Photo-controlled release and uptake of $Cu(hfac)_2$ in solution for a binuclear copper complex with a photochromic dithiazolylethene bridging ligand†

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A photochromic dithiazolylethene was used as bridging ligand to synthesize a series of homometallic binuclear complexes. It was found that the photochromic activity of the bridging ligand was maintained in solution only in the case of the copper binuclear complex. EPR studies revealed not only a weak magnetic coupling between the two copper ions, but also an interesting photo-controlled release and uptake of the $Cu(hfac)_2$ moiety in solution.

Introduction

Since the first report by Irie's group of di(heteroaryl)ethenes capable of undergoing fast and low fatigue photochemical reactions between two thermally stable isomers,[1] considerable efforts have been devoted to the synthesis of various photochromic di(heteroaryl)ethene-based derivatives for their potential as optical memory media and as efficient molecular switches.[2] For instance, elegant examples of photomodulation of magnetic coupling has been reported in a series of molecules where the magnetic interaction between two stable organic radicals (nitronyl nitroxide with $S = 1/2$) can be reversibly photo-switched by the photochromic reaction of a dithienylethene-based bridge connecting covalently the two radicals.[2b,3] However, use of organic radicals as spin carriers has a major limitation: it is very difficult to extend such studies to spin value S larger than 1/2 as most known organic radicals have a spin value of 1/2. On the other hand, clever combination of metal ions with photochromic di(heteroaryl)ethene-based ligands has already led to novel coordination systems displaying different photoswitchable behaviors.[4] Several systems associating magnetic metal ions with photochromic di(heteroaryl)ethene-based bridging ligands have also been described, but no magnetic coupling between the two metal ions has yet been detected, presumably due to a too large separation between the two metal centers.[5] Finally, an interesting approach combining two types of spin carriers (organic radical and metal ions) has also been reported.[6]

In the present work, we focus our investigation on a series of simple homometallic binuclear complexes (Scheme 1), where the two metal ions are bridged by 1,2-bis[5′-methyl-2′-(2″-pyridyl)thiazolyl]perfluorocyclopentene (denoted as **1o** and **1c** for its open and closed form, respectively),[7] and hfac is hexafluoroacetylacetonate.

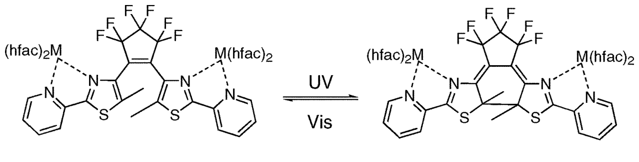
We have chosen **1o** as bridging ligand because, in addition to its good photochromic performance both in solution and in the crystalline state, its bis-chelating ability should allow to keep the two metal ions closer to each other than those already reported.[5] The main objective of this work is to investigate how the potential magnetic interaction, which should vary according to the nature of the metal ion, could be affected by the reversible structure changes of the photochromic bridging ligand **1**.

Results and discussion

Synthesis and crystal structures

All binuclear complexes were synthesized in a similar way by reacting **1o** with the corresponding $M(hfac)_2{\cdot}xH_2O$ in 1 : 2 molar ratio and they were characterized by elemental analysis and by single X-ray diffraction. The four binuclear complexes are isostructural and crystallize in the space group $P4_2/n$. The molecular structure of **$(hfac)_2Cu$-1o-$Cu(hfac)_2$** is shown in Fig. 1.

As expected, **1o** behaves as a chelating ligand *via* its two nitrogen atoms of pyridylthiazole moiety toward each Cu^{2+} ion, which sees its octahedral surroundings completed by four oxygen atoms of the two external hfac chelating ligands. More precisely, each Cu^{2+} ion has an elongated octahedral coordination sphere. The elongated axis runs through one



M: Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}.

Scheme 1 Expected photoreaction of **$(hfac)_2M$-1o-$M(hfac)_2$**.

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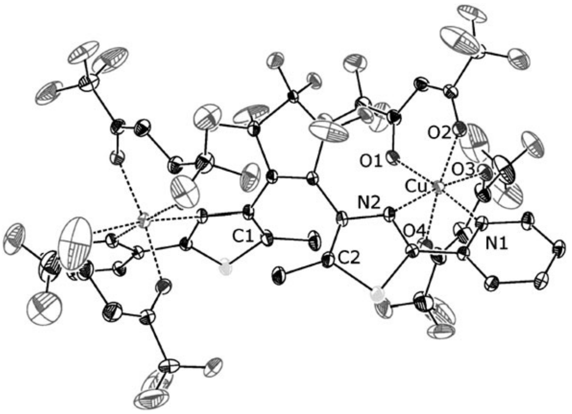

Fig. 1 ORTEP drawing of molecular structure of **(hfac)$_2$Cu-1o-Cu(hfac)$_2$** (30% probability). Hydrogen atoms are omitted for clarity.

oxygen atom of hfac, Cu^{2+} ion and the nitrogen atom of thiazole group, with $d_{Cu–O3}$ = 2.26 Å and $d_{Cu–N2}$ = 2.40 Å, respectively. These particularly large values are presumably due to the combination of Jahn–Teller distortion of Cu^{2+} ion and steric hindrance between hfac and the central perfluorocyclopentene ring. Finally, the intra-molecular distance separating the two Cu^{2+} ions is equal to 8.86 Å, shorter than those reported in the literature. Main metal–ligand bond lengths, distances between the two photoactive carbon atoms and the metal–metal separations for the four binuclear complexes are given in Table 1.

