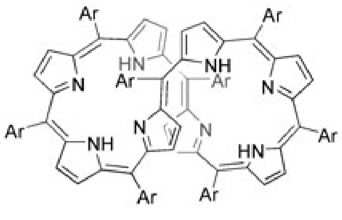
Metalloporphyrinoids

Dicopper and Disilver Complexes of Octaphyrin(1.1.1.1.1.1.1.1): Reversible Hydrolytic Cleavage of the Pyrrolic Ring to a Keto–Imine**

*Soji Shimizu, Yasuo Tanaka, Katsuyuki Youfu, and Atsuhiro Osuka**

Of the various expanded porphyrins developed in recent years,[1] octaphyrins hold a unique position in view of their dynamic figure-of-eight conformations as well as their ability to coordinate two metal ions,[2] while some octaphyrins are known to be planar and aromatic.[3] Curiously, the metalation of figure-of-eight octaphyrins is often accompanied by rather unexpected skeletal rearrangements.[4] Vogel et al. revealed an interesting equilibrium of the dipalladium complex of octaphyrin(1.1.1.0.1.1.1.0) and its bis-spiro derivative, and isolated the dinickel complex of a spirodicorrole upon metalation of dioxooctaphyrin(1.1.1.0.1.1.1.0).[5] Both processes involved large skeletal rearrangements. We also reported that complexation of [36]octaphyrin(1.1.1.1.1.1.1.1) **1** with copper provided the dicopper(II) complex **2**, which underwent a quantitative thermal splitting reaction into two copper(II) porphyrins, **3**, through an unprecedented metathesis that involved the scission and formation of at least two carbon–carbon bonds.[6] This reaction is thought to be driven by severe distortion of the complex **2**. Herein, we report the dimetalation of perfluorinated [36]octaphyrin(1.1.1.1.1.1.1.1) **4**[7] with copper(II) ions which leads to unusual hydrolytic ring opening of one pyrrole ring to give the keto–imine form. We also report facile dimetalations of **1** and **4** with silver ions to quantitatively provide figure-of-eight disilver complexes.



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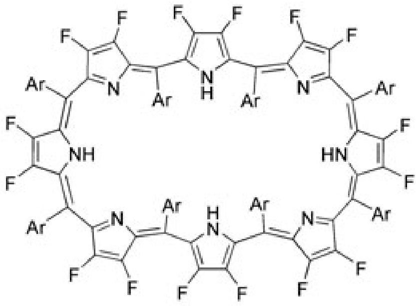

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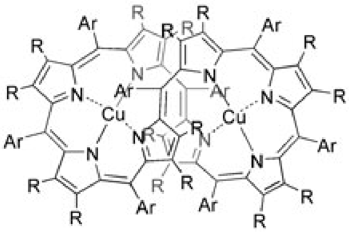
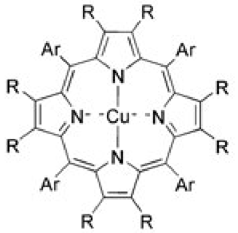


2: R = H
6: R = F



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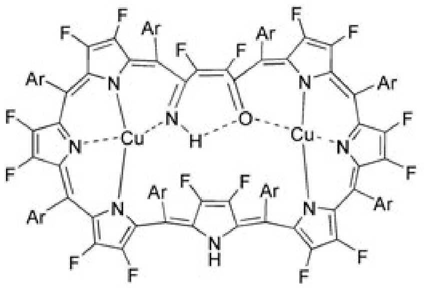
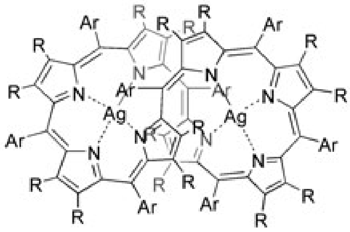


