Dinuclear Cu(II) molecules exhibiting reversible photochromism

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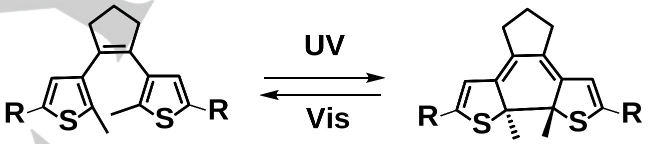
Abstract: We present here the design and preparation of several discrete coordination complexes exhibiting two Cu(II) ions separated by a dithienylcyclopentene as a photoswitchable spacer, proposed as models of molecular √SWAP quantum gates. These models use the two Cu(II) ions as realizations of qubits and the spacer as a light switch intended to trigger the gate by reversibly undergoing a ring closing isomerization. For this, a dicarboxylate species with a central diarylethene, H_2L1, has been used, together with bipyridine or phenatroline as capping ligands. Also, a new dinucleating ligand containing the photoactive moiety in between to tridentate coordinating pockets, H_4L2, has been designed and prepared for the same purpose. The four complexes have been characterized by single crystal X-ray diffraction. Three of them exhibit reversible photoswitching in solution.

Introduction

Quantum computing aims at exploiting the laws and properties of quantum mechanics for the processing of information with increased capacities to face challenges that are currently out of reach.[1] For this, algorithms have been developed while many technologies are being proposed and investigated to realize the quantum bits and gates (qubits and qugates).[2, 3] One possibility to achieve this is the coherent manipulation of the electronic spin within molecules.[4, 5] Recent proposals suggest that molecules exhibiting two transition metal aggregates or ions, each with a pure or effective $S = ½$ spin and separated by a redox switch capable of turning on and off the magnetic interaction between them could act as a √SWAP qugate.[6, 7] The latter is a 2qubit qugate that inverts the state of both qubits only if they feature opposite readings. We propose to use a photoactivated switch instead, to benefit from the advantages of light as versatile external stimulus. To test this possibility, it is necessary to design the synthesis of molecules with two $S = ½$ moieties separated by a photochromic unit able to change reversibly its chemical structure with light. There are several chemical groups that change reversibly their chemical structure by light irradiation.[8] One of the most appealing is that of dithienylethenes (Scheme I),[9] which undergo a process of light induced, reversible photocyclization, offering various relevant advantages; *i*) the photoisomerization is triggered with light of different wavelength for each direction, *ii*) in most systems, both isomers are thermally stable, *iii*) the switching process is fast and remarkably resistant to fatigue, and *iv*) this unit is easily amenable to chemical derivatization. Some groups have prepared ligands that interpose a dithienylethene in between donor atoms, to obtain complexes of metals connected by the photochromic unit.[10-18] On the same spirit, we have used in this paper the Cu(II) ion as realization of the qubit. With a d^9 configuration, it features a true and isolated $S = ½$ ground state, providing the two quantum states to encode the qubit. Complexes of this ion have demonstrated to exhibit very high quantum coherence, even at room temperature,[19, 20] which converts them into promising qubit realizations.



Scheme 1. Dithienylethene unit and its reversible photoisomerization using UV and visible light, respectively.

In order to link two Cu(II) ions with a dithienylethene spacer we have used a dicarboxylate derivative of the photochromic unit (H_2L1; Scheme 2).[21] In addition, a new ditopic ligand exhibiting two carbohydrazide-based chelating units at both sides of the photoactive spacer (H_4L2; Scheme 2) has been synthesized and crystallographically characterized. Two dinuclear complexes of Cu(II) with deprotonated H_2L1 and two with deprotonated H_4L2 have been obtained and characterized. We present here the structure and photochromic properties in solution of both ligands and of all these new coordination assemblies. Only the photochromic behaviour in solution is relevant for the purposes of this study, rather than in the solid state. The reason is that the future exploitation of molecular spin-based qugates can not be performed in the bulk, but rather on small ensembles or even on individual molecules deposited on the appropriate substrates.

Results and Discussion

Synthesis

A natural choice for linking two Cu(II) ions is the dicarboxylate ligand 1,2-(5-carboxy-2-methyl-thiophen-3-yl)-cyclopentene, H_2L1. The latter was obtained through a modified version of a

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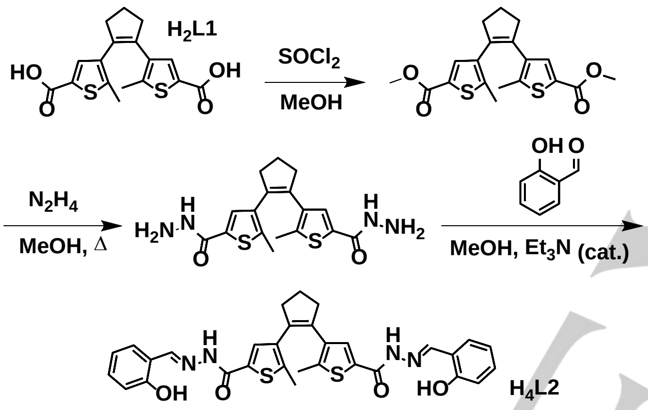
published procedure,[21] where the key step is the McMurry cyclisation of the linear diketone 1,5-bis(5-chloro-2-methylthiophen-3-yl)pentane-1,5-dione. Indeed, this ligand is a divergent difunctional node, previously reported reactions of H_2L1 with Cu(II) produced a linear polymer with formula $[Cu(L1)]_n$.[22] The latter could be prepared as two different solvathomorphs, and their photochromic properties were studied. This polymer had also some precedents with the perfluorinated version of H_2L1.[23] In order to isolate discrete Cu(II) dinuclear complexes, we introduced chelating ligands (2,2'-bipyridine or phenantroline) as capping ligands, intended to block some of the metals coordination positions thereby preventing the polymerization. Indeed, stoichiometric amounts of H_2L1, triethanolamine as base, $Cu(NO_3)_2$ and 2,2'-bipyridine (bpy) or phenantroline (phen), respectively, produce in MeOH, crystals of the dinuclear complexes $[Cu_2(L1)(bpy)_4](NO_3)_2$ (**1**) or $[Cu_2(L1)(phen)_4](NO_3)_2$ (**2**),‡ as intended.



