

## Molecular spintronics using noncollinear magnetic molecules

Alessandro Soncini\* and Liviu F. Chibotaru

*Institute for Nanoscale Physics and Chemistry (INPAC) and Division of Quantum and Physical Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, B-3001 Heverlee, Belgium*

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We investigate the spin transport through strongly anisotropic noncollinear magnetic molecules and find that *noncollinear magnetic quantum states* act as spin-switching devices for the current. Moreover, spin currents are shown to offer a viable route to selectively prepare the molecular device in one of two degenerate noncollinear magnetic states. Spin currents can be also used to create a nonzero density of toroidal magnetization in a recently characterized Dy<sub>3</sub> noncollinear magnet.

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One of the most ambitious directions in the quest for the ultimate miniaturization of electronic devices is represented by molecular spintronics.<sup>1,2</sup> Molecular nanomagnets are particularly promising for nanospintronics, especially in relation to the quest for magnetic molecular qubits,<sup>3</sup> since transport experiments<sup>4-6</sup> have shown a strong interplay between the current and the magnetic states of the molecules. To date, all theoretical investigations on molecular spintronics have addressed systems whose magnetism is only weakly anisotropic, thus exploring systems whose magnetization aligns along a single anisotropy axis (collinear magnetism).<sup>7-10</sup> The noncollinear regime of molecular magnetism, arising when the on-site magnetic anisotropy of single metal ions is one of the dominant energy scales, has only been explored very recently.<sup>11</sup> In the noncollinear regime magnetic molecules can be prepared in degenerate states characterized by nondipolar magnetic moments, such as the recently predicted<sup>11</sup> and found<sup>12,13</sup> toroidal (or anapole) moment in molecular wheels.

There are two main arguments that make spintronics of noncollinear magnets of great interest. The first follows from studies on spin transport through mesoscopic rings with noncollinear internal magnetic fields, which have been predicted to produce spin-switching effects.<sup>14</sup> The size of noncollinear molecular scatterers is expected to be more favorable to overcome dephasing, and lead to the observation of coherence and spin-switching effects. The second argument is related to the use of noncollinear states to implement molecular qubits. On the one hand, molecular spin qubits can easily be addressed via a magnetic field,<sup>15</sup> although intermolecular dipolar interactions lead to short dephasing times.<sup>16</sup> On the other hand, intermolecular interactions between nondipolar states are weak,<sup>11</sup> thus decoherence times longer, although these states cannot be addressed via uniform fields. Spintronics might offer a promising strategy to address noncollinear protected molecular qubits.

In this Letter we investigate spin transport through molecular noncollinear magnetic states, and provide evidence that these systems do offer strategies to (i) implement quantum-interference molecular devices capable of reversing the polarization of an injected spin current and to (ii) selectively populate specific noncollinear magnetic states. The most relevant transport regime has been shown to be the Coulomb blockade (CB).<sup>6</sup> The lowest lying states of a nanomagnet with  $n$  unpaired electrons well localized on  $N$  metal centers with local spin  $s$  is well described by the Hamiltonian

$$H_n = -J \sum_{\langle ij \rangle} \tilde{s}_i \cdot \tilde{s}_j + D \sum_i \tilde{s}_{z,i}^2, \quad (1)$$

consisting of the isotropic Heisenberg exchange coupling between nearest neighbors with strength  $J$ , and easy-axis zero-field splitting (ZFS) on-site (strength  $D$  with  $D < 0$ ). Note that the spin operator  $\tilde{s}_i$  has  $z$  component  $\tilde{s}_{i,z}$  parallel to the local ZFS axis. Whereas previous investigations<sup>10</sup> only considered the collinear weak-anisotropy regime, here we introduce two key ingredients for *noncollinearity*:<sup>11</sup> (i)  $|D| \gg |J|$  (ii) on-site easy axes *not parallel* to each other. In this work we will explore spin transport for a dimer (Fig. 1, top) and a three-centers molecular wheel (Fig. 1, bottom).