5



8: R = H
9: R = F

Ar = pentafluorophenyl

A solution of **4** in CH$_2$Cl$_2$ was stirred with Cu(OAc)$_2$ (50 equiv) and NaOAc for 6 hours at room temperature to provide two dicopper complexes, **5** and **6**, in respective yields of 58 and 14%. The parent-ion peak in the ESI-TOF (electrospray ionization/time of flight) mass spectrum for complex **5** was observed at $m/z = 2375$ ([$M-$H]$^-$), which is 16 mass units larger than the expected mass of a dicopper complex (see Table 1). The absorption spectrum of **5** comprises a broad band at 396 nm and a less intense band at 699 nm and is significantly different from that of **4** (Figure 1). The crystal structure of **5** was determined by single crystal X-ray diffraction analysis and is shown in Figure 2.[8] The complex exhibits a bent U-shaped ellipsoidal conformation, in which one pyrrole ring is hydrolytically cleaved to give a keto–imine. One of the two copper ions (Cu1) is bound to the keto-carbonyl oxygen atom (O1) and the nitrogen atoms of the nearby tripyrrolic subunit, while Cu2 is bound to the imine nitrogen atom (N5) and the nearby second tripyyrolic subunit. The coordination-bond lengths are in the range of 1.92–2.02 Å, and the distance between the two Cu ions is 5.41 Å.

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Table 1: Selected physical data for **5**, **8**, and **9**.

5: UV/Vis (CH_2Cl_2): λ_{max} (ε): 396 (6.25), 699 nm (2.16×10^{-4} $M^{-1}cm^{-1}$); HRMS (ESI-TOF): *m/z* calcd for $C_{88}N_8F_{56}OCu_2H$: 2374.7966; found: 2374.7966 (100%) $[M-H]^-$.

8: ^1H NMR (600.17 MHz, $CDCl_3$, 298 K): $\delta=7.98$ (d, $J=5.0$ Hz, 2H), 6.82 (d, $J=4.1$ Hz, 2H), 6.81 (d, $J=4.1$ Hz, 2H), 6.58 (d, $J=5.0$ Hz, 2H), 6.57 (d, $J=4.6$ Hz, 2H), 6.51 (d, $J=5.0$ Hz, 2H), 6.26 (d, $J=4.6$ Hz, 2H), 5.64 ppm (dd, $J_1=3.9$ Hz, $J_2=4.1$ Hz, 2H); ^{19}F NMR (564.73 MHz, $CDCl_3$, 298 K, C_6F_6): $\delta=-131.14$ (d, $J=22.5$ Hz, 2F; *o*-F), −136.28 (d, $J=22.5$ Hz, 2F; *o*-F), −136.86 (d, $J=19.1$ Hz, 2F; *o*-F), −138.10 (br d, $J=82.4$ Hz, 2F; *o*-F), −138.72 (m, 4F; *o*-F), −139.61 (d, $J=15.6$ Hz, 2F; *o*-F), −142.86 (s, 2F; *o*-F), −151.31 (t, $J=19.1$ Hz, 2F; *p*-F), −152.39 (t, $J=20.8$ Hz, 2F; *p*-F), −152.57 (t, $J=20.8$ Hz, 2F; *p*-F), −152.73 (br s, 2F; *p*-F), −160.30 (m, 2F; *m*-F), −161.32 (m, 2F; *m*-F), −161.53 (m, 4F; *m*-F), −161.77 (m, 2F; *m*-F), −162.37 (br s, 2F; *m*-F), −163.26 (m, 2F; *m*-F), −166.23 ppm (br d $J=93.2$ Hz, 2F; *m*-F); UV/Vis (CH_2Cl_2): λ_{max} (ε): 408 (0.57), 780 (0.88), 1151 nm (0.08×10^{-5} $M^{-1}cm^{-1}$); HRMS (ESI-TOF): *m/z* calcd for $C_{88}H_{16}N_8F_{40}Ag_2$: 2157.8967; found: 2157.8963 (100%) $[M]^-$.

