Design and Synthesis of New Differentiated Concurrent Mono- and Tridentate Ligands (Tectons) Based on Pyridine, Terpyridine, and Dihydrooxazole Units

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Dedicated to Professor *Jean-Claude Bünzli* on the occasion of his 65th birthday

The design, synthesis, and characterization of the 10 linear and bent acentric ligands **1** – **10** (tectons) based on the differentiation of two divergently disposed coordinating poles is reported. The nature of the two poles and their distance are varied by the use of different linear spacers. For these molecules, a monodentate coordinating site, *i.e.*, a pyridine ring, and a tridentate coordinating site, *i.e.*, a pyridine moiety bearing at the 2 and 6 positions either two thioether groups or two dimethylamino units (PySMe and $PyN(Me_2)_2$ type, resp.), a terpyridine, or a pyridine ring bearing two optically pure dihydrooxazole units, are combined.

Introduction. – Considering a molecular crystal as a supramolecular assembly [1] composed of molecular tectons [2][3] capable of mutual recognition opens the way to design new construction units and new crystalline architectures. This area, called molecular tectonics [2–4], has attracted considerable interest over the last *ca.* two decades. The molecular-tectonics approach, a subset of supramolecular chemistry in the solid state, is based on iterative recognition events occurring under self-assembly conditions. In other words, the formation of periodic architectures (1–3D) in the crystalline phase is achieved by self-assembly of molecular tectons bearing within their structure at least two specific interaction sites oriented in a divergent fashion. The recognition process may be based on any type of attractive forces. We shall here restrict the discussion to the use of coordination bonding as the dominant event generating the network [5][6]. This type of architecture is called coordination network since it is based on a coordinating organic tecton and a metal center or metal complex offering at least two free coordination sites. Thus, for this type of assembly, the recognition patterns are coordination motives resulting from the binding of the metal by the tecton. Through the repetitive coordination events, the recognition patterns become structural nodes of the network.

One of the major challenges in this area today remains the design of polar crystals (*Fig. 1*, **F**) resulting from the noncentrosymmetric arrangement of molecular tectons. Let us consider the formation of 1-D coordination networks (translated into a single direction of space of the coordination event) and their packing leading to hybrid crystals (*Fig. 1*). In this context, the formation of the crystal results from the packing of 1-D networks (see **B**) in two different planes, *i.e.*, the formation of sheets through

lateral packing of 1-D networks (see **C** and **D**) and the packing of sheets leading to the tridimensional crystalline solids (see **E** and **F**).

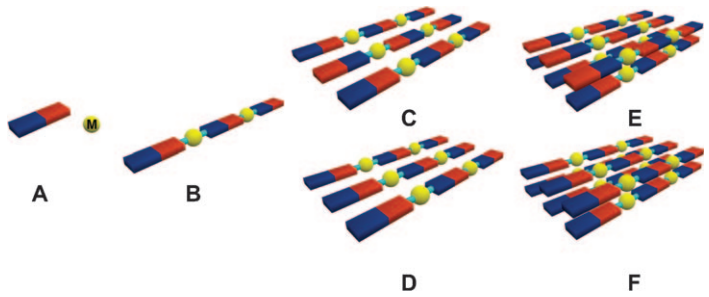


Fig. 1. *Schematic representation of 1-D directional coordination networks* **B** *formed by combining a directional tecton* **A** *and a metal center, and their packing, supposing a parallel mode of arrangement, into centric sheets* **C** *or directional sheets* **D** *and subsequent packing of the latter affording either apolar or polar 3-D architectures* **E** *or* **F**, *respectively*

A possible design strategy for the formation of polar crystals may be based on the use of a noncentrosymmetric organic tecton bearing two different coordinating sites (*Fig. 1*, **A**). The latter, in the presence of an appropriate metal center or complex, would lead to the formation of a 1-D directional network **B**. Supposing a parallel mode of packing, the consecutive 1-D networks may either be arranged in acentric (see **D**) or centric (see **C**) modes leading to the formation of directional and nondirectional sheets, respectively. Finally, whereas the packing of centric sheets **C** would generate an apolar crystal, for the acentric sheet **D**, either an acentric (see **F**) or a centric (see **E**) mode of arrangement are possible.

Our strategy to investigate this issue was based on the use of linear and bent noncentrosymmetric organic tectons of the type T1,3 bearing both a monodentate and a tridentate coordinating pole (for definition, see [7]). Indeed, the combination of such units with either a metal center adopting the square planar geometry **G** (*Fig. 2*) or with a metal center offering the octahedral geometry **H** with the two apical positions blocked by coordinating anions and thus offering four free coordination sites occupying the corner of a square should, by design, lead to the formation of 1-D directional networks. This principle was demonstrated in the crystalline phase by combining tectons **3** [8], **5** [7], or **7** [9] with $CoCl_2$. Furthermore, with tectons **9** [10] and **10** [11], the concept was extended to graphite-surface patterning in the presence of either $CoCl_2$ or $Pd(BF_4)_2$.

