

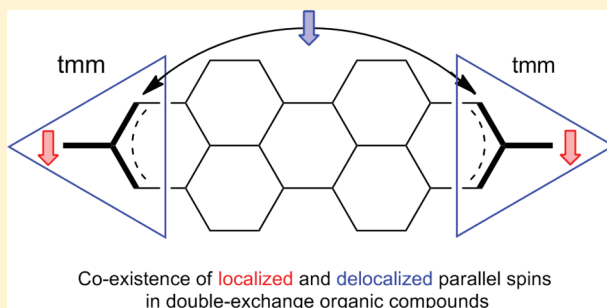
In Search of Organic Compounds Presenting a Double Exchange Phenomenon

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S Supporting Information

ABSTRACT: The objective of this paper is to design a consistent series of organic molecules that may present a double exchange mechanism and study their low energy spectrum using spin unrestricted Density Functional Theory. For this purpose, organic tetra-methylene methane units having an $S = 1$ spin ground state and diamagnetic organic bridges are taken as building blocks for constructing molecules having two or more magnetic units. When biunit systems are ionized, the ground state of the resulting molecular ions may be either a quartet, if the spectrum is ruled by a double exchange mechanism, or a doublet, if it obeys the logic of a mono-electronic picture. A strategy based on the physical analysis of the leading interactions is followed in order to energetically favor a high-spin ground state. It is shown that the most promising compounds involve bridges that have both a large gap between the highest occupied and the lowest unoccupied molecular orbitals and small coefficients on the atoms to which the magnetic units are connected. While the followed strategy enables one to conceive organic compounds exhibiting a double exchange phenomenon, it is shown that the electronic mechanism ruling the spectrum of such organic double exchange compounds is different from that of their inorganic homologues. A new method to reconstruct the spectrum of low energy from various spin unrestricted DFT solutions is proposed and applied. Finally monodimensional and bidimensional periodic lattices based on the most promising organic architecture are suggested.



1. INTRODUCTION

Owing to the Hund's rule, monometallic complexes having several unpaired electrons exhibit a nonzero spin ground state. Connecting these magnetic units through diamagnetic bridges leads to fascinating inorganic materials presenting remarkable properties such as ferro-, antiferro-, ferri-magnetism,¹ spin crossover,² superconductivity,³ magnetoresistive effects,⁴ etc. Recent interest in organic materials, including hydrocarbons, as an intriguing alternative to silicon and transition metals used currently in electronic devices, has grown considerably since they are easier and cheaper to produce. While magnetic properties in organic compounds are less commonly encountered, they have been the subject of a constant research.⁵ Organic chemists have synthesized and characterized organic single radicals such as nitroxides⁶ or verdazyl⁷ and also polyradicalar hydrocarbons such as assemblies of meta-xylylene.⁸ Spectacular architectures with spin up to $S = 80$ were even obtained by Rajca et al., though in a context of dendritic structures that cannot lead as such to periodic lattices.⁹ Playing with the donor and acceptor character of some molecules, it has also been possible to conceive conducting salts and even superconductive materials.¹⁰

Recently, a family of organic polyradicalar units presenting a nonzero spin ground state have been proposed.¹¹ They are based on fused poly benzenic hydrocarbons and may present a

high-spin ground state ($S = 5/2$ for instance) when certain specific carbons are saturated. Connecting these units using appropriate bridges can lead to ferro-, antiferro-, and ferrimagnetic materials.¹² In the present work, we study the possibility to assemble such magnetic units in order to conceive organic systems presenting double exchange phenomenon under doping. The first double exchange model had been proposed by Zener¹³ in order to rationalize the giant magnetoresistive effects observed in manganites. The underlying mechanism involves two populations of unpaired electrons: strongly localized electrons responsible for magnetic properties and delocalized electrons inducing conduction. It therefore represents interesting means to combine transport and magnetic properties, which can hardly be encountered simultaneously although their association is of prime interest in spintronics.¹⁴ Finally, it also appears a very promising means to prepare high-spin molecules.¹⁵ While the study of this phenomenon in inorganic systems has received a lot of attention from both chemists and physicists, examples of purely organic double exchange compounds are extremely rare. One should quote for instance a mixed-valence bis(semiquinone) biradical anion resulting from an electron reduction of an

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antiferromagnetically coupled triradical, reported by Shultz and co-workers.¹⁶

The double exchange mechanism happens in mixed valence compounds involving magnetic units having more than one unpaired electron. The mechanism implies three kinds of interactions, the on-site exchange integral K between the local magnetic orbitals of each magnetic unit, hopping integrals t of a hole (or an extra electron) between the magnetic units and intersite exchange interactions J between localized spin momenta, as illustrated in Figure 1. While the magnetic

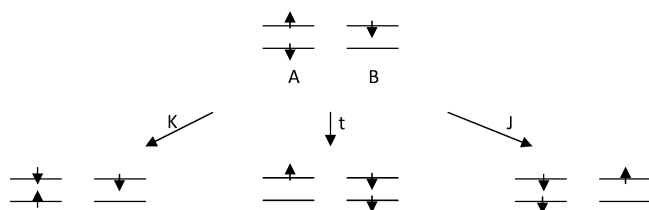


Figure 1. Illustration of the leading electronic interactions in double exchange phenomenon taking place between two magnetic units A and B.

couplings J are usually antiferromagnetic, the hopping integrals favor a ferromagnetic arrangement of all the spins. Since the itinerant electron or hole is usually delocalized between the most interacting orbitals of the units, the hopping integral between these orbitals dominates the physics of low energy and a high-spin ground state is obtained. In order to get organic compounds with such a property, several conditions should be fulfilled: (i) in the first place, the molecular frame should be seen as involving spin $S = 1$ magnetic units (before doping, i.e. ionization) such that two populations of electrons, itinerant and localized, can be obtained under doping, (ii) the organic bridges should not affect the magnetism of the units in the resulting doped architecture, (iii) the interactions through the bridges should be large enough in order to have a magnetic ordering of the spins at room temperature but not too large in order to keep a magnetic behavior, and (iv) finally, it is desirable that the pattern formed by the unit and the bridge be repeatable so that a periodic network can be formed.

The extraction of the double exchange interactions is straightforward from wave function methods calculations of

the lowest energy states.¹⁷ Due to the multideterminantal character of some of these states, it is much more complicated to determine these interactions from spin unrestricted DFT calculations. Recently, a procedure of extraction of double exchange interactions has been proposed.¹⁸ It consists of determining the interactions of a generalized Hubbard model from various DFT solutions and then expressing the interactions of the double exchange model as functions of the Hubbard ones. Unfortunately, this procedure is not accurate enough here due to the important covalence effects inherent to organic compounds. A refined method is therefore proposed that enables one to reconstruct the spectrum of the multiconfigurational states and then to extract rigorously the double exchange interactions.