9: ^{19}F NMR (564.73 MHz, $CDCl_3$, 298 K, C_6F_6): $\delta=-131.01$ (d, $J=22.4$ Hz, 2F; *o*-F), −136.68 (s, 2F; β-F), −137.94 (d, $J=22.5$ Hz, 2F; *o*-F), −138.85 (d, $J=100.1$ Hz, 2F; β-F), −139.35 (d, $J=19.0$ Hz, 2F; *o*-F), −139.72–−139.99 (m, 6F; *o*-F), −141.40 (dd, $J_1=15.5$ Hz, $J_2=88.8$ Hz, 2F; *o*-F), −141.43 (s, 2F; β-F), −143.19 (s, 2F; β-F), −143.35 (d, $J=20.7$ Hz, 2F; *o*-F), −143.80 (s, 2F; β-F), −144.19 (s, 2F; β-F), −144.91 (s, 2F; β-F), −147.86 (s, 2F; β-F), −148.66 (t, $J=17.3$ Hz, 2F; *p*-F), −149.47–−149.66 (m, 6F; *p*-F), −160.15 (m, 2F; *m*-F), −160.95 (m, 4F; *m*-F), −161.20 (m, 2F; *m*-F), −161.38 (m, 2F; *m*-F), −161.63 (m, 2F; *m*-F), −161.87 (br d, $J=82.9$ Hz, 2F; *m*-F), −163.42 ppm (br s, 2F; *m*-F); UV/Vis (CH_2Cl_2): λ_{max} (ε): 328 (0.47), 422 (0.73), 791 nm (1.24×10^{-5} $M^{-1}cm^{-1}$); HRMS (ESI-TOF): *m/z* calcd for $C_{88}N_8F_{56}Ag_2$: 1222.8721; found: 1222.8714 (100%) $[M]^{2-}$.

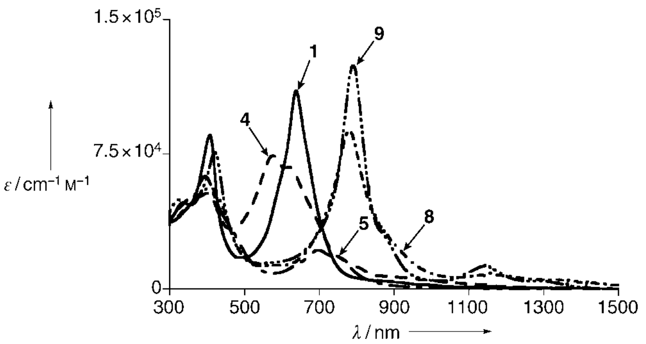

Figure 1. UV/Vis absorption spectra of **1** and **4**, and complexes **5**, **8**, and **9** in CH_2Cl_2.

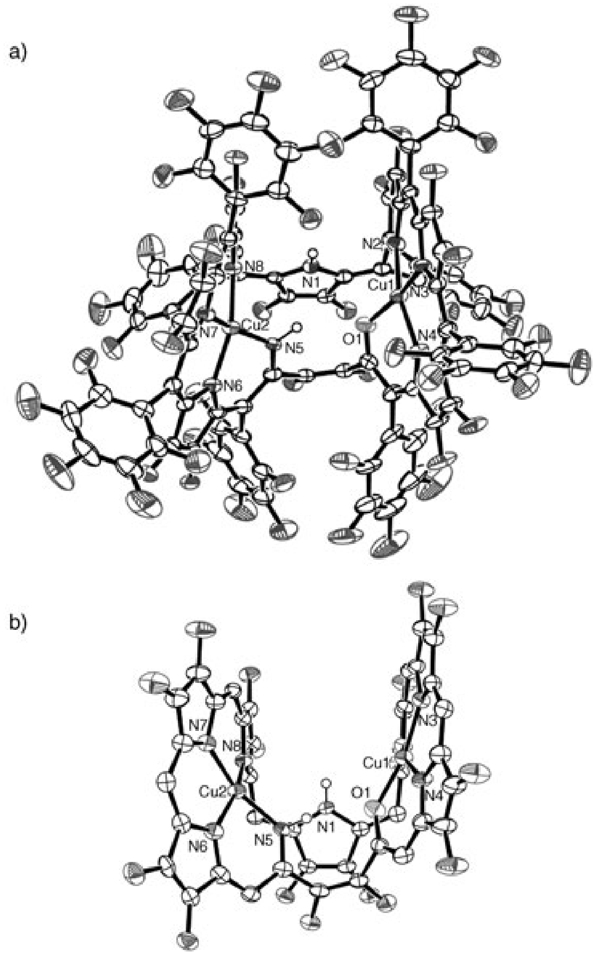

Figure 2. X-ray crystal structure of **5**: a) top view and b) side view. The thermal ellipsoids are scaled to the 50% probability level. Solvent molecules are omitted in the top view while *meso*-pentafluorophenyl substituents are also omitted in the side view for clarity.

