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Dual coordination in ditopic azabipyridines and azaterpyridines as a key for reversible switching†

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Dual coordination at two distinct nitrogen binding sites in various ditopic azabipyridines and azaterpyridines was evaluated by preparing 3- and 4-component complexes. The 4-aza-2,2′-bipyridine unit was implemented into a nanoswitch and used for reversible switching between open and closed forms.

Introduction

Metal–ligand coordination[1,2] is the key interaction in metallosupramolecular chemistry and thus is at the heart of a vast amount of two- and three-dimensional nanoarchitectures.[2a,b,3] Tuning this interaction by ligand design opens a multitude of opportunities to implement either specific geometrical arrangements or exciting functions by encrypting information both in binding sites and the covalent framework.

Nitrogen heterocycles such as phenanthrolines, pyridines,[4] bipyridines[5] and terpyridines[6] constitute an outstanding class of building blocks in view of many applications that are based on the physical, photophysical, electronic, and redox properties of their metal complexes.[6–8] Over many years, we have contributed to this field by studying the coordination behaviour of phenanthroline,[9] bipyridine[10] and terpyridine[11] ligands in dynamic heteroleptic metal complexes.

Various modifications of these heterocycles, particularly in oligopyridines, have already proven their value in fascinating architectures and functions.[12] Further diversification of phenanthroline, bipyridine and terpyridine ligands by introducing one extra nitrogen donor site at suitable positions may add a new facet to their usefulness. Indeed, the increased utility of such ligands has already been demonstrated by turning catalytic reactions on and off through input signals that operate *via* orthogonal[13] metal–ligand coordination at an azabipyridine site in molecular nanoswitches.[14] In the present paper, we describe the coordination behaviour of four recently designed multitopic azabipyridines and azaterpyridines,[15] each endowed with at least two independently addressable coordination sites. To demonstrate their mode of operation, we have probed the ligands in dual coordination scenarios with shielded copper(I) phenanthrolines on one side and zinc porphyrin on the other. Steric effects were found to be the governing factor controlling dual coordination. To illustrate the utility of such coordination scenarios, toggling between the open and close forms of a molecular nanoswitch is demonstrated.

Results and discussion

All azabipyridines and azaterpyridines **1**–**4** were prepared by a series of coupling reactions following a reported procedure.[15] Their multifarious complexation properties were then examined first toward Cu^+ and phenanthrolines **5** and **6** and second toward zinc porphyrin **7** (Chart 1) as an additional ligand in dual coordination scenarios.

At the onset, one equiv. of Cu^+ was reacted with shielded phenanthroline **5** or **6** in DCM, and subsequently one equiv. of azabipyridine **1** was added. The latter step was accompanied by a colour change from light yellow to deep red indicative of the formation of complex **8** = $[Cu(\mathbf{1})(\mathbf{5})]^+$ or **9** = $[Cu(\mathbf{1})(\mathbf{6})]^+$. In detail, the resulting heteroleptic complexes were characterised from ^1H and ^{13}C NMR, IR, ESI-MS and elemental analysis. ESI-MS show exclusive signals at *m*/*z* 715.7 (Fig. S49, ESI†) and 831.6 Da (Fig. S50, ESI†) that are attributed to **8** = $[Cu(\mathbf{1})(\mathbf{5})]^+$ and **9** = $[Cu(\mathbf{1})(\mathbf{6})]^+$, respectively, and whose experimental isotopic distributions perfectly match with computed ones. Quantitative formation of the complexes is furthermore supported by diagnostic shifts in the ^1H NMR spectrum. After adding **1** to a solution of $[Cu(\mathbf{5})]^+$, the mesityl protons are shifted from 6.90 to 6.20 and 6.35 ppm (Fig. S1, ESI†), which is very much indicative[16] of heteroleptic complex formation. Proton 4-H of the phenanthroline is shifted downfield from 8.32 to 8.66 ppm (Fig. S1, ESI†) in complex **8** and to 8.90 ppm (Fig. S5, ESI†) in complex **9**. The anthracenyl protons are split and shifted upfield due to shielding from **1**, which convincingly implies the presence of **6** in the complex. To check for quantitative complex formation, a ^1H NMR titration was performed. Upon

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†Electronic supplementary information (ESI) available: Full characterisation of all complexes and data on toggling nanoswitch **19**. See DOI: 10.1039/c3dt51780b

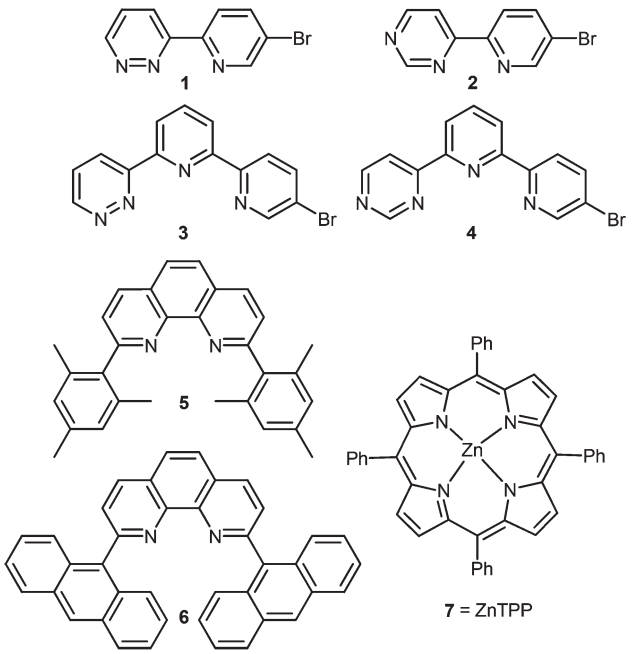


Chart 1 Compounds used in the present study.

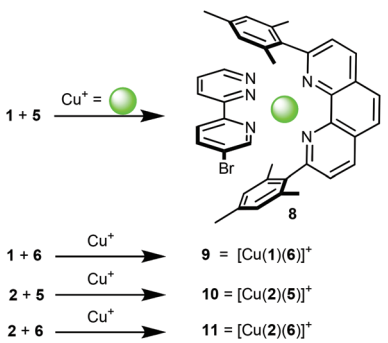
addition of 0.5 equiv. of **1** to a solution of either $[Cu(\mathbf{5})]^+$ (Fig. S3, ESI†) or $[Cu(\mathbf{6})]^+$ (Fig. S7, ESI†), the desired complex **8** or **9** is afforded along with 0.5 equiv. of $[Cu(\mathbf{5})]^+$ and $[Cu(\mathbf{6})]^+$ left free in solution. Addition of a further 0.5 equiv. of **1** to the above solution furnished the desired complexes **8** and **9**, exclusively.

Similarly, complexes **10** = $[Cu(\mathbf{2})(\mathbf{5})]^+$ and **11** = $[Cu(\mathbf{2})(\mathbf{6})]^+$ were received in quantitative yield when compound **2** was added to $[Cu(\mathbf{5})]^+$ or $[Cu(\mathbf{6})]^+$. Formation of **10** and **11** was confirmed from molecular ion peaks in the ESI-MS at *m*/*z* 715.7 (Fig. S51, ESI†) and 831.7 (Fig. S52, ESI†), respectively. Experimental isotopic distributions match with the theoretical ones. The ^{1}H NMR shows the characteristic shift of the mesityl proton from 6.90 to 6.29 and 6.34 ppm (Fig. S9, ESI†) in complex **10**. Equally, proton 4-H of the phenanthroline is shifted downfield from 8.32 to 8.70 ppm in complex **10** and to 8.93 ppm (Fig. S13, ESI†) in complex **11** (Scheme 1).

