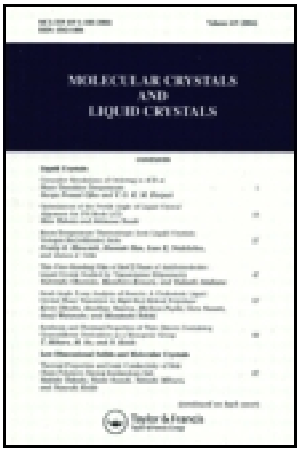

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Heterospin Systems Consisting of Organic Free Radicals and Magnetic Metal Ions by Self-Assembling Strategy. Diazodi(4-Pyridyl)Methane as Photo-Responsive Ligands for Metal-Carbene-Based Heterospin Magnets

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Version of record first published: 04 Oct 2006

To cite this article: Noboru Koga And & Hiizu Iwamura (1997): Heterospin Systems Consisting of Organic Free Radicals and Magnetic Metal Ions by Self-Assembling Strategy. Diazodi(4-Pyridyl)Methane as Photo-Responsive Ligands for Metal-Carbene-Based Heterospin Magnets, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 305:1, 415-424

To link to this article: http://dx.doi.org/10.1080/10587259708045076

Mol. Cryst. Liq. Cryst., 1997, Vol. 305, pp. 415–424
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HETEROSPIN SYSTEMS CONSISTING OF ORGANIC FREE RADICALS AND MAGNETIC METAL IONS BY SELF-ASSEMBLING STRATEGY. DIAZODI(4-PYRIDYL)METHANE AS PHOTO-RESPONSIVE LIGANDS FOR METAL-CARBENE-BASED HETEROSPIN MAGNETS

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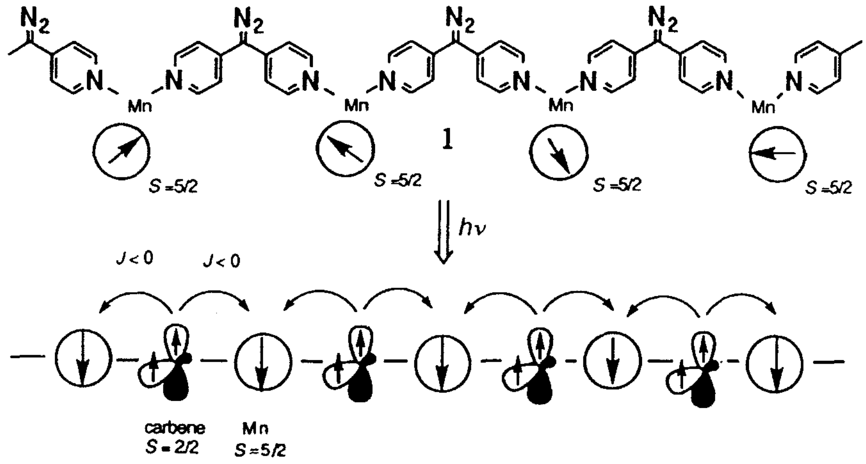
Abstract Diazodi(4-pyridyl)methane and Mn(hfac)$_2$ formed the orange-colored 1:1 complex having a spiral 1-D chain structure. While all the Mn (II) ions were found to be magnetically isolated before irradiation, a 1-D ferrimagnetic chain was established in the complex by an antiferromagnetic interaction of the 3d spins of Mn(II) with the 2p spins of photochemically generated carbenes (S = 2/2). Dark greenish bricks of the similar 1 : 1 complex from the diazo compound and Cu(hfac)$_2$ exhibited after photolysis a $\chi_{\mathrm{mol}}T$ -T profile characteristic of ferromagnetic interaction between the carbenes and the Cu(II) ions. The carbene centers were found to be stable up to ca. 230 K in both the complexes. The photochemically generated heterospin system will serve as a prototype of molecular photomagnetic recording devices.

INTRODUCTION

Diphenylcarbene with a triplet ground state has served as an important building block for designing and constructing molecules and molecular assemblies with high spin multiplicity.[1,2] Thus the connection of n carbene units through the m-phenylene, 1,3,5-benzenetriyl, and other ferromagnetic coupling units gives rise to various polycarbenes with $S = n$ ground states in which the highest record of the series reported so far is S = 9.[3] Efforts to increase the number of aligned spins have, however, been hampered by the development of antiferromagnetic intra- and/or interchain interactions between the carbene centers assembled in high local concentration; chemical bonds appear to be formed in the extreme.[4] Our last recourse is a strategy of assembling carbene centers into a rigid polymeric metal complex; ligation of the pyridyl nitrogens of diazodi(4-pyridyl)methane (**1**)[5] with coordinatively doubly unsaturated paramagnetic metal ions followed by photolysis has now been investigated (Scheme 1).



