Shape-Persistent Macrocycles with Bipyridine Units: Progress in Accessibility and Widening of Applicability

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Several new symmetrical and nonsymmetrical bipyridine-containing building blocks for shape-persistent macrocycles were developed, whereby much emphasis was placed on especially efficient procedures. The building blocks were used for the synthesis of several new cycles, the most important of which carry only one selectively addressable hydroxymethyl group at a corner. This group was converted into methacrylate- and norbornene-type polymerizable units for free radical and ROMP polymerizations, respectively, rendering the corresponding macrocycles the first macromonomers of this kind. Initial polymerization studies are also reported.

Introduction

Recently much attention has been focused on the synthesis of shape-persistent macrocycles.[1] Their reduced conformational mobility leads to an increased tendency to aggregate and/or adsorb on surfaces compared to similarly sized flexible cycles[2] and establishes them as novel rigid scaffolds. Shape-persistent macrocycles may open up fascinating avenues into the generation of cylindrical nanopores[3] and regular surface patterns as well as endocyclic catalysis or nanoconstructions. Most of these macrocycles known today have hexagonal structures and their available interior spans range from approximately one to several nanometers.[4] They can be divided into two subclasses: Ones whose backbones do not contain transition metals as integral part and ones that do. The latter are usually constructed from linear, shape-persistent units which carry terminal anchor groups for metal complexation and transition metal complexes. The linear units end up as sides of the oligons and the transition metals as corners. This approach produced a bouquet of beautiful and useful structures.[5] The price which has to be paid for this, however, is the use of a considerable amount of transition metal (e. g., Pt) which severely limits the amount available and also has other disadvantages. Consequently many of the cycles were only prepared on the milligram scale. This is where the subclass without integral transition metals is at an advantage, namely its generally better availability even though the involved synthetic effort as judged by the number of steps may be, by and large, higher. Several of their representatives were synthesized on the 100-mg scale,[6] some even on the gram scale.[7] Having made a couple of shape-persistent cycles with bipyridine (bpy) and terpyridine units typically on the 100-mg scale[8] we are presently aiming significantly beyond the cycles themselves. We are exploring potential applications by investigating the cycles' complexation behavior[9] and their polymerizability after conversion into macromonomers as well as their potential as repeat units for nanoconstructions including linear polymers in which cycles are held together by transition metals. In light of such goals, these cycles' better availability was not quite the golden opportunity it seemed anymore and improvements were necessary. We therefore set out to straighten some of the cycles' syntheses and to also make representatives available which carry variable exocyclic functionality. There were two options to improve the accessibility of bpy containing cycles such as **E** (Scheme 1). One was to straighten the sequences leading to the precursors for cyclization and the other was to improve the cyclization step itself. In the present contribution we describe significantly facilitated synthetic procedures to the main building blocks for cycle assembly which led to cycle syntheses on the 1-gram scale. Though the access to some of these cycles has been significantly improved, the synthetic procedures suffer from the fact that so far only symmetrical building blocks could be used. This in the end means that the cycles have to be closed from two precursors which by and large limit the yield of the final cycle formation step to a value of approximately 20%. It also and perhaps even more importantly prevents an nonsymmetrical decoration of the cycles which is of relevance, for example, in regard to their use as switches.[10] Thus, this paper also reports on a nonsymmetrical building block which, after some steps, would allow to close a cycle

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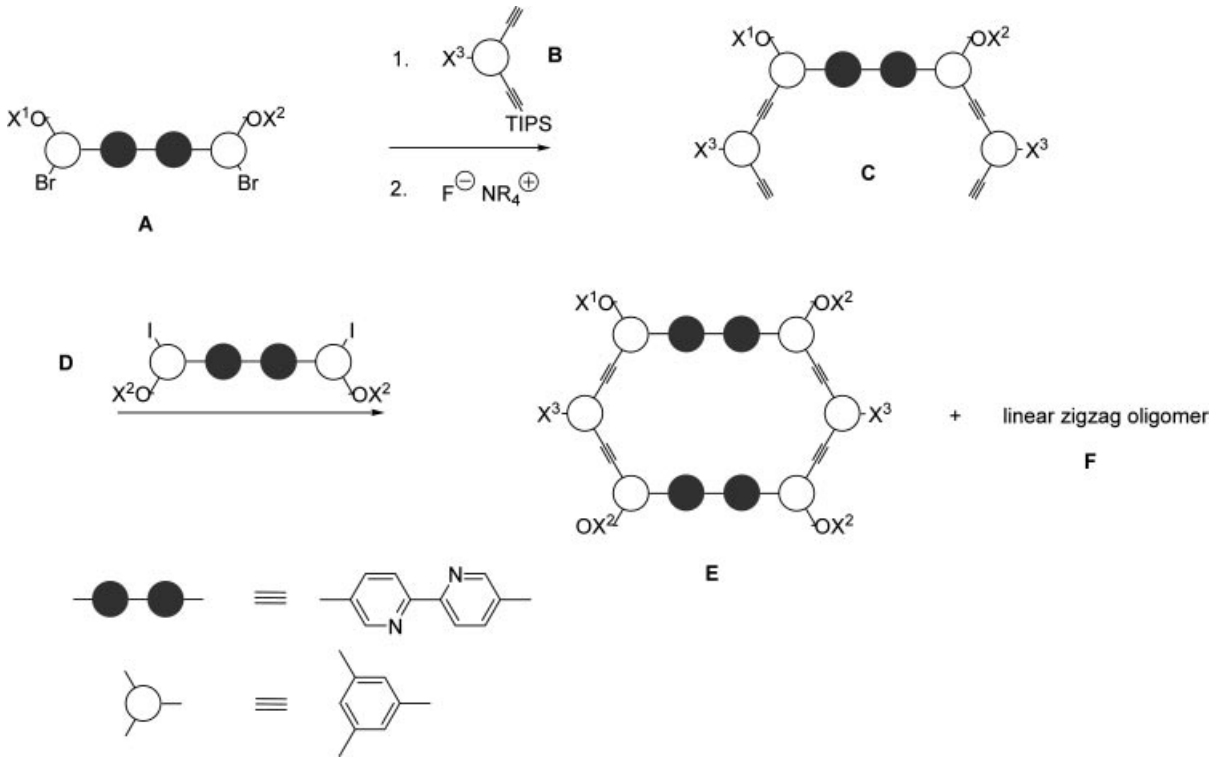


Scheme 1. The synthetic strategy to bipyridine macrocycles of kind **E**

from one precursor. For such ring closures yields of 70% have been obtained.[11] We finally report on the synthesis of two macrocyclic macromonomers and initial results of their polymerization according to free radical and ring-opening metathesis mechanisms.

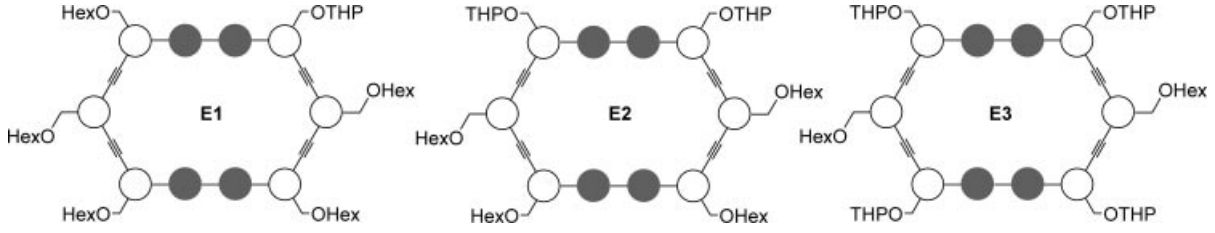
2. Results and Discussion

2a. General Remarks

The way by which the bpy-containing shape-persistent cycles of kind **E** are normally prepared requires two side stones **A** and **D** and a corner stone **B** (Scheme 1). Side **A** is reacted with the acetylenic cornerstone **B** under Sonogashira conditions to the cycle precursor **C** which, after silyl-deprotection, is then reacted with side **D** again according to a Sonogashira protocol and under pseudo high dilution conditions to give a roughly 1:4 mixture of cycle **E** and linear (zigzag) oligomers **F**. This mixture can additionally contain a few higher cycles and possible catenanes. The average yield based on numerous cyclization experiments is approximately 20%. The cyclizations themselves will not be treated here in any great detail anymore.

Side **A** carries two bromo functions for further growth, side **D** two iodo ones. In contrast to the cyclization of **C** and **D** where the rate of the cross-coupling has impact on the cyclization efficiency, the rate of assembly of **C** from **A** and **B** does not matter. Oligomerization does not compete. This is why side **D** and not side **A** is equipped with the more highly reactive iodo groups. Attempts to cyclize **C** with **A** gave practically zero cycle and only linear oligomer. Of course, also side **D** instead of **A** can be used to enter the sequence. Corner stones **B** carry acetylenes with selectively deprotectable acetylenes [e. g. trimethylsilyl (TMS) and triisoproyplsilyl (TIPS)] in order to allow for its selective coupling to **C**.

Sides **A** and **C** can be either symmetrical ($X^1 = X^2$) or nonsymmetrical ($X^1 \neq X^2$). Cycle **E** in Scheme 1 is shown for a nonsymmetrical side **A** and a symmetrical side **D**. Of the numerous possible combinations Scheme 2 shows combinations of peripheral substituent patterns which are considered especially interesting. **E1** with its one tetrahydropy-



Scheme 2. Different macrocycles with different substitution pattern

ranyl (THP) protected alcohol group is attractive for its further conversion into macromonomers in order to provide access to polymers with pendent macrocycles. **E2**[12] with its two THP groups is attractive as source for unconventional diols for polyesters, polyamides and alike, and, finally, **E4**[8b] for its decoration with dendrons, self-recognizing and/or polymerizable groups, the latter of which would potentially be useful for covalent stabilization of cylindrical cycle stacks by solid-state polymerization similar to Ringsdorf's[13] and Gadhiri's work.[14]

2b. Improvements and New Building Blocks

The main objectives of the sequences' overhaul was to reduce the number of steps, increase their yields, replace Stille cross-coupling wherever possible[15] by the generally more efficient Suzuki cross-coupling which, additionally, does not involve potentially toxic stannyl compounds, and improve work-up procedures.

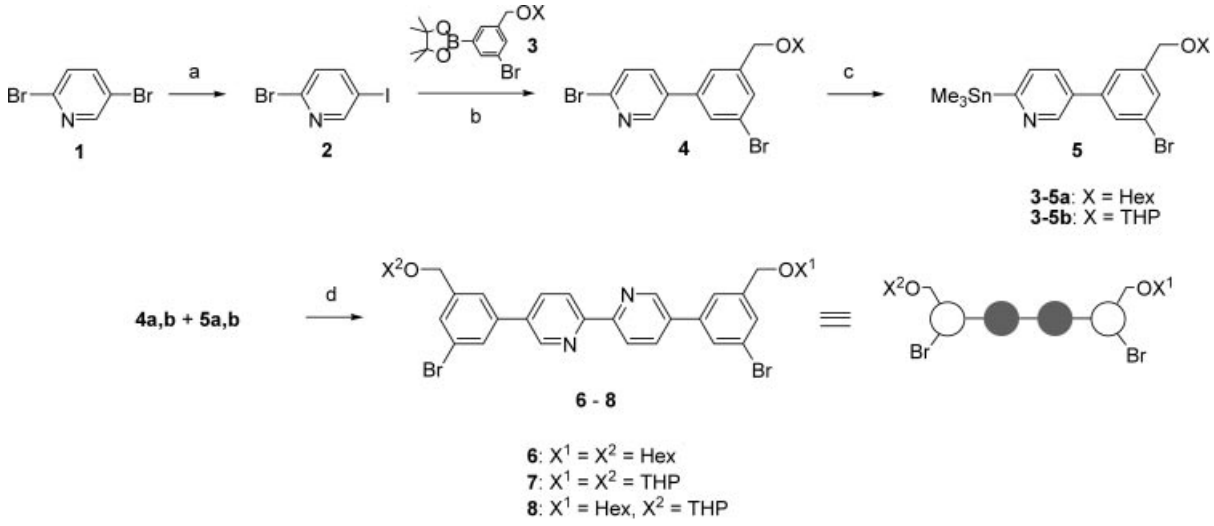
Improved Side Stones A: Sides **A** can be obtained symmetrically and nonsymmetrically depending on whether the X groups are like or unlike, respectively. Normally they are prepared such that the bpy unit (and thus the completed side) is generated in the last step by Stille cross-coupling between compounds **4** and **5** (Scheme 3). The route starts from 2,5-dibromopyridine (**1**) which was selectively converted into the iododerivative **2** by Schlosser's protocol.[16] Its iodo selective coupling with the phenylboronic acid ester **3** gave half sides **4a** (X = Hex) and **4b** (X = THP). Compound **3** was prepared on the 10-g scale as described earlier.[17] Both pyridines **4a** and **4b** were stannylated to **5a** and **5b**, respectively, by a conventional procedure.[15] The different combinations of these compounds gave the symmetrical sides **6** and **7** and the nonsymmetrical one **8**.[15] This Stille reaction is the last of formerly three such cross-couplings still remaining in the entire sequences to cycles **E** from two "halves".

Improved Side Stone D: Side **D** was prepared using the recently published facilitated synthesis of 5,5′-dibromo-2,2′-bipyridine (**9**) and the silylated phenyl derivative **10** under Suzuki cross coupling reaction conditions (Scheme 4). According to Sauvage's and Michl's procedure,[18] bpy **9** is now available on the 10-g scale. Compound **10** was basically prepared as described earlier[19] with one small but important modification. The esterification (pinacolization) of the free boronic acid precursor of **10** (not shown) was now done in toluene with concomitant removal of water. This change leads to an increase in yield for **10** from approximately 50% to an average of 80% which allowed its preparation on the 30-g scale. Having these compounds available at such large scale the obtainment of compound **11** on the 10-g scale was no problem. Silyl groups on aromatics are known to be place holders for various functional groups including iodo. This also refers to some heteroaromatic examples.[20] Compound **11** could thus be quantitatively converted into side **12** on the 10-g scale by reacting it with iodochloride. An alternative reaction pathway to compound **11** was also investigated (Scheme 4) though it is somewhat less attractive since the moment that the above-mentioned improved accessibility of compound **9** has been published. Compounds **10** and **2** were coupled to **13** which was subsequently homocoupled in presence of Sn_2Bu_6 and $[Pd(PPh_3)_4]$.