This paper is organized as follows. The next section recalls the theory of the double exchange model, the method of reconstruction of all the states of low energy and the procedure of extraction of the double exchange interactions from the energies of various spin unrestricted DFT solutions. Section III analyses and discusses the results obtained for a consistent series of designed compounds. The possibility to design promising hydrocarbons likely to present double exchange interaction from the simple calculations of the molecular orbitals diagrams at the Hückel level is presented in Supporting Information. From the knowledge acquired during the analysis of the studied compounds, new architectures likely to present improved features are proposed in section IV. Mono- and bidimensional periodic lattices based on the most promising molecular architecture are designed.

II. THEORETICAL INFORMATION

II.1. Studied Molecular Compounds and Computational Information. A consistent series of organic molecules likely to exhibit a double exchange phenomenon is represented in Figure 2. These molecules may be seen as constituted of two magnetic units, namely, the trimethylene methane (TMM) molecules, which have a triplet ground state in the isolated state and various diamagnetic bridges. The considered bridges have different lengths and different shapes. It is possible to anticipate the nature of the magnetic coupling between the two magnetic units using the Ovchinnikov's rule,¹⁹ which states that the spin of the ground state is given by the M_s component of the most alternant spin distribution of the π electrons. In all considered

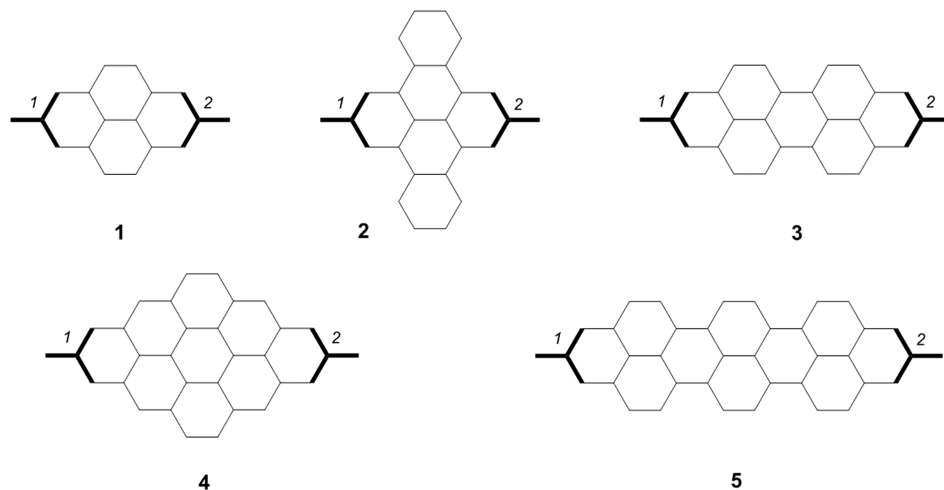


Figure 2. Schematic representation of the studied compounds.

cases, the connection ensures an antiferromagnetic coupling. As a consequence, before oxidation, the ground state of these compounds is expected to be a singlet. In the cation, the spin of the ground state is a result of the competition between the various double exchange interactions and might be either a doublet or a quartet.

The geometries of the designed compounds have been optimized for various electronic solutions, namely $M_s = 0$ and $M_s = 1$ for neutral molecules and $M_s = 1/2$ and $M_s = 3/2$ for cationic molecules, using the B3LYP functional of the GAUSSIAN package.²⁰ To optimize the singlet state geometry a recently proposed method²¹ of spin decontamination has been used. 6-311G** basis sets have been used for all atoms. Expectation values of S^2 have been computed for all solutions and are reported and discussed in the following.

II.2. Monoelectronic Picture versus Double Exchange Mechanism: Theory. Let us consider an organic molecular cation containing three unpaired electrons localized on two magnetic units A and B connected through a diamagnetic organic bridge. The local magnetic orbitals are called a_1 , a_2 on site A and b_1 , b_2 on site B. For a sake of simplicity, we shall first assume that the orbitals 1 and 2 belong to different irreducible representations; hence, there is no interaction between orbitals a_1 (a_2) and b_2 (b_1). For a symmetric cation (we will use the irreducible representation of the D_{2h} symmetry point group to which the studied molecules belong), the hole is completely delocalized between the units. One may expect that the interaction will be larger between the orbitals a_1 and b_1 than between the orbitals a_2 and b_2 . From the resulting molecular orbital diagram represented in Figure 3, one may also expect

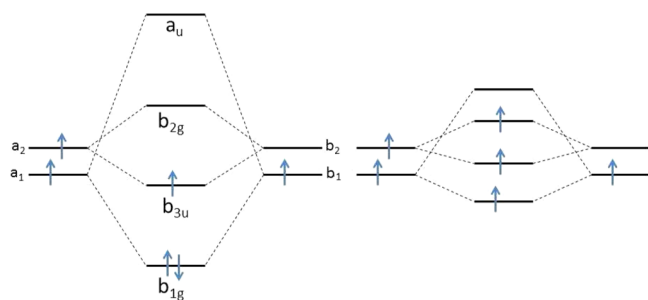


Figure 3. Molecular orbital diagrams obtained in case of strong (left) and weak (right) interactions for D_{2h} molecules such as **1**, **2**, **3**, **4**, and **5**. A doublet ground state can be anticipated in the left diagram while a quartet ground state is expected in the right diagram, that is, when the MOs are quasi-degenerate.

that the ground state is a doublet state with a single open shell, namely the bonding MO b_{3u} built from a_2 and b_2 . The first excited doublet state would result from an excitation from this MO to the corresponding antibonding MO b_{2g} . In both states, the hole is delocalized between the a_2 and b_2 orbitals. The quartet state, which would be obtained from the excitation of an electron from the b_{1g} bonding MO between a_1 and b_1 to the antibonding a_u MO and a spin change, usually lies much higher in energy than the two previously mentioned doublet states. This simple monolectronic picture reproduces qualitatively well the spectrum of most organic cations even though they are constituted of units that are magnetic when considered separately, such as the trimethylene methane TMM molecule, which has a triplet ground state. In order to reach a magnetic regime in which the spectrum of low energy would exhibit a

quartet ground state, these four MOs should be quasi-degenerate.