Scheme 1

PREPARATION OF THE 1:1 COMPLEXES [M(hfac)$_2$•1] {M = Mn(II) and Cu(II)}

1:1 Complex [Mn(hfac)$_2$•**1**] (Anal. Calcd for $C_{21}H_{12}N_4O_4F_{12}Mn$: C, 37.80; H, 1.81; N, 8.40. Found: C, 38.08; H, 1.74; N, 8.11) was obtained as orange bricks from a solution of anhydrous manganese(II) bis(hexafluoroacetylacetonate) [Mn(hfac)$_2$] and **1** in *n*-heptane/CH_2Cl_2 containing a small amount of methanol. Dark greenish brick-like crystals of [Cu(hfac)$_2$ •**1**] were obtained similarly in benzene/CH_2Cl_2/CH_3OH. Both the 1:1 complexes were recrystallized from the corresponding mixed solvents from which they were initially obtained.

X-RAY CRYSTAL AND MOLECULAR STRUCTURE OF THE 1:1 COMPLEX [Mn(hfac)$_2$•1]

A limited quality of the single crystal (orthorhombic and space group *Pbca* for [Mn(hfac)$_2$•**1**]) and its sensitivity to X-ray irradiation did not allow us to refine the residuals better than $R = 0.244$ and $R_w = 0.121$. The unrefined X-ray crystal and molecular structure data of [Mn(hfac)$_2$•**1**] thus obtained showed that a manganese ion is hexacoordinated with two pyridyl nitrogens from two different molecules of **1** in cis configuration and four hfac oxygen atoms (Figure 1). A spiral one-dimensional chain is established. An X-Ray crystal structure study was unsuccessful due to the limited quality of the crystals and the lability of the solvents included in the crystal. As **1** is a bismonodentate pyridyl ligand and [Cu(hfac)$_2$] is coordinatively doubly unsaturated, we

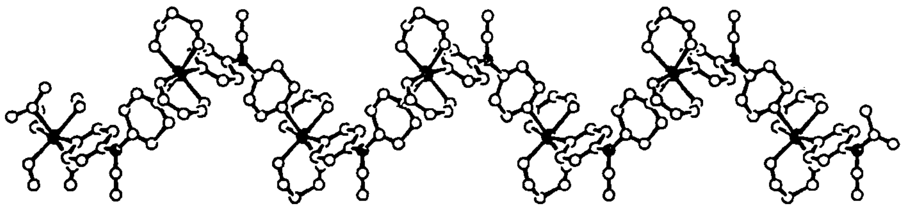


Figure 1. Ball-and-stick drawing of the X-ray structure of [Mn(hfac)$_2$•**1**].

may safely assume that the complex would have a one-dimensional chain structure similar to the [Mn(II)(hfac)$_2$] complex.

MAGNETIC PROPERTIES BEFORE AND AFTER IRRADIATION

Magnetic measurements of ca. 0.5 mg of fine crystalline samples of [Mn(hfac)$_2$•**1**] and [Cu(hfac)$_2$•**1**] were carried out on a SQUID susceptometer/magnetometer before and after irradiation with a 300-W Xenon lamp through an optical fiber[6] at or below 5 K. The 770 > λ > 400-nm light was used by a combination of a Kenko L-42 sharp-cut filter and an OCLI B cold mirror. The light intensity at the inside edge of the optical fiber was ca. 35 mW. The degree of the photolysis was estimated on an average to be 68 and 90 % complete for [Mn(hfac)$_2$•**1**] and [Cu(hfac)$_2$•**1**], respectively, by comparing the absorptivity at 2072 cm^{-1} due to the diazo groups of the complexes before and after the photolysis. The progress of the photolysis was found not to be even; the irradiated side of the crystalline samples suffered higher decomposition than the unirradiated side when inspected visually after the photolysis. Therefore the production of the carbene species on the irradiated side of the crystals is judged to be higher than the above estimates.