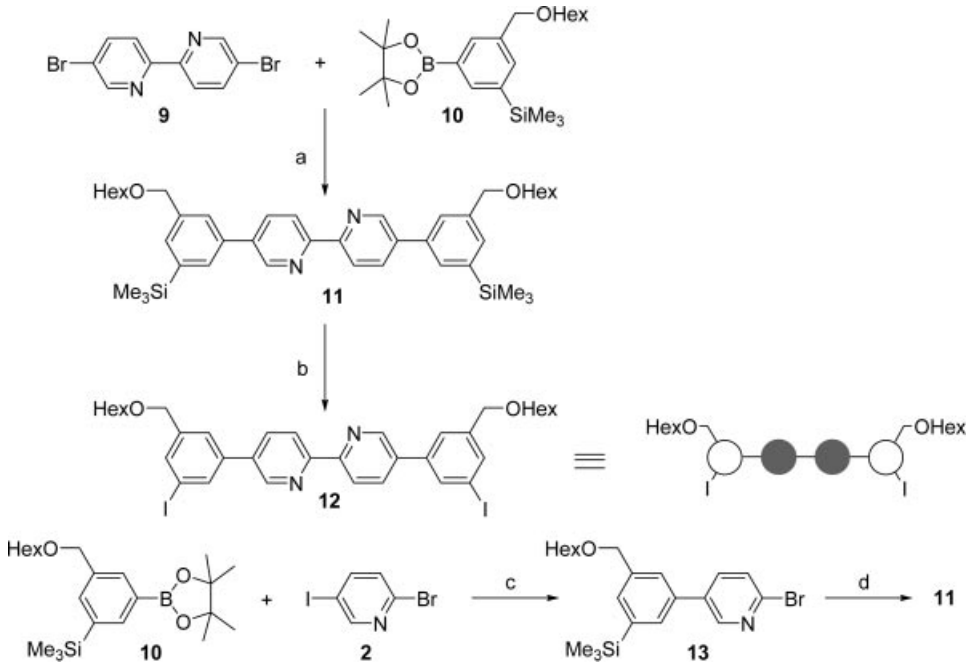
Corner Stones B: Compounds **B** (Scheme 1) did not need improvement. They are available on the 30-g scale.[8a]

New Cycle Precursors of Kind C and Their Cyclization: The new representatives of precursors **C**, **16** and **17**, were prepared according to known procedures (Scheme 5).[8a,8b] The ring closure was carried out under high dilution conditions by means of a Sonogashira–Hagihara-type reaction (Scheme 5). Cycles **E1** and **E4** were unambiguously characterized by NMR spectroscopy and mass spectrometry.

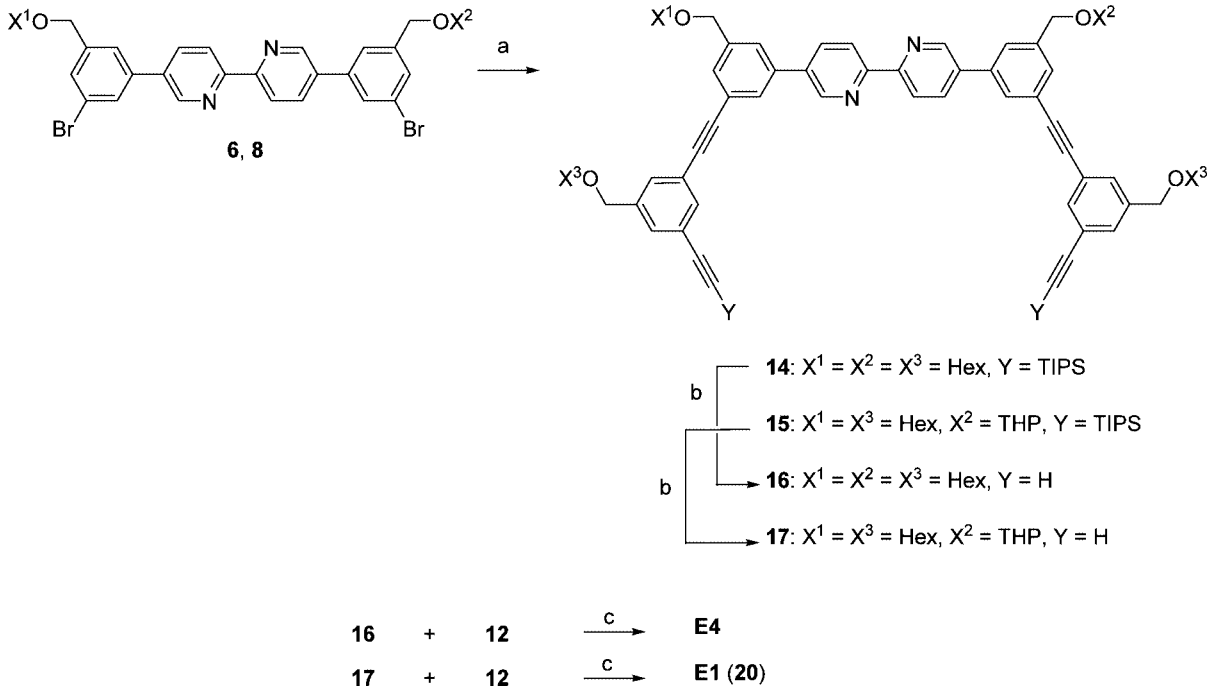
Another New Cycle Precursor and Its Ring Closure: In the case that only four substituents are needed or acceptable on a cycle, a specifically easy route was devised which is based



Scheme 3. Synthesis of symmetrical (**6**, **7**) and nonsymmetrical sides **A** (**8**); (a) *n*-butyllithium, 1.2-diiodoethane, diethyl ether, –78 °C, 75%; (b) $[Pd(PPh_3)_4]$, 2 M Na_2CO_3/water, toluene, r. f., 3 d, 80–85%; (c) *n*-butyllithium, $ClSnMe_3$, toluene, –78 °C; (d) $[Pd(PPh_3)_4]$, toluene, r. f., 5 d, 30–35%



Scheme 4. Synthesis of side **D**; (a) $[Pd(PPh_3)_4]$, toluene, 2 M Na_2CO_3, water, r. f., 3 d, 90%; (b) ICl, DCM, r. f., 2 d, 98%; (c) $[Pd(PPh_3)_4]$, toluene, 2 M Na_2CO_3, water, r. f., 3 d, 90%; (d) Sn_2Bu_6, $[Pd(PPh_3)_4]$, toluene, r. f., 5 d, 85%

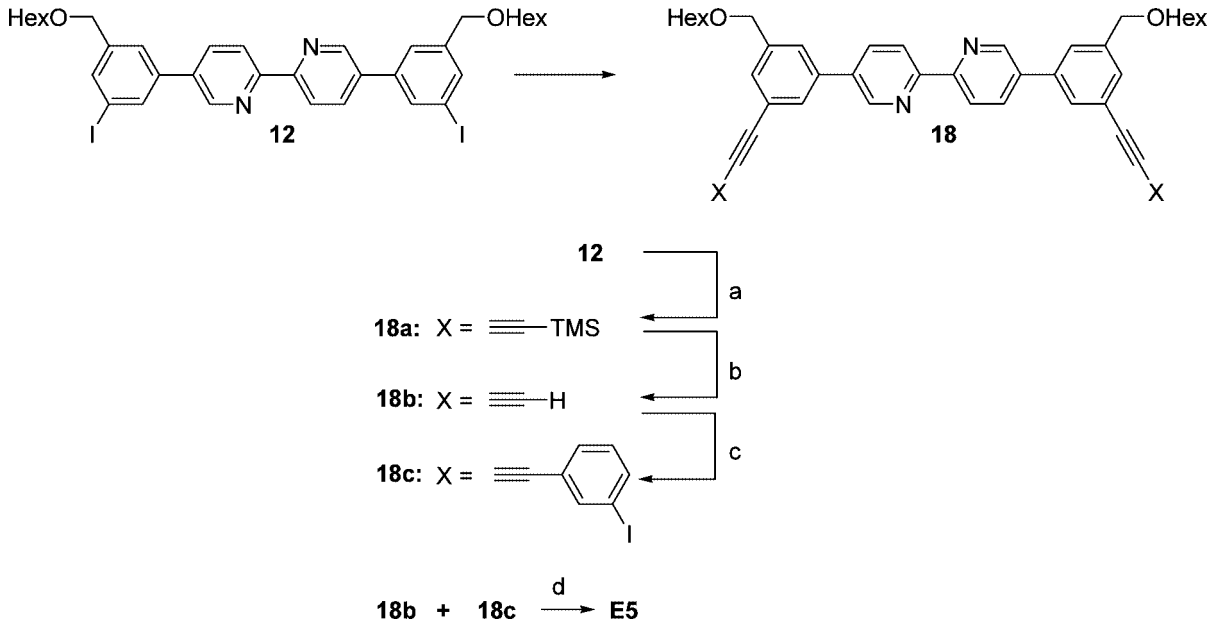


Scheme 5. (a) (2-(3-Ethynyl-5-((hexyloxy)methyl)phenyl)ethynyl)triisopropylsilane (**C**), $[Pd(PPh_3)_4]$, CuI, toluene, TEA, 80 °C, 2 d, 80–85%; (b) Bu_4NF, THF, room temp., 1 d, 95%

on the commercial availability of (trimethylsilyl)acetylene (TMSA) and 1,3-diiodobenzene and has a further reduced total number of steps from 17 to 13 (Scheme 6). It starts from **12** (side **D**) which is reacted with TMSA to give **18a** in an almost quantitative yield. After deprotection, **18b** is reacted with a large excess of 1,3-diiodobenzene to give the new cycle precursor **18c** in 60% yield and on the 2-g scale. Compound **18c** was cyclized with its own precursor, **18b**, to give the known cycle **E5** in a yield of 28% on the 540-mg scale.

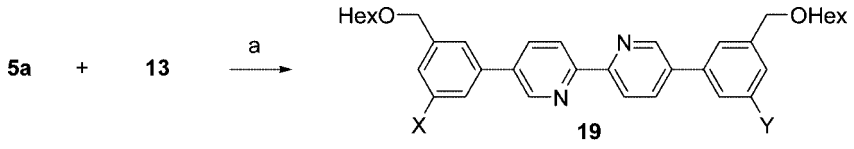
2c. A Nonsymmetrical Side

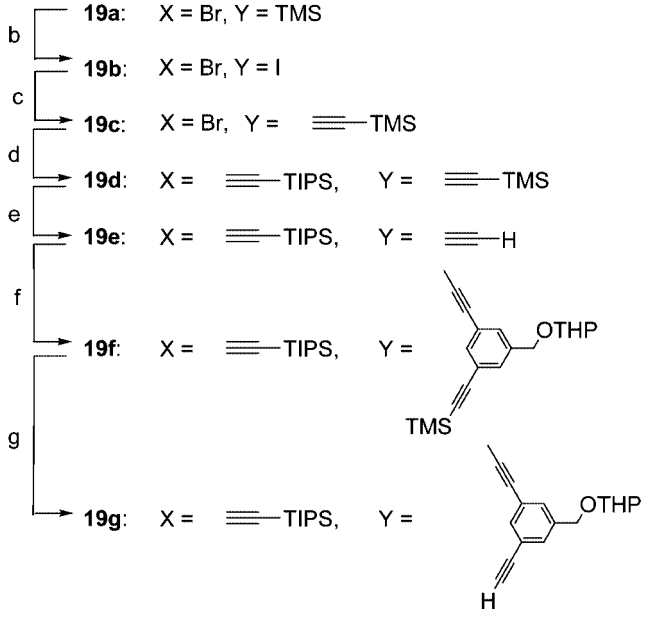
In the quest for a nonsymmetrical building block with two different, selectively addressable halogens which, after



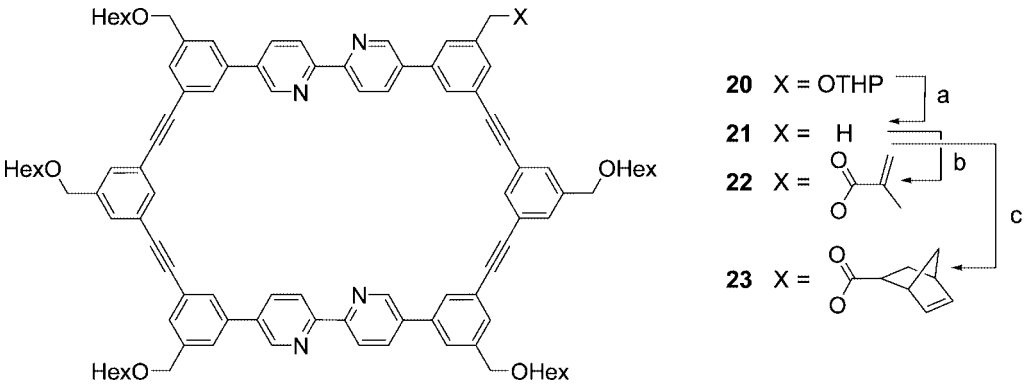
Scheme 6. (a) [Pd(PPh$_3$)$_4$], CuI, TMSA, toluene, TEA, 60 °C, 1 d, 90%; (b) NaOH, THF, methanol, room temp., 1 d, 94%; (c) 1,3-diiodobenzene, [Pd(PPh$_3$)$_4$], CuI, toluene, TEA, 60 °C, 3 d, 60%; (d) [Pd(PPh$_3$)$_4$], CuI, toluene, triethylamine, 60 °C, 5 d, 28%

some steps, would allow to close a cycle from one precursor, side **19b** with one bromo and one iodo function was considered an ideal candidate (Scheme 7). Its synthesis was achieved by first coupling the stannyl compound **5a** with the bromide **13** to give **19a**. As oftenly encountered in Stille coupling reactions not only the desired cross-coupling product but also the two homocoupling products were formed (ratio **19a**:**11**:**6** = 4:1:1). Fortunately, the side products could





Scheme 7. (a) [Pd(PPh$_3$)$_4$], toluene, r. f., 5 d, 44%; (b) ICl, DCM, r. f., 2 d, 79%; (c) TMSA, [Pd(PPh$_3$)$_4$], CuI, toluene, TEA, 60 °C, 1 d, 88%; d)TIPSA, [Pd(PPh$_3$)$_4$], CuI, toluene, TEA, 80 °C, 1 d, 75%; (e) NaOH, THF, methanol, room temp., 1 d, 89%; (f) (2-{3-bromo-5-[(tetrahydro-2*H*-pyran-2-yloxy)methyl]phenyl}ethynyl)trimethylsilane, [Pd(PPh$_3$)$_4$], CuI, toluene, TEA, 80 °C, 2 d, 71%; (g) NaOH, THF, methanol, room temp., 1 d, 95%



Scheme 8. (a) HCl, DCM, MeOH, 1 d, 98%; (b) MAC, DCM, DMAP, TEA, 18 d, 0 °C (82%); (c) *exo*-5-norbornene-2-carboxylic acid, DMAP, DCC, DCM, 0 °C, 18 h (96%)

