# Tethered 2,2′-Bipyridine Ligands – Synthesis and Coordination Properties

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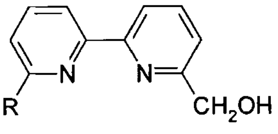
Bis-2,2′-bipyridine ligands tethered by phthalic- and terephthalic esters were synthesized. The coordination with copper(I) and silver(I) ions gave mononuclear complexes. With terepthalic acid as a spacer between 2,2′-bipyridines 2 + 2 assemblies were identified in traces. The coordination compounds were investigated by electrospray mass spectroscopy.

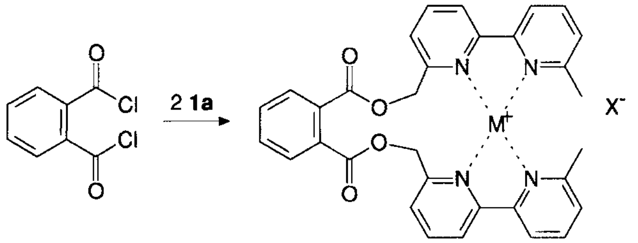
Self-assembly and self-organization have developed into a main theme of supramolecular chemistry[1]. Such is the case in particular with inorganic self-assembly as expressed in the spontanous formation of helicates[2], knots[3], or cages[4]. The self-assembly process is programmed by the coordination geometry and the preorganization of the ligands and the metal ions[5]. 2,2′-Bipyridines have been widely used in supramolecular chemistry due to their strong and defined coordination with various metal ions. Extended ligands with several 2,2′-bipyridine bindings sites linked by ether or amine bridges were synthesized by alkylation reactions[6]. However, coordinating oligomers and polymers of 2,2′-bipyridines are not accessible by this route, due to side reactions and low product solubility. The linkage of the coordination sites by a condensation reaction might be more feasible. In this paper we report on the synthesis of novel bis-2,2′-bipyridines linked by phthalic and terephthalic esters as model compounds for the coordination properties of 2,2′-bipyridine containing polyesters[7].

Hydroxymethyl-substituted 2,2′-bipyridines are the necessary starting material for ester formation[8]. Compound **1a** is conveniently accessible from 6,6′-dimethyl-2,2′bipyridine by the formation of the mono-*N*-oxide followed by rearrangement[9]. Monoprotected difunctional 2,2′-bipyridines[10] **1b** and **1c** were obtained by partial deprotection of diacetyl-6,6′-bis(hydroxymethyl)-2,2′-bipyridine or the reduction of one ester group in 6,6′-bis(carboxymethyl)-2,2′-bipyridine.



| | |
|---|---|
| R = $CH_3$ | 1a |
| $CH_3C{=}OOCH_2$ | 1b |
| $CH_3CH_2OC{=}O$ | 1c |

The reaction of **1a** with phthalic acid dichloride under standard conditions gave **3**. Treatment of **3** with Ag(I)$ClO_4$ as well as Cu(I)-$SO_3CF_3$ afforded the mononuclear complexes **4**. The FAB mass spectra shows their molecular ions with high intensity and clear isotopic patterns. No other coordination stoichiometries than 1:1 could be detected.



**2**

**3** ligand
**4** **a)** MX = Cu(I)$SO_3CF_3$
**b)** MX = Ag(I)$ClO_4$

By changing the spacer from a 1,2- to a 1,4-disubstituted benzene the geometry of the ligand **6-H**[11] should be more favorable for a 2:2 coordination stoichiometry.

However, treatment of **6-H** with Cu(I)$SO_3CF_3$ or Cu(I)-$(CH_3CN)_4PF_6$[12] still gave the mononuclear coordination compounds as the major product. The molecular ions of **7-H** and **7-Hex** were identified by electrospray mass spectrometry from their isotopic patterns. The 2:2 assembly **8**[13] was clearly detected by mass spectral analysis, but only in trace amounts. The $^1$H-NMR signals of the 2,2′-bipyridine methylene protons in **6** change upon coordination with copper(I) ions form a singlet ($A_2$ system) to an AB system, indicating a restricted mobility of the complex **7-H** on the NMR time scale.

