Supporting Information

for

Towards allosteric receptors – synthesis of β-
cyclodextrin-functionalised 2,2’-bipyridines and their
metal complexes

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Experimental data, NMR and ESI mass spectra

- Experimental part
- NMR spectra of compounds 1, 2, 3, 21, 22 and 6 and the metal complexes of
  1, 2, 3, 14, and 22.
- Mass spectra of metal complexes of 1, 2, 14, and 22.
Experimental

**General remarks:** All solvents were distilled and dried prior to use according to standard procedures. All syntheses with air- and moisture-sensitive compounds were performed using Schlenk techniques under argon atmosphere. Column chromatography was performed on silica gel 60 M (0.04–0.063 mm) from Macherey-Nagel. All solvents used as eluents for column chromatography were distilled prior to use. $^1$H and $^{13}$C NMR spectra were recorded at 293 K on a Bruker AM 300 ($^1$H: 300.1 MHz, $^{13}$C: 75.5 MHz) or a Bruker AM 400 ($^1$H: 400.1 MHz, $^{13}$C: 100.6 MHz). $^1$H NMR chemical shifts are reported on the $\delta$ scale (ppm) relative to residual non-deuterated solvent as internal standard. $^{13}$C NMR chemical shifts are given as $\delta$ values (ppm) relative to signals of the deuterated solvent as internal standards. Mass spectra were taken on a Bruker autoflex II TOF/TOF (MALDI) or a Bruker micrOTOF-Q (ESI, Hi-Res-ESI). Elemental analyses were carried out on a Heraeus Vario EL. Chemicals and reagents (except for the solvents) obtained from commercial sources were used as received. The following compounds were prepared according to published procedures: pyrrole-substituted 2-halogenopyridines 6 and 7,[1] bis(pyrrole)-substituted 2,2'-bipyridines 8 and 9,[1] as well as 10,[2] diamino-2,2'-bipyridines 11–13,[1] diisothiocyanato-2,2'-bipyridines 14–16,[3] 6$^A$-O-p-toluenesulfonyl-β-cyclodextrin (18)[4], 6$^A$-azido-6$^A$-deoxy-β-cyclodextrin (19)[5],

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2^A,2^B,2^C,2^D,2^E,2^F,2^G,3^A,3^B,3^C,3^D,3^E,3^F,3^G,6^B,6^C,6^D,6^E,6^F,6^G-icosa-O-acetyl-6^A-azido-
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6\textsuperscript{A}-desoxy-\textbeta-cyclodextrin (20)
\cite{6}, 6,7-dihydro-5\textH[1,4]di-azepino[1,2,3,4-\textl,\textm,\textn][1,10]-phenanthroline-4,8-dium dibromide (23)
\cite{7}, 3,6,7,9-tetrahydro-5\textH[1,4]diazepino[1,2,3,4-\textl,\textm,\textn][1,10]-phenanthroline-3,9-dione (24)
\cite{7}, 2,9-dichloro-1,10-phenanthroline (25)
\cite{8}, 2,6-dimethoxyphenylboronic acid (26)
\cite{9}, and 2,9-bis(2,6-dimethoxyphenyl)-1,10-phenanthroline (22)
\cite{10-12}.

2\textsuperscript{A},2\textsuperscript{B},2\textsuperscript{C},2\textsuperscript{D},2\textsuperscript{E},2\textsuperscript{F},2\textsuperscript{G},3\textsuperscript{A},3\textsuperscript{B},3\textsuperscript{C},3\textsuperscript{D},3\textsuperscript{E},3\textsuperscript{F},3\textsuperscript{G},6\textsuperscript{B},6\textsuperscript{C},6\textsuperscript{D},6\textsuperscript{E},6\textsuperscript{F},6\textsuperscript{G}-Icosa-O-acetyl-6\textsuperscript{A}-amino-6\textsuperscript{A}-desoxy-\textbeta-cyclodextrin (21): 3.92 g (1.96 mmol) of peracetylated azidocyclodextrin 20 were dissolved in 12 mL of dry acetone and 1.03 g (3.95 mmol) PPh\textsubscript{3} were added. The reaction mixture was stirred for two hours at rt, followed by the addition of 1 mL of water. After 30 minutes of reflux, the solvents were evaporated, the crude product was dissolved in dichloromethane and washed with water. After drying with MgSO\textsubscript{4}, the solvents were evaporated. Further purification could be achieved by column chromatography on silica gel (eluent: dichloromethane/EtOH 96:4 + 0.5% NEt\textsubscript{3}, \textit{R} = 0.32) to give 2.34 g (1.18 mmol, 60%) of the desired product as a white solid.