Scheme 2. Ligands H_2L1 and H_4L2, and synthesis of the latter.

A different strategy of obtaining dinuclear Cu(II) complexes with a dithienylethene spacer was to design a photochromic non-divergent dinucleating ligand. With this aim, the ligand 1,2-bis-(5-(N'-(2-hydroxybenzylidene)-carbohydrazide)-3-methyl-thien-3-yl)-cyclopentene (H_4L2) was prepared, which contains two external hydrazone-based tridentate chelating units (Scheme 2). This donor is prepared from the bis-carbohydrazide derivative of H_2L1, following the esterification of the latter. A Schiff base reaction between the bis-carbohydrazide and salicylaldehyde yields H_4L2 (Scheme 2), featuring the carbohydrazide spectral features (Fig. S1). Deprotonation of H_4L2 with Bu_4NOH, followed by addition of $CuBr_2$ in the mixture MeOH/pyridine leads to crystallization of the dinuclear neutral complex $[Cu_2(L2)(py)_2]$ (**3**). The infrared (IR) spectrum of this complex reveals a decrease of the stretching vibration of the C=O group from H_4L2, from 1634 cm^{-1} to near 1608 cm^{-1}, overlapping with the bad corresponding to the C=N, vibration of the carbohydrazide. The copper ions of complex **3** in the solid state establish weak axial interactions with the phenoxide oxygen atom of a neighboring molecule, leading to a one-dimensional chain (see below). These associations can be disrupted using a chelating capping ligand. Thus, the reaction in MeOH, upon addition of phenantroline, produces a precipitate that dissolves in DMF and generates crystals, after a process of slow evaporation, of the truly discrete complex $[Cu_2(L2)(phen)_2]$ (**4**). The IR of the complex indicates again the coordination of the carbohydrazide group (Fig S2), in addition to the presence of solvate DMF (C=O band at 1669 cm^{-1}).

Description of Structures

H_4L2. The crude of H_4L2 can be crystallized from DMF, producing crystals suitable for single crystal X-ray diffraction (SCXRD). The lattice of H_4L2 is described by the orthorhombic space group $P2_12_12_1$ (Table S1 and Fig. 1). The asymmetric unit is formed by one molecule of H_4L2 and two of DMF, which establish hydrogen bonds with the N–H fragments of the hydrazone groups (involving N2 and N3, Fig. S3). The other N atoms from these groups act as H-bond acceptors of their neighbouring phenol O–H units. The distance between carbon atoms C22 and C12 (relevant for the photocyclization) is 3.505 Å, thus suitable for observing photoisomerization in the solid state. The fragments of the molecule around each side of cyclopentene ring are approximately contained within two idealized planes forming an angle of 53.5°. The packing occurs through weak van der Waals intermolecular interactions and does not involve π···π stacking contacts.

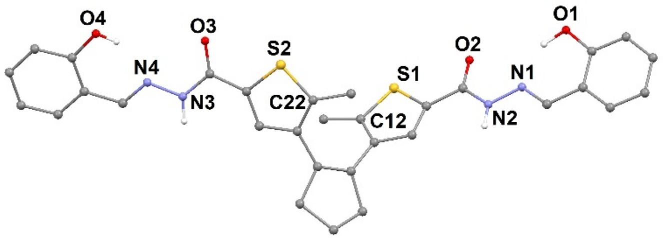


Figure 1. Molecular representation of H_4L2 as determined by SCXRD. Only H atoms bonded to heteroatoms are shown (in white colour).

$[Cu_2(L1)(bpy)_4](NO_3)_2$ (1). Compound **1** crystallizes in the triclinic $P\bar{1}$. space group. Its asymmetric unit comprises a $[Cu_2(L1)(bpy)_4]^{+2}$ cation, two NO_3^- anions, two molecules of methanol and three molecules of water. The complex cation (Fig. 2) contains two Cu(II) centers lying 9.982 Å apart, bridged by the photochromic species $L1^{2-}$ through its carboxylate groups, which chelate the metals, each via one short and one long bond (short/long bond distances, in Å, of 1.984/2.730 and 1.980/2.745 for Cu1 and Cu2, respectively). The coordination around each copper center is completed by two bipyridine ligands in cis conformation (with Cu–N bond distances in the range 1.988 to 2.185 Å, one bond being ≈9% longer than the other three at each metal ion, see Table S2). The coordination geometry around Cu(II) can be described as an extremely distorted octahedron, or close to a square-based pyramid plus the long Cu–O bond as additional weaker interaction (Fig. 3). In this pyramid, the apical position is taken by the long Cu–N bond. The methyl groups of the central photochromic are in the parallel conformation (Table S3), which should prevent, the photocyclization in the solid state. Each molecule establishes four π···π interactions with neighboring molecules through its four bpy ligands (Fig. S4). These contacts originate an extended network of interactions that keep the molecules organized in cationic sheets along the crystallographic ac planes (Fig. S5). All the lattice solvents and the anions are located in between sheets. The closest intermolecular Cu⋯Cu distance is 7.109 Å, almost 3 Å closer than within the molecule.