The temperature dependencies of the magnetic susceptibility χ_{mol} per formula units, [Mn(hfac)$_2$•**1**] and [Cu(hfac)$_2$•**1**], were investigated under constant fields of 500 and 5000 Oe below and above 70 K, respectively. Before irradiation, the $\chi_{\mathrm{mol}}T$ values of fine crystalline samples of [Mn(hfac)$_2$•**1**] and [Cu(hfac)$_2$•**1**] were nearly constant at 4.14 and 0.39 emu K mol^{-1} in the range 2 - 300 K. These values are consistent with theoretical spin-only values of 4.37 and 0.38 emu K mol^{-1} calculated for dilute paramagnets of S = 5/2 and 1/2, respectively, indicating that the d electrons of manganese (II) and copper(II) ions are magnetically isolated (the upper half of Scheme 1). When irradiated with a xenon lamp (λ > 400 nm),[6] the $\chi_{\mathrm{mol}}T$ values changed with irradiation time and leveled off after 16-18 hr.

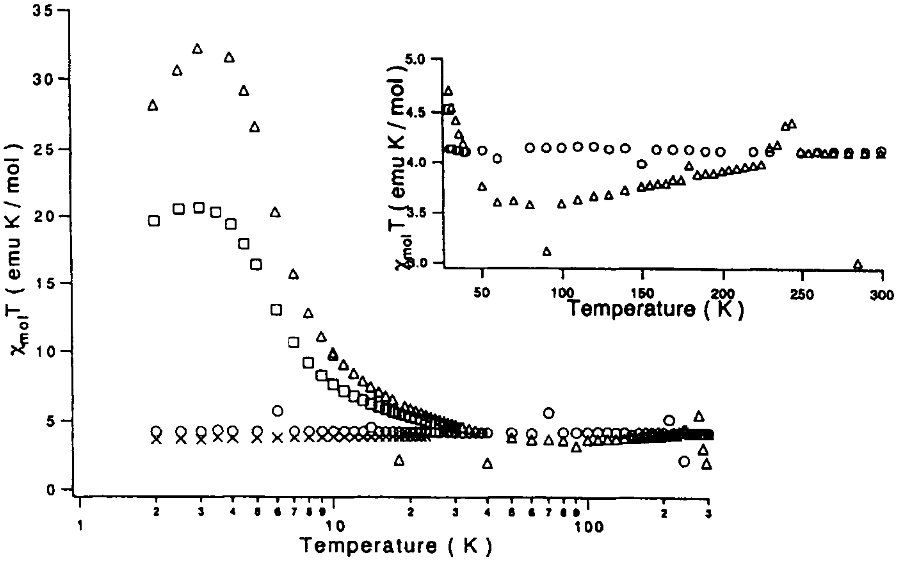


Figure 2. The temperature dependencies of the product $\chi_{\mathrm{mol}}T$ of "molar" paramagnetic susceptibility times temperature per formula [Mn(hfac)$_2$•**1**] of the crystalline samples: before (○) and after the irradiation for 2 hr (□) and 18 hr (△), and then after keeping at 300 K for one hour (X). The changes in the range 30-300 K are expanded in inset.[7]

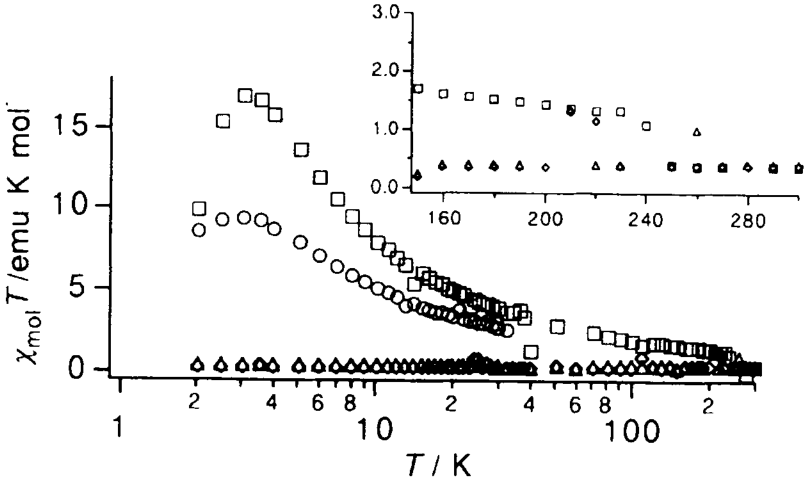


Figure 3. The plot of $\chi_{\mathrm{mol}}T$ vs T for a crystalline sample of [Cu(hfac)$_2$•**1**] before (△) and after irradiation for 2 hr (○), and 16 hr (□), and then after leaving at 300 K for 15 min (◇). The inset shows high temperature range 150 - 300 K.

