Electronic Supplementary Information

Catalytic machinery in motion: Controlling catalysis via speed

Emad Elramadi,‡ Amit Ghosh,‡ Isa Valiye, Pronay Kumar Biswas, Thomas Paululat, Michael Schmittel*

Center of Micro- and Nanochemistry and (Bio)Technology, Organische Chemie I & II, Universität Siegen, Adolf–Reichwein–Str. 2, D-57068 Siegen, Germany.

e-mail: schmittel@chemie.uni-siegen.de

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‡ Equal contribution.
1. Synthesis

1.1 General information. All reagents were purchased from commercial suppliers and used without further purification. Tetrahydrofuran (THF) was pre-dried over basic alumina and then distilled over potassium. Triethylamine (Et$_3$N) was distilled from calcium hydride.

Bruker Avance (400 MHz), Jeol ECZ (500 MHz) and Varian (600 MHz) spectrometer were used to record $^1$H-, $^{13}$C-, $^1$H-$^1$H-COSY, DOSY NMR spectra at 298 K applying the deuterated solvent as the lock. The chemical shifts refer to the residual protiated fraction of the solvent (CHCl$_3$: $\delta_H$ = 7.26 ppm, $\delta_C$ = 77.0 ppm; CHDCl$_2$: $\delta_H$ = 5.32 ppm, $\delta_C$ = 53.8 ppm). Coupling patterns of $^1$H NMR signals were described as follows (s: singlet, d: doublet, t: triplet, dd: doublet of doublets, ddd: doublet of doublets of doublets, brs: broad singlet, td: triplet of doublets, m: multiplet). Values of coupling constant(s) are reported in Hertz (Hz) and the number of protons is implied. The numbering of carbon atoms is usually not in accordance with IUPAC nomenclature guidelines.

Melting points were measured on a Büchi SMP-11 instrument. UV-vis spectra were measured on a Cary Win 50. Binding constants were determined through UV-vis titrations assuming a 1:1 binding scheme or with SPECFIT/32TM global analysis system from Spectrum Software Associates (Marlborough, MA). Electrospray ionization mass spectra (ESI-MS) were recorded on a Thermo-Quest LCQ Deca instrument. Infrared spectra were recorded using a Perkin Elmer Spectrum-Two FT-IR spectrometer. Column chromatography was performed on silica gel 60 (60–230 mesh). Thin layer chromatography (TLC) was performed using Merck silica gel (60 F254). The tris-phenanthroline deck 1$^1$ and compound 8$^2$ were synthesized according to known procedures. The spectral data of these compounds are in good agreement with those in the literature reports.
1.2 Ligands

Figure S1. Chemical structures of all ligands used in the present study.

1.3 Synthesis of ligands 2a, 2b

Scheme S1. Final step of the synthesis of ligand 2a.

Scheme S2. Final step of the synthesis of ligand 2b.
1.4 Characterization of ligands 1, 2a, 2b and 2c.

**Deck 1**:  

![Diagram of ligand 1](image)

MP > 250 °C, $^1$H NMR (CDCl$_3$, 500 MHz): $\delta = 2.04$ (s, 18H, e-H), 2.11 (s, 18H, f-H), 2.31 (s, 9H, h-H), 2.47 (s, 18H, d-H), 6.93 (s, 6H, g-H), 7.21 (d, $^3$J = 8.0 Hz, 6H, b-H), 7.58-7.62 (m, 9H, c-, 8-H), 7.73 (s, 3H, a-H), 7.86 (d, $^3$J = 8.0 Hz, 3H, 6-H), 7.90 (d, $^3$J = 8.0 Hz, 3H, 5-H), 8.30 (d, $^3$J = 8.0 Hz, 3H, 7-H), 8.51 (s, 3H, 4-H) ppm.
Compounds 13 (50.0 mg, 108 µmol) and 14 (181 mg, 216 µmol) were added to a degassed mixture of Et₃N (20 mL) and anhydrous THF (15 mL). Then, Pd(PPh₃)₄ (12.5 mg, 10.8 µmol) was added and the mixture was heated at 60 °C for 20 h. After cooling to rt the solvent was evaporated under reduced pressure. The residue was dissolved in DCM (25 mL) and subsequently washed with water (2 × 30 mL). The organic layer was dried over anhydrous MgSO₄ and evaporated in vacuo. The residue was purified by column chromatography (Rf = 0.4, EtOAc: hexane = 1:4) on silica gel using 20% EtOAc in hexane then it was precipitated out from DCM by adding pentane to furnish compound 2 as a yellow solid (110 mg, 58.2 µmol, 54%). Mp: 210-212 °C. **H NMR (CDCl₃, 400 MHz):** δ = 2.51 (s, 12H, g-H), 2.54 (s, 12H, a-H), 7.10 (s, 4H, b-H), 7.37 (t, J = 8.0 Hz, 2H, d-H), 7.49 (dt, J = 8.0 Hz, J = 1.6 Hz, 2H, c/e-H), 7.55 (dt, J = 8.0 Hz, J = 1.6 Hz, 2H, e/c-H), 7.72 (t, J = 1.6 Hz, 2H, f-H) ppm. **C NMR (CDCl₃, 100 MHz):** δ = 18.4, 24.4, 87.8, 89.4, 91.9, 97.1, 122.1, 122.8, 123.2, 124.3, 128.6, 131.3, 131.4, 131.7, 134.5, 135.9, 157.9 ppm. Anal. Calcd. for C₄₄H₃₆N₂•¼CH₂Cl₂: C, 86.56; H, 5.99; N, 4.56. Found C, 86.53; H, 6.02; N, 4.30. **ESI-MS:** m/z (%) = 593.7 (100) [M+H]+.
Ligand 2b

Compound 16 (1.63 g, 2.34 mmol) and 4-iodo-2-methylpyridine (15, 1.54 g, 7.02 mmol) were dissolved in a mixture of freshly distilled anhydrous THF (15 mL) and anhydrous Et$_3$N (15 mL). The solution was subjected to freeze pump-thaw cycles. Then, Pd(PPh$_3$)$_4$ (135 mg, 117 µmol) was added under N$_2$ atmosphere to the mixture, which was subjected to heating at 65 °C for overnight. The reaction mixture then was cooled and solvents were evaporated under reduced pressure. The crude mixture was purified by column chromatography ($\Phi = 2.5$ cm, $l = 15$ cm) eluting with 1-8% DCM in n-hexane on silica gel ($R_f = 0.36$, SiO$_2$, 8% DCM in n-hexane) to furnish 3 as a yellow solid (1.62 g, 1.85 mmol, 79%).

**Mp:** 74-75 °C. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta = 0.86$ (t, $^3J = 7.1$ Hz, 6H, u-H), 1.22-1.33 (m, 28H, n,o,p,q,r,s,t-H), 1.39 (m, 4H, m-H), 1.56 (m, 4H, l-H), 1.86 (m, 4H, k-H), 2.58 (s, 6H, a-H), 4.05 (t, $^3J = 6.5$ Hz, 4H, j-H), 7.02 (s, 2H, i-H), 7.20 (dd, $^3J = 5.2$ Hz, $^4J = 1.2$ Hz, 2H, d-H), 7.27 (brs, 2H, b-H), 7.36 (t, $^3J = 7.8$ Hz, 2H, f-H), 7.50 (dt, $^3J = 7.8$ Hz, $^4J = 1.9$ Hz, 2H, h-H), 7.54 (dt, $^3J = 7.8$ Hz, $^4J = 1.9$ Hz, 2H, e-H), 7.72 (t, $^4J = 1.9$ Hz, 2H, h-H), 8.50 (d, $^3J = 5.2$ Hz, 2H, c-H) ppm. $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta = 14.1$, 22.6, 26.1, 29.3, 29.4, 29.6, 29.7, 31.9, 69.6, 86.8, 87.3, 92.4, 93.7, 113.9, 117.0, 122.6, 124.0, 125.1, 128.6, 131.3, 131.5, 132.0, 134.7, 149.2, 153.7, 158.6 ppm. **Anal.:** Calcd for C$_{62}$H$_{72}$N$_2$O$_2$: C, 84.89; H, 8.27; N, 3.19. Found, C, 84.80; H, 7.93; N, 3.16. **ESI-MS:** $m/z$ (%) = 877.7 (100) [2+H]$^+$. 