$[Cu_2(L1)(phen)_4](NO_3)_2$ (2). The crystal lattice of compound **2** belongs to the triclinic space group $P\bar{1}$. Its asymmetric unit is composed by a $[Cu_2(L1)(phen)_4]^{+2}$ cation, together with two NO_3^- anions and five molecules of methanol. The dinuclear complex (Fig. 2) is analogous to the cation of **1**, with phenantroline ligands instead of bipyridine. The Cu(II) ions are here slightly more separated (10.035 Å) and exhibit the same peculiar coordination geometry (Fig. 3). The short/long Cu–O distances (in Å) are here 1.985/2.549 and 1.982/2.641 for Cu1 and Cu2, respectively. Again, of the four Cu–N distances at each metal, one is distinctly longer than the other three (by ≈10%). These bond distances span the 2.004 to 2.226 Å range. As in compound 1, the methyl groups on the thienyl rings lay in the parallel conformation. All the phenantroline ligands of the complex are engaged in π⋯π interactions with their counterparts from four neighbouring molecules (Fig. S6). These weak bonds cement the disposition of the cations in form of positively charged layers contained on the *ac* plane of the lattice (Fig. S7). In between these layers one can find the NO_3^- anions and the molecules of MeOH. The molecules place the Cu ions from different complexes as close as 8.447 Å.

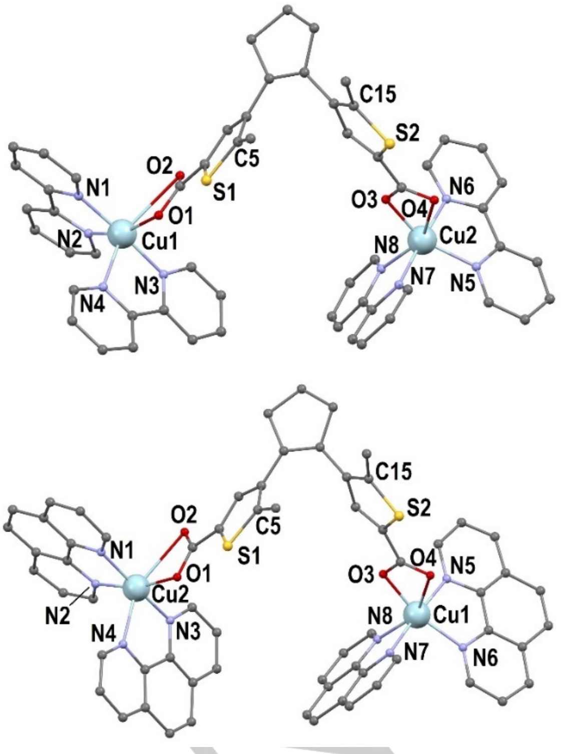


Figure 2. Molecular SCXRD representation of $[Cu_2(L1)(bpy)_4]^{+2}$ and $[Cu_2(L1)(phen)_4]^{+2}$ of **1** and **2**, respectively. H atoms are not shown.

$[Cu_2(L2)(py)_2]$ (3). The crystal lattice of complex **3** is found in the triclinic space group $P\bar{1}$. The asymmetric unit includes the coordination compound, in addition to one molecule of MeOH. This complex (Fig. 4) features two Cu(II) ions chelated in *mer* fashion by the tridentate O_2N pockets of the hydrazone units of $L2^{4-}$, while being kept 14.934 Å apart by this ligand. The equatorial environment of each metal is completed by a pyridine ligand. In the solid state, each Cu(II) exhibits a weak interaction with the phenoxide oxygen atom of a neighboring molecule (with Cu–O distances of 2.659 and 2.839 Å, for Cu1 and Cu2, respectively) thus leading in the lattice to infinite chains of molecules connected by their ends (Fig. S8), with short intermetallic separations of 3.391 Å. In this manner, the coordination environment around the metal centers can be described as square-based pyramidal, with these weak interactions occupying the apical positions (Fig. 3). The equatorial Cu–O bond lengths range, 1.903 to 1.954 Å, while the Cu–N distances span the 1.930 to 2.009 Å range, the bonds to azine being longer than these to pyridine. The molecule of methanol is acting as donor of a H-bond with one azine N atom of the complex. The polymers of **3** are only weakly interacting *via* Van der Waals interactions.

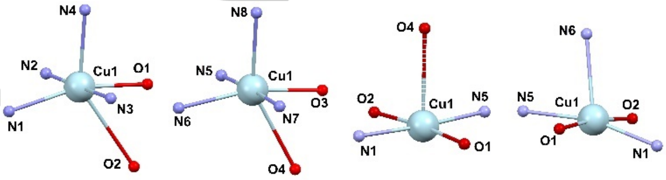


Figure 3. Representation of the first coordination sphere of the metal ions in complexes **1**, **2**, **3** and **4** (from left to right). For all complexes, Cu1 is shown, while Cu2 is essentially the same, in each case.

