, 127.33, 127.20, 126.31, 62.57. HR-ESI-MS (pos): ($C_{28}H_{23}O_6$ [M+H]$^+$; 455.1489) 455.1480.

(5-Bromo-2-iodophenyl)methanol (**4**). To a solution of benzoate (5.3 g, 15.3 mmol, 1 equiv.) in dry CH_2Cl_2 (30 mL) was slowly added DIBAL-H (1.2 M in toluene, 29 mL, 34.8 mmol, 2.2 equiv.) at 0 °C. The mixture was gradually warmed up to r.t. and kept stirring until full conversion was confirmed by TLC (cyclohexane/AcOEt 7:3). The resulting mixture was diluted with AcOEt, and the reaction slowly quenched with MeOH and subsequently water. The resulting two-layer system was extracted with AcOEt (three times). The organic fractions were combined, dried with Na_2SO_4 and concentrated under reduced pressure yielding the alcohol as a white solid (4.8 g, 99 %). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.65 (*d*, *J*=8.3, 1H), 7.62 (*dd*, *J*=2.5, 0.8, 1H), 7.13 (*ddd*, *J*=8.3, 2.4, 0.6, 1H), 4.63 (*d*, *J*=5.8, 2H), 2.06–2.00 (*m*, 1H). ^{13}C-NMR (126 MHz, $CDCl_3$): 144.75, 140.45, 132.33, 131.32, 123.15, 94.77, 68.86. HR-ESI-MS (neg.): 310.8565 ($C_7H_5BrIO^-$, [*M*−H]$^-$; calc. 310.8574).

***tert*-Butyl {[4′-Bromo-2′-(hydroxymethyl)[1,1′-biphenyl]-4-yl]methyl}carbamate** (**9$_H$**). To a 100 mL *Schlenk* tube, (5-bromo-2-iodophenyl)methanol (1520 mg, 4.86 mmol, 1 equiv.), *tert*-butyl {[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]methyl}carbamate (1943 mg, 5.83 mmol, 1.2 equiv.) and Na_2CO_3 (2060 mg, 19.4 mmol, 4 equiv.) were added and cycled between vacuum and argon three times. The solids were dispersed in 60 mL THF/H_2O (4:1) and the mixture was degassed for 15 min with argon. $PdCl_2$(dppf) (249 mg, 0.34 mmol, 0.07 equiv.) was added under inert atmosphere, and the mixture was heated up to 65 °C. After 16 h, the mixture was cooled down to r.t. and diluted in AcOEt and washed with two times H_2O and one time brine. The organic fractions were collected, dried with Na_2SO_4 and concentrated under vacuum. The crude was purified through SiO_2 column chromatography (cyclohexane/AcOEt 8:2) obtaining the product in the 3rd band as a colorless wax (1560 mg, 82 %). R_f (SiO_2, cyclohexane/AcOEt 9:1) 0.10. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.71 (*d*, *J*=2.2, 1H), 7.44 (*dd*, *J*=8.1, 2.2, 1H), 7.33–7.20 (*m*, 4H, overlap $CDCl_3$), 7.09 (*d*, *J*=8.1, 1H), 4.90 (*s*, 1H), 4.54 (*d*, *J*=5.4, 2H), 4.34 (*d*, *J*=6.0, 2H), 1.80 (*t*, *J*=5.7, 1H), 1.45 (*s*, 9H). ^{13}C-NMR (126 MHz, $CDCl_3$): 156.11, 140.37, 139.70, 138.69, 138.55, 131.69, 131.19, 130.68, 129.33, 127.55, 121.88, 79.84, 62.66, 44.48, 28.56. HR-ESI-MS (pos): 414.0672 ($C_{19}H_{22}BrNNaO_3{}^+$, [*M*+Na]$^+$; calc. 414.0675).

***tert*-Butyl {[4′-Bromo-2′-(bromomethyl)[1,1′-biphenyl]-4-yl]methyl}carbamate** (**3$_H$**). Alcohol **9$_H$** (933 mg, 2.38 mmol, 1 equiv.) and PPh_3 (699 mg, 2.64 mmol, 1.1 equiv.) were dissolved in 20 mL dry CH_2Cl_2 under inert atmosphere and cooled down to 0 °C. CBr_4 (881 mg, 2.66 mmol, 1.1 equiv.) was added portion wise to the mixture which was allowed to react at r.t. for 5 h before it was quenched with sat. NaBr solution. The resulting two-phase mixture was extracted with CH_2Cl_2 three times, and the organic fractions were combined, dried with Na_2SO_4 and concentrated in vacuum. The crude was purified with SiO_2 column chromatography (cyclohexane/AcOEt 9:1) obtaining the product in the 2nd band as a white solid (748 mg, 70 %). R_f (SiO_2, cyclohexane/AcOEt 9:1) 0.38. ^{1}H-NMR (500 MHz, CD_2Cl_2): 7.68 (*d*, *J*=2.1, 1H), 7.48 (*dd*, *J*=8.3, 2.1, 1H), 7.37 (*s*, 4H), 7.13 (*d*, *J*=8.2, 1H), 5.06 (*s*, 1H), 4.39 (*s*, 2H), 4.36 (*d*, *J*=6.1, 2H), 1.46 (*s*, 9H). ^{13}C-NMR (126 MHz, CD_2Cl_2): 156.27, 141.16, 139.60, 138.35, 137.90, 133.97, 132.50, 131.94, 129.43, 127.67, 121.79, 79.68, 44.55, 31.39, 28.53. HR-ESI-MS (pos): 475.9824 ($C_{19}H_{22}Br_2NO_2Na^+$, [*M*+Na]$^+$; calc. 478.9831).

