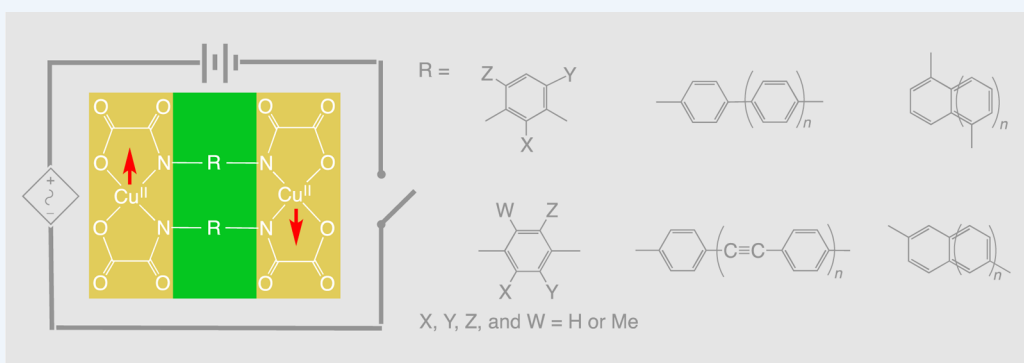


Dicopper(II) Metallacyclophanes as Multifunctional Magnetic Devices: A Joint Experimental and Computational Study

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CONSPECTUS: Metallosupramolecular complexes constitute an important advance in the emerging fields of molecular spintronics and quantum computation and a useful platform in the development of active components of spintronic circuits and quantum computers for applications in information processing and storage. The external control of chemical reactivity (electro- and photochemical) and physical properties (electronic and magnetic) in metallosupramolecular complexes is a current challenge in supramolecular coordination chemistry, which lies at the interface of several other supramolecular disciplines, including electro-, photo-, and magnetochemistry. The specific control of current flow or spin delocalization through a molecular assembly in response to one or many input signals leads to the concept of developing a molecule-based spintronics that can be viewed as a potential alternative to the classical molecule-based electronics. A great variety of factors can influence over these electronically or magnetically coupled, metallosupramolecular complexes in a reversible manner, electronic or photonic external stimuli being the most promising ones. The response ability of the metal centers and/or the organic bridging ligands to the application of an electric field or light irradiation, together with the geometrical features that allow the precise positioning in space of substituent groups, make these metal–organic systems particularly suitable to build highly integrated molecular spintronic circuits. In this Account, we describe the chemistry and physics of dinuclear copper(II) metallacyclophanes with oxamato-containing dinucleating ligands featuring redox- and photoactive aromatic spacers. Our recent works on dicopper(II) metallacyclophanes and earlier ones on related organic cyclophanes are now compared in a critical manner. Special focus is placed on the ligand design as well as in the combination of experimental and computational methods to demonstrate the multifunctionality nature of these metallosupramolecular complexes. This new class of oxamato-based dicopper(II) metallacyclophanes affords an excellent synthetic and theoretical set of models for both chemical and physical fundamental studies on redox- and photo-triggered, long-distance electron exchange phenomena, which are two major topics in molecular magnetism and molecular electronics. Apart from their use as ground tests for the fundamental research on the relative importance of the spin delocalization and spin polarization mechanisms of the electron exchange interaction through extended π -conjugated aromatic ligands in polymetallic complexes, oxamato-based dicopper(II) metallacyclophanes possessing spin-containing electro- and chromophores at the metal and/or the ligand counterparts emerge as potentially active (magnetic and electronic) molecular components to build a metal-based spintronic circuit. They are thus unique examples of multifunctional magnetic complexes to get single-molecule spintronic devices by controlling and allowing the spin communication, when serving as molecular magnetic couplers and wires, or by exhibiting bistable spin behavior, when acting as molecular magnetic rectifiers and switches. Oxamato-based dicopper(II) metallacyclophanes also emerge as potential candidates for the study of coherent electron transport through single molecules, both experimentally and theoretically. The results presented herein, which are a first step in the metallosupramolecular approach to molecular spintronics, intend to attract the attention of physicists and materials scientists with a large expertise in the manipulation and measurement of single-molecule electron transport properties, as well as in the processing and addressing of molecules on different supports.

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■ INTRODUCTION

Supramolecular coordination chemistry, referred to as metallo-supramolecular chemistry, is an outstanding research area that offers convenient tools to move from molecular magnetism and molecular electronics toward molecular spintronics.¹ The structural modulation and external control of the magnetic and electronic coupling in metallosupramolecular complexes, combined with their nanometer size and easy handling, can be exploited in the development of active molecular components of spintronic circuits and quantum computers for future applications in information processing and storage.^{2–4} These include metal *meso*-helicates (so-called mesocates), which are proposed as examples of magnetic wires and switches⁵ by analogy with the more familiar electronic wires and switches based on metal strings,⁶ but also metal helicates and metal grids, which would serve to encode binary information on the molecular scale in spin-based quantum computing devices such as magnetic quantum bits (qubits)⁷ and quantum cellular automata (QCA).⁸

Metallacyclophanes are indeed a unique class of metallosupramolecular complexes because they combine the inherent optical, redox, and magnetic properties of the intervening metal centers with those of the parent, purely organic cyclophanes.⁹ The design and synthesis of novel types of electro- and photoactive noninnocent aromatic bridging ligands constitute thus a major goal in the field of metallosupramolecular chemistry. They should be able to self-assemble with paramagnetic first-row transition metal ions, while mediating both magnetic and electronic coupling effects between the metallic centers across the extended π -conjugated aromatic spacers in a switchable manner. This requires both a skillful organic synthesis and a deep understanding of the electron exchange (EE) mechanism. With the advent of calculations based on the density functional (DF) theory combined with the broken-symmetry (BS) approach, it has been possible not only to reproduce but also to predict the molecular and electronic structures of polymetallic complexes.¹⁰

The strategy developed by our group in this area is based on the use of dinucleating ligands having two oxamato donor groups separated by more or less rigid noninnocent, extended π -conjugated aromatic spacers that self-assemble with Cu^{II} ions to form double-stranded dicopper(II) metallacyclic complexes of

the cyclophane type (Scheme 1, left). The almost perpendicular disposition among the two coplanar metal basal planes and the two parallel planes of the aromatic spacers ensures an unusual π -type orbital pathway for the propagation of the EE interaction between the unpaired electrons occupying the σ -type $d_{x^2-y^2}$ (Cu) orbitals (so-called “magnetic orbitals”) (Scheme 1, right). This situation leads to the occurrence of a σ - π interaction due to hyperconjugation within the π -system of the aromatic diamidate bridges, involving the sp^2 (N) orbitals that are oriented nearly parallel to the p_z (C) orbitals.

The variation of the aromatic spacer in this family of oxamato-based dicopper(II) metallacyclophanes may control their overall structure and magnetic properties, as summarized in Table 1.^{11–18} The influence of different factors such as the topology and conformation of the bridging ligand and its noninnocent character on the sign and strength of the magnetic coupling as well as on the electro- and photochemical behavior can then be investigated in a systematic way, which would ultimately allow achieving potentially switchable, long-distance EE interactions. Indeed, the variety of single-molecule magnetic behaviors herein reported illustrates the potential of electro- and photoactive, exchange-coupled dicopper(II) metallacyclophanes as prototypes of multifunctional magnetic devices in the emerging area of molecular spintronics.