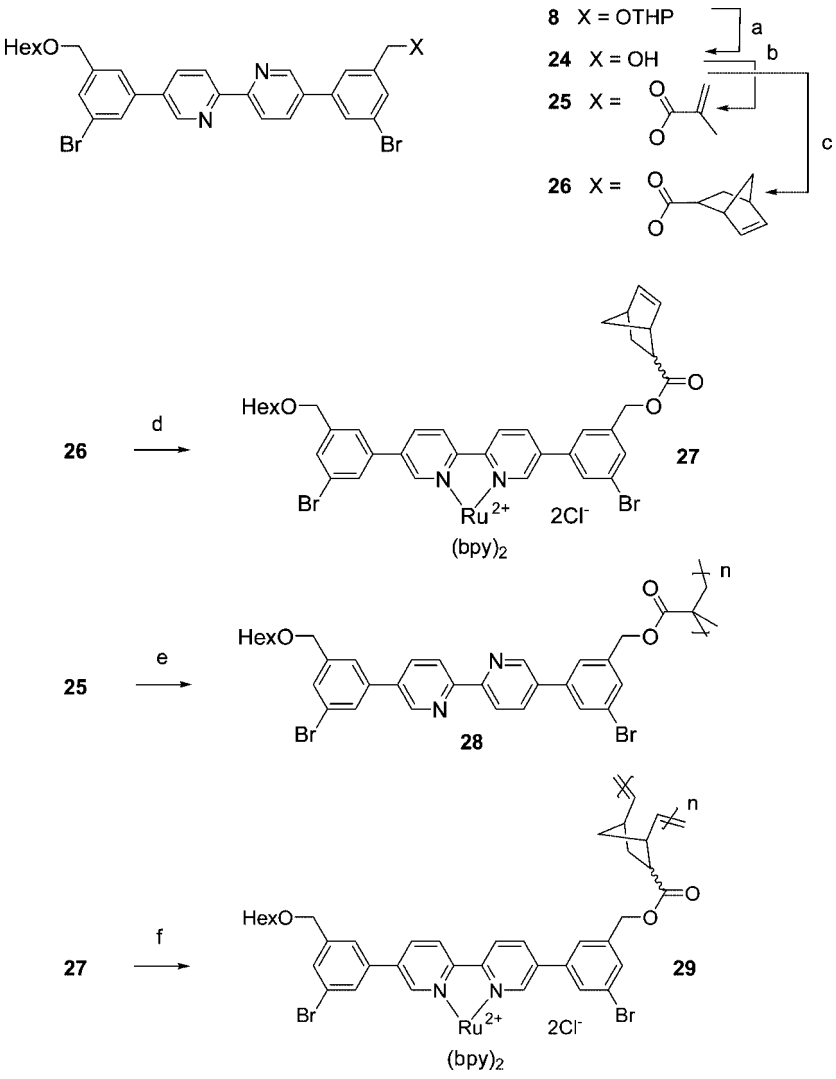
be easily removed by column chromatography. Iododesilylation of pure **19a** afforded **19b** on the 2-g scale as analytically pure material. Some further steps towards a cycle were also done. **19b** was subjected to a series of Sonogashira-type coupling reactions with various silyl-protected acetylenes to give **19g**. All these procedures went absolutely smoothly and were high-yielding so that **19g** could be isolated on the not yet optimized 500-mg scale. We consider this a good starting point for the missing steps to cycle as well as other purposes.

2d. Polymerization of Macrocycles with Pendant Polymerizable Units

A motivation for research in the area of shape-persistent macrocycles is to reach their self-assembly into columnar stacks in which each pair of two consecutive cycles lies directly on top of each other. This way cylindrical confinements with long pores would be generated which eventually could lead to the generation of, for example, atomically thin metal wires. In many of the single crystals obtained from bpy and tpy containing macrocycles, the formation of cylindrical stacks, however, is avoided and more complex arrangements are preferred. One potential way to nevertheless achieve a columnar packing[3,21] is to attach them to a polymer backbone. Spurred by this consideration the possibility of polymerizing macrocycles with pendent polymerizable units, like **22** and **23** was explored (Scheme 8). Such an enterprise would also be of interest to polymer synthesis because no such monomers have ever been subjected to polymerizations. Given their high molar mass as compared with conventional monomers like methacrylate or norbornene, **22** and **23** are to be considered macromonomers. Polymerizations of macromonomers tend to suffer from an enhanced chain transfer and the difficult to achieve extremely high monomer concentrations required in order to achieve decent molar masses. Free radical (FRP) and ring-opening metathesis polymerizations (ROMP) are known to be relatively robust procedures and were therefore selected for these initial studies.

First model studies were done by using the noncyclic macromonomers **25** and **27** derived from the nonsymmetrical side **8** (Scheme 9). This way the conditions for both the attachment of the polymerizable units and the polymerization itself could be explored. The tetrahydropyranyl (THP) protecting group on **8** was removed under acidic conditions and the resulting alcohol **24** reacted with freshly distilled methacrylic acid chloride to give the FRP macromonomer **25**. The norbornenic unit was introduced by active ester chemistry using the commercially available *exo*/*endo* (2:8) mixture of norbornenic acid. For this test purpose the use of a mixture was considered acceptable. The bpy unit of **26** was blocked by converting it into the corresponding Ru complex **27**. Attempted ROMP of **26** with first generation Grubbs catalyst[22] gave basically unreacted material presumably because of a detrimental interference of its bpy unit with the catalyst. FRP of **25** was done with AIBN in toluene and actually gave polymer **28** (yield: 65%) with gel permeation chromatography (GPC) molar masses versus polystyrene standard of M_p 20,300 g/mol and M_w = 27,600 g/mol (PDI = 1.56). The molar mass distribution was monomodal. Also ROMP of **27** to furnish polymer **29** could be accomplished though the molar mass determination was not yet achieved. Polymer **29** carries two positive charges per repeat unit and is thus a polyelectrolyte. An accurate molar mass determination of polyelectrolytes is a rather complex matter. The ^{1}H NMR spectrum of polymer **29** shows the complete disappearence of olefinic signals ensuring at least its oligomeric regime. **29** is soluble in chloroform, DMF, and NMP, but not in THF.

Next the macrocyclic macromonomers **22** and **30** were prepared (Scheme 8, Scheme 10). Given the experience with monomer **26**, monomer **23** was not directly subjected to ROMP conditions but rather first converted into its "protected" Ru complex **30** (Scheme 10). For the latter the *exo* diastereomer of norbornenic acid was used.[23] Both monomers were obtained on the 150–300-mg scale according to routine procedures and obtained as fully characterized, analytically pure substances. FRP of **22** was done like for model **25** at a monomer concentration of approximately 0.11 M. In macromonomer polymerization the application of an as high as possible concentration is essential. Otherwise the concentration of the polymerizable units is so low



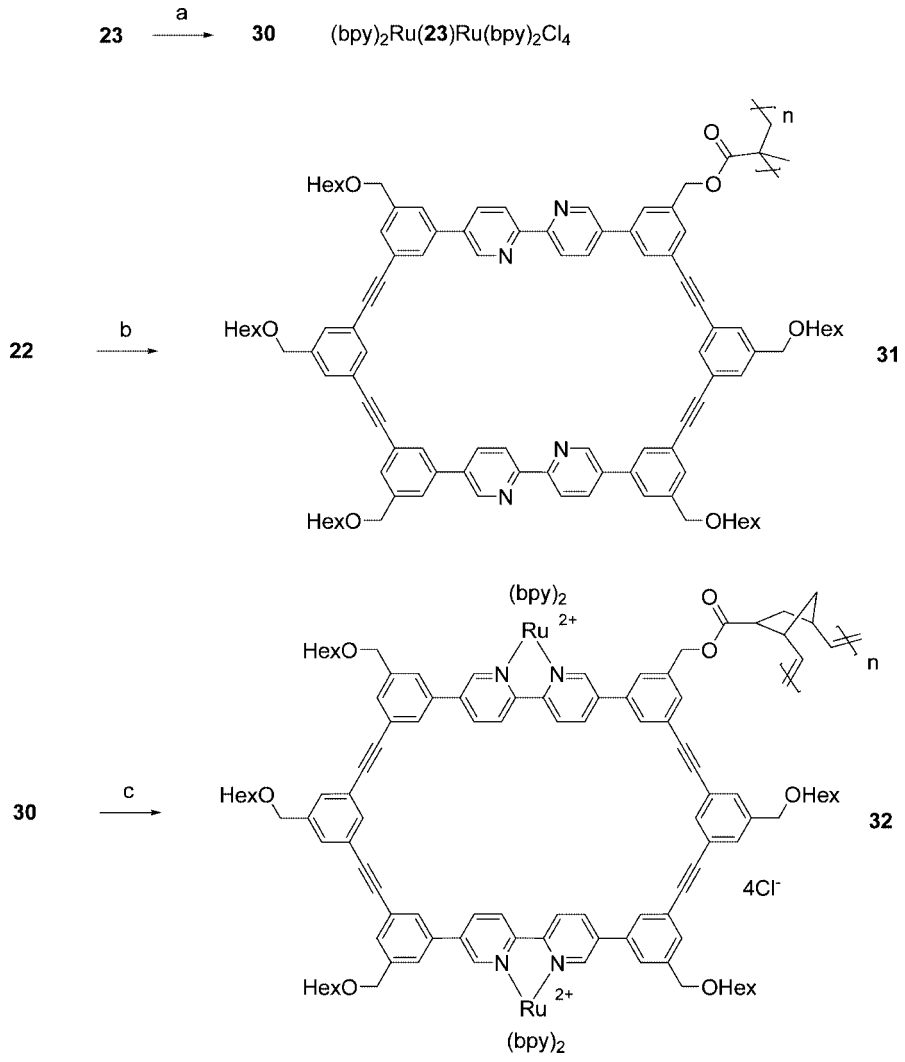
Scheme 9. (a) HCl, DCM, MeOH, 1 d, 93%; (b) MAC, DCM, DMAP, TEA, 18 d, 0 °C, 95%; (c) *exo-endo*-5-norbornene-2-carboxylic acid, DMAP, DCC, DCM, 0 °C, 18 d, 70%; (d) $[Ru(bpy)_2Cl_2]$, ethanol, water, r. f., 24 d, 66%; (e) toluene, AIBN, 80 °C, 1 d, 65%; (f) $(Cy_3P)_2Cl_2Ru{=}CHPh$, DCM, room temp.

that the polymerization is slowed to the extent that side reactions can take over.[24] A soluble product, to which structure **31** is assigned, was obtained from precipitation and had GPC molar masses of M_n = 10,500 g/mol and M_w = 13,800 g/mol (PDI = 1.35). Figure 1 compares the ^1H NMR spectrum of monomer **22** and polymer **31**. As expected the olefinic signals of **22** are absent for **31** and all signals are broadened. It is noteworthy that the signals associated with the cyclic substituent on **31**'s backbone suffer a considerable highfield shift of approximately 0.5 ppm. This reflects the cycles' close proximity and thus their mutual influence. The bulk structure of polymer **31** is presently under investigation.

The polymerization of **30** under the above ROMP conditions gave polymer **32**. Its ^1H NMR spectrum shows the ring-opened norbornene and gives no evidence for end groups. Especially characteristic is the disappearance of the norbornenic olefin signals at δ = 6.1 ppm with concommitant appearance the olefinic signals of **32** which absorb at δ = 4.9 and 5.3 ppm as is typical for norbornene ROMP polymers (see ESI).[25] The polymerization was carried out in dichloromethane solution from which the polymer precipitated. GPC measurements could not yet be performed because of **32**'s polyelectrolyte character.

Experimental Section

General: All reactions involving air-sensitive compounds were carried out under nitrogen using standard Schlenk techniques and dry, oxygen-free solvents. Diethyl ether, toluene, THF, and triethylamine were distilled under nitrogen from sodium/benzophenone and dichloromethane was distilled from CaH_2. All reagents were purchased from Aldrich or Acros and used without further purification. BuLi was used as a 1.6 M solution in hexane. Compounds **B**,[8a]**3a**,[17] **6**, **7**, 2-(3,5-dibromobenzyloxy)tetrahydropyran[15] **9**,[18] **10**,[19] and **18a**,**b**,[8e] and *exo*-norbornenic acid ester[26] were prepared according to the literature procedures. Compounds **2**,[27]**4a**,**b**,[15] and **12**,[8a] are known, but were prepared by different



Scheme 10. (a) $[Ru(bpy)_2Cl_2]$, dioxane, propylene glycol, 24 h (54%); (b) benzene, AIBN, 80 °C, 5 d, 62%; (c) $[(Cy_3P)_2Cl_2Ru{=}CHPh]$, DCM, room temp.

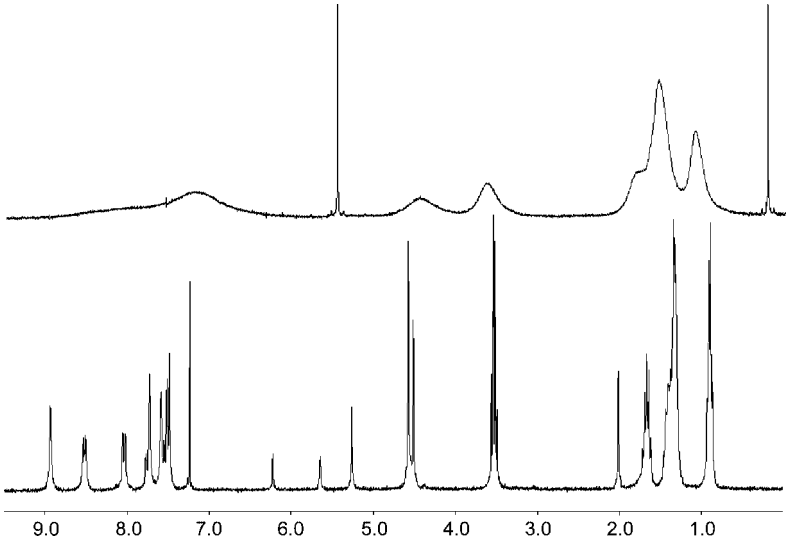


Figure 1. ^1H NMR spectra of **22** ($CDCl_3$, 20 °C, 270 MHz) and of corresponding polymer **31** (CD_2Cl_2, 20 °C, 270 MHz)

procedures. Therefore their analytical and spectroscopic data are not given. All other compounds are new. All polymers were not fully characterized by organic chemistry standards. Melting points: Büchi SMP 510 (open capillaries, uncorrected values). NMR: Bruker AC-250, AM-270, AMX-500 (^{1}H: $CDCl_3$ at δ = 7.24 ppm, ^{13}C: $CDCl_3$ at δ = 77.00 ppm as internal standards, 20 °C). MS: Perkin–Elmer Varian MAT-711, electron-impact (EI) mode. Elemental analyses: Perkin–Elmer EA-240. Column chromatography: Merck silica gel 60, 0.040–0.063 mm (230–400 mesh).

General Procedure for the Coupling of Terminal Acetylene with Aryl Iodides or Aryl Bromides: A thick-walled flask was charged with the terminal acetylene, aryl iodide or aryl bromides, $[Pd(PPh_3)_4]$ (0.02 equiv. per coupling), CuI (0.02 equiv. per coupling), dry triethylamine, and dry toluene. The reaction mixture was evacuated, flushed with nitrogen, sealed with a Teflon screw cap, and stirred at 60 °C for 24 h for iodo compounds and at 80 °C for bromo ones, respectively. The reaction mixture was filtered and the solvent removed. The compounds were purified by column chromatography through silica gel.