Photochromic properties

From the crystal structures of **(hfac)$_2$M-1o-M(hfac)$_2$**, one may expect to observe crystalline state photochromism for the four binuclear complexes because the bridging ligand **1o** fulfills the two conditions usually formulated:[8] anti-parallel conformation and distance shorter than 4.2 Å between the two (potentially photo-active) carbon atoms bearing the methyl groups. However, none of them was found to be photochromic, under our experimental conditions. More surprisingly, all but the copper complex, were also not photochromic even in solution (toluene, $CHCl_3$). The photochromic behavior of the binuclear copper complex, **(hfac)$_2$Cu-1o-Cu(hfac)$_2$**, is shown in Fig. 2.

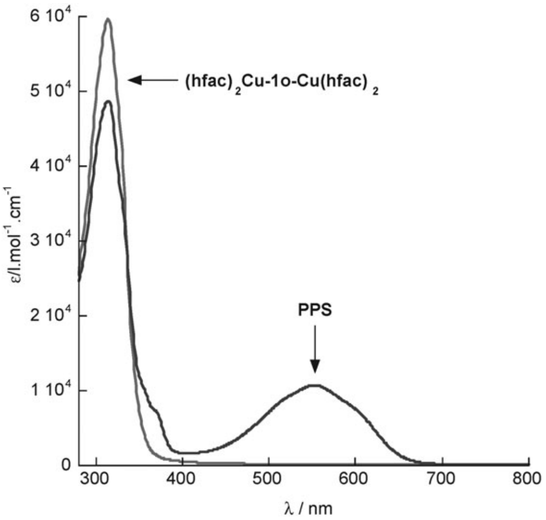

Fig. 2 Electronic absorption spectra of **(hfac)$_2$Cu-1o-Cu(hfac)$_2$** before UV irradiation at 313 nm and in the photostationary state.

The reasons for such a strong inhibition of photochromic activity, both in the crystalline state and in solution, by metal coordination are, as yet, not clear. However, the fact that only **(hfac)$_2$Cu-1o-Cu(hfac)$_2$** is found to be photochromic in solution indicates that the paramagnetic or diamagnetic nature of the metal ions is clearly not the main cause, as Cu^{2+}, Co^{2+} and Ni^{2+} ions are paramagnetic while Zn^{2+} ion is diamagnetic. This prompted us to examine therefore more closely the potential structural differences that may account, at least partly, for their contrasting photochromic activities observed in solution.

It is clear from Table 1 that the most significant structural difference between **(hfac)$_2$Cu-1o-Cu(hfac)$_2$** and the three other binuclear complexes concerns the bond length between the metal ion and the nitrogen atom of the thiazole moiety. This bond length is slightly larger than the usual M–N value for the

Table 1 Metal–ligand bond lengths, C1–C2 distance and M···M separation

	$d_{M–O}$/Å	$d_{M–N}$/Å	$d_{C1–C2}$/Å	$d_{M\cdots M}$/Å
(hfac)$_2$Cu-1o-Cu(hfac)$_2$	Cu–O1: 1.962(3) Cu–O2: 1.964(3) Cu–O3: 2.255(3) Cu–O4: 1.975(3)	Cu–N1: 2.012(3) Cu–N2: 2.401(3)	3.864(5)	8.856(2)
(hfac)$_2$Co-1o-Co(hfac)$_2$	Co–O1: 2.031(5) Co–O2: 2.046(5) Co–O3: 2.071(5) Co–O4: 2.058(5)	Co–N1: 2.094(6) Co–N2: 2.205(5)	4.014(11)	8.493(4)
(hfac)$_2$Ni-1o-Ni(hfac)$_2$	Ni–O1: 2.011(3) Ni–O2: 2.021(3) Ni–O3: 2.036(3) Ni–O4: 2.032(4)	Ni–N1: 2.047(4) Ni–N2: 2.183(3)	4.025(7)	8.524(3)
(hfac)$_2$Zn-1o-Zn(hfac)$_2$	Zn–O1: 2.049(2) Zn–O2: 2.060(2) Zn–O3: 2.094(2) Zn–O4: 2.090(2)	Zn–N1: 2.102(3) Zn–N2: 2.250(3)	3.933(5)	8.579(2)

three non-photochromic binuclear complexes (Table 1), but it is particularly long in the case of the copper complex, indicating that the Cu^{2+} ion is only weakly coordinated by the nitrogen atom of the thiazole group. As electrocyclization of **1o** requires rotation of the thiazole group and this rotation would be hampered by the metal–thiazole coordination, it is reasonable to expect a difference in the photochromic activity between the copper and other metal complexes given their differences in the metal–thiazole bond length.