Ligand 2c

![Diagram of ligand 2c]

Synthesis of ligand 2c was accomplished using the literature-known procedure.\(^3\)

\(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)): \(\delta = 2.53\) (s, 12H, g-H), 7.41 (d, \(^3J = 6.0\) Hz, 4H, b-H), 7.43 (td, \(^3J = 8.0\) Hz, \(^5J = 0.4\) Hz, 2H, d-H), 7.55 (dt, \(^3J = 8.0\) Hz, \(^4J = 1.6\) Hz, 2H, e-H), 7.60 (dt, \(^3J = 8.0\) Hz, \(^4J = 1.6\) Hz, 2H, c-H), 7.77 (td, \(^4J = 1.6\) Hz, 5J = 0.4 Hz, 2H, f-H), 8.60 (d, \(^3J = 6.0\) Hz, 4H, a-H) ppm.

2. Synthesis and characterization of model complexes

All solid components of the complexes were placed in an NMR tube and dissolved in CD\(_2\)Cl\(_2\).

Complex C1\(^4\)

In an NMR tube, [Cu(CH\(_3\)CN)\(_4\)]PF\(_6\) (870 µg, 2.33 µmol) and ligand 9 (970 µg, 2.33 µmol) were dissolved in 500 µL of CD\(_2\)Cl\(_2\). The NMR spectrum indicated quantitative formation of the complex C1 = [Cu(9)]\(^+\). \(^1\)H NMR (CD\(_2\)Cl\(_2\), 400 MHz): \(\delta = 2.03\) (s, 12H, a-H), 2.36 (s, 6H, c-H), 7.01 (s, 4H, b-H), 7.90 (d, \(^3J = 8.0\) Hz, 2H, 3-H), 8.14 (s, 2H, 5-H), 8.67 (d, \(^3J = 8.0\) Hz, 2H, 4-H) ppm.
Complex C2

To the NMR tube containing complex C1 (2.33 mmol) in CD₂Cl₂ (500 µL) and ligand 10 (433 µg, 2.33 µmol) in 15 µl of CDCl₃ was added. The NMR spectrum indicated quantitative formation of the complex C₂ = [Cu(9)(10)]⁺. ¹H NMR (CD₂Cl₂, 400 MHz): δ = 1.99 (s, 12H, a-H), 2.12 (s, 6H, d-H), 2.22 (s, 6H, c-H), 6.82 (s, 4H, b-H), 7.10 (s, 4H, e-H), 7.92 (d, ³J = 8.0 Hz, 2H, 3-H), 8.17 (s, 2H, 5-H), 8.70 (d, ³J = 8.0 Hz, 2H, 4-H) ppm.

Complex C3

In an NMR tube, [Cu(CH₃CN)₄]PF₆ (490 µg, 1.31 µmol), ligand 9 (540 µg, 1.31 µmol) as solid and compound 3 (140 µg, 1.31 µmol) in 10 µl of CDCl₃ were dissolved in CD₂Cl₂ (500 µL). The NMR spectrum indicated quantitative formation of complex C₃ = [Cu(9)(3)]⁺. ¹H NMR (CD₂Cl₂, 400 MHz): δ = 1.90 (s, 12H, a-H), 2.03 (s, 6H, c-H), 6.55 (s, 4H, b-H), 7.60 (ddd, ³J = 5.1, 7.7 Hz, ⁴J = 1.2 Hz, 1H, i-H), 7.72 (d, ³J = 7.7 Hz, 1H, g-H), 7.89 (d, ³J = 8.0 Hz, 2H, 3-H), 8.04 (dt, ³J = 7.7 Hz, ⁴J = 1.4 Hz, 1H, h-H), 8.17 (s, 2H, 5-H), 8.26 (d, ³J = 5.1 Hz, 1H, j-H), 8.68 (d, ³J = 8.0 Hz, 2H, 4-H), 9.58 (s, 1H, f-H) ppm.
Complex C4

An NMR tube containing complex C3 (1.31 µmol) and ligand 4 (190 µg, 1.31 µmol) was filled with 500 µL of CD₂Cl₂ holding traces of CDCl₃. The NMR spectrum showed 95% formation of the complex C⁴ = [Cu(5)(9)]⁺. ¹H NMR (CD₂Cl₂, 400 MHz): δ = 1.55 (s, 6H, a'/a-H), 1.58 (s, 6H, a/a'-H), 1.85 (s, 6H, c-H), 6.17 (s, 2H, b'/b-H), 6.29 (s, 2H, b/b'-H), 7.17 (ddd, ³J = 6.8, 5.5 Hz, ⁴J = 1.3 Hz, 1H, i-H), 7.43-7.47 (m, 2H, l-o-H), 7.50 (ddd, ³J = 6.8 Hz, 5.2 Hz, ⁴J = 1.2 Hz, 1H, h-H), 7.70 (d, ³J = 8.0 Hz, 1H, n-H), 7.77 (d, ³J = 8.0 Hz, 2H, 3-H), 7.79 (d, ³J = 7.4 Hz, 1H, m-H), 7.92 (d, ³J = 6.8 Hz, 1H, g-H), 8.21 (s, 2H, 5-H), 8.26 (dd, ³J = 5.5 Hz, ⁴J = 1.2 Hz, 1H, j-H), 8.37 (dd, ³J = 6.0 Hz, ⁴J = 1.2 Hz, 1H, k-H), 8.63 (d, ³J = 8.0 Hz, 2H, 4-H), 8.74 (d, ³J = 8.4 Hz, 1H, p-H), 8.94 (s, 1H, f-H) ppm.

Complex C⁵

In an NMR tube, a solution of iron(II) tetrafluoroborate hexahydrate (0.28 mg, 0.83 µmol) in 30 µL of CD₃CN, ligand 3 in 10 µL CDCl₃ (180 µg, 1.66 µmol) and ligand 4 (240 µg, 1.66 µmol) were dissolved in 500 µL of CD₂Cl₂. The NMR spectrum showed quantitative formation of C⁵ = [Fe(5)₂]²⁺. ¹H NMR (CD₂Cl₂, 600 MHz): δ = 7.17 (m, 4H, i,l-H), 7.61 (ddd, ³J = 6.8, 5.2 Hz, ⁴J = 1.2 Hz, 2H, h-H), 7.86 (dd, ³J = 8.0 Hz, ⁴J = 1.2 Hz, 2H, m-H), 8.08 (d, ³J = 5.2 Hz, 2H, j-H), 8.09 (t, ³J = 7.2 Hz, 2H, o-H), 8.11 (d, ³J = 6.8 Hz, 2H, g-H), 8.12 (d, ³J = 7.2 Hz, 2H, n-H), 8.56 (dd, ³J = 7.8 Hz, ⁴J = 1.2 Hz, 2H, k-H), 9.37 (d, ³J = 7.6 Hz, 2H, p-H), 10.99 (s, 2H, f-H) ppm.
Dynamic mixture C6 = [Cu(9)]+ + 2×[Cu(9)(10)]+

In an NMR tube, [Cu(CH3CN)4]PF6 (640 µg, 1.72 µmol) and ligand 9 (720 µg, 1.72 µmol) were dissolved in 475 µL of CD2Cl2 and ligand 10 (210 µg, 1.14 µmol) in 25 µL of CDCl3 was added at a ratio 3:3:2 respectively. The NMR spectrum indicates quantitative formation of the rapidly exchanging mixture of complexes C1 + C2 = [Cu(9)]+ + 2×[Cu(9)(10)]+ as judged from a single set of signals. 1H NMR (CD2Cl2, 400 MHz): δ = 1.99 (s, 36H, a-H), 2.12 (s, 12H, d-H), 2.21 (s, 18H, c-H), 6.81 (brs, 12H, b-H), 7.10 (s, 4H, e-H), 7.92 (d, 3J = 8.0 Hz, 6H, 3-H), 8.18 (s, 6H, 5-H), 8.71 (d, 3J = 8.0 Hz, 6H, 4-H) ppm.