General Procedure for the Deprotection of Acetylenic Trimethylsilyl Groups: A catalytic amount of 1 M NaOH solution was added to the silyl compound in a mixture of THF/methanol (1:1) and stirred at room temp. for 16 h. Then the reaction mixture was diluted with diethyl ether and brine, and the phases were separated. The aqueous phase was extracted with diethyl ether and the combined organic phases were dried over $MgSO_4$, the solvent was removed, and the compound purified by column chromatography through silica gel.

General Procedure for the Deprotection of Acetylenic Tri(isopropyl) silyl Groups: To a stirred solution of the silyl compound in THF, tetrabutylammonium fluoride trihydrate (1 equiv. per deprotection) was added and the reaction stirred for 24 h at room temp. The reaction mixture was diluted with diethyl ether and brine and the phases were separated. The aqueous phase was extracted with diethyl ether and the combined organic phases were dried over $MgSO_4$. The solvent was removed and the compound purified by column chromatography through silica gel.

General Procedure for Macrocycle Synthesis: A solution of **C** (0.98 mmol) and **D** (0.98 mmol) in a mixture of dry triethylamine (320 mL) and dry toluene (320 mL) was carefully degassed. After the addition of $[Pd(PPh_3)_4]$ (0.04 equiv.) and CuI (0.04 equiv.), the mixture was stirred under nitrogen at 60 °C for 4 d and then at 95 °C for 24 h. The solvent was removed, the residue dissolved in CH_2Cl_2 (300 mL), and the resulting mixture treated with a solution of KCN (265 mg) in water (200 mL). The phases were separated, the aqueous one was extracted with CH_2Cl_2, and the combined organic phases were washed with water. It was then dried with $MgSO_4$ and the solvent removed. The macrocycles were purified by preparative GPC (Yields: 20–35%).

2-Bromo-5-iodopyridine (2): To a stirred suspension of 2,5-dibromopyridine (**1**) (10 g, 42.2 mmol) in dry diethyl ether (280 mL) a solution of 1.6 M BuLi in hexane (28 mL, 44.8 mmol) was added drop wise at –78 °C. After 3 h diiodoethane was added in solid form (12.7 g, 45.1 mmol) to the resulting red suspension and the mixture was warmed to room temp. Then water (100 mL) was added and the phases were separated. The aqueous phase was extracted with diethyl ether (2 × 100 mL) and the combined organic phases were washed with water. The organic phase was dried ($MgSO_4$), the solvent was removed, and the resulting solid was purified by column chromatography over silica gel (hexane/ethyl acetate, 10:1) to give 9 g of **2** (75%) as a white solid.

2-[3-Bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyloxy]tetrahydropyran (3b): To a stirred solution of 2-(3,5-dibromobenzyloxy)tetrahydropyran (20 g, 57.1 mmol) in dry diethyl ether (200 mL) at –78 °C, a solution of 1.6 M BuLi in hexane (39.3 mL, 62.8 mmol) was added over a period of 15 min. After 3 d, triisopropyl borate (13 g, 68.8 mmol) was added and the mixture warmed to room temperature. The organic phase was washed with water and the aqueous one extracted with diethyl ether. The combined organic phases were dried with $MgSO_4$. The solvent was removed and the resulting oil used for the esterification without further purification. The crude boronic acid and 2,3-dimethylbutane-2,3-diol (5.91 g, 50.0 mmol) were dissolved in toluene (100 mL), and refluxed for 2 d. The formed water was removed from the reaction using a Dean–Stark trap. The solvent was removed and the oil was purified by column chromatography through silica gel (hexane/ethyl acetate, 20:1) to give 4.65 g of **3b** (83%) as colorless oil. R_f (hexane/ethyl acetate, 20:1) = 0.12. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.31 (s, 12 H, CH_3), 1.46–1.91 (m, 6 H, THP), 3.53 (m, 1 H, THP), 3.90 (m, 1 H, THP), 4.43 (d, 1 H, benzyl-H), 4.66 (s, 1 H, THP), 4.72 (d, 1 H, benzyl-H), 7.60 (s, 1 H, phenyl-H), 7.66 (s, 1 H, phenyl-H), 7.84 (s, 1 H, phenyl-H) ppm. ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 19.28, 24.83, 25.42, 30.48, 62.08, 68.01, 84.15, 97.92, 122.51, 132.45, 133.46, 136.57, 140.04 ppm. MS (EI, 80 eV): *m/z* (%) = 380.2 (1.20), 296.4 (60.67), 216.7 (21.90), 196.5 (14.75), 115.8 (12.68), 84.9 (100.00). $C_{18}H_{26}BBrO_4$ (397.11): calcd. C 54.44, H 6.60; found C 54.41, H 6.35.

General Procedure for the Synthesis of Pyridines 4a,b: To a degassed mixture of the boronic ester **3** (11.10 g, 27.95 mmol), 2-bromo-5-iodopyridine **2** (7.93 g, 27.95 mmol), Bu_4NBr (9.01 g, 27.95 mmol) in toluene (160 mL) and aq. 2 M Na_2CO_3 (80 mL), $[Pd(PPh_3)_4]$ (600 mg, 0.52 mmol) was added and the reaction degassed once more. After the mixture was refluxed for 4 d the layers were separated and the aqueous one extracted with toluene (2 × 50 mL). The combined organic phases were dried ($MgSO_4$) and evaporated under reduced pressure. The crude product was purified by column chromatography through silica gel (hexane/ethyl acetate, 25:1) to give **4** as a white solid (85–90%).

General Procedure for the Synthesis of Symmetrical and Nonsymmetrical Building Blocks A: To a stirred solution of **4** (10.9 mmol) in dry toluene (120 mL) a 1.6 N solution of BuLi in hexane (7.2 mL, 11.5 mmol) was added drop wise at –78 °C. After 2 h, to the resulting red solution Me_3SnCl (2.4 g, 12 mmol) was added in solid form. The mixture was let to warm to room temp. and then compound **4** (10.9 mmol) was added to the brownish solution of **5**. The mixture was degassed, $[Pd(PPh_3)_4]$ (3 mol%) added, and the reaction mixture degassed again. After refluxing for 5 d the mixture was cooled to room temp. An aq. satd. KF solution (90 mL) was added to the organic phase followed by an aq. 2 N Na_2CO_3 solution (150 mL). The phases were separated, the aqueous one was extracted with toluene (2 × 100 mL). The combined organic phases were washed with water (100 mL) and dried ($MgSO_4$). The solvent was removed to give a brown oil which was purified by column chromatography trough silica gel.

5′-[3-Bromo-5-(hexyloxymethyl)phenyl]-5-[3-bromo-5-(tetrahydropyran-2-yloxymethyl)phenyl]-2,2′-bipyridinyl (8): **4a** (4.64 g, 10.86 mmol) and **4b** (4.64 g, 10.86 mmol). The reaction mixture was purified by column chromatography trough silica gel (hexane/ethyl acetate, 4:1) to give 2.5 g (30–35%) of **8** as a white solid. R_f (hexane/ethyl acetate, 4:1) = 0.38. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.42 (t, 3 H, CH_3), 1.24–1.45 (m, 6 H, γ-, δ-, ε-CH_2), 1.50–2.00 (m, 8 H, β-CH_2, THP), 3.47 (t, 2 H, α-CH_2), 3.60 (t, 1 H, THP), 3.91 (m, 1 H, THP), 4.56 (s, 2 H, benzyl-H), 4.56 (d, 1 H, benzyl-

H), 4.76 (t, 1 H, THP), 4.85 (d, 1 H, benzyl-CH_2), 7.53 (s, 2 H, phenyl-H), 7.59 (s, 2 H, phenyl-H), 7.71 (s, 2 H, phenyl-H), 8.00 (dd, ^3J = 8, ^4J = 2 Hz, 2 H, pyridyl-H,), 8.53 (d, ^3J = 8 Hz, 2 H, pyridyl-H), 8.88 (s, 2 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 14.00, 19.29, 22.58, 25.38, 25.84, 29.66, 30.48, 31.64, 62.22, 67.87, 71.04, 71.85, 98.10, 121.12, 123.22, 124.60, 124.82, 129.03, 130.06, 130.23, 135.16, 135.33, 139.55, 141.58, 141.58, 142.00, 147.52, 153.18, 154.82 ppm. MS (EI, 80 eV): *m/z* (%) = 694 (8.67), 612 (17.07), 594 (100). $C_{35}H_{38}Br_2N_2O_3$ (694.50): calcd. C 60.53, H 5.52, N 4.03; found 60.46, H 5.24, N 3.84.

5,5′-Bis[3-hexyloxymethyl-5-(trimethylsilanyl)phenyl]-2,2′-bipyridinyl (11). First Route: To a degassed mixture of **10** (15.32 g, 39.2 mmol) and 5,5-dibromo-2,2′-bipyridine (**9**) (5.60 g, 17.8 mmol) in toluene/aq. 2 M Na_2CO_3 2:1 (360 mL) [$Pd(PPh_3)_4$] (1.20 g, 1.04 mmol) was added and the mixture degassed once more. The reaction mixture was refluxed for 3 d and then the phases were separated. The aqueous one was extracted with toluene (2 × 100 mL) and the combined organic phases were dried with $MgSO_4$. The solvent was removed and the resulting oil purified by column chromatography through silica gel (hexane/ethyl acetate, 4:1) to give 11 g of **11** (90%) as a white solid. R_f (hexane/ethyl acetate, 9:1) = 0.35.

Second Route: To a degassed solution of **13** (4.64 g, 11.04 mmol) in dry toluene (140 mL) 3 mL (50 mol%) of hexa-*n*-butyldistannane and [$Pd(PPh_3)_4$] (290 mg, 0.25 mmol) were added and the reaction mixture was degassed again. After refluxing for 5 d the mixture was poured into aqueous EDTA (1 M, 40 mL). After stirring for 15 min the phases were separated. The aqueous one was extracted with toluene and the combined organic phases were dried ($MgSO_4$). After evaporation of the solvent, the raw product was purified by column chromatography through silica gel (hexane/ethyl acetate, 9:1) to give 3.23 g of **11** (85%) as a white solid. R_f (hexane/ethyl acetate, 9:1) = 0.35. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.35 [s, 18 H, $Si(CH_3)_3$], 0.93 (t, 6 H, CH_3), 1.24–1.45 (m, 12 H, γ-, δ-, ε-CH_2), 1.68 (m, 4 H, β-CH_2), 3.58 (t, 4 H, α-CH_2), 4.64 (s, 4 H, benzyl-H), 7.54 (s, 2 H, phenyl-H), 7.63 (s, 2 H, phenyl-H), 7.72 (s, 4 H, phenyl-H), 8.06 (d, ^3J = 8 Hz, 2 H, pyridyl-H), 8.55 (d, ^3J = 8 Hz, 2 H, pyridyl-H), 8.97 (s, 2 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 63 MHz): δ = –1.10, 14.02, 22.62, 25.94, 29.76, 31.70, 70.83, 72.85, 120.91, 126.92, 131.17, 132.35, 135.36, 136.80, 137.12, 138.88, 141.80, 147.80, 154.59 ppm. MS (EI): *m/z* (%) = 680 (100), 580 (22.26), 375 (13.14). HRMS ($C_{42}H_{60}N_2O_2Si_2$): calcd. 680.41931; found 680.41756.

5,5′-Bis(3-hexyloxymethyl-5-iodophenyl)-2,2′-bipyridinyl (12): Compound **11** (7.58 g, 11.02 mmol) was placed into a flask, which was evacuated and refilled with N_2. On the Schlenk line, dry CH_2Cl_2 (550 mL) and iodine monochloride (7.22 g, 44.47 mmol) were added under nitrogen. The mixture was heated to 45 °C for 48 h. Once it had cooled to room temperature, a solution of NaOH (2.22 g, 55 mmol) and $Na_2S_2O_3$ (6 g, 44.58 mmol) in water (140 mL) was added and the mixture stirred for 12 h. The phases were then separated, the aqueous one was extracted with CH_2Cl_2 (2 × 100 mL), and the combined organic phases were washed with 2 N NH_4OH (140 mL) and then dried with $MgSO_4$. Removal of the solvent gave 8.00 g of **12** (98%) as a white solid.

2-Bromo-5-[3-hexyloxymethyl-5-(trimethylsilanyl)phenyl]pyridine (13): To a degassed mixture of 2-bromo-5-iodopyridine **2** (5.17 g, 18.2 mmol) and **10** (7.11 g, 18.2 mmol) in toluene (110 mL) and aq. 2 M Na_2CO_3 (55 mL) [$Pd(PPh_3)_4$] (410 mg, 0.35 mmol) was added. The mixture was degassed once more and refluxed for 3 d. Then the phases were separated, the aqueous one was extracted with toluene (2 × 100 mL) and the combined organic phases dried with $MgSO_4$. The solvent was removed under reduced pressure. The product was purified by column chromatography through silica gel (hexane/ethyl acetate, 9:1) to give 6.88 g of **13** (90%) as a white solid. R_f (hexane/ethyl acetate, 6:1) = 0.74. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.31 (s, 9 H, $Si(CH_3)_3$), 0.88 (t, 3 H, CH_3), 1.30–1.41 (m, 6 H, γ-, δ-, ε-CH_2), 1.63 (m, 2 H, β-CH_2), 3.52 (t, 2 H, α-CH_2), 4.57 (s, 2 H, benzyl-H), 7.50–7.56 (m, 4 H, phenyl-H, pyridyl-H), 7.74 (dd, ^3J = 8 Hz, 1 H, pyridyl-H), 8.58 (s, 1 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 63 MHz): δ = –1.15, 14.01, 22.60, 25.91, 29.72, 31.67, 33.10, 70.89, 72.69, 126.77, 127.91, 131.05, 132.59, 136.02, 136.35, 137.09, 139.01, 142.05, 148.61, 153.13 ppm. MS (EI, 80 eV): *m/z* (%) = 421.0 (44.13), 418.9 (42.34), 406.0 (66.00), 404.0 (61.49), 321 (100.00), 318.9 (95.72). $C_{21}H_{30}BrNOSi$ (420.46): calcd. C 59.99, H 7.19, N 3.33; found C 59.93, H 6.98, N 3.22.