It is interesting to note that in the crystalline phase, although the combination of tectons **5** [7] or **7** [8] with $CoCl_2$ indeed leads to the formation of neutral 1-D directional networks **H** (*Fig. 2*), unfortunately, the packing of consecutive networks takes place in the centric mode and consequently, the crystals obtained are apolar. However, with the chiral and optically pure tecton **3**, the arrangement of chiral 1-D networks in the plane leads to the formation of polar sheets **D** and the packing of the latter generates a polar cystal **F** (*Fig. 1*) [8].

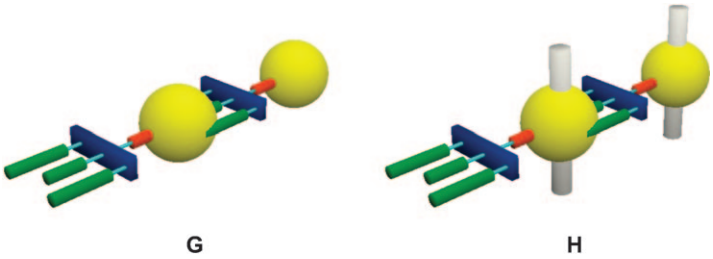
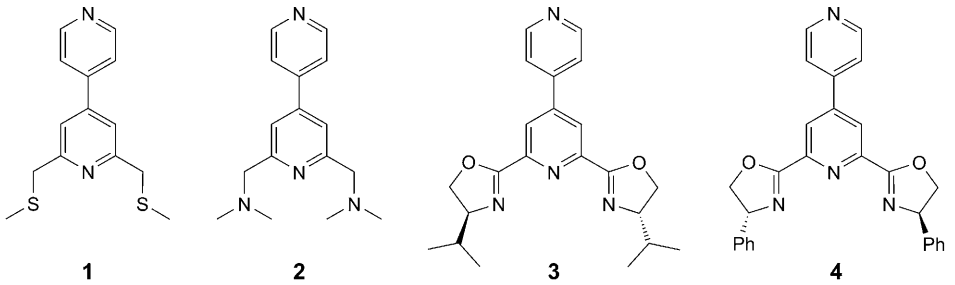


Fig. 2. *Schematic representation of 1-D directional coordination networks formed upon combining an acentric organic tecton based on a monodentate and a tridentate coordinating pole with metal centers adopting either a square planar geometry* **G** *or an octahedral geometry* **H** *with protected apical positions*

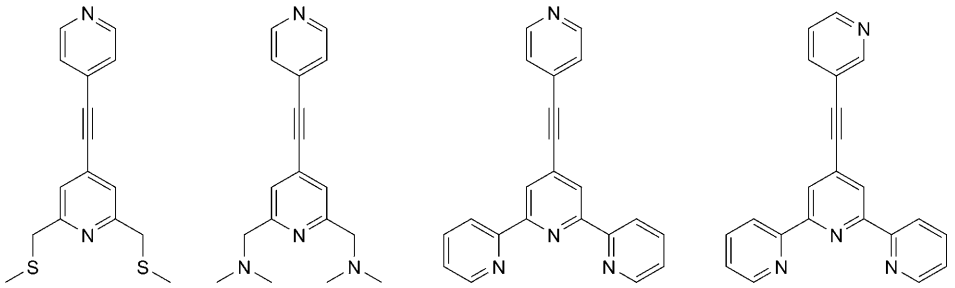
Here we report on the design, synthesis, and characterization of noncentric tectons **1**–**10**. The noncentric tectons **3** [8], **5** [7], **7** [9], and **9** [10] have briefly been described, and the synthesis of **10** has already been reported [11].

Results and Discussion. – Tectons **1** and **2** are based on a pyridine unit behaving as a monodentate coordinating site, and a tridentate pole composed of a pyridine moiety bearing either two thioether groups ($PySMe_2$ type) or two dimethylamino groups ($PyN(Me_2)_2$ type) at the 2 and 6 positions. The synthesis of **1** and **2** was based on the *Suzuki* coupling reaction between the pyridin-4-ylboronic acid and the bromo compounds **15** and **16**, respectively. Starting with the commercially available chelidamic acid (=4-hydroxypyridine-2,6-dicarboxylic acid; **11**), bromination with PBr_5 followed by esterification of the two COOH groups with EtOH afforded diester **12** in 61% yield [12]. The latter was reduced with $NaBH_4$ in dry EtOH to diol **13** in 62% yield [13]. Although the preparation of compound **14** from diol **13** with PBr_3 was reported [13], we found that the bromination with 33% HBr/AcOH at 125° for 5 h was much more efficient and produced compound **14** in 89% yield. The treatment of **14** with MeSNa in dry THF for 48 h at room temperature afforded the precursor **15** in 70% yield, and the condensation of **14** with Me_2NH in MeCN afforded the tridentate diamine **16** [14]. The synthesis of ligands **1** and **2** was achieved by coupling pyridin-4-ylboronic acid with the bromopyridine derivatives **15** and **16**, respectively, in the presence of $[Pd(Ph_3P)_4]$ and Cs_2CO_3 in DMF at 90° overnight. The pure compounds **1** and **2** were obtained as yellowish viscous oils in 81 and 78% yield, respectively, after chromatography (Al_2O_3).

