Electronic Supporting Information

for

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

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$^1$H, $^{13}$C, and COSY Spectra of Complexes:

**Figure S1**: $^1$H NMR spectrum (400 MHz) of complex 8 in CD$_2$Cl$_2$ at 298 K.

**Figure S2**: Partial $^1$H-$^1$H COSY spectrum (400 MHz) of complex 8 in CD$_2$Cl$_2$ at 298 K.
Figure S3: $^1$H NMR spectra (400 MHz) of [Cu(MeCN)$_4$]PF$_6$ and 5 (1:1) in CD$_2$Cl$_2$ at 298 K with (top) 0.5 equiv. of 1 being added, and (bottom) with a total of 1.0 equiv. of 1 being added affording complex 8.

Figure S4: $^{13}$C NMR spectrum (100 MHz) of complex 8 in CD$_2$Cl$_2$ at 298 K.
Figure S5: $^1$H NMR spectrum (400 MHz) of complex 9 in CD$_2$Cl$_2$ at 298 K.

Figure S6: $^1$H-$^1$H COSY spectrum (400 MHz) of complex 9 in CD$_2$Cl$_2$ at 298 K.
Figure S7: $^1$H NMR spectra (400 MHz) of [Cu(MeCN)$_4$]PF$_6$ and 6 (1:1) in CD$_2$Cl$_2$ at 298 K with (top) 0.5 equiv. of 1 being added, and (bottom) with a total of 1.0 equiv. of 1 being added affording complex 9.

Figure S8: $^{13}$C NMR spectrum (100 MHz) of complex 9 in CD$_2$Cl$_2$ at 298 K.
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Figure S 11: $^1$H NMR spectra (400 MHz) of [Cu(MeCN)$_4$]PF$_6$ and 5 (1:1) in CD$_2$Cl$_2$ at 298 K with (top) 0.5 equiv. of 2 being added, and (bottom) with a total of 1.0 equiv. of 2 being added affording complex 10.

Figure S12: $^{13}$C NMR spectrum (100 MHz) of complex 10 in CD$_2$Cl$_2$ at 298 K.
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**Figure S14**: $^1$H-$^1$H COSY spectrum (400 MHz) of complex 11 in CD$_2$Cl$_2$ at 298 K.
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**Figure S16:** $^{13}$C NMR spectrum (100 MHz) of complex 11 in CD$_2$Cl$_2$ at 298 K.
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**Figure S18:** Partial $^1$H-$^1$H COSY spectrum (400 MHz) of complex 12 in CD$_2$Cl$_2$ at 298 K.
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Figure S20: $^{13}$C NMR spectrum (100 MHz) of complex 12 in CD$_2$Cl$_2$ at 298 K.
**Figure S21**: $^1$H NMR spectrum (400 MHz) of complex 13 in CD$_2$Cl$_2$ at 298 K.

**Figure S22**: $^1$H-$^1$H COSY spectrum (400 MHz) of complex 13 in CD$_2$Cl$_2$ at 298 K.
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Figure S29: $^1$H NMR spectra (400 MHz) of 4 and 6 (1:1) in CD$_2$Cl$_2$ at 298 K with (top) 0.5 equiv. of [Cu(MeCN)$_4$]PF$_6$ being added, and (bottom) with a total of 1.0 equiv. of [Cu(MeCN)$_4$]PF$_6$ being added affording complex 15.
Figure S30: $^{13}$C NMR spectrum (100 MHz) of complex 15 in CD$_2$Cl$_2$ at 298 K.

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Figure S32: Partial $^1$H-$^1$H COSY spectrum (400 MHz) of complex 16 in CD$_2$Cl$_2$ at 298 K.

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Figure S38: $^{13}$C NMR spectrum (100 MHz) of complex 18 in CD$_2$Cl$_2$ at 298 K.
Figure S39: $^1$H NMR spectra (400 MHz) in CD$_2$Cl$_2$ at 298 K of (top) complex 8, and (bottom) complex 8 in presence of ZnTPP (7). Congruent blue coloured peaks for 1 in both spectra (see a-H and b-H) indicate that 1 is not axially coordinated to the added ZnTPP.

Figure S40: $^1$H NMR spectra (400 MHz) in CD$_2$Cl$_2$ at 298 K of (top) complex 9, and (bottom) complex 9 in presence of ZnTPP (7). Congruent blue coloured peaks for 1 in both spectra (see a-H and b-H) indicate that 1 is not axially coordinated to the added ZnTPP.
**Figure S41:** $^1$H NMR spectra (400 MHz) in CD$_2$Cl$_2$ at 298 K of (top) complex 12, and (bottom) complex 12 in presence of ZnTPP. The different shifts (blue colour) for 3 in both spectra (see a-H and b-H) indicate that 3 is axially coordinated to the added ZnTPP.

**Figure S42:** $^1$H NMR spectra (400 MHz) in CD$_2$Cl$_2$ at 298 K of (top) complex 13, and (bottom) complex 13 in presence of ZnTPP. The different shifts (blue colour) for 3 in both spectra (see a-H and b-H) indicate that 3 is axially coordinated to the added ZnTPP.
Figure S43: $^1$H NMR spectrum (400 MHz) of complex 20 in CD$_2$Cl$_2$ at 298 K.
Figure S44: Concentration dependence of the $^1$H NMR (400 MHz) shifts of protons a-H and b-H at the bipy unit in complex 20. The downfield shift with decreasing concentration points to intermolecular coordination.

Figure S45: $^{13}$C NMR spectrum (150 MHz) of unlocked complex 20 in CD$_2$Cl$_2$ at 298 K.
Figure S46: Partial $^1$H NMR spectrum (400 MHz) showing reversible switching between the open and closed form. (A) Only nanoswitch 19. (B) 19 after addition of one equivalent of [Cu(5)]$^{+}$. (C) After addition of one equivalent of cyclam to solution B. Only the characteristics protons a-H, b-H, and mes-H are shown.
**DOSY Spectra of Complexes:**

![DOSY Spectrum](image)

**Figure S47:** DOSY spectrum (400 MHz) of complex 10 at 298 K.
Figure S48: DOSY spectrum (400 MHz) of complex 16 at 298 K.
ESI-MS of Complexes:

Figure S49: ESI-MS of complex 8.
Figure S50: ESI-MS of complex 9.
Figure S51: ESI-MS of complex 10.
Figure S52: ESI-MS of complex 11.
Figure S53: ESI-MS of complex 12.
Figure S54: ESI-MS of complex 13.
Figure S55: ESI-MS of complex 14.
Figure S56: ESI-MS of complex 15.