The temperature dependencies of the $\chi_{mol}T$ values were contrasting between [Mn(hfac)$_2$•**1**] and [Cu(hfac)$_2$•**1**]. As the temperature was increased from 2 K, the $\chi_{mol}T$ values for [Mn(hfac)$_2$•**1**] increased, reached a maximum of 32.2 emu K mol^{-1} at 3 K, rapidly decreased to a shallow minimum of 3.58 emu K mol^{-1} at ca. 80 K, and then gradually increased until 230 K. An abrupt change in the $\chi_{mol}T$ value was observed at 230 K above which it traced the horizontal line before irradiation. Subsequent measurements of the $\chi_{mol}T$ values at 2-300 K of the same sample left at 300 K for an hour showed temperature independent horizontal lines overlapped with those before irradiation (Figure 2). In the case of [Cu(hfac)$_2$•**1**], the $\chi_{mol}T$ values increased steeply, reached a maximum at 3.0 K, and then decreased gradually until 230 K. After irreversible change at 230 K, they exactly traced the data obtained before irradiation. In a consecutive measurement for the same sample left at 300 K, the $\chi_{mol}T$ values again traced the ones before irradiation even at low temperatures (Figure 3).

DISCUSSION

The temperature independent $\chi_{mol}T$ values before irradiation and after irradiation followed by annealing at > 230 K clearly demonstrate that the diazo ligand **1** and the chemically quenched carbene ligand are insulating magnetic couplers (Scheme 1). The temperature dependence ($T < 230$ K) of the $\chi_{mol}T$ values after photolysis of [Mn(hfac)$_2$•**1**] and [Cu(hfac)$_2$•**1**] are best interpreted in terms of the formation of a ferri- and ferromagnetic chains made by alternating units of triplet di(4-pyridyl)carbenes on the one hand and high-spin d^5 manganese(II) and low-spin d^9 copper(II) ions on the other, respectively. As the temperature is lowered, the antiferromagnetic coupling of the unpaired electrons of the manganese ion ($S = 5/2$) and the carbene center (2/2) dominates thermal fluctuation and produces a minimum in the $\chi_{mol}T$ vs T plot as in a number of hetero-spin systems.[8,9] The correlation of increasing length along the ferrimagnetic chain leads to the increase in $\chi_{mol}T$ values; the correlation length at 3 K is estimated to be the ordering over ca. 40 units in [Mn(hfac)$_2$•**1**] (the lower half of Scheme 1).

The magnitude of the antiferromagnetic exchange coupling J/k_B (in Scheme 1) between the adjacent manganese ion and the carbene center was estimated to be ca. -20 K from two independent methods. A 1:2 complex, [Mn(hfac)$_2$•**2**$_2$], was prepared as a reference complex by using two equivalent moles of diazophenyl(4-pyridyl)methane (**2**)[5] in a manner similar to the preparation of [Mn(hfac)$_2$•**1**]. X-ray crystal and molecular structure data of [Mn(hfac)$_2$•**2**$_2$][10] showed that the two pyridyl nitrogens are ligated to a manganese ions in *trans* form (Figure 4). The bond distances of Mn-N and

Mn-O are 2.28 and 2.15 Å, respectively; the coordination geometry is an elongated distorted octahedron. As the temperature was increased from 2 to 300 K in the dark

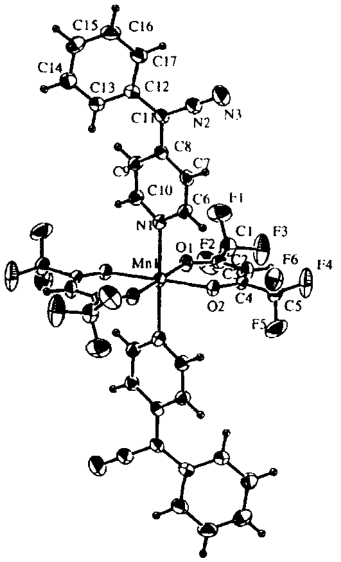


Figure 4. ORTEP drawing of the [Mn(hfac)$_2$•**2**$_2$] at 30 % probability.