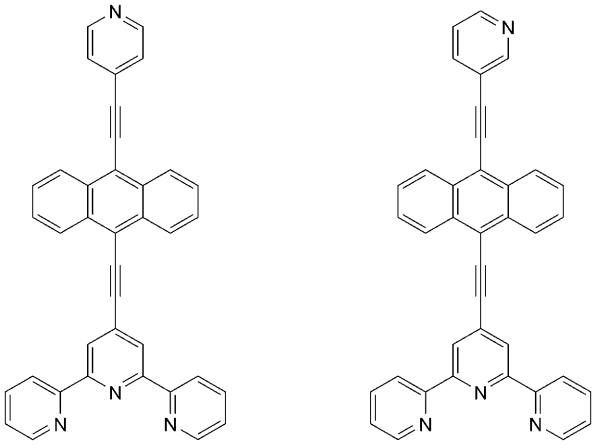
The C_2 chiral tectons **3** and **4** are again based on two coordination poles composed of a pyridine unit connected at the 4-position to a pyridine unit bearing at the 2 and 6 positions two optically active monodentate dihydrooxazole moieties. The strategy for the synthesis of **3** and **4** was also based on the *Suzuki* coupling between **18** [15] or **19**, which were prepared by slight modifications of the reported procedure [15], and pyridin-4-ylboronic acid. Chelidamic acid (**11**) was again the starting material. The treatment of the latter with $SOCl_2$ in the presence of a drop of DMF afforded the acyl chloride derivative **17**. The chirality of the final ligands **3** and **4** was imposed upon treatment of **17** with (*S*)-valinol (=(2*S*)-2-amino-3-methylbutan-1-ol) or (−)-(*R*)-2-phenylglycinol (=(2*R*)-2-amino-2-phenylethanol) in THF (0° to room temp.) in the presence of Et_3N affording **18** and **19** in 79 and 68% yield, respectively. The *Suzuki*



1 **2** **3** **4**

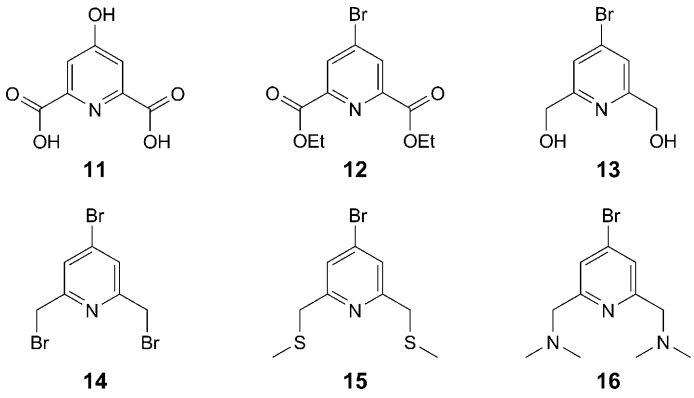


5 **6** **7** **8**

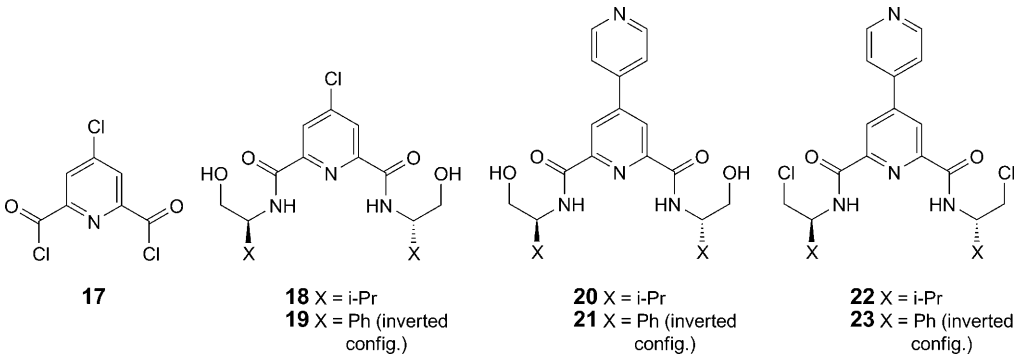


9 **10**

coupling between **18** or **19** and pyridin-4-ylboronic acid or its cyclic ester 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine [16] in the presence of $[Pd(Ph_3P)_4]$ in DMF and in the presence of Cs_2CO_3 afforded the 4,4′-bipyridine derivatives **20** and **21** in 89 and 91% yield, respectively. It is worth noting that no difference in yields was observed upon substitution of the boronic acid by the cyclic boronic ester. The chlorination of compounds **20** and **21** upon treatment with $SOCl_2$ under reflux afforded the dichloro derivatives **22** and **23** in *ca.* 95% yield. Finally, the desired ligands **3** and **4**