Metal ion coordination of ether-linked 2,2′-bipyridines leads to helical interstrand assemblies as previous shown by Lehn[2]. The coordination properties of **3** and **6** indicate that the entropically favored intramolecular binding of copper(I) ions can be expected for oligomeric esters of terephthalic acid and hydroxymethyl-2,2′-bipyridines.

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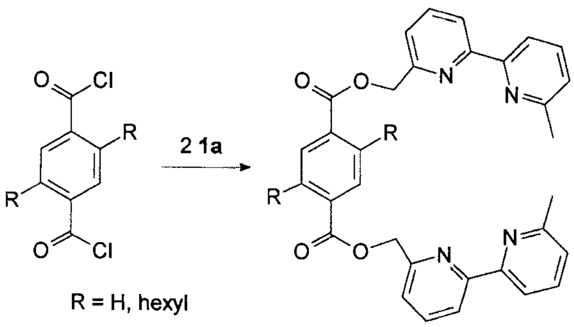
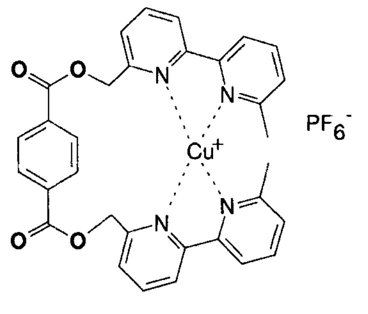
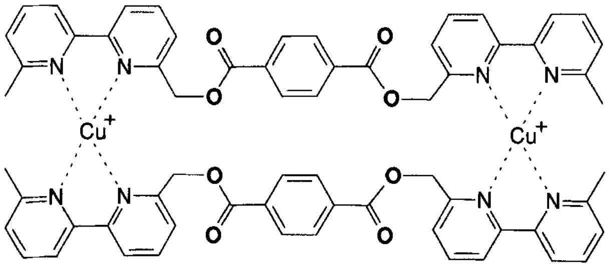


**5** **6**



**7-H**



**8** $2\ SO_3CF_3^-$

der Chemischen Industrie for a Liebig stipendium, Dr. *M. Nimtz* (Gesellschaft für Biotechnologische Forschung, Braunschweig) for recording the electrospray mass spectra and Prof. Dr. *H. Hopf* for his support.

## Experimental

$^1H$ NMR: Bruker AM 400; internal standard TMS, $\delta$ = 7.26 for chloroform. – $^{13}C$ NMR: AM 400; $\delta$ = 77.0 for $CDCl_3$; the multiplicity of the $^{13}C$-NMR signals was determined by the DEPT technique (distortionless enhancement by polarization transfer) and quoted as (+) for $CH_3$ and CH groups, (–) for $CH_2$- and ($C_{quart}$) for quarternary carbon atoms. – IR: Nicolet 320 FT-IR. – MS: Finnigan MAT 8430. – UV/Vis: Hewlett Packard 8452A. – Melting points: hot-plate microscope apparatus, not corrected. – Column chromatography (CC): Merck silica gel 60, mesh 70–230; PE (60/70) means petroleum ether with a boiling range of 60–70°C; EE means ethyl acetate. – TLC: silica gel (Macherey-Nagel; Sil (G/UV$_{254}$).

1,5-Dihexylterephthalic acid[14] and 6-hydroxymethyl-6'-methyl-2,2'-bipyridine (**1a**)[7] were prepared according to literature procedures.