The electronic absorption spectrum of **(hfac)$_2$Cu-1o-Cu(hfac)$_2$** in toluene is characterized by an intense band in the UV region (λ_{max} = 313 nm) and a very low intensity band in the visible region (λ_{max} = 720 nm) which, though not visible in Fig. 2, imparts the green color to the complex; λ_{max} of this d–d band is shifted to lower energy as compared to that of $Cu(hfac)_2 \cdot xH_2O$ in toluene (λ_{max} = 670 nm), suggesting thereby the integrity of dimeric entity being maintained in solution. The much higher ε of the absorption band at 310 nm of **(hfac)$_2$Cu-1o-Cu(hfac)$_2$** is due to the presence of hfac in the $Cu(hfac)_2$ moiety, which absorbs at almost the same wavelength as **1o**.

Upon UV irradiation (313 nm), this pale green solution rapidly turned dark purple, characterized by the appearance of a broad band at 546 nm. The purple color was stable in the dark at room temperature, but could be easily bleached by visible irradiation (550 nm), with total recovery of the initial spectrum. These spectral changes are similar to those of **1o** alone. The conversion of **1o** to **1c** in the complex was estimated to be about the same (90%) in the photostationary state (313 nm) as for **1o** alone in the same solvent (toluene) by using a literature reported method.[6] Finally, the back reaction (**1c** to **1o**) in toluene under 547 nm irradiation was found to proceed with almost equal efficiency for both the binuclear copper complex and the photochromic bridging ligand alone. This is rather surprising as one would expect it being affected by metal binding. The quantum yield of the coloration process (**1o** to **1c**) was more difficult to access because of absorption of the hfac moiety at similar wavelengths as **1o**.

The photo-induced conversion of the bridging ligand **1o** to **1c** is also expected to bring about modifications of copper centered d–d band. However, monitoring of the d–d band evolution upon UV irradiation turned out to be impossible as it was totally masked by the red edge of the intense and large band of **1c**.

EPR studies

EPR spectroscopy was used to investigate the photo-switching of potential magnetic interaction between the two Cu^{2+} ions in **(hfac)$_2$Cu-1o-Cu(hfac)$_2$** because of its high sensitivity to small magnetic perturbations. In the present case, even though the two Cu^{2+} ions are closer than those reported in the literature,[5] the potential magnetic interaction is expected to be very weak. In order to have a reference EPR spectrum for such a study, a non-photochromic copper monomer with an identical coordination sphere (denoted as **(hfac)$_2$Cu-2**) was synthesized and structurally characterized (Fig. 3).

In the $g_{\parallel}$ portion of the EPR spectrum of **(hfac)$_2$Cu-1o-Cu(hfac)$_2$**, pairs of lines can clearly be distinguished. To first order, these pairs are centered on the hyperfine lines of the monomer **(hfac)$_2$Cu-2** (Fig. 4(a)) and split by 54.5 mT on average (Fig. 4(b)). The $g_{\perp}$ region is also broader in the dimer spectrum compared to the monomer species. The spectrum with split features is characteristic of a weak magnetic coupling between two $S = 1/2$ species. Spectra recorded with increasing dilution factors did not affect the shape of the EPR spectrum, indicating that the coupling is intramolecular. We therefore attribute the origin of the EPR spectrum to the magnetic interaction between the two copper ions coordinated

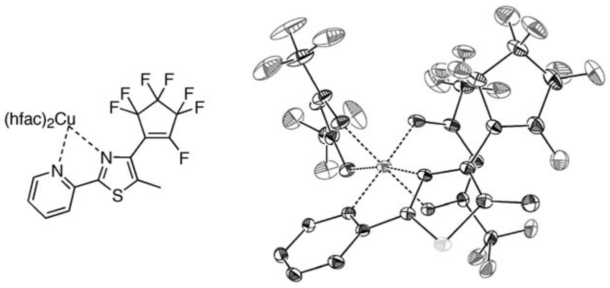

Fig. 3 Schematic representation and ORTEP drawing of molecular structure of **(hfac)$_2$Cu-2** (30% probability). Hydrogen atoms are omitted for clarity.