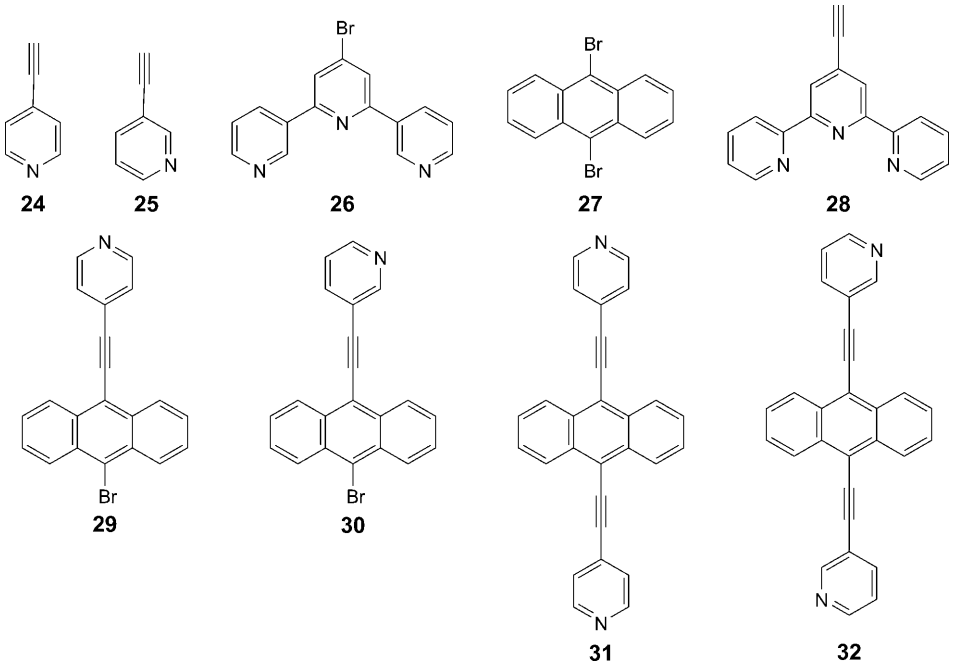


were obtained upon treatment of **22** with NaH in THF, and of **23** with NaOH in H_2O/MeOH in 79% and 86% yield, respectively.



Tecons **5** and **6** are longer analogues of ligands **1** and **2**. Indeed, for these two compounds, the two coordinating poles are preserved. However, to investigate the role played by the distance between the poles on the formation of 1-D networks and their packing, the two poles were separated by an ethynyl spacer which was chosen because of its cylindrical shape and small diameter avoiding thus steric issues. The synthesis of both **5** and **6** was based on the *Sonogashira* coupling reaction between compounds **15** or **16** with 4-ethynylpyridine (**24**). The latter was prepared according to a published procedure [17]. Thus, the coupling of **24** with either bromo compound **15** or **16** in the presence of $[Pd(OAc)_2]/Ph_3P$ in Et_3N afforded the desired compounds **5** and **6** in 62 and 94% yield, respectively.

Compounds **7** and **8**, which may be regarded as achiral analogues of **3** and **4**, are based on a pyridine unit connected at the position 4 and 3, respectively, to a terpyridine moiety through an ethynyl spacer. The difference between **7** and **8** resides in the orientation of the monodentate site with respect to the tridentate pole imposed by the connecting position (4 for **7** and 3 for **8**). The synthesis of **7** and **8** was achieved again by



the *Sonogashira* coupling reactions with $[Pd(OAc)_2]/Ph_3P$ as the catalyst. The condensation of bromoterpyridine **26** [18], prepared according to a published procedure with either 4-ethynylpyridine (**24**) [17] or 3-ethynylpyridine (**25**) [19] afforded the desired compounds **7** and **8** in 98 and 84% yield, respectively.

The two tectons **9** and **10** are longer analogues of ligands **7** and **8**. They are constructed around a spacer composed of an anthracene moiety bearing two ethynyl units at positions 9 and 10. One of the two ethynyl spacers is connected to a pyridine moiety either at position 4 (compound **9**) or 3 (compound **10**), and the remaining triple bond is attached to a terpyridine group. Again, **9** and **10** differ only by the orientation of the pyridine unit with respect to the terpyridine unit. To increase the interactions with the graphite surface, the anthracene moiety was used to link the two ethynyl units [10][11]. The synthesis of **9** and **10** [11] was based on a double *Sonogashira* reaction with $[Pd(OAc)_2]/Ph_3P$ as catalyst. Starting with 9,10-dibromoanthracene (**27**), the first *Sonogashira* coupling reaction with 4-ethynylpyridine (**24**) [17] or with 3-ethynylpyridine (**25**) [19] afforded the mono-functionalized anthracene derivatives **29** and **30** in 34 and 30% yields, respectively. The second coupling reaction between either **29** or **30** and ethynylterpyridine **28**, prepared according to a reported procedure [20], gave the final compounds **9** and **10** in 80 and 87% yields, respectively. It is worth noting that the above-mentioned condensation of **27** either with **24** or **25**, in addition to the desired compounds **29** and **30** gave the centrosymmetric bis-monodentate ligands **31** and **32** [11] in 25 and 40% yields, respectively. These compounds are also interesting as tectons and are currently employed for the formation of coordination networks.