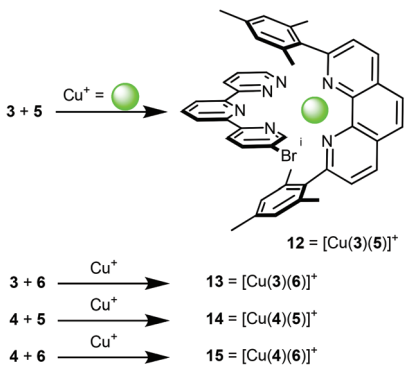
In addition, a ^{1}H NMR titration showed that upon addition of 0.5 equiv. of **2** to one equiv. of $[Cu(\mathbf{5})]^+$ (Fig. S11, ESI†) or $[Cu(\mathbf{6})]^+$ (Fig. S15, ESI†), free $[Cu(\mathbf{5})]^+$ and $[Cu(\mathbf{6})]^+$ were present along with complexes **10** and **11**. In contrast, only the desired complexes **10** and **11** were detectable when a further 0.5 equiv. of **2** was added to the above solution. DOSY NMR (Fig. S47, ESI†) furthermore confirmed the presence of only one species in solution. From ESI-MS and NMR data, it was thus ascertained that the bipyridine unit of compounds **1** and **2** forms heteroleptic complexes with both shielded phenanthrolines **5** and **6** in the presence of Cu^+ as a metal ion.

Complexation of azaterpyridines **3** and **4** was examined in a similar way. Thus, Cu^+ was first reacted with one of the shielded phenanthrolines **5** or **6**. Then, azaterpyridine **3** was added to $[Cu(\mathbf{5})]^+$ or $[Cu(\mathbf{6})]^+$ to furnish complexes **12** = $[Cu(\mathbf{3})(\mathbf{5})]^+$ and **13** = $[Cu(\mathbf{3})(\mathbf{6})]^+$, respectively, that were thoroughly characterised (Scheme 2). For $[Cu(\mathbf{3})(\mathbf{5})]^+$ the ESI-MS data show a molecular ion peak at *m*/*z* = 792.8 (Fig. S53, ESI†) with the experimental isotopic distribution neatly matching the theoretical one. Complex $[Cu(\mathbf{3})(\mathbf{6})]^+$ exhibits a molecular ion peak at *m*/*z* = 908.7 (Fig. S54, ESI†) again with fully matching isotopic distribution. Mesityl protons in complex **12** appear at 6.36 instead of 6.90 ppm (Fig. S17, ESI†). Proton 4-H of the phenanthroline is shifted downfield from 8.32 to 8.61 ppm for **12** and to 8.85 ppm (Fig. S21, ESI†) for **13** due to complex formation. The anthracenyl protons of **13** show similar shifts as in the case of **9**. Again ^{1}H NMR titration experiments were carried out to further corroborate quantitative complex formation. After addition of 0.5 equiv. of Cu^+ to a 1 : 1 solution of either **3** and **5** (Fig. S19, ESI†) or **3** and **6** (Fig. S24, ESI†), the expected complexes **12** and **13** were formed leaving all other components free in solution. When an additional 0.5 equiv. of Cu^+ was added, the desired complexes **12** and **13** were formed exclusively. The above pieces of information corroborate quantitative formation of the heteroleptic complexes.

Complexes **14** and **15** were synthesised following a similar procedure to that for **12** and **13**. Complexes **14** = $[Cu(\mathbf{4})(\mathbf{5})]^+$ and **15** = $[Cu(\mathbf{4})(\mathbf{6})]^+$ were readily identified from NMR, ESI-MS and elemental analysis. In the case of **14**, the mesityl protons are shifted from 6.90 to 6.29 and 6.35 ppm (Fig. S25, ESI†) again being indicative of heteroleptic complex formation. The



Scheme 1 Fabrication of three-component azabipyridine complexes.



Scheme 2 Fabrication of three-component azaterpyridine complexes.

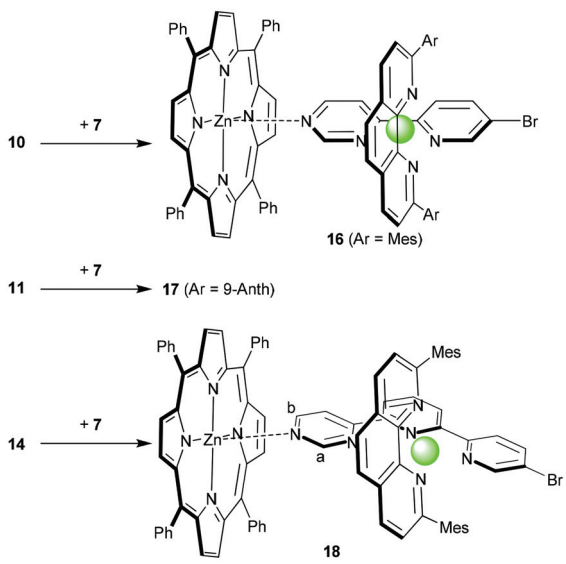
downfield shift of proton 4-H of the phenanthroline from 8.32 ppm to 8.64 ppm in complex **14** and to 8.90 ppm (Fig. S28, ESI†) in complex **15** again supports our structure assignment. In addition, ^{1}H NMR titration as before and ESI-MS data provide clear information for heteroleptic complex formation. In ESI-MS, the molecular ion peaks show up at *m*/*z* 792.8 (Fig. S55, ESI†) and 908.7 (Fig. S56, ESI†) with isotopic distributions being attributable to $[Cu(\mathbf{4})(\mathbf{5})]^+$ and $[Cu(\mathbf{4})(\mathbf{6})]^+$, respectively.

To explore the ditopic nature of ligands **1–4** within the heteroleptic complexes, their coordination capability at the remaining free nitrogen was explored toward added zinc tetraphenylporphyrin (**7** = ZnTPP) (Scheme 3). At first, **7** was added to complexes **8** (Fig. S39, ESI†) and **9** (Fig. S40, ESI†). Diagnostically, the ^{1}H NMR spectrum did not show any upfield shift of protons a-H and b-H of azabipyridine **1** indicating that the nitrogen is not available for further coordination to ZnTPP possibly due to steric reasons.

In contrast, the free nitrogen of azabipyridine **2** in complexes **10** and **11** was found to coordinate to ZnTPP. After addition of ZnTPP to **10** and **11**, the protons b-H and a-H of the pyrimidine subunit in complex **16** were shifted upfield from 8.09 and 7.77 ppm to 6.72 and 6.84 ppm (Fig. 1) in the ^{1}H NMR. The upfield shift is readily explained due to immersion of the pyrimidine subunit into the zone of the porphyrin ring current in complex **16**.

An analogous phenomenon was observed in the case of **17** where protons b-H and a-H are shifted from 8.32 and 7.45 ppm to 6.54 and 6.32 ppm (Fig. S34, ESI†), respectively. The same spectrum was observed when all components were added together in DCM indicating that the formation of the final compound was fully reversible and independent of the sequence of addition.

The coordinating properties of the free nitrogen in the azaterpyridine ligands were likewise probed by adding ZnTPP to complexes **12–15**. Contrary to complex **15**, ^{1}H NMR data of **14**



Scheme 3 Fabrication of four-component complexes.