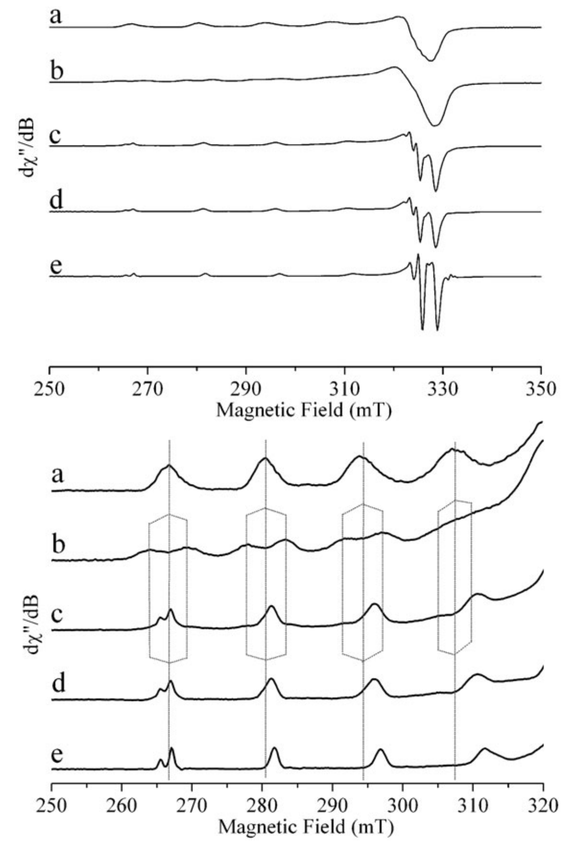

Fig. 4 X-Band EPR spectra recorded at 100 K (1 mM for copper concentration in toluene matrix, 9.386 GHz) (top) and magnified $g_{\parallel}$ portions of the spectra (bottom): (a) **(hfac)$_2$Cu-2**; (b) **(hfac)$_2$Cu-1o-Cu(hfac)$_2$**; (c) photostationary state of **(hfac)$_2$Cu-1o-Cu(hfac)$_2$** (313 nm); (d) photostationary state with residual contribution from **(hfac)$_2$Cu-1o-Cu(hfac)$_2$** removed; (e) one solution species of $Cu(hfac)_2 \cdot xH_2O$.

by the open form of the photochromic ligand **1o**. It is also worth noting that simple mixing of **1o** and $Cu(hfac)_2\cdot xH_2O$ in stoichiometric ratio in toluene gives the same EPR spectrum as that of crystals of **(hfac)$_2$Cu-1o-Cu(hfac)$_2$** dissolved in toluene, indicating a strong affinity of **1o** for $Cu(hfac)_2\cdot xH_2O$ to form **(hfac)$_2$Cu-1o-Cu(hfac)$_2$**.

The EPR spectrum recorded on the same sample after UV irradiation at 313 nm is strongly modified (Fig. 4(c)). The spectrum of the photostationary state (313 nm) now resembles that of a monomeric species and, in addition, all the features, including the $g_\perp$ region, have a much narrower linewidth. A small contribution (*ca.* 10%) from the original coupled binuclear complex is still present in the photostationary state and a difference spectrum, with this contribution removed, is presented in Fig. 4(d). The resulting spectrum differs from the monomeric complex **(hfac)$_2$Cu-2** (Fig. 4(a)) both in spectral line positions as well as in linewidth, indicating a different coordination sphere for the copper ion. Indeed, the EPR spectrum is more reminiscent of that observed for one of the solution species in $Cu(hfac)_2\cdot xH_2O$ (Fig. 4(e)),‡ strongly suggesting photo-ejection of the $Cu(hfac)_2$ entity upon photo-isomerization of the bridging ligand **1o** to **1c**. This is also consistent with the fact that the back reaction (**1c** to **1o**) was found to proceed with similar quantum yields for the copper binuclear complex and for the photochromic bridging ligand alone. Finally, it is noteworthy that the initial EPR spectrum is perfectly restored when the solution of above photo-stationary state is irradiated with visible light (550 nm).

Such a reversible photo-release and uptake of the $Cu(hfac)_2$ entity is clearly related to the difference in the affinity for the $Cu(hfac)_2$ entity between the open and closed forms of the bridging ligand. The weaker ligating properties of **1c** for the $Cu(hfac)_2$ entity is also supported by the X-ray diffraction analysis of single crystals, obtained from the photostationary state of **(hfac)$_2$Cu-1o-Cu(hfac)$_2$** (see Experimental section), which reveals the expected copper binuclear structure: **(hfac)$_2$Cu-1c-Cu(hfac)$_2$** with **1c** bridging two $Cu(hfac)_2$ entities (Fig. 5).

The bond lengths between the two copper ions and the corresponding thiazole groups are 2.521(4) and 2.576 (4) Å, respectively. These values, much larger than that (2.400(3) Å) found in **(hfac)$_2$Cu-1o-Cu(hfac)$_2$**, clearly indicate a much weaker affinity of **1c** for the $Cu(hfac)_2$ entity. This binuclear structure could appear to be in contradiction with the photo-ejection of $Cu(hfac)_2$ entity formulated above. However, one has to keep in mind that the crystal structure is only indicative of the molecular structure in solution, which can sometimes differ significantly. Moreover, the fact that the EPR spectrum of the photostationary state resembles that of one of the solution species of $Cu(hfac)_2\cdot xH_2O$ also means that photo-ejection of the $Cu(hfac)_2$ entity proceeds with its concomitant complexation by water molecules present in toluene, making such a process more favorable. Finally, it has to be noted that single crystals of **(hfac)$_2$Cu-1c-Cu(hfac)$_2$** for X-ray diffraction analysis were obtained, not directly from the solution of the photostationary state in toluene but in a mixture of different solvents.