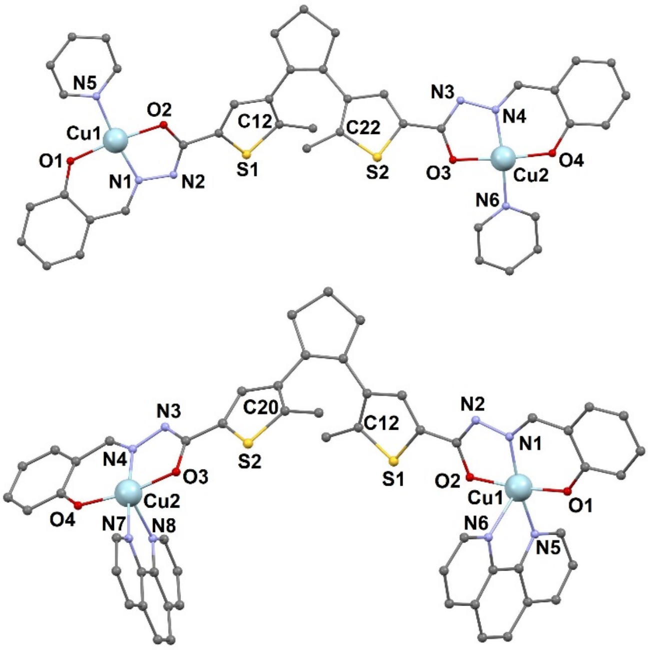


Figure 4. Molecular SCXRD representation of $[Cu_2(L2)(py)_2]$ (**3**) and $[Cu_2(L2)(phen)_2]$ (**4**). H atoms are not shown.

[Cu_2(L2)(phen)$_2$] (4). Unlike all the other compounds in this report, complex **4** is part of a lattice organized in the monoclinic space group $P2_1/n$. The asymmetric unit contains one complex molecule, three molecules of water and one of DMF. The complex (Fig. 4) also features one L2^{4-} ligand chelating and bridging two Cu(II) ions, this time separated by 13.73 Å. The metals are in a distorted square-based pyramidal coordination geometry (Fig. 3). Three of the positions are occupied by the tridentate O_2N hydrazone pockets of L2^{4-} (Cu−O and Cu−N distances in the range 1.878 to 1.963 Å and 1.927 to 1.942 Å, respectively) while the remaining two sites are filled with one chelating phenantroline donor (with Cu−N distance ranges of 2.007 to 2.257 Å, in both cases one short and one ≈13% longer). The apical position of the pyramid is formed by the long bond to phenantroline. Each molecule of **4** establishes a set of π···π interactions through its phenantroline ligands with two neighboring molecules, thereby leading to infinite chains in the lattice (Fig. S9). The shortest intermolecular Cu···Cu separation is 6.914 Å.

Mass Spectrometry

Mass spectrometry (MS) helped in the characterization of new ligand H_4L2 (see experimental). Complexes **1** to **4** were also investigated with this technique, employing positive and negative electrospray ionization (ESI) MS. The experiments revealed that the dicarboxylate bridged compounds **1** and **2** do not hold the experimental conditions necessary to bring them to the detector. Thus, only fragments of the molecular moiety investigated were obtained (not shown). This is a consequence of the relatively labile binding existing between Cu(II) and the carboxylates, which is not really chelating since it consists of a coordination and a pseudo-coordination bond (see above). Complex **3** was indeed detected, although only in the negative mode, in form of the adducts [Cu_2(L2)(OH)]$^-$, [Cu_2(L2)(OH)$_2$]$^{2-}$ and [[Cu_2(L2)]$_2$(OH)]$^-$ (Fig. S10). These results demonstrate that the [Cu_2(L2)] core is more robust, since the Cu(II) ions are encapsulated within tridentate pockets. It becomes apparent that the pyridine ligands may be easily removed and eventually be substituted by H_2O or OH^- ligands. The positive mode did not yield any result, presumably from difficulties in generating detectable positive fragments. Complex **4** was not detected in the negative mode, presumably because, contrary to pyridine, chelating phenantroline is much harder to remove, thus rendering the formation of negatively charged fragments by OH^- coordination difficult. In this case, it was however possible to detect the [M+H]$^+$ fragment, [HCu_2(L2)(phen)$_2$]$^+$ (Fig. S11).

Photochromic Properties

The photochromic properties of H_2L1 in the solid state were previously reported by some of us.[22] These were studied through reflectivity measurements and Raman spectroscopy, both reflecting essentially on the behavior at the surface of the system. These studies demonstrated that H_2L1 exhibits a distinct and reversible full photochromic process that proceeds with UV light (365 nm) in one direction and with visible radiation (455 nm) in the other. We further characterized here the photochromic behavior of H_2L1 in solution and compared it with that of H_4L2, *via* absorption spectroscopy (Fig. 5).