When connected to source, drain and gate electrodes, under bias voltage  $V_B$  and gate voltage  $V_G$ , the molecule will become charged. The migrating electron will be consecutively accommodated at different metal sites,<sup>17</sup> described here by a set of  $N$  atomic orbitals localized on the metal centers. The molecular Hamiltonian for a charged state with an excess of  $Q$  electrons with respect to the isolated nanomagnet is given by

$$H_{n+Q} = H_n + (\epsilon - eQV_G) \sum_p \sum_{\sigma}^{\uparrow\downarrow} n_{p\sigma} + t \sum_{\langle pq \rangle} \sum_{\sigma}^{\uparrow\downarrow} c_{p\sigma}^{\dagger} c_{q\sigma} + U \sum_p n_{p\uparrow} n_{p\downarrow} + J_H \sum_p \sum_{\alpha}^{\uparrow\downarrow} \sum_{\beta}^{\uparrow\downarrow} \tilde{s}_p \cdot \sigma_{p,\alpha\beta} c_{p\alpha}^{\dagger} c_{p\beta}, \quad (2)$$

where  $\epsilon$  is the energy of the localized orbitals,  $c_{p\sigma}^{\dagger}$  are creation operators for the on-site spin orbitals,  $n_{p\sigma} = c_{p\sigma}^{\dagger} c_{p\sigma}$ ,  $t$  is a hopping parameter between centers,  $U$  is the Coulomb repulsion between two electrons on the same center,  $\sigma_p$  are Pauli matrices associated to an electronic spin injected on-site  $p$ , and  $J_H$  is the Hund's rule coupling between the spin of the excess electron on-site  $p$ , and the spin moment  $\tilde{s}_p$  on that center ( $J_H < 0$ ). Here we confine ourselves with the region around the first CB diamond, where only singly-charged states are relevant together with the neutral ones. This is formally achieved by setting  $U \rightarrow \infty$ . Finally, a tunneling Hamiltonian  $H_{\text{mix}}$  between electrodes and device is introduced in the usual manner,<sup>7-10</sup> with tunneling amplitudes estimated to be at most  $0.3 \text{ cm}^{-1}$ .<sup>6,9</sup> Given the weak molecule-lead coupling, the transition rates  $W$  between molecule and contacts are calculated with the Fermi golden rule using  $H_{\text{mix}}$ , assuming a Fermi-Dirac distribution in the two leads,

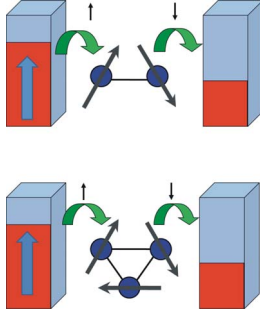


FIG. 1. (Color online) The two molecular spintronics setups considered in this work. Top, a noncollinear antiferromagnetic dimer with on-site spin  $s=3/2$  and coplanar on-site ZFS easy axes, tilted with respect to the normal to the intermetal distance by  $\pm 30^\circ$ . Bottom, a three-center antiferromagnetic wheel with on-site  $s=3/2$  and coplanar on-site ZFS easy axes, arranged tangentially to the wheel's circumference (cf. Refs. 11 and 12).

kept at different chemical potential  $\mu_L - \mu_R = eV_B$ . Next, using the rates  $W$ , a master equation for the nonequilibrium populations of charged and neutral states of the device is set up and solved in the steady-state regime. This choice is consistent with the available experimental data<sup>4-6</sup> and previous theoretical work.<sup>7-10</sup> The resulting populations are used to compute the input ( $I_L^\uparrow - I_L^\downarrow$ ) and the output ( $I_R^\uparrow - I_R^\downarrow$ ) spin currents.

Consider first the dimer molecule with local spin  $s=3/2$  (e.g., a Co(II) dimer). We assume co-planar local ZFS axes, forming angles  $\theta = \pm 30^\circ$  with the perpendicular ( $z$  direction) to the Co-Co bond, (Fig. 1, top). We choose here  $D=4J$ , with antiferromagnetic isotropic exchange coupling  $J=-50 \text{ cm}^{-1}$ . The dominant energy scale in Eq. (2) is the on-site Hund-coupling exchange  $J_H$ , chosen here as  $J_H=4D=800 \text{ cm}^{-1}$ . Moreover, the source contact is assumed to be ferromagnetic, the drain nonmagnetic. The spin-polarization axis for the ferromagnetic source is coplanar to the ZFS axes and parallel to  $z$  (Fig. 1). The Heisenberg states of lower energy of the Co dimer can be described in terms of almost pure noncollinear Ising states  $|m_1 m_2\rangle$ , where  $m_i$  is the projection of the local spin moment  $s$  along the tilted easy axis.<sup>11</sup> For the present choice of parameters, denoting “+” and “-” the on-site spin-states  $|\pm 3/2\rangle$ , the ground state is quasidegenerate and corresponds to the in- and out-of-phase superposition of the noncollinear Neel states  $|+-\rangle$ , and  $| -+\rangle$ . The tunneling gap is  $\Delta \approx 0.57 \text{ cm}^{-1}$ .