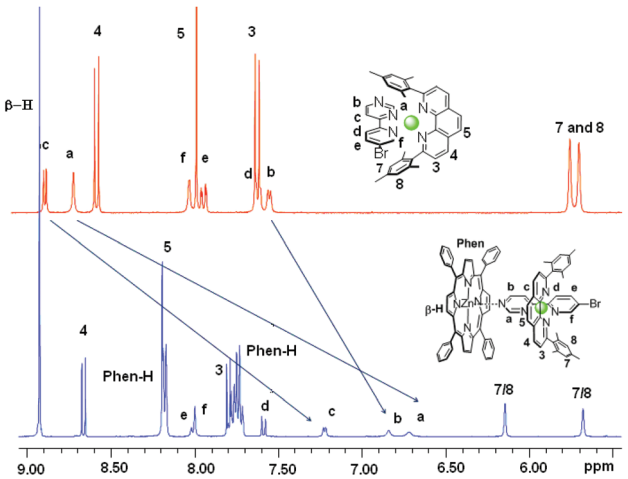
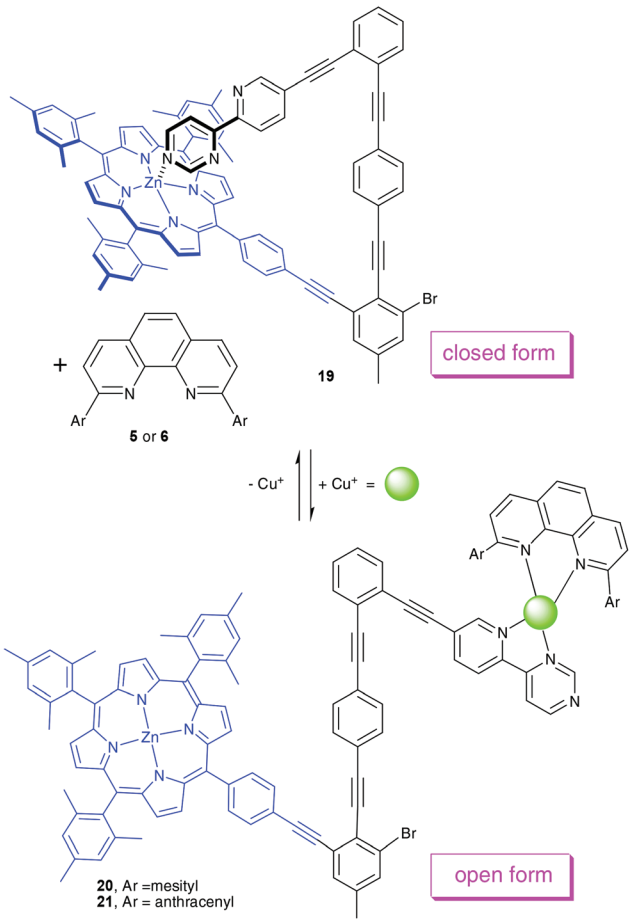


Fig. 1 (Top) ^{1}H NMR spectrum of complex **10** in CD_2Cl_2 at 298 K. (Bottom) Complex **10** after addition of ZnTPP. The upfield shifts indicate axial coordination of **10** to ZnTPP.

indicate that despite engagement of the terpyridine segment, the left-over nitrogen of azaterpyridine **4** can still coordinate to ZnTPP. Pyrimidine protons a-H and b-H are now shifted upfield from ~7.80 and 8.57 to 6.18 and 7.04 ppm (Fig. S37, ESI†), respectively, due to shielding by the porphyrin ring. Amazingly, terpyridine **3** is also able to coordinate to ZnTPP in complexes **12** and **13** as evidenced from the ^{1}H NMR spectrum. For complex **12**, protons a-H and b-H are now upfield shifted from 8.89 and 7.45 ppm to 8.69 and 7.34 ppm upon coordination to ZnTPP (Fig. S41, ESI†). Similarly, coordination of complex **13** to ZnTPP resulted in a shift of protons a-H and b-H from 8.56 and 7.19 ppm to 8.16 and 7.10 ppm, respectively (Fig. S42, ESI†).

The recent preparation of nanoswitch **19**[14a] with its azabipyridine arm allowed us to probe the ditopic role of "subunit **2** (py-pym)" in an intramolecular setting. In **19**, *i.e.* the closed form of the nanoswitch, the py-pym unit is intramolecularly coordinated to the zinc porphyrin. To drive the unlocking process chemically, we reacted **19** at its py-pym unit with the shielded copper(I) phenanthroline complex $[Cu(\mathbf{6})]^+$ to form the heteroleptic complex **21** as the open form (Scheme 4).[14a]

In contrast, addition of $[Cu(\mathbf{5})]^+$ to **19** works differently. In order to understand this difference, we studied the resulting complex **20** = $[Cu(\mathbf{5})(\mathbf{19})]^+$ in detail. It was first characterised by ESI-MS, ^{1}H NMR, UV-vis spectroscopy and elemental analysis. The peak at *m*/*z* = 1857.3 (Fig. 2) in the ESI-MS is clearly attributed to M^+ as the experimental isotopic distribution neatly matches with the theoretical one. From a comparison (Fig. 3) of the ^{1}H NMR data of **20** with those of **16**, it became evident that the pyrimidine nitrogen N1 in both **20** = $[Cu(\mathbf{5})(\mathbf{19})]^+$ and $[Cu(\mathbf{2})(\mathbf{5})(\mathbf{7})]^+$ is coordinated to ZnTPP. Upon addition of $[Cu(\mathbf{5})]^+$ to **19**, the characteristic sharp signals at 2.9 and 3.3 ppm (protons a-H and b-H of the locked state) broaden and shift to 6.8 and 6.7 ppm, respectively. Broadening suggests that the py-pym unit is dynamically coordinated at N1 to the zinc porphyrin, but now in an intermolecular fashion.



Scheme 4 Switching between open and closed forms in a nanoswitch.

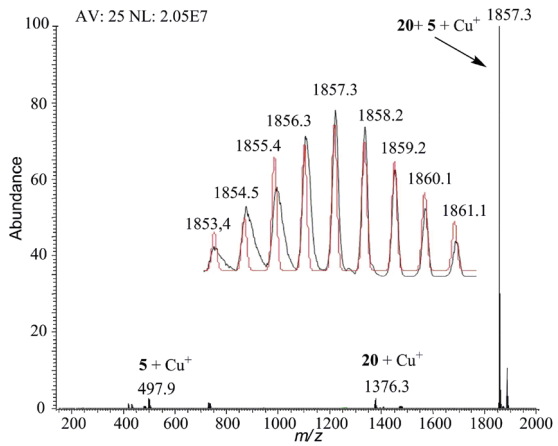


Fig. 2 ESI-MS spectrum of **20** = [Cu(**5**)(**19**)]$^+$ in DCM.