Mixture C7 = 2×[Cu(9)(10)]+ + [Cu(9)(3)]+

Ligand 3 (60.0 µg, 0.570 µmol) in 500 µL of CD2Cl2 and 25 µL of CDCl3 was added to the NMR tube (experiment f) loaded with C1 (0.570 µmol) and C2 (1.14 µmol). The NMR data suggested quantitative formation of complexes 2xC2 + C3 = 2×[Cu(9)(10)]+ + [Cu(9)(3)]+. 1H NMR (CD2Cl2, 400 MHz): δ = 1.99 (s, 36H, a-H), 2.11 (s, 18H, c-H), 2.21 (s, 12H, d-H), 6.66 (brs, 12H, b-H), 7.16 (s, 4H, e-H), 7.63 (ddd, 3J = 5.1, 7.7 Hz, 4J = 1.2 Hz, 1H, i-H), 7.72 (d, 3J = 7.7 Hz, 1H,
Mixture C8 = 2×[Cu(9)(10)]⁺ + [Cu(9)(5)]⁺

Ligand 4 (82.0 µg, 0.570 µmol) in 500 µL of CD₂Cl₂ and 25 µL of CDCl₃ was added to the NMR tube (experiment g) containing C3 (0.570 µmol) and C2 (1.14 µmol). The NMR spectrum indicates 97% formation of the mixture 2×C2 + C4 = 2×[Cu(9)(10)]⁺ + [Cu(9)(5)]⁺. ¹H NMR (CD₂Cl₂, 400 MHz): δ = 1.55 (s, 6H, a'/a''-H), 1.58 (s, 6H, a''/a'-H), 1.85 (s, 6H, c'-H), 1.99 (s, 24H, a-H), 2.18 (s, 12H, d-H), 2.33 (s, 12H, c-H), 6.16 (s, 2H, b''/b'-H), 6.29 (s, 2H, b'/b''-H), 6.75 (brs, 8H, b-H), 7.14 (s, 4H, e-H), 7.17 (ddd, ³J = 7.2, 5.4 Hz, ⁴J = 1.2 Hz, 1H, i-H), 7.43-7.58 (m, 3H, h-,l-,o-H), 7.70 (d, ³J = 8.0 Hz, 1H, n-H), 7.77 (d, ³J = 8.0 Hz, 2H, 3-H), 7.79 (d, ³J = 7.4 Hz, 1H, m-H), 7.89 (d, ³J = 7.8 Hz, 4H, 3'-H), 7.95 (t, ³J = 7.6 Hz, ⁴J = 1.4 Hz 1H, g-H), 8.16 (s, 4H, 5'-H), 8.21 (s, 2H, 5-H), 8.26 (dd, ³J = 5.4 Hz, ⁴J = 1.2 Hz, 1H, j-H), 8.56 (d, ³J = 6.0 Hz, 1H, k-H), 8.63 (d, ³J = 8.0 Hz, 2H, 4-H), 8.67 (d, ³J = 8.5 Hz, 5H, 4'-,p-H), 8.94 (s, 1H, f-H) ppm.
Mixture $C9 = [Cu(9)]^+ + 2\times[Cu(9)(10)]^+ + [Fe(5)_2]^{2+}$

A solution of iron(II) tetrafluoroborate hexahydrate in CD$_3$CN (96.0 µg, 0.285 µmol) was added to the NMR tube of experiment h containing a mixture of complexes $C4$ (0.570 µmol) and $C2$ (1.14 µmol) in 500 µL of CD$_2$Cl$_2$ and traces of CDCl$_3$. The NMR spectrum indicated clean formation of the mixture of complexes $C9 = [Cu(9)]^+ + 2\times[Cu(9)(10)]^+ + [Fe(5)_2]^{2+}$. $^1$H NMR (CD$_2$Cl$_2$, 400 MHz): $\delta = 1.98 \ (s, \ \text{36H}, \ \text{a-H}), 2.13 \ (s, \ \text{18H}, \ \text{c-H}), 2.17 \ (s, \ \text{12H}, \ \text{d-H}), 6.76 \ (\text{brs}, \ \text{12H}, \ \text{b-H}), 7.18 \ (\text{m}, \ \text{8H}, \ \text{e,i,l-H}), 7.62 \ (\text{d}, \ ^3J = 5.2 \ Hz, \ \text{2H}, \ \text{h-H}), 7.88 \ (\text{t}, \ ^3J = 8.0 \ Hz, \ \text{2H}, \ \text{m-H}), 7.92 \ (\text{d}, \ ^3J = 8.0 \ Hz, \ \text{6H}, \ \text{3-H}), 8.07 \ (\text{d}, \ ^3J = 7.2 \ Hz, \ \text{4H}, \ \text{j,o-H}), 8.12 \ (\text{d}, \ ^3J = 6.8 \ Hz, \ \text{2H}, \ \text{g-H}), 8.15 \ (\text{d}, \ ^3J = 7.2 \ Hz, \ \text{2H}, \ \text{n-H}), 8.19 \ (\text{s}, \ \text{6H}, \ \text{5-H}), 8.51 \ (\text{d}, \ ^3J = 6.0 \ Hz, \ \text{2H}, \ \text{k-H}), 8.71 \ (\text{d}, \ ^3J = 8.0 \ Hz, \ \text{6H}, \ \text{4-H}), 9.31 \ (\text{d}, \ ^3J = 7.6 \ Hz, \ \text{2H}, \ \text{p-H}), 10.89 \ (\text{s}, \ \text{2H}, \ \text{f-H})$ ppm.
Table 1. Assignment of ligand 9 through NMR shifts in model complexes

![Chemical structure diagram]

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<th>Complex</th>
<th>a'-H</th>
<th>a-H</th>
<th>c-H</th>
<th>b-H</th>
<th>b'-H</th>
<th>3-H</th>
<th>5-H</th>
<th>4-H</th>
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<tr>
<td><strong>C1 = [Cu(9)]^+</strong></td>
<td>-</td>
<td>2.03</td>
<td>2.36</td>
<td>7.01</td>
<td>-</td>
<td>7.90</td>
<td>8.14</td>
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<td><strong>C2 = [Cu(9)(10)]^+</strong></td>
<td>-</td>
<td>1.99</td>
<td>2.22</td>
<td>6.82</td>
<td>-</td>
<td>7.92</td>
<td>8.17</td>
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<tr>
<td><strong>C3 = [Cu(9)(3)]^+</strong></td>
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<td>1.90</td>
<td>2.03</td>
<td>6.55</td>
<td>-</td>
<td>7.89</td>
<td>8.17</td>
<td>8.68</td>
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<tr>
<td><strong>C4 = [Cu(9)(5)]^+</strong></td>
<td>1.55</td>
<td>1.58</td>
<td>1.85</td>
<td>6.17</td>
<td>6.29</td>
<td>7.77</td>
<td>8.21</td>
<td>8.63</td>
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<tr>
<td><strong>C6 = [Cu(9)]^+ + 2xCu(9)(10)]^+</strong></td>
<td>-</td>
<td>1.99</td>
<td>2.21</td>
<td>6.81</td>
<td>-</td>
<td>7.92</td>
<td>8.18</td>
<td>8.71</td>
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<tr>
<td><strong>C7 = [Cu(9)(3)]^+ + 2xCu(9)(10)]^+</strong></td>
<td>-</td>
<td>1.99</td>
<td>2.11</td>
<td>6.66</td>
<td>-</td>
<td>7.92</td>
<td>8.19</td>
<td>8.71</td>
</tr>
<tr>
<td><strong>C8 = [Cu(9)(5)]^+ + 2xCu(9)(10)]^+</strong></td>
<td>1.55, 1.58</td>
<td>1.99</td>
<td>1.85, 2.33</td>
<td>6.75, 6.16, 6.29</td>
<td>7.77, 7.89, 8.21</td>
<td>8.16, 8.63, 8.67</td>
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</tr>
<tr>
<td><strong>C9 = [Cu(9)]^+ + 2xCu(9)(10)]^+ + [Fe(5)]^2+</strong></td>
<td>-</td>
<td>1.98</td>
<td>2.13</td>
<td>6.76</td>
<td>-</td>
<td>7.92</td>
<td>8.19</td>
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3. Synthesis and characterization of the final complexes