■ DICOPPER(II) META- AND PARACYCLOPHANES AS PROTOTYPES OF MOLECULAR MAGNETIC COUPLERS

“Molecular ferro- and antiferromagnetic couplers” (MFCs and MACs) are molecular components that would align in either parallel or antiparallel manner, respectively, the spin of the spin carriers along the spintronic circuit, as illustrated by Scheme 2.

The concept of magnetic couplers was earlier used to control the spin alignment in organic molecules.^{19,20} For instance, the distinct triplet and singlet ground spin states in the *meta*- and *para*-phenylenebis(diphenylcarbene) diradicals can be rationally interpreted on the basis of the MFC and MAC concepts, respectively (Scheme 3a). Depending on the substitution pattern of the phenylene linker involved in the “through-bond” EE pathway, the unpaired π -electrons on each diphenylcarbene

Scheme 1. General Chemical Structure of the Oxamato-Based Dicopper(II) Metallacyclophanes Illustrating the Relative Orientation of the $d_{x^2-y^2}$ Magnetic Orbitals of the Square Planar Cu^{II} Ions with Respect to the p_z Orbitals of the Extended π -Conjugated Aromatic R Spacers (See Table 1)

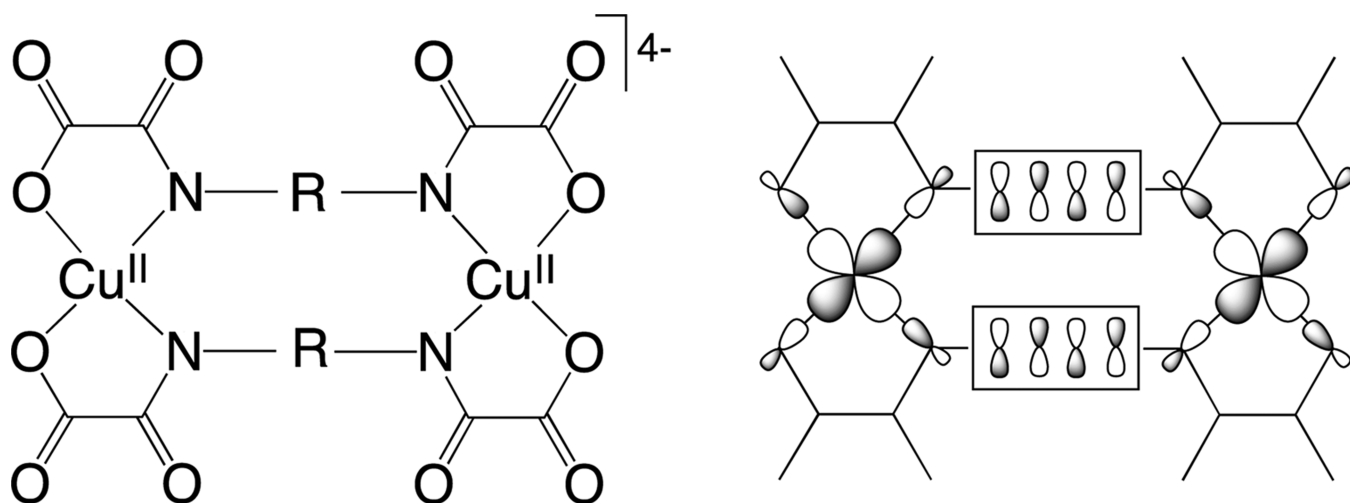
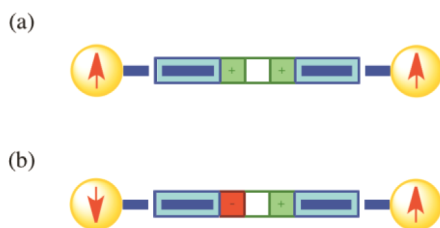


Table 1. Selected Structural and Magnetic Data for Oxamato-Based Dicopper(II) Metallacyclophanes

Entry	Complex ^a	R ^b	r (Å) ^c	J ^d (cm ⁻¹)
1	Na ₄ [Cu ₂ (mpba) ₂] · 8H ₂ O		6.8	+16.8
2	(Bu ₄ N) ₄ [Cu ₂ (Mempba) ₂] · 4H ₂ O		7.2	+16.4
3	(Bu ₄ N) ₄ [Cu ₂ (Me ₃ mpba) ₂] · 12H ₂ O		7.3	+15.9
4	Na ₄ [Cu ₂ (ppba) ₂] · 11H ₂ O		7.9	-81
5	Li ₄ [Cu ₂ (Meppba) ₂] · 7H ₂ O		7.9	-100
6	(Ph ₄ P) ₄ [Cu ₂ (Me ₄ ppba) ₂] · 15H ₂ O		7.9	-144
7	Na ₄ [Cu ₂ (bpba) ₂] · 12H ₂ O		n = 1	-9.5
8	(Ph ₄ P) ₄ [Cu ₂ (tpba) ₂] · 10H ₂ O		n = 2	-2.1
9	(Bu ₄ N) ₄ [Cu ₂ (dpeba) ₂] · 4MeOH · 2Et ₂ O		n = 1	-3.9
10	(Bu ₄ N) ₄ [Cu ₂ (tpeba) ₂] · 12H ₂ O		n = 2	-0.9
11	(Ph ₄ P) ₄ [Cu ₂ (naba) ₂] · 8H ₂ O		8.3	-20.7
12	(Bu ₄ N) ₄ [Cu ₂ (anba) ₂]		12.5	-23.9

^aAbbreviations used: H₄mpba = N,N'-1,3-phenylenebis(oxamic acid); H₄Mempba = N,N'-2-methyl-1,3-phenylenebis(oxamic acid); H₄Me₃mpba = N,N'-2,4,6-trimethyl-1,3-phenylenebis(oxamic acid); H₄ppba = N,N'-1,4-phenylenebis(oxamic acid); H₄Meppba = N,N'-2-methyl-1,4-phenylenebis(oxamic acid); H₄Me₄ppba = N,N'-2,3,5,6-tetramethyl-1,4-phenylenebis(oxamic acid); H₄bpba = N,N'-4,4'-biphenylenebis(oxamic acid); H₄tpba = N,N'-1,4-di(4-phenyl)phenylenebis(oxamic acid); H₄bpeba = N,N'-4,4'-diphenylethynebis(oxamic acid); H₄tpeba = N,N'-1,4-di(4-phenylethynyl)phenylenebis(oxamic acid); H₄naba = N,N'-1,5-naphthalenebis(oxamic acid); H₄anba = N,N'-2,6-anthracenebis(oxamic acid). ^bSee Scheme 1. ^cr is the intermetallic distance. ^dJ is the magnetic coupling constant, the spin Hamiltonian being defined as $H = -JS_1 \cdot S_2$ (with $S_1 = S_2 = S_{Cu} = 1/2$).

Scheme 2. Illustration of a Molecular Ferro- and Antiferromagnetic Coupler Showing the (a) Parallel and (b) Antiparallel Spin Alignment, Respectively



monoradical unit will be ferro- or antiferromagnetically coupled for an odd (*meta* isomer) or even number (*para* isomer) of carbon atoms, respectively. These simple topological arguments are ultimately based on the alternance of the spin densities at the adjacent carbon atoms of the phenylene linker, which results from the double (or dynamic) spin polarization (DSP).²¹ The concerted DSP effects by the unpaired π electrons of the trivalent carbon atoms in this family of isomeric bis(diphenylcarbene) diradicals are additive for a parallel spin alignment in the *meta* isomer or, conversely, for an antiparallel spin alignment in the *para* isomer, favoring then the triplet or the singlet state, respectively.

