magnetochemistry

Review

When Molecular Magnetism Meets Supramolecular Chemistry: Multifunctional and Multiresponsive Dicopper(II) Metallacyclophanes as Proof-of-Concept for Single-Molecule Spintronics and Quantum Computing Technologies?

Renato Rabelo [1], Salah-Eddine Stiriba [1], Danielle Cangussu [2], Cynthia L. M. Pereira [3], Nicolás Moliner [1], Rafael Ruiz-García [1,*], Joan Cano [1,*], Juan Faus [1], Yves Journaux [4] and Miguel Julve [1,*]

[1] Instituto de Ciencia Molecular (ICMol), Universitat de València, Paterna, 46980 València, Spain; Renato.Rabelo@uv.es (R.R.); stiriba@uv.es (S.-E.S.); Fernando.Moliner@uv.es (N.M.); Juan.Faus@uv.es (J.F.)
[2] Instituto de Química, Universidade Federal de Goiás, Goiânia-GO 74001-970, Brazil; danielle_cangussu@ufg.br
[3] Departamento de Química, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Pampulha, Belo Horizonte, Minas Gerais 31270-901, Brazil; lopescynthia@yahoo.com.br
[4] Institut Parisien de Chimie Moléculaire, Sorbonne Universités UPMC Univ Paris 06, 75005 Paris, France; yves.journaux@gmail.com
* Correspondence: rafael.ruiz@uv.es (R.R.-G.); joan.cano@uv.es (J.C.); miguel.julve@uv.es (M.J.)

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Abstract: Molecular magnetism has made a long journey, from the fundamental studies on through-ligand electron exchange magnetic interactions in dinuclear metal complexes with extended organic bridges to the more recent exploration of their electron spin transport and quantum coherence properties. Such a field has witnessed a renaissance of dinuclear metallacyclic systems as new experimental and theoretical models for single-molecule spintronics and quantum computing, due to the intercrossing between molecular magnetism and metallosupramolecular chemistry. The present review reports a state-of-the-art overview as well as future perspectives on the use of oxamato-based dicopper(II) metallacyclophanes as promising candidates to make multifunctional and multiresponsive, single-molecule magnetic (nano)devices for the physical implementation of quantum information processing (QIP). They incorporate molecular magnetic couplers, transformers, and wires, controlling and facilitating the spin communication, as well as molecular magnetic rectifiers, transistors, and switches, exhibiting a bistable (ON/OFF) spin behavior under external stimuli (chemical, electronic, or photonic). Special focus is placed on the extensive research work done by Professor Francesc Lloret, an outstanding chemist, excellent teacher, best friend, and colleague, in recognition of his invaluable contributions to molecular magnetism on the occasion of his 65th birthday.

Keywords: copper complexes; electron exchange; electron transport; ligand design; metallacyclic complexes; metallosupramolecular chemistry; molecular magnetism; molecular spintronics; nanotechnology; quantum computing

1. Introduction and Background: Molecular Magnetism Meets Metallosupramolecular Chemistry for Single-Molecule Spintronics and Quantum Computing

The metallosupramolecular chemistry term was coined by Constable in 1994 to describe an emerging research area in the field of supramolecular chemistry [1,2], where the advantage of coordination chemistry is taken to control the metal-directed assembly of supramolecular systems [3–10]. Metallosupramolecular chemistry provides convenient tools for the current evolution from molecular magnetism [11–18] toward single-molecule spintronics [19–28] and quantum computing [29–45]. The internal (steric and electronic modulation) and external control (chemo-, electro- and photostimulation) of the magnetic coupling through ligand design have been successfully achieved in simple metallosupramolecular complexes, such as metal strings [46–55], rings [56–61] and grids [62–74], or more complex supramolecular aggregates of polynuclear complexes which behave as molecular nanomagnets [75–92]. They include both homo- and heterometallic fluoride wheels [75–79] and cyanide polyhedra [80–85], as well as homo- and heterovalent metal-oxo clusters [86–92]. These specific characteristics, combined with their nanometer size and easy handling, can be used to make the active molecular components of spintronic circuits and quantum computers. In fact, they could serve as encoders of binary information in molecular-scale spin-based quantum computing devices, including magnetic wires and switches [49,71,88], or magnetic quantum bits (qubits) [50–52,87] and quantum cellular automata (QCA) [69].

Detecting the response of the spins of a single magnetic molecule to an external stimulus and, by using such a platform (in the form of well-established stimulus-response correlations), being able to implement quantum logic memory capabilities, is the key to applications in single-molecule spintronics and quantum computing, according to Sanvito [21]. Two unique examples of divanadium(IV) complexes which have been proposed as prototypes of molecular magnetic transistors (MTs) and molecular quantum gates (QGs) for the physical implementation of quantum information processing (QIP) illustrate this idea [93–96].

On the one hand, a dual electroswitching (ON/OFF) magnetic behavior upon one-electron metal reduction and oxidation of the *trans*-diaminomaleonitrile-bridged divanadium(IV) complex of formula $V_2(\mu\text{-}C_4N_4)(CN)_4(tmtacn)_2$ (tmtacn = *N*,*N*′,*N*′′-1,4,7-trimethyl-1,4,7-triazacyclononane) has been reported by Long et al., as shown in Figure 1 [93]. The magnetic bistability responsible for the MT behavior in this electron spin-based system would arise from the conversion between the antiferromagnetically coupled V^{IV}_2 complex with an $S = 0$ ground state (OFF) and the mixed-valence, ferromagnetically coupled $V^{III,IV}_2$ or paramagnetic $V^{IV,V}_2$ species, possessing $S = 3/2$ and $1/2$ ground states (ON), respectively [94]. The electron exchange (EE) interactions between the V^{IV} ($S_V = 1/2$) ions through the $C_4N_4{}^{4-}$ bridge account for the strong antiferromagnetic coupling in the $S = 0$ V^{IV}_2 neutral molecule (Figure 1, middle) [93]. In contrast, the very strong ferromagnetic coupling in the reduced $S = 3/2$ $V^{III,IV}_2$ anion results from the double exchange (DE) interactions between the V^{III} ($S_V = 1$) and V^{IV} ($S_V = 1/2$) ions due to the delocalization of the added electron through the $C_4N_4{}^{4-}$ bridge (Figure 1, left) [93].

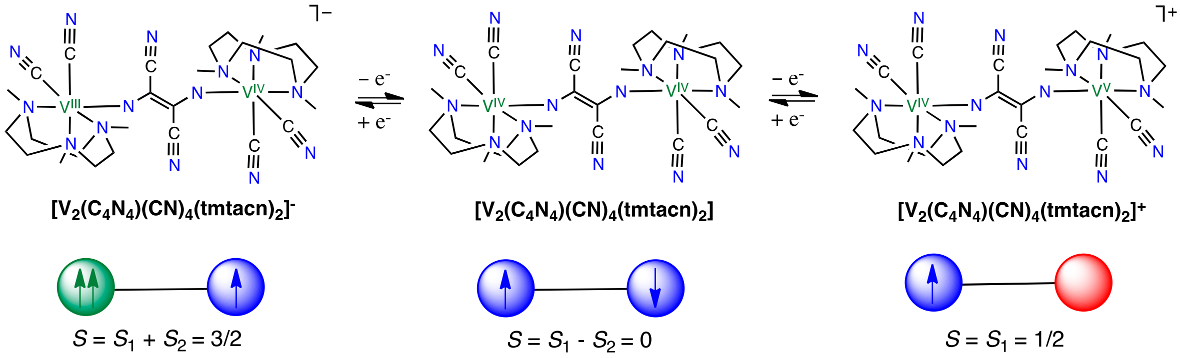


Figure 1. Illustration of the electroswitching of the magnetic coupling in a *trans*-diaminomaleonitrile-bridged dinuclear vanadium(IV) complex proposed as a prototype of the molecular magnetic transistor.

On the other hand, the *p*-phenylenediamidocatecholate-bridged divanadyl(IV) metallacyclic complex of the cyclophane type of formula $(Ph_4P)_4[(VO)_2(\mu\text{-ppbacat})_2]$ [ppbacat = *N*,*N*′-bis(2,3-dihydroxybenzoyl)-1,4-phenylendiamine] reported by Atzori et al. allows for the electron spin-mediated switching of the nuclear spins of each V^{IV} ion, as shown in Figure 2 [96]. The QG behavior in this nuclear spin-based double quantum bit (qubit) system results from the fast electronic spin excitations within the $S = 1$ state promoted by the application of uniform electron paramagnetic resonance (EPR) pulses. The controlled entanglement between the nuclear spin-based qubits in this very weak magnetically coupled V^{IV}_2 complex is ultimately made possible by the large hyperfine coupling between the electron and nuclear spins of each V^{IV} moiety ($S_V = 1/2$ and $I_V = 7/2$), as clearly found in the parent mononuclear vanadyl(IV) complex featuring long spin coherence times [95]. This related pair of mono- and dinuclear vanadyl(IV) complexes illustrates, in a certain manner, the transition from classic molecular (Werner) to modern supramolecular coordination chemistry by using binucleating aromatic diamidocatecholates ligands as bridges.