Slider-on-deck S1a

In an NMR tube, [Cu(CH3CN)4]PF6 (710 µg, 1.92 µmol), deck 1 (1.20 mg, 0.640 µmol) and ligand 2a (340 µg, 0.640 µmol) were dissolved in 500 µL of CD2Cl2. The NMR spectrum indicated quantitative formation of S1a = [Cu3(1)(2a)]3+. 1H NMR (600 MHz, CD2Cl2): δ = 1.99 (s, 18H, e-H), 2.03 (s, 18H, f-H), 2.15 (s, 12H, a’-H), 2.21 (s, 9H, h-H), 2.36 (s, 12H, g’-H), 2.55 (s, 18H, d-H), 6.86 (s, 6H, g-H), 7.03 (s, 4H, b’-H), 7.28 (d, 3J = 7.6 Hz, 6H, b-H), 7.45 (t, 3J = 7.6 Hz, 2H, d’-H), 7.55 (d, 3J = 7.6 Hz, 2H, e’-H), 7.63 (d, 3J = 7.6 Hz, 8H, c,c’-H), 7.73 (s, 3H, a-H), 7.80 (s, 2H, f’-H), 7.95 (d, 3J = 8.0 Hz, 3H, 8-H), 8.19 (d, 3J = 8.9 Hz, 3H, 6-H), 8.22 (d, 3J = 8.9 Hz, 3H, 5-H), 8.74 (d, 3J = 8.0 Hz, 3H, 7-H), 8.87 (s, 3H, 4-H) ppm. **Elemental analysis:** Anal. Calcd for C167H135Br3Cu18N8P3½CH2Cl2: C, 63.63; H, 4.34; N, 3.54. Found: C, 63.70; H, 4.35; N, 3.77. **ESI-MS:** m/z (%) = 895.5 (100) [[Cu3(1)(2a)]3+].
In an NMR tube, [Cu(\text{CH}_3\text{CN})_4]PF_6 (711 µg, 1.91 µmol), deck 1 (1.20 mg, 0.640 µmol), ligand 2a (415 µg, 0.640 µmol) and pyridine carboxaldehyde 3 (60.0 µg, 0.640 µmol) dissolved in 10 µL of CDCl$_3$ were added to 490 µL of CD$_2$Cl$_2$. The NMR spectrum indicated quantitative formation of SIIa = [Cu$_3$\textcolor{red}{(1)(2a)(3)}]$^{3+}$. $^1$H NMR (600 MHz, CD$_2$Cl$_2$): $\delta = 1.96$ (brs, 18H, e'-H), 2.00 (brs, 30H, f,a'-H), 2.15 (s, 9H, h-H), 2.28 (s, 12H, g'-H), 2.55 (s, 18H, d-H), 6.80 (s, 6H, g-H), 7.03 (s, 4H, b'-H), 7.27 (d, $^3J = 7.6$ Hz, 6H, b-H), 7.45 (t, $^3J = 7.6$ Hz, 2H, d'-H), 7.50 (ddd, $^3J = 7.4$, 5.2 Hz, $^4J = 1.2$ Hz, 1H, 1-H), 7.53 (d, $^3J = 7.6$ Hz, 2H, e'-H), 7.62 (d, $^3J = 7.6$ Hz, 8H, c,c'-H), 7.70 (s, 3H, a-H), 7.84 (d, $^3J = 7.4$ Hz, 1H, j-H), 7.79 (s, 2H, f'-H), 7.96 (d, $^3J = 8.1$ Hz, 3H, 8-H), 7.99 (t, $^3J = 7.4$ Hz, 1H, k-H), 8.19 (d, $^3J = 8.8$ Hz, 3H, 5/6-H), 8.23 (d, $^3J = 8.8$ Hz, 3H, 6/5-H), 8.45 (d, $^3J = 5.2$ Hz, 1H, m-H), 8.74 (d, $^3J = 8.1$ Hz, 3H, 7-H), 8.87 (s, 3H, 4-H), 9.76 (s, 1H, i-H) ppm. 

**Elemental analysis:** Anal. Calcd for C$_{173}$H$_{140}$Br$_3$Cu$_3$F$_{18}$N$_9$OP$_3$•½CH$_2$Cl$_2$: C, 63.75; H, 4.35; N, 3.86. Found: C, 63.72; H, 4.34; N, 3.86. **ESI-MS:** $m/z$ (%) = 930.5 (100) [Cu$_3$(1)(2a)(3)]$^{3+}$. 
In an NMR tube, freshly prepared SIIa (0.64 µmol) and 8-amino quinoline (4) (90 µg, 0.64 µmol) were dissolved in 500 µL of CD₂Cl₂. The NMR spectrum indicated quantitative formation of SIIla = [Cu₃(1)(2a)(5)]³⁺. **¹H NMR** (600 MHz, CD₂Cl₂): δ = 1.56 (s, 6H, f''-H), 1.95 (brs, 18H, d'',e''-H), 2.02 (s, 15H, f,h''-H), 2.15 (brs, 33H, a',e,h -H), 2.27 (s, 12H, g'-H), 2.54 (s, 12H, d-H), 6.18 (s, 1H, g''/g'''-H), 6.33 (s, 1H, g'''/g'"-H), 6.80 (s, 4H, g-H), 7.04 (s, 4H, b'-H), 7.14 (ddd, 3J = 7.2, 5.5 Hz, 4J = 1.2 Hz, 1H, l-H), 7.25 (brs, 6H, b-H), 7.35-7.47 (m, 7H, d',e',k,o,r-H), 7.52-7.64 (m, 12H, q,c,c',a-H), 7.68 (d, 3J = 7.0 Hz, 1H, j-H), 7.76-7.80 (m, 3H, 8',f''-H), 7.83 (d, 3J = 8.5 Hz, 1H, p-H), 7.96 (d, 3J = 8.0 Hz, 2H, 8-H), 8.13-8.27 (m, 6H, 5,6,5',6'-H), 8.33 (d, 3J = 5.5 Hz, 1H, m-H), 8.48 (brs, 1H, n-H), 8.64 (d, 3J = 8.0 Hz, 1H, 7'-H), 8.75 (d, 3J = 8.0 Hz, 2H, 7-H), 8.81 (s, 2H, 4-H), 8.86 (brs, 2H, 4',s-H), 9.00 (s, 1H, i-H) ppm. **Elemental analysis:** Anal. Calcd for C₁₇₂H₁₄₆Br₃Cu₃F₁₈N₁₁P₅•½CH₂Cl₂: C, 64.57; H, 4.36; N, 4.54. Found: C, 64.53; H, 4.35; N, 4.66. **ESI-MS:** m/z (%) = 973.6 (100) [Cu₃(1)(2a)(5)]³⁺.
Slider-on-deck S1a + [Fe(5)\textsubscript{2}]\textsuperscript{2+}