If complex **20** = [Cu(**5**)(**19**)]$^+$ were a single species, it should exhibit a UV-vis absorption at 422 nm, typical of an axially noncoordinated zinc porphyrin. Fig. 4 displays the UV-vis titration of **19** (1 μM) *vs.* copper phenanthroline complex [Cu(**5**)]$^+$. Notably, only after addition of 3 equiv. of [Cu(**5**)]$^+$, the band at 429 nm completely shifted to 422 nm implying that only at

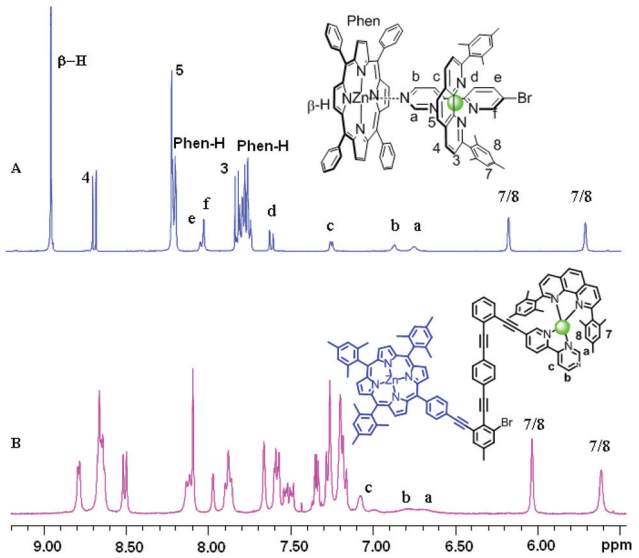


Fig. 3 Partial ^{1}H NMR of complexes (A) **16** and (B) **20** = [Cu(**5**)(**19**)]$^+$.

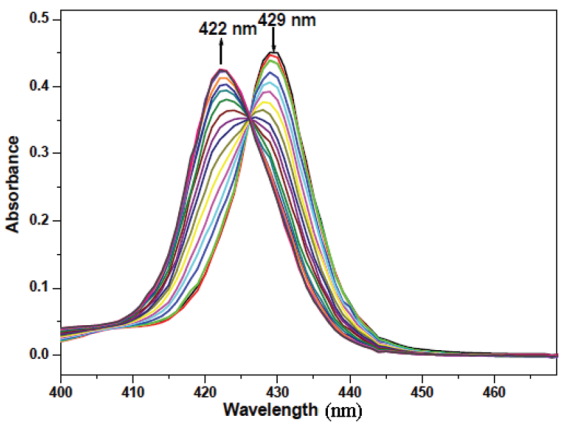


Fig. 4 UV-vis titration of **19** (1 μM) *vs.* [Cu(**5**)]$^+$ (0.1 mM) in DCM at 298 K. After 3 equivalents of copper complex addition, the intensity at 422 nm remains constant.

this ratio, **20** is fully in the unlocked state. Apparently, after addition of one equivalent of [Cu(**5**)]$^+$, N1 of pyrimidine in the resulting [Cu(**5**)(**19**)]$^+$ still remained coordinated to the zinc(II) porphyrin. Thus, the steric effect exerted by phenanthroline **5** was not sufficient to prevent binding of N1 of the pyrimidine unit to zinc porphyrin, quite in contrast to the situation in **21**.

To evaluate whether this coordination was intra- or intermolecular in [Cu(**5**)(**19**)]$^+$, ^{1}H NMR spectra were taken at different concentrations. Notably, signals of the pyrimidine protons a-H and b-H were shifted downfield with decreasing concentration from 10.8 to 1.67 mM (Fig. S44, ESI†). This evidence suggests that the pyrimidine N1 is coordinated intermolecularly after addition of one equiv. of [Cu(**5**)]$^+$ to **19**, rendering this reaction less suitable for toggling nanoswitch **19** than with input [Cu(**6**)]$^+$.[14a]

The closed form **19** of the molecular switch was regenerated by removing Cu^+ from complex **20** by adding one equiv. of cyclam. After addition of cyclam to complex **20**, the py-pym protons in the ^{1}H NMR spectrum reappear as signals at 2.9 and 3.3 ppm (Fig. S46, ESI†). Moreover, the Soret band moves back to 429 nm. Thus, both ^{1}H NMR and UV-vis data confirm that the self-locking molecule **19** is regenerated in its closed form after removal of Cu^+ with cyclam.

In summary, we describe the heteroleptic coordination behaviour of four ditopic azabipyridine and azaterpyridine ligands with Cu^+ and shielded phenanthrolines. Depending on the spatial availability of the extra nitrogen, an additional complexation with a zinc porphyrin and thus formation of 4-component complexes was realised. For instance, with pyrimidine terminals an extra coordination was established, while with pyridazine-terminated ligands, the extra nitrogen was not available on steric grounds. The utility of azabipyridine **2** was investigated in the context of switching the molecular nanoswitch **19**. Due to the availability of both mono- and bidentate nitrogen sites in the azabipyridine arm, a closed form was established by intramolecular coordination of the monodentate nitrogen to the zinc porphyrin, while complexation of $[Cu(\mathbf{5})]^+$ at the bidentate site led to the open form. Nanoswitch **19** could be toggled reversibly between open and closed forms.

Experimental

General information

The commercially available reagents were used without any further purification. All solvents for column chromatography were distilled prior to use. Thin-layer chromatography was performed using thin-layer chromatography plates (silica gel 60 F_{254}, Merck). Silica gel 60 was used for column chromatography. Nuclear magnetic resonance (NMR) spectra were recorded using Bruker Avance 400 MHz and Varian 600 MHz spectrometers using the deuterated solvent as the lock and the residual solvent as the internal reference. In the assignments, the chemical shift (in ppm) is given first, followed, in brackets, by the multiplicity of the signal (s: singlet, d: doublet, t: triplet, dd: doublet of doublets, ddd: doublets of doublets of doublet, dt: doublet of triplets, m: multiplet, bs: broad singlet), the value of the coupling constants in hertz if applicable, the number of protons implied, and finally the assignment of the proton wherever possible. The numbering of the carbon atoms of the molecular formulae shown in the Experimental section is only used for the assignments of the NMR signal and is not in accordance with IUPAC nomenclature rules. Melting points of compounds were measured after evaporating the solvent and drying under vacuum uisng a Büchi (BÜCHI 510) melting point apparatus and were uncorrected. IR spectra were recorded using a Perkin-Elmer FT-IR 1750. Electrospray ionisation mass spectra (ESI-MS) were recorded using a Thermo-Quest LCQ Deca. Microanalyses were performed using a Euro elemental analyser from EuroVector.‡

Synthesis of complex 8. A mixture of 3-(5-bromopyridin-2-yl) pyridazine (2.14 mg, 9.07 μmol), 2,9-dimesityl-1,10-phenanthroline (3.78 mg, 9.07 μmol) and $[Cu(CH_3CN)_4]PF_6$ (3.38 mg, 9.07 μmol) was placed in an NMR tube, and then dichloromethane-d_2 was added furnishing a clear deep red solution. NMR was measured without purification. Yield: Quantitative. **Melting point:** 242 °C. **IR (KBr):** ν = 3050, 2922, 2855, 1614, 1585, 1549, 1459, 1381, 1310, 1144, 1105, 1024, 842, 780, 733, 650, 622, 558. **^{1}H NMR (400 MHz, CD_2Cl_2):** δ = 1.76 (s, 6 H, mes-CH_3), 1.82 (s, 6 H, mes-CH_3), 1.93 (s, 6 H, mes-CH_3), 6.20 (s, 2 H, 6/7-H), 6.35 (s, 2 H, 7/6-H), 7.77 (dd, ^3J = 8.8 Hz, ^3J = 4.9 Hz, 1 H, b-H), 7.80 (d, ^3J = 8.4 Hz, 1 H, d-H), 7.87 (d, ^3J = 8.2 Hz, 2 H, 3-H), 8.09–8.15 (m, 2 H, c-, e-H), 8.17 (s, 2 H, 5-H), 8.25 (s, 1 H, f-H), 8.66 (d, ^3J = 8.2 Hz, 2 H, 4-H), 9.07 (dd, ^3J = 4.9 Hz, ^4J = 1.6 Hz, 1 H, a-H) ppm. **^{13}C NMR (100 MHz, CD_2Cl_2):** δ = 20.1, 20.8 (2 C), 122.7, 123.9, 125.4, 126.9 (2 C), 127.0, 127.5, 127.7, 128.1, 135.0, 135.8, 137.3, 137.8, 138.5, 140.0, 144.2, 148.0, 149.1, 152.4, 152.8, 159.5 ppm. **ESI-MS:** *m*/*z* (%): 715.7 (100) $[Cu(\mathbf{1})(\mathbf{5})]^+$. **Elemental analysis** ($C_{39}H_{34}N_5BrCuPF_6{\cdot}CH_3OH$): Calcd C, 53.79; H, 4.29; N, 7.84. Found: C, 54.03; H, 3.89; N, 7.48.

