Supporting Information

Di- and Tetranclear Transition Metal Complexes of a Tetrakisguanidino-Substituted Phenazine Dye by Stepwise Coordination

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Comparison between the results from TD-DFT calculations and the measured UV/Vis spectra as well as assignment of the lowest-energy electronic transitions

Figure S1 a) Comparison between the experimentally obtained electronic absorption spectrum for \([\text{I(NiCl}_2]\) dissolved in CH\(_3\)CN solution (—) and a simulation (- - -) based on a TD-DFT calculation at the B3LYP-D3/def2-TZVP level; b) Isodensity surfaces of the orbitals contributing to the two most-intense bands at 448 (black) and 472 nm (red).
Figure S2 a) Comparison between the UV/Vis spectrum for [1+2Bn]Br₂ in CH₃CN solution (—) and a simulation (- - -) based on TD-DFT calculations at the B3LYP-D3/def2-TZVP level; b) Isodensity surfaces of the orbitals contributing to the band at 525 nm.

Figure S3 a) Comparison between the UV/Vis spectrum of [1(NiCl₂)₂(CuCl(CH₃CN))]₂ in CH₃CN solution (—) and a simulation (- - -) based on a TD-DFT calculations on the B3LYP-D3/def2-TZVP level. b) Isodensity surfaces of the orbitals contributing to the band at 516 nm.

Photos of solutions of 1, [1(CuCl₂)₂], [1(NiCl₂)₂] and [1+2Bn]Br₂ (from left to right) in CH₃CN.
Analytical data for all compounds

EPR spectra for $[1(CuCl_2)_2]$

**Figure S4** EPR-spectrum (RT, solid): $g_1 = 2.216$, $g_2 = 2.096$, $g_3 = 2.057$ ($\nu = 9.638289 \text{ GHz}$).

**Figure S5** EPR-spectrum (RT, CH$_2$Cl$_2$ solution): $g = 2.120$ ($\nu = 9.63795 \text{ GHz}$).
Absorption and emission spectra for 1

Figure S6 Electronic absorption (red) and emission (black) spectra for 1 in the solid material, in CH$_3$CN solution, in an Ar matrix (4 K) as well as calculated (B3LYP/TZVP) absorption spectra without and with simulation of the solvent effect by COSMO ($\epsilon_r = 37.5$).
Analytical data for [1+2R]Br₂

Figure S7 $^1$H NMR spectrum (600 MHz) of [1+2Bn]Br₂ dissolved in CD₃CN.

Figure S8 $^1$H NMR spectrum (600 MHz) of [1+2(p-NO₂Bn)]Br₂ dissolved in CD₃CN.
Figure S9 $^1$H NMR (400 MHz) of [1+2(F$_3$Bn)]Br$_2$ dissolved in DMSO-$d_6$.

Figure S10 $^1$H NMR (600 MHz) of [1+2(m-MeOBn)]Br$_2$ dissolved in CD$_3$CN.
**Analytical data for [2+Bn]Br**

![Graph 1](image1)

**Figure S11** Electronic absorption and emission spectra (normalized) of [2+Bn]Br in CH$_3$CN and a simulation based on TD-DFT calculations at the B3LYP/TZVP level.

![Graph 2](image2)

**Figure S12** $^1$H NMR spectrum (600 MHz) of [2+Bn]Br dissolved in CD$_3$CN.
EPR spectrum for [1(CuCl)$_2$(CuCl)$_2$]

**Figure S13** EPR spectrum of [1(CuCl)$_2$(CuCl)$_2$] in a frozen CH$_2$Cl$_2$ solution at 35 K. The fit was obtained with the following parameters: $g_\parallel = 2.258$, $g_\perp = 2.072$, $A_\parallel = 75$ G, $A_\perp = 25$ G.
Analytical data for $[1(NiCl_2)_2(CuCl(CH_3CN))_2]$  

**Figure S14** $^1$H NMR spectra (200 MHz) of $[1(NiCl_2)_2]$ (bottom) and $[1(NiCl_2)(CuCl(CH_3CN))_2]$ (top) dissolved in CD$_3$CN.

**Figure S15** Variable temperature $^1$H NMR spectra from 300 to 340 K (from bottom to top) of $[1(NiCl_2)_2]$ dissolved in CD$_3$CN.
Figure S16 Variable temperature $^1$H NMR spectra from 300 to 340 K (from bottom to top) of [1(NiCl$_2$)$_2$(CuCl(CH$_2$CN))$_2$] dissolved in CD$_2$CN.
Analytical data for [2(NiCl₂)]

Figure S17 UV/Vis spectrum of [2(NiCl₂)] dissolved in CH₃CN.

Figure S18 Structure of the complex [2(NiCl₂)]. Vibrational ellipsoids drawn at the 50% probability level. Hydrogen atoms omitted for clarity. Selected structural parameters (bond distances in Å, angles in °): Ni-Cl1 2.2302(18), Ni-Cl2 2.2294(17), Ni-N1 1.991(4), Ni-N4 1.986(4), N1-C1 1.369(7), N1-C13 1.338(7), N4-C2 1.397(7), N4-C18 1.334(7), (Cl1-Ni-Cl2, N1-Ni-N4) 68.86.
Section of the mixed-valent coordination polymer [1(CuCl)2(CuCl)]n. A ball-and-stick representation is shown. Hydrogen atoms omitted for clarity. Selected structural parameters (bond distances in Å, angles in °): Cu1-N1 1.987(4), Cu1-N4 1.964(4), Cu1-C11 2.2420(14), Cu1-C12 2.2265(15), Cu2-N7 1.981(5), Cu2-C13 2.102(3), Cu2-C13' 2.669(3), N1-C1 1.388(6), N1-C7 1.342(6), N4-C2 1.368(7), N4-C12 1.329(7), N1-Cu1-N4 82.21(17), Cl1-Cu1-Cl2 99.45(6), N7-Cu2-Cl3 152.69(16), N7-Cu2-Cl3' 118.33(15), Cl3-Cu-C13' 88.88(9). Please note that the crystals were of bad quality. Therefore, the structural parameters are afflicted with a large error.

Crystal data: C33.8H55.6Cl8.6Cu3N14: Mr = 1153.61, 0.50 × 0.20 × 0.10 mm3, monoclinic, space group C2/c, a = 21.862(4), b = 24.311(5), c = 14.152(3) Å, β = 117.18(3)°, V = 6691(3) Å3, Z = 4, dcalc = 1.145 Mg m–3, Mo-Kα radiation (λ = 0.71073 Å), T = 100 K, θrange 4.2 to 60.00°. Reflections measured. 55915, indep. 9742, Rint = 0.1217. Final R indices [I > 2s(I)]: R1 = 0.0842, wR2 = 0.2351.

Figure S19
SQUID data for [1(NiCl$_2$)$_2$]
Fit parameters: $J = 1.534; \ g_1 = g_2 = 2.07; \ D_1 = D_2 = 11.917; \ E/D_1 = E/D_2 = 2.091$