To the previous NMR tube containing S\textsubscript{III}a = [Cu\textsubscript{3}(1)(2a)(5)]\textsuperscript{3+}, a solution of iron(II) tetrafluoroborate hexahydrate (80.0 µg, 0.235 µmol) in 15 µL of CD\textsubscript{3}CN was added in 500 µL of CD\textsubscript{2}Cl\textsubscript{2}. The NMR spectrum suggested full conversion to S1a + [Fe(5)\textsubscript{2}]\textsuperscript{2+}.
In an NMR tube, deck 1 (1.11 mg, 0.584 µmol), biped 2b (0.512 mg, 0.584 µmol), and 3.0 equiv of [Cu(CH₃CN)₄]PF₆ (0.653 mg, 1.75 µmol) were dissolved in 500 µL of CD₂Cl₂ affording [Cu₃(1)(2b)]³⁺ in quantitative yield. ¹H NMR (CD₂Cl₂, 600 MHz): δ = 0.84 (t, ³J = 7.2 Hz, 6H, u’-H), 1.25 (m, 16H, q’,r’,s’,t’-H), 1.32 (m, 4H, p’-H), 1.40 (m, 4H, o’-H), 1.57 (m, 8H, m’,n’-H), 1.87 (m, 8H, k’,l’-H), 1.95 (s, 6H, a’-H), 2.01 (s, 18H, e-H), 2.03 (s, 18H, f-H), 2.23 (s, 9H, h-H), 2.35 (s, 18H, d-H), 4.08 (t, ³J = 6.4 Hz, 4H, j’-H), 6.87 (s, 6H, g-H), 7.07 (s, 2H, i’-H), 7.10 (d, ³J = 6.5 Hz, 2H, d’-H), 7.17 (s, 2H, b’-H), 7.31 (d, ³J = 8.2 Hz, 6H, b-H), 7.44 (t, ³J = 7.4 Hz, 2H, f’-H), 7.54 (d, ³J = 6.5 Hz, 2H, c’-H), 7.56 (d, 2H, ³J = 7.4 Hz, e’-H), 7.59 (d, ³J = 7.4 Hz, 2H, g’-H), 7.64 (d, ³J = 8.2 Hz, 6H, c-H), 7.75 (s, 3H, a-H), 7.78 (s, 2H, h’-H), 7.95 (d, ³J = 8.2 Hz, 3H, 8-H), 8.18 (d, ³J = 9.0 Hz, 3H, 6-H), 8.21 (d, ³J = 9.0 Hz, 3H, 5-H), 8.72 (d, ³J = 8.2 Hz, 3H, 7-H), 8.87 (s, 2H, 4-H) ppm. **Elemental analysis**: Anal. Calcd for C₁₈S₁₇₁Br₃Cu₃F₁₈N₈O₃P₃•½CH₂Cl₂: C, 64.65%; H, 5.03%; N, 3.25. Found: C, 64.57%; H, 4.97%; N, 3.37. **ESI-MS**: m/z (%) 989.2 (100) [Cu₃(1)(2b)]³⁺.
In an NMR tube, deck 1 (1.15 mg, 0.605 µmol), biped 2b (0.530 mg, 0.605 µmol), and 3.0 equiv of [Cu(CH$_3$CN)$_4$]PF$_6$ (0.676 mg, 1.81 µmol) were dissolved in 450 µL of CD$_2$Cl$_2$ then 1.0 equiv. of 3 (0.065 mg, 0.605 µmol) was added as solution in 5 µl of CDCl$_3$ furnishing [Cu$_3$(I)(2b)(3)]$^{3+}$ in quantitative yield. $^1$H NMR (CD$_2$Cl$_2$, 600 MHz): δ = 0.84 (t, $^3J$ = 7.2 Hz, 6H, u'-H), 1.25 (m, 16H, q',r',s',t'-H), 1.32 (m, 4H, p'-H), 1.42 (m, 4H, o'-H), 1.57 (m, 8H, m',n'-H), 1.88 (m, 8H, k',l'-H), 1.96 (s, 24H, a', e-H), 2.00 (s, 18H, f-H), 2.13 (s, 9H, h-H), 2.26 (s, 18H, d-H), 4.07 (t, $^3J$ = 6.4 Hz, 4H, j'-H), 6.74 (s, 6H, g-H), 7.09 (s, 2H, i'-H), 7.10 (d, $^3J$ = 6.5 Hz, 2H, d'-H), 7.17 (s, 2H, b'-H), 7.30 (d, $^3J$ = 8.2 Hz, 6H, b-H), 7.44 (t, $^3J$ = 7.4 Hz, 2H, f'-H), 7.54-7.58 (m, 4H, c',e'-H), 7.59 (d, $^3J$ = 7.4 Hz, 2H, g'-H), 7.64 (d, $^3J$ = 8.2 Hz, 6H, c-H), 7.65 (ddd, $^3J$ = 7.4, 5.2 Hz, $^4J$ = 1.2 Hz, 1H, i-H), 7.72 (s, 3H, a-H), 7.78 (s, 2H, h'-H), 7.80 (d, $^3J$ = 7.4 Hz, 1H, j-H), 7.95 (d, $^3J$ = 8.2 Hz, 3H, 8-H), 8.04 (t, $^3J$ =7.4 Hz, 1H, k-H), 8.18 (d, $^3J$ = 9.0 Hz, 3H, 6-H), 8.21 (d, $^3J$ = 9.0 Hz, 3H, 5-H), 8.33 (d, $^3J$ = 5.2 Hz, 1H, m-H), 8.72 (d, $^3J$ = 8.2 Hz, 3H, 7-H), 8.87 (s, 2H, 4-H), 9.65 (s, 1H, i-H) ppm. Elemental analysis: Anal. Calcd for C$_{191}$H$_{176}$Br$_3$Cu$_3$F$_{18}$N$_9$O$_3$P$_3$• $\frac{1}{2}$CH$_2$Cl$_2$: C, 64.73; H, 5.02; N, 3.55. Found: C, 64.95; H, 4.93; N, 3.56. ESI-MS: m/z (%) 1024.7 (100) [Cu$_3$(I)(2b)(3)]$^{3+}$. 
In an NMR tube, deck 1 (1.01 mg, 0.531 μmol), ligand 2c (285 μg, 0.531 μmol), and 3.0 equiv. of [Cu(CH3CN)4]PF6 (594 μg, 1.59 μmol) were dissolved in 500 μL of CD2Cl2 affording [Cu3(1)(2c)]3+ in quantitative yield. 1H NMR (CD2Cl2, 600 MHz): δ = 2.07 (s, 36H, e,f-H), 2.39 (s, 9H, h-H), 2.50 (s, 12H, g'-H), 2.58 (s, 18H, d-H), 6.55 (brs, 4H, a'-H), 7.03 (s, 6H, g-H), 7.14 (d, 3J = 6.2 Hz, 4H, b'-H), 7.33 (d, 3J = 8.2 Hz, 6H, b-H), 7.47 (t, 3J = 8.0 Hz, 2H, d'-H), 7.58 (d, 3J = 8.0 Hz, 2H, e'-H), 7.64 (d, 3J = 8.0 Hz, 2H, c'-H), 7.69 (d, 3J = 8.2 Hz, 6H, c-H), 7.80 (s, 3H, a-H), 7.87 (d, 2H, f'-H), 7.94 (d, 3J = 8.2 Hz, 3H, 8-H), 8.10 (d, 3J = 9.0 Hz, 3H, 6-H), 8.22 (d, 3J = 9.0 Hz, 3H, 5-H), 8.72 (d, 3J = 8.0 Hz, 3H, 7-H), 8.89 (s, 3H, 4-H) ppm. Elemental analysis: Anal. Calcd for C163H127Br3Cu3F18N8P2•CH2Cl2: C, 62.57; H, 4.13; N, 3.56. Found: C, 62.50; H, 3.98; N, 3.56. ESI-MS: m/z (%) 876.3 (100) [Cu3(1)(2c)]3+. 
In an NMR tube, deck 1 (1.10 mg, 0.578 µmol), ligand 2c (310 µg, 0.578 µmol), 3.0 equiv. of [Cu(CH3CN)4]PF6 (647 µg, 1.73 µmol) and 3 (61.9 µg, 0.578 µmol) in 5 µL of CDCl3 were mixed with 500 µL of CD2Cl2 furnishing [Cu3(1)(2c)(3)]3+ in quantitative yield. $^1$H NMR (CD2Cl2, 600 MHz): δ = 2.00 (s, 36H, e,f-H), 2.25 (s, 9H, h-H), 2.35 (s, 12H, g'-H), 2.57 (s, 18H, d-H), 6.71 (brs, 4H, a'-H), 6.84 (s, 6H, g-H), 7.15 (d, $^3$J = 6.2 Hz, 4H, b'-H), 7.30 (d, $^3$J = 8.0 Hz, 6H, b-H), 7.46 (t, $^3$J = 8.0 Hz, 2H, d'-H), 7.57 (d, $^3$J = 8.0 Hz, 2H, e'-H), 7.65 (ddd, $^3$J = 7.4, 5.2 Hz, $^4$J = 1.2 Hz, 1H, 1-H), 7.67 (d, $^3$J = 8.0 Hz, 8H, c',c-H), 7.73 (d, $^3$J = 7.4 Hz, 1H, j-H), 7.76 (s, 3H, a-H), 7.86 (s, 2H, f'-H), 7.94 (d, $^3$J = 8.2 Hz, 3H, 8-H), 8.10 (t, $^3$J = 7.4 Hz, 1H, k-H), 8.12 (d, $^3$J = 5.2 Hz, 1H, m-H), 8.18 (d, $^3$J = 9.0 Hz, 3H, 6-H), 8.22 (d, $^3$J = 9.0 Hz, 3H, 5-H), 8.73 (d, $^3$J = 8.2 Hz, 3H, 7- H), 8.88 (s, 3H, 4-H), 9.61 (s, 1H, i-H) ppm. **Elemental analysis**: Anal. Calcd for C169H132Br3Cu3F18N9OP3•½CH2Cl2: C, 63.25; H, 4.16; N, 3.94. Found: C, 63.12; H, 4.46; N, 3.94. **ESI-MS**: m/z (%) 912.0 (100) [Cu3(1)(2c)(3)]3+. 
4. NMR spectra

Figure S2. $^1$H NMR spectrum (CDCl$_3$, 400 MHz) of compound 2a.

Figure S3. $^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of compound 2a.
Figure S4. $^1$H NMR spectrum (CDCl$_3$, 400 MHz) of compound 2b.

Figure S5. $^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of compound 2b.
Figure S6. $\text{^1H NMR spectrum (CD}_2\text{Cl}_2, 400 MHz) of complex C1.}$

Figure S7. $\text{^1H NMR spectrum (CD}_2\text{Cl}_2, 400 MHz) of complex C2.}$
Figure S8. $^1$H NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of complex C3.

Figure S9. $^1$H-$^1$H COSY NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of complex C3.
Figure S10. $^1$H NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of complex C4.

Figure S11. $^1$H-$^1$H COSY NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of complex C4.
Figure S12. $^1$H NMR spectrum (CD$_2$Cl$_2$, 600 MHz) of complex C5.

Figure S13. $^1$H-$^1$H COSY NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of complex C5.
Figure S14. $^1$H NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of complex C6.

Figure S15. $^1$H NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of complex C7.
Figure S16. $^1$H NMR spectrum ($\text{CD}_2\text{Cl}_2$, 400 MHz) of complex C8.

Figure S17. $^1$H NMR spectrum ($\text{CD}_2\text{Cl}_2$, 400 MHz) of complex C9.
Figure S18. $^1$H NMR spectrum (CD$_2$Cl$_2$, 600 MHz) of nanoslider S1a.