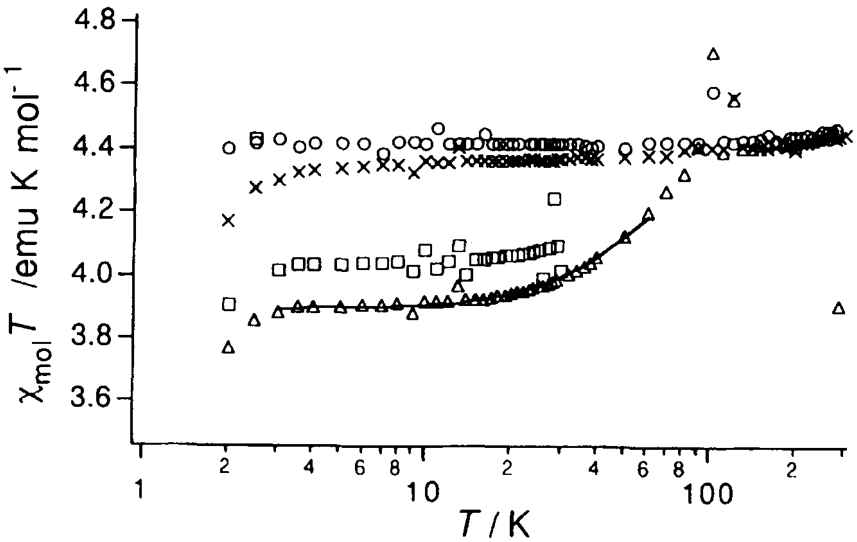


Figure 5. The temperature dependencies of products $\chi_{mol}T$ of "molar" magnetic susceptibilities times temperature per formula [Mn(hfac)$_2$•**2**$_2$] of the crystalline samples: before (○) and after the irradiation for 2 hr (□) and 18 hr (△), and then after keeping at 300 K for one hour (X). Solid curve is a theoretical one calculated on the based of the linear three spin system with optimized parameters given in text.

after the photolysis, $\chi_{\mathrm{mol}}T$ values of $[\mathrm{Mn(hfac)_2 \cdot 2_2}]$ remained nearly constant at 3 - 20 K, gradually increased until ca. 90 K, and then exactly traced those before irradiation (Figure 5), a behavior characteristic of three-spin systems having an antiferromagnetic interaction between the generated carbene centers and the manganese ion. The observed $\chi_{\mathrm{mol}}T$ vs T plots obtained between 3 - 60 K after irradiation for 18 hr were analyzed on the basis of spin Hamiltonian:

$$H = -2J(S_1S_M + S_MS_2) \qquad (1)$$

for the linear three spin system S_1-S_M-S_2 revealed by the X-ray crystal and molecular structure. Photolysis factor F, Weiss temperature θ, and Lande factor g, were obtained by means of a least-squares method to give the best fitting parameters: $J/k_B = -17.8 \pm 0.4$ K, $\theta = -0.011 \pm 0.007$ K, $g = 2.06 \pm 0.01$, and $F = 18.0 \pm 0.1$ %. The theoretical curve is included in Figure 5.

Alternatively, the data for $[\mathrm{Mn(hfac)_2 \cdot 1}]$ in Figure 2 was analyzed theoretically on the basis of a ferrimagnetic chain model consisting of a $S = 5/2$ classical and $S = 2/2$ quantum spins to give a preliminary result of $J/k_B = -25.6$ K and $g = 2$.[11]

The latter method based on a model of the $S = 1/2$ and $S = 2/2$ Heisenberg ferromagnetic chain ($g = 2$) for $[\mathrm{Cu(hfac)_2 \cdot 1}]$ gave $J/k_B = +66.8$ K.[11]

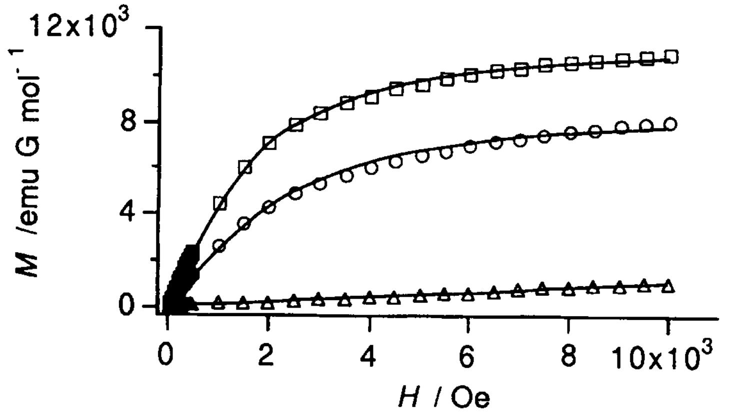


Figure 6. The plot of M vs H for a crystalline sample of $[\mathrm{Cu(hfac)_2 \cdot 1}]$ at 3.5 K before (△) and after irradiation for 2 hr (○) and 16 hr (□). Solid curves are theoretical ones calculated on the basis of the Brillouin function with $S = 1/2$, 18.8, and 26.4.