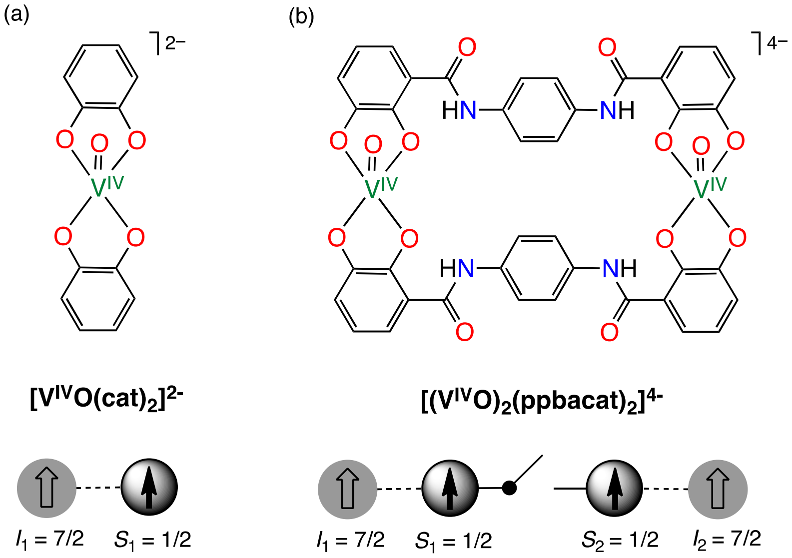


Figure 2. Illustration of the hyperfine coupling and electron spin-mediated switching of the nuclear spin quantum coherence in the mononuclear bis(catecholate)vanadyl(IV) complex (**a**) and the related *p*-phenylenediamidocatecholate-bridged dinuclear vanadyl(IV) complex (**b**) proposed as a prototype of the two qubit-based molecular quantum gate.

In addition, two related examples of dicopper(II) and copper(II)-organic radical complexes are known, featuring a chemo- and photoswitchable (ON/OFF) magnetic behavior between antiferro- or ferromagnetically coupled states (ON) and magnetically isolated ones (OFF) [97,98]. These two case studies of ligand-based chemo- and photo-active, bistable dynamic magnetic systems would constitute suitable candidates for single-molecule spintronics and quantum computing nanotechnologies [17].

On the one hand, the tweezer-type dicopper(II) complex of formula $[Cu_2(terpytbsalphen)]$ $[H_4terpy\text{-}tbsalphen$ 6,6″-bis(4-ethenyl-*N*,*N*′-1,2-phenylene-bis(3,5-diterbutysalicylideneimine)-2,2′:6′,2″-terpyridine] reported by Doisteau et al. provides an elegant example of the mechanically assisted chemical switching of the magnetic coupling after coordination of the Zn^{II} ion to the central terpy linker, to give the corresponding $[ZnCu_2(terpytbsalphen)]Cl_2$ species, as shown in Figure 3 [97]. A concomitant conformational change of the terpy–tbsalphen bridging ligand occurs, which is eventually responsible for the switching between the magnetically uncoupled (W-shaped) open isomer and the weak antiferromagnetically coupled (U-shaped) closed isomer. The lack of through-bond EE interactions between the Cu^{II} ($S_{Cu} = 1/2$) ions at such a long intermetallic distance ($r = 21.4$ Å) accounts for the negligibly small magnetic coupling observed in the open isomer (Figure 3, left). Otherwise, the presence of direct through-space EE interactions between the two parallel stacked, copper(II)-salphen fragments at a short intermetallic distance ($r = 4.03$ Å) is the origin of the weak but non-negligible antiferromagnetic coupling found in the closed isomer (Figure 3, right).

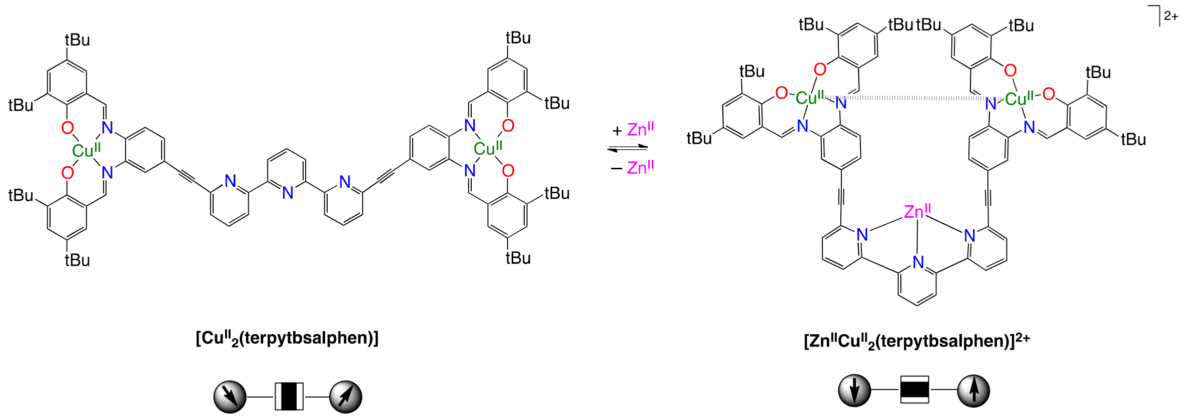


Figure 3. Illustration of the chemoswitching of the magnetic coupling upon zinc(II) coordination in a terpyridine-bridged dicopper(II) complex proposed as a prototype of the two qubit-based molecular quantum gate.

On the other hand, the copper(II)-organic radical complex of formula Cu(hfac)$_2$(phendaeNNO) (hfac = hexafluoroacetylacetonate and phendaeNNO = 1-[6-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)-2-methylbenzothiophen-3-yl]-2-[6-(1,10-phenanthroline-2-yl)-2-methylbenzothiophen-3-yl]-3,3,4,4,5,5-hexafluorocyclopentene) reported by Takayama et al. constitutes an example of the photoswitching of the magnetic coupling by using a tailor-made coordinating group-substituted, photoactive nitronyl nitroxide (NNO) radical ligand, as shown in Figure 4 [98]. The reversible intramolecular photocycloaddition of the diarylethene-type photochromic linker that occurs after UV and visible light irradiation is responsible for the switching between the magnetically uncoupled open-ring (*o*) and the presumably weak ferromagnetically coupled closed-ring (*c*) isomers of the Cu^{II}-NNO radical species. The magnetic coupling in the open isomer is very weak, if not negligible, as expected because of the absence of through-bond EE interaction between the Cu^{II} (S_{Cu} = 1/2) ion and the NNO radical (S_R = 1/2) (Figure 4, left). Otherwise, the fully conjugated π-electron system of the closed isomer substantially increases the magnitude of the EE interaction, giving rise to a weak but non-negligible ferromagnetic coupling due to the strict orthogonality of the magnetic orbitals of the Cu^{II} ion and the NNO radical ligand (Figure 4, right).