Bis[(4-bromo-4′-{[(tert-butoxycarbonyl)amino]-methyl}[1,1′-biphenyl]-2-yl)methyl] 1^4,4^4-Bis(hydroxymethyl)[1^1,2^1:2^4,3^1:3^4,4^{1}quaterphenyl]-2^3,3^2-dicarboxylate (**1$_H$**). A 100 mL round-bottom flask was charged with diacid 2 (290 mg, 0.64 mmol, 1 equiv.), carbamate **3$_H$** (720 mg, 1.58 mmol, 2.5 equiv.) and CsF (295 mg, 1.94 mmol, 3 equiv.). The solids were cycled between vacuum and argon three times before 50 mL dry DMF was added and the solution was stirred at room temperature for 24 h under inert atmosphere. The mixture was diluted with AcOEt and washed two times with H_2O followed by two times brine. The organic fraction was collected, dried with Na_2SO_4, concentrated under reduced pressure and purified by SiO_2 column chromatography (cyclohexane/AcOEt 6:4 5 CV →1:1 over 3 CV). Obtaining the 4th band yielded the product as a colorless wax (580 mg, 76 %). R_f (SiO_2, cyclohexane/AcOEt 1:1)

0.17. ^{1}H-NMR (500 MHz, CD_2Cl_2): 8.09 (*d*, *J*=2.2, 2H), 7.71 (*dt*, *J*=8.0, 2.2, 2H), 7.62–7.56 (*m*, 4H), 7.48 (*dd*, *J*=8.3, 2.0, 4H), 7.37 (*s*, 2H), 7.33–7.29 (*m*, 2H), 7.26 (*dd*, *J*=7.9, 1.9, 2H), 7.19 (*d*, *J*=7.8, 4H), 7.10 (*dd*, *J*=8.2, 2.1, 4H), 7.00 (*d*, *J*=8.1, 2H), 5.07–5.01 (*m*, 2H), 4.96 (*s*, 4H), 4.74 (*s*, 4H), 4.20 (*d*, *J*=6.0, 4H), 2.32 (br. *s*, 2H), 1.44 (*s*, 18H). ^{13}C-NMR (126 MHz, CD_2Cl_2): 167.03, 156.28, 141.87, 141.57, 140.93, 140.02, 139.16, 138.83, 138.42, 135.33, 132.75, 131.95, 131.58, 131.38, 130.31, 130.15, 129.49, 128.83, 127.78, 127.65, 127.47, 121.51, 79.69, 65.08, 64.41, 44.51, 28.54. HR-ESI-MS (pos): ($C_{66}H_{62}Br_2N_2O_{10}Na^+$, $[M+Na]^+$; calc. 1223.2663) 1223.2653.

Bis{[4′-{[(*tert*-butoxycarbonyl)amino]methyl}-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)[1,1′-biphenyl]-2-yl]methyl} 1^4,4^4-Bis(hydroxymethyl)-[1^1,2^1:2^4,3^1:3^4,4^1quaterphenyl]-2^3,3^2-dicarboxylate (10$_\mathbf{H}$). Dibromo **1$_\mathbf{H}$** (480 mg, 0.40 mmol, 1 equiv.), B_2Pin_2 (237 mg, 0.92 mmol, 2.3 equiv.) and KOAc (233, 2.37 mmol, 6 equiv.) were loaded into a 25 mL flame-dried *Schlenk* tube and cycled between vacuum and argon three times. Dry DMSO (12 mL) was added, and the mixture was degassed with argon for 15 min. $PdCl_2$(dppf) (40 mg, 0.04 mmol, 0.1 equiv.) was added, and the mixture was heated to 80 °C. The reaction was tracked through LC/MS, and after full consumption (4 h) of the starting material, the mixture was cooled down to room temperature, diluted with AcOEt, and washed three times with water. The organic phase was collected, dried with Na_2SO_4 and concentrated under reduced pressure obtaining the crude mixture which was used in the next step without further purification.