Figure S19. $^1$H-$^1$H COSY NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of nanoslider S1a.
Figure S20. $^1$H NMR spectrum (CD$_2$Cl$_2$, 600 MHz) of nanoslider SIIa.

Figure S21. $^1$H-$^1$H COSY NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of nanoslider SIIa.
Figure S22. $^1$H NMR spectrum (CD$_2$Cl$_2$, 600 MHz) of nano-assembly SIIIa.

Figure S23. $^1$H-$^1$H COSY NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of nano-assembly SIIIa.
Figure S24. $^1$H NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of nanoslider S1a + [Fe(5)$_2$]$^{2+}$.

Figure S25. $^1$H–$^1$H COSY NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of nanoslider S1a + [Fe(5)$_2$]$^{2+}$. 
Figure S26. $^1$H NMR spectrum (CD$_2$Cl$_2$, 600 MHz) of nanoslider SIIb.

Figure S27. $^1$H NMR spectrum (CD$_2$Cl$_2$, 600 MHz) of nanoslider SIIb.
Figure S28. $^1$H NMR spectrum (CD$_2$Cl$_2$, 600 MHz) of nanoslider SIlc.

Figure S29. $^1$H NMR spectrum (CD$_2$Cl$_2$, 600 MHz) of nanoslider SIIlc.
5. Model studies

Self-sorting was tested by mixing 2, 3, 4, 5 and [Cu(CH$_3$CN)$_4$]PF$_6$ (2.33 μmol) in a molar ratio of

Scheme S30. Schematic illustration of self-sorting of ligands 3, 4, 5, 9, and 10, in presence [Cu(CH$_3$CN)$_4$]PF$_6$ and Fe(BF$_4$)$_2$•6H$_2$O.

Figure S31. Comparison of $^1$H NMR spectra (CD$_2$Cl$_2$, 400 MHz) of model complexes C1, C6, C7, C8, and C9.
Figure S32. Comparison of $^1$H NMR spectra (CD$_2$Cl$_2$, 400 MHz) of model complexes C6, C7, C3 and SIIa.

Figure S33. Comparison of $^1$H NMR spectra (CD$_2$Cl$_2$, 400 MHz) of model complexes C6, C8, C4 and SIIIa.
Figure S34. Comparison of $^1$H NMR spectra (CD$_2$Cl$_2$, 400 MHz) of model complexes C6, C9, C5 and S1a.
6. Comparison of NMR spectra

Figure S35. Partial $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$, 298 K) of 2a, [Cu$_3$(1)]$^{3+}$ and [Cu$_3$(1)(2a)]$^{3+}$.

Figure S36. Partial $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$, 298 K) of the conversion SIIa → SIIla → SIIla → SIIa (from bottom to top).
7. DOSY NMR spectra

Calculation of hydrodynamic radius. The diffusion coefficient \( D \) for \( \text{SI-IIIa, SI-II(b,c)} \) were obtained from their corresponding DOSY spectrum. The hydrodynamic radius \( r \) was calculated by using the Stokes Einstein equation

\[
r = \frac{k_BT}{6\pi\eta D}
\]

![DOSY NMR spectrum](image)

**Figure S37.** DOSY NMR of \( \text{SIa} \) in \( \text{CD}_2\text{Cl}_2 \) (600 MHz, 298 K). Diffusion coefficient \( D = 3.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \), hydrodynamic radius \( r = 15.2 \text{ Å} \).
Figure S38. DOSY NMR of SIIa in CD$_2$Cl$_2$ (600 MHz, 298 K). Diffusion coefficient \( D = 3.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \), hydrodynamic radius \( r = 14.8 \text{ Å} \).

Figure S39. DOSY NMR of SIIIa in CD$_2$Cl$_2$ (600 MHz, 298 K). Diffusion coefficient \( D = 3.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \), hydrodynamic radius \( r = 14.8 \text{ Å} \).
Figure S40. DOSY NMR of SⅠb in CD$_2$Cl$_2$ (600 MHz, 298 K). Diffusion coefficient $D = 3.8 \times 10^{-10}$ m$^2$ s$^{-1}$, hydrodynamic radius $r = 14.6$ Å.

Figure S41. DOSY NMR of SⅡb in CD$_2$Cl$_2$ (600 MHz, 298 K). Diffusion coefficient $D = 3.8 \times 10^{-10}$ m$^2$ s$^{-1}$, hydrodynamic radius $r = 14.6$ Å.
Figure S42. DOSY NMR of S\text{Ic} in CD\textsubscript{2}Cl\textsubscript{2} (600 MHz, 298 K). Diffusion coefficient $D = 4.0 \times 10^{-10}$ m$^2$ s$^{-1}$, hydrodynamic radius $r = 13.3$ Å.

Figure S43. DOSY NMR of S\text{Iic} in CD\textsubscript{2}Cl\textsubscript{2} (600 MHz, 298 K). Diffusion coefficient $D = 4.0 \times 10^{-10}$ m$^2$ s$^{-1}$, hydrodynamic radius $r = 13.3$ Å.
8. ESI-MS spectra

Figure S44. ESI-MS of 2a in CH₂Cl₂.

Figure S45. ESI-MS of 2b in CH₂Cl₂.
Figure S46. ESI-MS of S1a in CH$_2$Cl$_2$.

Figure S47. ESI-MS of SIIa in CH$_2$Cl$_2$. 
Figure S48. ESI-MS of SIIIa in CH₂Cl₂.
Figure S49. ESI-MS of S1a + [Fe(5)2]²⁺ in CH₂Cl₂.

Figure S50. ESI-MS of S1b in CH₂Cl₂.
Figure S51. ESI-MS of SIIb in CH$_2$Cl$_2$.

Figure S52. ESI-MS of SIC in CH$_2$Cl$_2$. 
Figure S53. ESI-MS of SIIc in CH₂Cl₂.
9. Variable temperature studies and determination of kinetic parameters

Figure S54. Partial $^1$H VT-NMR (CD$_2$Cl$_2$, 600 MHz) of S1a showing the splitting of proton g-H (red asterisk marked).

Figure S55. (a) Experimental and simulated $^1$H VT-NMR (CD$_2$Cl$_2$, 600 MHz) of S1a show the splitting of g-H (red asterisk marked) and (b) Eyring plot for rotational exchange in S1a.
Figure S56. Partial $^1$H VT-NMR (CD$_2$Cl$_2$, 600 MHz) of SIIa showing the splitting of proton g-H (red asterisk marked).

Figure S57. (a) Experimental and simulated $^1$H VT-NMR (CD$_2$Cl$_2$, 600 MHz) of SIIa show the splitting of mesityl proton g-H (red asterisk marked) and (b) Eyring plot for rotational exchange in SIIa.
Figure S58. Partial $^1$H VT-NMR (CD$_2$Cl$_2$, 600 MHz) of SIIb showing the splitting of proton 4-H (red asterisk marked).

Figure S59. (a) Experimental and simulated $^1$H VT-NMR (CD$_2$Cl$_2$, 600 MHz) of SIIb show the splitting of mesityl proton 4-H (red asterisk marked) and (b) Eyring plot for rotational exchange in SIIb.
Figure S60. Partial $^1$H VT-NMR (CD$_2$Cl$_2$, 600 MHz) of S1c showing the splitting of proton g-H (red asterisk marked).

Figure S61. (a) Experimental and simulated $^1$H VT-NMR (CD$_2$Cl$_2$, 600 MHz) of S1c shows the splitting of mesityl proton g-H (red asterisk marked) and (b) Eyring plot for rotational exchange in S1c.
Figure S62. Partial $^1$H VT-NMR (CD$_2$Cl$_2$, 600 MHz) of SIIc showing the splitting of proton 4-H (red asterisk marked).

Figure S63. (a) Experimental and simulated $^1$H VT-NMR (CD$_2$Cl$_2$, 600 MHz) of SIIc shows the splitting of mesityl proton 4-H (red asterisk marked) and (b) Eyring plot for rotational exchange in SIIc.
Figure S64. Partial $^1$H-$^1$H ROESY NMR (500 MHz, 298 K, mixing time = 300 ms) of SIIIa in CD$_2$Cl$_2$ shows no exchange between HETPYP-I complexed phenanthroline protons (denoted as g) and terpy like complexed phenanthroline protons (designated as g’, g’’) in aromatic and aliphatic region. None of the phenanthrolines and phenanthroline-substituted mesityl and duryl signals show exchange correlation.
10. Catalysis

General procedure for the catalytic reaction

All catalytic experiments were performed in CD$_2$Cl$_2$ directly in an NMR tube that was put into a thermostat. Solids were transferred first, followed by addition of the solvent, and finally liquids were added (as standard solutions in CDCl$_3$). Product yields were determined by using 1,3,5-trimethoxybenzene as an internal standard. The $^1$H NMR was recorded first. Then, the reaction mixture was heated at 40 °C for 10, 20, and 30 h. After cooling to room temperature, the sample was immediately subjected to $^1$H NMR measurement. The yields of product 8 with different assemblies are shown in Figure S65.