Conclusion. – A series of linear or bent acentric tectons based on the differentiation of two coordinating poles were designed and synthesized by *Suzuki* or *Sonogashira* coupling reactions. The nature of the two poles and their distance were varied by the use of different linear spacers. Thus, these molecules **1**–**10** are composed of a monodentate (pyridine) and a tridentate coordinating sites. The latter site consists of a pyridine ring bearing at the 2 and 6 positions either two thioether groups (PySMe type) or two dimethylamino units ($PyN(Me_2)_2$ type), a terpyridine, or a pyridine ring bearing two optically pure dihydrooxazole units at positions 2 and 6. With some of these tectons, the validity of the design principle, *i.e.*, generation of infinite directional coordination networks both in the crystalline phase [7–9] or on surfaces [10][11] was demonstrated previously. The use of the remaining tectons for the formation of oriented architectures is currently under investigation.

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Experimental Part

General. All commercially available reagents were used without further purification. THF was distilled over Na. Compounds **10** [11], **12** [12], **13** [13] **14** [13], **16** [14], **24** [17], **25** [19], **26** [18], **28** [20], **30** [11], **31** [21], and **32** [11] were prepared according to published procedures. ^{1}H- and ^{13}C-NMR Spectra: *Bruker* spectrometers, at 300 and 75 MHz, resp.; in $CDCl_3$ unless otherwise specified; δ in ppm rel. to Me_4Si as internal standard, J in Hz. Microanalyses were performed by the Service de Microanalyses de la Fédération de Recherche Chimie, Université de Strasbourg.

4-Bromo-2,6-bis[(methylsulfanyl)methyl]pyridine (**15**). A soln. of 4-bromo-2,6-bis(bromomethyl)-pyridine (**14**; 1 g, 2.9 mmol) and MeSNa (0.65 g, 9.27 mmol) in THF (25 ml) was stirred at r.t. for 48 h. The soln. was concentrated, the org. residue dissolved in Et_2O (50 ml), the mixture filtered, and the filtrate washed with H_2O (2×10 ml), dried, and concentrated affording a pure colorless oil which crystallized upon standing overnight: **15** (0.57 g, 70%). ^{1}H-NMR: 7.38 (*s*, 2 H); 3.68 (*s*, 4 H); 2.02 (*s*, 6 H). ^{13}C-NMR: 159.7; 133.8; 124.3; 39.6; 15.3. Anal. calc. for $C_9H_{12}BrNS_2$ (278.23): C 38.85, H 4.35, N 5.03; found: C 38.95, H 4.42, N 4.98.

4-Chloro-N^2*,*N^6*-bis[(1S)-1-(hydroxymethyl)-2-methylpropyl]pyridine-2,6-dicarboxamide* (**18**) and *4-Chloro-*N^2*,*N^6*-bis[(1R)-2-hydroxy-1-phenylethyl]pyridine-2,6-dicarboxamide* (**19**) were prepared following the same procedure. For **19**, chelimadic acid (**11**; 1 g, 5.4 mmol) was treated with $SOCl_2$ (25 ml) in the presence of 2 drops of DMF under reflux for 36 h. Excess of $SOCl_2$ was then evaporated to give the diacyl chloride **17**. To a soln. of (−)-(*R*)-2-phenylglycinol (13.2 mmol) and Et_3N (5 ml) in THF (20 ml) was slowly added a soln. of the diacyl chloride **17** in THF (30 ml) at 0°. The mixture was stirred at r.t. for 24 h. The THF was evaporated, the residue extracted with CH_2Cl_2 (100 ml), the extract washed with aq. $NaHCO_3$ soln. (60 ml), dried, and concentrated, and the residue purified by column chromatography (CC; silica gel (SiO_2)): pure.

19 (68%). M.p. 63°. ^{1}H-NMR: 8.68 (*d*, $J = 7.6$, 2 H); 8.18 (*s*, 2 H); 7.35–7.23 (*m*, 10 H); 5.22–5.17 (*m*, 2 H); 3.92 (*d*, $J = 4.9$, 4 H); 3.41 (*s*, 2 H). ^{13}C-NMR: 162.6; 150.1; 147.8; 138.6; 128.9; 127.9; 126.6; 125.4; 65.9; 55.7. Anal. calc. for $C_{23}H_{22}ClN_3O_4$ (439.90): C 62.80, H 5.04, N 9.55; found: C 63.01, H 5.14, N 9.73.

18: Yield 79%. For data, see [15].

Suzuki *Coupling: General Method.* [$Pd(Ph_3P)_4$] (0.06 g, 0.05 mmol) was added to a degassed soln. of pyridin-4-ylboronic acid (0.33 g, 2.68 mmol), a halopyridine derivative (2.0 mmol), and Cs_2CO_3 (1.8 mol) in DMF (15 ml). The mixture was heated to 90° under Ar for the time indicated (TLC monitoring). After evaporation of the solvent, the residue was purified by CC (Al_2O_3) with the indicated eluent.

2,6-Bis[(methylsulfanyl)methyl]-4,4′-bipyridine (**1**): For 24 h; eluent cyclohexane/CH_2Cl_2 50:50. Yield 81%. Yellowish oil. ^{1}H-NMR: 8.72 (*d*, $J = 6.1$, 2 H); 7.55 (*d*, $J = 6.1$, 2 H); 7.49 (*s*, 2 H); 3.86 (*s*, 4 H);

2.10 (*s*, 6 H). ^{13}C-NMR: 159.4; 150.4; 147.0; 145.7; 121.5; 119.0; 40.0; 15.3. Anal. calc. for $C_{14}H_{16}N_2S_2$ (276.42): C 60.83, H 5.83, N 10.13; found: C 60.73, H 5.76, N 10.03.