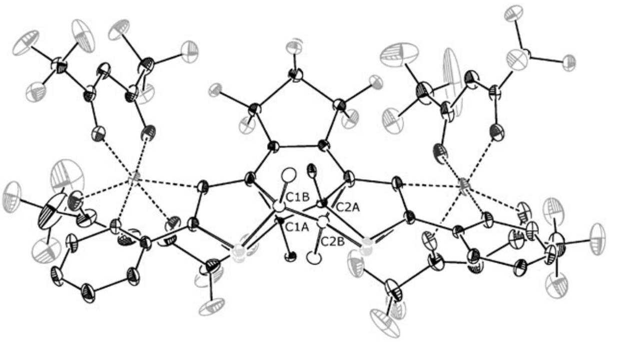

Fig. 5 ORTEP drawing of molecular structure of **(hfac)$_2$Cu-1c-Cu(hfac)$_2$** (30% probability). Disordered atoms are shown and hydrogen atoms are omitted for clarity.

Conclusion

A series of homometallic binuclear complexes with a photochromic dithiazolylethene as bridging ligand were prepared and structurally characterized. Metal binding was found to strongly inhibit the photochromic activity of the bridging ligand both in crystalline phase and in solution, except in the case of the copper binuclear complex. EPR studies revealed not only the capability of such a dithiazolylthene to mediate magnetic couplings between two metal centers, but also, to our knowledge, an unique photo-controlled release and uptake of the $Cu(hfac)_2$ entity in solution. We are currently applying this hybrid approach for the design of new coordination compounds with novel and different photo-responsive behaviors.

Experimental

General

^1H NMR spectra were recorded at a Bruker 250 MHz spectrometer in $CDCl_3$. UV-Vis spectra were recorded on a Varian Cary 5E at room temperature. X-Band EPR spectra were recorded on a Bruker Elexsys E500 spectrometer equipped with a continuous-flow cryostat (Oxford Instruments). Elemental analyses were performed at Service de Microanalyse, ICSN-CNRS, Gif sur Yvette, France. Irradiation was provided by a 200 W high pressure mercury–Xe lamp (Oriel) through narrow band interference filters of appropriate wavelength.

Chemicals

Reagents and chemicals were used as supplied (Acros, Alfa Aesar or Aldrich) unless otherwise stated. Octafluorocyclopentene was generously provided by Zeon Corporation (Japan). 2-(2′-Pyridyl)-4-bromo-5-methylthiazole and 1,2-bis[5′-methyl-2′-(2″-pyridyl)thiazolyl]perfluorocyclopentene (**1o**) were prepared according to the published procedures.[7]

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‡ When $Cu(hfac)_2\cdot xH_2O$ is dissolved in toluene, its X-band EPR spectrum recorded at 100 K clearly shows the presence of two copper species, presumably $Cu(hfac)_2$ with one and two water molecules in the coordination sphere of copper ion. The proportion of the two species depends on the content of water molecules present in solution. Also consistent with above observation is the crystal structure determination of two hydrated $Cu(hfac)_2$ species described in the literature.[12]

Synthesis

1-[5′-Methyl-2′-(2″-pyridyl)thiazolyl]perfluorocyclopentene (2). 2-(2-Pyridyl)-4-bromo-5-methylthiazole (1.27 g, 5 mmol) was dissolved under argon in *ca.* 60 mL of Et_2O distilled from sodium and benzophenone. The solution was cooled to −78 °C with partial reprecipitation of starting compound. *n*-BuLi in hexane (2.5 M, 2.2 mL, 5.5 mmol) was slowly added to the mixture over *ca.* 15 min. After stirring for 30 min at the same temperature, octafluorocyclopentene (0.67 mL, 5 mmol) was added at once into the red–brown mixture. The stirring was continued for 2 h at the same temperature and then allowed to slowly warm to room temperature and stirred over night. An aqueous HCl solution (0.6 M, 20 mL) was added to the red–brown solution with some suspension. After *ca.* 30 min of stirring the pH of the aqueous phase was brought to *ca.* 8 with solid $NaHCO_3$. The aqueous phase was extracted with Et_2O (20 mL). The combined organic phase, after being dried over Na_2SO_4 and filtered, was evaporated under reduced pressure. After chromatography (SiO_2, CH_2Cl_2) of the residue, **2** was obtained as an off white powder in 48% yield.

^{1}H NMR ($CDCl_3$): δ 2.11 (s, 3H), 7.34 (m, 1H), 7.51 (td, 1H), 8.10 (d, 1H), 8.57 (d, 1H).

(hfac)$_2$Cu-2. Cu(hfac)$_2$·*x*H_2O (15 mg, 0.03 mmol) in heptane (10 mL) was refluxed until a clear solution was obtained. Reflux was maintained for about 15 min and the solution was allowed to slightly cool to 50–60 °C before **2** (11 mg, 0.03 mmol) in CH_2Cl_2 (5 mL) was added with continuing stirring. The solution turned immediately emerald green. Slow cooling of the solution to room temperature afforded **(hfac)$_2$Cu-2** as emerald green crystals, directly suitable for X-ray diffraction, in 72% yield.