Since the interaction is ferromagnetic, there is no minimum in the $\chi_{\mathrm{mol}}T$ vs. T plot for $[\mathrm{Cu(hfac)_2 \cdot 1}]$. The field dependence of magnetization, M, for the same sample of $[\mathrm{Cu(hfac)_2 \cdot 1}]$ at 3.5 K before and after irradiation for 16 hr are reproduced in Figure 6. Before irradiation the M values were nearly linear in good agreement with a $S = 1/2$

paramagnet. Fitting of a theoretical curve based on the Brillouin function[12] gave S = 26.4 ± 0.2 after photolysis. The ferromagnetic coupling between the Cu(II) ion and the coordinated triplet di(4-pyridyl)carbene is interpreted in terms of the orthogonality of the singly occupied $d_{x^2-y^2}$ atomic orbital of Cu(II) and the π-orbital on the pyridyl nitrogen which carries spin density due to the carbene center at the *p*-position.

CONCLUSION

It is concluded that the photochemical generation of the triplet carbene centers induces polarization of the π-electrons on the pyridine rings which in turn effects the coupling of magnetically isolated 3d spins of the Mn and Cu ions along the one-dimensional chains (Scheme 1). These results provide the first example of the formation of extended ferri- and ferromagnetic chains containing photochemically generated 2p spins: a prototype of the molecular photomagnetic recording device in which only the irradiated domain of the non- or weakly magnetic materials becomes strongly magnetic. Once the ordering of the spins is established for samples having higher dimensional structure (Figure 7),[13] the photochemically generated heterospin systems will serve as molecular photomagnetic recording devices just as photoresists become functional for printing circuit elements.[14]

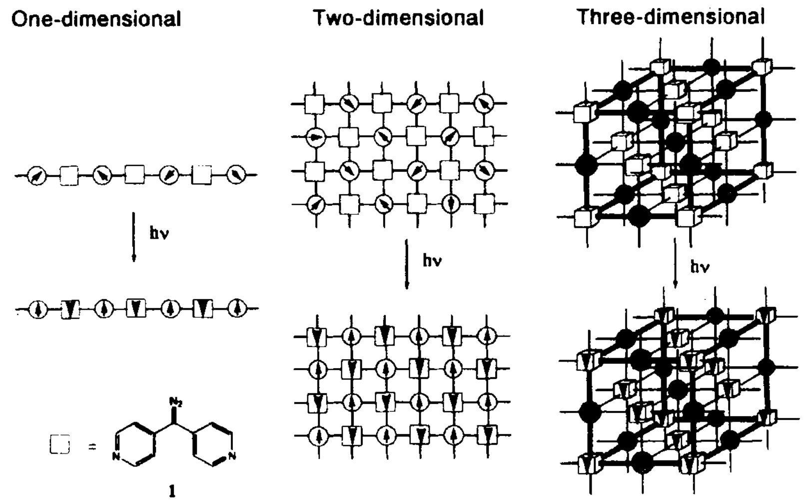


Figure 7. Schematic drawings of the one-, two- and three-dimensionally aligned spins consisting of magnetic metal ions and photo-responsive spins and/or magnetic coupling units.

Acknowledgment. This work was supported by a Grant-in-Aid for COE Research "Design and Control of Advanced Molecular Assembly Systems" from the Ministry of Education, Science and Culture, Japan (#08CE2005).

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10. [Mn(hfac)$_2$•**2**$_2$]: Anal. Calcd for $C_{34}H_{22}N_6O_4F_{12}Mn$: C, 47.40; H, 2.57; N, 9.76. Found: C, 47.45; H, 2.51; N, 9.89. The following crystal parameters for [Mn(hfac)$_2$•**2**$_2$] have been obtained: monoclinic, space group $P2_1/c$(#14), a = 12.432(3) Å, b = 6.739(4) Å, c = 22.192(3) Å, β = 104.87(1)° V = 1797(1) Å^3, Z = 3, D_{calcd} = 1.267 g/cm^{-1}, R = 0.039 and R_w = 0.026.
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12. $M = NgS\,\mu_B B(x)$ where B(x) is the Brillouin function and $x = gS\,\mu_B H/(k_B T)$. The other symbols have their usual meanings.
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14. For practical applications, sensitivity to oxygen and thermal reactivity of the triplet carbene centers may pose problems and should be overcome.