Another formulation of the problem is provided by the double exchange mechanism. The simpler double exchange model proposed by Zener¹³ is based on the idea that the spectrum of the biunits can be reproduced by considering the magnetic units in their atomic ground states. In the considered case, the magnetic units have either a triplet or a doublet ground state depending on the position of the hole. Two families of states can be generated according to the symmetry of the orbitals in which the hole is delocalized. The family (called 1 here after) to which the high-spin ground state belongs is such that the hole is delocalized between the most interacting orbitals, a_1 and b_1 , for instance. The dominant electronic interaction is the corresponding hopping integral t_1 of the hole between these orbitals. In double exchange systems, this delocalization generates two quartet states Q_+^1 and Q_-^1 and two doublet states D_+^1 and D_-^1 . As shown by Girerd and Papaefthymiou,²² the interaction between the electrons occupying the less interacting orbitals a_2 and b_2 is a magnetic coupling J_1 (contribution of Heisenberg type) that rules the relative energies of the doublet spin states in comparison to the quartet ones in family 1. Similar states, noted Q_+^2 , Q_-^2 , D_+^2 , and D_-^2 constitute family 2, in which the hole is delocalized between the orbitals a_2 and b_2 and the localized electrons occupy the a_1 and b_1 orbitals. In the particular case of a symmetric biunit system, the eigenenergies of the usual double exchange model (here noted the ZGP model in reference to Zener, Girerd, and Papaefthymiou) are analytically known. Energies $E(S, \pm)$ of the different states of total spin S are given by the expression:

$$E_i^{(ZGP)}(S, \pm) = \Delta\epsilon(1 - \delta_{2i}) \pm \frac{t_i}{S_{\max} + 1/2} \left(S + \frac{1}{2} \right) - \frac{J_i}{2} (S(S+1) - S_{\max}(S_{\max}+1)) \quad (1)$$

where S_{\max} is the highest total spin of the double exchange model (here $S = 3/2$), δ is the Kronecker symbol, and the zero of energy is taken as the energy centroid of the highest-spin states of family 2, here the quartet states. The index i (1 or 2) indicates the family of states. The energy difference between the energy centroids of the two families of states is essentially given by the energy difference $\Delta\epsilon = \epsilon(a_1) - \epsilon(a_2)$ between the orbitals a_1 (b_1) and a_2 (b_2). The first term of eq 1 is generally dominant and accounts for the appearance of a high-spin ground state, that is, a ferromagnetic order in family 1. Due to the presence of a bridging ligand, the t_1 integral is expected to be dominated by the through-ligand contribution. The second family of states (higher in energy) is generated by the delocalization t_2 of the hole in the less interacting orbitals a_2 and b_2 and a magnetic coupling J_2 between the electrons localized in the most interacting orbitals a_1 and b_1 . The hopping integral t_2 between a_2 and b_2 may be very small while the magnetic coupling J_2 , which is proportional to t_1 , is usually antiferromagnetic and large, so that one usually observes that the doublet states are lower in energy than the quartets in that family.

When the local excited singlet state (called the non-Hund state in inorganic compounds) of the units is low in energy, as expected in organic compounds, it may affect the energy spacing between the various states. The Anderson Hasegawa model²³ takes only into account the non-Hund states.

Combining both contributions leads to the more appropriate following expressions:¹⁷

$$\begin{aligned}
 {}^4E_i^{(\text{AH/GP})}(S_{\text{max}}, \pm) &= \Delta\epsilon(1 - \delta_{2i}) \pm t_i \\
 {}^2E_i^{(\text{AH/GP})}(S \neq S_{\text{max}}, \pm) &= \Delta\epsilon(1 - \delta_{2i}) + K - \sqrt{K^2 + t_i(t_i \pm K)} \\
 &\quad - \frac{J_i}{2}(S(S+1) - S_{\text{max}}(S_{\text{max}}+1))
 \end{aligned} \quad (2)$$

where AH stands for Anderson Hasegawa. In inorganic compounds the non-Hund states are quite high in energy; however, due to the delocalized character of magnetic orbitals in organic compounds, one may expect that these states can be quite low in energy and may be dominant in the wave function of some of the doublet states.

Figure 4 represents schematically the two families of states (including only the two lowest doublet states) as functions of

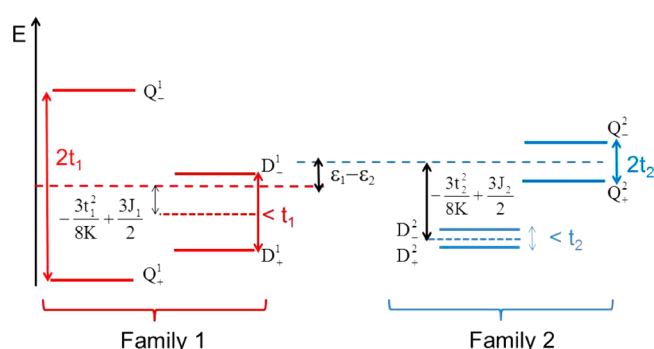


Figure 4. Schematic representation of the spectrum of the two families of states of a double exchange compound. The expression of the energy differences between the energy centroids of the quartet and doublet states is derived from perturbation expansion.

the various interactions in organic (or covalent systems). It should be noticed that while t_1 is the dominant interaction in the first family of states, J_2 is the most important interaction of the second family. For covalent compounds such as organic molecules, J_2 can be so large that the lowest doublet of family 2 can be lower in energy than the quartet state of family 1. In such a case, the double exchange model would predict the same ground state as the simple mono-electronic picture, but in such a case, one should be careful about the applicability of the double exchange model for the analysis of the spectra.

II.3. Reconstruction of the Spectrum of Low Energy and Extraction of the Double Exchange Interactions from DFT Calculations. The real difficulty in getting the low energy spectrum of double exchange compounds from spin unrestricted DFT calculations comes from the determination of accurate energies of the doublet states. Indeed, these doublet states are usually multiconfigurational while the spin unrestricted calculated DFT solutions are single determinants and quite certainly not eigenfunctions of S^2 . While techniques of spin decontamination in the case of magnetic undoped systems are fairly simple, the situation is highly complex for the case of double exchange. For both the doublets with a single open shell and the quartets, the deviations of the expectation value of S^2 from the expected values, $3/4$ and $15/4$, respectively, are relatively small. Nevertheless, it is no longer true for three-open-shell $M_s = 1/2$ solutions. In order to get reliable estimates

of the energies of such doublet states, we will use a method that slightly differs from the one proposed by some of the authors in a previous work;¹⁸ this refined proposed method is more rigorous and more appropriate for organic compounds. It consists of determining the crucial interactions that are ruling the spectrum of low energy and then reconstructing the spectrum from these interactions. For this purpose, the various DFT solutions that are needed to extract all the interactions of a generalized Hubbard model are calculated. This Hamiltonian differs from the usual Hubbard model, which only considers intersite hopping integrals t_1 , t_2 and on-site repulsion U_1 , U_2 , by the introduction of the on-site exchange integral $K = K_{a1a2} = K_{b1b2}$. This model is then numerically solved to get the energies of all doublet states, and the spectrum is reconstructed. The interactions of the double exchange model are consequently extracted from the reconstructed spectrum. This last extraction only makes sense for the states, which are ruled by a double exchange model, that is, the states of family 1 for systems for which the quartet is the ground state.

All needed interactions can be calculated from the seven DFT solutions represented in Figure 5.