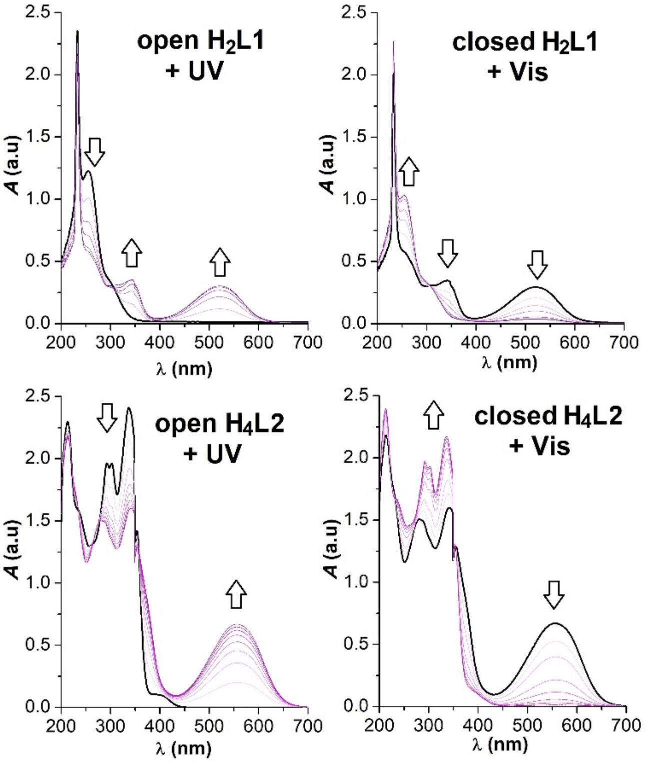


Figure 5. Absorption spectra of H_2L1 (top) H_4L2 (bottom) in H_2O/DMSO (99:1) and MeOH solution, respectively, and their evolution upon irradiation first with UV light (< 425 nm, left panels) and then with visible light (> 430 nm, right panels). The initial spectra before each series are the black thick traces.

The evolution of the absorption spectrum of H_2L1 in H_2O/DMSO (99:1) upon irradiation with UV light (< 425 nm) denotes a decrease of a high-energy band attributed to a π···π transitions (near 256 nm) together with the growth of the typical wide and intense band in the visible region (522 nm). The latter confers an intense color to the cyclized species and originates from the conjugated polyene system that arises with this isomerization (Scheme 1). The same study was carried out for H_4L2, using methanol as a solvent. Here, UV irradiation causes the decline of two bands at 298 and 336 nm, while generating a strong and wide band at 556 nm. Photo-stationary states (PSSs) are reached in approximately 120 and 100 s, respectively. Upon irradiation with visible light (> 430 nm), the spectrum of both compounds is restored 100 % to that of the initial, open form in approximately 300 and 90 s, respectively.

The photochromic behaviour of complexes **1** to **4** was also investigated (Fig. 6 and S12).‡ Complexes **1** and **2** were studied in the same solvent used for ligand H_2L1. In the solid state, the configuration of their central photochromic moiety is not suitable to observe the photo-isomerization, since both methyl groups of the thienyl rings are oriented to the same side (Fig. 2). However, these molecules are flexible enough to reach a suitable conformation in solution. In both cases a clear photochromic response was observed. Thus, illumination with UV light turns light greenish solutions of **1** and **2** in H_2O/DMSO (99:1) into purple ones, causing the rapid growth of a large band at 515 nm in their electronic spectra (Fig. 6). This characteristic band is less pronounced than seen for the ligand. It has been seen before that the electronic interaction between the photochromic unit and metals contained in the same molecule can partially or completely quench the activity of the photosensitive unit.[18]

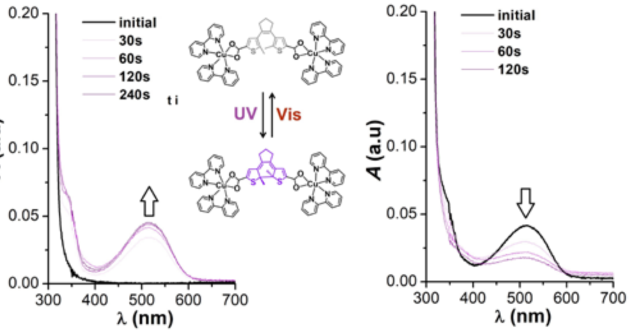


Figure 6. Absorption spectrum of complex **1** in H_2O/DMSO (99:1) and its evolution upon irradiation first with UV light (< 425 nm, left panel) and then with visible light (> 430 nm, right panel). The initial spectra before each series are the black thick traces.

Complex **3** was irradiated with UV light in DMSO or DMF. In both cases the response was very similar, with a colour change from light brown to purple. The electronic spectrum revealed the growth of a broad band near 560 nm, with a weaker relative intensity (Fig S13) than seen for complexes **1** and **2**, reaching a PSS after 35 min. This process was completely reversible, and the original spectrum and the initial colour of the solution were restored upon illumination with visible light only after 5 min. Interestingly, complex **4** does not show any photochromic activity, perhaps as a result of the coupling between the metal in this environment and the central photochromic unit, blocking the photo-switching of the latter.[18]

Conclusions

Photo-switchable ligands H_2L1 and H_4L2, the latter designed and characterized during this work, are able to assemble pairs of Cu(II) ions into discrete dinuclear complexes separated by a photoactive spacer. The reversible photo-switching activity exhibited by H_2L1 and H_4L2 in solution is conserved by three of the complexes, yielding potential models of √SWAP qugates. Subsequent studies will involve the evaluation of the eventual quantum coherence properties of the spin centres present in these molecules, as well as the possible effect on the weak magnetic interaction of the reversible cycloisomerization caused by irradiation, when these molecules are in solution.