Next, we find the eigenstates of Eq. (2). We explore here two limiting situations: a weak-transfer limit with  $t=0.5D$ , and a strong-transfer limit with  $t=4D=J_H$ . In the weak-transfer limit, we expect the additional electron spin to follow “adiabatically” the noncollinear magnetic texture of the molecular device, so that the ground state of the charged system will be doubly degenerate and dominated by either the  $|+-\rangle$  or the  $| -+\rangle$  component of the Neel doublet, carrying an additional electron on either center, with the spin parallel to the local magnetic moment via Hund-rule coupling. These expectations are confirmed by full diagonalization, leading to the following ground state for the  $n+1$  magnet (unless otherwise stated, we report components whose weight is larger than 10%)

$$\Psi_{0,1}^{n+1} \approx C_{\uparrow,0}|+-\rangle|\uparrow 0\rangle + C_{0,\downarrow}|+-\rangle|0\downarrow\rangle,$$

$$\Psi_{0,2}^{n+1} \approx C_{\downarrow,0}| -+\rangle|\downarrow 0\rangle + C_{0,\uparrow}| -+\rangle|0\uparrow\rangle, \quad (3)$$

where the kets  $|\uparrow 0\rangle$  denote the determinant of two spin-orbitals centered on the two metals, the first with spin  $\uparrow$ , the second empty. We find  $|C_{\uparrow,0}|^2 = |C_{\downarrow,0}|^2 \approx 0.45$  and  $|C_{0,\downarrow}|^2 = |C_{0,\uparrow}|^2 \approx 0.42$ . On the other hand, in the strong-transfer limit, intercenter hopping processes have the same rate as Hund-coupling spin-polarization processes, so that transport is not expected to be adiabatic. This is confirmed by full diagonalization, where the ground state is dominated by noncollinear Ising states favoring spin-preserving hopping processes such as  $|++\rangle|\uparrow 0\rangle$  and  $|++\rangle|0\uparrow\rangle$ . Thus, in this regime the overlap with the neutral noncollinear Neel states is very small. The voltage  $V_G$  is taken large enough to bring in resonance the ground states of the neutral and charged systems, separated by about  $8000 \text{ cm}^{-1}$ . Without loss of generality, we set the equilibrium chemical potential lying in between the ground- and first-excited state of the neutral molecule and the temperature to  $T=0.1 \text{ K}$ .

In Fig. 2(a) (weak transfer) and Fig. 2(c) (strong transfer), we report the spin current-voltage diagrams obtained for the two limits of the hopping parameter. Since the source is fully spin polarized, the input spin current (bullets) always corresponds to the total charge current. Interestingly, in the weak-transfer limit the output spin current (squares) has a negative sign: *the spin polarization of the input current is reversed in the output nonmagnetic electrode*. On the other hand, in the strong-transfer regime this *spin-switching* effect is strongly quenched. These results are easily interpreted analyzing the ground state wave functions for the neutral and charged states. In the weak-transfer limit, the charged ground state (3) is a coherent state describing the adiabatic hopping of an injected electron spin between the two metals, in which process the additional electron always aligns its spin parallel to the magnetic polarization of the local metal ion. Thus we define this limit as the *adiabatic-transport limit*, in analogy with the findings reported in Ref. 14. Although the CB regime is noncoherent, the transition rates entering the master equation are determined by the overlap amplitudes between the tunneling combinations of the ground noncollinear Neel doublet, and the charged ground-state doublet (3). Due to the full  $\uparrow$ -spin polarization of the source, the injected electron on the first metal center creates an excess of nonequilibrium population in the state  $\Psi_{0,1}^{n+1}$  (see Figs. 2(b) and 2(d), diamonds), which can host an electron with spin up on the first metal. The electron is then coherently transported through  $\Psi_{0,1}^{n+1}$  on the second metal center, where, as described by the  $|0\downarrow\rangle$  component of  $\Psi_{0,1}^{n+1}$ , its spin polarization is reversed. Output tunneling events from the second metal center into the drain will thus occur more frequently with opposite spin polarization.