Coordination features of the two copper ions in **5** are likely closer to a square-planar geometry than the highly distorted structure of **2**. The mean planes defined by Cu1, N2, N3, and N4, and by Cu2, N6, N7, and N8, are relatively flat and almost parallel to each other. The ligating carbonyl oxygen atom O1 and imine nitrogen atom N5 are somewhat deviated from these planes (O1 by 0.8 Å; N5 by 1.2 Å). Interestingly, **5** was quantitatively demetalated to give **4** upon treatment with trifluoroacetic acid and H_2SO_4 with concomitant recyclization of the keto–imine unit to the pyrrole ring. Measurement of the magnetic susceptibility (χ) by SQUID revealed that the copper ions in **5** were both present as paramagnetic d^9 forms of Cu^{II} ($\chi_pT=0.81$ emu K mol^{-1} at room temperature), in accord with the crystal structure.[9]

The minor product **6** exhibits an absorption spectrum that is quite similar to that of **2** (see Supporting Information), and its high-resolution ESI-MS spectrum showed a peak for the molecular ion at $m/z=2357.7978$ (calcd for $C_{88}N_8F_{56}Cu_2=2357.7938$) with the expected isotopic peak pattern. Although efforts to obtain suitable crystals of **6** for X-ray analysis were unsuccessful, these data suggest that **6** is a dicopper complex that adopts a figure-of-eight structure, similar to **2**. Upon heating complex **6** in solution, it underwent hydrolysis to give **5** with concomitant decomposition, whereas, interestingly, thermolysis of **6** in the solid state led to its splitting into perfluorinated Cu^{II} porphyrin **7**.[10] One possible route to **5** may be through initial formation of **6** followed by subsequent hydrolytic ring opening of one pyrrole ring, facilitated by the strongly electron-deficient nature of the perfluorinated macrocycle in **6**.

Among the transition-metal salts tested, we found that complexation of **1** and **4** with salts of silver(I), a heavier congener of copper, proceeded smoothly without any rearrangement of the macrocyclic ring, in sharp contrast to dimetalation with copper, to provide disilver(I) complexes. A solution of **1** in a mixture of $CHCl_3$ and methanol (3:1) was heated at reflux in the presence of AgOAc (10 equiv) for 15 minutes. Disilver complex **8** was obtained as a blue solid in 98% yield. The parent-ion peak for this complex appeared at $m/z = 2158$ (M^-; calcd for $C_{88}H_{16}N_8F_{40}Ag_2 = 2158$) in the ESI-TOF mass spectrum (see Table 1). The structure of **8** was revealed by single-crystal X-ray diffraction analysis (Figure 3) to adopt a near-C_2-symmetric figure-of-eight conformation, in which two silver ions are each bound within porphyrin-like hemicyclic cavities with Ag–N bond distances in the range of 2.27–2.37 Å.[11] Tripyrrolic units consisting of pyrroles A, B, and C, and E, F, and G are relatively flat, while pyrroles D and H are tilted by 33 and 43°, respectively, from these planes. As a consequence, the structure of **8** is rather distorted from square-planar geometry, but the extent of this distortion is modest relative to **2**. Interestingly, pentafluorophenyl substituents at the crossing *meso* position lie just over the silver atoms in parallel with the tripyrrolic units, with an interplanar distance of approximately 3.2 Å, while pyrroles D and H are placed below silver ions with Ag–βC distances of 2.89 and 2.87 Å, respectively. Relative to the structures of silver complexes of porphyrins and porphyrinoids,[12] relatively long Ag–N distances lead to the assignment of **8** as a disilver(I) complex of [34]octaphyrin(1.1.1.1.1.1.1.1).