Experimental Section

Synthesis

All chemicals were purchased from commercial sources and used without further purification. All coordination chemistry reactions were performed under aerobic conditions. The precursor 1,2-bis-(5-carboxy-2-methyl-thiophen-3-yl)-cyclopentene (H_2L1) was synthesized according to a previously reported procedure.[21]

1,2-bis-(5-acetyl-2-methyl-thiophen-3-yl)-cyclopentene. To a solution of 1,2-bis-(5-carboxy-2-methyl-thiophen-3-yl)-cyclopentene (H_2L1, 0.5 g, 1.4 mmol) in dry methanol (20 mL) was added an excess of $SOCl_2$ (2 mL, 22.8 mmol). The mixture was stirred under reflux for 2 h and then overnight at room temperature. The solvent was then removed *in vacuo* and the remaining brown oil was re-dissolved in diethyl ether and washed several times to remove the HCl biproduct. The organic phase was separated, dried with Na_2SO_4 and treated by rotary evaporation, yielding a brown oil (0.52 g, 98% yield). ^{1}H-NMR (400 MHZ, $CDCl_3$) δ(ppm): 7.51 (s, 2H, tph), 3.85 (s, 6H, Me), 2.79 (t, 4H, cp), 2.07 (m, 2H, cp), 1.91 (s, 6H, Me).

1,2-bis-(5-carbohydrazide-2-methyl-thien-3-yl)-cyclopentene. To a solution of 1,2-bis-(5-acetyl-2-methyl-thiophen-3-yl)-cyclopentene (1.88 g, 5 mmol) in dry methanol (20 mL) was added an excess of hydrazine hydrate (10 mL) and the mixture was refluxed for 3 h. The system was allowed to cool to room temperature and a white precipitate was collected by filtration, washed repeatedly with MeOH and a last time with diethyl ether, leaving a white powder (1.41 g, 75 % yield). ^{1}H-NMR (400 MHz, *d*$_6$-DMSO) δ(ppm): 9.55 (s, 2H, NH), 7.43 (s, 2H, tph), 4.35 (s, 4H, NH_2), 2.72 (t, 4H, cp), 2.00 (m, 2H, cp), 1.84 (s, 6H; Me).

1,2-bis-(5-(N'-(2-hydroxybenzylidene)-carbohydrazide)-2-methyl-thien-3-yl)-cyclopentene (H_4L2). To a solution of 1,2-bis-(5-carbohydrazide-2-methyl-thiophen-3-yl)-cyclopentene (0.7 g, 1.86 mmol) and salicylaldehyde (0.39 mL, 3.72 mmol) in dry methanol (20 mL) were added a few drops of Et_3N (≈0.5 mL) and the mixture was refluxed overnight. After reaching room temperature, the system was filtered and the collected precipitate was washed with MeOH and diethyl ether to produce a white powder (0.87 g, 80.5 % yield). IR (KrB pellet, cm^{-1}): 3176, 3059, 2915, 2841, 1634, 1619, 1606, 1568, 1486, 1454, 1374, 1296, 1264, 1199, 1178, 1152, 1136, 1035, 974, 925, 846, 751, 669, 650. ^{1}H-NMR (400 MHz, *d*$_6$-DMSO) δ(ppm):11.95 (s, 2H, NHene), 11.05 (s, 2H, OH), 8.5 (s, 2H, NH), 7.73 (s, 2H, tph), 7.52 (d, 2H, Ar), 7.27 (t, 2H, Ar), 6.84 (m, 4H, Ar), 2.82 (t, 4H, cp), 2.06 (m, 2H, cp), 1.88 (s, 6H, Me)). MS (ESI+) m/z: 585.14 $[C_{29}H_{26}O_4N_4S_2+H]^+$.

$[Cu_2(L1)(bpy)_4](NO_3)_2$ (1). A solution of H_2L1 (30 mg, 0.086 mmol) and triethylamine (24 µl, 0.18 mmol) in methanol (10 mL) was added to a solution of $Cu(NO_3)_2{\cdot}3H_2O$ (41.54 mg, 0.18 mmol) and 2,2'-bypyridine (53.6 mg, 0.36 mmol) in methanol (10 mL). The resulting green solution was mixed for 2 hours, filtered and the filtrate was allowed to slowly incorporate ether by vapor diffusion. After two week , blue crystals were collected by filtration (59 mg, yield 57% in average). IR (KrB pellet, cm^{-1}): 3426, 3060, 2917, 2847, 1578, 1465, 1439, 1378, 1239, 1147, 1030, 973, 769, 734, 647. Anal., found (calc% for $[C_{57}H_{50}Cu_2N_{10}O_{12}S_2]$; **1**·$H_2O$): C, 53.93 (54.41); H, 3.80 (4.01); N, 11.75 (11.13).

$[Cu_2(L1)(phen)_4](NO_3)_2$ (2). A solution of H_2L1 (30 mg, 0.086 mmol) and triethylamine (24 µl, 0.18 mmol) in methanol (10 mL) was added to a solution of $Cu(NO_3)_2{\cdot}3H_2O$ (20.77 mg, 0.09 mmol) and phenantroline (31 mg, 0.18 mmol) in methanol (10 mL). The resulting green solution was mixed for 2 hours, filtered and the filtrate was allowed to slowly incorporate ether by vapor diffusion. After 4 days, blue crystals were collected by filtration (32 mg, yield 31 %). IR (KrB pellet, cm^{-1}): 3421, 3056, 2939, 1586, 1517, 1426, 1382, 1143, 1100, 852, 778, 721, 639. Anal., found (calc% for $[C_{65}H_{60}Cu_2N_{10}O_{17}S_2]$; **2**·$7H_2O$): C, 53.05 (54.05); H, 3.31 (4.19); N, 8.32 (9.70).‡