Elemental analysis: calc. (%) for $C_{24}H_9CuF_{19}N_2O_4S$ (845.9): C 34.08, H 1.07, N 3.31; found: C 33.85, H 0.98, N 3.36.

General procedure for (hfac)$_2$M-1o-M(hfac)$_2$

M(hfac)$_2$·*x*H_2O (0.11 mmol) in heptane (20 mL) was refluxed until a clear solution was obtained and reflux was continued for further 20 min. After allowing the solution to slightly cool to 50–60 °C, **1o** (26 mg, 0.05 mmol) in CH_2Cl_2 (5 mL) was added at once. The solution was then allowed to slowly cool to room temperature to give **(hfac)$_2$M-1o-M(hfac)$_2$** as a microcrystalline powder.

(hfac)$_2$Cu-1o-Cu(hfac)$_2$. Microcrystalline green powder in 68% yield.

Elemental analysis: calc. (%) for $C_{43}H_{18}Cu_2F_{30}N_4O_8S_2$ (1479.8): C 34.90, H 1.23, N 3.79; found: C 34.79, H 1.19, N 3.91.

(hfac)$_2$Co-1o-Co(hfac)$_2$. Microcrystalline orange powder in 88% yield.

Elemental analysis: calc. (%) for $C_{43}H_{18}Co_2F_{30}N_4O_8S_2$ (1470.6): C 35.12, H 1.23, N 3.81; found: C 35.74, H 1.31, N 3.82.

(hfac)$_2$Ni-1o-Ni(hfac)$_2$. Microcrystalline green-grey powder in 66% yield.

Elemental analysis: calc. (%) for $C_{43}H_{18}Ni_2F_{30}N_4O_8S_2$ (1470.1): C 35.13, H 1.23, N 3.81; found: C 35.80, H 1.40, N 3.82.

(hfac)$_2$Zn-1o-Zn(hfac)$_2$. Microcrystalline white powder in 42% yield.

Elemental analysis: calc. (%) for $C_{43}H_{18}Zn_2F_{30}N_4O_8S_2$ (1483.5): C 34.81, H 1.22, N 3.78; found: C 35.25, H 1.30, N 3.91.

Single-crystal structure determination

(hfac)$_2$M-1o-M(hfac)$_2$. All single crystals were grown in the same way as following: 10–15 mg of **(hfac)$_2$M-1o-M(hafc)$_2$** were dissolved in EtOAc (a few mL) and then heptane (*ca.* 5 mL) were added. Slow evaporation at room temperature of EtOAc gave directly suitable single crystals for X-ray analysis.

(hfac)$_2$Cu-1c-Cu(hfac)$_2$: Slow evaporation in the dark of a toluene solution of **(hfac)$_2$Cu-1o-Cu(hfac)$_2$** in its photostationary state (313 nm) failed to give a crystalline material. However, once this dark red solid residue was redissolved in a mixture of EtOAc and heptane, slow evaporation in the dark at room temperature gave few dark red crystals, suitable for X-ray diffraction.

X-Ray diffraction data were collected by using a Kappa CCD Bruker-Nonius diffractometer with graphite-monochromated Mo$_{K\alpha}$ radiation (λ = 0.71073 Å) at 150 K for **(hfac)$_2$Cu-1o-Cu(hfac)$_2$** and **(hfac)$_2$Co-1o-Co(hfac)$_2$**, at 100 K for **(hfac)$_2$Cu-1c-Cu(hfac)$_2$** and **(hfac)$_2$Zn-1o-Zn(hfac)$_2$**, and at room temperature for **(hfac)$_2$Ni-1o-Ni(hfac)$_2$** and **(hfac)$_2$Cu-2**. The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SHELXS-97[9] and refined against F^2 by full-matrix least-squares techniques using SHELXL-97[10] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.[11]

Main crystallographic data. For the four isomorphous binuclear metallic complexes that crystallize in space group $P4_2/n$, the imposed twofold symmetry axis passes through the perfluorocyclopentene ring with the central CF_2 group disordered over two sites.

(hfac)$_2$Cu-1o-Cu(hfac)$_2$. $C_{43}H_{18}Cu_2F_{30}N_4O_8S_2$, M = 1479.85, tetragonal, space group $P4_2/n$ (no. 86), $a = b$ = 17.879(8), c = 17.607(8) Å, U = 5628(4) Å^3, T = 150(1) K, Z = 4, 113 444 reflections measured, 8920 unique (R_{int} = 0.0508), 6423 with $I > 2\sigma(I)$ which were used in all calculations. The final $R(F^2)$ was 0.0634 (observed data).

(hfac)$_2$Co-1o-Co(hfac)$_2$. $C_{43}H_{18}Co_2F_{30}N_4O_8S_2$, M = 1470.61, tetragonal, space group $P4_2/n$ (no. 86), $a = b$ = 17.718(5), c = 17.836(5) Å, U = 5599(3) Å^3, T = 150(2) K, Z = 4, 18 745 reflections measured, 4380 unique (R_{int} = 0.0581), 2956 with $I > 2\sigma(I)$ which were used in all calculations. The final $R(F^2)$ was 0.0734 (observed data).