Mp (°C): 150°C. \textsuperscript{1}H NMR (300.1 MHz, CDCl\textsubscript{3}): \( \delta [\text{ppm}] = 5.23-5.40 (\text{m}, 7\text{H}, \text{H-3}\text{A-G}); 5.17 (\text{d}, \( {3}J = 3.8 \text{ Hz}, 1\text{H}, \text{H-1}\text{A})); 5.03-5.35 (\text{m}, 6\text{H}, \text{H-1}\text{B-G}); 4.72-4.86 (\text{m}, 7\text{H}, \text{H-2}\text{A-G}), 4.48-4.62 (\text{m}, 6\text{H}, \text{H-6}\text{B-G}); 4.19-4.35 (\text{m}, 6\text{H}, \text{H-6}\text{B-G}); 4.02-4.19 (\text{m}, 7\text{H}, \text{H-5}\text{A-G}); 3.82-3.98 (\text{m}, 2\text{H}, \text{H-6}\text{A}), 3.64-3.77 (\text{m}, 7\text{H}, \text{H-4}\text{A-G}); 1.95-2.20 (\text{m}, 60\text{H}, -\text{COOMe}).

\textsuperscript{13}C NMR (75.5 MHz, CDCl\textsubscript{3}): \( \delta [\text{ppm}] = 169.38-170.77 (-\text{COOMe}); 96.79-98.42 (\text{C-1}\text{A-G}); 76.51-77.40 (\text{C-4}\text{A-G}); 69.38-71.24 (\text{C-2}\text{A-G}, \text{C-3}\text{A-G}, \text{C-5}\text{A-G}); 62.44-62.78

((C-6^B-G); 41.59 (C-6^A); 20.77 (-COOMe). MS (ESI (+)): m/z = 1974.4 ([([7]+H]^+); 999.2
([([7]+H+Na)^+). Elemental analysis: calcd. for C_{82}H_{111}NO_{54} (%): C, 49.87; H, 5.67; N,
0.71; found (%): C, 49.53; H, 5.90; N, 0.89.

N,N’-(2,2’-Bipyridine)-4,4’-diylbis(N’-2^A,2^B,2^C,2^D,2^E,2^F,2^G,3^A,3^B,3^C,3^D,3^E,3^F,3^G,
6^B,6^C,6^D,6^E,6^F,6^G-icosa-O-acetyl-6^A-desoxy-β-cyclodextrin-6^A-yl)thiourea) (1)

0.05 g (0.2 mmol) of 4,4’-diisothiocyanato-2,2’-bipyridine (14) and 0.9 g (0.46 mmol,
2.3 equiv) of 2^A,2^B,2^C,2^D,2^E,2^F,2^G,3^A,3^B,3^C,3^D,3^E,3^F,3^G,6^B,6^C,6^D,6^E,6^F,6^G-icosa-O-
acetyl-6^A-amino-6^A-desoxy-β-cyclodextrin (21) were dissolved in 20 mL of dry
dichloromethane and stirred for 24 hours at rt, followed by evaporation of the solvent.
Column chromatography on silica gel (eluent: dichloromethane:EtOH 96:4, R_f = 0.32)
gave 0.77 g (0.18 mmol, 92%) of the desired product as a slightly off-white
amorphous solid.