We note that the coupling between  $|+-\rangle|\uparrow 0\rangle$  and  $| -+\rangle|0\downarrow\rangle$  in Eq. (3), which determines the spin-switching transport, is triggered by the Hund-Hamiltonian, via the intermediate state  $|+-\rangle|\downarrow 0\rangle$  (about 4.5% of  $\Psi_{0,1}^{n+1}$ ). Importantly, if the angle  $\theta$  is set to zero, i.e., within the collinear regime, the Hund mechanisms leading to the superposition (3) are not

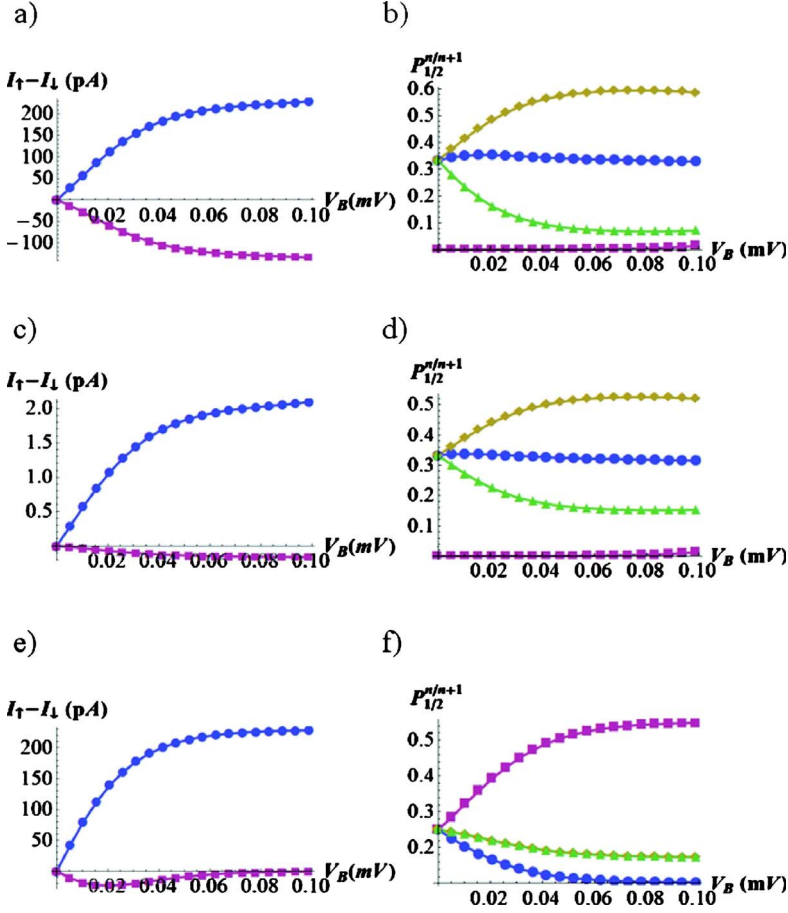


FIG. 2. (Color online) Input (bullets) and output (squares) spin current vs voltage curves (left column) and (right column) nonequilibrium populations of neutral (bullets for in-phase and  $|+-\rangle$  and  $| -+\rangle$ ) and charged states (diamonds for  $\Psi_{0,1}^{n+1}$ , triangles for  $\Psi_{0,2}^{n+1}$ ) for the noncollinear magnetic dimer, with the following type of exchange interaction and values of  $t(D=-200 \text{ cm}^{-1})$ : (a) and (b) Heisenberg,  $t=0.5D$ , (c) and (d) Heisenberg,  $t=4.0D$ , (e) and (f) noncollinear Ising,  $t=1.0D$ .