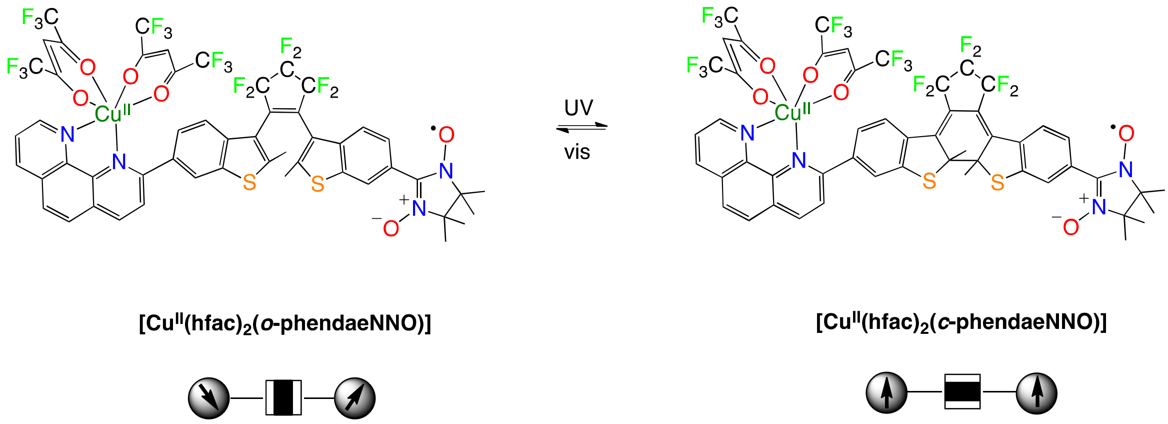
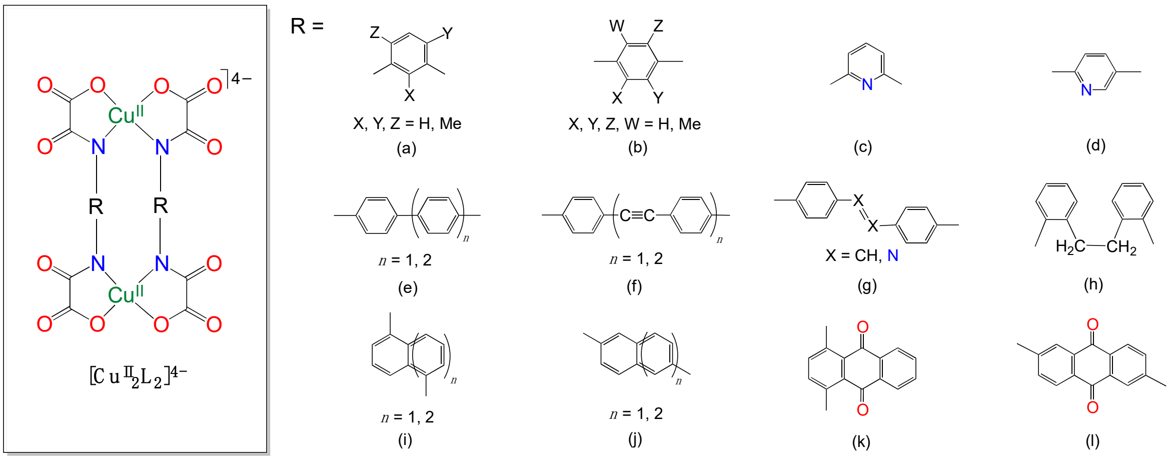


Figure 4. Illustration of the photoswitching of the magnetic coupling upon light irradiation in a diarylethene-bridged copper(II)-nitronyl nitroxide radical complex proposed as a prototype of the molecular magnetic transistor.

The state-of-the-art in metallosupramolecular chemistry concerns the design and synthesis of novel classes of chemo-, electro- and photo-active, extended π-conjugated aromatic bridging ligands, which should be able to self-assemble with paramagnetic transition metal ions to give new multifunctional and multiresponsive metallacyclic complexes [7]. This is nicely exemplified in the work by Lloret and co-workers on the rich metallosupramolecular chemistry of a novel class of ligands bearing two oxamato donor groups separated by more or less rigid non-innocent, extended π-conjugated aromatic spacers, which transmit both magnetic and electronic coupling effects between the metal centers in efficient and switchable ways [99,100].

In this review, we summarize old and more recent achievements, as well as future perspectives, dealing with the ligand design strategy to control the nature and magnitude of the intramolecular magnetic coupling between distant metal centers, through both internal and external factors, in a diverse family of oxamato-based dicopper(II) metallacyclophanes, as illustrated in Scheme 1 [99,100]. These double-stranded dicopper(II) metallacyclic complexes of the cyclophane type, resulting from the self-assembly of dinucleating aromatic oxamato ligands with Cu^{II} ions, include a variety of potentially chemo-, electro- and/or photoactive, extended π-conjugated organic spacers, such as polymethyl-substituted *m*- or *p*-phenylenes (Scheme 1a,b), *m*- or *p*-pyridines (Scheme 1c,d), oligo-*p*-phenylenes or oligo-*p*-phenylene-ethynes (Scheme 1e,f), stilbene or azobenzene (Scheme 1g), *o*-phenylene-ethylenes (Scheme 1h), oligo-α,α'- or oligo-β,β'-acenes (Scheme 1i,j), and 1,4- or 2,6-anthraquinones (Scheme 1k,l). Herein, we will highlight how this new class of multifunctional and multiresponsive metallosupramolecular complexes are up-and-coming candidates as a proof-of-concept (POC) design in the development of molecular magnetic devices, such as wires and switches, for information processing and storage applications in the emerging fields of single-molecule spintronics and quantum computing.



Scheme 1. General chemical structure for the series of oxamato-based dicopper(II) metallacyclophanes with different chemo-, electro- and/or photoactive, extended π-conjugated aromatic spacers: polymethyl-substituted *m*- or *p*-phenylenes (**a**,**b**), *m*- or *p*-pyridines (**c**,**d**), oligo-*p*-phenylenes or oligo-*p*-phenylene-ethynes (**e**,**f**), stilbene or azobenzene (**g**), *o*-phenylene-ethylenes (**h**), oligo-α,α'- or oligo-β,β'-acenes (**i**,**j**), and 1,4- or 2,6-anthraquinones (**k**,**l**).

2. Dinuclear Copper(II) Metallacyclophanes in the Proof-of-Concept (POC) Design of Molecular Magnetic Wires

The basic components of a molecular spintronic circuit are molecular magnetic wires (MWs), which would facilitate the magnetic communication between the spin carriers along the circuit [100,101]. MWs offer a new design concept for the transfer of information over long distances based on EE interactions and without current flow [102–115], in contrast to conventional charge transport-based electronic wires [116–122], as stated by Lloret [100]. Indeed, setting a long-range magnetic coupling between two distant spin centers connected by a long organic spacer that ultimately extends over infinite distances ("wire-like magnetic coupling") is the cornerstone. That being so, a perturbation induced by an externally applied magnetic field on the spin center located at the beginning of the wire generates a change on the spin center located at the end of it, as shown in Figure 5.

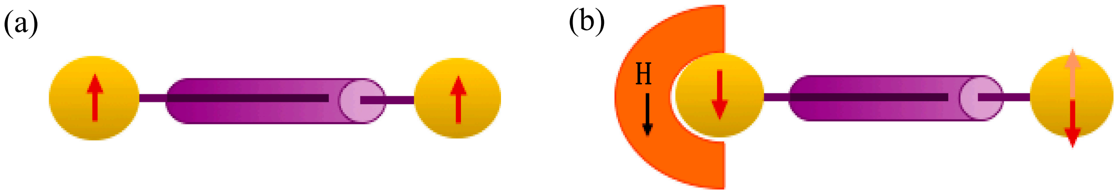


Figure 5. Illustration of the transfer of information in a molecular magnetic wire before (**a**) and after (**b**) the operation of a perturbation induced by an external applied magnetic field. Adapted with permission from Castellano et al. (reprinted with permission from [100], American Chemical Society, 2015).

The transmission of spin information between the metal centers occurs through either σ- or π-pathways, depending on the nature of the linker. The σ-pathway is very efficient over short distances but nearly negligible for long organic spacers. In contrast, the π-pathway is more efficient over long distances. In this latter case, two different situations can be envisaged for long organic spacers, as shown in Figure 6.

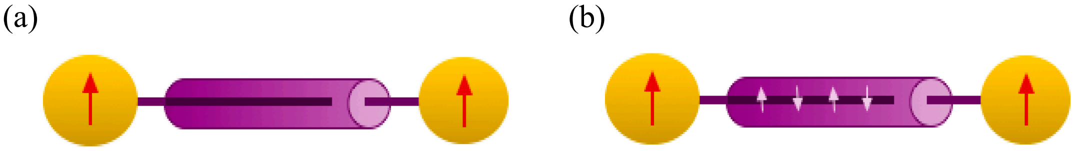


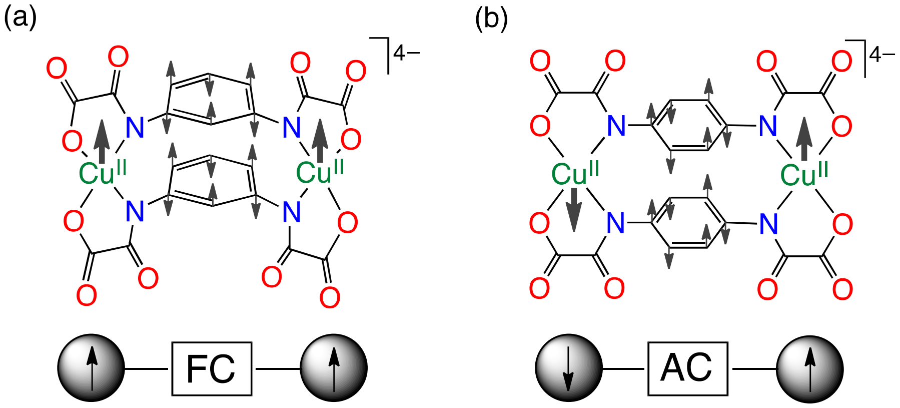
Figure 6. Illustration of the long-range magnetic coupling in a molecular magnetic wire with non-polyradical (**a**) or polyradical (**b**) spacers.