Iwamura and co-workers successfully extended this work to related paracyclophane derivatives incorporating two facing diphenylcarbene triplet diradicals ($S_A = S_B = S_R = 1$) in pseudo-*meta* or pseudo-*para* configurations that favor their antiferro- or ferromagnetic coupling to give singlet ($S = S_A - S_B = 0$) or

quintet ($S = S_A + S_B = 2$) ground spin states, respectively (Scheme 3b).²² In fact, each diphenylcarbene diradical unit possesses two unpaired electrons occupying orthogonal orbitals of σ - and π -type symmetries, with a “robust” triplet ground spin state. The σ -electrons are mainly localized on the divalent carbon atoms, while the π -electrons are largely delocalized and partially polarized within the benzene rings leading to an alternance of the spin densities of adjacent carbon atoms. Depending on the connectivity pattern of the paracyclophane bridging skeleton, the “through-space” EE interactions between the nearest-neighbor carbon atoms of the two facing spin-polarized benzene rings favor the overall antiparallel alignment of the electron pairs on each diphenylcarbene diradical unit in the pseudo-*meta* isomer or, conversely, their parallel spin alignment in the pseudo-*para* isomer. This family of isomeric bis(phenylmethylene)[2.2]-paracyclophanes thus served as ground tests of the McConnell model for the topological control of the magnetic coupling in organic polyradicals.²³

The appropriate choice of the topology (substitution pattern) of the bridging ligand in building oxamato-based dicopper(II) metallacyclophanes with 1,3- and 1,4-phenylene spacers also allows controlling the sign and strength of the magnetic coupling in polymeric complexes.^{11,13} The different substitution pattern of the phenylene spacers in the corresponding oxamato-based dicopper(II) meta- and paracyclophanes (Figure 1) is found to be responsible for the observed moderate to strong, ferro- and antiferromagnetic coupling (see Table 1, entries 1 and 4, respectively).^{11,13} In each case, the *meta*- and *para*-substituted phenylene spacers act as MFC and MAC,

Scheme 3. (a) Chemical Structure of the Bis(Diphenylcarbene) Diradicals with *meta*- or *para*-substituted Phenylene Spacers Showing the Different Antiparallel (Left) or Parallel (Right) Spin Alignments, Resulting from the Alternance of the Spin Densities. (b) Chemical Structure of the Pseudo-*meta* or Pseudo-*para* Isomers of the Bis(Diphenylcarbene) [2.2]Paracyclophane Tetraradicals Showing the Different Overall Ferro- (Left) and Antiferromagnetic (Right) Couplings, Respectively, According to the McConnell Model. The Thick Arrows are the Unpaired Electrons of the Tri- or Divalent Carbon Atoms, While the Narrow Arrows Represent the Spin-Polarized π -Electron System of the Benzene Rings.

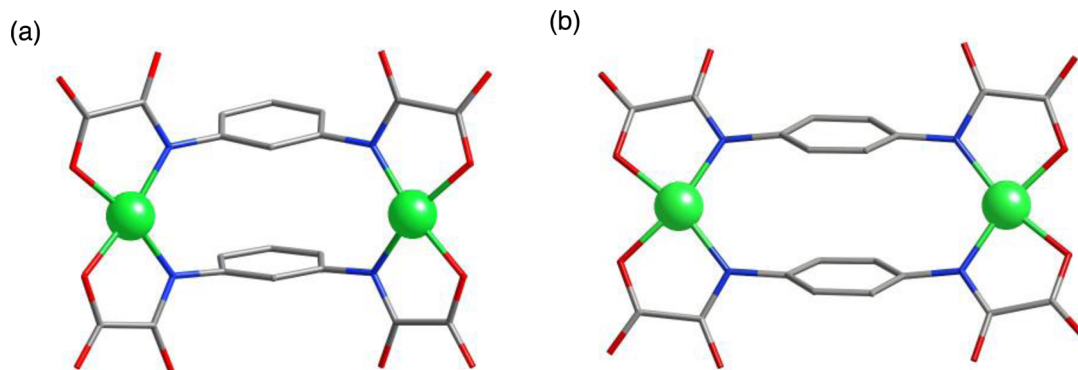
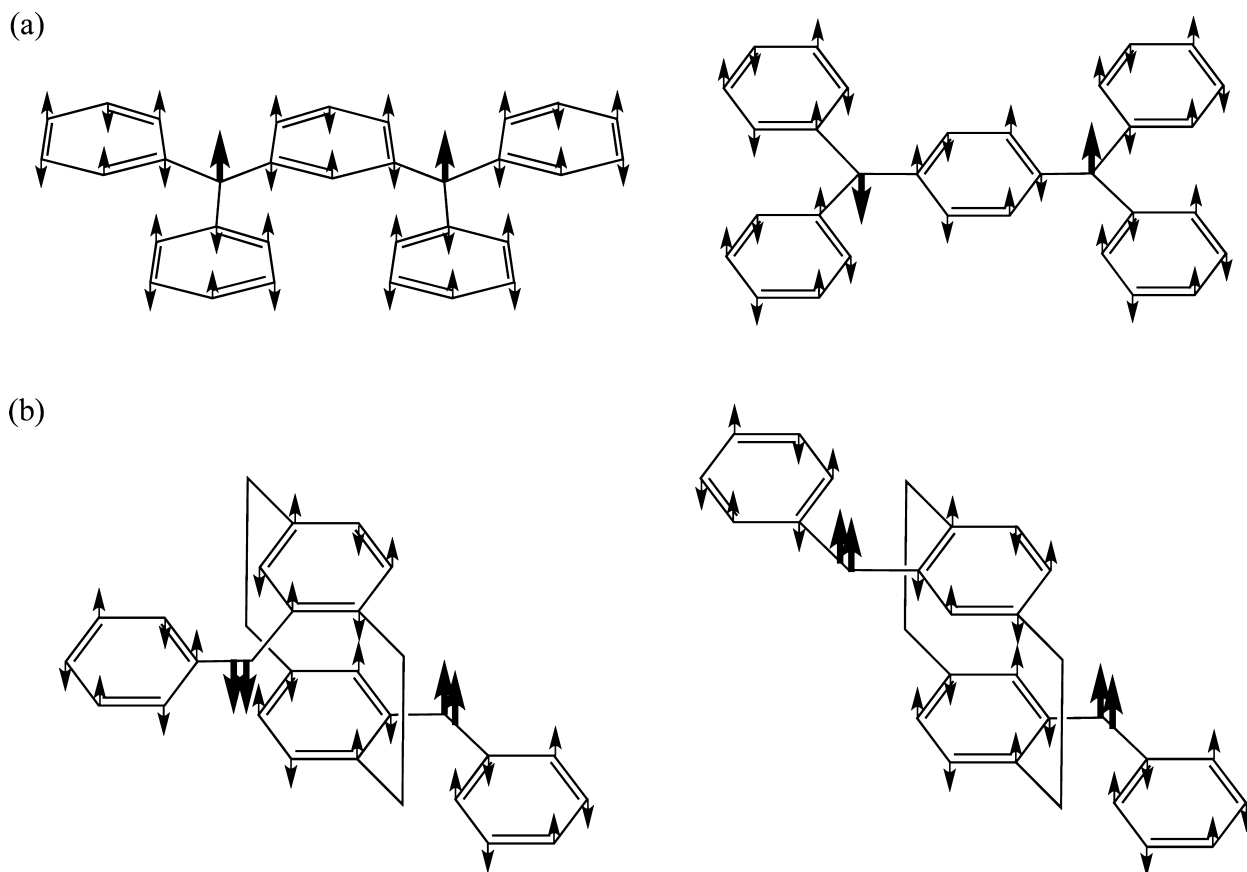