5,5′-Bis(3-hexyloxymethyl-5-{3-hexyloxymethyl-5-[(triisopropylsilanyl)ethynyl]phenylethynyl}phenyl)-2,2′-bipyridinyl (14): B (X^3 = CH_2OHex) (3.41 g, 8.6 mmol), 6 (2.01 g, 2.90 mmol), triethylamine (40 mL), toluene (20 mL). Column chromatography through silica gel (hexane/ethyl acetate, 10:1) gave 3.07 g of **14** (80%) as a colorless oil. R_f (hexane/ethyl acetate, 4:1) = 0.48. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.92 (t, 12 H, CH_3), 1.12 [s, 42 H, $Si(C_3H_7)_3$], 1.30–1.48 (m_c, 24 H, γ-, δ-, ε-CH_2), 1.64 (m_c, 8 H, β-CH_2), 3.28 (m, 8 H, α-CH_2), 4.40 (s, 4 H, benzyl-H), 4.60 (s, 4 H, benzyl-H), 7.42 (s, 2 H, phenyl-H), 7.48 (s, 2 H, phenyl-H), 7.56 (s, 2 H, phenyl-H) 7.60 (s, 2 H, phenyl-H) 7.70 (s, 2 H, phenyl-H) 7.72 (s, 2 H, phenyl-H), 8.04 (d, ^3J = 8 Hz, 2 H, pyridyl-H), 8.52 (d, ^3J = 8 Hz, 2 H, pyridyl-H), 8.96 (s, 2 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 11.28, 14.03, 18.64, 22.61, 25.84, 29.67, 31.67, 70.81, 70.95, 71.92, 72.22, 89.17, 89.42, 91.41, 106.05, 121.03, 123.25, 123.98, 126.14, 129.25, 130.30, 130.43, 130.91, 134.15, 135.26, 135.63, 138.04, 139.37, 140.18, 147.67, 154.95 ppm. MS (EI, 80 eV): *m/z* (%) = 1326 (10) [M^+], 1282 (100). HRMS ($C_{88}H_{120}N_2O_4Si_2$): calcd. 1280.81607; found 1280.81120.

5′-(3-Hexyloxymethyl-5-{3-hexyloxymethyl-5-[(triisopropylsilanyl)-ethynyl]phenylethynyl}phenyl)-5-{3-[3-hexyloxymethyl-5-[(triisopropylsilanyl)ethynyl]phenylethynyl]-5-(tetrahydropyran-2-yloxymethyl)phenyl}-2,2′-bipyridinyl (15): 8 (1.78 g, 2.56 mmol), **B** (X^3 = CH_2OHex) (3.01 g, 7.60 mmol), triethylamine (40 mL), toluene (20 mL). Column chromatography through silica gel (hexane/ethyl acetate, 6:1) gave 2.79 g of **15** (82%) as colorless oil. R_f (hexane/ethyl acetate, 3:1) = 0.36. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.86 (t, 9 H, CH_3), 1.12 [s, 42 H, $Si(C_3H_7)_3$], 1.23–1.42 (m_c, 18 H, β-, γ-, δ-CH_2), 1.50–1.90 (m_c, 12 H, β-CH_2, 6 H-THP), 3.45–3.6 (m, 7 H, α-CH_2, THP), 3.90 (m, 1 H, THP), 4.39 (s, 4 H, benzyl-H), 4.51 (s, 2 H, benzyl-H), 4.56 (d, ^2J = 12 Hz, 1 H, benzyl-H), 4.73 (t, 1 H, THP), 4.88 (d, ^2J = 12 Hz, 1 H, benzyl-H), 7.41 (s, 2 H, phenyl-H), 7.48 (s, 2 H, phenyl-H), 7.53 (s, 1 H, phenyl-H), 7.56 (s, 2 H, phenyl-H), 7.61 (s, 3 H, phenyl-H), 7.71 (s, 2 H, phenyl-H), 7.53 (d, ^3J = 8 Hz, 2 H, pyridyl-H), 8.00 (d, ^3J = 8 Hz, 2 H, pyridyl-H), 8.91 (s, 2 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 11.17, 13.93, 18.19, 19.20, 22.51, 25.34, 25.74, 29.56, 30.41, 31.55, 61.98, 66.90, 68.03, 70.67, 70.81, 71.75, 72.04, 89.07, 89.37, 91.22, 97.86, 105.98, 120.89, 123.13, 123.83, 12589, 126.11, 129.03, 130.26, 130.71, 133.97, 135.02, 135.39, 137.79, 139.30, 139.68, 140.10, 147.42, 154.64 ppm. MS (FAB): *m/z* (%) = 1327 (7.20) [M + H]$^+$, 496 (32.29). $C_{87}H_{116}N_2O_5Si_2$ (1326.03): calcd. C 78.80, H 8.82, N 2.11; found C 78.42, H 8.83, N 1.94.

5,5′-Bis{3-[3-ethynyl-5-(hexyloxymethyl)phenylethynyl]-5-(hexyloxymethyl)phenyl}-2,2′-bipyridinyl (16): 14 (2.72 g, 2.05 mmol), ammonium fluoride trihydrate (1.36 g, 4.25 mmol). The compound was purified by column chromatography through silica gel (ethyl acetate/hexane, 1:6) to give 1.97 g of **16** (95%) as a white solid. R_f

= 0.07 (ethyl acetate/hexane, 1:3). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.89 (t, 12 H, CH_3), 1.29 (m_c, 24 H, β-, γ-, δ-CH_2), 1.63 (m_c, 8 H, β-CH_2), 3.1 (s, 2 H, acetylene-H), 3.50 (m, 8 H, α-CH_2), 4.46 (s, 4 H, benzyl-H), 4.59 (s, 4 H, benzyl-H), 7.42 (s, 2 H, phenyl-H), 7.52 (s, 2 H, phenyl-H), 7.57 (s, 2 H, phenyl-H) 7.59 (s, 2 H, phenyl-H) 7.62 (s, 2 H, phenyl-H) 7.72 (s, 2 H, phenyl-H), 8.04 (d, ^3J = 9 Hz, 2 H, pyridyl-H), 8.55 (d, ^3J = 9 Hz, 2 H, pyridyl-H), 8.95 (s, 2 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 14.04, 22.62, 25.85, 25.90, 29.69, 31.68, 70.89, 70.99, 71.85, 72.24, 88.97, 121.07, 122.59, 123.57, 123.95, 126.24, 129.28, 130.32, 130.92, 134.16, 135.29, 135.71, 138.1, 139.64, 140.25, 147.70, 153.57, 154.99 ppm. MS (FAB): *m*/*z* (%) = 1014 (100), 926 (57.53). $C_{70}H_{80}N_2O_4$ (1013.40): calcd. C 82.96, H 7.96, N 2.76 found C 81.21, H 7.59, N 2.53.

5′-{3-[3-Ethynyl-5-(hexyloxymethyl)phenylethynyl]-5-(hexyloxymethyl)phenyl}-5-{3-[3-ethynyl-5-(hexyloxymethyl)phenylethynyl]-5-(tetrahydropyran-2-yloxymethyl)phenyl}-2,2′-bipyridinyl (17): 15 (2.90 g, 2.19 mmol), ammonium fluoride trihydrate (1.45 g, 4.52 mmol). The compound was purified by column chromatography through silica gel (hexane/ethyl acetate, 1:3) to give 2.15 g **17** (97%) as a white solid. R_f (ethyl acetate/hexane, 1:3) = 0.36. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.86 (t, 9 H, CH_3), 1.18–1.38 (m_c, 18 H, γ-, δ-, ε-CH_2), 1.50–2.00 (m_c, 12 H, β-CH_2, THP), 3.09 (s, 2 H, acetylene-H), 3.35–3.57 (m, 7 H, α-CH_2, THP), 3.91 (m, 1 H, THP), 4.39 (s, 4 H, benzyl-H), 4.47 (s, 2 H, benzyl-H), 4.51 (d, ^2J = 12 Hz, 1 H, benzyl-H), 4.71 (t, 1 H, THP), 4.82 (d, ^2J = 12 Hz, 1 H, benzyl-H), 7.36 (s, 2 H, phenyl-H), 7.45 (s, 2 H, phenyl-H), 7.5 (s, 2 H, phenyl-H) 7.55 (s, 4 H, phenyl-H) 7.65 (s, 2 H, phenyl-H) 7.94 (d, ^3J = 8 Hz, 2 H, pyridyl-H), 8.48 (d, ^3J = 8 Hz, 2 H, pyridyl-H), 8.86 (s, 2 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 13.87, 19.17, 22.45, 25.29, 25.74, 29.51, 30.37, 31.49, 61.93, 67.98, 70.66, 71.56, 71.50, 77.81, 82.63, 88.86, 89.52, 97.85, 120.81, 122.42, 123.25, 123.70, 123.73, 125.82, 126.05, 128.93, 130.00, 130.18, 130.58, 130.68, 131.03, 133.89, 134.86, 135.21, 137.73, 139.47, 139.67, 140.07, 147.34, 154.63 ppm. MS (FAB): *m*/*z* (%) = 1013 (12.30), 927 (6.35). $C_{69}H_{76}N_2O_5$ (1013.35): calcd. C 81.78, H 7.56, N 2.76; found C 81.22, H 7.34, N 2.38.

Macrocycle E4: (X^1 = X^2 = Hex, X^3 = CH_2OHex, Scheme 1). **16** (300 mg, 0.30 mmol), **12** (236 mg, 0.30 mmol), triethylamine (100 mL), toluene (100 mL), [$Pd(PPh_3)_4$] (0.04 equiv.), and CuI (0.04 equiv.), gave 83 mg of cycle **E4** (19%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.91 (t, 18 H, CH_3), 1.20–1.49 (m_c, 36 H, γ-, δ-, ε-CH_2), 1.67 (m_c, 12 H, β-CH_2), 3.53 (m, 12 H, α-CH_2), 4.51 (s, 4 H, benzyl-H), 4.59 (s, 8 H, benzyl-H), 7.5 (s, 4 H, phenyl-H), 7.55 (s, 4 H, phenyl-H), 7.62 (s, 4 H, phenyl-H) 7.75 (s, 6 H, phenyl-H), 8.06 (dd, ^3J = 8, ^4J = 2 Hz, 4 H, pyridyl-H), 8.53 (d, ^3J = 8 Hz, 4 H, pyridyl-H), 8.96 (s, 4 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 14.03, 22.63, 23.91, 25.89, 29.14, 29.74, 31.70, 70.90, 70.98, 71.99, 72.27, 89.23, 89.70, 121.11, 123.55, 124.04, 125.91, 129.55, 129.99, 130.16, 134.48, 135.12, 135.40, 137.92, 139.65, 140.25, 147.59, 154.96 ppm. MS (FAB): *m*/*z* (%) = 1546 (100), 1460 (57.85). $C_{106}H_{120}N_4O_6$ (1546.11): calcd. C 82.34, H 7.82, N 3.62; found C 81.27, H 7.54, N 3.50.

Macrocycle E1 (20): (X^1 = THP, X^2 = Hex, X^3 = CH_2OHex, Scheme 1). **17** (1.84 g, 1.82 mmol), **12** (1.44 g, 1.82 mmol), triethylamine (600 mL), toluene (600 mL), [$Pd(PPh_3)_4$] (80 mg, 0.04 equiv.), CuI (13 mg, 0.04 equiv.), gave 0.66 g of cycle **20** (23%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ= 0.88 (t, 15 H, CH_3), 1.20–1.44 (m_c, 30 H, γ-, δ-, ε-CH_2), 1.50–2.00 (m_c, 16 H, THP, β-CH_2), 3.40–3.64 (m, 11 H, THP, α-CH_2), 3.92 (m, 1 H, THP), 4.46 (s, 4 H, benzyl-H), 4.52 (s, 7 H, THP, benzyl-H), 4.76 (t, 1 H, THP), 5.84 (d, 1 H, benzyl-H), 7.36–7.60 (m, 12 H, phenyl-H), 7.68 (s, 6 H, phenyl-H), 8.00 (dd, ^3J = 8 Hz, 4 H, pyridyl-H), 8.52 (d, 4 H, ^3J = 8 Hz, pyridyl-H), 8.88 (s, 4 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 14.05, 19.42, 22.65, 25.49, 25.92, 28.73, 30.61, 31.72, 62.29, 68.24, 70.93, 71.04, 71.99, 72.20, 89.35, 89.56, 98.15, 121.56, 123.45, 124.07, 125.51, 129.15, 130.14, 134.35, 135.32, 135.43, 136.96, 139.51, 139.77, 140.18, 146.69, 153.36 ppm. MS (FAB): *m*/*z* (%) = 1546 (19.72), 1462 (6.81). $C_{105}H_{116}N_4O_7$ (1546.07): calcd. C 81.57, H 7.56, N 3.62; found C 81.18, H 7.42, N 3.76.

5,5′-Bis{3-hexyloxymethyl-5-[(3-iodophenyl)ethynyl]phenyl}-2,2′-bipyridyl (18c): 18b (2.00 g, 3.42 mmol), 1,3-diiodobenzene (23 g, 70 mmol), toluene (230 mL), triethylamine (230 mL), [$Pd(PPh_3)_4$] (0.04 equiv.) and CuI (0.04 equiv.), 3 d. The solvent was removed and the crude product purified by column chromatography through silica gel (hexane/ethyl acetate, 6:1) to give 2.00 g of **18c** (60%) as white solid. R_f (hexane/ethyl acetate, 6:1) = 0.17. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.91 (t, 6 H, CH_3), 1.23–1.42 (m, 12 H, γ-, δ-, ε-CH_2), 1.65 (m, 4 H, β-CH_2), 3.53 (t, 4 H, α-CH_2), 4.56 (s, 4 H, benzyl-H), 7.06 (t, 2 H, phenyl-H), 7.42 (d, 2 H, phenyl-H), 7.45 (s, 2 H, phenyl-H), 7.53 (s, 2 H, phenyl-H), 7.59 (d, 2 H, phenyl-H), 7.64 (s, 2 H, phenyl-H), 7.83 (s, 2 H, phenyl-H), 7.96 (dd, ^3J = 8, ^4J = 2 Hz, 2 H, pyridyl-H), 8.54 (d, ^3J = 8 Hz, 2 H, pyridyl-H), 8.94 (d, ^4J = 2 Hz, 2 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 14.00, 22.58, 25.84, 29.68, 31.64, 70.95, 72.13, 88.18, 90.26, 93.67, 121.01, 123.70, 125.07, 126.22, 129.16, 129.81, 130.22, 130.69, 135.16, 135.51, 137.38, 138.00, 140.17, 140.21, 147.59, 154.88 ppm. MS (EI, 80 eV): *m*/*z* (%) = 988.9 (57.17), 988.0 (96.83), 888.9 (43.63), 887.9 (100), 761.9 (26.69), 127.9 (45.09), 42.0 (49.08). HRMS: ($C_{52}H_{50}I_2N_2O_2$): calcd. 988.19617; found 988.19436.

Macrocycle E5: 18c (1.9 g, 1.92 mmol), **18b** (1.12 g, 1.92 mmol), triethylamine (600 mL), toluene (800 mL), [$Pd(PPh_3)_4$] (0.04 equiv.), copper iodide (0.04 equiv.), gave 540 mg of cycle **E5** (28%).