*6-Hydroxymethyl-6'-acetylmethyl-2,2'-bipyridine* (**1b**): 300 mg (1 mmol) of 6,6'-bis(acetylhydroxymethyl)-2,2'-bipyridine[15] and KOH (60 mg, 1.1 mmol) in 20 ml of methanol were stirred for 10 min at room temp. A saturated aqueous solution of $NH_4Cl$ (50 ml) and ether (50 ml) were added, the organic phase was dried with $MgSO_4$ and the solvent was evaporated in vacuo. CC (EE/PE, 1:1) of the residue and recrystallization of the crude product from *n*-heptane gave 90 mg (35%) of **1b** ($R_f$ = 0.5) as white crystals, m. p. 70°C. – IR (KBr): $\tilde{\nu}$ = 1742 $cm^{-1}$, 1582, 1258. – UV ($CH_3CN$): $\lambda_{max}$ (lg $\varepsilon$) = 196 (4.605) nm, 238 (3.997), 288 (4.200). – $^1H$ NMR ($CDCl_3$): $\delta$ = 2.20 (s, 3H), 3.99 (bs, 1H), 4.83 (s, 2H), 5.32 (s, 2H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.82 (dd, *J* = 8.0 Hz, *J* = 7.7 Hz, 2H), 8.36 (d, *J* = 8.0 Hz, 2H). – $^{13}C$ NMR ($CDCl_3$): $\delta$ = 20.93 (+), 63.82 (–), 66.92 (–), 119.87 (+), 119.96 (+), 120.49 (+), 121.64 (+), 137.57 (+), 137.64 (+), 155.14 ($C_{quart}$), 155.38 ($C_{quart}$), 158.04 ($C_{quart}$), 170.64 ($C_{quart}$). – MS (70 eV), *m/z* (%): 258 (40) [$M^+$], 257 (40) [$M^+$ – 1], 215 (100) [$M^+$ – $COCH_3$]. – $C_{14}H_{14}N_2O_3$ (258.3): calcd. C 65.11, H 5.46, N 10.85; found C 64.96, H 5.21, N 10.62. – Mol. mass 258 (MS).

*6-Hydroxymethyl-6'-ethoxycarbonyl-2,2'-bipyridine* (**1c**): To a solution of diethyl-2,2'-bipyridine-6,6'-dicarboxylate[16] (330 mg, 1.1 mmol) in 20 ml of THF and 1 ml of ethanol were added LiBr (200 mg, 2.3 mmol) and $NaBH_4$ (83 mg, 2.2 mmol) and the reaction mixture was stirred at room temp. for 1 h. Usual workup and separation from unreacted starting material and 6,6'-bis(hydroxymethyl)-2,2'-bipyridine by CC (PE:EE, 3:1) yielded 90 mg (32%) of **1c** ($R_f$ = 0.8), as a white solid, m. p. 82°C. – IR (KBr): $\tilde{\nu}$ = 3419 $cm^{-1}$, 2928, 1736, 1581, 767. – $^1H$ NMR ($CDCl_3$): $\delta$ = 1.46 (t, *J* = 7.2 Hz, 3H), 3.90 (bs, 1H), 4.49 (q, *J* = 7.2 Hz, 2H), 4.83 (s, 2H), 7.27 (dd, *J* = 7.6 Hz, *J* = 0.7 Hz, 1H), 7.84 (t, *J* = 7.6 Hz, 1H), 7.96 (t, *J* = 7.9 Hz, 1H), 8.12 (dd, *J* = 7.7 Hz, *J* = 1.0 Hz, 1H), 8.48 (dd, *J* = 7.9 Hz, *J* = 0.7 Hz, 1H), 8.60 (dd, *J* = 7.9 Hz, *J* = 1.0 Hz, 1H). – $^{13}C$ NMR ($CDCl_3$): $\delta$ = 14.35 (+), 61.49 (–), 63.98 (–), 120.42 (+), 120.97 (+), 123.98 (+), 125.08 (+), 137.84 (+), 137.89 (+), 147.94 ($C_{quart}$), 154.00 ($C_{quart}$), 155.85 ($C_{quart}$), 158.25 ($C_{quart}$), 165.28 ($C_{quart}$). – MS (70 eV), *m/z* (%): 258 (25) [$M^+$], 257 (20) [$M^+$ – 1], 186 (100). – $C_{14}H_{14}N_2O_3$ (258.3): calcd. C 65.11, H 5.46, N 10.85; found C 64.94, H 5.31, N 10.90. – Mol. mass 258 (MS).