Figure 1. Perspective views of the anionic *meta*- and *paracyclophane* dinuclear units, respectively, of (a) $\text{Na}_4[\text{Cu}_2(\text{mpba})_2] \cdot 10\text{H}_2\text{O}$ and (b) $\text{Na}_4[\text{Cu}_2(\text{ppba})_2] \cdot 11\text{H}_2\text{O}$ (see Table 1 for ligand abbreviations).

respectively, between the two Cu^{II} ions ($S_A = S_B = S_{\text{Cu}} = 1/2$) leading to either triplet ($S = S_A + S_B = 1$) or singlet ($S = S_A - S_B = 0$) ground spin states for the Cu^{II}_2 metallacyclophane molecule, as shown in Figure 2.

In these metallacyclic analogues of the *m*- and *p*-phenylenebis(diphenylcarbene) organic diradicals, the ferro- and antiferromagnetic nature of the EE interaction results from a spin polarization mechanism through the extended π -conjugated bond system of the *meta*- and *para*-substituted phenylene spacers,

respectively, as supported by DF calculations.^{11,13} In each case, the spin densities at the nitrogen donor atoms possess the same sign as those at the copper atoms due to the spin delocalization in the Cu–N bonds, while the adjacent benzene-carbon atoms show alternating positive and negative spin densities because of the concerted polarizations by the unpaired electrons of the Cu^{II} ions, having identical (*meta* substitution) or opposite signs (*para* substitution) of the spin density (Figure 2, left and right, respectively).

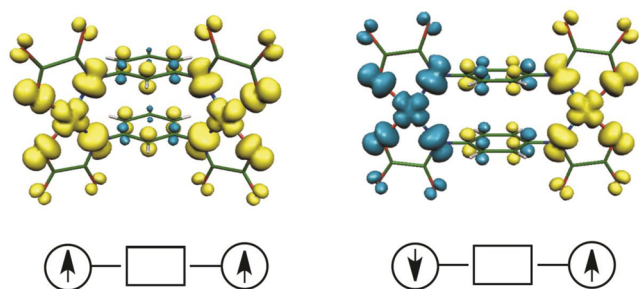
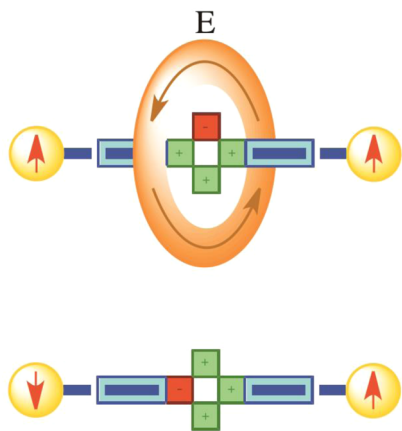


Figure 2. Perspective views of the calculated spin density distribution for the ground triplet and BS singlet spin states, respectively, of the orthogonal models of the dicopper(II) meta- (left) and paracyclophanes (right) illustrating the molecular ferro- and antiferromagnetic coupler concepts (yellow and blue contours represent positive and negative spin densities, respectively).

■ PERMETHYLATED DICOPPER(II) PARACYCLOPHANES AS PROTOTYPES OF MOLECULAR MAGNETIC RECTIFIERS

“Molecular magnetic rectifiers” (MMRs) are molecular components that would invert the spin alignment between the spin carriers along the spintronic circuit by means of an electrical potential (“threshold voltage”), as illustrated by Scheme 4.

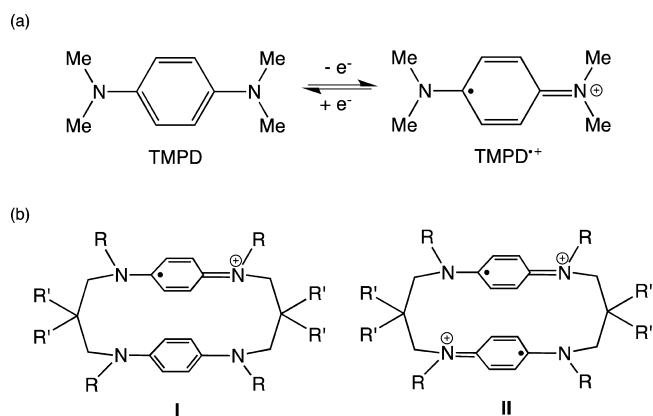
Scheme 4. Illustration of a Molecular Magnetic Rectifier Showing the Inversion of the Spin Alignment from Parallel to Antiparallel Induced by an External Applied Electric Field



This spin-current rectification phenomenon, which is related to the spin-polarized nature of the current in molecular spintronics, is the counterpart of the more familiar charge-current rectification, which is being investigated for transition metal complexes of donor-bridge-acceptor diradicals.²⁴ The required bistable magnetic molecules acting as MMRs are likely to be built from two spin-containing units whose spin alignment can be switched from parallel to antiparallel, or vice versa, by means of an electroswitchable magnetic coupler.

The first step through our ligand design approach to multifunctional magnetic devices was then the incorporation of electroactive aromatic spacers in the oxamato-based dicopper(II) metallacyclophanes to get a magnetic rectification. The aforementioned dicopper(II) paracyclophanes are appealing candidates as MMRs because of the redox noninnocent nature of the polymethyl-substituted *p*-phenylene spacers.^{12,13} In fact, the parent *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) is easily oxidized to the corresponding π -radical iminium cation

Scheme 5. (a) Redox Equilibrium of *N,N,N',N'*-Tetramethyl-*p*-Phenylenediamine. (b) Chemical Structures of the π -Stacked Radical (I) and Diradical (II) Redox Forms of Polyalkyl-Substituted, Doubly Trimethylene-Bridged Bis(*p*-Phenylenediamine) Derivatives.