di-*tert*-butyl [{2,7-Bis[4-(hydroxymethyl)phenyl]-9,24-dioxo-9,24-dihydro-11*H*,22*H*-12,16:17,21-di-(metheno)dibenzo[*c*,*e*][1,8]dioxacycloicosine-13,20-diyl}bis(4,1-phenylenemethylene)]biscarbamate (C$_{\mathbf{1,H}}$). Crude diboronic ester **10$_\mathbf{H}$** (1 equiv.) was added to a 1 L *Erlenmeyer* flask and dissolved in 350 mL THF. $PdCl_2(PPh_3)_2$ (158 mg, 0.225 mmol, 0.5 equiv.) and boric acid (134 mg, 2.15 mmol, 5.4 equiv.) were added, and the mixture was stirred vigorously for 15 min. KF (104 mg, 1.77 mmol, 4.4 equiv.) was added followed by the addition of water (35 mL) and the mixture was stirred for 16 h at room temperature open to the atmosphere. THF was removed under reduced pressure and the remaining aqueous phase was extracted with CH_2Cl_2 three times. The organic fractions were combined, dried over Na_2SO_4 and concentrated in vacuum. The crude was subjected to SiO_2 column chromatography (CH_2Cl_2/AcOEt 8:2 to 6:4 *v/v*) collecting the 2nd fraction which yielded a yellow solid after solvent evaporation. The solid was washed with cold MeOH to obtain the product as a fine white powder (220 mg, 52 %) over two steps. R_f (SiO_2, CH_2Cl_2/AcOEt (6:4) 0.46. ^{1}H-NMR (500 MHz, DMSO-d$_6$): 8.45 (*d*, *J*=2.1, 2H), 7.99 (*dd*, *J*=8.1, 2.1, 2H), 7.75–7.69 (*m*, 6H), 7.49–7.31 (*m*, 18H), 7.21 (*s*, 2H), 5.76 (*d*, *J*=14.6, 2H), 5.24 (*t*, *J*=5.8, 2H), 4.98 (*d*, *J*=14.5, 2H), 4.55 (*d*, *J*=5.8, 4H), 4.20 (*d*, *J*=6.2, 4H), 1.41 (*s*, 18H). ^{13}C-NMR (126 MHz, DMSO-d$_6$): 165.04, 155.85, 143.50, 142.42, 139.70, 139.13, 138.40, 138.13, 137.25, 137.03, 134.14, 132.03, 130.47, 130.26, 128.76, 128.15, 127.15, 127.07, 126.79, 126.37, 124.52, 124.00, 77.83, 63.40, 62.54, 43.07, 28.26. HR-ESI-MS (pos): 1065.4291 ($C_{66}H_{62}N_2NaO_{10}^+$, $[M+Na]^+$; calc. 1065.4297).

Di-*tert*-butyl {[2,7-Bis(4-formylphenyl)-9,24-di-oxo-9,24-dihydro-11*H*,22*H*-12,16:17,21-di(meth-eno)dibenzo[*c*,*e*][1,8]dioxacycloicosine-13,20-diyl]-bis(4,1-phenylenemethylene)}biscarbamate (C$_{\mathbf{2,H}}$). To cross **C$_{\mathbf{1,H}}$** (72 mg) 5 mL THF/CH_2Cl_2 (4:1) was added and the suspension was cooled to 0 °C, followed by the portion wise addition of *Dess-Martin* periodane (67 mg, 2.3 equiv.). The mixture was allowed to warm up to r.t. and was stirred for 1.5 h before a mix of sat. $NaHCO_3$ and sat. $NaHSO_3$ was added. The water phase was extracted with CH_2Cl_2 three times, and the organic fractions were combined, dried with Na_2SO_4 and concentrated under reduced pressure. The crude was purified by SiO_2 column chromatography (CH_2Cl_2/AcOEt (10:0 to 9:1 *v/v*)) collecting the first band yielded the product as a white solid (66 mg, 92 %). R_f (SiO_2, CH_2Cl_2/AcOEt 19:1) 0.43. ^{1}H-NMR (500 MHz, CD_2Cl_2): 10.05 (*s*, 2H), 8.58 (*d*, *J*=2.0, 2H), 8.00–7.95 (*m*, 4H), 7.93 (*dd*, *J*=8.0, 2.0, 2H), 7.90–7.84 (*m*, 4H), 7.60 (*dd*, *J*=7.9, 1.9, 2H), 7.46 (*d*, *J*=8.0, 2H), 7.41–7.36 (*m*, 6H), 7.35–7.29 (*m*, 6H), 5.88 (*d*, *J*=14.1, 2H), 5.11 (*s*, 2H), 4.94 (*d*, *J*=14.1, 2H), 4.36 (*d*, *J*=6.1, 4H), 1.47 (*s*, 18H). ^{13}C-NMR (126 MHz, CD_2Cl_2): 192.08, 165.96, 156.29, 145.86, 145.54, 139.54, 139.33, 139.26, 139.18, 138.90, 136.09, 134.77, 132.19, 131.04, 130.73, 130.60, 130.09, 129.62, 128.05, 127.96, 127.72, 125.98, 124.99, 79.65, 64.16, 44.56, 28.54. HR-ESI-MS (pos): 1061.3971 ($C_{66}H_{58}N_2NaO_{10}^+$, $[M+Na]^+$; calc. 1061.3984). FT-ATR-IR: 3427*m* (ν(N–H)), 3363*w*, 2976*m* (ν(C–H)), 2929*m* (ν(C–H)), 2826*w* (ν(C–H, aldehyde)), 2731*w* (ν(C–H, aldehyde)), 1699*s* (ν(C=O)), 1602*m* (ν(C=C)), 1573*w*, 1502*m*, 1484*m*, 1423*w*, 1305*w*, 1220*s*, 1163*s*, 1074 *m*, 1049*w*, 1002 *m*, 933*w*, 854*w*, 819*s*, 792*w*, 754*w*, 734*w*, 680*w*, 601*w*, 497*w*, 445*w*.