N^2,N^2,N^6,N^6-Tetramethyl[4,4′-bipyridine]-2,6-dimethanamine (**2**): For 24 h, CH_2Cl_2. Yield 78%. Yellowish oil. ^{1}H-NMR: 8.67 (*d*, *J* = 6.1, 2 H); 7.57 (*d*, *J* = 6.1, 2 H); 7.55 (*s*, 2 H); 3.64 (*s*, 4 H); 2.30 (*s*, 12 H). ^{13}C-NMR: 159.7; 150.4; 146.4; 145.9; 121.4; 119.0; 65.7; 45.6. Anal. calc. for $C_{16}H_{22}N_4$ (270.37): C 71.08, H 8.20, N 20.72; found: C 70.88, H 8.17, N 20.66.

N^2,N^6-Bis[(1S)-1-(hydroxymethyl)-2-methylpropyl][4,4′-bipyridine]-2,6-dicarboxamide (**20**): For 15 h; eluent 2% MeOH/CH_2Cl_2. Yield 89%. M.p. 115°. ^{1}H-NMR: 8.72 (*d*, *J* = 6.1, 2 H); 8.53 (*s*, 2 H); 8.13 (*d*, *J* = 8.64, 2 H); 7.60 (*d*, *J* = 6.1, 2 H); 3.98–3.94 (*m*, 2 H); 3.87–3.84 (*m*, 2 H); 3.27 (*s*, 2 H); 2.11–2.02 (*m*, 2 H); 1.03–0.96 (*m*, 12 H). ^{13}C-NMR: 18.7; 19.6; 29.3; 57.2; 63.6; 121.3; 122.5; 143.9; 148.7; 149.9; 150.7; 163.6. Anal. calc. for $C_{22}H_{30}N_4O_4$ (414.50): C 63.75, H 7.30, N 13.52; found: C 63.96, H 7.11, N 13.60.

N^2,N^6-Bis[(1R)-2-hydroxy-1-phenylethyl][4,4′-bipyridine]-2,6-dicarboxamide (**21**): For 48 h; eluent 2% MeOH/CH_2Cl_2. Yield 91%. M.p. 118°. ^{1}H-NMR (MeOD): 8.66 (*d*, *J* = 6.1, 2 H); 8.60 (*s*, 2 H); 7.88 (*d*, *J* = 6.1, 2 H); 7.47 (*d*, *J* = 7.4, 4 H); 5.31 (*t*, *J* = 7.3, 2 H); 3.97 (*d*, *J* = 7.4, 4 H). ^{13}C-NMR (MeOD): 56.1; 64.8; 122.0; 122.4; 126.7; 127.2; 128.2; 139.4; 145.56; 147.9; 149.4; 150.4; 164.1. Anal. calc. for $C_{28}H_{26}N_4O_4$ (482.53): C 69.70, H 5.43, N 11.61; found: C 69.90, H 5.61, N 11.62.

N^2,N^6-Bis[(1S)-1-(chloromethyl)-2-methylpropyl][4,4′-bipyridine]-2,6-dicarboxamide (**22**) and *N^2,N^6-Bis[(1R)-2-chloro-1-phenylethyl][4,4′-bipyridine]-2,6-dicarboxamide* (**23**) were prepared following an identical procedure: To **20** or **21** (2 mmol) was added $SOCl_2$ (20 ml), and the mixture was heated under reflux for 7 h. The $SOCl_2$ was evaporated, and the crude product was purified by CC (Al_2O_3, 1% MeOH/CH_2Cl_2.

Data at **22**: Yield 95%. White solid. M.p. 162°. ^{1}H-NMR: 8.76 (*d*, *J* = 6.1, 2 H); 8.53 (*s*, 2 H); 8.04 (*d*, *J* = 8.7, 2 H); 7.63 (*d*, *J* = 6.1, 2 H); 4.19–4.13 (*m*, 2 H); 3.88–3.83 (*m*, 2 H); 3.78–3.72 (*m*, 2 H); 2.12–2.07 (*m*, 2 H); 1.04–0.98 (*m*, 12 H). ^{13}C-NMR: 18.80; 19.3; 29.6; 46.8; 54.9; 121.3; 122.7; 143.9; 149.1; 149.6; 150.7; 162.6. Anal. calc. for $C_{22}H_{28}Cl_2N_4O_2$ (451.39): C 58.54, H 6.25, N 12.41; found: C 58.43, H 6.11, N 12.29.