Synthesis of complex 9. 2,9-Dianthracenyl-1,10-phenanthroline (2.13 mg, 4.00 μmol) and $[Cu(CH_3CN)_4]PF_6$ (1.49 mg, 4.00 μmol) were loaded into an NMR tube followed by addition of CD_2Cl_2 to afford a clear solution. 3-(5-Bromopyridin-2-yl)-pyridazine (945 μg, 4.00 μmol) was added to furnish the deep red complex. All spectroscopic measurements were performed without further purification. Yield: Quantitative. **Melting point:** >275 °C. **IR (KBr):** ν = 3049, 2953, 2923, 2856, 2363, 2339, 1620, 1579, 1497, 1436, 1353, 1264, 1197, 1120, 1094, 1017, 842, 734, 625, 555, 499. **^{1}H NMR (400 MHz, CD_2Cl_2):** δ = 6.80 (d, ^4J = 2.0 Hz, 1 H, f-H), 6.99–7.04 (m, 4 H, anth-H), 7.08–7.12 (m, 2 H, b, d-H), 7.13–7.16 (m, 2 H, anth-H), 7.19–7.24 (m, 6 H, anth-H), 7.36 (dd, ^3J = 8.8 Hz, ^4J = 1.2 Hz, 1 H, c-H), 7.44–7.49 (m, 4 H, anth-H), 7.55 (dd, ^3J = 8.4 Hz, ^4J = 2.0 Hz, 1 H, e-H), 7.85 (s, 2 H, 9′-H), 7.90 (dd, ^3J = 4.8 Hz, ^4J = 1.2 Hz, 1 H, a-H), 8.24 (d, ^3J = 8.4 Hz, 2 H, 3-H), 8.38 (s, 2 H, 5-H), 8.90 (d, ^3J = 8.4 Hz, 2 H, 4-H) ppm. **^{13}C NMR (100 MHz, CD_2Cl_2):** δ = 120.9, 122.9, 124.0, 125.2, 125.3, 125.5 (2C), 125.8, 126.3, 126.6, 127.4, 127.8, 128.2, 128.3, 128.5, 128.8, 129.5, 129.8, 130.3, 130.4, 134.3, 137.7, 138.9, 144.4, 146.0, 148.4, 150.5, 151.5, 157.4 ppm. **ESI-MS:** *m*/*z* (%): 831.6 (100) $[Cu(\mathbf{1})(\mathbf{6})]^+$. **Elemental analysis** ($C_{49}H_{30}N_5BrCuPF_6{\cdot}2/3CH_2Cl_2$): Calcd C, 57.70; H, 3.05; N, 6.77. Found: C, 57.38; H, 2.85; N, 6.65.

Synthesis of complex 10. 4-(5-Bromopyridin-2-yl)pyrimidine (503 μg, 2.13 μmol) and 2,9-dimesityl-1,10-phenanthroline (888 μg, 2.13 μmol) were loaded into an NMR tube, and then $[Cu(CH_3CN)_4]PF_6$ (795 μg, 2.13 μmol) and CD_2Cl_2 were added to afford a clear deep red solution. Spectroscopic measurements were performed without further purification.

‡Complexes were isolated for elemental analysis by transferring them from the NMR tube into a flask rinsing with CH_2Cl_2 as a solvent and drying under high vacuum.

Yield: Quantitative. **Melting point:** 255 °C. **IR (KBr):** ν = 3051, 2922, 2856, 1615, 1581, 1506, 1476, 1436, 1381, 1355, 1291, 1244, 1145, 1096, 1024, 842, 627, 559. **^{1}H NMR (400 MHz, CD_2Cl_2):** δ = 1.80 (s, 12 H, 8-H), 1.95 (s, 6 H, 9-H), 6.29 (s, 2 H, 6/7-H), 6.34 (s, 2 H, 7/6-H), 7.86–7.92 (m, 4 H, 3-, d-, b-H), 8.15–8.23 (m, 4 H, 5-, e-, f-H), 8.70 (d, ^3J = 8.4 Hz, 2 H, 4-H), 8.81 (s, 1 H, a-H), 8.95 (d, ^3J = 5.2 Hz, 1 H, c-H) ppm. **^{13}C NMR (100 MHz, CD_2Cl_2):** δ = 20.1, 20.8 (2 C), 117.3, 123.7, 124.9, 127.0, 127.1 (2 C), 127.9, 128.0, 128.3, 135.1, 137.3, 138.2, 138.7, 140.3, 144.2, 147.8, 149.6, 156.7, 157.0, 158.2, 159.5 ppm. **ESI-MS:** *m*/*z* (%): 715.7 (100) $[Cu(2)(5)]^+$. **Elemental analysis** ($C_{39}H_{34}N_5BrCuPF_6 \cdot 1/3CH_2Cl_2$): Calcd C, 53.11; H, 3.93; N, 7.87. Found C, 52.98; H, 3.84; N, 7.54.

Synthesis of complex 11. An equimolar mixture of 2,9-dianthracenyl-1,10-phenanthroline (3.36 mg, 6.31 μmol), 4-(5-bromopyridin-2-yl)pyrimidine (1.49 mg, 6.31 μmol) and $[Cu(CH_3CN)_4]PF_6$ (2.35 mg, 6.31 μmol) was loaded in an NMR tube. Deuterated dichloromethane was added affording a deep red solution. NMR and other spectroscopic measurements were performed without further purification. Yield: Quantitative. **Melting point:** 284 °C. **IR (KBr):** ν = 3055, 3051, 2925, 2857, 2366, 1587, 1500, 1459, 1391, 1363, 1314, 1197, 1144, 1103, 1024, 842, 734, 625, 557. **^{1}H NMR (400 MHz, CD_2Cl_2):** δ = 6.90 (d, ^4J = 2.0 Hz, 1 H, f-H), 7.04–7.08 (m, 2 H, anth-H), 7.09–7.19 (m, 12 H, anth-, d-, c-H), 7.44–7.48 (m, 5 H, anth-, a-H), 7.53 (dd, ^3J = 8.4 Hz, ^4J = 2.0 Hz, 1 H, e-H), 7.89 (s, 2 H, 9-H), 8.25 (d, ^3J = 8.4 Hz, 2 H, 3-H), 8.32 (d, ^3J = 5.2 Hz, 1 H, b-H), 8.41 (s, 2 H, 5-H), 8.93 (d, ^3J = 8.4 Hz, 2 H, 4-H) ppm. **^{13}C NMR (100 MHz, CD_2Cl_2):** δ = 115.5, 121.7, 124.0, 125.0, 125.1, 125.5, 125.6, 126.6, 126.8, 127.5, 127.8, 128.1, 128.5 (2 C), 128.8, 129.6, 129.7, 130.5, 130.6, 134.4, 137.9, 139.1, 144.4, 145.7, 148.5, 154.9, 156.0, 157.0, 157.5 ppm. **ESI-MS:** *m*/*z* (%): 831.7 (100) $[Cu(2)(6)]^+$. **Elemental analysis** ($C_{49}H_{30}N_5BrCuPF_6 \cdot 1/2CH_2Cl_2$): Calcd C, 58.31; H, 3.06; N, 6.87. Found: C, 58.00; H, 2.94; N, 6.63.