(TMPD^{•+}) (Scheme 5a), which is one of the oldest known stable organic radical cations (referred to as Wurster blue).²⁵ This work has been recently extended to related π -stacked radical (I) and diradical (II) iminium cations resulting from the stepwise two-electron oxidation of polyalkyl-substituted, doubly trimethylene-bridged bis(*p*-phenylenediamine) derivatives (Scheme 5b with R = Me, Et, or *i*Pr and R' = H or Me), which belong to the large class of tetraza[5.5]paracyclophanes (so-called Wurster blue cyclophanes).²⁶

The corresponding oxamato-based dicopper(II) metallacyclophanes with polymethyl-substituted 1,4-phenylene spacers, $-C_6H_{(4-x)}Me_x-$ ($x = 0, 1, \text{ and } 4$) (Figure 3), exhibit two well-separated one-electron oxidations in acetonitrile solution, with only the first one being reversible, possessing relatively low formal potential values that decrease with the increasing number of electron-donating methyl substituents [$E_1 = +0.33$ ($x = 0$), $+0.24$ ($x = 1$), and $+0.15$ V vs SCE ($x = 4$) and $E_2 = +0.79$ ($x = 0$), $+0.80$ ($x = 1$), and $+0.86$ V vs SCE ($x = 4$)].^{12,13} These two redox processes correspond to the stepwise ligand-centered oxidation of each of the two facing polymethyl-substituted *p*-phenylenediamide bridges to give the corresponding dicopper(II) π -radical and diradical species, which are the metallacyclic analogues of the aforementioned purely organic Wurster blue cyclophanes (see forms I and II in Scheme 5b).

This new class of oxamato-based permethylated dicopper(II) paracyclophanes can then be viewed as prototypes of MMRs, as shown in Figure 4. The magnetic bistability is due to the change from antiparallel to parallel spin alignment of the two unpaired electrons of the Cu^{II} ions ($S_1 = S_2 = S_{Cu} = 1/2$) by means of the antiferromagnetic interaction with the unpaired electron of the delocalized π -stacked radical ligand ($S_3 = S_R = 1/2$) generated upon one-electron oxidation of the double tetramethyl-*p*-phenylenediamide bridge skeleton. Such observation was supported by DF calculations on the optimized molecular geometries of the permethylated dicopper(II) paracyclophane and its monooxidized dicopper(II) π -radical cation species in acetonitrile solution.^{12,13}

The spin density distribution for the ground singlet spin state of the permethylated dicopper(II) paracyclophane precursor shows spin densities of opposite sign at the Cu^{II} ions, together with small but non-negligible spin densities of alternating sign at the adjacent carbon atoms of the benzene rings resulting from

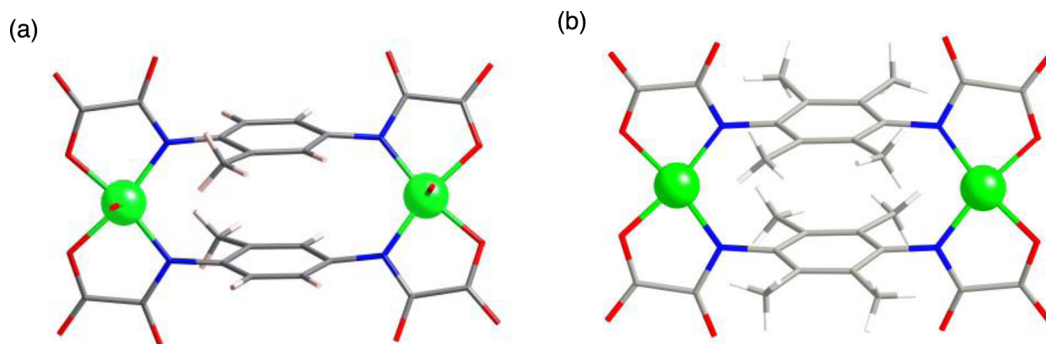


Figure 3. Perspective views of the anionic paracyclophane dinuclear units of (a) $\text{Li}_4[\text{Cu}_2(\text{Meppba})_2] \cdot 7\text{H}_2\text{O}$ and (b) $(\text{Ph}_4\text{P})_4[\text{Cu}_2(\text{Me}_4\text{ppba})_2] \cdot 15\text{H}_2\text{O}$ (see Table 1 for ligand abbreviations).

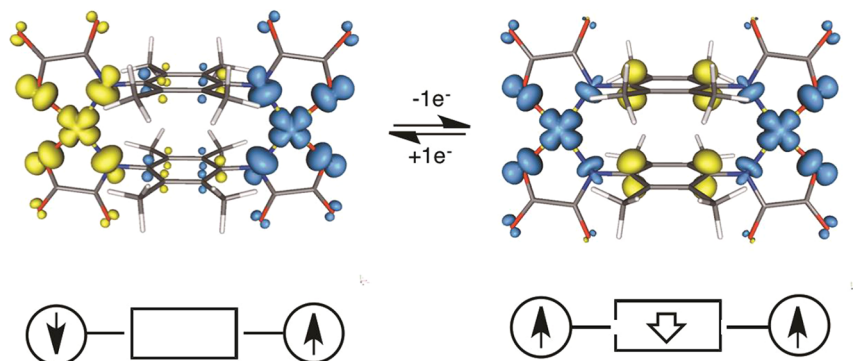


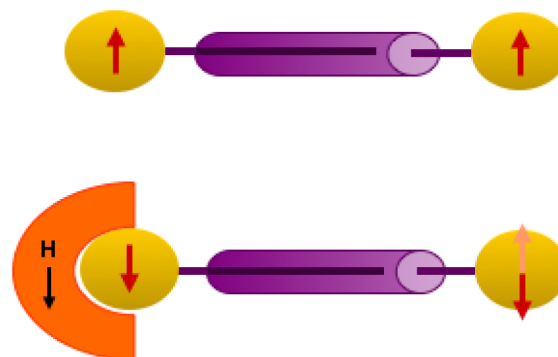
Figure 4. Perspective views of the calculated spin density distribution for the ground BS singlet and doublet spin states, respectively, of the optimized molecular geometries in acetonitrile of the permethylated dicopper(II) paracyclophane precursor (left) and the corresponding monooxidized dicopper(II) π -radical cation species (right) illustrating the molecular magnetic rectifier concept (blue and yellow contours represent positive and negative spin densities, respectively).

spin polarization effects by the nitrogen atoms of the amidate donor groups (Figure 4, left). In contrast, the spin density distribution for the ground doublet spin state of the monooxidized dicopper(II) π -radical cation species reflects spin densities of the same sign at the Cu^{II} ions, alongside a large amount of spin density of opposite sign mainly delocalized on each of the carbon atoms of the two facing benzene rings directly attached to the nitrogen atoms of the amidate donor groups (Figure 4, right). This picture clearly corresponds to that expected for a fully delocalized π -stacked radical cation species, as recently shown for the 2,2-dimethylpropylene-bridged N,N',N'',N''' -tetramethyl-tetraza[5.5]paracyclophane (see form I in Scheme 5b with $R = R' = \text{Me}$).²⁶

■ DICOPPER(II) OLIGO-*p*-PHENYLENO/PHENYLETHYNYLENOPHANES AND OLIGO- $\alpha,\alpha'/\beta,\beta'$ -ACENOPHANES AS PROTOTYPES OF MOLECULAR MAGNETIC WIRES

“Molecular magnetic wires” (MMWs) are the basic molecular components that would allow the magnetic communication between the spin carriers along the spintronic circuit. In contrast to conventional charge transport-based electronic wires, MMWs may offer a new design concept for the transfer of information over long distances based purely on EE interactions and without electric current flow. A spin reorientation induced by an external applied magnetic field on the magnetic center located at the beginning of the wire leads thus to a change on that located at the end of it, as illustrated by Scheme 6.