^1^H NMR (300.1 MHz, CDCl_3): δ [ppm] = 8.87 (b, 2H, NH); 8.46 (d, 3 J = 5.7 Hz, 2H,
H-6^B_{bip}); 8.13 (s, 2H, H-3^B_{bip}); 7.97 (b, 2H, H-5^B_{bip}); 6.89 (b, 2H, NH); 5.22-5.45 (m,
14H, H-3^A-G); 4.96-5.24 (m, 14H, H-1^A-G); 4.69-4.93 (m, 14H, H-2^A-G), 3.93-4.66 (m,
38H, H-5^A-G, H-6^B-G); 3.61-3.88 (m, 18H, H-6^A; H-4^A-G ); 1.91-2.28 (m,
120H, -COOMe). ^13^C NMR (75.5 MHz, CDCl_3): δ [ppm] = 180.5 (C=S); 169.4-171.3 (-
COOMe); 155.9 (C-4^B_{bip}); 150.0 (C-2^B_{bip}); 147.2 (C-6^B_{bip}); 114.6 (C-5^B_{bip}); 111.8 (C-
3^B_{bip}); 96.3-98.1 (C-1^A-G); 76.5-77.4 (C-4^A-G); 69.5-71.8 (C-2^A-G, C-3^A-G, C-5^A-G); 62.4-
63.1 (C-6^A-G); 20.6 (-COOMe). MS (MALDI-TOF): m/z = 4219.8 ([([1]+H]^+). Elemental
analysis: calcd. for C_{176}H_{229}N_{6}O_{108}S_{2} · 7 CH_{2}Cl_{2} (%): C, 45.66; H, 5.07; N, 1.75; S:
1.33; found (%): C, 45.82; H, 5.12; N, 1.85; S, 1.82.
N,N’-(2,2’-Bipyridine)-6,6’-diylbis(N’-2A,2B,2C,2D,2E,2F,2G,3A,3B,3C,3D,3E,3F,3G, 
6B,6C,6D,6E,6F,6G-icosa-O-acetyl-6A-desoxy-β-cyclodextrin-6A-yl thiourea) (2)

0.02 g (0.07 mmol) of 6,6’-diisothiocyanato-2,2’-bipyridine (15) and 0.34 g (0.17 
mmol, 2.3 equiv) of 2A,2B,2C,2D,2E,2F,2G,3A,3B,3C,3D,3E,3F,3G,6B,6C,6D,6E,6F,6G-icosa-
O-acetyl-6A-amino-6A-desoxy-β-cyclodextrin (21) were dissolved in 10 mL of dry 
dichloromethane and stirred for 48 hours at rt, followed by evaporation of the solvent. 
Column chromatography on silica gel (elucent: dichloromethane:EtOH 96:4, Rf = 0.38) 
gave 0.29 g (0.069 mmol, 93%) of the desired product as a slightly off-white 
amorphous solid.

1H NMR (400.1 MHz, CDCl3): δ [ppm] = 11.81 (s, 2H, N-H); 8.97 (s, 2H, N-H); 7.77 
(dd, 3J = 7.9 Hz, 2H, H-4Bipy); 7.59 (d, 3J = 7.9 Hz, 2H, H-3Bipy); 7.02 (d, 3J = 7.9 Hz, 
2H, H-5Bipy); 5.10-5.40 (m, 14H, H-3A-G); 4.91-5.09 (m, 14H, H-1A-G); 4.64-4.83 (m, 
14H, H-2A-G), 3.88-4.27 (m, 38H, H-5A-G, H-6B-G); 3.42-3.81 (m, 18H, H-6A; H-4A-G); 
1.82-2.52 (m, 120H, -COOMe). 13C NMR (100.1 MHz, CDCl3): δ [ppm] = 180.2 
(C=S); 169.2-171.5 (-COOMe); 153.0 (C-6Bipy); 151.8 (C-2Bipy); 139.6 (C-4Bipy); 114.9 
(C-3Bipy); 113.4 (C-5Bipy); 96.3-97.5 (C-1A-G); 76.1-78.1 (C-4A-G); 68.5-72.0 (C-2A-G, 
C-3A-G, C-5A-G); 62.4-65.2 (C-6A-G); 20.8-21.1 (-COOMe). MS (MALDI-TOF): m/z = 
4217.9 ([2]+H’). Elemental analysis: calcd. for C176H228N6O108S2 : 2 CH2Cl2 (%): C, 
48.70; H, 5.33; N, 1.91; S, 1.46; found (%): C, 48.39; H, 5.48; N, 1.56; S, 1.85.

N,N’-(2,2’-Bipyridine)-4,6’-diylbis(N’-2A,2B,2C,2D,2E,2F,2G,3A,3B,3C,3D,3E,3F,3G, 
6B,6C,6D,6E,6F,6G-icosa-O-acetyl-6A-desoxy-β-cyclodextrin-6A-yl thiourea) (3)

0.02 g (0.07 mmol) of 4,6’-diisothiocyanato-2,2’-bipyridine (16) and 0.34 g (0.17 
mmol, 2.3 equiv) of 2A,2B,2C,2D,2E,2F,2G,3A,3B,3C,3D,3E,3F,3G,6B,6C,6D,6E,6F,6G-O-
acetyl-6A-amino-6A-desoxy-β-cyclodextrin were dissolved in 10 mL of dry 
dichloromethane and stirred for 48 hours at rt, followed by evaporation of the solvent.
Column chromatography on silica gel (eluent: dichloromethane:EtOH 96:4, \( R_f = 0.38 \)) gave 0.27 g (0.06 mmol, 86%) of the desired product as a slightly off-white amorphous solid.