Synthesis of complex 12. $[Cu(CH_3CN)_4]PF_6$ (2.23 mg, 5.98 μmol) was added to a solution of 2,9-dimesityl-1,10-phenanthroline (2.49 mg, 5.98 μmol) in CD_2Cl_2 affording a light yellow solution. 5-Bromo-6′-(pyridazin-3-yl)-2,2′-bipyridine (1.87 mg, 5.97 μmol) was added affording a deep red solution. NMR was measured without further purification. Yield: Quantitative. **Melting point:** 230 °C. **IR (KBr):** ν = 3060, 2952, 2919, 2858, 2366, 2339, 1611, 1580, 1502, 1479, 1448, 1374, 1360, 1103, 1012, 806, 743, 625, 557. **^{1}H NMR (400 MHz, CD_2Cl_2):** δ = 1.64 (bs, 12 H, 7-H), 2.01 (bs, 6 H, 6-H), 6.36 (bs, 4 H, mes-H), 7.45 (dd, ^3J = 8.4 Hz, ^4J = 4.9 Hz, 1 H, b-H), 7.52–7.55 (m, 2 H, g-, i-H), 7.67 (dd, ^3J = 8.0 Hz, ^4J = 0.8 Hz, 1 H, h-H), 7.77 (d, ^3J = 8.4 Hz, 2 H, 3-H), 7.96–7.98 (m, 2 H, c-, f/d-H), 8.03 (dd, ^3J = 7.6 Hz, ^4J = 0.8 Hz, 1 H, d/f-H), 8.12 (dd, ^3J = 8.0 Hz, ^3J = 7.6 Hz, 1 H, e-H), 8.17 (s, 2 H, 5-H), 8.61 (d, ^3J = 8.4 Hz, 2 H, 4-H), 8.89 (dd, ^4J = 4.9 Hz, ^5J = 1.2 Hz, 1 H, a-H) ppm. **^{13}C NMR (100 MHz, CD_2Cl_2):** δ = 20.0 (2 C), 20.9, 121.8, 123.2, 123.3, 124.6, 125.3, 126.4, 127.0 (2 C), 127.1, 127.8 (2 C), 128.2, 135.4, 137.1, 137.5 (2 C), 138.2, 138.3, 139.0, 149.3, 150.8, 151.8, 152.0, 152.6, 154.2, 159.3 ppm. **ESI-MS**: *m*/*z* (%): 792.8 (100) $[Cu(5)(3)]^+$. **Elemental analysis** ($C_{44}H_{37}N_6BrCuPF_6 \cdot 1/4CH_2Cl_2$): Calcd C, 55.39; H, 3.94; N, 8.76. Found C, 55.50; H, 3.85; N, 8.80.

Synthesis of complex 13. $[Cu(CH_3CN)_4]PF_6$ (1.33 mg, 3.57 μmol) was first combined with 2,9-dianthracenyl-1,10-phenanthroline (1.90 mg, 3.57 μmol) in CD_2Cl_2 affording a light yellow hue. 5-Bromo-6′-(pyridazin-3-yl)-2,2′-bipyridine (1.12 mg, 3.58 μmol) was then added to furnish a deep red solution. NMR was measured without purification. Yield: Quantitative. **Melting point:** >275 °C. **IR (KBr):** ν = 3052, 2925, 2365, 2348, 1578, 1500, 1448, 1385, 1263, 1195, 1143, 1102, 1013, 842, 738, 626, 556. **^{1}H NMR (400 MHz, CD_2Cl_2):** δ = 6.48 (dd, ^3J = 7.6 Hz, ^3J = 7.2 Hz, 2 H, anth-H), 6.74 (d, ^3J = 9.2 Hz, 2 H, anth-H), 6.91–6.95 (m, 4 H, anth-H), 7.01–7.12 (m, 6 H, anth-, terpy-H), 7.18–7.22 (m, 1 H, trpy-H), 7.24–7.30 (m, 2 H, trpy-H), 7.42–7.49 (m, 6 H, anth-, terpy-H), 7.58–7.61 (m, 1 H, terpy-H), 7.86 (s, 2 H, 9-H), 8.10 (d, ^3J = 8.4 Hz, 2 H, 3-H), 8.41 (s, 2 H, 5-H), 8.55–8.57 (m, 1 H, a-H), 8.85 (d, ^3J = 8.4 Hz, 2 H, 4-H) ppm. **^{13}C NMR (100 MHz, CD_2Cl_2):** δ = 121.3, 121.7 (2 C), 122.7, 124.7, 125.0, 125.3 (2 C), 125.4, 125.5 (2 C), 126.0, 126.1, 127.5 (2 C), 127.8, 128.1 (2C), 128.2, 128.9, 129.2, 129.6, 130.5, 134.2, 136.8, 137.3, 138.6, 144.8, 148.2, 148.3, 149.2, 151.3, 153.6, 156.9 ppm. **ESI-MS:** *m*/*z* (%): 908.7 (100) $[Cu(4)(5)]^+$. **Elemental analysis** ($C_{54}H_{33}N_6BrCuPF_6 \cdot 1/2CH_2Cl_2$): Calcd C, 59.68; H, 3.12; N, 7.66. Found C, 59.52; H, 2.99; N, 7.85.

Synthesis of complex 14. In an NMR tube 5-bromo-6′-(pyrimidin-4-yl)-2,2′-bipyridine (1.21 mg, 3.86 μmol) was added to a mixture of 2,9-dimesityl-1,10-phenanthroline (1.61 mg, 3.86 μmol) and $[Cu(CH_3CN)_4]PF_6$ (1.44 mg, 3.86 μmol) in CD_2Cl_2 to furnish a clear deep-red solution. NMR was measured without purification. Yield: Quantitative. **Melting point:** 220 °C. **IR (KBr):** ν = 3052, 2918, 2852, 2359, 1613, 1589, 1481, 1441, 1383, 1335, 1298, 1202, 1171, 1066, 997, 842, 749, 703, 556. **^{1}H NMR (400 MHz, CD_2Cl_2):** δ = 1.54 (bs, 6 H, mes-CH_3), 1.64 (bs, 6 H, mes-CH_3), 1.98 (bs, 6 H, mes-CH_3), 6.29 (bs, 2 H, mes-H), 6.35 (bs, 2 H, mes-H), 7.69 (d, ^3J = 8.0 Hz, 1 H, h/g-H), 7.71 (bs, 1 H, i-H), 7.76–7.82 (m, 4 H, a-, c-, 3-H), 8.02 (d, ^3J = 7.2 Hz, 2 H, d-, f-H), 8.10 (t, ^3J = 7.2 Hz, 1 H, e-H), 8.15 (d, ^3J = 8.0 Hz, 1 H, g/h-H), 8.20 (s, 2 H, 5-H), 8.57 (bs, 1 H, b-H), 8.64 (d, ^3J = 8.0 Hz, 2 H, 4-H) ppm. **^{13}C NMR (100 MHz, CD_2Cl_2):** δ = 20.1 (2 C), 20.9, 116.8, 118.3, 122.3, 123.1, 124.5, 124.7, 127.1, 127.2, 128.0, 128.2, 135.1, 135.3, 137.1, 137.7, 138.4, 138.5 (2 C), 139.4, 144.1, 149.2, 150.5, 150.8, 152.6, 157.2, 157.7, 159.3 ppm. **ESI-MS**: *m*/*z* (%): 792.8 (100) $[Cu(4)(5)]^+$. **Elemental analysis** ($C_{44}H_{37}BrCuF_6N_6P \cdot CH_2Cl_2$): Calcd C, 52.83; H, 3.84; N, 8.21. Found C, 53.11; H, 3.68; N, 8.05.