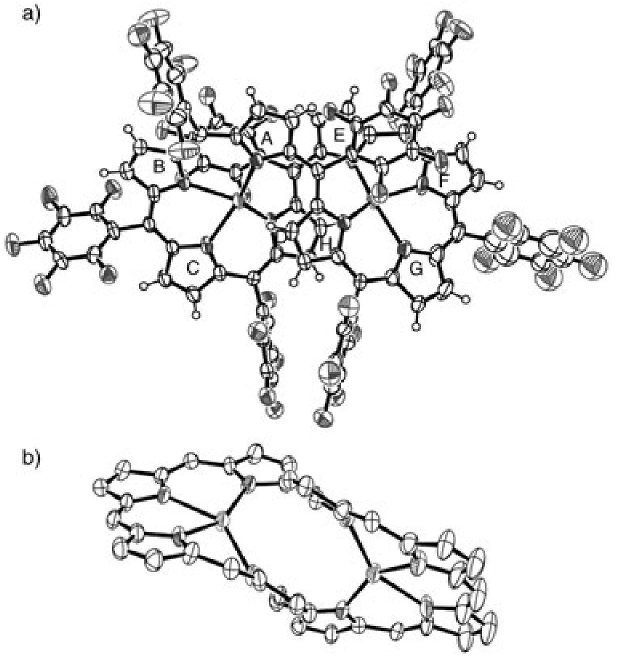

Figure 3. X-ray crystal structure of **8**: a) top view and b) side view. The thermal ellipsoids are scaled to the 50% probability level. Solvent molecules are omitted in the top view while *meso*-pentafluorophenyl substituents and β-hydrogen atoms are also omitted in the side view for clarity.

In accord with this assignment, the ^1H NMR spectrum of **8** revealed eight sharp signals for the peripheral β protons of which seven signals were observed as doublets in the range of $\delta = 7.98$–6.26 ppm and one signal was observed at $\delta =$ 5.64 ppm as a double-doublet. The observed double-doublet signal cannot be explained by considering only proton–proton coupling, but can be accounted for in terms of additional through-space coupling with the proximal Ag^I ion as the Ag^I ion ($I = 1/2$) is placed close to the β-CH protons of pyrroles D and H (see Supporting Information). In the ^{19}F NMR spectrum of **8**, the peaks from the *ortho* and *meta* fluorine atoms that are close to the Ag^I ions are split similarly.[13] While the absorption spectrum of **1** displayed a broad Soret-like band at 638 nm, the spectrum of **8** displayed Soret-like bands at 408 and 780 nm and a Q-like band at 1151 nm, probably reflecting the 34-π-electron system of the macrocycle. As an excess of AgOAc was needed for complete metalation, the initial step may be silver(I)-promoted oxidation of [36]octaphyrin to [34]octaphyrin, which then may bind two Ag^I ions inside the porphyrin-like hemi-macrocycles.

In an analogous manner, treatment of **4** with CF_3COOAg (10 equiv) in a mixture of CH_2Cl_2 and methanol (10:1) for 40 minutes at room temperature provided almost quantitatively the disilver complex **9** as a dark green solid. Complex **9** displayed its parent-ion peak at $m/z = 2445$ [M^-] in the ESI-TOF mass spectrum and its ^{19}F NMR spectrum revealed sharp signals, which indicate its diamagnetic nature and a C_2-symmetric structure in solution (see Table 1). The absorption spectrum of **9** displayed bands at 422 and 791 nm and Q-band-like bands at 1143 and 1287 nm (Figure 1). The final structural confirmation of **9** was provided by single-crystal X-ray analysis.[14] As shown in Figure 4, complex **9** has a figure-of-eight conformation in the solid state which is quite similar to that of **8**. Pyrrole rings D and H are located below the silver

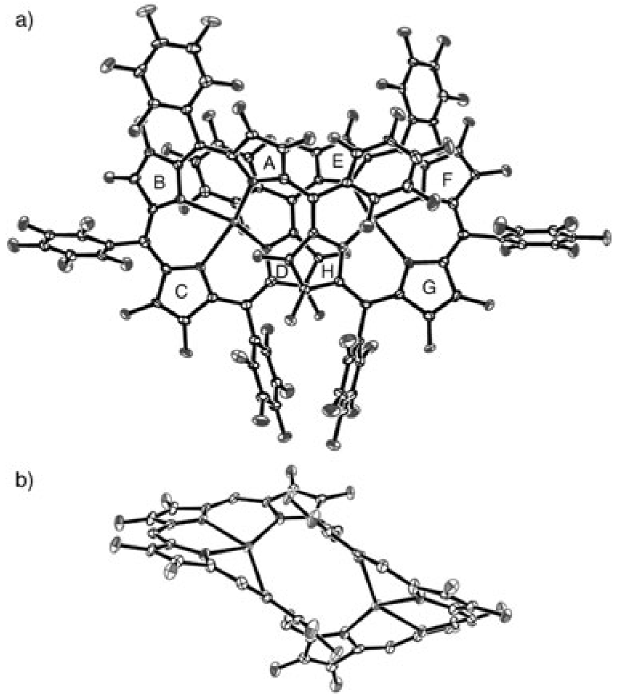

Figure 4. X-ray crystal structure of **9**: a) top view and b) side view. The thermal ellipsoids are scaled to the 50% probability level. Solvent molecules are omitted in the top view while *meso*-pentafluorophenyl substituents are also omitted in the side view for clarity.