\(^1\)H NMR (300.1 MHz, CDCl\(_3\)): \( \delta \) [ppm] = 12.26 (b, 1H, N-H); 9.11 (s, 1H, H-3\textsubscript{Bipy}); 8.63 (b, 1H, N-H); 8.53 (d, \(^3\)J = 5.5 Hz, 1H, H-6\textsubscript{Bipy}); 8.30 (b, 1H, N-H); 7.95 (d, \(^3\)J = 7.9 Hz, 1H, H-3\textsubscript{Bipy}); 7.69 (m, 2H, H-4\textsubscript{Bipy}, H-5\textsubscript{Bipy}); 7.09 (b, 1H, N-H); 7.00 (d, \(^3\)J = 7.9 Hz, 1H, H-5\textsubscript{Bipy}); 5.22-5.40 (m, 14H, H-3\textsubscript{A-G}); 4.96-5.22 (m, 14H, H-1\textsubscript{A-G}); 4.65-4.93 (m, 14H, H-2\textsubscript{A-G}), 4.03-4.63 (m, 38H, H-5\textsubscript{A-G}, H-6\textsubscript{B-G}); 3.57-3.91 (m, 18H, H-6\textsubscript{A-G}; H-4\textsubscript{A-G}); 1.75-2.23 (m, 120H, -COO\textsubscript{Me}).

\(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)): \( \delta \) [ppm] = 180.1 (C=S); 169.1-171.1 (-COO\textsubscript{Me}); 155.3 (C-4\textsubscript{Bipy}); 152.7 (C-6\textsubscript{Bipy}); 150.5 (C-6\textsubscript{Bipy}); 147.2 (C-2\textsubscript{Bipy}); 139.7 (C-4\textsubscript{Bipy}); 115.7 (C-3\textsubscript{Bipy}); 115.0 (C-5\textsubscript{Bipy}); 113.0 (C-5\textsubscript{Bipy}); 112.2 (C-3); 95.5-97.9 (C-1\textsubscript{A-G}); 75.9-78.4 (C-4\textsubscript{A-G}); 68.7-72.3 (C-2\textsubscript{A-G}, C-3\textsubscript{A-G}, C-5\textsubscript{A-G}); 62.0-63.1 (C-6\textsubscript{A-G}); 20.4 (-COO\textsubscript{Me}). MS (ESI (+)): \( m/z = 2132.5 \) ([(CO)\(_3\)Re(14)]\(^+\)Na\(^2+\)). Hi-Res-MS (ESI (+)): calcd. for \([C\textsubscript{176}H\textsubscript{228}N\textsubscript{6}O\textsubscript{108}S\textsubscript{2}Na\textsubscript{2}]^{+}\): \( m/z = 2131.5880 \); found: \( m/z = 2131.5813 \) (\( \Delta = 3.1 \) ppm). Elemental analysis: calcd for C\textsubscript{176}H\textsubscript{228}N\textsubscript{6}O\textsubscript{108}S\textsubscript{2} (%): C, 50.09; H, 5.45; N, 1.99; S, 1.52; found (%): C, 49.72; H, 5.69; N, 1.58; S, 1.57.

\([(\text{CO})\textsubscript{3}\text{Re(14)}\text{Cl}]\)

0.02 g (0.07 mmol) of 14 and 0.03 mg (0.016 mmol) pentacarbonylrhenium(I) chloride were dissolved in 2 mL CHCl\(_3\). The solution was stirred at 40 °C. After 7 d, when \(^1\)H NMR measurements showed complete conversion, the solvent was evaporated.