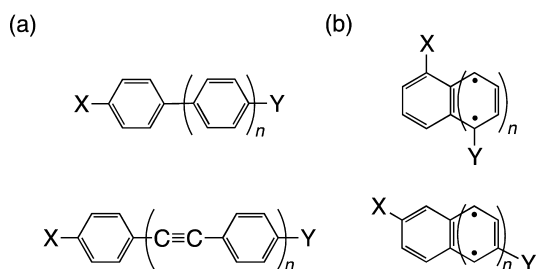
Scheme 6. Illustration of a Molecular Magnetic Wire Showing the Transfer of Information through the Operation of a Spin Reorientation Induced by an External Applied Magnetic Field



The target in this field is to get a long-range magnetic coupling between two distant spin-containing units connected by a long organic spacer that ultimately extends over infinite distances (“wire-like magnetic coupling”), as illustrated by recent studies on organic diradicals with extended π -conjugated aromatic bridges.²⁷ Our ligand design approach to MMWs is based on the incorporation of extended π -conjugated aromatic spacers, as those depicted by Scheme 7, within the oxamato-based dicopper(II) metallacyclophanes to get a wire-like magnetic coupling.^{14–17}

Among the plethora of organic oligomers and co-oligomers at hand, rodlike spacers like oligo-*p*-phenylenes (OPs) and oligo-*p*-phenylethylenes (OPEs) are very appealing candidates as molecular wires (Scheme 7a).^{28,29} Due to their planar conformation,

Scheme 7. Chemical Structures of (a) Rodlike Oligo- (*p*-phenylenes or *p*-phenylene-ethynylenes) and (b) Flatlike Oligo(α,α' - or β,β' -acenes) as Illustrative Examples of Molecular Wires, Showing the Predicted “Open-Shell” Singlet Diradical Ground State for the Longer Derivatives of the Latter Ones



OPEs possess an extended π -conjugation between the *para*-substituted benzene rings across the triple carbon–carbon bonds, which would certainly match up that found in nonplanar OPs, whereby the *para*-substituted benzene rings are significantly tilted around the carbon–carbon single bond because of the repulsive interactions between their *ortho-ortho'* hydrogen atoms. This is exemplified by the corresponding oxamato-based dicopper(II) metallacyclophanes with 4,4'-diphenylene and 4,4'-diphenylethynylene spacers (Figure 5), which exhibit a moderate to weak

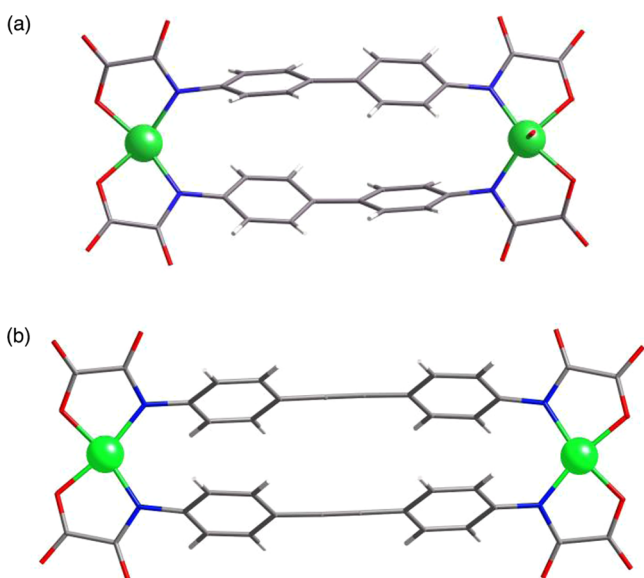


Figure 5. Perspective views of the anionic diphenylenophane and diphenylene-ethynylenophane dinuclear units of (a) Na₄[Cu₂(bpba)₂·(H₂O)₂]·10H₂O and (b) (Bu₄N)₄[Cu₂(dpeba)₂]·4MeOH·2Et₂O (see Table 1 for ligand abbreviations).

antiferromagnetic coupling at a relatively large intermetallic distance (see Table 1, entries 7 and 9, respectively),^{14,15} showing thus that one nanometer was definitely not the upper limit for the observation of magnetic coupling in dicopper(II) complexes.³⁰ Yet a very weak but non-negligible antiferromagnetic coupling is observed for the related oxamato-based dicopper(II) metallacyclophanes with the longer 1,4-di(4-phenyl)- and 1,4-di(4-phenylethynyl)phenylene spacers (see Table 1, entries 8 and 10, respectively).¹⁶

Further developments may be envisaged for molecular wires based on flatlike spacers such as oligoacenes (OAs), which

consist of linearly fused benzenoid units differently substituted at the α,α' - or β,β' -carbon atoms of the terminal benzene rings (Scheme 7b). In fact, earlier DF calculations predicted an “open-shell” singlet diradical ground state for the longer OAs, instead of the common “closed-shell” singlet ground state typical of the shorter OAs.³¹ Surprisingly, the corresponding oxamato-based dicopper(II) metallacyclophane with 2,6-anthracene spacers shows a moderately stronger antiferromagnetic coupling than that with 1,5-naphthalene spacers (Figure 6), in spite of the

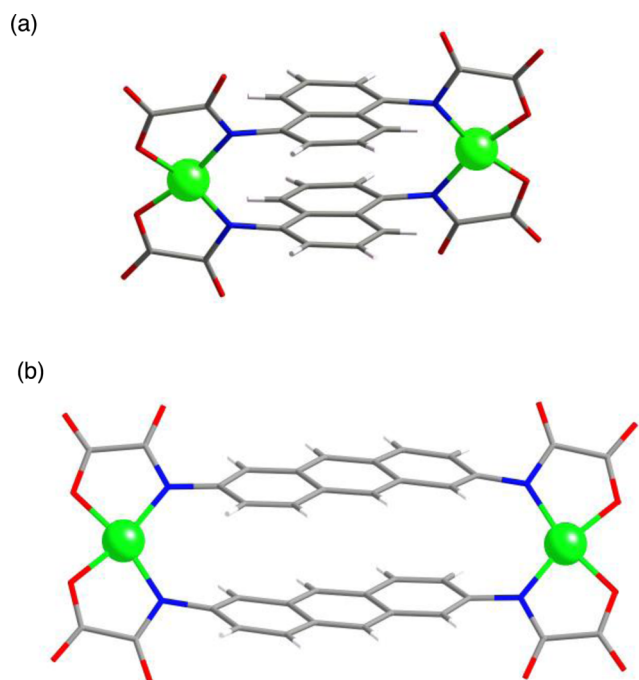


Figure 6. Perspective views of the anionic naphthalenophane and anthracenophane dinuclear units, respectively, of (a) (Ph₄P)₄[Cu₂(naba)₂]·8H₂O and (b) (Bu₄N)₄[Cu₂(anba)₂] (see Table 1 for ligand abbreviations).

significantly greater intermetallic distance (see Table 1, entries 12 and 11, respectively).^{17,18} Once again, these features reflect the relevant role that the substitution pattern of the aromatic spacer applies on the transmission of EE interactions through π -type orbital pathways in oxamato-based dicopper(II) metallacyclophanes.¹⁷

DF calculations on the orthogonal models of this family of oxamato-based dicopper(II) metallacyclophanes with *p*-disubstituted OPs or OPEs [$-(C_6H_4)_{n+1}-$ or $-C_6H_4(C\equiv CC_6H_4)_n-$ with $n = 1-4$] and α,α' - or β,β' -disubstituted OAs [$-(C_{6+4n}H_{4+2n})-$ with $n = 1-9$] predict a different distance dependence of the magnetic coupling when increasing the number of repeating units on the rod- or flatlike spacers, respectively, as depicted by Figure 7.