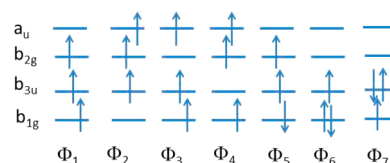


Figure 5. DFT solutions, which are used to extract the interactions of the Hubbard model (D_{2h} symmetry).

Their Hubbard energies are given by the following expressions:

$$\begin{aligned}
 E(\Phi_1) &= \Delta\epsilon - |t_1| \\
 E(\Phi_2) &= \Delta\epsilon + |t_1| \\
 E(\Phi_3) &= -|t_2| \\
 E(\Phi_4) &= +|t_2| \\
 E(\Phi_5) &= \Delta\epsilon + K - |t_1| \\
 E(\Phi_6) &= -2|t_1| - |t_2| + \left(\frac{4K + U_1}{4}\right) \\
 E(\Phi_7) &= \Delta\epsilon - 2|t_2| - |t_1| + \left(\frac{4K + U_2}{4}\right)
 \end{aligned} \quad (3)$$

Solving this system of equations enables one to assess values to the interactions, K , t_1 , t_2 , U_1 , and U_2 . Due to strong covalence effects expected in organic compounds, it is not possible to get reliable values of the exchange integrals of the double exchange model from their perturbative expressions, as done in ref 18. The procedure proposed by the authors consists in determining variationally the energies of the doublet states. The neutral doublet (N) functions of the double exchange model are coupled with the ionic (I of energy U), the pseudo-ionic (pseudo I , of energy $3K$) and the non-Hund functions (NH of energy $2K$). Left-right combination of these functions furnishes a symmetric basis of gerade and ungerade functions for the doublet state of family 2:

$$\begin{aligned}
{}^2\Psi_1^N &= \left| \frac{1}{\sqrt{6}} \left[\sqrt{2} (|a_1 a_2 \bar{b}_1| - |\bar{a}_1 b_1 b_2|) \right. \right. \\
&\quad + \left. \left(\frac{|a_1 b_1 \bar{b}_2| + |a_1 \bar{a}_1 b_2|}{\sqrt{2}} \right. \right. \\
&\quad \left. \left. - \frac{|a_1 \bar{a}_2 b_1| + |\bar{a}_1 a_2 b_1|}{\sqrt{2}} \right) \right] \right\rangle \\
{}^2\Psi_2^{NH} &= \left| \frac{1}{\sqrt{2}} \left(\frac{|a_1 \bar{a}_2 b_1| - |\bar{a}_1 a_2 b_1|}{\sqrt{2}} \right. \right. \\
&\quad \left. \left. - \frac{|a_1 b_1 \bar{b}_2| - |\bar{a}_1 \bar{b}_1 b_2|}{\sqrt{2}} \right) \right\rangle \\
{}^2\Psi_3^{\text{pseudoI}} &= \left| \frac{1}{\sqrt{2}} (|a_2 b_1 \bar{b}_1| - |a_1 \bar{a}_1 b_2|) \right\rangle \\
{}^2\Psi_4^I &= \left| \frac{1}{\sqrt{2}} (|a_1 \bar{a}_1 a_2| - |b_1 \bar{b}_1 b_2|) \right\rangle
\end{aligned} \quad (4)$$

The 4×4 matrix of the Hubbard Hamiltonian working in this basis is

$$\hat{H}_{D_+}^{\text{Hubbard}} = \begin{pmatrix} -\frac{t_2}{2} & -\frac{\sqrt{3}t_2}{2} & -\sqrt{\frac{3}{2}}t_1 & -\sqrt{\frac{3}{2}}t_1 \\ -\frac{\sqrt{3}t_2}{2} & 2K + \frac{t_2}{2} & -\frac{t_1}{\sqrt{2}} & -\frac{t_1}{\sqrt{2}} \\ -\sqrt{\frac{3}{2}}t_1 & -\frac{t_1}{\sqrt{2}} & 3K & -t_2 \\ -\sqrt{\frac{3}{2}}t_1 & -\frac{t_1}{\sqrt{2}} & -t_2 & U_1 \end{pmatrix} \quad (5)$$

Similar matrices can be calculated for the doublet states of family 1 and for the second doublet state of family 2. The following matrix describes the energy of the lowest doublet state of family 1:

$$\hat{H}_{D_+}^{\text{Hubbard}} = \begin{pmatrix} -\frac{t_1}{2} + \Delta\epsilon & -\frac{\sqrt{3}t_1}{2} & -\sqrt{\frac{3}{2}}t_2 & -\sqrt{\frac{3}{2}}t_2 \\ -\frac{\sqrt{3}t_1}{2} & 2K + \frac{t_1}{2} + \Delta\epsilon & -\frac{t_2}{\sqrt{2}} & -\frac{t_2}{\sqrt{2}} \\ -\sqrt{\frac{3}{2}}t_2 & -\frac{t_2}{\sqrt{2}} & 3K + \Delta\epsilon & -t_1 \\ -\sqrt{\frac{3}{2}}t_2 & -\frac{t_2}{\sqrt{2}} & -t_1 & U_2 + \Delta\epsilon \end{pmatrix} \quad (6)$$

Using the numerical values of all the interactions determined from eqs 3, one may diagonalize all these matrices. The energy of the four doublet states of interest is given by the lowest eigenvalue of each matrix. Finally, when the system is ruled by a double exchange mechanism one may extract values of the effective magnetic couplings J^{eff} and local exchange K^{eff} interactions using the energies of the various states and the expression given in eq 2. Effective interactions incorporate correlation effects, which do not appear in the model space but which are accounted for in the numerical DFT calculations.

III. RESULTS AND DISCUSSION

III.1. Analysis of the DFT Results and Extraction of the Leading Interactions. The Singly Occupied Molecular Orbitals (SOMOs) of an isolated TMM unit are represented in Figure 6. It can be seen that connecting such a unit by two of

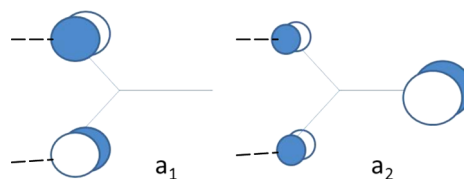


Figure 6. Magnetic orbitals of the TMM magnetic unit. Dotted lines indicate the connection to the bridge.

its carbon atoms will lead to a stronger interaction between the bridge and the unit for orbital a_1 than for orbital a_2 . The opposite result would be obtained in the case of a connection via a single carbon atom. As a consequence one may expect larger values for t_1 than for t_2 in the studied compounds.