(hfac)$_2$Ni-1o-Ni(hfac)$_2$. $C_{43}H_{18}Ni_2F_{30}N_4O_8S_2$, $M = 1470.13$, tetragonal, space group $P4_2/n$ (no. 86), $a = b = 17.8094(3)$, $c = 18.0024(6)$ Å, $U = 5709.9(2)$ Å^3, $T = 273(2)$ K, $Z = 4$, 35 272 reflections measured, 6790 unique ($R_{\text{int}} = 0.0258$), 4689 with $I > 2\sigma(I)$ which were used in all calculations. The final $R(F^2)$ was 0.0772 (observed data).

(hfac)$_2$Zn-1o-Zn(hfac)$_2$. $C_{43}H_{18}Zn_2F_{30}N_4O_8S_2$, $M = 1483.53$, tetragonal, space group $P4_2/n$ (no. 86), $a = b = 17.681(5)$, $c = 17.726(5)$ Å, $U = 5542(3)$ Å^3, $T = 100(1)$ K, $Z = 4$, 55 891 reflections measured, 7680 unique ($R_{\text{int}} = 0.0363$), 5718 with $I > 2\sigma(I)$ which were used in all calculations. The final $R(F^2)$ was 0.0542 (observed data).

(hfac)$_2$Cu-1c-Cu(hfac)$_2$. $C_{43}H_{18}Cu_2 F_{30}N_4O_8S_2$, $M = 1479.85$, monoclinic, space group $P2_1/c$ (no. 14), $a = 17.699(5)$, $b = 17.418(5)$, $c = 17.916(5)$ Å, $\beta = 106.609(5)°$, $U = 5293\ (3)$ Å^3, $T = 100(1)$ K, $Z = 4$, 86102 reflections measured, 12886 unique ($R_{\text{int}} = 0.0247$), 11090 with $I > 2\sigma(I)$ which were used in all calculations. The final $R(F^2)$ was 0.0641 (observed data). For this complex, the C1–C2 bond is disordered over two orientations, with occupancy factors of 0.691 (**A**) and 0.309 (**B**), respectively.

(hfac)$_2$Cu-2. $C_{24}H_9CuF_{19}N_2O_4S$, $M = 845.95$, triclinic, space group $P\bar{1}$ (no. 2), $a = 14.4416(4)$, $b = 15.5291(4)$, $c = 15.5304(3)$ Å, $\alpha = 107.0200(10)$, $\beta = 100.3160(10)$, $\gamma = 104.6300(10)°$, $U = 3099.57(13)$ Å^3, $T = 293(2)$ K, $Z = 4$, $Z' = 2$, 21 991 reflections measured, 14 111 unique ($R_{\text{int}} = 0.0227$), 8320 with $I > 2\sigma(I)$ which were used in all calculations. The final $R(F^2)$ was 0.0706 (observed data).