Data of **23**: Yield 92%. White solid. M.p. 180° (dec.). ^{1}H-NMR: 8.76 (*d*, *J* = 6.1, 2 H); 8.64 (*d*, *J* = 8.27, 2 H); 8.62 (*s*, 2 H); 7.64 (*d*, *J* = 6.1, 2 H); 7.43–7.33 (*m*, 10 H); 4.03–3.98 (*m*, 2 H); 4.01 (*m*, 4 H). ^{13}C-NMR: 48.3; 53.8; 121.5; 123.0; 126.6; 128.4; 128.9; 139.4; 144.2; 149.0; 149.6; 150.5; 162.5. Anal. calc. for $C_{28}H_{24}Cl_2N_4O_2$ (519.42): C 64.75, H 4.66, N 10.79; found: C 64.68, H 4.59, N 10.71.

2,6-Bis[(4S)-4,5-dihydro-4-(1-methylethyl)-1,3-oxazol-2-yl]-4,4′-bipyridine (**3**). To a suspension of NaH (0.023 g, 0.95 mmol) in THF (10 ml), **22** (0.18 g, 0.4 mmol) was added. The mixture was stirred at r.t. for 3 h. After filtration and concentration, Et_2O (20 ml) was added and the residue filtered. The crude mixture was recrystallized from Et_2O/hexane: **3** as (79%). White needles. M.p. 118°. ^{1}H-NMR: 8.76 (*d*, *J* = 6.2, 2 H); 8.47 (*s*, 2 H); 7.67 (*d*, *J* = 6.2, 2 H); 4.56 (*dd*, *J* = 8.2, 9.1, 2 H); 4.20 (*t*, *J* = 8.3, 2 H); 4.19–4.14 (*m*, 2 H); 1.93–1.85 (*m*, 2 H); 1.07 (*d*, *J* = 6.7, 6 H); 0.96 ((*d*, *J* = 6.7, 6 H). ^{13}C-NMR: 18.2; 19.0; 32.8; 71.1; 73.0; 121.5; 123.3; 144.1; 147.9; 150.8; 162.0. Anal. calc. for $C_{22}H_{26}N_4O_2$ (378.47): C 69.82, H 6.92, N 14.80; found: C 69.75, H 6.87, N 14.66.

2,6-Bis[(4R)-4,5-dihydro-4-phenyl-1,3-oxazol-2-yl]-4,4′-bipyridine (**4**). Compound **23** (0.42 g, 0.8 mmol) was treated with a soln. of NaOH (0.3 g, 7.5 mmol) in H_2O (5 ml) and MeOH (12 ml) at r.t. for 20 h. After extraction with CH_2Cl_2 (2 × 50 ml), the org. layer was dried ($MgSO_4$) and concentrated and the residue purified by CC (SiO_2, 2% MeOH/CH_2Cl_2): **4** (86%). White solid. M.p. 116°. ^{1}H-NMR: 8.75 (*d*, *J* = 6.2, 2 H); 8.61 (*s*, 2 H); 7.66 (*d*, *J* = 6.2, 2 H); 7.43–7.28 (*m*, 10 H); 5.49 (*dd*, *J* = 8.6, 9.2, 2 H); 4.96 (*dd*, *J* = 8.6, 9.2, 2 H); 4.46 (*dd*, *J* = 8.6, 9.2, 2 H). ^{13}C-NMR: 70.4; 75.7; 121.5; 123.9; 126.9; 127.9; 128.9; 141.4; 143.8; 147.4; 147.8; 150.8; 163.3. Anal. calc. for $C_{28}H_{22}N_4O_2$ (446.51): C 75.32, H 4.97, N 12.55; found: C 75.11, H 5.12, N 12.71.

4-[2-(10-Bromoanthracen-9-yl)ethynyl]pyridine (**29**). To a degassed mixture of 4-ethynylpyridine (**24**; 0.50 g, 4.8 mmol) and 9,10-dibromoanthracene (2 g, 5.9 mmol) in Et_3N (20 ml) (*Schlenk* flask) were added [$Pd(OAc)_2$] (0.024 g, 0.1 mmol) and Ph_3P (0.054 g, 0.2 mmol). The mixture was refluxed for 24 h, after which the solvent was evaporated. The crude product was purified by CC (SiO_2, CH_2Cl_2/MeOH 99 : 1): **29** (0.6 g, 34%) and 4,4′-(anthracene-9,10-diyldiethyne-2,1-diyl)bis[pyridine] (**31**; 25%). For anal. data of **31**, see [21]. **29**: M.p. 112°. ^{1}H-NMR: 7.71 (*d*, *J* = 6.3, 2 H); 8.65–8.58 (*m*, 4 H); 7.68–7.61 (*m*,

6 H). ^{13}C-NMR: 149.9; 135.9; 130.3; 129.0; 128.4; 127.6; 127.3; 126.8; 126.4; 123.7; 119.4; 86.9; 80.6. Anal. calc. for $C_{21}H_{12}BrN$ (358.23): C 70.41, H 3.38, N 3.91; found: C 70.44, H 3.67, N 3.88.