On the one hand, an exponential decay law as $|J| = J_0 \exp(-\gamma r)$ is calculated for the two related series of dicopper(II) oligo-*p*-phenylenophanes and oligo-*p*-phenylethylenophanes, with the calculated γ value for the OPE spacers being slightly smaller than that found for the OP spacers (red and blue solid lines, respectively, in Figure 7). This feature suggests that the inclusion of additional carbon–carbon triple bond between the benzene rings occurs without any loss of π -conjugated aromatic character, as experimentally found.^{14,16} In contrast, the calculated γ value for

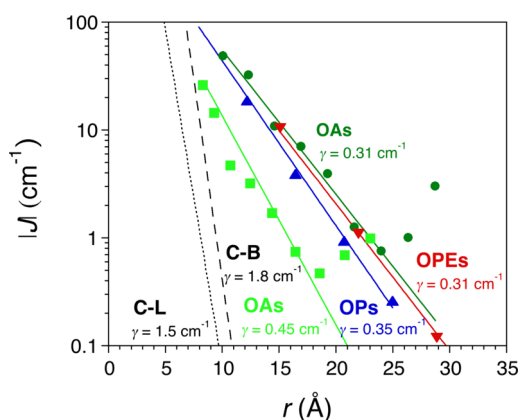


Figure 7. Decay law of the calculated magnetic coupling constant (J) with the intermetallic distance (r) for the orthogonal models of the oxamato-based dicopper(II) metallacyclophanes with oligo(*p*-phenylene) (blue \blacktriangle), oligo(*p*-phenylene-ethynylene) (red \blacktriangledown), oligo(α,α' -acene) (light green \blacksquare), and oligo(β,β' -acene) spacers (dark green \bullet). The solid lines correspond to the best-fit curves, while the dashed and dotted lines are the well-known Coffman–Buettner (C-B) and related relationship by Cano–Lloret (C-L) based on experimental magneto-structural data from simple dicopper(II) complexes (see text).

the shorter members of the dicopper(II) oligo- β,β' -acenophanes is significantly smaller than that found for those of the dicopper(II) oligo- α,α' -acenophanes (dark and light green solid lines, respectively, in Figure 7), supporting the better efficiency of the β,β' - over α,α' -substitution pattern on long-range magnetic coupling, as experimentally found.¹⁷ Earlier relationships obtained by Coffman and Buettner³⁰ and by some of us,¹⁴ which were based on experimental magneto-structural data from simple dicopper(II) complexes with aromatic bridging ligands, predict a dramatically faster decay of the magnetic coupling with the intermetallic distance (dashed and dotted black lines, respectively, in Figure 7). This establishes the relative efficiency of π - vs σ -type EE pathways, as expected because of the larger spin delocalization and spin polarization contributions to the ground state electronic structure in the former case.

On the other hand, a unique wirelike magnetic coupling was predicted for the longer members of the flatlike OA spacers independently of the substitution pattern,¹⁷ with a rise of the magnetic coupling constant at very long intermetallic distances which was not found for the rod-like OP or OPE spacers.^{14,16} These two related series of oxamato-based dicopper(II) oligo- α,α' and β,β' -acenophanes were then proposed as suitable prototypes of MMWs because of the occurrence of a ligand-based polyradical mechanism for the long OA spacers instead of the common nonpolyradical spin polarization mechanism which is operative for the shorter OA spacers, as shown in Figure 8 for the α,α' -disubstituted derivatives with $n = 1$ and 3.¹⁷ When compared with naphthalene spacers (Figure 8, left), larger amounts of spin densities of global opposite sign are found in tetracene spacers, which are delocalized along each of the two oligoacetylene ribbons and partially polarized at the carbon atoms connecting the two oligoacetylene halves (Figure 8, right). Such long oligoacene spacers would then behave as two oligoacetylene monoradicals that are connected by C–C bonds to afford an “open-shell” diradical singlet ground state, in agreement with earlier calculations for oligoacene themselves (see Scheme 7b with $X = Y = H$).³¹

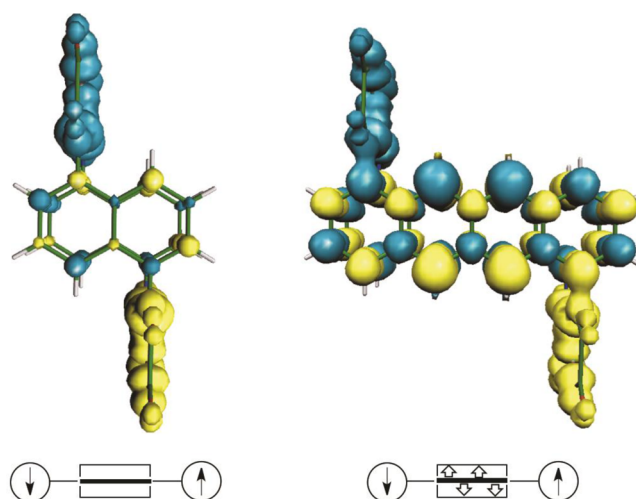


Figure 8. Top projection views of the calculated spin density distribution for the BS singlet spin state of the orthogonal models of the dicopper(II) 1,5-naphthalenophane (left) and 1,5-tetracenophane (right) illustrating the molecular magnetic wire concept (yellow and blue contours represent positive and negative spin densities, respectively).

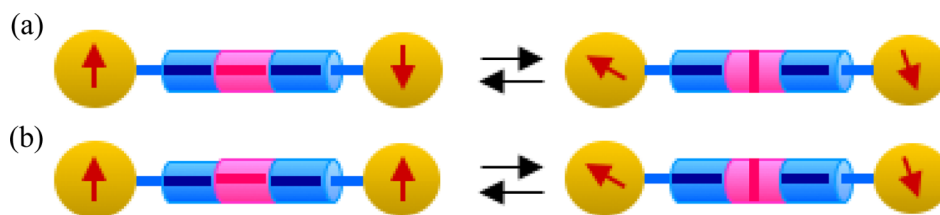
DICOPPER(II) ANTHRACENOPHANES AS PROTOTYPES OF MOLECULAR MAGNETIC SWITCHES

“Molecular magnetic switches” (MMSs) are molecular components that would allow for the interruption and restoration of the magnetic communication between the spin carriers along the spintronic circuit. MMSs present two metastable states having totally different magnetic properties, which can be reached in a reversible manner through the operation of some external stimuli. The spins of the magnetic centers would be antiferro- or ferromagnetically coupled in one of the states (ON), whereas they would be magnetically uncoupled in the other one (OFF), as illustrated by Scheme 8. Among others, the external stimuli responsible for the magnetic switching can be electronic or photonic, as exemplified by earlier studies on organic diradicals or hybrid metal–organic triradicals with redox- or photoactive aromatic bridges.^{32,33}