2-(5-{3-Bromo-5-[(hexyloxy)methyl]phenyl}pyridin-2-yl)-5-{3-[(hexyloxy)methyl]-5-(trimethylsilyl)phenyl}pyridine (19a): To a stirred solution of **4a** (3.03 g, 7.09 mmol) in dry toluene (50 mL) a 1.6 N solution of BuLi in hexane (4.7 mL, 7.52 mmol) was added dropwise at –78 °C. To the resulting red solution Me_3SnCl (1.53 g, 7.68 mmol) was added in solid form after 2 h. The mixture was let to warm to room temp. (overnight). Compound **13** (2.98 g, 7.09 mmol) was then added to the brownish solution of **5a**. The mixture was degassed and [$Pd(PPh_3)_4$] (3 mol%) added. The reaction mixture was degassed once more and refluxed for 5 d. Then it was cooled to room temp. and an aq. satd. KF solution (90 mL) added followed by an aq. 2 N Na_2CO_3 solution (150 mL). The phases were separated, the aqueous one was extracted with toluene (2 × 100 mL) and the combined organic phases washed with water (100 mL) and dried ($MgSO_4$). The solvent was removed and the crude brown oil purified by column chromatography through silica gel (hexane/ethyl acetate, 9:1) to give 2.18 g of **19a** (44%) as a white solid, together with the homocoupling products **6** (0.64 g) and **11** (0.43 g). ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.43 [s, 9 H, $Si(CH_3)_3$], 0.75–0.95 (m, 6 H, CH_3), 1.20–1.40 (m, 12 H, γ-, δ-, ε-CH_2), 1.60–1.75 (m, 4 H, β-CH_2), 3.45–3.55 (m, 4 H, α-CH_2), 4.53 (s, 2 H, benzyl-H), 4.59 (s, 2 H, benzyl-H), 7.53 (s, 3 H, phenyl-H), 7.61 (s, 1 H, phenyl-H), 7.68 (s, 2 H, phenyl-H), 7.98 (dd, ^3J = 8, ^4J = 2 Hz, 1 H, pyridyl-H), 8.03 (dd, ^3J = 8, ^4J = 2 Hz, 1 H, pyridyl-H), 8.52 (d, ^3J = 8 Hz, 2 H, pyridyl-H), 8.93 (s, 1 H, pyridyl-H), 8.93 (s, 1 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 63 MHz): δ = –1.24, 13.60, 13.88, 22.22, 22.45, 25.71, 25.78, 29.52, 29.60, 31.27, 31.52, 31.79, 33.65, 70.62, 70.80, 71.62, 72.62, 120.72, 120.81, 123.04, 124.25, 126.65, 128.67, 129.69, 130.89, 132.15, 134.59, 134.86, 135.00, 136.63, 136.81, 138.74, 139.43, 141.49, 141.82, 147.30, 147.58, 154.09, 155.00 ppm. MS (EI): *m*/*z* (%) = 688 (100),

586 (35). HRMS ($C_{39}H_{51}BrN_2O_2Si$): calcd. 686.290319, found: 686.29333.

2-(5-{3-Bromo-5-[(hexyloxy)methyl]phenyl}pyridin-2-yl)-5-{3-[(hexyloxy)methyl]-5-iodophenyl}pyridine (19b): To a solution of **19a** (4.79 g, 6.96 mmol) in dry dichloromethane (350 mL), ICl (3.39 g, 20.8 mmol) was added under nitrogen. The reaction mixture was refluxed for 2 d. After it was cooled to room temp., a solution of NaOH (1 g) and $Na_2S_2O_3$ (2.8 g) in water (30 mL) was added and stirring continued for 2 h. The organic phase was separated, washed with 2 N NH_4OH (65 mL) and dried with $MgSO_4$. The solvent was removed and the mixture purified by column chromatography through silica gel (hexane/ethyl acetate, 9:1) to give 1.86 g of **19b** (79%) as a white solid. R_f (hexane/ethyl acetate, 4:1) = 0.59. M. p. 87 °C. ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.87 (t, 6 H, CH_3), 1.10–1.40 (m, 12 H, γ-, δ-, ε-CH_2), 1.75–1.60 (m, 4 H, β-CH_2), 3.50 (t, 4 H, α-CH_2), 4.50 (s, 2 H, benzyl-H), 4.53 (s, 2 H, benzyl-H), 7.52 (s, 2 H, phenyl-H), 7.55 (s, 1 H, phenyl-H), 7.67 (s, 1 H, phenyl-H), 7.72 (s, 1 H, phenyl-H), 7.87 (s, 1 H, phenyl-H), 7.97 (m, ^3J = 8 Hz, 2 H, pyridyl-H), 8.48 (d, ^3J = 8 Hz, 2 H, pyridyl-H) 8.86 (s, 2 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 68 MHz): δ = 14.03, 22.60, 25.85, 29.66, 31.64, 71.02, 71.72, 71.84, 95.01, 121.03, 123.20, 124.61, 125.34, 128.99, 130.03, 134.94, 134.98, 135.23, 136.00, 139.61, 139.68, 141.89, 141.95, 147.57, 154.98 ppm. MS (FAB): *m/z* (%) = 741 (9.78) $[M]^+$. $C_{36}H_{42}BrIN_2O_2$ (741.54): calcd. C 58.31, H 5.71, N 3.78; found 58.22, H 5.52, N 3.56.

2-(5-{3-Bromo-5-[(hexyloxy)methyl]phenyl}pyridin-2-yl)-5-{3-[(hexyloxy)methyl]-5-[2-(trimethylsilyl)ethynyl]phenyl}pyridine (19c): 19b (3.83 g, 5.14 mmol), trimethylsilylethyne (0.53 g, 5.32 mmol), triethylamine (70 mL), toluene (40 mL), reaction time: 24 h at 60 °C. The crude product was purified by column chromatography through silica gel (hexane/ethyl acetate, 10:1) to give 3.21 g of **19c** (88%) as colorless oil. ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.25 [s, 9 H, $Si(CH_3)_3$], 0.75–0.98 (t, 6 H, CH_3), 1.20–1.45 (m, 12 H, γ-, δ-, ε-CH_2), 1.55–1.75 (m, 4 H, β-CH_2), 3.42 (t, 4 H, α-CH_2), 4.41 (s, 2 H, benzyl-H), 4.44 (s, 2 H, benzyl-H), 7.42 (s, 3 H, phenyl-H), 7.47 (s, 1 d, phenyl-H), 7.56 (s, 1 H, phenyl-H), 7.59 (s, 1 H, phenyl-H), 7.81–7.89 (m, 2 H, pyridyl-H), 8.39 (d, ^3J = 8 Hz, 2 H, pyridyl-H), 8.75 (s, 1 H, pyridyl-H), 8.80 (s, 1 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 68 MHz): δ = 0.24, 13.87, 22.40, 25.66, 29.47, 31.44, 70.60, 70.71, 71.52, 71.86, 94.65, 104.44, 120.63, 122.93, 123.80, 124.12, 125.76, 128.54, 129.15, 129.60, 130.29, 134.47, 134.72, 135.14, 137.42, 139.25, 139.76, 141.68, 147.20, 147.25, 154.35, 154.71 ppm. MS (EI, 80 EV): *m/z* (%) = 712.2 (21) $[M]^+$, 611.9 (100), $[M - OHex]^+$. HRMS ($C_{41}H_{51}O_2N_2Si^{79}Br$): calcd. 710.29034; found 710.29211.

2-(5-{3-[(Hexyloxy)methyl]-5-[2-(triisopropylsilyl)ethynyl]phenyl}-pyridin-2-yl)-5-{3-[(hexyloxy)methyl]-5-[2-(trimetylsilyl)ethynyl]-phenyl}pyridine (19d): 19c (1.68 g, 2.36 mmol), triisopropylsilylethyne (0.54 g, 3.07 mmol), triethylamine (50 mL), toluene (35 mL), 24 d, at 80 °C. The compound was purified by column chromatography through silica gel (hexane/ethyl acetate, 4:1) to give 1.44 g of **19d** (75%) as colorless oil. R_f (hexane/ethyl acetate, 4:1) = 0.53. ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.23 [s, 9 H, $Si(CH_3)_3$], 0.83 (t, 6 H, CH_3), 1.10 [s, 21 H, $Si(C_3H_7)_3$], 1.20–1.40 (m, 12 H, γ-, δ-, ε-CH_2), 1.50–1.60 (m, 4 H, β-CH_2), 3.40 (t, 4 H, α-CH_2), 4.41 (s, 2 H, benzyl-H), 4.43 (s, 2 H, benzyl-H), 7.30–7.45 (m, 4 H, phenyl-H), 7.58 (s, 2 H, phenyl-H), 7.87 (m, 2 H, pyridyl-H), 8.44 (d, ^3J = 8 Hz, 2 H, pyridyl-H) 8.81 (s, 2 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 68 MHz): δ = –0.31, 11.06, 13.81, 18.43, 22.39, 25.66, 29.45, 31.42, 70.53, 71.79, 90.84, 94.45, 104.46, 106.44, 120.54, 123.78, 124.14, 125.63, 129.08, 129.19, 130.16, 130.23, 134.63, 135.01, 135.10, 137.46, 137.51, 139.74, 147.21, 154.47 ppm. MS (EI): *m/z* (%) = 812.5 (5) $[M]^+$, 769.4 (25), $[M - C_3H_7]^+$. HRMS ($C_{52}H_{72}N_2O_2Si_2$): calcd. 812.51324, found 812.51533.

5-{3-Ethynyl-5-[(hexyloxy)methyl]phenyl}-2-(5-{3-[(hexyloxy)-lxmethyl]-5-[2-(triisopropylsilyl)ethynyl]phenyl}pyridin-2-yl)pyridine (19e): 19d (1.28 g, 1.57 mmol), THF (20 mL), methanol (10 mL), catalytic amount of 1 M NaOH solution, 24 h. The compound was purified by column chromatography through silica gel (hexane/ethyl acetate, 4:1) to give 1.14 g of **19e** (89%) as colorless oil. R_f (hexane/ethyl acetate, 4:1) = 0.61. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.86 (t, 6 H, CH_3), 1.13 (s, 21 H, $Si(C_3H_7)_3$), 1.20–1.40 (m, 12 H, γ-, δ-, ε-CH_2), 1.61 (quintet, 4 H, β-CH_2), 3.13 (s, 1 H, ethynyl-H), 3.42–3.55 (m, 4 H, α-CH_2), 4.50 (s, 2 H, benzyl-H), 4.51 (s, 2 H, benzyl-H), 7.47 (s, 2 H, phenyl-H), 7.54 (s, 1 H, phenyl-H), 7.57 (s, 1 H, phenyl-H), 7.65 (s, 2 H, phenyl-H), 7.90–8.05 (m, 2 H, pyridyl-H), 8.48 (d, ^3J = 8 Hz, 2 H, pyridyl-H) 8.87 (s, 1 H, pyridyl-H), 8.89 (s, 1 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 68 MHz): δ = 11.12, 13.85, 18.49, 22.42, 25.69, 29.50, 31.48, 70.64, 71.79, 71.90, 77.75, 83.07, 90.98, 106.47, 120.63, 122.84, 124.21, 125.68, 125.99, 129.31, 130.34, 134.71, 134.74, 134.99, 135.21, 137.57, 137.62, 139.77, 139.92, 147.25, 154.49, 154.58 ppm. MS (EI): *m/z* (%) = 740.4 (14) $[M]^+$, 697.6 (100) $[M - C_3H_7]^+$, 655.6 (23), [M – Hex]. HRMS ($C_{49}H_{64}O_2N_2Si$): calcd. 740.47369; found 740.47522.

5-{3-[(Hexyloxy)methyl]-5-(2-{3-[2-(trimethylsilyl)ethynyl]-5-[(tetrahydro-2*H*-pyran-2-yloxy)methyl]phenyl}ethynyl)phenyl}-2-(5-{3-[(hexyloxy)methyl]-5-[2-(triisopropylsilyl)ethynyl]phenyl}pyridin-2-yl)pyridine (19f): 15e (1.14 g, 1.54 mmol), (2-{3-bromo-5-[(tetrahydro-*2H*-pyran-2-yloxy)methyl]phenyl}ethynyl)trimethylsilane (0.68 g, 1.85 mmol), triethylamine (30 mL), toluene (40 mL), at 80 °C for 24 h. The compound was purified by column chromatography through silica gel (hexane/ethylacetate, 6:1) to give 1.12 g of **15f** (71%) as colorless oil. R_f (hexane/ethyl acetate, 4:1) = 0.48. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.24 [s, 9 H, $Si(CH_3)_3$], 0.75–0.95 (m, 6 H, CH_3), 1.12 [s, 21 H, $Si(C_3H_7)_3$], 1.20–1.90 (m, 22 H, β-, γ-, δ-, ε-CH_2, THP-H), 3.40–3.58 (m, 5 H, α-CH_2, THP), 3.80–3.89 (m, 1 H, THP), 4.43 (d, ^2J = 12 Hz, 1 H, benzyl-H), 4.52 (s, 2 H, benzyl-H), 4.53 (s, 2 H, benzyl-H), 4.68 (s, 1 H, THP), 4.71 (d, ^2J = 12 Hz, 1 H, benzyl-H), 7.41 (s, 1 H, phenyl-H), 7.47–7.57 (m, 6 H, phenyl-H), 7.64 (s, 1 H, phenyl-H), 7.69 (s, 1 H, phenyl-H), 7.99 (d, ^3J = 8 Hz, 2 H, pyridyl-H), 8.50 (d, ^3J = 8 Hz, 2 H, pyridyl-H) 8.90 (s, 2 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 68 MHz): δ = –0.20, 11.22, 13.96, 18.56, 19.13, 22.55, 25.33, 25.82, 29.61, 29.65, 30.36, 31.60, 61.89, 67.67, 70.78, 70.34, 72.08, 89.02, 89.42, 91.20, 94.88, 97.67, 103.99, 106.49, 120.85, 123.20, 123.49, 123.87, 124.37, 125.92, 129.06, 129.51, 130.11, 130.57, 130.82, 134.02, 135.05, 135.42, 135.53, 137.76, 137.89, 138.91, 139.90, 140.10, 147.52, 154.73, 154.80 ppm. MS (EI): *m/z* (%) = 1014.8 (10.82), 983.5 (27.09), 870.3 (8.88). HRMS ($C_{63}H_{79}N_2O_4Si_2$) $[M-C_3H_7]^+$: calcd. 983.55784; found 983.55705.