4′-{2-{10-[2-(Pyridin-4-yl)ethynyl]anthracen-9-yl}ethynyl}-2,2′:6′,2″-terpyridine (**9**). As described for **29**, with 4′-ethynyl-2,2′:6′,2″-terpyridine (0.107 g, 0.41 mmol), **29** (0.150 g, 0.41 mmol), Et_3N (20 ml), $Pd(OAc)_2$ (0.024 g, 0.1 mmol), and Ph_3P (0.054 g, 0.2 mmol). CC (Al_2O_3, CH_2Cl_2) afforded **9** (0.160 g, 80%). Orange solid. M.p. 190° (dec.). ^{1}H-NMR: 8.81 – 8.77 (*m*, 6 H); 8.72 (*dd*, *J* = 2.7, 6.3, 2 H); 8.69 (*d*, *J* = 8, 2 H); 8.66 – 8.63 (*m*, 2 H); 7.92 (*td*, *J* = 7.9, 1.8, 2 H); 7.74 – 7.70 (*m*, 4 H); 7.43 – 7.39 (*m*, 2 H); 7.63 (*dd*, *J* = 2.7, 6.3, 2 H). Anal. calc. for $C_{38}H_{22}N_4$ (534.62): C 85.37, H 4.15, N 10.48; found: C 85.63, H 4.25, N 10.56.

Sonogashira *Coupling: General Method.* To a degassed mixture of 4-ethynylpyridine (**24**; 0.8 g, 0.78 mmol) and a halopyridine derivative (0.50 mmol) in Et_3N (20 ml) (*Schlenk* flask) were added [$Pd(OAc)_2$] (0.024 g, 0.1 mmol) and Ph_3P (0.054 g, 0.2 mmol).The mixture was refluxed for 48 h, after which the solvent was evaporated. The crude product was purified by CC.

2,6-Bis[(methylsulfanyl)methyl]-4-[2-(pyridin-4-yl)ethynyl]pyridine (**5**). CC (SiO_2, CH_2Cl_2/MeOH 99 : 1). Yield 94%. Oil. ^{1}H-NMR: 2.08 (*s*, 6 H); 3.79 (*s*, 4 H); 7.31 (*s*, 2 H); 7.38 (*d*, *J* = 6, 2 H); 8.63 (*d*, *J* = 6, 2 H). ^{13}C-NMR: 15.3; 39.9; 90.05; 90.1; 123.0; 125.6; 130.3; 131.5; 150.0; 158.8. Anal. calc. for $C_{16}H_{16}N_2S_2$ (300.44): C 63.97, H 5.37, N 9.32; found: C 64.10, H 5.66, N 9.15.

N^2,N^2,N^6,N^6-Tetramethyl-4-[2-(pyridin-4-yl)ethynyl]pyridine-2,6-dimethanamine (**6**). CC (Al_2O_3, hexane/AcOEt). Yield 92%. Oil. ^{1}H-NMR (200 MHz): 2.26 (*s*, 12 H, Me); 3.55 (*s*, 2 CH_2); 7.3 (*dd*, *J* = 6, 1.6, 2 H); 7.38 (*s*, 2 H); 8.57 (*dd*, *J* = 6, 1.6, 2 H). ^{13}C-NMR: 45.7; 65.6; 89.8; 91.5; 123.1; 125.6; 128.5; 130.7; 149.9; 159.3. Anal. calc. for $C_{18}H_{22}N_4$ (294.39): C 73.44, H 7.53, N 19.03; found: C 73.12, H 7.22, N 18.85.

4′-[2-(Pyridin-4-yl)ethynyl]-2,2′:6′,2″-terpyridine (**7**). CC (Al_2O_3, hexane/AcOEt 90 : 10). Yield 99%. White solid from AcOEt. M.p. 217°. ^{1}H-NMR: 8.72 (*d*, *J* = 4, 2 H); 8.66 – 8.62 (*m*, 4 H); 8.60 (*s*, 2 H); 7.88 (*J* = 6.1, 1.71, 2 H); 7.42 (*d*, *J* = 4.65, 2 H); 7.39 – 7.35 (*m*, 2 H). ^{13}C-NMR: 155.9; 155.6; 150.1; 149.4; 137.1; 132.3; 130.7; 125.8; 124.3; 123.1; 121.4; 91.7; 90.5. Anal. calc. for $C_{22}H_{14}N_4$ (334.36): C 79.02, H 4.22, N 16.76; found: C 79.22, H 4.10, N 16.46.

4′-[2-(Pyridin-3-yl)ethynyl]-2,2′:6′,2″-terpyridine (**8**). CC (Al_2O_3, CH_2Cl_2/AcOEt). Yield 84%.White solid from AcOEt. M.p. 186°. ^{1}H-NMR: 8.81 (*d*, *J* = 2, 1 H); 8.72 (*ddt*, *J* = 4.6, 1, 2 H); 8.64 (*s*, 1 H); 8.61 (*s*, 2 H); 8.59 (*s*, 2 H); 7.90 – 7.84 (*m*, 3 H); 7.38 – 7.33 (*m*, 3 H). ^{13}C-NMR: 155.7; 155.5; 152.5; 149.2; 138.8; 136.9; 132.6; 124.1; 123.2; 122.8; 121.3; 119.8; 90.7; 90.1. Anal. calc. for $C_{22}H_{14}N_4 \cdot 0.5\ C_2H_6O$ (357.41): C 77.29, H 4.79, N 15.67; found: C 77.62, H 4.61, N 15.15.

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