The electronic density of the metal centers is partially delocalized, and occasionally polarized, on the ligands when they possess a non-polyradical character (with a closed-shell singlet ground state) (Figure 6a). In such a case, the double spin polarization mechanism through the π-electron system of the organic spacer allows for the transmission of spin information over very long distances (long-range magnetic coupling), provided that there is a relatively small highest-occupied molecular orbital (HOMO)/lowest-unoccupied molecular orbital (LUMO) energy gap [108]. The magnetic coupling between the metal centers is expected to decay continuously with the intermetallic distance in a more or less marked way, depending on the extended π-conjugated nature of the organic spacer. In contrast, a strong magnetic coupling between metal centers could be anticipated when the ligands have a unique polyradical character (with an open-shell singlet ground state) (Figure 6b). In this case, the unpaired electrons of the polyradical spacer act as intermediates in the transmission of spin information, providing thus two strongly spin-correlated metal centers. This situation is reminiscent of the hopping mechanism of electrical conduction over a wire [119]. The magnetic coupling in these polyradical systems is much stronger than that found for the non-polyradical ones (*vide infra*). More importantly, it remains more or less constant with the intermetallic distance from a certain length of the organic spacer (wire-like magnetic behavior).

2.1. Non-Polyradical Spacers

In a pioneering work, Ruiz and Cano demonstrated that the appropriate choice of the topology (substitution pattern) and the number of methyl substituents of the bridging ligand allows for controlling the nature and magnitude of the intramolecular magnetic coupling on oxamato-based dicopper(II) metallacyclophanes with polymethyl-substituted 1,3- and 1,4-phenylene spacers (Scheme 1a,b) [123–126]. This is appropriately expressed by the variation in the sign and magnitude of the magnetic coupling parameter (J) in the phenomenological spin Hamiltonian $H = -J\, S_A \cdot S_B$ ($S_A = S_B = S_{Cu} = 1/2$) [127]. Density functional theory (DFT) calculations provide a clear-cut answer to the relative importance of the spin delocalization and spin polarization mechanisms for the through-ligand EE interaction along these two series of oxamato-based dicopper(II) metallacyclophanes [100].

In the parent oxamato-based dicopper(II) meta- and paracyclophanes (Scheme 1a,b, X = Y = Z = W = H), the distinct nature of the ground spin state can be nicely interpreted based on the concept of molecular ferro- and antiferromagnetic couplers (FCs and ACs), as illustrated in Scheme 2. In each case, the *meta*- and *para*-substituted phenylene spacers act as FCs and ACs, respectively, between the two Cu^{II} ions leading to either a triplet ($S = S_A + S_B = 1$) or a singlet ($S = S_A - S_B = 0$) ground spin state for the corresponding dicopper(II) meta- and paracyclophanes ($J = 16.8$ and -94 cm^{-1}, respectively) [123,125]. In both cases, the perpendicular arrangement of the oxamate donor groups with the central benzene ring allows a strong interaction of the magnetic orbitals of the Cu^{II} ions with the π-electron system of the bridging ligands. This leads to an efficient spin polarization mechanism which accounts for the parallel or antiparallel spin alignments resulting from alternating spin densities on the *m*- and *p*-phenylene spacers with an even or odd number of carbon atoms, respectively [127]. In a more general way, this particular geometrical configuration will allow any chemical or physical action occurring in the π-electron system of the bridging ligands to have drastic repercussions on the electron spin configuration of the Cu^{II} ions, as we will see in the next section.

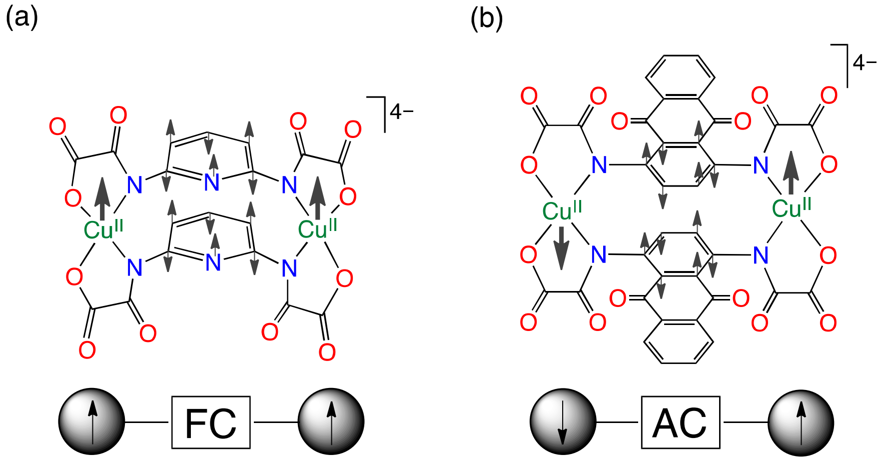


Scheme 2. Proof-of-concept (POC) design of molecular ferro- and antiferromagnetic couplers based on oxamato-based dicopper(II) metacyclophanes (**a**) and paracyclophanes (**b**), showing the different parallel and antiparallel spin alignments, respectively, which arise from the alternating spin densities on the phenylene spacers. Adapted with permission from Castellano et al. (reprinted with permission from [99], Elsevier, 2015).

Likewise, the antiferromagnetic coupling in the series of polymethyl-substituted oxamato-based dicopper(II) paracyclophanes continuously increases with the number of methyl substituents ($J = -94$, -124, and -144 cm^{-1}, with $x = 0$, 1, and 4, respectively) (Scheme 1b) [125,126]. They act thus as a kind of adjusting screws in a putative molecular antiferromagnetic transformer (AT). The observed AT behavior points out that the magnitude of the antiferromagnetic coupling along this series is mainly governed by electronic factors associated with the electron donor properties of the methyl group, as supported by DFT calculations [126].

In subsequent works, Cangussu and Julve, on the one hand, and Armentano and Lloret, on the other hand, provided further support of the occurrence of a spin polarization mechanism in the related oxamato-based dicopper(II) metallacyclophanes with 2,6-pyridine and 1,4-anthraquinone spacers (Scheme 1c,k) [128–131]. In each case, the ferro- or antiferromagnetic nature of the EE interaction is likely explained by the *meta*- or *para*-substitution pattern of the 2,6-pyridine and 1,4-anthraquinone spacers, respectively, as illustrated in Scheme 3. In both cases, however, the magnitude of the ferro- and antiferromagnetic coupling for these novel oxamato-based dicopper(II) metapyridenophanes and paraanthraquinophanes ($J = 7.9$ and -84 cm^{-1}, respectively) decreases when compared with their parent unsubstituted dicopper(II) meta- and paracyclophanes. This feature is likely explained by the reduction in the Lewis basicity of the amidate donor groups from the electron-poor 2,6-pyridine and

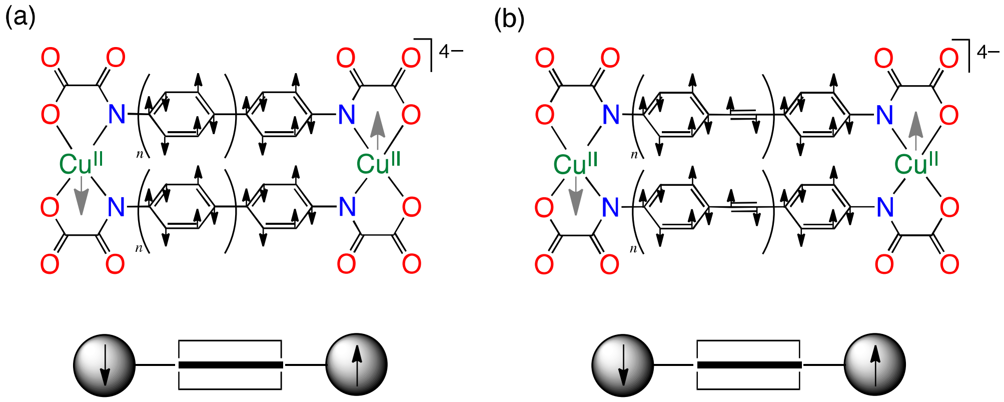
1,4-anthraquinone spacers, which causes a decrease in the metal-ligand covalency and thus of the electron spin delocalization and polarization effects on the bridging ligands, as supported by DFT calculations [128,131].



Scheme 3. POC design of molecular ferro- and antiferromagnetic couplers based on oxamato-based dicopper(II) metapyridenophanes (**a**) and paraanthraquinophanes (**b**), showing the different parallel and antiparallel spin alignments, respectively, which arise from the alternating spin densities on the pyridine and anthraquinophane spacers.