![Figure S65. Product yield % of click reaction catalyzed by different assemblies showing higher rate in relation to model complexes.](image)
a) Model system catalytic experiment A

In an NMR tube, \( \textbf{9} \) (240 \( \mu \)g, 0.580 \( \mu \)mol) and \( \textbf{10} \) (70.0 \( \mu \)g, 0.390 \( \mu \)mol) were combined in presence of \([\text{Cu(CH}_3\text{CN)}_4]\text{PF}_6\) (0.220 mg, 0.580 \( \mu \)mol) to afford \( \textbf{C6} = [\text{Cu}(9)]^+ + 2\times[\text{Cu}(\textbf{10})]^+ \). 4-Ethynyl-\( N,N\)-dimethyl aniline (6) (850 \( \mu \)g, 5.85 \( \mu \)mol), benzyl azide (7) (780 \( \mu \)g, 5.85 \( \mu \)mol) and 1,3,5-trimethoxybenzene (980 \( \mu \)g, 5.85 \( \mu \)mol) were added in CD$_2$Cl$_2$. The $^1$H NMR spectrum was recorded. The mixture was heated for 10 h at 40 °C, then the NMR spectrum was recorded to determine the yield of product. Afterwards, the consumed amounts of both reactants 6 and 7 as well as of 2-pyridine carboxaldehyde (3) as a stock solution in CDCl$_3$ (20 \( \mu \)g, 0.19 \( \mu \)mol) were added, the latter generating \( \textbf{C7} = [\text{Cu}(9)(3)]^+ + 2\times[\text{Cu}(\textbf{10})]^+ \). The solution was heated for another 10 h at 40 °C. The $^1$H NMR spectrum was measured. Upon addition of consumed amounts of substrates and of 8- aminoquinoline (4) (30 \( \mu \)g, 0.19 \( \mu \)mol) to yield \( \textbf{C8} = [\text{Cu}(9)(5)]^+ + 2\times[\text{Cu}(\textbf{10})]^+ \), the mixture was heated for the same time. The yield of \( \textbf{8} \) was calculated from the $^1$H NMR spectra as shown in Figure S66. In contrast, the catalytic activity of \( \textbf{C2} = [\text{Cu}(\textbf{10})]^+ \) was also examined under same conditions and concentration, however, the NMR spectrum showed only 2% yield.

![Figure S66](image)

**Figure S66.** a) Partial $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$, 298 K) of the reaction of substrates 6 and 7 in presence of catalytic amounts of C6, C7, C8 and C2 at 40 °C in CD$_2$Cl$_2$ for 10 h each. Product 8 shows up at 5.52 ppm in the spectrum. b) Table showing product yield formed in presence of different assemblies.
b) Final system catalytic experiment B using 2a as biped

In an NMR tube, deck 1 (361 µg, 0.190 µmol) and ligand 2a (112 µg, 0.190 µmol) were mixed with [Cu(CH$_3$CN)$_4$]PF$_6$ (220 µg, 0.570 µmol) to furnish SⅠa. 4-Ethynyl N,N-dimethyl aniline (6) (850 µg, 5.85 µmol), benzyl azide (7) (780 µg, 5.85 µmol) and 1,3,5-trimethoxybenzene (980 µg, 5.85 µmol) were added to SⅠa in CD$_2$Cl$_2$. The $^1$H NMR spectrum was recorded. Then, the mixture was heated for 10 h at 40 °C. After recording an NMR spectrum, the consumed amounts of both reactants 6 and 7 were added as well as 2-pyridine carboxaldehyde (3) (20.0 µg, 0.190 µmol) to form SⅡa. The solution was heated for another 10 h at 40 °C. After recording another $^1$HNMR spectrum, consumed amounts of substrates were replaced and 8-aminoquinoline (4) (27.0 µg, 0.190 µmol) was added to yield SⅢa. The mixture was heated for the same time at 40 °C and the $^1$H NMR was recorded. Lastly, to regain SⅠa, Fe(BF$_4$)$_2$$\cdot$6H$_2$O (0.033 mg, 0.095 µmol) was added and a 2nd full cycle using the same conditions and concentrations was performed. In between the consumed amount of 6 and 7 were added and the yield was determined for each state after 10 h of heating immediately by $^1$H NMR as shown in Figure S67.

![Figure S67](image_url)

**Figure S67.** Partial $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$, 298 K) of the reaction of substrates 6 and 7 in presence of catalytic amounts of SⅠa, SⅡa, and SⅢa at 40 °C in CD$_2$Cl$_2$ for 10 h each. Product 8 shows up at 5.52 ppm in the spectrum.
Figure S68. a) Product yield of the click reaction catalyzed in the different states (S1a, SIIa, SIIIa) over two cycles showing decreasing catalytic activity. b) Table: Product yield obtained after catalysis by the different final assemblies S1a, SIIa, and SIIIa.

c) Final system catalytic experiment C using 2b as biped

Use of same concentrations, the same conditions and procedures. The $^1$H NMR spectrum of S1b in presence of substrates 6, 7 was recorded. Then, the mixture was heated for 10 h at 40 °C. After recording an NMR spectrum, the consumed amounts of both reactants 6 and 7 were added as well as 2-pyridine carboxaldehyde (3) (20.0 µg, 0.190 µmol) to form SIIb. The solution was heated for another 10 h at 40 °C and the $^1$H NMR was immediately recorded. The consumed amounts of substrates were replaced and 8-aminoquinoline (4, 27.0 µg, 0.190 µmol) was added to yield SIIIb. The mixture was heated for the same time at 40 °C and the $^1$H NMR was recorded as shown in Figure S69. Accordingly, the yield furnished by the catalyst S1b is 70% of 8, but after addition of 3 the catalytic activity of SIIb is way less (only 8% increase in yield). Finally, SIIIb proved to be catalytically inactive.
Figure S69. Partial $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$, 298 K) of the reaction of substrates 6 and 7 in presence of catalytic amounts of $\text{SI-IIIb}$ at 40 °C in CD$_2$Cl$_2$ for 10 h each. Product 8 shows up at 5.52 ppm in the spectrum.

d) Final system catalytic experiment D using 2c as biped

Use of same concentrations, under the same conditions and procedures. The $^1$H NMR spectrum of $\text{SIc}$ in presence of substrates 6, 7 was recorded. Then, the mixture was heated for 10 h at 40 °C. After recording an NMR spectrum, the consumed amounts of both reactants 6 and 7 were added as well as 2-pyridine carboxaldehyde (3) (20.0 µg, 0.190 µmol) to form $\text{SIIc}$. The solution was heated for another 10 h at 40 °C, immediately another $^1$HNMR spectrum was recorded. Afterwards, the consumed amounts of substrates were replaced and 8-aminoquinoline (4, 27.0 µg, 0.190 µmol) was added to yield $\text{SIIIc}$. The mixture was heated for the same time at 40 °C and the $^1$H NMR was recorded as shown in Figure S70. The yield produced by the catalyst $\text{SIc}$ is 75% of 8 while after addition of 3 the catalytic activity of $\text{SIIc}$ declined drastically with only 5% increase in yield. The final state $\text{SIIIc}$ turned out to be catalytically inactive.
**Figure S70.** Partial $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$, 298 K) of the reaction of substrates 6 and 7 in presence of catalytic amounts of S-IIIc at 40 °C in CD$_2$Cl$_2$ for 10 h each. Product 8 shows up at 5.52 ppm in the spectrum.

e) Direct analysis of the catalytic activity of states SIIa and SIIc

Deck 1 (361 µg, 0.190 µmol) and biped (2a, 2c) (0.190 µmol) in presence of 3 (20.0 µg, 0.190 µmol) and [Cu(CH$_3$CN)$_4$]PF$_6$ (220 µg, 0.570 µmol) were mixed in 500 µL of CD$_2$Cl$_2$. Substrates 6 & 7 (5.85 µmol each) were added, and the mixture heated for 10 h at 40 °C. The yield was consistent with experiments B and D, since SIIa furnished 15% yield of 8 and SIIc afforded just 5% of 8 (Figure S71).

**Figure S71.** Partial $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$, 298 K) of the reaction of substrates 6 and 7 in presence of catalytic amounts of SIIa and SIIb at 40 °C in CD$_2$Cl$_2$ for 10 h each. Product 8 shows up at 5.52 ppm in the spectrum.
Table S2. Yield of 8 vs. sliding frequency of S1a,b,c , SIIa,b,c.