{[2,7-Bis(4-formylphenyl)-9,24-dioxo-9,24-dihydro-11*H*,22*H*-12,16 : 17,21-di(metheno)dibenzo-[*c*,*e*][1,8]dioxacycloicosine-13,20-diyl]di(4,1-phenylene)}dimethanaminium Bis(trifluoroacetate) (M_H). Cross $\mathbf{C_{2,H}}$ (30 mg, 0.029 mmol, 1 equiv.) was dissolved in 4 mL CH_2Cl_2 and trifluoroacetic acid (0.5 mL, 6.66 mmol, 230 equiv.) was added dropwise. The mixture was stirred at room temperature for 30 min before poured in 100 mL cold heptane. Solvents were evaporated under reduced pressure obtaining the free amine TFA salt in quantitative yield as a white solid. ^{1}H-NMR (500 MHz, DMSO-d_6): 10.08 (*s*, 2H), 8.56 (*d*, $J=2.1$, 2H), 8.26 (*s*, 6H), 8.13 (*dd*, $J=8.1$, 2.0, 2H), 8.09–7.98 (*m*, 8H), 7.75 (*dd*, $J=8.0$, 1.9, 2H), 7.58 (*d*, $J=8.3$, 4H), 7.51 (*d*, $J=8.0$, 6H), 7.37 (*d*, $J=7.8$, 2H), 7.23 (*d*, $J=2.1$, 2H), 5.79 (*d*, $J=14.6$, 2H), 5.00 (*d*, $J=14.4$, 2H), 4.13 (*d*, $J=5.7$, 4H). ^{13}C-NMR (101 MHz, DMSO-d_6): 192.79, 164.87, 144.58, 144.27, 139.05, 138.40, 138.08, 138.03, 135.49, 134.10, 132.12, 133.53, 130.98, 130.95, 130.58, 130.55, 130.30, 129.16, 129.11, 127.49, 126.94, 124.71, 124.13, 63.41, 41.99. Signals: 132.12, 124.13, 63.41 are extracted from 2D-NMR. ^{19}F-NMR {1H}: (376 MHz, DMSO): −73.67 (not referenced). HR-ESI-MS (pos): 839.3103 ($C_{56}H_{43}N_2O_6^+$, $[M+H]^+$; calc. 839.3116). FT-ATR-IR: 3032*m* (ν(C–H)), 2945 (br., ν(N$^+$-H)), 2930*m* (ν(C–H)), 2854*w* (ν(C–H, aldehyde)), 2737*w* (ν(C–H, aldehyde)), 2628*w*, 1726*s* (ν(C=O)), 1700*s* (ν(C=O)), 1605*m* (ν(C=C)), 1480*w*, 1427*w*, 1373*w*, 1306*w*, 1203*s*, 1174*m*, 1133*m*, 1073 *m*, 1004*w*, 971*w*, 909*w*, 821*s*, 796*m*, 720*m*, 679*w*, 597*w*, 515*w*.

Synthesis of $\mathbf{M_{OH}}$ and $\mathbf{M_{OMe}}$ and its precursors can be found in the *Supporting Information*.

The crystallographic data for this paper can be found under deposition number 2220993 for $\mathbf{C_C}$ and 2221018 for $\mathbf{C_{1,H}}$. These data are provided by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Author Contribution Statement

C. C. E. K. performed the synthesis, characterized the compounds and wrote the manuscript; *A. D'A.* performed the DFT-calculations; *A. P.*, *O. F.*, and *D. F.* analyzed the solid-state structures; *M. M.* supervised the work and wrote the manuscript. All authors commented on the manuscript.

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