\(^1\)H NMR (300.1 MHz, CDCl\(_3\)): \( \delta \) [ppm] = 8.98 (d, \(^3\)J = 6.0 Hz, 2H, H-6); 7.85 (d, \(^4\)J = 2.1 Hz, 2H, H-3); 7.31 (dd, \(^3\)J = 6.0 Hz, \(^4\)J = 2.1 Hz, 2H, H-5). MS (ESI (+)): \( m/z = 605.0 \) ([(CO)\(_3\)Re(14)]\(^+\)+2 MeOH\(^+\))\(^+\); 623.0 ([(CO)\(_3\)Re(14)]\(^+\)+2 MeOH+H\(_2\)O\(^+\)).
Hi-Res.-MS (ESI (+)): calcd. for [C_{15}H_6N_4O_3ReS_2(CH_3OH)_2]^+: m/z = 604.9950; found: m/z = 604.9940 (Δ = 1.7 ppm).

[Zn(1)\textsubscript{2}](OTf\textsubscript{2})

0.7 mg (0.002 mmol) of Zn(OTf\textsubscript{2}) were in dissolved in 0.5 mL of C\textsubscript{6}D\textsubscript{6}/CD\textsubscript{3}CN (1:1). 0.3515 mL of this solution were transferred into a solution of 8 mg (0.002 mmol) of 1 in 0.1985 mL of C\textsubscript{6}D\textsubscript{6}/CD\textsubscript{3}CN (1:1) and stirred for 1 h at 40 °C.

\textsuperscript{1}H NMR (400.1 MHz, C\textsubscript{6}D\textsubscript{6}/CD\textsubscript{3}CN): δ [ppm] = 9.58 (b, 2H, N-H); 8.66 (s, 2H, H-3\textsubscript{Bipy}); 8.57 (d, \textsuperscript{3}J = 6.1 Hz, 2H, H-6\textsubscript{Bipy}); 8.39 (b, 2H, H-5\textsubscript{Bipy}); 7.6 (b, 2H, N-H); 5.32-5.43 (m, 14H, H-3\textsubscript{A-G}); 5.01-5.13 (m, 14H, H-1\textsubscript{A-G}); 4.70-4.83 (m, 14H, H-2\textsubscript{A-G}); 4.08-4.62 (m, 38H, H-5\textsubscript{A-G}, H-6\textsubscript{B-G}); 3.69-3.96 (m, 18H, H-6\textsubscript{A}; H-4\textsubscript{A-G}); 1.85-2.01 (m, 120H, -COO\textsubscript{Me}). MS (MALDI-TOF): m/z = 4432.4 [[Zn(1)]OTf]\textsuperscript{+}; 8654.7 [[Zn(1)\textsubscript{2}]OTf]\textsuperscript{+}.

[Cu(2)]PF\textsubscript{6}

2 mg (0.00537 mmol) of Cu(MeCN\textsubscript{4})PF\textsubscript{6} were dissolved in 0.5 mL of C\textsubscript{6}D\textsubscript{6}/CD\textsubscript{3}CN (1:1). 0.177 mL of this solution were transferred into a solution of 8 mg (0.00186 mmol) of 2 in 0.423 mL of C\textsubscript{6}D\textsubscript{6}/CD\textsubscript{3}CN (1:1). The yellow solution was stirred for 1 h at 40 °C.

\textsuperscript{1}H NMR (400.1 MHz, C\textsubscript{6}D\textsubscript{6}/CD\textsubscript{3}CN): δ [ppm] = 12.04 (b, 2H, N-H); 9.79 (b, 2H, N-H); 7.91 (m, 2H, H-4\textsubscript{Bipy}); 7.81 (m, 2H, H-3\textsubscript{Bipy}); 7.31 (m, 2H, H-5\textsubscript{Bipy}); 5.30-5.63 (m, 14H, H-3\textsubscript{A-G}); 5.03-5.25 (m, 14H, H-1\textsubscript{A-G}); 4.7-4.96 (m, 14H, H-2\textsubscript{A-G}), 4.10-4.70 (m, 38H, H-5\textsubscript{A-G}, H-6\textsubscript{B-G}); 3.73-4.05 (m, 18H, H-6\textsubscript{A}; H-4\textsubscript{A-G}); 1.90-2.25 (m, 120H, -COO\textsubscript{Me}). MS (MALDI-TOF): m/z = 4283.3 [[Cu(2)]\textsuperscript{+}].
[Zn(2)](OTf)₂

1 mg (0.00275 mmol) of Zn(OTf)₂ were dissolved in 0.5 mL of C₆D₆/CD₃CN (1:1). 0.338 mL of this solution were transferred into a solution of 8 mg (0.00186 mmol) 2 in 0.162 mL of C₆D₆/CD₃CN (1:1) and stirred for 1 h at 40 °C.