ions on the opposite hemi-macrocycle with their pyrrolic β-fluorine atoms close to the silver ion, while the pentafluorophenyl substituents at the *meso* positions between pyrroles D and E and between pyrroles A and H also lie close to the silver ions. These structural features lead to through-space coupling of the related fluorine atoms with silver ions.[15] The Ag–N bond distances are in the range of 2.27–2.40 Å. We thus assigned complex **9** as a disilver(I) complex of perfluorinated [34]octaphyrin.

Despite the figure-of-eight structures that are similar to that of **2**, both disilver complexes **8** and **9** are thermally stable and do not exhibit any splitting reactivity, as observed for **2**. A major reason for the absence of thermal splitting reactivity may be the 34-π-electron systems of **8** and **9** which rationally preclude splitting into two 18-π-electron porphyrins. We thus attempted the reduction of **8** and **9** with $NaBH_4$ which caused spontaneous demetalation of the complexes to provide the respective free-base [38]octaphyrins.

In summary, metalation of the perfluorinated octaphyrin **4** with copper resulted in the formation of the dicopper complex **5** with an unprecedented concomitant hydrolytic ring opening of one of the pyrrole units. The octaphyrin framework was restored by demetalation with TFA and H_2SO_4. In contrast, metalation of both octaphyrin **1** and **4** with silver proceeded with initial two-electron oxidation of the ligands to give twisted figure-of-eight disilver(I) complexes of [34]octaphyrins that are thermally very stable. The structures and properties of dimetal complexes of octaphyrins are diverse and depend on the individual properties of the metal ion and the ligand, and they hail great potential for expanded porphyrins, which are actively pursued in our laboratory.

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[1] a) A. Jasat, D. Dolphin, *Chem. Rev.* **1997**, *97*, 2267; b) T. D. Lash, *Angew. Chem.* **2000**, *112*, 1833; *Angew. Chem. Int. Ed.* **2000**, *39*, 1763; c) H. Furuta, H. Maeda, A. Osuka, *Chem. Commun.* **2002**, 1795; d) J. L. Sessler, D. Seidel, *Angew. Chem.* **2003**, *115*, 5292; *Angew. Chem. Int. Ed.* **2003**, *42*, 5134; e) T. K. Chandrashekar, S. Venkatraman, *Acc. Chem. Res.* **2003**, *36*, 676; f) A. Ghosh, *Angew. Chem.* **2004**, *116*, 1952; *Angew. Chem. Int. Ed.* **2004**, *43*, 1918; g) J.-Y. Shin, H. Furuta, K. Yoza, S. Igarashi, A. Osuka, *J. Am. Chem. Soc.* **2001**, *123*, 7190.

[2] a) A. Werner, M. Michels, L. Zander, J. Lex, E. Vogel, *Angew. Chem.* **1999**, *111*, 3866; *Angew. Chem. Int. Ed.* **1999**, *38*, 3650; b) J. Setsune, Y. Katakami, N. Iizuna, *J. Am. Chem. Soc.* **1999**, *121*, 8957; c) N. Sprutta, L. Latos-Grażyński, *Chem. Eur. J.* **2001**, *7*, 5099.

[3] a) V. G. Anand, S. K. Pushpan, S. Venkatraman, A. Dey, T. K. Chandrashekar, B. S. Joshi, R. Roy, W. Teng, K. Ruhlandt-Senge, *J. Am. Chem. Soc.* **2001**, *123*, 8620; b) D. Seidel, V. Lynch, J. L. Sessler, *Angew. Chem.* **2002**, *114*, 1480; *Angew. Chem. Int. Ed.* **2002**, *41*, 1422.

[4] L. Latos-Grażyński, *Angew. Chem.* **2004**, *116*, 5234; *Angew. Chem. Int. Ed.* **2004**, *43*, 5124.