On the other hand, oxamato-based dicopper(II) metallacyclophanes with oligo-*p*-phenylene (OP) and oligo-*p*-phenylene-ethyne (OPE) spacers have been examined by Cano and Lloret as potential candidates to obtain molecular antiferromagnetic wires (Scheme 1e,f) [132–134]. In fact, OP and OPE spacers have been demonstrated to be really effective in mediating EE interactions between paramagnetic metal centers which are separated by relatively long distances in discrete metallacyclic entities, as supported by DFT calculations [132,134]. The EE interaction between the two Cu^{II} ions decreases from the parent complexes with 4,4′-diphenylene and 4,4′-diphenylene-ethyne spacers (J = −8.7 and −3.9 cm^{-1}, respectively) (Scheme 1e,f, with n = 1) to the longer homologues with 4,4′-terphenylene and 1,4-di(4-phenylethynyl)phenylene ones (J = −1.8 and −0.9 cm^{-1}, respectively) (Scheme 1e,f, with n = 2) [132,134]. Indeed, the rather low exponential decay of the antiferromagnetic coupling with the intermetallic distance along both series of oxamato-based dicopper(II) oligo-*p*-phenyleno- and oligo-*p*-phenylene-ethynophanes indicates that the EE interaction through these rigid rod-like aromatic spacers obeys a non-polyradical spin polarization mechanism, as illustrated in Scheme 4.

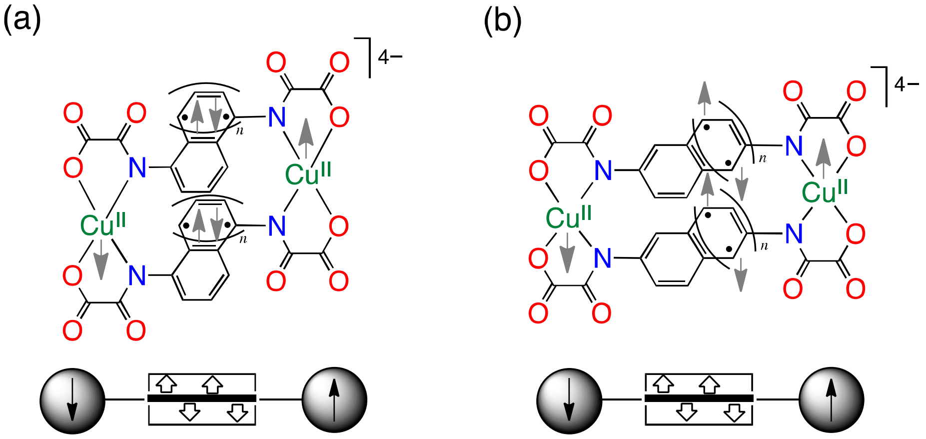
Interestingly, a much better magnetic communication between very distant metal centers is predicted for the series of oxamato-based dicopper(II) oligophenylethynylenophanes than for the parent dicopper(II) oligophenylenophanes (Scheme 4a,b), as reflected by the calculated values of the exponential decay factor (β = 0.31 and 0.35 $Å^{-1}$) [132,134]. This feature clearly indicates that introducing an ethynylene group between the phenylene spacers does not interrupt the magnetic communication between the spins of the metal centers [133]. Instead, a strong orbital overlap occurs between the π-type orbitals of the *para*-substituted benzene rings across the carbon–carbon triple bonds due to the almost planar configuration of the OPE spacers, when compared to the slightly twisted configuration of the OP spacers. This situation is in agreement with time-dependent density functional theory (TD-DFT) calculations, which point out the linear decay of the π–π* transition energy with the HOMO-LUMO energy gap along this series of dicopper(II) oligophenylethynylenophanes [134].



Scheme 4. POC design of molecular magnetic wires based on oxamato-based dicopper(II) oligo-*p*-phenylenophanes (**a**) and oligo-*p*-phenylethynylenophanes (**b**), showing the non-polyradical spin polarization mechanism responsible for the long-range magnetic coupling. Adapted with permission from Castellano et al. (reprinted with permission from [99], Elsevier, 2015).

2.2. Polyradical Spacers

Oxamato-based dicopper(II) metallacyclophanes with flat-like oligo-α,α'- and oligo-β,β'-acene (OA) spacers have been investigated by Ruiz and Cano as unique examples of MWs (Scheme 1i,j) [135–137]. As such, they have found a moderately strong antiferromagnetic coupling between the two Cu^{II} ions separated by relatively large intermetallic distances (J = −18.6 and −23.9 cm^{-1} with r = 8.3 and 12.5 Å, respectively) for the former members of these series with the shorter 1,8-naphthalene and 2,6-anthracene spacers (Scheme 1i,j, with n = 1 and 2, respectively) [137]. These results show thus that one nanometer is definitely not the upper limit for the observation of magnetic coupling in dicopper(II) complexes [138–140]. More importantly, they have predicted a wire-like magnetic behavior for these two series of oxamato-based dicopper(II) oligo-α,α'- and oligo-β,β'-acenophanes, regardless of the substitution pattern, as supported by DFT calculations [135]. This unprecedented wire-like magnetic behavior arises from the polyradical character of the longer OA spacers ($n \geq 3$), as illustrated in Scheme 5.



Scheme 5. POC design of molecular magnetic wires based on oxamato-based dicopper(II) oligo-α,α'-(**a**) and β,β'-anthracenophanes (**b**), showing the polyradical mechanism that is responsible for the wire-like magnetic coupling through the longer OA spacers ($n \geq 3$). Adapted with permission from Castellano et al. (reprinted with permission from [99], Elsevier, 2015).

This wire-like magnetic behavior is accompanied by a change from antiferro- to ferromagnetic coupling for the latter members of both series of oxamato-based dicopper(II) oligo-α,α'- and oligo-β,β'-acenophanes (Scheme 5a,b). Notably, DFT calculations predict a weak but non-negligible ferromagnetic coupling ($J = 3.0$ cm^{-1}) between the two Cu^{II} ions separated by a very large intermetallic distance ($r \approx 3$ nm) through the decacene spacers in the series of β,β'-disubstituted OA spacers (Scheme 1j, with $n = 9$) [135]. The current efforts in our group are devoted to the preparation of dicopper(II) metallacyclophanes with longer tetracene and pentacene spacers (Scheme 1i,j, with $n = 4$ and 5) as unique prototypes of MWs for single-molecule spintronics.

3. Dinuclear Copper(II) Metallacyclophanes in the POC Design of Molecular Magnetic Switches

Molecular magnetic switches (MSs) which would allow for the interruption and restoration of the magnetic communication between the spin carriers are also basic components of a molecular spintronic circuit [100,141]. MSs are archetypical examples of bistable dynamic systems presenting two separately stable equilibrium states (or two distinctly accessible states) having totally different magnetic properties, which can be transformed in a reversible manner under some external stimuli. The external stimuli that are responsible for the magnetic switching behavior can be chemical, electronic, or photonic, among others, as occurs in conventional molecular electronic switches [142–148].

MSs formed by two localized spins whose magnetic communication can be switched by means of a chemical, redox, or photonic event ("chemo-, electro-, or photo-switching magnetic behavior") constitute the simplest molecules to be tested [93,94,97,98,149–165]. In principle, the spins of the metal 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 shown in Figure 7. MSs offer an alternative design concept to encode binary information in their corresponding ON ("1") and OFF ("0") states, because of the switching of the magnetic coupling between the spin carriers, as stated by Lloret [100]. A transistor-like magnetic behavior at the molecular scale can be achieved, opening thus the way for the potential applications of MSs in quantum computing [94].

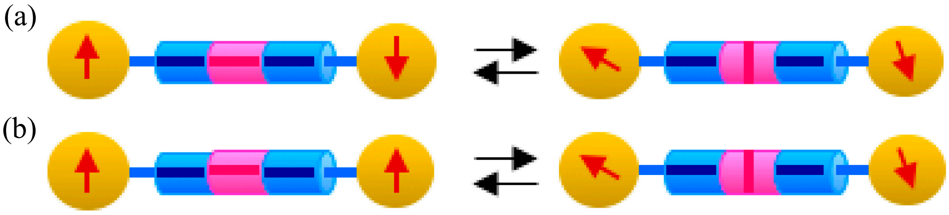


Figure 7. Illustration of the transistor behavior in a molecular magnetic switch showing the interruption and restoration of the parallel (**a**) or antiparallel (**b**) spin alignment. Adapted with permission from Castellano et al. (reprinted with permission from [100], American Chemical Society, 2015).