¹H NMR (400.1 MHz, C₆D₆/CD₃CN): δ [ppm] = 10.58 (s, 2H, N-H); 8.43 (s, 2H, N-H); 7.87 (dd, 3J = 8.1 Hz, 3J = 8.1 Hz, 2H, H-4_Bipy); 7.70 (d, 3J = 8.1 Hz, 2H, H-3_Bipy); 7.33 (d, 3J = 8.1 Hz, 2H, H-5_Bipy); 5.35-5.50 (m, 14H, H-3_A-G); 4.91-5.21 (m, 14H, H-1_A-G); 4.68-4.95 (m, 14H, H-2_A-G); 4.05-4.59 (m, 42H, H-5_A-G, H-6_A-G); 3.75-3.92 (m, 14H, H-4_A-G); 1.82-2.08 (m, 120H, -COO.Me). MS (ESI(+)): m/z = 1429.2 ([Zn(2)]+H)³⁺).

[Cu(22)]PF₆

5 mg (0.01341 mmol) of Cu(MeCN)₄PF₆ were dissolved in 0.5 mL of C₆D₆/CD₃CN (1:1). 0.297 mL of this solution were transferred into a solution of 3.6 mg (0.00796 mmol) of 22 in 0.5 mL of C₆D₆/CD₃CN (1:1). A yellow solution was obtained.

¹H NMR (400.1 MHz, C₆D₆/CD₃CN 1:1): δ [ppm] = 8.09 (d, 3J₃,₄ = 8.3 Hz, 2H, H-4); 7.54 (s, 2H, H-5); 7.52 (d, 3J₃,₄ = 8.3 Hz, 2H, H-3); 7.3 (dd, 3J₃',₄' = 8.4 Hz, 2H, H-3'); 6.57 (d, 3J₃',₄' = 8.4 Hz, 4H, H-3'); 3.43 (s, 12H, -O Me). MS (ESI(+)): m/z = 515.2 ([Cu(22)]⁺). Hi-Res.-MS (ESI(+)): calcd. for [C₂₈H₂₄CuN₂O₄]⁺: m/z = 515.1026; found: m/z = 515.1027 (Δ = 0.2 ppm).

[Zn(22)₂](OTf)₂

5 mg (0.014 mmol) of Zn(OTf)₂ were dissolved in 0.3 mL of C₆D₆/CD₃CN (1:1). 0.289 mL of this solution were transferred into a solution of 5 mg (0.01105 mmol) of 22 in 0.4 mL of C₆D₆/CD₃CN (1:1). The colourless solution was stirred at 40 °C for 1 h.

¹H NMR (400.1 MHz, C₆D₆/CD₃CN): δ [ppm] = 8.34 (d, 3J₃,₄ = 8.4 Hz, 2H, H-4); 7.86 (s, 2H, H-5); 7.45 (d, 3J₃,₄ = 8.4 Hz, 2H, H-3); 7.45 (dd, 3J₃',₄' = 8.4 Hz, 2H, H-4'). 6.70
(d, \( ^3J_{3',4'} = 8.4\) Hz, 4H, H-3'); 3.31 (s, 12H, -OMe). MS (ESI (+)): \(m/z = 258.0\) ([M+Zn]^{2+}); 484.1 ([Zn(22)]^{2+}); 665.1 ([[Zn(11)]OTf]^+). Hi-Res.-MS (ESI (+)): calcd. for [C_{29}H_{24}F_{3}N_{2}O_{7}SZn]^+: \(m/z = 665.0542\); found: \(m/z = 665.0522\) (\(\Delta = 3\) ppm).

[Cu(1)(22)]PF₆

2 mg (0.005366 mmol) of Cu(MeCN)₄PF₆ were dissolved in 0.4 mL of C₆D₆/CD₃CN (1:1). 0.3295 mL of this solution were transferred to a solution of 2 mg (0.00442 mmol) of 22 in 0.4 mL of C₆D₆/CD₃CN (1:1). From this solution, 0.3129 mL were taken and added to a solution of 8 mg (0.001896 mmol) of 1 in 0.3 mL of C₆D₆/CD₃CN (1:1). The resulting solution has a deep red colour.