References

1. M. Irie and M. Mohri, *J. Org. Chem.*, 1989, **53**, 803.
2. Reviews and some recent and selected examples: (*a*) M. Irie, *Chem. Rev.*, 2000, **100**, 1685; (*b*) K. Matsuda and M. Irie, *J. Photochem. Photobiol., C*, 2004, **5**, 169; (*c*) T. Fukaminato, T. Sasaki, T. Kawai, N. Tamai and M. Irie, *J. Am. Chem. Soc.*, 2004, **126**, 14843; (*d*) K. Higashiguchi, K. Matsuda, N. Tanifuji and M. Irie, *J. Am. Chem. Soc.*, 2005, **127**, 8922; (*e*) T. Fukaminato, T. Umemoto, Y. Iwata, S. Yokojima, M. Yoneyama, S. Nakamura and M. Irie, *J. Am. Chem. Soc.*, 2007, **129**, 5932; (*f*) H. Tian and S. Wang, *Chem. Commun.*, 2007, 781; (*g*) D. Sud, T. J. Wigglesworth and N. R. Branda, *Angew. Chem., Int. Ed.*, 2007, **46**, 8017; (*h*) V. Lemieux, M. D. Spantulescu, K. K. Baldridge and N. R. Branda, *Angew. Chem., Int. Ed.*, 2008, **47**, 5034; (*i*) A. J. Kronemeijer, H. B. Akerman, T. Kudernac, B. J. van Wees, B. L. Feringa, P. W. M. Blom and B. de Boer, *Adv. Mater.*, 2008, **20**, 1467; (*j*) T. Okuyama, Y. Tani, K. Miyaka and Y. Yokoyama, *J. Org. Chem.*, 2007, **72**, 1634; (*k*) S. D. Straight, P. A. Liddell, Y. Terazono, T. A. Moore, A. L. Moore and D. Gust, *Adv. Funct. Mater.*, 2007, **17**, 777; (*l*) M. Berberich, A. M. Krause, M. Orlandi, F. Scandola and F. Würthner, *Angew. Chem., Int. Ed.*, 2008, **47**, 6616; (*m*) C. C. Corredor, Z. L. Huang, K. D. Belfield, A. R. Morales and M. V. Bondar, *Chem. Mater.*, 2007, **19**, 5165; (*n*) M. Bossi, V. Belov, S. Polyakova and S. W. Hell, *Angew. Chem., Int. Ed.*, 2006, **45**, 7462; (*o*) Y. Zou, T. Yi, S. Xiao, F. Li, C. Li, X. Gao, J. Wu, M. Yu and C. Huang, *J. Am. Chem. Soc.*, 2008, **130**, 15750; (*p*) T. A. Golovkova, D. V. Kozlov and D. C. Neckers, *J. Org. Chem.*, 2005, **70**, 5545; (*q*) M. K. Hossain, M. Takeshita and T. Yamato, *Eur. J. Org. Chem.*, 2005, 2771; (*r*) K. E. Maly, P. Zhang, M. D. Wand, E. Buncel and R. P. Lemieux, *J. Mater. Chem.*, 2004, **14**, 2806; (*s*) A. Mulder, A. Jukovic, J. Huskens and D. N. Reinhoudt, *Org. Biomol. Chem.*, 2004, **2**, 1748; (*t*) S. J. Lim, J. Seo and S. Y. Park, *J. Am. Chem. Soc.*, 2006, **128**, 14542; (*u*) Y. Chen, D. X. Zeng, N. Xie and Y. Z. Dang, *J. Org. Chem.*, 2005, **70**, 5001; (*v*) S. Kobatake and Y. Terakawa, *Chem. Commun.*, 2007, 1698; (*w*) H. Ikeda, A. Sakai, H. Namai, A. Kawabe and K. Mizuno, *Tetrahedron Lett.*, 2007, **48**, 8338; (*x*) A. El Yahyaoui, G. Félix, A. Heynderickx, C. Moustrou and A. Samat, *Tetrahedron*, 2007, **63**, 9482; (*y*) G. Guirado, C. Coudret, M. Hliwa and J. P. Launay, *J. Phys. Chem. B*, 2005, **109**, 17445; (*z*) T. Nakashima, M. Goto, S. Kwai and T. Kawai, *J. Am. Chem. Soc.*, 2008, **130**, 14570.
3. N. Tanifuji, M. Irie and K. Matsuda, *J. Am. Chem. Soc.*, 2005, **127**, 13344.
4. Some selected exemples: (*a*) H. Kai, S. Nara, K. Kinbara and T. Aida, *J. Am. Chem. Soc.*, 2008, **130**, 6725; (*b*) P. H. M. Lee, C. C. Ko, N. Zhu and V. W. W. Yam, *J. Am. Chem. Soc.*, 2007, **129**, 6058; (*c*) Y. Liu, C. Lagrost, K. Costuas, N. Tchouar, H. Le Bozec and S. Rigaut, *Chem. Commun.*, 2008, 6117; (*d*) V. Aubert, V. Guerchais, E. Ishow, K. Hoang-Thi, I. Ledoux, K. Nakatani and H. Le Bozec, *Angew. Chem., Int. Ed.*, 2007, **47**, 577; (*e*) K. Motoyama, T. Koike and M. Akita, *Chem. Commun.*, 2008, 5812; (*f*) D. V. Kozlov and F. N. Castellano, *J. Phys. Chem. A*, 2004, **108**, 10619; (*g*) T. Nakagawa, K. Atsumi, T. Nakashima, Y. Hasegawa and T. Kawai, *Chem. Lett.*, 2007, **36**, 372; (*h*) M. T. Indelli, S. Carli, M. Ghirotti, C. Chiorboli, M. Ravaglia, M. Garavelli and F. Scandola, *J. Am. Chem. Soc.*, 2006, **130**, 7286.
5. (*a*) K. Matsuda, K. Takayama and M. Irie, *Inorg. Chem.*, 2004, **43**, 482; (*b*) J. Han, M. Maekawa, Y. Suenaga, H. Ebisu, A. Nabei, T. Kuroda-Sowa and M. Munakata, *Inorg. Chem.*, 2007, **46**, 3313.
6. K. Yakayama, K. Matsuda and M. Irie, *Chem.–Eur. J.*, 2003, **9**, 5605.
7. M. Giraud, A. Léaustic, M. F. Charlot, P. Yu, M. Césario, C. Philouze, R. Pansu, K. Nakatani and E. Ishow, *New J. Chem.*, 2005, **29**, 439.
8. M. Morimoto and M. Irie, *Chem. Commun.*, 2005, 3895.
9. G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Göttingen, Germany, 1997.
10. G. M. Sheldrick, SHELXL-97, Program for the refinement of crystal structures from diffraction data, University of Göttingen, Göttingen, Germany, 1997.
11. L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.
12. A. W. Maverick, F. R. Fronczek, E. F. Maverick, D. R. Billodeaux, Z. T. Cygan and R. A. Isovitsch, *Inorg. Chem.*, 2002, **41**, 6488.