Synthesis of complex 15. 2,9-Dianthracenyl-1,10-phenanthroline (1.96 mg, 3.68 μmol) and $[Cu(CH_3CN)_4]PF_6$ (1.37 mg, 3.68 μmol) were added to an NMR tube followed by CD_2Cl_2. After receiving a clear solution, 5-bromo-6′-(pyrimidin-4-yl)-2,2′-bipyridine (1.15 mg, 3.67 μmol) was added to furnish a deep red colour. All spectroscopic measurements were performed without further purification. Yield: Quantitative. **Melting point:** >270 °C. **IR (KBr):** ν = 3052, 2924, 2854, 1623, 1575, 1502, 1444, 1356, 1291, 1256, 1197, 1149, 1100, 1014,

950, 842, 737, 626, 557. **^{1}H NMR (400 MHz, CD_2Cl_2):** δ = 6.50 (m, 2 H, anth-H), 6.72 (d, ^3J = 8.0 Hz, 2 H, anth-H), 6.92–7.12 (m, 10 H, a-, g-, anth-H), 7.29–7.36 (m, 3 H, c-, f-, d-H), 7.44–7.48 (m, 5 H, h-, anth-H), 7.62 (t, ^3J = 8.0 Hz, 1 H, e-H), 7.69 (s, 1 H, i-H), 7.85 (s, 2 H, 9′-H), 8.16 (d, ^3J = 8.4 Hz, 2 H, 3-H), 8.45 (s, 2 H, 5-H), 8.48 (d, ^3J = 4.8 Hz, 1 H, b-H), 8.90 (d, ^3J = 8.4 Hz, 2 H, 4-H) ppm. **^{13}C NMR (100 MHz, CD_2Cl_2):** δ = 116.9, 117.9, 121.4, 121.8, 122.5, 123.3, 125.0, 125.3, 125.4, 125.8, 126.2, 127.7, 127.8, 128.2, 128.3, 128.4, 129.0, 129.1, 129.6, 130.5 (2 C), 134.0, 137.1, 137.6, 138.6, 144.3, 147.8, 148.0, 148.0, 149.7, 156.7, 157.4, 157.5, 158.0 ppm. **ESI-MS:** *m*/*z* (%): 908.7 (100) $[Cu(\mathbf{4})(\mathbf{6})]^+$. **Elemental analysis** ($C_{54}H_{33}BrCuF_6N_6P\cdot 1/2CH_2Cl_2$): Calcd C, 59.68; H, 3.12; N, 7.66. Found C, 59.38; H, 2.93; N, 7.57.

Synthesis of complex 16. In an NMR tube, complex **10** was first prepared by mixing equimolar amounts of 2,9-dimesityl-1,10-phenanthroline (2.52 mg, 6.05 μmol), 4-(5-bromopyridin-2-yl)pyrimidine (1.43 mg, 6.06 μmol) and $[Cu(CH_3CN)_4]PF_6$ (2.26 mg, 6.06 μmol) in CD_2Cl_2. Then, zinc tetraphenylporphyrin (4.11 mg, 6.06 μmol) was added furnishing a pink solution. The NMR was measured without purification. Yield: Quantitative. **Melting point:** >300 °C. **IR (KBr):** ν = 3049, 3021, 2916, 2855, 2361, 1587, 1480, 1378, 1336, 1201, 1173, 1067, 996, 842, 751, 702, 656, 555. **^{1}H NMR (400 MHz, CD_2Cl_2):** δ = 1.32 (s, 6 H, mes-CH_3), 1.60 (s, 6 H, mes-CH_3), 1.70 (s, 6 H, mes-CH_3), 5.68 (s, 2 H, mes-H), 6.15 (s, 2 H, mes-H), 6.72 (bs, 1 H, b-H), 6.84 (bs, 1 H, a-H), 7.22 (d, ^3J = 5.2 Hz, 1 H, c-H), 7.58 (d, ^3J = 9.6 Hz, 1 H, d-H), 7.71–7.81 (m, 14 H, 3-, b′-, c′-H), 8.00–8.02 (m, 2 H, e-, f-H), 8.17–8.20 (m, 10 H, a′-, 5-H), 8.66 (d, ^3J = 8.0 Hz, 2 H, 4-H), 8.93 (s, 8 H, β-H) ppm. **^{13}C NMR (100 MHz, CD_2Cl_2):** δ = 19.6, 19.8, 20.5, 116.5, 117.0, 121.4, 123.6, 125.1, 126.9 (3 C), 127.1, 127.4, 127.5, 127.8, 128.1, 132.3, 134.7 (2 C), 134.8, 137.0, 138.2, 138.3, 140.3, 143.2, 143.8, 146.8, 149.1, 150.6, 154.1, 154.8, 156.4, 159.3 ppm. **Elemental analysis** ($C_{83}H_{62}N_9BrZnCuPF_6$): Calcd C, 64.76; H, 4.06; N, 8.19. Found C, 64.72; H, 4.20; N, 7.89.

Synthesis of complex 17. Complex **11** (4.54 mg, 3.98 μmol) was prepared first in an NMR tube following the previous procedure. Then zinc tetraphenylporphyrin (2.70 mg, 3.98 μmol) was added furnishing a pink solution. The NMR was measured without purification. Yield: Quantitative. **Melting point:** 270 °C. **IR (KBr):** ν = 3049, 1587, 1485, 1436, 1340, 1200, 1172, 1069, 997, 841, 734, 702, 624, 556. **^{1}H NMR (400 MHz, CD_2Cl_2):** δ = 6.32 (s, 1 H, a-H), 6.42 (t, ^3J = 8.0 Hz, 2 H, 3′/6′-H), 6.53–6.55 (m, 2 H, f-, b-H), 6.77–6.84 (m, 5 H, d-, 4′/5′-, 2′/7′-H), 7.03–7.14 (m, 7 H, c-, anth-H), 7.27 (d, ^3J = 8.4 Hz, 2 H, 1′/8′-H), 7.34–7.37 (m, 3 H, e-, anth-H), 7.67 (s, 2 H, 9′-H), 7.76–7.83 (m, 12 H, b′-, c′-H), 8.20 (d, ^3J = 8.0 Hz, 10 H, 3-, a′-H), 8.41 (s, 2 H, 5-H), 8.89 (d, ^3J = 8.0 Hz, 2 H, 4-H), 8.92 (s, 8 H, β-H) ppm. **^{13}C NMR (100 MHz, CD_2Cl_2):** δ = 115.3, 121.5, 121.6, 124.1, 124.7, 124.9, 125.3, 125.5, 126.4, 126.6, 127.0 (3 C), 127.5, 127.7, 127.9 (2 C), 128.1, 128.2, 128.4, 128.7, 129.3, 129.6, 130.2, 130.4, 132.3 (3 C), 134.0, 134.9 (2 C), 137.9, 139.0, 143.1, 144.2, 145.2, 148.2, 150.5 (2 C), 154.6, 154.8, 155.7, 157.4 ppm. **Elemental analysis** ($C_{93}H_{58}BrCuF_6N_9PZn$) Calcd C, 67.48; H, 3.53; N, 7.62. Found C, 67.36; H, 4.00; N, 7.78.