Both neutral and cationic molecules have been studied. Let us first concentrate on the results obtained for the neutral molecules. The energies and $\langle S^2 \rangle$ values of the $M_s = 0$ and $M_s = 1$ solutions computed for the optimized geometries of both the triplet and the spin decontaminated singlet are reported in Table 1. From the various solutions, vertical and adiabatic energy differences between the lowest singlet (spin decontaminated) and triplet states of the five molecules have been computed and are also reported in Table 1. The vertical energy difference between the real singlet and the triplet is equal to the effective exchange interaction of the Heisenberg Hamiltonian when the system is magnetic.

The various spin unrestricted DFT solutions needed for the reconstruction of the spectra of the cations have been computed. The geometries of the lowest in energy $M_s = 3/2$ and $M_s = 1/2$ solutions have been optimized and the corresponding values of their energies and of $\langle S^2 \rangle$ are reported in Table 2. The energies of the $M_s = 1/2$ solutions having three open shells at the geometries of the $M_s = 3/2$ solutions are also reported in Table 2. Table 3 collects all the values of the interactions of the Hubbard model for all systems and those of the double exchange one when the spectrum is ruled by a double exchange mechanism, that is, for family 1 of compounds 4 and 5. The spectra reconstructed using the method presented in section II.3 are represented in Figure 7.

The t_1 and t_2 parameters, which have been extracted from the cations energies would be slightly different for the neutral molecules. One may, however, expect that the observed trends for the extracted parameters in this consistent series of molecules would be identical for both the neutral and cationic systems, and their relative values will be used to rationalize the observed trends in both neutral and cationic molecules.

The molecular orbitals have been optimized for the ground state of the cations. These orbitals are very similar for both neutral and cationic molecules. Those optimized for compounds 1 and 4 are represented in Figures 8 and 9. All the trends observed in the series can be correlated with the shape of these four MOs. These orbitals can be seen as resulting from bonding and antibonding combinations of the local orbitals (a_1 , a_2 , b_1 , and b_2) of the TMM units with delocalization tails on the bridging ligand. The SOMO (b_{3u}) shows large components on the extracyclic carbons of both TMM. It can be seen as a

Table 1. Neutral Molecules^{a,b}

		$\langle S^2 \rangle$	E (au or eV)
1	triplet (vert.)	2.03	−693.253712
	triplet	2.03	−693.256048
	BS $M_s = 0$ (“vert.”)	0.92	−693.265296
	BS $M_s = 0$	0.80	−693.266979
	ΔE_{ST} (vertical)		0.616
	ΔE_{ST} (adiabatic)		0.532
2	triplet (vert.)	2.04	−1000.604739
	triplet	2.04	−1000.608011
	BS $M_s = 0$ (“vert.”)	0.88	−1000.617184
	BS $M_s = 0$	0.71	−1000.619331
	ΔE_{ST} (vertical)		0.614
	ΔE_{ST} (adiabatic)		0.520
3	triplet (vert.)	2.05	−1076.854431
	triplet	2.05	−1076.854547
	BS $M_s = 0$ (“vert.”)	1.09	−1076.857159
	BS $M_s = 0$	1.09	−1076.857267
	ΔE_{ST} (vertical)		0.183
	ΔE_{ST} (adiabatic)		0.167
4	triplet (vert.)	2.05	−1229.338761
	triplet	2.04	−1229.339042
	BS $M_s = 0$ (“vert.”)	1.27	−1229.343328
	BS $M_s = 0$ (“vert.”)	1.27	−1229.343328
	ΔE_{ST} (vertical) ^c		0.302
	ΔE_{ST} (adiabatic) ^c		0.264
5	triplet (vert.)	2.07	−1460.451337
	triplet	2.07	−1460.451356
	BS $M_s = 0$ (“vert.”)	1.13	−1460.449958
	BS $M_s = 0$	1.14	−1460.452359
	ΔE_{ST} (vertical)		0.062
	ΔE_{ST} (adiabatic)		0.061

^aUDFT-calculated energies for 1 to 5, with corresponding singlet-triplet energy differences after spin decontamination. vert (resp. “vert”) refers to the geometry of the ground state (resp. excited state).

^bThe spin-decontaminated values are obtained from the UDFT energies and $\langle S^2 \rangle$ values, assuming an harmonic geometry dependency of the energy and a linear geometry dependency of the spin decontamination factor λ . ^cIn this case, the $\langle S^2 \rangle$ values for the $M_s = 0$ solution compel to use a spin-decontamination factor $\lambda = 2$.

bonding combination between the outermost and hence less interacting orbitals of the TMM (a_2 and b_2). The b_{1g} MO, which results from a bonding combination between the most interacting orbitals of the TMM (a_1 and b_1 , which have large components on the cyclic carbons), is delocalized inside the bridge, revealing a stronger covalence between the local orbitals of the magnetic units and the orbitals of the bridge. These observations are true for all compounds. However, comparing the orbitals of compounds 1 and 4, one may easily see that the covalence, evidenced by the importance of the tails inside the bridge, decreases from compound 1 to compound 4.

Looking at the results obtained for the **neutral** molecules several conclusions can be drawn:

- The spin multiplicity of the ground state of the five molecules is a singlet confirming the antiferromagnetic nature of the interactions between the two TMMs. As expected the values of ΔE_{ST} decrease with the length of the bridge.
- The expectation value of S^2 in the lowest $M_s = 0$ solution shows that there is mainly a single open shell per TMM units, revealing that these units cannot be considered as a

Table 2. Cationic Molecules^a

		$\langle S^2 \rangle$	energy (au)
1	quartet (vert.)	3.81	−692.993238
	quartet	3.81	−693.003177
	BS $M_s = 1/2$ (“vert.”)	0.82	−693.027045
	BS $M_s = 1/2$	0.81	−693.036818
2	quartet (vert.)	3.81	−1000.345431
	quartet	3.82	−1000.354809
	BS $M_s = 1/2$ (“vert.”)	0.85	−1000.385054
	BS $M_s = 1/2$	0.83	−1000.394285
3	quartet (vert.)	3.84	−1076.620122
	quartet	3.85	−1076.627585
	BS $M_s = 1/2$ (“vert.”)	0.83	−1076.627146
	BS $M_s = 1/2$	0.83	−1076.634478
4	BS $M_s = 1/2$ (“vert.”) 3 open-shell (ϕ_s)	1.77	−1229.110294
	BS $M_s = 1/2$ (“vert.”)	0.84	−1229.113133
	BS $M_s = 1/2$	0.83	−1229.119439
	quartet (vert.)	3.85	−1229.118140
5	quartet	3.85	−1229.123853
	BS $M_s = 1/2$ (“vert.”) 3 open-shells (ϕ_s)	1.78	−1460.229159
	BS $M_s = 1/2$ (“vert.”)	0.85	−1460.225720
	BS $M_s = 1/2$	0.85	−1460.231719
	quartet (vert.)	3.86	−1460.232461
	quartet	3.87	−1460.238495

^aUDFT-calculated energies of the lowest $M_s = 1/2$ and $M_s = 3/2$ solution for 1 to 5. $\langle S^2 \rangle$ values are also reported. vert (resp. “vert”) refers to the geometry of the ground state (resp. excited state).