The next step in our ligand design approach to multifunctional magnetic devices was then the incorporation of photoactive aromatic spacers in the corresponding oxamato-based dicopper(II) metallacyclophanes to get a magnetic photoswitching. The aforementioned dicopper(II) oligoacenophanes are very appealing candidates as MMWs because of the unique photochromic properties of the OA spacers.¹⁸ In particular, the thermally reversible photodimerization of anthracene through the carbon atoms at the 9,10- and 9',10'- (*meso*) positions of the central benzene rings to give the corresponding intermolecular [4 + 4] photocycloaddition product is one of the oldest known photochemical reactions and a classical text-book example (Scheme 9a).³⁴ They are much less reactive than purely organic cyclophane derivatives, such as [2.2](9,10)anthracenophane, reflecting thus the importance of the entropic effects associated with the cyclic structure in the higher efficiency and faster kinetics of the pressure reversible, intramolecular (“pseudo-bimolecular”) [4 + 4] photocycloaddition (Scheme 9b).³⁵

Interestingly, the thermally reversible intramolecular photocycloaddition reaction of the two facing anthracene spacers in oxamato-based dicopper(II) 2,6-anthracenophanes is accompanied by a switch from a moderate antiferromagnetically

Scheme 8. Illustration of a Molecular Magnetic Switch Showing the (a) Antiferro- or (b) Ferromagnetic Coupling in One of the States (Left) and the Negligible Magnetic Coupling in the Other One (Right)



Scheme 9. (a) Thermally-Reversible Photodimerization of Anthracene; (b) Pressure-reversible Photodimerization of the [2.2](9,10)-Anthracenophane Derivative

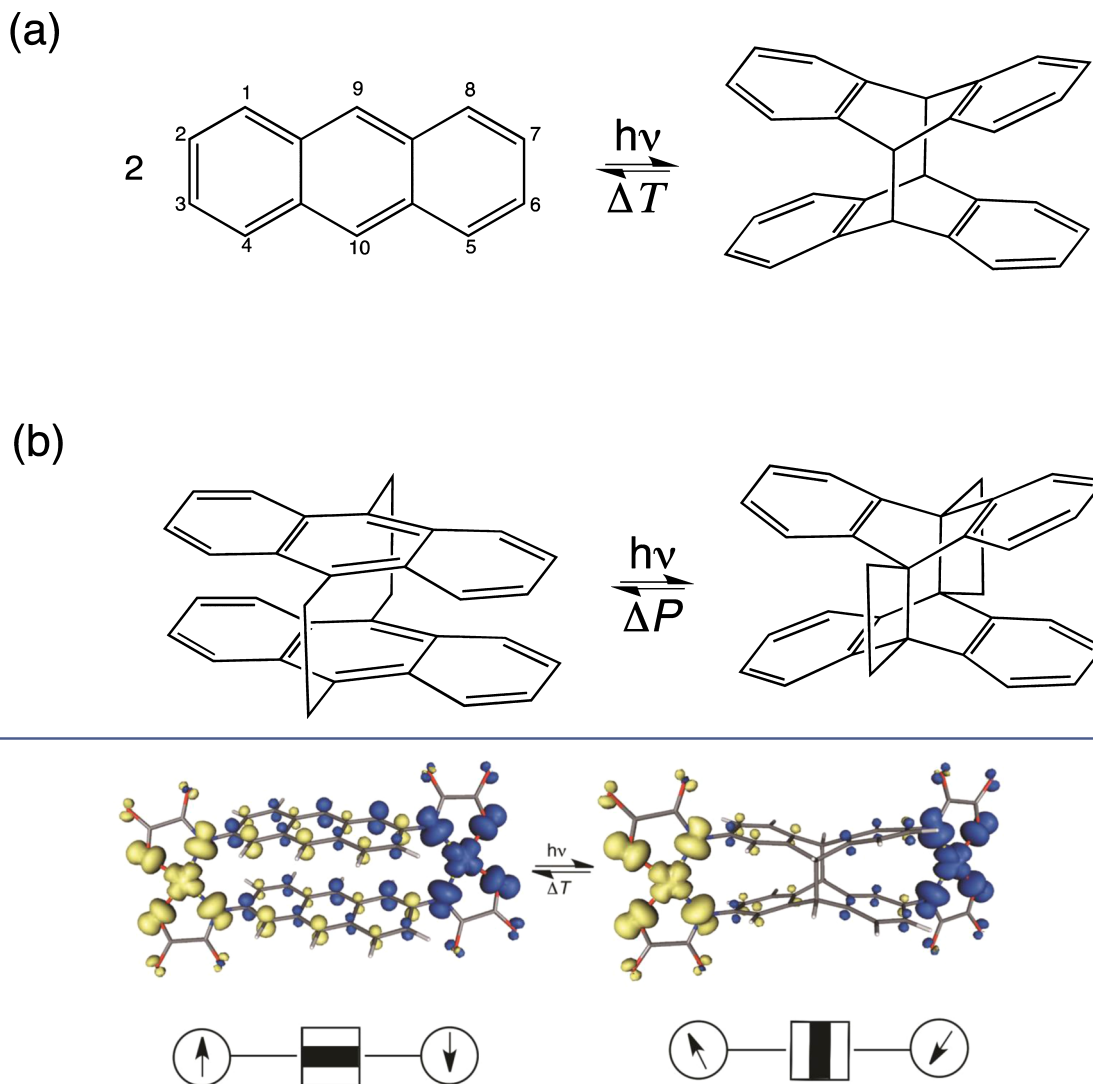


Figure 9. Perspective views of the calculated spin density distribution for the ground BS singlet spin state of the optimized molecular geometries in acetonitrile of the oxamato-based dicopper(II) 2,6-anthracenophane (left) and the corresponding [4 + 4] photocycloaddition product (right) illustrating the molecular magnetic switch concept (yellow and blue contours represent positive and negative spin densities, respectively).

coupled dicopper(II) precursor (ON state) to a magnetically uncoupled dicopper(II) photodimer product (OFF state),¹⁸ so that they can be viewed as prototypes of phototriggered MMSs, as shown in Figure 9.

This magnetic photoswitching is consistent with DF calculations on the optimized molecular geometries of the dicopper(II) 2,6-anthracenophane precursor and its putative photodimer product in acetonitrile, which evidence a complete loss of the

extended π -conjugated character upon [4 + 4] photocycloaddition of the two facing anthracene spacers.¹⁸ So, the spin polarization and spin delocalization effects onto the extended π -conjugated anthracenediamidate bridges of the dicopper(II) 2,6-anthracenophane lead to significant values of the spin density of opposite sign at the adjacent carbon atoms of the fused benzene rings (Figure 9, left). On the contrary, the spin polarization and spin delocalization effects across the

nonconjugated anthracenediamidate photodimer bridge skeleton in the corresponding [4 + 4] photocycloaddition product are found to be restricted to the four lateral benzene rings, the values of the spin density at the tertiary bridgehead, sp^3 -hybridized carbon atoms of the central cyclohexadiene rings being strictly zero (Figure 9, right).

CONCLUSIONS

A ligand design approach for the topological, redox, and photochemical control of the magnetic coupling between distant metal centers in a diverse class of oxamato-based dinuclear copper(II) metallacyclophanes is reported. This new family of electro- and photoactive, exchange-coupled dicopper(II) metallacyclophanes could be viewed as a set of prototypes for the development of multifunctional magnetic devices for molecular spintronics. Indeed, they may emerge as potentially active molecular components to build a metal-based spintronic circuit, such as spin couplers and rectifiers or spin wires and switches.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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DEDICATION

This work is dedicated to the memory of Prof. Alessandro Bencini.

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