*Bis(6'-2,2'-bipyridyl)phthalate* (**3**): Compound **2** (35 µl, 0.25 mmol) was added to a suspension of **1a** (100 mg, 0.5 mmol) in 1 ml of dry pyridine. The reaction mixture was heated for 30 min at 100°C and stirred at room temp. for 12 h. 10 ml of ice and 30 ml of $CH_2Cl_2$ were added, the organic phase was washed with water (2 × 30 ml), dried with $MgSO_4$ and the solvent was evaporated in vacuo. CC on silica gel (PE:EE, 1:2) yielded 74 mg (56%) of pure **3** ($R_f$ = 0.8), as a viscous oil. – IR (KBr): $\tilde{\nu}$ = 1731 $cm^{-1}$, 1574, 1287. – UV ($CH_3CN$): $\lambda_{max}$ (lg $\varepsilon$) = 198 (5.005) nm, 238 (4.366), 290 (4.467). – $^1H$ NMR ($CDCl_3$): $\delta$ = 2.60 (s, 6H), 5.47 (s, 4H), 7.13 (d, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.70 (m, 8H), 8.16 (d, *J* = 7.7 Hz, 2H), 8.31 (d, *J* = 7.6 Hz, 2H). – $^{13}C$ NMR ($CDCl_3$). $\delta$ = 24.59 (+), 68.16 (–), 118.21 (+), 120.16 (+), 121.42 (+), 123.23 (+), 129.21 (+), 131.31 (+), 131.91 ($C_{quart}$), 136.96 (+), 137.48 (+), 154.68 ($C_{quart}$), 155.17 ($C_{quart}$), 156.03 ($C_{quart}$), 157.76 ($C_{quart}$), 167.18 ($C_{quart}$). – MS (70 eV), *m/z* (%): 530 (40) [$M^+$], 199 (100). – $C_{32}H_{26}N_4O_4$ (530.6): calcd. C 72.44, H 4.94, N 10.56; found C 72.18, H 4.40, N 10.99. – Mol. mass 530 (MS).

*Bis(6′-2,2′-bipyridyl)phthalate-copper(I) Trifluoromethanesulfonic Acid* (**4a**): A solution of **3** (30 mg, 0.06 mmol) and 32 mg (0.06 mmol) of $Cu(CF_3SO_3)(C_6H_6)_{0.5}$ in 2 ml of $CH_3CN$ was stirred under $N_2$ for 2 h. The solvent was removed in vacuo and CC ($CH_2Cl_2$:methanol, 20:1) of the residue yielded 28 mg (80%) of **4a** ($R_f$ = 0.5) as a red solid, m. p. >300°C. – IR (KBr): $\tilde{\nu}$ = 1731 $cm^{-1}$, 1260, 643. – $^1H$ NMR ($CH_3CN$): $\delta$ = 2.18 (s, 6H), 5.32 (bs, 4H), 7.46 (d, $J$ = 7.7 Hz, 2H), 7.66 (m, 4H), 7.80 (dd, $J$ = 7.6 Hz, $J$ = 0.5 Hz, 2H), 8.03 (t, $J$ = 7.9 Hz, 2H), 8.20 (t, $J$ = 7.9 Hz, 2H), 8.31 (m, 2H), 8.48 (d, $J$ = 7.6 Hz, 2H). – MS (FAB$^+$, NBA), $m/z$ (%): 593/594/595/596/597 (100/40/50/20/6) [M$^+$]. – $C_{33}H_{26}CuF_3N_4O_7S$ (743.2): calcd. C 53.33, H 3.53, N 7.54; found C 53.01, H 3.52, N 7.50. – Mol. mass 743 (MS).

*Bis(6′-2,2′-bipyridyl)phthalate-silver(I) Perchlorate* (**4b**): 24 mg (0.05 mmol) of **3** was treated with 12 mg (0.06 mmol) of $AgClO_4$ in 2 ml of $CH_3CN$ and the reaction mixture was stirred for 2 h in the dark. It was subsequently poured into 20 ml of diethyl ether, the precipitate collected and dried in vacuo to yield 27 mg (85%) of **4b** as a white solid, m. p. >300°C. – IR (KBr): $\tilde{\nu}$ = 1731 $cm^{-1}$, 1262. – $^1H$ NMR ($CH_3CN$): $\delta$ = 2.38 (s, 6H), 5.32 (s, 4H), 7.47 (d, $J$ = 7.6 Hz, 2H), 7.59 (m, 2H), 7.66 (m, 2H), 7.72 (dd, $J$ = 7.6 Hz, $J$ = 0.7 Hz, 2H), 7.98 (t, $J$ = 7.9 Hz, 2H), 8.10 (t, $J$ = 7.9 Hz, 2H), 8.16 (d, $J$ = 7.9 Hz, 2H), 8.31 (dd, $J$ = 8.0 Hz, $J$ = 0.6 Hz, 2H). – $^{13}C$ NMR ($CDCl_3$): $\delta$ = 26.71 (+), 71.46 (−), 121.31 (+), 123.87 (+), 126.72 (+), 130.17 (+), 131.94 ($C_{quart}$), 132.89 (+), 140.67 (+), 141.43 (+), 151.64 ($C_{quart}$), 153.08 ($C_{quart}$), 155.39 ($C_{quart}$), 159.68 ($C_{quart}$), 167.58 ($C_{quart}$). – MS (FAB$^+$, NBA), $m/z$ (%): 637/638/639/640/641 (95/35/100/35/10) [M$^+$].