active. Note in fact that for  $\theta=0$  the total spin projection  $S_z$  is a constant of motion, so that  $|+-\rangle|\uparrow 0\rangle$  and  $|+-\rangle|\downarrow 0\rangle$  are not allowed to mix. The spin-conserving hopping Hamiltonian, in turn, cannot mix in the spin-reversal component  $|+-\rangle|0\downarrow\rangle$ . On the other hand, if  $\theta \neq 0$ ,  $S_z$  is not conserved,  $|+-\rangle|\uparrow 0\rangle$  and  $|+-\rangle|\downarrow 0\rangle$  are allowed to mix and the spin-conserving hopping Hamiltonian can in turn mix  $|+-\rangle|\downarrow 0\rangle$  with  $|+-\rangle|0\downarrow\rangle$ , thus leading to the spin-switching transport process. Hence, *noncollinearity is found to be a crucial ingredient for the realization of the spin-switching effect*. In the nonadiabatic regime, the spin-switch effect is quenched [Fig. 2(c)] due to the negligible presence of spin-switch coherences in the charged ground state. The current magnitude is much smaller due to the small overlap between charged and neutral states [see Fig. 2(c)].

It is interesting to investigate the case of exact degeneracy between  $|+-\rangle$  and  $| -+\rangle$ , implied by the noncollinear Ising exchange Hamiltonian:

$$H_n = -J_I \sum_{\langle ij \rangle} \tilde{s}_{i,z} \tilde{s}_{j,z} + D \sum_i \tilde{s}_{z,i}^2. \quad (4)$$

The ground state of the charged system is still doubly degenerate and given by Eq. (3), with  $|C_{\uparrow,0}|^2 = |C_{0,\downarrow}|^2 = |C_{\downarrow,0}|^2 = |C_{0,\uparrow}|^2 = 0.41$ . The full  $\uparrow$ -spin polarization of the source electrode will favor population-transfer processes mainly between the  $|+-\rangle$  Neel state and the *spin-switch* excited state  $\Psi_{0,1}^{n+1}$ , via the Hund-coupling mechanism. However, now only half of the input  $\uparrow$  current is converted to  $\downarrow$  current, so

that the current is nonpolarized in the drain [see Fig. 2(e)]. However, the dominant population-transfer process remains  $|+-\rangle \rightarrow \Psi_{0,1}^{n+1}$ , and, as seen from Fig. 2(f), this fact has a fundamental consequence: *at nonzero bias voltage the spin current causes a net excess of population of one of the two degenerate noncollinear Neel states*. Thus, the neutral system is prepared in the  $| -+\rangle$  state.

Finally, we consider a three-center molecular wheel with local ZFS axes contained in the molecular plane and tangential to the wheel's circumference. This system is of special interest, being a model for the experimentally characterized lanthanide wheel  $\text{Dy}_3$ ,<sup>18</sup> which has been recently shown to have almost tangential on-site anisotropy axes, leading to toroidal magnetization.<sup>12</sup> For simplicity, here we consider an analog of this system with  $s=3/2$  on metal sites. The collective states are modeled by the noncollinear Ising Hamiltonian (1), with ferromagnetic exchange  $J_I=25 \text{ cm}^{-1}$ , and easy-axis ZFS parameter  $D=8J_I$ . The ground state of the three-wheel is a doubly-degenerate Kramer's doublet characterized by a toroidal magnetic moment  $\tau = \mu_B R \sum_p \tilde{s}_{z,p}$ ,<sup>11,12</sup> where  $R$  is the radius of the triangle and  $\mu_B$  is the Bohr magneton. We denote the two states with  $|+++ \rangle$  ( $\tau = +9/2R\mu_B$ ) and  $| --- \rangle$  ( $\tau = -9/2R\mu_B$ ), where the first position refers to the atom more strongly bound to the ferromagnetic source, and the second position refers to the atom bound to the nonmagnetic drain. The singly-charged system is investigated for  $J_H=4D$ , and for  $t=0.05D$  (adiabatic transfer) and  $t=D$  (strong transfer). The ground state of the singly-charged system is always fourfold degenerate. The