Table 3. Values of the Interactions of the Hubbard and Double Exchange Models^a

	t_1	t_2	u_1	u_2 (eV)	K (eV)	K_{DE}	J_1
1	1.677	0.612	1.504	3.332	0.419	1.175	
2	1.831	0.653	1.171	3.546	0.345	1.149	
3	1.186	0.291	1.058	3.664	0.317	0.512	
4	0.802	0.234	1.554	4.066	0.369	0.509	−0.092
5	0.793	0.082	1.031	4.159	0.254	0.272	−0.014

^a t_1 , t_2 , U_1 , U_2 , and K are the interactions of the Hubbard model while $\Delta\epsilon$, t_1 , J_1 , and K^{DE} are the interactions of the double exchange model for family 1.

unit of spin $S = 1$ (for which $\langle S^2 \rangle = 3$) in the neutral compounds. As a consequence, the $M_s = 2$ solution which of course involves four open-shells is very high in energy (17138 $\text{cm}^{-1} = 49 \text{ kcal}\cdot\text{mol}^{-1}$ higher than the $M_s = 0$ solution in compound 1 and 22 $\text{kcal}\cdot\text{mol}^{-1}$ in compound 5). Comparing the values of $\langle S^2 \rangle$, one may notice that even if they always support a diradical character in compounds 4 and 5 the values are slightly larger than 1. The spin polarization due to the contributions of four-open-shells determinants $|b_{1b}\bar{b}_{3u}\bar{b}_{2g}a_u|$ and $|\bar{b}_{1b}b_{3u}b_{2g}\bar{a}_u|$ introduces quintet components in the $M_s = 0$ solution resulting in $\langle S^2 \rangle$ values larger than 1. Actually, since these contributions are larger for systems for which the b_{1g} and a_u orbitals are close in energy, that is, for small values of t_1 , one may easily correlate the increase of the $\langle S^2 \rangle$ values with the decrease of t_1 (Tables 1 and 3).

- Another confirmation of the diradical character of these compounds is brought by the comparison between the t_2 hopping integrals and the energy difference between the singlet and the triplet states in the series. The decrease of

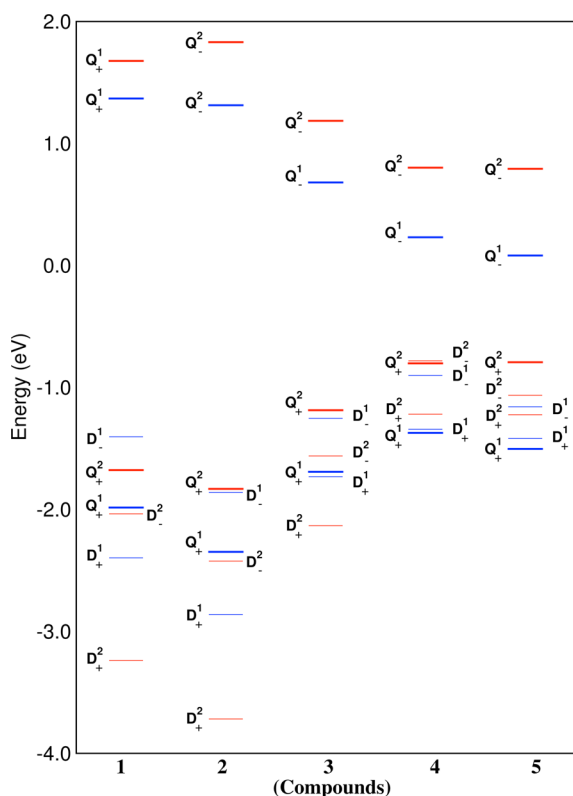


Figure 7. Reconstructed spectra of the cationic compounds 1, 2, 3, 4, and 5 indicated in abscissa. Energy levels of quartet states are represented with thick lines while that of the doublet state are represented with thin lines. Family 1 appears in blue and family 2 in red.

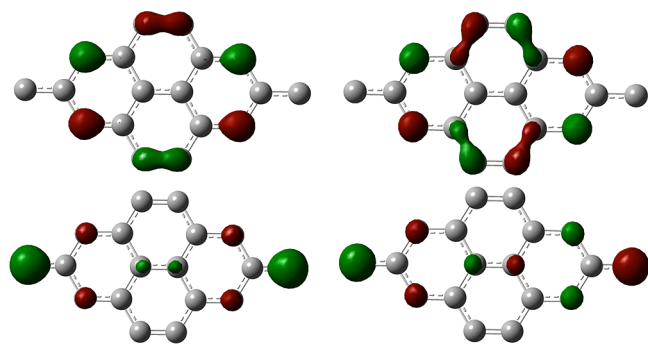


Figure 8. DFT molecular orbitals b_{1g} (top left), a_u (top right), b_{3u} (bottom left) b_{2g} (bottom right) optimized for the doublet ground state ($b_{1g}^2 b_{3u}^1$) of compound 1.

ΔE_{ST} (Table 1) is actually correlated with the decrease of t_2 integrals (Table 3). The single open shells localized on the TMM are mainly the a_2 and b_2 orbitals while the b_{1g} MO obtained from the local a_1 and b_1 orbitals which undergo strong covalent interactions via the bridge is finally doubly occupied. This result is consistent with the strong values of the t_1 integrals in all compounds. One may also notice that while compound 4 has the smallest value of t_1 , its value of t_2 is quite large rationalizing the obtaining of a large ΔE_{ST} .

The comparison of the results obtained for the cations deserves the following comments:

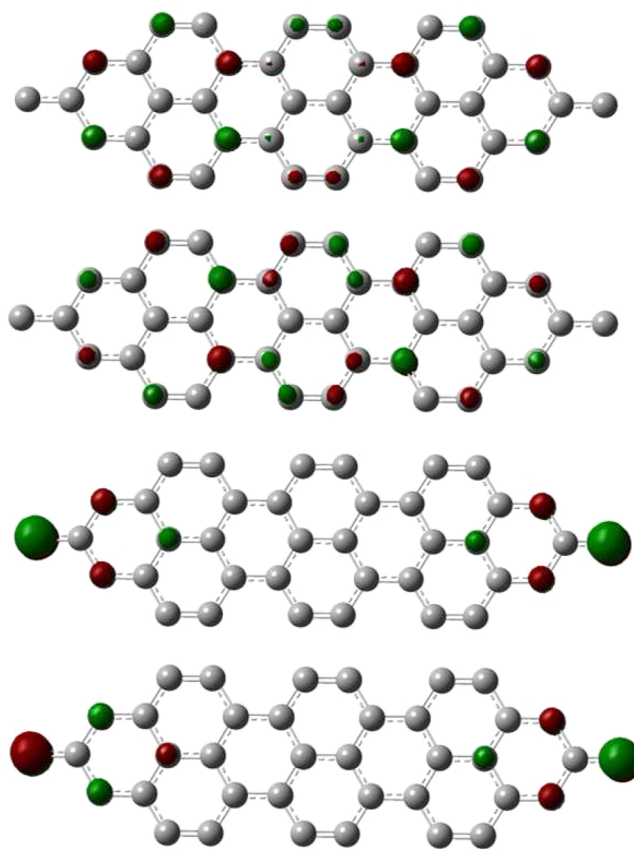


Figure 9. DFT molecular orbitals optimized for the lowest $M_s = 3/2$ solution ($b_{1g}^1 b_{3u}^1 b_{2g}^1$) of compound 5: from top to bottom b_{1g} , a_u , b_{3u} and b_{2g} .