*Bis(6′-2,2′-bipyridyl)terephthalate* (**6-H**): Compound **1a** (400 mg, 2 mmol) and **5-H** (203 mg, 1 mmol) were allowed to react in 5 ml of pyridine as described for **3**. The reaction mixture was hydrolyzed with 30 ml of ice and extracted with 200 ml of $CHCl_3$. The organic phase was washed with water (2 × 100 ml), dried and the solvent was evaporated in vacuo. Recrystallization of the crude product from $CHCl_3$ gave 290 mg (55%) of **6-H** as a white solid, m. p. >300°C. – IR (KBr): $\tilde{\nu}$ = 1715 $cm^{-1}$, 1665, 1356. – $^1H$ NMR ($CDCl_3$): $\delta$ = 2.56 (s, 6H), 5.53 (s, 4H), 7.11 (d, $J$ = 7.5 Hz, 2H), 7.37 (d, $J$ = 7.5 Hz, 2H), 7.62 (t, $J$ = 7.5 Hz, 2H), 7.78 (t, $J$ = 7.6 Hz, 2H), 8.13 (d, $J$ = 7.5 Hz, 2H), 8.17 (s, 4H), 8.30 (d, $J$ = 7.6 Hz, 2H). – MS (70 eV), $m/z$ (%): 530 (35) [M$^+$], 199 (100). – $C_{32}H_{26}N_4O_4$: calcd. C 530.1954, found 530.1954 (MS).

*Bis(6′-2,2′-bipyridyl)terephthalate-copper(I) Hexafluorophosphate* (**7-H**): A solution of 30 mg (0.06 mmol) of **6-H** and 22 mg (0.06 mmol) of $Cu[(CH_3CN)_4]PF_6$ in 2 ml of $CH_3CN$ was stirred at room temp. for 12 h. The reaction mixture was poured into 20 ml of ether, the precipitate was collected by filtration, washed with methanol, dichloromethane and ether, then dried in vacuo to yield 24 mg (55%) of **7-H** as a red solid, m. p. >300°C. – IR (KBr): $\tilde{\nu}$ = 1719 $cm^{-1}$, 1655, 1111. – UV ($CH_3CN$): $\lambda_{max}$ (lg $\varepsilon$) = 194 (4.982) nm, 246 (4.554), 300 (4.506), 448 (3.710). – $^1H$ NMR ([$D_6$]DMSO): $\delta$ = 2.07 (s, 6H), 4.82 (d, $J$ = 13.4 Hz, 2H), 4.97 (d, $J$ = 13.4 Hz, 2H), 7.55 (d, $J$ = 7.5 Hz, 2H), 7.63 (s, 4H), 7.70 (m, 2H), 8.21 (m, 4H), 8.70 (m, 4H). – MS (ESI), $m/z$ (%): 593.2/593.8/594.2 (100/70/100) [M$^+$]. – $C_{32}H_{26}CuF_6N_4O_4P$ (739.1): calcd. C 52.00, H 3.55, N 7.58; found C 51.65, H 3.53, N 7.21. – Mol. mass 739 (MS).