Synthesis of complex 18. 5-Bromo-6′-(pyrimidin-4-yl)-2,2′-bipyridine (1.55 mg, 4.95 μmol) in CD_2Cl_2 was added to a mixture of 2,9-dimesityl-1,10-phenanthroline (2.06 mg, 4.95 μmol) and $[Cu(CH_3CN)_4]PF_6$ (1.85 mg, 4.96 μmol) in an NMR tube providing a clear deep red solution. Zinc tetraphenylporphyrin (3.36 mg, 4.95 μmol) was then added furnishing a pink solution. All spectroscopic measurements were performed without purification. Yield: Quantitative. **Melting point:** >270 °C. **IR (KBr):** ν = 3052, 2918, 2852, 2359, 1613, 1589, 1481, 1441, 1383, 1335, 1298, 1202, 1171, 1066, 997, 842, 749, 703, 556. **^{1}H NMR (400 MHz, CD_2Cl_2):** δ = 1.02 (bs, 6 H, mes-CH_3), 1.44 (bs, 6 H, mes-CH_3), 1.78 (s, 6 H, mes-CH_3), 5.70 (bs, 1 H, mes-H), 5.86 (s, 1 H, mes-H), 5.97 (s, 1 H, mes-H), 6.18 (bs, 2 H, mes-, a-H), 7.04 (d, ^3J = 4.4 Hz, 1 H, b-H), 7.42 (s, 1 H, i-H), 7.46 (d, ^3J = 8.4 Hz, 1 H, g/h-H), 7.59 (d, ^3J = 8.0 Hz, 1 H, d/f-H), 7.70 (d, ^3J = 8.0 Hz, 2 H, 3-H), 7.73–7.81 (m, 14 H, b′-, c′-, h/g-, c-H), 7.84 (d, ^3J = 8.0 Hz, 1 H, f/d-H), 7.95 (t, ^3J = 8.0 Hz, 1 H, e-H), 8.12 (s, 2 H, 5-H), 8.19 (d, ^3J = 8.0 Hz, 8 H, a′-H), 8.56 (d, ^3J = 8.0 Hz, 2 H, 4-H), 8.93 (s, 8 H, β-H) ppm. **^{13}C NMR (100 MHz, CD_2Cl_2):** δ = 19.8 (2 C), 20.7, 117.4, 121.4 (2 C), 122.0, 123.1, 124.1, 125.1, 126.9 (2 C), 127.0 (2 C), 127.8 (2 C), 128.0, 132.3 (2 C), 134.9 (2 C), 136.8, 137.7, 138.3, 138.4, 139.2, 143.2 (2 C), 143.8, 149.1, 149.7, 150.6 (2 C), 151.0, 152.7, 155.1, 158.9, 159.3 ppm. **Elemental analysis** ($C_{88}H_{65}BrCuF_6N_{10}PZn\cdot CH_2Cl_2$): Calcd C, 62.83; H, 3.97; N, 8.23. Found: C, 63.17; H, 3.82; N, 8.00.

Formation of unlocked complex $[Cu(5)(19)]^+$

In an NMR tube, $[Cu(CH_3CN)_4]PF_6$ (993 μg, 2.66 μmol) was added to a solution of 2,9-dimesityl[1,10]phenanthroline (1.11 mg, 2.66 μmol) in CD_2Cl_2. Compound **19** (3.66 mg, 2.66 μmol) was then added to the solution and the mixture was sonicated for 2–3 minutes. Spectroscopic measurements were performed without further purification. **Yield:** Quantitative. **Melting point**: >300 °C. **IR (KBr):** ν = 3045, 2916, 2852, 2363, 2339, 2209, 1611, 1583, 1508, 1478, 1456, 1377, 1331, 1201, 1062, 996, 840, 798, 556. **^{1}H NMR (400 MHz, CD_2Cl_2):** δ = 1.47 (s, 6 H, 8-H), 1.54 (s, 12 H, 7-H), 1.69 (s, 12 H, p′-,n′-H), 1.74 (s, 6 H, o′-H), 2.52 (s, 3 H, o-H), 2.57 (s, 6 H, s′-, q′-H), 2.59 (s, 3 H, r′-H), 5.59 (s, 2 H, 6/9-H), 6.03 (s, 2 H, 9/6-H), 6.60 (bs, 1 H, b-H), 6.72 (bs, 1 H, a-H), 7.05 (d, ^3J = 4.0 Hz, 1 H, c-H), 7.17 (d, ^3J = 8.0 Hz, 2 H, k/l-H), 7.20 (bs, 4 H, m′-, k′-H), 7.25 (bs, 2 H, l′-H), 7.26 (d, ^3J = 8.0 Hz, 2 H, l/k-H), 7.31–7.37 (m, 2 H, i-, h-H), 7.48–7.50 (m, 1 H, g-/j-H), 7.52–7.54 (m, 1 H, j/g-H), 7.56–7.59 (m, 3 H, 3-, d-H), 7.66 (s, 2 H, m-, n-H), 7.86–7.90 (m, 3 H, e-, a′/b′-H), 7.96 (s, 1 H, f-H), 8.10 (s, 2 H, 5-H), 8.13 (d, ^3J = 7.6 Hz, 2 H, b′/a′-H), 8.51 (d, ^3J = 7.6 Hz, 2 H, 4-H), 8.63–8.67 (m, 6 H, e′-, f′-, g′-H), 8.78 (d, ^3J = 4.4 Hz, 2 H, h′-H) ppm. **^{13}C NMR (150 MHz, CD_2Cl_2):** δ = 19.5, 19.8, 20.5, 21.4, 21.5 (2 C), 21.7 (2 C), 21.9, 88.3, 89.2, 89.9, 90.3, 93.2, 94.8, 96.3, 97.0, 107.7, 116.3, 116.4, 119.0, 119.1, 119.2, 122.1, 122.4, 123.3, 123.4, 124.0, 124.5, 124.9, 126.0, 126.8, 127.3 (2 C), 127.4, 127.6, 127.7, 128.0 (3 C), 129.0, 130.0, 130.2, 131.0, 131.4, 131.5, 131.6, 131.7, 132.1, 132.3, 132.4, 132.6, 133.9, 134.3, 134.7, 135.0, 136.7, 137.9, 138.0, 138.1, 138.2, 139.2 (3 C), 141.1, 143.6, 144.4, 146.4, 149.9, 150.1, 150.2, 150.3,

150.4, 154.1, 154.5, 156.7, 159.1 ppm. **ESI-MS:** *m*/*z* (%): 1857.4 (100) $C_{119}H_{92}BrCuN_9Zn$, calcd **MS** *m*/*z* 1857.5. **Elemental analysis** ($C_{119}H_{92}N_9BrCuF_6ZnP{\cdot}CH_2Cl_2$): Calcd C, 69.07; H, 4.54; N, 6.04. Found C, 69.16; H, 4.75; N, 6.42.

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