Other possibilities exist for the design of an MS, whereby the spins of the magnetic centers would be antiferromagnetically coupled in one of the states (OFF) and ferromagnetically coupled in the other one (ON), as shown in Figure 8. In this case, the spin alignment can be switched from antiparallel to parallel or vice versa through the action of a switchable magnetic coupler. The idea behind this design concept is to be able to invert the spin alignment of the spin-polarized current along the molecular circuit by means of an electric potential ("threshold voltage"), so that a rectifier-like magnetic behavior on the molecular scale can be achieved [166–168].

Molecular magnetic transistors (MTs) and molecular magnetic rectifiers (MRs) appear thus as some particular cases of MSs. A large variety of factors can influence over these MSs in a reversible way, such as pH, electrochemical potential, or light irradiation, leading to chemo-, electro- or photo-switching magnetic behaviors, as we will see hereafter.

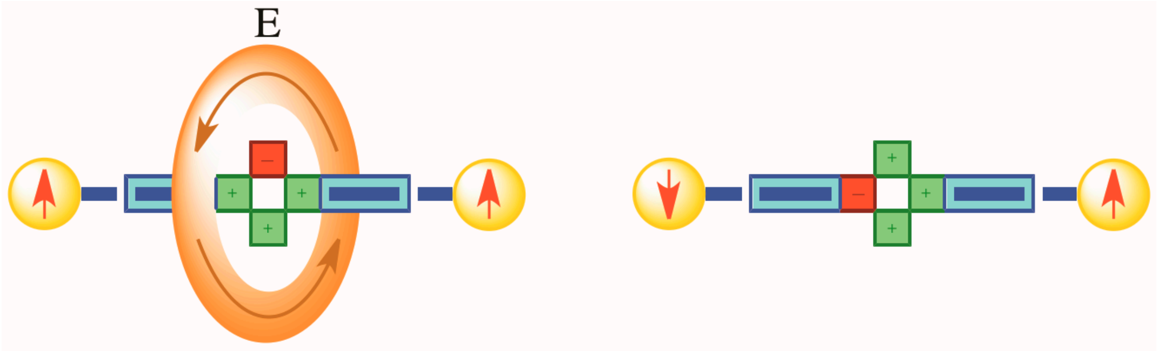
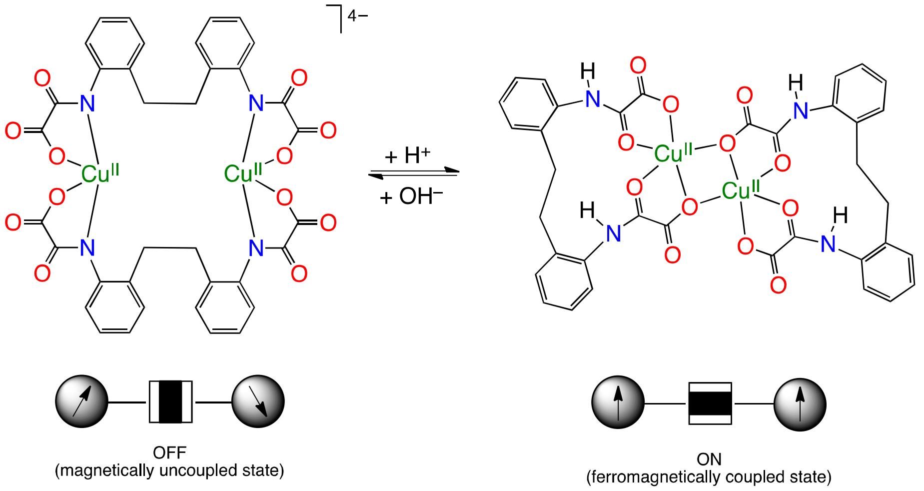


Figure 8. Illustration of the rectifying behavior in a molecular magnetic switch showing the inversion of the spin alignment from parallel to antiparallel induced by an external applied electric field. Adapted with permission from Castellano et al. (reprinted with permission from [100], American Chemical Society, 2015).

3.1. Chemoactive Spacers

Pereira and Julve have recently reported a unique, pH-triggered, structural and magnetic switching behavior for a related pair of oxamato-based dicopper(II) metallacyclic complexes with the flexible 4,4′-biphenylethylene spacer (Scheme 1h). It can adopt either *syn* (in alkaline media) or *anti* conformations (in slightly acidic media) depending on the protonation degree, as illustrated in Scheme 6 [169–171].



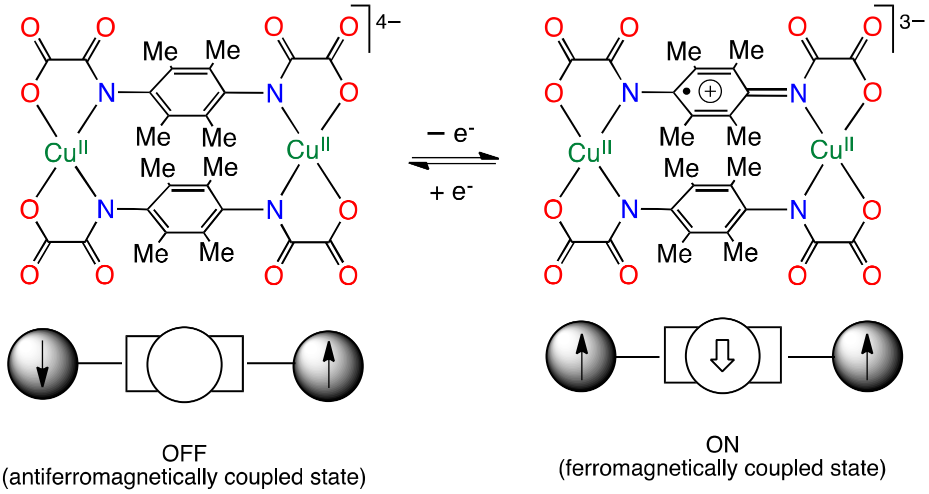
Scheme 6. POC design of a molecular ferromagnetic switch based on oxamato-based permethylated dicopper(II) 2,2′-biphenylethylenophanes showing the reversible chemoswitching magnetic behavior between the deprotonated *syn* and protonated *anti* isomers upon ligand protonation of the amido donor groups. Adapted with permission from Do Pim et al. (reprinted with permission from [17], Elsevier, 2017).

A reversible *syn–anti* conformational change of the ligand occurs in aqueous solution upon protonation of the two amide groups in the double-stranded dicopper(II) metallacyclic complex of the cyclophane-type [169]. This gives rise to the corresponding bis(monohydrogenoxamato)-bridged dimer of single-stranded copper(II) metallacyclic species by free rotation around the central single carbon–carbon bond of the 2,2′-ethylenediphenylene spacer. This bistable pair of dicopper(II) metallacyclic complexes shows a switching from non-interacting spins (OFF) for the deprotonated *syn* isomer, to parallel spin alignment (ON) for the protonated *anti* isomer. In the latter case, the weak ferromagnetic coupling (J = 2.93 cm^{-1}) is due to the accidental orthogonality of the magnetic orbitals of the two Cu^{II} ions through the out-plane exchange pathway involving the axial carboxylate groups.

In the former case, the extended non-conjugated π-pathway of the 2,2′-ethylenediphenylene spacers connecting the two Cu^{II} ions is unable to mediate any significant EE interaction, as supported by DFT calculations [169]. Interestingly, this multifunctional dicopper(II) complex can be easily anchored over niobium oxyhydroxide or adsorbed on hybrid silica-based porous materials [170,171], opening thus the way for future applications as magnetic nanodevices in single-molecule spintronics.

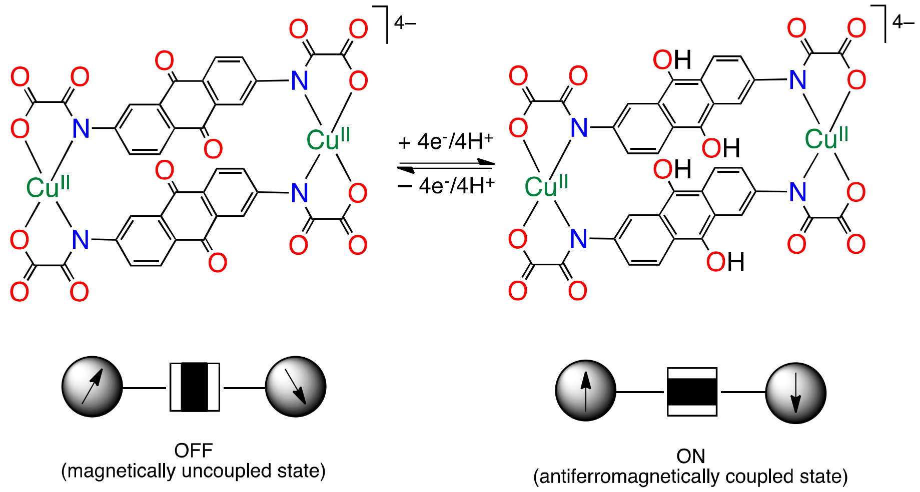
3.2. Electroactive Spacers

The aforementioned oxamato-based dicopper(II) paracyclophanes can be considered appealing candidates for MSs [125,126]. Because of the redox-active ("non-innocent") nature of their polymethyl-substituted 1,4-phenylene spacers, the permethylated dicopper(II) paracyclophane exhibits a unique redox-triggered magnetic rectifying behavior [125]. In this case, the magnetic bistability brings about a change from antiparallel (OFF) to parallel (ON) alignments of the spins of the two Cu^{II} ions. This fact adheres to the polarization by the π-stacked delocalized monoradical ligand, which is generated upon one-electron oxidation of the double tetramethyl-*p*-phenylenediamidate bridging skeleton, as illustrated in Scheme 7.