5-{3-(2-{3-Ethynyl-5-[(tetrahydro-2*H*-pyran-2-yloxy)methyl]-phenyl}ethynyl)-5-[(hexyloxy)methyl]phenyl}2-(5-{3-[(hexyloxy)methyl]-5-[2-(triisopropylsilyl)ethynyl]phenyl}pyridin-2-yl)-pyridine (19g): 19f (1 g, 0.97 mmol), THF (20 mL), methanol (15 mL). Purification by column chromatography through silica gel (hexane/ethyl acetate, 6:1) gave 0.88 g of **19g** (95%) as colorless oil. R_f (hexane/ethyl acetate, 6:1) = 0.38. ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.84 (t, 6 H, CH_3), 1.11 (s, 21 H, $Si(C_3H_7)_3$), 1.20–1.50 (m, 12 H, γ-, δ-, ε-CH_2), 1.50–1.95 (m, 10 H, THP, β-CH_2), 3.09 (s, 1 H, acetylene-H), 3.40–3.52 (m, 5 H, α-CH_2, THP), 3.78–3.89 (m, 1 H, THP), 4.45 (d, ^2J = 12 Hz, 1 H, benzyl-H), 4.48 (s, 2 H, benzyl-H), 4.49 (s, 2 H, benzyl-H), 4.66 (t, 1 H, THP), 4.69 (d, ^2J = 12 Hz, 1 H, benzyl-H), 7.40 (s, 1 H, phenyl-H), 7.45 (s, 1 H, phenyl-H), 7.51 (s, 2 H, phenyl-H), 7.52 (s, 1 H, phenyl-H), 7.55 (s, 1 H, phe-

nyl-H), 7.62 (s, 1 H, phenyl-H), 7.66 (s, 1 H, phenyl-H), 7.96 (d, ^3J = 8 Hz, 2 H, pyridyl-H), 8.48 (d, ^3J = 8 Hz, 2 H, pyridyl-H) 8.87 (s, 2 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 68 MHz): δ = 11.10, 13.87, 18.49, 19.01, 22.44, 25.21, 25.71, 29.50, 30.20, 31.48, 61.74, 67.48, 70.67, 71.91, 77.83, 82.54, 88.75, 89.45, 91.05, 97.63, 106.30, 120.76, 122.40, 123.17, 123.62, 124.23, 125.79, 128.92, 129.35, 129.98, 130.45, 130.75, 133.90, 134.90, 135.28, 137.64, 138.98, 139.76, 139.97, 147.36, 154.55 ppm. MS (FAB+): *m*/*z* (%) = 955.4 (5.24), 884.9 (2.10). HRMS ($C_{60}H_{73}N_2O_4Si$): calcd. 913.53396; found 913.53219.

Macrocycle 21: A solution of **20** (**E1**) (0.47 g, 0.30 mmol) in DCM (150 mL) and methanol (50 mL) was treated with a solution of hydrochloric acid (25%, 1.5 mL). The mixture was stirred at ambient temperature for 24 h and then treated with a solution of $NaHCO_3$ (pH = 7). The phases were separated and the organic one was washed with brine and dried with $MgSO_4$ to give 0.43 g of **21** (98%) as a white solid. ^{1}H NMR ($CDCl_3$, 270 MHz): to prevent aggregation some triethylammonium hydrochloride salt (TEA·HCl) was added into the NMR tube: δ = 0.80–0.95 (m, 15 H, CH_3), 1.25–1.50 (m, 30 H, γ-, δ-, ε-CH_2), 1.60–1.70 (m, 10 H, β-CH_2), 3.43–3.52 (m, 10 H, α-CH_2), 4.44 (s, 4 H, benzyl-H), 4.50 (s, 6 H, benzyl-H), 4.72 (s, 2 H, benzyl-H), 7.41 (s, 4 H, phenyl-H), 7.44 (s, 3 H, phenyl-H), 7.49 (s, 1 H, phenyl-H), 7.51 (s, 3 H, phenyl-H), 7.59 (s, 1 H, phenyl-H), 7.64 (s, 6 H, phenyl-H), 7.96 (d, ^3J = 8 Hz, 4 H, pyridyl-H), 8.43 (d, ^3J = 8 Hz, 4 H, pyridyl-H), 8.86 (s, 4 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 14.04, 22.63, 25.90, 29.69, 31.72, 70.90, 71.12, 71.99, 72.23, 88.95, 89.48, 120.46, 123.21, 123.33, 123.43, 124.71, 128.49, 129.30, 129.83, 133.80, 134.07, 136.52, 136.69, 138.89, 139.02, 141.96, 146.69, 154.18 ppm. MS (FAB): *m*/*z* (%) = 1462.8 (100) $[M + H]^+$; monoisotopic mass calcd. for $C_{100}H_{109}N_4O_6^+$: 1462.83; found: 1462.80.

Macromonomer 22: To a mixture of alcohol **21** (0.2 g, 0.14 mmol), triethylamine (70 μL), and catalytic amounts of 4-(dimethylamino) pyridine (2.6 mg) in dry dichloromethane (60 mL) freshly distilled methacryloyl chloride (60 μL) was added at 0 °C and the resulting mixture stirred for 20 h. After letting it warm to room temp. a saturated solution of $NaHCO_3$ was added and the phases were separated. The organic phase was washed with brine and dried with $MgSO_4$. The solvent was removed at room temp. The white solid was dissolved in the minimum amount of tetrahydrofurane and precipitated with methanol. The suspension was centrifugated, the white solid collected, and then dried at high vacuum to give 0.17 g of **22** (82%) as a white solid. ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.80–1.02 (m, 15 H, CH_3), 1.30–1.50 (m, 30 H, γ-, δ-, ε-CH_2), 1.60–1.75 (m, 10 H, β-CH_2), 2.02 (s, 3 H, CH_3), 3.45–3.60 (m, 10 H, α-CH_2), 4.48 (s, 4 H, benzyl-H), 4.50 (s, 6 H, benzyl-H), 5.19 (s, 2 H, benzyl-H), 5.66 (s, 1 H, C=CH_2), 6.24 (s, 1 H, C=CH_2), 7.49 (s, 4 H, phenyl-H), 7.52 (s, 3 H, phenyl-H), 7.55 (s, 1 H, phenyl-H), 7.59 (s, 4 H, phenyl-H), 7.73 (s, 5 H, phenyl-H), 7.77 (s, 1 H, phenyl-H), 8.04 (d, ^3J = 8 Hz, 4 H, pyridyl-H), 8.52 (d, ^3J = 8 Hz, 4 H, pyridyl-H), 8.94 (s, 4 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 68 MHz): δ = 14.04, 18.40, 22.62, 25.62, 29.74, 31.69, 65.66, 70.93, 71.93, 72.20, 89.09, 89.63, 120.85, 123.46, 123.83, 124.21, 125.49, 125.86, 126.17, 129.12, 129.78, 130.11, 134.22, 134.72, 136.02, 137.44, 137.74, 139.41, 139.92, 147.27, 154.65, 160.74 ppm. MS (MALDI-TOF) 1529.87. MS (FAB): *m*/*z* (%) = 1255.1 (100) $[M + Na]^+$. $C_{104}H_{112}N_4O_7$ (1530.02): calcd. C 81.64, H 7.38, N 3.66; found: C 81.48, H 6.94, N 3.29.

Macrocycle 23: *exo*-5-Norbornene-2-carboxylic acid (50 mg, 0.36 mmol), **21** (0.22 g, 0.15 mmol), DMAP (44 mg, 0.36 mmol), and dry dichloromethane (50 mL) were placed in a flask. DCC (74 mg, 0.36 mmol) was added to the solution at 0 °C. The solution was stirred for 20 d, during which time the reaction warmed to room temp. The solvent was removed, the solid dissolved in the minimum amount of tetrahydrofurane, and the compound precipitated by addition of methanol. The suspension was centrifugated and the precipitate filtered and dried in vacuo to give 0.23 g of **23** (96%) as a white solid. ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.80–0.95 (m, 15 H, CH_3), 1.25–1.50 (m, 32 H, γ-, δ-, ε-CH_2, norbornene), 1.58 (d, 1 H, norbornene), 1.60–1.72 (m, 10 H, β-CH_2), 1.95–2.05 (m, 1 H, norbornene), 2.30–2.40 (m, 1 H, norbornene), 2.95 (s, 1 H, norbornene), 3.12 (s, 1 H, norbornene), 3.50–3.65 (m, 10 H, α-CH_2), 4.50 (s, 4 H, benzyl-H), 4.55 (s, 6 H, benzyl-H), 5.17 (s, 2 H, benzyl-H), 6.14 (s, 2 H, norbornene), 7.46 (s, 5 H, phenyl-H), 7.48 (s, 4 H, phenyl-H), 7.54 (s, 4 H, phenyl-H), 7.67 (s, 4 H, phenyl-H), 7.71 (s, 1 H, phenyl-H), 7.99 (d, ^3J = 8 Hz, 4 H, pyridyl-H), 8.48 (d, ^3J = 8 Hz, 4 H, pyridyl-H), 8.90 (s, 4 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 500 MHz): δ = 13.99, 22.56, 25.88, 29.68, 30.45, 31.66, 41.62, 43.05, 46.35, 46.60, 70.82, 70.87, 71.90, 72.10, 88.91, 89.13, 89.31, 89.52, 120.50, 123.13, 123.53, 123.88, 124.90, 125.35, 128.56, 129.11, 129.46, 129.85, 129.95, 133.73, 133.90, 134.04, 134.13, 135.63, 136.87, 137.18, 138.05, 139.06, 139.10, 139.45, 146.80, 154.24, 154.33, 154.54, 175.73. MS (FAB): *m*/*z* (%) = 1582.8 (1.5), 448 (2.7), 391.6 (100) ppm. MS(MALDI-TOF, dithranol): 1581.83 $[M]^+$; monoisotopic mass calcd. for $C_{108}H_{116}N_4O_7$ 1581.89, found 1581.83. $C_{108}H_{116}N_4O_7$ (1582.10): calcd. C 81.99, H 7.39, N 3.54; found C 80.63, H 7.16, N 3.30.

{3-Bromo-5-[6-(5-{3-bromo-5-[(hexyloxy)methyl]phenyl}pyridin-2-yl)pyridin-3-yl]phenyl}methanol (24): To a stirred solution of **8** (1.5 g, 2.16 mmol) in THF/methanol, 1:1 (60 mL), hydrochloric acid (35%, 1 mL) was added. The reaction mixture was stirred at room temp. for 24 h. Then DCM (100 mL) and a saturated aqueous solution of $NaHCO_3$ (20 mL) were added and the phases separated. The aqueous one was extracted with dichloromethane (50 mL) and the combined organic phases were dried with $MgSO_4$. The solvent was removed to give 1.23 g of **24** (93%) as a white solid. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.84 (t, 3 H, CH_3), 1.20–1.40 (m, 6 H, γ-, δ-, ε-CH_2), 1.62 (m, 2 H, β-CH_2), 3.34 (s, 1 H, OH), 3.50 (t, 2 H, α-CH_2), 4.52 (s, 2 H, benzyl-H), 4.72 (s, 2 H, benzyl-H), 7.46 (s, 4 H, phenyl-H), 7.56 (s, 1 H, phenyl-H), 7.64 (s, 1 H, phenyl-H), 7.82 (d, 1 H, pyridyl-H), 7.92 (d, 1 H, pyridyl-H), 8.40 (2d overlapped in t, 2 H, pyridyl-H), 8.72 (s, 1 H, pyridyl-H), 9.89 (s, 1 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 13.98, 22.56, 25.82, 29.63, 31.62, 64.05, 71.05, 71.82, 121.11, 123.21, 123.26, 123.83, 124.53, 128.80, 128.92, 129.40, 130.04, 134.88, 135.08, 135.13, 135.22, 139.44, 141.94, 144.21, 147.40, 147.48, 154.77 ppm. MS (EI): *m*/*z* (%) = 610 (40.30), 509.8 (99.11), 430.7 (100). $C_{30}H_{30}Br_2N_2O_2$ (610.38): calcd. C 59.03, H 4.95, N 4.59; found C 59.01, H 4.66, N 4.46.

3-Bromo-5-[6-(5-{3-bromo-5-[(hexyloxy)methyl]phenyl}-pyridin-2-yl)pyridin-3-yl]benzyl Methacrylate (25): To a mixture of alcohol **24** (50 mg, 0.08 mmol), triethylamine (30 μL), and catalytic amounts of 4-(dimethylamino)pyridine (1.3 mg) in dry dichloromethane (2 mL) freshly distilled methacryloyl chloride (15 μL) was added at 0 °C and the resulting mixture stirred for 20 h before it was let to warm to room temp. Then a saturated solution of $NaHCO_3$ was added and the phases were separated. The organic one was washed with brine and dry over $MgSO_4$. The solvent was removed at room temp. and the compound dried to give 51 mg of **25** (95%) as a white solid. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.88 (t, 3 H, CH_3), 1.3–1.45 (m, 6 H, γ-, δ-, ε-CH_2), 1.65 (m, 2 H, β-CH_2), 1.99 (s, 3 H, CH_3), 3.52 (t, 2 H, α-CH_2), 4.54 (s, 2 H, benzyl-H), 5.24 (s, 2 H, benzyl-H), 5.63 (s, 1 H, C=CH_2), 6.20 (s, 1 H, C=CH_2) 7.54 (s, 2 H, phenyl-H), 7.56 (s, 2 H, phenyl-H), 7.68 (s, 1 H, phenyl-H), 7.73 (s, 1 H, phenyl-H), 7.99 (d, ^3J = 8 Hz, 2 H,

pyridyl-H), 8.51 (d, 2 H, ^3J = 8 Hz, pyridyl-H), 8.88 (s, 2 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 13.99, 18.31, 22.56, 25.82, 29.63, 31.60, 65.19, 71.00, 71.81, 121.10, 123.20, 124.59, 125.13, 126.31, 128.96, 129.69, 130.07, 130.41, 135.30, 141.93, 147.47, 155.01, 176.87 ppm. MS (EI): *m*/*z* (%) = 678 (71.9) [M^+], 578 (100), 497 (61.5). HRMS ($C_{34}H_{34}Br_2N_2O_3$): calcd. 678.09155; found: 678.09355.