\(^1\)H NMR (400.1 MHz, C₆D₆/CD₃CN): \(\delta [ppm] = 9.10\) (b, 2H, N-H); 8.26 (b, 2H, H-3Bipy); 8.14 (d, \( ^3J = 8.3\) Hz, 2H, H-4Phen); 7.85 (b, 2H, H-5Bipy); 7.82 (d, \( ^3J = 5.7\) Hz, 2H, H-6Bipy); 7.60 (s, 2H, H-5Phen); 7.52 (d, \( ^3J = 8.3\) Hz, 2H, H-3Phen); 7.19 (b, 2H, N-H); 6.79 (dd, \( ^3J = 8.4\) Hz, 2H, H-4'Phen); 6.01 (d, \( ^3J = 8.4\) Hz, 4H, H-3'Phen); 5.35-5.48 (m, 14H, H-3\(^A\)-G); 5.02-5.18 (m, 14H, H-1\(^A\)-G); 4.70-4.85 (m, 14H, H-2\(^A\)-G); 4.05-4.55 (m, 38H, H-5\(^A\)-G, H-6\(^B\)-G); 3.69-3.92 (m, 18H, H-6\(^A\); H-4\(^A\)-G); 3.21 (s, 12H, -OMe); 1.85-1.98 (m, 120H, -COOMe). MS (MALDI-TOF): 4735.9 ([Cu(1)(22)]^+).

[Zn(1)(22)](OTf)₂

2.5 mg (0.00688 mmol) of Zn(OTf)₂ were dissolved in 0.6 mL C₆D₆/CD₃CN (1:1). 0.4821 mL of this solution were transferred into a solution of 2.5 mg (0.00553 mmol) of 22 in 0.6 mL C₆D₆/CD₃CN (1:1). From this solution, 1.0211 mL were taken and added to a solution of 22 mg (0.005214 mmol) of 1 in 0.3 mL of C₆D₆/CD₃CN (1:1). The colourless mixture was stirred for 1 h at 40 °C.

\(^1\)H NMR (400.1 MHz, C₆D₆/CD₃CN): \(\delta [ppm] = 9.79\) (b, 2H, N-H); 8.54 (s, 2H, H-3Bipy); 8.41 (d, \( ^3J = 8.4\) Hz, 2H, H-4Phen); 8.17 (d, \( ^3J = 6.0\) Hz, 2H, H-6Bipy); 7.92 (s,
2H, H-5\textsubscript{Phen}); 7.75 (b, 2H, N-H); 7.67 (d, $^3\text{J} = 8.4$ Hz, 2H, H-3\textsubscript{Phen}); 7.66 (d, $^3\text{J} = 6.0$ Hz, 2H, H-5\textsubscript{Bipy}); 6.92 (dd, $^3\text{J} = 8.4$ Hz, 2H, H-4$'$\textsubscript{Phen}); 6.13 (m, 4H, H-3$'$\textsubscript{Phen}); 5.35-5.50 (m, 14H, H-3\textsubscript{A-G}); 5.02-5.19 (m, 14H, H-1\textsubscript{A-G}); 4.68-4.80 (m, 14H, H-2\textsubscript{A-G}); 4.10-4.48 (m, 42H, H-5\textsubscript{A-G}, H-6\textsubscript{A-G}); 3.75-3.90 (m, 14H, H-6\textsubscript{A}; H-4\textsubscript{A-G}); 3.19 (s, 12H, -OMe); 1.86-1.98 (m, 120H, -COO\textsubscript{Me}). MS (MALDI-TOF): $m/z = 4884.6$ ([Zn(1)(22)]OTf)$^+$. 

**Crystal structure determination:** The data collection was performed on a NONIUS KappaCCD diffractometer (area detector) using graphite monochromated Mo $K_\alpha$ radiation ($\lambda = 0.71073$ Å). The diffractometer was equipped with a low-temperature device (Cryostream 600er series, Oxford Cryosystems, 123(2) K). Intensities were measured by fine-slicing $\omega$ and $\phi$-scans and corrected for background, polarization and Lorentz effects. An empirical absorption correction was applied for all data sets according to Blessing’s method.$^{[13]}$ The structures were solved by direct methods and refined anisotropically by the least-squares procedure implemented in the ShelX program system.$^{[14]}$ Hydrogen atoms were included isotropically using the riding model on the bound carbon atoms.