- (i) Looking at the reconstructed spectra (Figure 7), one may see that for compounds 1, 2, and 3 the ground state is the lowest doublet of family 2. For compounds 4 and 5, the ground state is the quartet state of family 1, demonstrating that one may conceive hydrocarbons exhibiting a double exchange phenomenon. This result shows that while the magnetic units must be considered as a spin $S = 1/2$ unit in the neutral molecules, it may behave as a spin $S = 1$ in cationic molecules.
- (ii) The analysis of the occupation numbers of the orbitals of the ground state and of the $\langle S^2 \rangle$ values in compounds 1, 2, and 3 (table 2) reveals that the lowest $M_s = 1/2$ DFT solution essentially has a single open shell, for both the lowest doublet and quartet optimized geometries. This result is in agreement with the occurrence of two open-shells only in the lowest solutions of the corresponding neutral molecules. The spectrum of these cations obeys the logic of the mono-electronic picture, which predicts that the ground state is the lowest doublet state of family 2. A simple building block logic consisting in bridging magnetic unit by any diamagnetic bridge and then ionizing the system does not necessary succeed to generate a double exchange phenomenon.
- (iii) In order to favor the occurrence of a high-spin ground state, the b_{1g} MO (Figure 3) should be destabilized; that is, the value of the hopping integral t_1 must be weak. The here-followed logic consists in extending the π system in order to decrease the energy differences between the orbitals at the Fermi level. Comparing the energies of the

lowest doublet of family 2 and of the lowest quartet of family 1 (Table 2) in the series of compounds, one can notice the correlation between the decrease of t_1 and the relative stability of the quartet state, showing the crucial role of the magnitude of t_1 (Table 3) in the occurrence of a double exchange phenomenon. Looking more precisely at the consistent series 1, 3, and 5 (which have similar bridges that only differ by their length) shows the correlation of the decrease of t_1 with the length of the bridge. Interestingly enough, comparing t_1 in the full series, that is, including compounds 2 and 4, which have slightly different bridges, leads to the conclusion that the t_1 values also depend on the shape of the bridge and may significantly decrease for some specific thickenings, as it occurs in compound 4.

- (iv) The correlation of the decrease of t_1 with the stabilization of the quartet state is meaningful for all compounds. However, from this quantity only, one may not anticipate the relative stability of the lowest quartet and doublet states of family 1. Actually in compounds 1, 2, and 3 this doublet is lower in energy than the quartet state, showing that it may be not sufficient to focus on the value of t_1 in order to reach a double exchange regime. In order to get more insight on the factors governing the relative stability of this doublet state, we have analyzed the physical content of its wave function, that is, of the eigenstate of the 4×4 matrices (see eq 6). In the first place, it is interesting to note that the weight of the non-Hund state in this doublet is large but constant in the series (for instance it is 0.15 in compound 1 and 0.13 in compound 5). The main difference comes from the weight of the pseudoionic and ionic functions, which are respectively 0.13 and 0.06 for compound 1 and 0.05 and 0.01 in compound 5. While the values of U_2 and K are rather similar from one compound to another, the t_2 values which determine the coupling between the neutral Hund's function and the pseudoionic and ionic functions dramatically decrease in the series, rationalizing the strong stabilizing contributions of these excited functions in the doublet state wave functions of compound 1, 2, and 3. As a conclusion, one may say that the relative stability of the quartet and doublet states of family 1 is essentially determined by the value of the hopping integral t_2 between the weakly interacting orbitals.
- (v) The analysis of the wave functions of the doublet states also reveals that the excited doublet states are slightly dominated by the non-Hund function in family 1. For instance, the relative weights of the Hund and non-Hund functions are 0.62 and 0.38 in the second doublet state of family 1 of compound 1. This result will always be true as long as $t_1 > 2K$.
- (vi) Finally, the parameters K^{DE} and J_1 of the double exchange model have been extracted for the family 1 of compounds 4 and 5 (see Table 3). One may notice that the values of K^{DE} differ from the Hubbard K values. One should recall that in eq 2, the Non-Hund functions are treated variationally while the ionic and pseudo ionic functions are treated perturbatively through the J parameter. As a consequence, the exchange parameter of the double exchange model described using eq 2 should be seen as an effective parameter and may be slightly different from the *ab initio* calculated one (expected to be very close to the Hubbard one). Finally

one may note that the intersite exchange integral J_1 decreases between compounds 4 and 5 in agreement with the decrease of t_2 .

As shown in Supporting Information, the extension of the π system of the bridge cannot rationalize by itself the observed trend: the shape of the bridge should be accounted for. Using the topological Hückel method combined with the fragment theory in terms of two TMM and the closed-shell bridge, one may rationalize the magnitude of the hopping integrals in the various studied compounds. It is interesting to note that such a simple method enables one to anticipate and therefore conceive molecular architectures susceptible to exhibit a double exchange phenomenon.

IV. OTHER POSSIBLE ARCHITECTURES AND LOW-DIMENSIONAL PERIODIC LATTICES LIKELY TO PRESENT A DOUBLE EXCHANGE PHENOMENON

One way to decrease the covalent interaction between the bridge and the TMM, would be to connect the TMM through only one of its carbon atoms. In such a case, the orbitals, which would generate the most important interactions, would be the a_1 (b_1) orbital. Saturating one of the orbitals of the bridge should diminish the interactions through the bridge and distinguish one of the carbon atoms of the TMM. Such a molecule is represented in Figure 10 (compound 6). Another



Figure 10. Schematic representation of compounds 6 and 7.

possibility consists in considering a nonsymmetric compound such as compound 7 also represented in Figure 10. In both compounds, the dissymmetry introduced in the molecule changes the nature of the most interacting orbital and one may expect that the proposed compounds would have smaller hopping integrals and therefore exhibits a double exchange mechanism. Due to the lack of symmetry, the two families interact and it is no more possible to make any extractions of the parameters from DFT calculations. Table 4 shows the energies of the $M_s = 3/2$ and $M_s = 1/2$ solutions having only

Table 4. UDFT-Calculated Energies of the Lowest $M_s = 1/2$ and $M_s = 3/2$ Solution for 6 and 7^a

		$\langle S^2 \rangle$	energy (au)
6	BS $M_s = 1/2$ ("vert.")	1.50	−617.914525
	BS $M_s = 1/2$	1.35	−617.917603
	quartet (vert.)	3.84	−617.922641
	quartet	3.84	−617.926125
7	BS $M_s = 1/2$ ("vert.")	1.59	−1000.361133
	BS $M_s = 1/2$	1.50	−1000.362330
	quartet (vert.)	3.85	−1000.366575
	quartet	3.85	−1000.367770

^a $\langle S^2 \rangle$ values are also reported.

one unpaired electron. In both cases, the $M_s = 3/2$ solution is the lowest solution, which is quite encouraging.