26: *exo*,*endo*-5-Norbornene-2-carboxylic acid (115 μL, 0.5 mmol), **24** (0.3 g, 0.5 mmol), DMAP (0.12 g, 1 mmol), and dry dichloromethane (4 mL) were placed in a flask. DCC (0.2 g, 1 mmol) was added to the solution at 0 °C. The solvent was stirred under nitrogen at room temp. for 18 h. After removal of the solvent, the product was dissolved in acetone and a solution of 10% HCl was added (pH = 7) followed by the addition of NH_4PF_6 (0.8 g). The resulting solid was collected and washed with water. The aqueous phase was extracted with dichloromethane (2 × 100 mL). The solvent was removed and the solid washed with diethyl ether. The ether phase was treated with triethylamine and diluted with dichloromethane and water. The organic phase was separated and dried with $MgSO_4$ to give 0.4 g of **26** (70%) as white solid. ^{1}H NMR mixture of *endo*/*exo* 3:1 (from integration of the benzyl protons) ($CDCl_3$, 270 MHz): *exo*δ = 0.75 (t, 3 H, CH_3), 1.10–1.55 (m, 10 H, β-, γ-, δ-, ε-CH_2, nornornene-H), 1.58–1.68 (m, 2 H, norbornene-H), 2.15–2.25 (s, 1 H, norbornene), 2.85–3.00 (m, 2 H, norbornene), 3.36 (t, 2 H, α-CH_2), 4.36 (s, 2 H, benzyl-H), 5.01 (s, 2 H, benzyl-H), 5.95–6.30 (m, 2 H, norbornene), 7.35 (s, 4 H, phenyl-H), 7.49 (s, 1 H, phenyl-H), 7.53 (s, 1 H, phenyl-H), 7.75 (d, ^3J = 8 Hz, 2 H, pyridyl-H), 8.29 (d, ^3J = 8 Hz, 2 H, pyridyl-H), 8.67 (s, 2 H, pyridyl-H); *endo*: δ = 0.75 (t, 3 H, CH_3), 1.10–1.55 (m, 11 H, β-, γ-, δ-, ε-CH_2, nornornene), 1.72–1.90 (m, 2 H, norbornene), 2.78 (s, 1 H, norbornene), 3.12 (s, 1 H, norbornene), 3.36 (t, 2 H, α-CH_2), 4.36 (s, 2 H, benzyl-H), 4.96 (s, 2 H, benzyl-H), 5.75–5.80 (m, 1 H, norbornene), 6.03–6.10 (m, 1 H, norbornene), 7.35 (s, 4 H, phenyl-H), 7.49 (s, 1 H, phenyl-H), 7.53 (s, 1 H, phenyl-H), 7.75 (d, ^3J = 8 Hz, 2 H, pyridyl-H), 8.29 (d, ^3J = 8 Hz, 2 H, pyridyl-H), 8.67 (s, 2 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 63 MHz) for the *exo*-*endo* mixture: δ = 13.71, 22.27, 25.53, 28.96, 29.33, 30.13, 31.31, 41.33, 42.24, 42.71, 42.96, 45.48, 46.02, 46.30, 49.30, 64.37, 64.64, 66.64, 70.61, 71.37, 120.53, 122.80, 122.88, 122.92, 123.99, 124.45, 124.59, 126.45, 128.39, 128.98, 129.07, 129.50, 129.81, 129.93, 131.89, 132.18, 134.06, 134.43, 134.55, 135.28, 136.33, 137.53, 137.75, 139.03, 139.09, 139.15, 139.26, 139.32, 139.38, 141.67, 147.04, 147.08, 154.36, 154.63, 173.69, 175.23. MS (EI, 80 eV) *m*/*z* (%): 730.2 (100), 665.4 (17), 344.6 (57) ppm. HRMS ($C_{38}H_{38}{}^{79}Br_2N_2O_3$): calcd. 728.12673; found 728.12494.

[26·Ru(bpy)$_2$(PF$_6$)$_2$] (27): A stirred solution of **26** (0.33 g, 0.45 mmol) and $[Ru(bpy)_2Cl_2] \times 2H_2O$ (245 mg, 0.43 mmol) in a mixture of ethanol (8 mL) and H_2O (3 mL) was refluxed for 24 h. Then the solvent was removed and the residual orange material purified by column chromatography through silica gel (methanol/2 M NH_4Cl/nitromethane, 7:2:1). The combined orange fractions were diluted with CH_2Cl_2, the organic phase was separated, and the solvent removed to give an orange solid 0.36 g of **27** (66%). A small part of this solid was dissolved in methanol and added to a concentrated solution of NH_4PF_6. The precipitated solid was separated by filtration and washed with H_2O several times. The compound was characterized as PF_6 salt.

The product was obtained as a mixture of diastereoisomers with an *endo*/*exo* ratio of 1:3. Its ^{1}H NMR spectrum is therefore quite complex and the number of atoms which cause the signals are not given. ^{1}H NMR ([D]acetonitrile, 270 MHz): δ = 0.89 (t, CH_3), 1.25–1.45 (m, γ-, δ-, ε-CH_2, norbornene-H), 1.58–1.62 (m, β-CH_2), 1.56–1.85 (m, norbornene-H), 2.93 (s, norbornene-H), 3.00–3.05 (m, norbornene-H), 3.21 (s, norbornene-H), 3.49 (t, α-CH_2), 4.46 (s, benzyl-H), 5.03 (s, norbornene-H), 5.08 (s, norbornene-H), 6.15–6.18 (m, norbornene-H), 7.33 (s, phenyl-H), 7.50–7.60 (m, pyridyl-H, phenyl-H), 7.65–7.70 (m, pyridyl-H), 7.79 (d, ^3J = 6 Hz, pyridyl-H), 7.82–7.88 (m, pyridyl-H), 8.05–8.15 (m, pyridyl-H), 8.25 (d, ^3J = 8 Hz, pyridyl-H), 8.51 (d, ^3J = 8 Hz, pyridyl-H), 8.61 (dd, ^3J = 8, ^4J = 3 Hz, pyridyl-H) ppm. ^{13}C NMR ([D]acetonitrile, 126 MHz): δ = 14.10, 22.73, 25.94, 29.33, 29.77, 31.77, 42.72, 43.37, 45.99, 49.81, 64.60, 71.19, 71.46, 123.40, 124.51, 124.75, 124.95, 125.67, 128.14, 128.44, 129.02, 129.67, 131.57, 131.88, 132.35, 136.45, 136.55, 136.71, 136.96, 138.18, 138.38, 138.52, 138.91, 139.21, 140.46, 143.03, 144.06, 148.81, 151.96, 155.75, 156.73, 157.13, 175.83 ppm. MS (FAB) *m*/*z* (%) $C_{58}H_{54}N_6O_3Br_2RuCl_2$: 1178.7 (18), 1158.1 (25), 1143.1 (88) ppm. $C_{58}H_{54}Br_2F_{12}N_6O_3P_2Ru$ (1433.83): calcd. C 48.59, H 3.79, N 5.86; found C 48.54, H 3.56, N 5.68.

Polymerization of 25 (28): To a solution of **25** (63 mg, 0.1 mmol) in freshly degassed toluene (50 μL) 100 μL (5 mol-%) of a 0.05 M AIBN solution in toluene were added. The mixture was stirred in a sealed tube at 80 °C for 24 h. The product was purified by preparative GPC to give 41 mg of **28** (65%). ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.81 (br. s, 3 H, CH_3), 1.23 (br. s, 6 H, γ-, δ-, ε-CH_2), 1.55 (br. s, 2 H, β-CH_2), 3.40 (s, 2 H, α-CH_2), 4.39 (s, 2 H, benzyl-H), 4.91 (s, 2 H, benzyl-H), 7.46 (br. m, 6 H, phenyl-H), 7.69 (br. s, 2 H, pyridyl-H), 8.18 (br. s, 2 H, pyridyl-H), 8.62 (br. s, 2 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, 68 MHz): δ = 14.06, 22.55, 25.80, 29.65, 31.62, 71.00, 71.77, 120.87, 123.20, 124.34, 125.15, 129.37, 130.05, 130.90, 132.53, 133.86, 134.80, 139.49, 147.27, 154.53, 171.98 ppm.

Polymerization of 27 (29): Monomer **27** (360 mg, 0.3 mmol) was dissolved in CH_2Cl_2 (0.5 mL) and stirred under nitrogen. The catalyst ([M]/[C] 20:1) was placed in a second flask containing dried and degassed CH_2Cl_2 (0.2 mL) and was added dropwise to the monomer solution which was then stirred for 2 h at room temp. followed by another 16 h at 40 °C. Nitromethane (1 mL) and ethyl vinyl ether were then added to the reaction mixture. The solvent was removed and the compound was dried at high vacuum pump. ^{1}H NMR (CD_3NO_2, 250 MHz): δ = 0.80 (br., 3 H, CH_3), 1.24 (br., 7 H, γ-,δ-, ε-CH_2, CH), 1.50–1.80 (br., 4 H, β-CH_2, CH_2), 2.30–3.00 (br., 4 H), 3.43 (br., 2 H, α-CH_2), 4.41 (s, 2 H, benzyl-H), 4.97 (br., 2 H, benzyl-H), 5.20–5.50 (br., 2 H, CH =), 7.30–7.60 (br., 10 H, phenyl-H, pyridyl-H), 7.90–8.15 (br., 10 H, pyridyl-H), 8.31 (br., 2 H, pyridyl-H), 8.53 (br., 4 H, pyridyl-H), 8.64 (br.,2 H, pyridyl-H) ppm. The polymer was not sufficiently soluble to record a ^{13}C NMR spectrum.

Macromonomer [(bpy)$_2$Ru·(23)·Ru(bpy)$_2$](Cl)$_4$ (30): A stirred suspension of **23** (0.23 mg, 0.14 mmol) and $[Ru(bpy)_2Cl_2] \times 2H_2O$ (155 mg, 0.30 mmol) in a mixture of dioxane (70 mL) and ethylene glycol (23 mL) was refluxed for 24 h. The solvent was removed and the residual orange material purified by column chromatography through silica gel (methanol/2 M NH_4Cl/nitromethane, 7:2:1). The combined orange fractions were diluted with DCM, the organic phase was separated, and the solvent removed to give 0.2 g of **30** (54%) as an orange solid. A small amount of the complex was precipitated by adding a solution of the complex in methanol to a saturated solution of NH_4PF_6 in H_2O (1 mL). The precipitated solid was separated by filtration, washed with H_2O (4 × 2 mL), and dried in vacuo (this complex was used for characterization). The chloride complex was used for polymerization because of its higher solubility in DCM. ^{1}H NMR ($CDCl_3$, CD_3NO_2, 270 MHz): δ = 0.83 (t, 15 H, CH_3), 1.25–1.48 (m, 32 H, γ-, δ-, ε-CH_2, 2 norbornene-H), 1.50–1.59 (m, 12 H, β-CH_2, 2 norbornene-H), 2.18–2.25 (m, 1 H, norbornene-H), 2.90 (s, 1 H, norbornene-H), 2.98 (s, 1 H,

norbornene H), 3.40–3.50 (m, 10 H, α-CH_2), 4.38 (s, 6 H, benzyl-H), 4.45 (s, 4 H, benzyl-H), 4.99 (s, 2 H, benzyl-H), 6.00–6.10 (m, 2 H, norbornene-H), 7.03 (s, 4 H, phenyl-H), 7.42–7.52 (m, 18 H, 8 pyridyl-H, 10 phehyl-H), 7.63 (s, 3 H, phenyl-H), 7.69 (s, 1 H, phenyl-H), 7.75 (s, 4 H, phenyl-H), 7.81 (s, 8 H, pyridyl-H), 7.95 – 8.07 (m, 8 H, pyridyl-H), 8.31 (d, ^3J = 8 Hz, 4 H, pyridyl-H), 8.42 (d, ^3J = 8 Hz, 8 H, pyridyl-H), 8.68 (d, ^3J = 8 Hz, 4 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, CD_3NO_2, 63 MHz): δ = 13.84, 22.47, 25.66, 29.53, 30.32, 31.52, 41.51, 42.93, 46.22, 46.44, 70.82, 70.93, 71.57, 71.67, 88.97, 89.74, 123.17, 123.95, 124.27, 124.41,124.77, 124.88, 125.00, 127.89, 128.27, 129.93, 130.98, 132.68, 133.62, 134.61, 134.97, 135.45, 136.30, 137.76, 138.09, 138.19, 139.29, 139.84, 140.83, 147.80, 151.41, 151.65, 155.50, 156.33, 156.87 ppm, C=O missing. MS (MALDI-TOF, dithranol): *m/z* = 2843.75 [M – PF_6]$^+$, 2785.82 [M – PF_6 – C_4H_9]$^+$, 2698.82 [M – $2PF_6$]$^+$, 2553.86 [M – $3PF_6$]$^+$; monoisotopic mass calcd. for: $C_{148}H_{148}F_{18}N_{12}O_7P_3Ru_2$ 2843.86, found 2843.75. $C_{148}H_{148}F_{24}N_{12}O_7P_4Ru_2$ (2988.83): calcd. C 59.47, H 4.99, N 5.62; found C 58.82, H 4.96, N 5.31.

Polymerization of 22 (31): To a solution of monomer **22** (0.17 mg, 0.11 mmol) in degassed benzene (1 mL), a 0.05 M AIBN initiator solution in benzene (112 μL, 5 mol-%) was added. The resulting mixture was stirred in a sealed tube at 80 °C for 5 d. The purification of the oligomer was done by GPC using THF as solvent to give 108 mg of polymer **31** (62%). ^{1}H NMR (270 MHz, CD_2Cl_2): δ = 0.75–1.10 (br., 18 H, CH_3), 1.20–1.90 (br., 42 H, β-, γ-, δ-, ε-CH_2, CH_2), 3.25–3.70 (br., 12 H, 10 α-CH_2, 2 benzyl-H), 4.00–4.55 (br., 10 H, benzyl-H), 6.50–8.80 (br., 30 H, phenyl-H, pyridyl-H) ppm. ^{13}C NMR (CD_2Cl_2, 63 MHz): δ = 14.36, 21.37, 23.19, 26.50, 29.25, 30.33, 32.32, 71.46, 72.56, 89.34, 89.90, 120.50, 123.79, 128.47, 130.02, 133.84, 136.62, 139.68, 146.78, 154.29, 156.84, 172.30 ppm.

Polymerization of 30 (32): Monomer **30** (100 mg, 0.04 mmol) was dissolved in CH_2Cl_2 (0.5 mL) and stirred under nitrogen. 130 μL of a catalyst stock solution prepared from 12 mg of [$(Cy_3P)_2Cl_2Ru$=CHPh] in 1 mL DCM, corresponding to monomer/catalyst ratio of 20:1, was added dropwise to the monomer solution which was then stirred for 24 h. The product was dried at high vacuum. ^{1}H NMR ($CDCl_3$/CD_3NO_2): δ = 0.60–1.90 (br. 15 H, CH_3), 1.10–1.45 (br. 34 H, γ-, δ-, ε-CH_2, CH_2), 1.45–1.60 (br., 11 H, β-CH_2, CH), 1.60–2.0 (br., 2 H, CH), 3.80–3.50 (br., 10 H, α-CH_2), 4.3–4.48 (2 s, 10 H, benzyl-H), 4.60 (br., 2 H, benzyl-H), 4.85–5.10 (br., 1 H, = CH), 5.20–5.50 (br., 1 H, = CH), 7.0–7.23 (br., 4 H, Ph-H), 7.24–7.60, 7.60–7.90 (br., 34 H, pyridyl-H, Ph-H), 7.90–8.15 (br., 8 H, pyridyl-H), 8.15–8.45 (br., 4 H, pyridyl-H), 8.70–9.10 (br., 8 H, pyridyl-H), 9.10–9.40 (br., 8 H, pyridyl-H) ppm. ^{13}C NMR ($CDCl_3$, CD_3NO_2): δ = 13.36, 22.05, 25.58, 25.72, 26.21, 26.40, 29.11, 31.10, 34.26, 45.44, 70.50, 71.21, 88.67, 89.29, 122.80, 123.93, 124.78, 125.89, 127.38, 127.77, 129.73, 130.59, 134.22, 134.67, 136.36, 137.69, 138.74, 139.66, 140.38, 147.43, 150.95, 155.45, 156.32, 156.83 ppm, C=O missing.

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