$[Cu_2(L2)(py)_2]$ (3). A solution of H_4L2 (20 mg, 0.034 mmol) and Bu_4NOH (0.136 ml, 0.136 mmol) in methanol (10 mL) was added to a solution of $CuBr_2$ (15.22 mg, 0.068 mmol) in methanol (10 mL). The resulting green solution was stirred for 2 hours. After this, a precipitate appeared, and pyridine was then added dropwise until the complete re-dissolution of the former. The system was left in air unperturbed for the slow evaporation of the solvent. After 1 day, dark brown crystals were collected (23 mg, 73% yield). IR (KBr pellet, cm^{-1}): 3442, 3065, 2926, 2839, 1608, 1500, 1469, 1343, 1195, 1139, 1078, 873, 752, 730, 695. Anal. Found (calc% for [$C_{42}H_{36.9}Cu_2N_6O_{6.45}S_2$]; **3**·MeOH·1.45$H_2O$): C 55.9 (55.8), H 4.22 (4.11), N 9.25 (9.3). MS (ESI-) m/z: 724.98 [$C_{31}H_{25}O_5N_4S_2$]$^-$, 370.99 [$C_{31}H_{26}O_6N_4S_2$]$^{2-}$, 1430.96 [$C_{62}H_{50}O_9N_8S_4$]$^-$.

[Cu_2(L2)(phen)$_2$] (4). A solution of H_4L2 (20 mg, 0.034 mmol) and Bu_4NOH (0.204 ml, 0.204 mmol) in methanol (10 mL) was added to a solution of $CuBr_2$ (15.22 mg, 0.068 mmol) in methanol (10 mL). The resulting green solution was stirred for 10 minutes and phenantroline (13.75 mg, 0.068mmol) was then, while the stirring was maintained further for 30 min at 50 °C. After cooling to room temperature, a precipitate was collected by filtration and re-dissolved with DMF. The solution was left unperturbed and after two weeks, dark brown crystals were collected (18 mg, 42% yield). IR (KBr pellet, cm^{-1}): 3439, 3052, 2917, 2831, 1669, 1613, 1500, 1465, 1426, 1330, 1191, 1026, 943, 839, 721, 665, 562. Anal. Found (calc% for [$C_{58}H_{54}Cu_2N_9O_8S_2$; **4**·DMF·3$H_2O$): C 58.11 (58.23), H 4.51(4.55), N 10.50 (10.54). MS (ESI+) m/z: 1069.12 [$C_{55}H_{40}Cu_2N_8O_4S_2$ + H]$^+$.

Physical Measurements

Elemental analyses were performed with a Perkin-Elmer Series II CHNS/O Analyzer 2400, at the Servei de Microanàlisi of CSIC, Barcelona, Spain. IR spectra were recorded as KBr pellet samples on a Nicolet 5700 FTIR spectrometer. UV-Vis experiments were performed with a Varian Cary-100 spectrophotometer with 1nm of resolution using a cuvette of 1cm light-pass. ^{1}H-NMR spectra were recorded at room temperature with a Varian Unity 400 MHz spectrometer. Photconversions were carried out using a Xenon Light Source 300W Monochromatic lamp with two filters (<425 and >430 nm) from ASAHI SPECTRA Co.

X-ray Crystallography

Data for compounds **H_4L2**, **2**, **3** and **4** were collected at 100 K on a Bruker APEXII QUAZAR diffractometer equipped with a microfocus multilayer monochromator with MoKα radiation (λ = 0.71073 Å). Data for compound **1** were obtained at 100 K on a Bruker APEX II CCD diffractometer at the Advanced Light Source beam-line 11.3.1 at Lawrence Berkeley National Laboratory, from a silicon 111 monochromator (λ = 0.77490 Å). For **H_4L2**, **1**, **3** and **4** data reduction for and absorption corrections were performed with SAINT and SADABS, respectively.[24] Compound **1** was refined as a perfect 2-component twin. Twinning was found within APEX using RLATT, and then analyzed with CELL_NOW[25] that found the proper unit cell, twinning law and ascribed reflections to either or both components. Cell refinement and integration were then performed by SAINT as a 2-component twin, keeping the cell of both components identical. TWINABS was used for absorption corrections and produced HKLF4 and HKLF5 data, respectively for initial structure solution and final refinement. The structures were solved by intrinsic phasing with SHELXT,[26] and refined by full-matrix least-squares on F^2 with SHELXL.[27] All details can be found in CCDC 1941688-1941692 (**H_4L2**-**1**-**2**-**3**-**4**) that contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via https://summary.ccdc.cam.ac.uk/structure-summary-form.
Crystallographic and refinement parameters are summarized in Table S1. Selected bond lengths and intermolecular distances are given in Tables S2 and S3.

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Keywords: Photoisomerization • Quantum bit • Cu(II) • Coordination Chemistry • Ligand Design

‡ The elemental analysis of complex **2** shows deviations that slightly exceed (max. divergence 1.38%) the accepted values for purity. It was not possible to obtain better results from seemingly homogeneous polycrystalline phases. For this reason, we have only exploited the crystallographic information from this compound but refrained from emphasizing its bulk properties.

[1] M. A. Nielsen, I. L. Chuang, *Quantum Computation and Quantum Information*, Cambridge University Press, **2000**.

[2] R. P. Feynman, *Foundations of Physics* **1986**, *16*, 507-531.

[3] T. D. Ladd, F. Jelezko, R. Laflamme, Y. Nakamura, C. Monroe, J. L. O'Brien, *Nature* **2010**, *464*, 45-53.