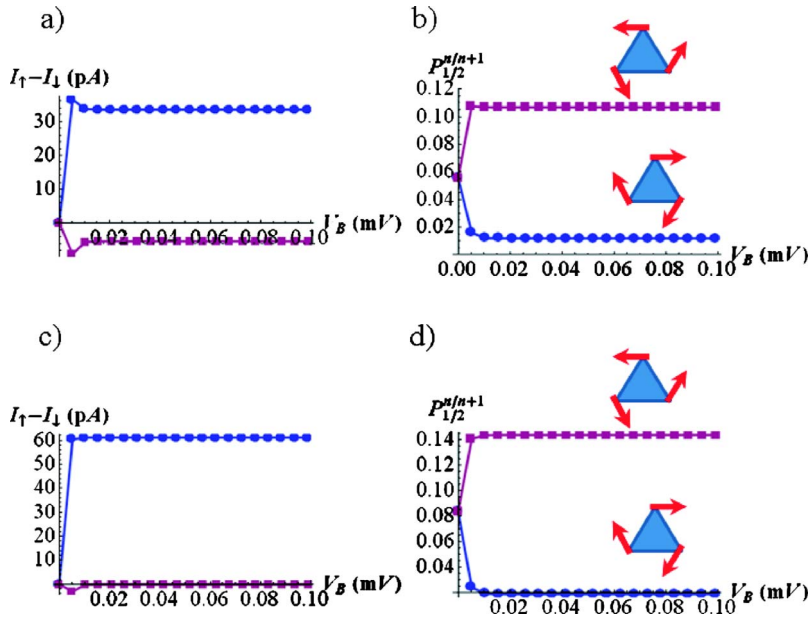


FIG. 3. (Color online) Input (bullets) and output (squares) spin current vs voltage curves (left) and (right) nonequilibrium populations of the neutral doublet ground state (bullets for  $|---\rangle$  and squares for  $|+++ \rangle$ ) for the three-center non-collinear magnetic wheel, with the following values of  $t$ : (a) and (b)  $t=0.05D$ , (c) and (d)  $t=1.0D$  ( $D=-200$  cm $^{-1}$ ).

present spintronics setup (bottom of Fig. 1, spin-polarization axis of the source coplanar with the wheel's plane, and perpendicular to the bond between metal 1 and metal 2) implies that only those components of the charged ground state overlapping with the  $|---\rangle$  toroidal state reported in Fig. 1 will be significantly populated, by virtue of the Hund's coupling rule. In the adiabatic limit these states correspond to spin-switching states, i.e., to states which represent coherent hopping from center 1 to center 2, with inversion of spin polarization, and found to be

$$\Psi_{0,1}^{n+1} \approx |---\rangle (a_1 |\uparrow 00\rangle + b_1 |0\downarrow 0\rangle)$$

$$\Psi_{0,2}^{n+1} \approx |---\rangle \times (a_2 |\uparrow 00\rangle + b_2 |0\downarrow 0\rangle + c_2 |00\uparrow\rangle + c_2 |00\downarrow\rangle)$$

with  $|a_1|^2=0.4$ ,  $|b_1|^2=0.38$ ,  $|a_2|^2=0.21$ ,  $|b_2|^2=0.27$ , and  $|c_2|^2=0.19$ . In the nonadiabatic limit the weight of the spin-switching components becomes smaller (although does not vanish), in favor of states representing spin-conserving hopping processes.

In Fig. 3(a) (adiabatic) and Fig. 3(c) (nonadiabatic) we report the spin current-voltage diagrams obtained for the two

limits of the hopping parameter: as for the dimer system, we observe spin switching only in the adiabatic limit. However, due to the spin polarization of the source electrode, the population transfer from the  $|---\rangle$  toroidal neutral state to the charged manifold always dominates the noncoherent kinetics, producing an excess of population of  $|+++ \rangle$ , in both weak and strong transfer limits [Figs. 3(b) and 3(d)]. This demonstrates a viable spintronics strategy to prepare a non-zero density of toroidal molecular magnetization in the sample.

In conclusion, we have investigated spin transport through noncollinear magnetic molecules in the sequential tunneling regime. Two fundamental phenomena are identified here. The first, the *spin-switching effect*, is caused by the action of the noncollinear quantum states on the spin current. The second, the *selective population bias* of one of the two partners of a noncollinear doublet, is determined by the effect of a spin current on the noncollinear states. Noncollinearity is found to be a crucial ingredient in these phenomena. This work represents a first step into the domain of noncollinear molecular spintronics, expected to have a significant impact on the quest for protected molecular qubits.

\*alessandro.soncini@chem.kuleuven.be

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