<table>
<thead>
<tr>
<th>State</th>
<th>Slider-on-deck</th>
<th>$k_{298}$ / kHz</th>
<th>$\Delta G^\ddagger$ / kJ mol$^{-1}$</th>
<th>Yield of 8 /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1a</td>
<td>[Cu$_3$(1)(2a)]$^{3+}$</td>
<td>2.4</td>
<td>53.7</td>
<td>33</td>
</tr>
<tr>
<td>SIIa</td>
<td>[Cu$_3$(1)(2a)(3)]$^{3+}$</td>
<td>1.6</td>
<td>55.2</td>
<td>13</td>
</tr>
<tr>
<td>S1b</td>
<td>[Cu$_3$(1)(2b)]$^{3+}$</td>
<td>20</td>
<td>48.2</td>
<td>70</td>
</tr>
<tr>
<td>SIIb</td>
<td>[Cu$_3$(1)(2b)(3)]$^{3+}$</td>
<td>11</td>
<td>49.8</td>
<td>8</td>
</tr>
<tr>
<td>S1c</td>
<td>[Cu$_3$(1)(2c)]$^{3+}$</td>
<td>42</td>
<td>46.5</td>
<td>75</td>
</tr>
<tr>
<td>SIIc</td>
<td>[Cu$_3$(1)(2c)(3)]$^{3+}$</td>
<td>26</td>
<td>47.8</td>
<td>5</td>
</tr>
</tbody>
</table>

As displayed in Table S2, the catalytic activity of the sliders-on-deck shows that S1a,b,c furnishes more yield as the rotational frequency increases. In contrast, SIIa,b,c produced more yield as the rotational frequency decreased.

Figure 72. A representation of direct and inverse relation of yield % vs sliding frequency of S1a,b,c , SIIa,b,c respectively.
11. Determination of log $K$ of complex SIIa

A UV-vis titration was performed to measure the binding constants between $\text{SIIa} = [\text{Cu}_3(\text{1})(\text{2a})]^{3+}$ and 3. A solution of $[\text{Cu}_3(\text{1})(\text{2a})]^{3+}$ ($2.76 \times 10^{-6}$ M) was titrated with a $4.2 \times 10^{-4}$ M solution of 3 in dichloromethane. The UV-vis response was analyzed by nonlinear curve-fitting. $\Delta A$ values were monitored at 271 nm. The following equation$^5$ was used for the fitting:

$$\Delta A = \frac{L \times (K \times (P + x) + 1) - \sqrt{((K \times (P + x) + 1)^2 - 4 \times K \times K \times P \times x)})}{2 \times K \times P}.$$  

With $x$ and $P$ representing $[\text{Guest}]_{\text{total}}$ and $[\text{Host}]_{\text{total}}$, respectively; $L$ denoting $\Delta A$ at 100% complexation; $L$ and $K$ are parameters.

![UV-vis titration of SIIa](image.png)

**Figure S73.** UV-vis titration of SIIa $[\text{Cu}_3(\text{1})(\text{2a})]^{3+}$ ($2.76 \times 10^{-6}$ M) with 3 ($4.2 \times 10^{-4}$ M) furnishing log $K$ = 3.62 ± 0.15.
12. Species distribution curves

a) Speciation analysis of pyridine aldehyde (3) in relation to [Cu(9)]\(^+\) = C1

The species distribution was calculated by the Hyperquad software HySS2009® version using log \( K = 3.83 \pm 0.35 \) as binding constant between [Cu(9)]\(^+\) with 3 (0 → 0.42 mM) (at 298 K in dichloromethane).

From the speciation distribution curve, we derive that 87% of complex [Cu(9)(3)]\(^+\) was formed in solution, thus leaving 13% of pyridine aldehyde (3) unbound. Reciprocally, it means that 13% of copper(I) ion are exposed to catalyze the cycloaddition reaction between 6 and 7.

Figure S74. Calculated species distribution between C1 = [Cu(9)]\(^+\) with 3 (0 → 0.42 mM) with log \( K = 3.83 \pm 0.35 \).
b) Percentage of 3 liberated by different assemblies

Figure S75. $^1$H NMR of 3 (CD$_2$Cl$_2$, 298 K, 400 MHz) as pure compound (bottom) and in the various complexes. The chemical shift of proton C(=O)-H of 3 (see red asterisk) in SIIa, SIIb reveals that 3 is increasingly liberated into solution the higher the binding ability of the biped 2. This conclusion is supported by its chemical shift approaching that of free 3.

Table 3. NMR shift and amount of 3 liberated from SIIa, SIIb, SIIc and [Cu(9)]$^+$ at $c = 1.14$ mM.

<table>
<thead>
<tr>
<th>Assemblies/ Compounds</th>
<th>δ / ppm$^a$</th>
<th>3 / %$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>10.04</td>
<td>100</td>
</tr>
<tr>
<td>[Cu$_3$(1)(2a)(3)$]^{3+}$ = SIIa</td>
<td>9.76</td>
<td>47</td>
</tr>
<tr>
<td>[Cu$_3$(1)(2b)(3)$]^{3+}$ = SIIb</td>
<td>9.65</td>
<td>26</td>
</tr>
<tr>
<td>[Cu$_3$(1)(2c)(3)$]^{3+}$ = SIIc</td>
<td>9.61</td>
<td>19</td>
</tr>
<tr>
<td>[Cu(9)(3)]$^+$</td>
<td>9.58</td>
<td>13</td>
</tr>
</tbody>
</table>

$^a$ The chemical shift of proton -C(=O)-H of 3 (CD$_2$Cl$_2$, 298 K, 400 MHz) in free 3 (top) and in various dynamic complexes. $^b$ The percentage of 3 liberated from the different complexes.
A prerequisite of the current analysis is that the equilibration liberating 3 from [Cu₃(1)(2)(3)]⁺⁺⁺ or [Cu(9)(3)]⁺⁺ is fast on the NMR time scale providing an averaged shift.

The speciation analysis (SI, Figure S74) showed that 13% of 3 are freed in solution in [Cu(9)(3)]⁺⁺ at the concentration \( c = 2.76 \times 10^{-6} \) M used in the UV experiments. By means of the known chemical shifts of free 3 (\( \delta = 10.04 \) ppm) and that (\( \delta = 9.58 \) ppm) representing the equilibrium of \([\text{Cu}(9)]^+ + 3 \rightleftharpoons [\text{Cu}(9)(3)]^+ = 13 : 87\) (SI, Figure S74) on can derive the amount of 3 liberated from the assemblies SIIa,b,c as follows:

\[ \Delta \delta = \text{chemical shift difference of product } 3 \text{ (ald-H) between free (100%) and 13% unbound state in } [\text{Cu}(9)(3)]^+, 10.04 - 9.58 = 0.46 \text{ ppm.} \]

On the other hand, \( \Delta \delta^1, \Delta \delta^2 \) and \( \Delta \delta^3 \) are chemical shift differences of product 3 (ald-H) in the free and the bound state in SIIa,b,c respectively.

- **SIIa** binds 3 in a yield = \((100\%-13\%) \times (\Delta \delta^1/\Delta \delta) = [87\% \times (0.28/0.46)] = 53\%. \) Therefore 47% of 3 is liberated from SIIa.
- **SIIb** binds 3 in a yield = \((100\%-13\%) \times (\Delta \delta^2/\Delta \delta) = [87\% \times (0.39/0.46)] = 74\%. \) Therefore 26% of 3 is liberated from SIIb.
- **SIIc** binds 3 in a yield = \((100\%-13\%) \times (\Delta \delta^3/\Delta \delta) = [87\% \times (0.43/0.46)] = 81\%. \) Therefore 19% of 3 is liberated from SIIc.

c) Binding constant of ligand to copper loaded shielded phenanthroline

<table>
<thead>
<tr>
<th>Complexes</th>
<th>(log K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(phenAr₂)]⁺⁺ + pyridine⁷</td>
<td>3.20</td>
</tr>
<tr>
<td>[Cu(phenAr₂)]⁺⁺ + picoline⁸</td>
<td>3.43 ± 0.01</td>
</tr>
<tr>
<td>[Cu(phenAr₂)]⁺⁺ + pyridine aldehyde⁶</td>
<td>3.83 ± 0.35</td>
</tr>
<tr>
<td>[Cu(phenAr₂)]⁺⁺ + lutidine⁹</td>
<td>4.50 ± 0.21</td>
</tr>
</tbody>
</table>

*Table 4. Association constants of pyridine, picoline and lutidine to [Cu(phenAr₂)]⁺⁺*
14. References