[5] E. Vogel, M. Michels, L. Zander, J. Lex, N. S. Tuzum, K. N. Houk, *Angew. Chem.* **2003**, *115*, 2964; *Angew. Chem. Int. Ed.* **2003**, *42*, 2857.

[6] Y. Tanaka, W. Hoshino, S. Shimizu, K. Youfu, N. Aratani, N. Maruyama, S. Fujita, A. Osuka, *J. Am. Chem. Soc.* **2004**, *126*, 3046.

[7] S. Shimizu, J.-Y. Shin, H. Furuta, R. Ismael, A. Osuka, *Angew. Chem.* **2003**, *115*, 82; *Angew. Chem. Int. Ed.* **2003**, *42*, 78.

[8] Crystal data for **5**: $C_{88}H_4F_{56}N_8O_3Cu_2$, $M_W = 2412.07$, monoclinic, space group $P2_1/n$ (no. 14), $a = 17.7961(14)$, $b = 23.5392(18)$, $c = 22.4783(17)$ Å, $\beta = 92.598(2)^\circ$, $V = 9406.6(13)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.703\ \mathrm{g^{cm^{-3}}}$, $T = -153\,^\circ C$. $R = 0.0648$, $R_w = 0.1731$ (all data), GOF = 0.972 ($I > 2\sigma(I)$).

[9] In the temperature range 20–2 K, the susceptibility value slightly decreased ($\chi_p T = 0.70\ \mathrm{emu\,K\,mol^{-1}}$ at 2 K), which can be accounted for in terms of weak antiferromagnetic coupling of the two copper(II) ions ($J = -0.306\ \mathrm{cm^{-1}}$, $g = 2.110$) despite the long separation (5.41 Å). See Supporting Information.

[10] Differential scanning calorimetry (DSC) measurement on **6** revealed sharp exothermic responses around 170–200 °C (see Supporting Information).

[11] Crystal data for **8**: $C_{114}H_{28}F_{50}N_{10}Ag_2O_7$, $M_W = 2815.19$, triclinic, space group $P\bar{1}$ (no. 2), $a = 15.908(8)$, $b = 15.978(7)$, $c = 21.28(1)$ Å, $\alpha = 99.02(4)$, $\beta = 94.61(4)$, $\gamma = 106.71(4)^\circ$, $V = 5071(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.843\ \mathrm{g\,cm^{-3}}$, $T = -150\,^\circ C$. $R = 0.092$, $R_w = 0.253$ (all data), GOF = 1.298 ($I > 2\sigma(I)$).

[12] a) W. R. Scheidt, J. U. Mondal, C. W. Eigenbrot, A. Adler, L. J. Radonovich, J. L. Hoard, *Inorg. Chem.* **1986**, *25*, 795; b) H. Furuta, T. Ogawa, Y. Uwatoko, K. Araki, *Inorg. Chem.* **1999**, *38*, 2676; c) C. Brücker, C. A. Barta, R. P. Brinas, J. A. Krause Bauer, *Inorg. Chem.* **2003**, *42*, 1673.

[13] Similar through-space coupling of the protons of a *p*-phenylene moiety with cadmium(II) ions was reported, see: a) M. Stępień, L. Latos-Grażyński, *J. Am. Chem. Soc.* **2002**, *124*, 3838; b) M. Stępień, L. Latos-Grażyński, *Acc. Chem. Res.* **2005**, *38*, 88.

[14] Crystal data for **9**: $C_{90}H_2F_{56}N_8Cl_2Ag_2O_3$, $M_W = 2593.61$, triclinic, space group $P\bar{1}$ (no. 2), $a = 14.820(2)$, $b = 17.797(2)$, $c = 19.159(3)$ Å, $\alpha = 67.010(2)$, $\beta = 87.229(2)$, $\gamma = 66.519(2)^\circ$, $V = 4232.2(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.035\ \mathrm{g\,cm^{-3}}$, $T = -183\,^\circ C$. $R = 0.061$, $R_w = 0.117$ ($I > 3\sigma(I)$), GOF = 0.945. CCDC-264267 (**5**), 264268 (**9**), and 264302 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[15] Selected signals of the β-, *o*-, and *m*-fluorine atoms were coupled with Ag^I ions probably as a result of through-space interactions (see Supporting Information).