CCDC-974931 ([CO\textsubscript{3}Re(14)C]), CCDC-974932 ([Cu(22)(H\textsubscript{2}CCN)\textsubscript{2}]PF\textsubscript{6}), and CCDC-974933 ([Zn(22)\textsubscript{2}](OTf)\textsubscript{2}) contain the supplementary crystallographic data for this paper, which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.


$^{14}$ Sheldrick, G. M.; *SHELXS97* and *SHELXL97*, University of Göttingen, Germany, 1997.
Table S1: Crystallographic data for [(CO)$_3$Re(14)Cl], [Cu(22)(H$_3$CCN)$_2$]PF$_6$, and [Zn(22)$_2$](OTf)$_2$.

<table>
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<tr>
<th>Parameters</th>
<th>[(CO)$_3$Re(14)Cl]</th>
<th>[Cu(22)(H$_3$CCN)$_2$]PF$_6$</th>
<th><a href="OTf">Zn(22)$_2$</a>$_2$</th>
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Figure S1: $^1$H NMR spectrum (400.1 MHz, in CDCl$_3$ at 293 K) of 1.

Figure S2: $^{13}$C NMR spectrum (100.6 MHz, in CDCl$_3$ at 293 K) of 1.
Figure S3: $^1$H NMR spectrum (400.1 MHz, in CDCl$_3$ at 293 K) of 2.

Figure S4: $^{13}$C NMR spectrum (100.6 MHz, in CDCl$_3$ at 293 K) of 2.
Figure S5: $^1$H NMR spectrum (400.1 MHz, in CDCl$_3$ at 293 K) of 3.

Figure S6: $^{13}$C NMR spectrum (100.6 MHz, in CDCl$_3$ at 293 K) of 3.
Figure S7: $^1$H NMR spectrum (400.1 MHz, in CDCl$_3$ at 293 K) of 21.

Figure S8: $^{13}$C NMR spectrum (100.6 MHz, in CDCl$_3$ at 293 K) of 21.
**Figure S9:** $^1$H NMR spectrum (400.1 MHz, in CDCl$_3$ at 293 K) of [(CO)$_3$Re(14)Cl].

**Figure S10:** ESI–MS (positive mode, sprayed from benzene/acetonitrile 1:1) of [(CO)$_3$Re(14)Cl].
Figure S11: Aromatic region of the $^1$H NMR spectra (100.6 MHz, 400.1 MHz, 293 K, benzene-$d_6$/acetonitrile-$d_3$ 1:1) of a) 2 and b) [Cu(2)]PF$_6$.

Figure S12: MALDI–MS (sample prepared from benzene/acetonitrile (1:1) solution using DCTB as matrix) of [Zn(1)$_2$(OTf)$_2$].
Figure S13: ESI–MS (positive mode, sprayed from benzene/acetonitrile 1:1) of [Zn(2)][OTf]₂.

Figure S14: Aromatic region of the ¹H NMR spectra (100.6 MHz, 400.1 MHz, 293 K, benzene-₆/acetonitrile-₃ 1:1) of a) 3 and b) a 1:2 mixture of Zn(OTf)₂ and 3.
**Figure S15:** $^1$H NMR spectrum (100.6 MHz, 400.1 MHz, 293 K, benzene-$d_6$/acetonitrile-$d_3$ 1:1) of a 1:1 mixture of CuPF$_6$ and 22.

**Figure S16:** MALDI–MS (sample prepared from a benzene/acetonitrile (1:1) solution using DCBT as matrix) of [Cu(22)]PF$_6$. 
Figure S17: $^1$H NMR spectrum (100.6 MHz, 400.1 MHz, 293 K, benzene-$d_6$/acetonitrile-$d_3$ 1:1) of a 1:1 mixture of Zn(OTf)$_2$ and 22.

Figure S18: ESI–MS (positive mode, sprayed from benzene/acetonitrile 1:1) of [Zn(22)](OTf)$_2$. 

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Figure S19: Aromatic region of the $^1$H NMR spectra (100.6 MHz, 400.1 MHz, 293 K, benzene-$d_6$/acetonitrile-$d_3$ 1:1) of a) 1, b) a 1:1:1 mixture of CuPF$_6$, 1, and 22, and c) 22.

Figure S20: MALDI–MS (sample prepared from a benzene/acetonitrile (1:1) solution using DCTB as matrix) of [Zn(22)(1)][OTf]$_2$. 