Scheme 7. POC design of a molecular magnetic rectifier based on oxamato-based permethylated dicopper(II) paracyclophanes showing the reversible electroswitching magnetic behavior upon ligand oxidation of the phenylene spacer to the corresponding monoradical cation. Adapted with permission from Castellano et al. (reprinted with permission from [99], Elsevier, 2015).

Our group is currently investigating a novel series of oxamato-based dicopper(II) metallacyclophanes with flat-like electroactive 1,4- or 2,6-anthraquinone (OAQ) spacers (Scheme 1k,l) as new examples of MSs. In this latter case, a complete electrochemical reversibility may be reached upon four proton/electron-coupled reduction and oxidation in the dicopper(II) 2,6-anthraquinophane, as reported earlier for the related dicopper(II) 1,4-anthraquinophane, which acts as a prototype of a molecular magnetic capacitor (MC) [130,131]. In the former case, the spins of the Cu^{II} ions would be antiferromagnetically coupled through the extended π-conjugated, fully reduced dihydroanthraquinolate (ON), whereas they are magnetically uncoupled across the non-conjugated π-pathway of the 2,6-anthraquinone spacers (OFF), as illustrated in Scheme 8.



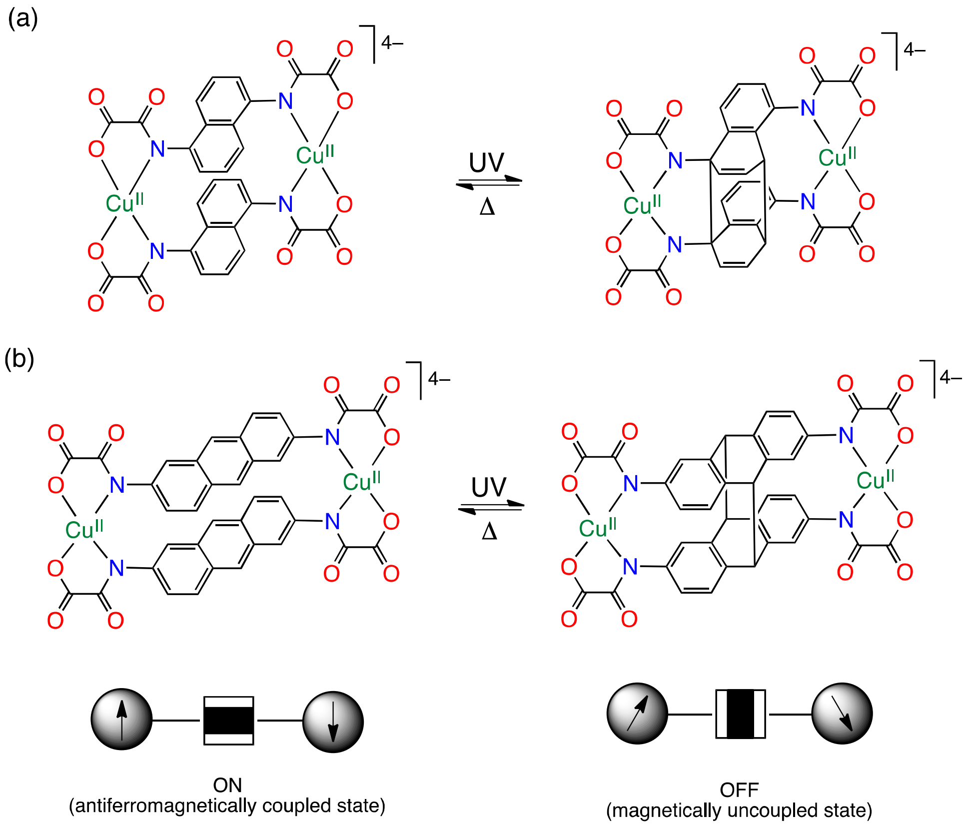
Scheme 8. POC design of a molecular antiferromagnetic switch in oxamato-based dicopper(II) 2,6-anthraquinophanes showing the electroswitching magnetic behavior upon ligand reduction of the anthraquinone spacers.

3.3. Photoactive Spacers

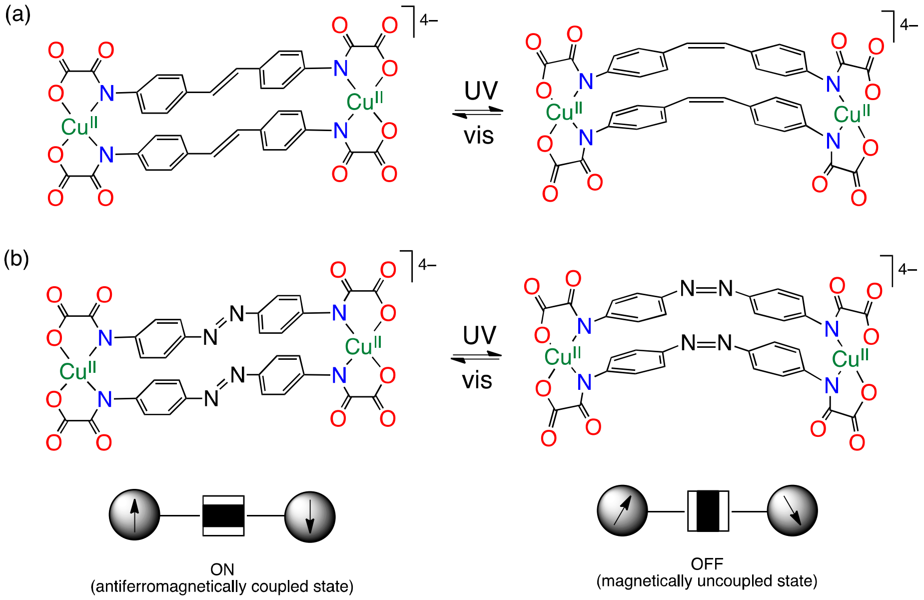
Oxamato-based dicopper(II) oligoacenophanes are appealing candidates as MSs because of the photoactive ("non-innocent") nature of the OA spacers [135–137]. As such, the aforementioned dicopper(II) 1,5-naphthalenophane and 2,6-anthracenophane exhibit a photo-triggered magnetic transistor behavior [136,137]. The reported photomagnetic bistability arises from the more or less complete and thermally reversible conversion of the weak antiferromagnetically coupled dicopper(II) oligocenophane (ON) to the corresponding magnetically uncoupled dicopper(II) photodimer product (OFF) resulting from the intramolecular [4 + 4] photocycloaddition reaction of the two facing oligoacene spacers under UV light irradiation and heating, as illustrated in Scheme 9.

This intramolecular ("pseudo-bimolecular") photocycloaddition reaction constitutes a unique example of coordination-driven self-assembly for the supramolecular control of photochemical reactivity and photophysical properties in the solid state [99]. The lower photochemical efficiency and thermal reversibility of the dicopper(II) 1,5-naphthalenophane when compared to those of the 2,6-anthracenophane derivative agree with the different reactivity toward the photodimerization of anthracene and naphthalene themselves [137]. However, their photochemical efficiency and thermal reversibility are comparable to those reported for the intramolecular [4 + 4] photocycloaddition of purely organic naphthalenophane and anthracenophane analogues, reflecting thus the importance of the entropic effects associated with the cyclic or metallacyclic structures.

A novel series of oxamato-based dicopper(II) metallacyclophanes with rod-like photoactive oligo(*p*-phenylenevinylene)-(OPV) and oligo(*p*-phenyleneazo) (OPA) spacers, such as 4,4′-stilbene or 4,4′-azobenzene (Scheme 1g), is currently under investigation by some of us. As such, a complete and totally reversible photochemical transformation may be reached after successive irradiation, with UV and visible light, of the dicopper(II) 4,4′-stilbenophane and 4,4′-azobenzenophane featuring a *cis–trans* geometric isomerization, as illustrated in Scheme 10. The spins of the Cu^{II} ions are antiferromagnetically coupled through the planar *trans*-azobenzene spacers (ON state) in the former case, whereas they are magnetically uncoupled across the non-planar *cis*-azobenzene spacers (OFF state) in the latter one because of the steric repulsion between the *ortho* hydrogen atoms from the two benzene rings.