From one of the most promising architectures (compound 4), it is possible to conceive monodimensional and bidimensional periodic lattices. Fragments of the two proposed low dimensional lattices are represented in Figures 11 and 12.

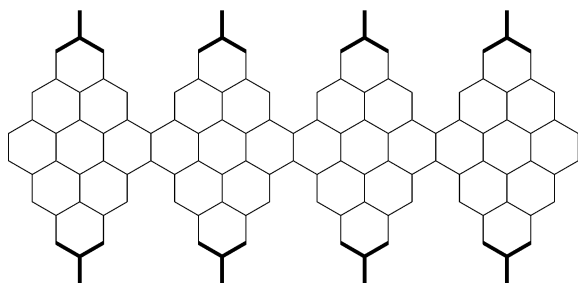


Figure 11. Example of 1D lattice constituted of compound 4 units.

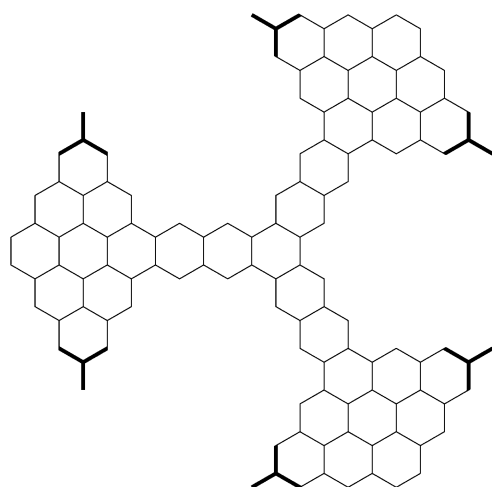


Figure 12. Example of 2D lattice constituted of compound 4 units.

V. CONCLUSION

Magnetism and double exchange phenomenon are more likely to occur in inorganic compounds, for which the hopping integrals between magnetic centers are often weak due to the strong localization of the magnetic orbitals. The spectrum of magnetic inorganic compounds hence usually obeys simple physical models as the Heisenberg or double exchange ones. In contrast, organic systems for which the magnetic orbitals are delocalized over several centers are more sensitive to chemical factors, such as the geometrical features of the bridge and the strength of covalent interactions. As a consequence, their spectrum of low energy may or may not be well reproduced by simple physical models. This paper discusses the possible occurrence of a double exchange phenomenon in a consistent series of organic molecules. Both neutral and cationic molecules have been studied. While for neutral magnetic systems well-known spin decontamination techniques can be used to determine the energy difference between the lowest magnetic states, the determination of the energies of the doublet states of double exchange compounds is more complicate. A method that consists in determining the leading interactions of the Hubbard model from series of UDFT calculations and then uses the numerical values of these interactions in order to

reconstruct the spectra has been proposed and applied here. The mains conclusions of this work are the following:

- (i) While these molecules may be seen as involving TMM units that have a triplet ground state (when isolated), these units cannot be considered as $S = 1$ magnetic units when they are bridged by the here-considered diamagnetic bridges in the resulting neutral compounds. The energy difference between the singlet and triplet lowest states results from an antiferromagnetic coupling between $S = 1/2$ momenta strongly localized on the extracyclic carbon atoms.
- (ii) In contrast, two of the corresponding cations exhibit a quartet ground state showing that the TMM of such molecules may behave as a $S = 1$ unit **under doping**.
- (iii) The comparison of the spectra reveals that the real challenge in order to get a double exchange phenomenon is to control the factors governing the relative stability of the quartet ground state of family 1 and the lowest doublet state of family 2. We have shown that the main factor is the hopping integral t_1 between the most interacting orbitals between the TMMs, the magnitude of which is determined by the strength of the covalence between the TMM and the bridge. The other leading factor is the hopping integral t_2 between the weakly interacting orbitals which is decisive for the relative stability of the lowest quartet and doublet states of a same family.
- (iv) While the magnitude of the t_2 integral essentially depends on the length of the bridge, t_1 is also sensitive to the shape of the bridge, in the studied compounds. Both the relative stability of the magnetic orbitals and the impact of the shape of the bridge on the leading interactions can be easily anticipated using the Hückel method (see Supporting Information). This simple model combined with a deep analysis of the leading interactions of the double exchange model can be a predictive tool in order to anticipate organic systems likely to present a double exchange phenomenon.
- (v) Finally, it is interesting to note that the lowest local excited state of the TMM, that is, the non-Hund state, is particularly low in energy and plays an important role in the physics of these systems. The weight of these local states is important in the wave functions of the lowest doublets states of both families and it is dominant in the wave functions of the second doublets states. As a consequence, the model of Girerd and Papaefthymiou²² cannot be used to describe the physics of the double exchange mechanism in these organic compounds. Due to the delocalized character of magnetic orbitals, one may expect that the role of non-Hund states will generally be more important in organic compounds than in inorganic ones. In order to account for both the non-Hund and the ionic and pseudo ionic functions which all may have a large coefficient in the wave functions of the lowest states, the relevant double exchange model should account for both the Anderson–Hazegawa and Girerd–Papaefthymiou contributions. Moreover, in order to extract all the parameters of the model, it is necessary to use also the expression describing the energy of the non-Hund states (which are discarded in the usual model since they are expected to be highly excited).

Other architectures in which the interactions go through a single carbon atom of the TMM have been proposed in section IV. The comparison between the energies of the lowest $M_s = 3/2$ and $M_s = 1/2$ spin unrestricted DFT solutions indicate that these molecules are likely to exhibit a double exchange phenomenon. Unfortunately, due to the lack of symmetry, the energies of the real doublets could not be determined using the proposed method.

Finally, one- and two-dimensional periodic lattices have been designed from the most promising compounds **4** and **5**. One may expect that under doping such lattices could present both magnetic and conductive properties of potential interest in spintronics. A forthcoming work will be devoted to the study of spin polarized current in such systems.

■ ASSOCIATED CONTENT

Supporting Information

A Hückel based rationalization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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