[4] G. Aromí, D. Aguilà, P. Gamez, F. Luis, O. Roubeau, *Chem. Soc. Rev.* **2012**, *41*, 537-546.

[5] A. Gaita-Ariño, F. Luis, S. Hill, E. Coronado, *Nature Chem.* **2019**, *11*, 301-309.

[6] J. Lehmann, A. Gaita-Arino, E. Coronado, D. Loss, *Nat. Nanotechnol.* **2007**, *2*, 312-317.

[7] J. Ferrando-Soria, E. Moreno Pineda, A. Chiesa, A. Fernandez, S. A. Magee, S. Carretta, P. Santini, I. J. Vitorica-Yrezabal, F. Tuna, G. A. Timco, E. J. L. McInnes, R. E. P. Winpenny, *Nature Commun.* **2016**, *7*, 11377.

[8] I. Yildiz, E. Deniz, F. M. Raymo, *Chem. Soc. Rev.* **2009**, *38*, 1859-1867.

[9] M. Irie, *Chem. Rev.* **2000**, *100*, 1685-1716.

[10] Z. Y. Li, J. W. Dai, M. Damjanovic, T. Shiga, J. H. Wang, J. Zhao, H. Oshio, M. Yamashita, X. H. Bu, *Angew. Chem., Int. Ed.* **2019**, *58*, 4339-4344.

[11] T. Shiga, H. Miyasaka, M. Yamashita, M. Morimoto, M. Irie, *Dalton Trans.* **2011**, *40*, 2275-2282.

[12] M. Estrader, J. S. Uber, L. A. Barrios, J. Garcia, P. Lloyd-Williams, O. Roubeau, S. J. Teat, G. Aromi, *Angew. Chem., Int. Ed.* **2017**, *56*, 15622-15627.

[13] M. Han, R. Michel, B. He, Y.-S. Chen, D. Stalke, M. John, G. H. Clever, *Angew. Chem. Int. Ed.* **2013**, *52*, 1319-1323.

[14] A. Presa, L. Barrios, J. Cirera, L. Korrodi-Gregório, R. Pérez-Tomás, S. J. Teat, P. Gamez, *Inorg. Chem.* **2016**, *55*, 5356-5364.

[15] J. Salinas-Uber, M. Estrader, J. Garcia, P. Lloyd-Williams, A. Sadurni, D. Dengler, J. van Slageren, N. F. Chilton, O. Roubeau, S. J. Teat, J. Ribas-Arino, G. Aromi, *Chem., Eur. J.* **2017**, *23*, 13648-13659.

[16] Y. Tanaka, A. Inagaki, M. Akita, *Chem. Commun.* **2007**, 1169-1171.

[17] E. C. Harvey, B. L. Feringa, J. G. Vos, W. R. Browne, M. T. Pryce, *Coord. Chem. Rev.* **2015**, *282*, 77-86.

[18] E. C. Harvey, B. L. Feringa, J. G. Vos, W. R. Browne, M. T. Pryce, *Coord. Chem. Rev.* **2015**, *282-283*, 77-86.

[19] K. Bader, D. Dengler, S. Lenz, B. Endeward, S.-D. Jiang, P. Neugebauer, J. Van Slageren, *Nature Commun.* **2014**, *5*, 5304.

[20] J. M. Zadrozny, J. Niklas, O. G. Poluektov, D. E. Freedman, *ACS Cent. Sci.* **2015**, *1*, 488-492.

[21] Linda N. Lucas, Jaap J. D. d. Jong, Jan H. v. Esch, Richard M. Kellogg, Ben L. Feringa, *Eur. J. Org. Chem.* **2003**, *2003*, 155-166.

[22] J. S. Uber, M. Estrader, C. Mathoniere, R. Clerac, O. Roubeau, G. Aromí, *Cryst. Growth Des.* **2016**, *16*, 4026-4033.

[23] K. Matsuda, K. Takayama, M. Irie, *Inorg. Chem.* **2004**, *43*, 482-489.

[24] G. M. Sheldrick, Bruker AXS Inc., Madison, Wisconsin, USA, **2012**.

[25] G. M. Sheldrick, Bruker AXS Inc., Madison, Wisconsin, USA, **2012**.

[26] G. Sheldrick, *Acta Crystallogr., A* **2015**, *71*, 3-8.

[27] G. Sheldrick, *Acta Crystallogr., C* **2015**, *71*, 3-8.

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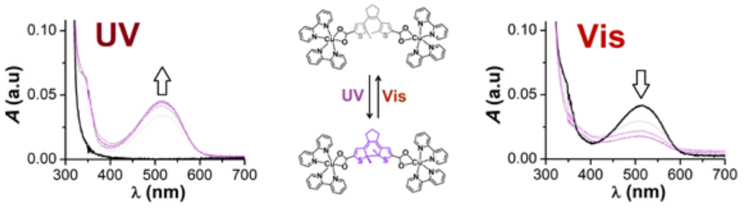

Two ligands have been prepared (one designed here) with the aim of coordinating two Cu(II) ions (S=1/2) separated by a dithienylethene photoswitchable spacer. Four dinuclear complexes have been obtained and crystallographically characterized. Their reversible photoswitching behaviour in solution is revealed *via* electronic spectroscopy.

Photoswitchable Complexes*

*Jorge Salinas-Uber, Leoní A. Barrios, Marta Estrader, Olivier Roubeau, and Guillem Aromí**

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Dinuclear Cu(II) molecules exhibiting reversible photochromism