*2,5-Dihexyl-bis(6′-2,2′-bipyridyl)terephthalate* (**6-Hexyl**): The compounds **1a** (200 mg, 1 mmol) and **5-Hexyl** (168 mg, 0.5 mmol) were allowed to react in 3 ml of dry pyridine and the reaction mixture was worked up as described for **3**. CC (PE:EE, 3:1) gave 283 mg (81%) of **6-Hexyl** ($R_f$ = 0.65) as an off-white solid, m.p. 65°C. – IR (KBr): $\tilde{\nu}$ = 2925 $cm^{-1}$, 1724, 1440. – $^1H$ NMR ($CDCl_3$): $\delta$ = 0.74 (m, 6H), 1.14 (m, 12H), 1.48 (m, 4H), 2.55 (s, 6H), 2.85 (t, $J$ = 7.5 Hz, 4H), 5.47 (s, 4H), 7.09 (d, $J$ = 7.6 Hz, 2H), 7.33 (d, $J$ = 7.6 Hz, 2H), 7.60 (t, $J$ = 7.7 Hz, 2H), 7.75 (t, $J$ = 7.7 Hz, 2H), 7.78 (s, 2H), 8.14 (d, $J$ = 7.7 Hz, 2H), 8.30 (d, $J$ = 7.7 Hz, 2H). – $^{13}C$ NMR ($CDCl_3$): $\delta$ = 14.02 (+), 22.54 (−), 24.55 (+), 29.31 (−), 31.63 (−), 31.70 (−), 33.85 (−), 67.53 (−), 118.31 (+), 120.28 (+), 121.42 (+), 123.39 (+), 132.42 ($C_{quart}$), 132.90 (+), 137.05 (+), 137.53 (+), 141.81 ($C_{quart}$), 155.03 ($C_{quart}$), 155.21 ($C_{quart}$), 156.15 ($C_{quart}$), 157.86 ($C_{quart}$), 166.98 ($C_{quart}$). – MS (70 eV), $m/z$ (%): 698 (10) [M$^+$], 199 (100). – $C_{44}H_{50}N_4O_4$ (698.9): calcd. C 75.62, H 7.21, N 8.02; found C 75.26, H 7.26, N 7.82. – Mol. mass 698 (MS). – $C_{44}H_{50}N_4O_4$: calcd. 698.3832, found 698.3830 (MS).

*2,5-Dihexyl-bis(6′-2,2′-bipyridyl)terephthalate-copper(I) Hexafluorophosphate* (**7-Hexyl**): A solution of **6-Hexyl** (280 mg, 0.4 mmol) and $Cu[(CH_3CN)_4]PF_6$ (150 mg, 0.4 mmol) in 3 ml of $CH_3CN$ was stirred at room temp. for 12 h. The product was precipitated by the addition of 20 ml of ether, collected by filtration, and purified by CC ($CH_2Cl_2$/methanol, 20:1) to give 280 mg (77%) of **7-Hexyl** ($R_f$ = 0.6) as a red solid, m.p. >300°C. – $^1H$ NMR (DMSO-[$D_6$]): $\delta$ = 0.90 (m, 6H), 1.14 (m, 12H), 2.10 (m, 10H), 2.85 (m, 4H), 5.00 (m, 4H), 7.20–8.90 (m, 14H). – MS (ESI), $m/z$ (%): 761.4/761.9/762.4/762.9 (80/90/100/80) [M$^+$]. – $C_{44}H_{50}CuF_6N_4O_4P$ (907.4): calcd. C 58.24, H 5.55, N 6.17; found C 58.12, H 5.37, N 5.95. – Mol. mass 907 (MS).

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[7] [7a] For the synthesis of a block copolymer containing 2,2′-bipyridine units see: C. D. Eisenbach, A. Göldel, M. Terskan-Reinold, U. S. Schubert, *Macromol. Chem. Phys.* **1995**, *196*, 1077–1091. – [7b] To our knowledge ester-linked bis-2,2′-bipyridines like **3** or **6** and their coordination properties have not been described in the literature. While bis-2,2′-bipyridines tethered by a short ether bridge yield helical structures upon coordination with copper(I) or silver(I) ions this is not necessarily the case for **6**.

[8] The reaction of 2,2′-bipyridinecarboxylic acids with diols might lead to the formation of ester linkages. However, electron-withdrawing ester substituents signficantly reduce the 2,2′-bipyridine coordination ability.

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ters. See ref. [6a] for an example of functionalized oligo(bipyridines). The more accessible **1a** was used for the preparation of **3** and **6**.

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