Scheme 9. POC design of a molecular antiferromagnetic switch based on oxamato-based dicopper(II) 1,5-naphthalenophanes (**a**) and 2,6-anthracenophanes (**b**), showing the thermally reversible photoswitching magnetic behavior upon ligand photocycloaddition of the two facing naphthalene and anthracene spacers. Adapted with permission from Castellano et al. (reprinted with permission from [99], Elsevier, 2015).



Scheme 10. POC design of a molecular magnetic switch in oxamato-based dicopper(II) 4,4′-stilbenophanes (**a**) and 4.4′-azobenzenophanes (**b**) showing the photoswitching magnetic behavior upon *cis–trans* geometrical photoisomerization of the aromatic spacers.

4. Conclusions and Outlook: Metallosupramolecular Chemistry Acts as a Rail from Single-Molecule Spintronics to Quantum Computing

Metallosupramolecular complexes are particularly attractive systems for the construction of molecular magnetic devices for highly integrated molecular spintronic circuits. The chemical, electro- and photo-chemical reactivities of the metal centers and/or the ligand spacers, their ability to respond to changes in chemical and electrochemical potential or photoexcitation, and the geometrical features that allow positioning of substituent groups, allow for the exploration of a vast amount of molecular magnetic wires (MWs) and switches (MSs) [19–28]. The extension of the control of charge localization (or current flow) through MWs and MSs in response to one or several input signals is mandatory in the development of molecule-based logic circuits for quantum computing. The controlled entanglement through a very weak (but non-negligible) switchable magnetic interaction between a pair of highly coherent spin carriers acting as individual quantum bits (qubits) is crucial for the physical implementation of quantum information processing (QIP) through quantum gates. In contrast to current computational methodology based on classical bits, QIP may offer a new paradigm for performing quantum logic operations that exploits the quantum coherence properties of electron spin-based qubits in forming part of a quantum gate in future quantum computers [29–45].

The present review provides a brief overview on the evolution of the field of oxamato-based dicopper(II) metallacyclophanes, from the simple systems with ferro- and antiferromagnetic interactions, depending on the substitution pattern of the *m*- and *p*-phenylene, 2,6-pyridine or 1,4-anthraquinophane spacers, to a plethora of multifunctional magnetic systems, playing with the chemical, electro- and photo-chemical properties of the oligo-*o*-phenylethylene, oligo-*p*-phenylene or *p*-phenylethyne, and oligo-α,α'- or β,β'-acene spacers (see Scheme 1). Oxamato-based dicopper(II) metallacyclophanes constitute thus a unique class of metalosupramolecular complexes because they combine the inherent magnetic properties of the intervening metal centers with the chemical, electro- and photo-chemical reactivity of the organic bridging ligands. Besides their use as ground tests for the fundamental research on electron exchange (EE) magnetic interactions through extended π-conjugated aromatic ligands (both experimentally and theoretically), they have emerged as ideal model systems for the proof-of-concept design of molecule-based multifunctional magnetic devices in the emerging fields of single-molecule spintronics and quantum computing, as shown in Figure 9 [99,100].

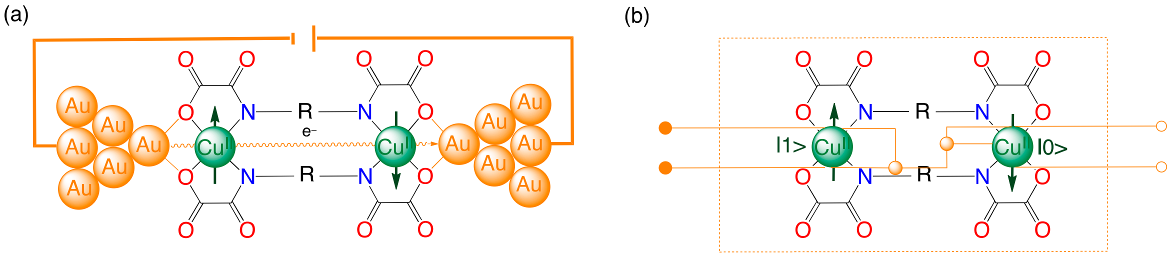


Figure 9. Oxamato-based dicopper(II) metallacyclophanes as multifunctional molecular magnetic devices for electrical (**a**) and logic circuits (**b**) of single-molecule spintronics and quantum computing.

Oxamato-based dicopper(II) metallacyclophanes appear thus as suitable candidates for the study of spin-dependent electron transport (ET) across single-molecule junctions when they are connected to two gold electrodes through their carboxylate-oxygen donor atoms (Figure 9a), as proposed earlier [99]. A topological control of the ET can be envisaged in dicopper(II) meta- and paracyclophanes (Scheme 1a,b). The parallel spin alignment observed in the former case would lead to a greater electrical conductance than the antiparallel one found in the latter case [172,173]. Alternatively, the application of a moderate magnetic field that reverses the spin alignment from antiparallel to parallel would allow for a magnetic rectification of ET in dicopper(II) oligophenylenophanes and oligophenylethynylenophanes (Scheme 1e,f). In both cases, the energy difference between the parallel (triplet) and antiparallel (singlet) spin states can be chemically tuned by the length of the spacer [119,120]. Likewise, the electrical rectification of the ET seems feasible in dicopper(II) anthraquinophanes (Scheme 1k,l). A change of the spin alignment from antiparallel to parallel is predicted after the successive reduction of the two anthraquinone spacers under an applied voltage of the electrical current [166]. Another possibility is to get an optical switching of the ET through molecular wires in dicopper(II) oligoacenophanes (Scheme 1i,j). In this case, the photocycloaddition of the oligoacene spacers by UV light irradiation would lead to the interruption of the electrical conductance, and thermal relaxation by heating would restore it [174–177].

One further step in this area will be the use of oxamato-based dicopper(II) metallacyclophanes as basic logic units (quantum gates) for the future generation of quantum computers (Figure 9b). The recent work by Rüffer and Kataev on the quantum coherence (QC) properties of related mononuclear oxamato-containing copper(II) complexes is particularly encouraging, as it shows that sufficiently long spin coherence times for quantum gate operations can be achieved in these simple systems [178]. However, this is not an easy task because it implies the rational design of very weakly interacting ("entangled") and potentially switchable molecules before applications could be envisaged, as illustrated by the impressive work of Winpenny on supramolecular arrays of metal rings [75–79].

In this respect, the two novel classes of electro- and photo-active, oxamato-based dicopper(II) 4,4′-azobenzenophanes and 2,6-anthraquinophanes (Scheme 1g,l) are particularly interesting as prototypes of double qubit-based quantum gates. In both cases, each Cu^{II} ion ($S_{Cu} = \frac{1}{2}$) constitutes a two-state magnetic quantum system represented by the pair of $m_S = \pm 1/2$ states, which may be viewed as a basic unit of quantum information or a "single" qubit, the quantum analogue of the classical bit with "0" and "1" values. That being so, the two potentially switchable Cu^{II} ions may function as a "double" qubit with up to four degenerated |00>, |01>, |10>, and |11> quantum states. In fact, a completely reversible electro- or photo-magnetic switching could be achieved in the resulting dicopper(II) 2,6-anthraquinophane and 4,4′-azobenzenophane after redox cycling or under irradiation with UV and visible light (Schemes 8 and 10a, respectively). The spins of the Cu^{II} ions are antiferromagnetically coupled through the extended π-conjugated, 2,6-anthraquinolate and *trans*-azobenzene spacers ("coupled" state), whereas they very weakly interact across the non-extended 2,6-anthraquinone and non-planar *cis*-azobenzene spacers ("entangled" state).

Indeed, this review on the use of oxamato-based dicopper(II) metallacyclophanes as prototypes of multifunctional and multiresponsive molecular magnetic devices for single-molecule spintronics and quantum computing is more a proposal than a real achievement. This is rightly expressed in the voice of the most famous Portuguese poet, Fernando Pessoa: "Não sou nada./Nunca serei nada./Não posso querer ser nada./À parte isso, tenho em mim todos os sonhos do mundo" (extracted from the poem Tabacaria by Álvaro de Campos). In the years to come, we would like to accomplish some of these dream worlds concerning the physical realization of QIP in future quantum computers. In this respect, this review is also meant to be a tribute letter to Professor Francesc Lloret, who introduced us to the fantastic experience of molecular magnetism, on the occasion of his 65th birthday, and hoping that he will continue to pursue his dreams, from both professional and personal viewpoints.

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Conflicts of Interest: The authors declare no conflict of interest.

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