

Adam Sokołowski · Wojciech Grochala

Towards a tunable molecular memory that fits into a $(10 \text{ \AA})^3$ cube

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Abstract Using DFT calculations we predict a novel family of small amino acid-based memory-exhibiting molecules, namely complexes of triply deprotonated cysteine (or its derivatives) with selected hexavalent transition metals. We show that the energy difference of the 0 and 1 electromers—corresponding to two chemically distinct oxidation states of a metal, M(VI) and M(IV)—can be tuned towards the thermodynamic equilibrium via deliberate chemical substitutions in the cysteine ligand. Although the thermal stability of both electromers is computed to be rather small at ambient temperatures (due to facile interchange of states 0 and 1 via a low-lying M(V) configuration), we hope to improve stability in related systems.

Keywords Molecular memory · Molybdenum complexes · Disulphide bond · Density functional theory · Electronic bistability · Electromers

Introduction

Fast development of data-storage techniques increases demand for a new data-storage medium, which would make possible an unprecedentedly high data-storage density (DSD). DSD today reaches 23 GB on each side of a 4.72in diameter disc (BlueRay technology [1]); this translates to around 50 MB/cm^2 . Along with the persistent improvement of existing read/write devices, development of the novel data storage media is

progressing. Such media should be thermally stable (to eliminate data loss at ambient temperatures), rewritable, and of course built of cheap chemical constituents.

Many diverse approaches have been elaborated towards tunable molecular memory which might be read and written by visible light or electric nanocurrents. The list of potential candidates for high-tech memory carriers of the future now encompasses nanotubes [2], fullerenes [3], metalloporphyrins [4, 5], diaryl- and bisporphyrinylethenes [6–8], fulgides [9, 10], spiropyrans and spirooxazines [11], derivatives of bacteriorhodopsin [12], dihydropyrenes [13, 14], derivatives of oligo-(phenyleneethylene) [15], molecular glasses based on phthalein dyes [16], cyanoferrate ions, iron-bis(cyclopentadienyl) and salene complexes [17–19], larger functional supramolecular assemblies [20, 21], thin films of various molecules and polymers [22, 23] and entire crystals built from spin-crossover compounds [24–26]. Read-only and 3D memory also undergoing vigorous development [10, 27]. The properties of known families of materials for molecular electronics (in particular: for single-molecule-based memory), have recently been reviewed [28, 29].

In this paper we describe an entirely novel hypothetical family of molecules that might serve as molecular memory of theoretical DSD close to 1 TB/cm^2 . The memory is based on an intramolecular $2e^-$ redox process.

Methods

The geometry of complexes of cysteine and its derivatives¹ with transition-metal cations was optimized while

This paper is dedicated to our dear teacher and friend, Professor Lucjan Piela.

A. Sokołowski · W. Grochala (✉)
Department of Chemistry,
University of Warsaw, Pasteur 1,
02093 Warsaw, Poland
E-mail: wg22@cornell.edu
Tel.: +48-22-8220211
Fax: +48-22-8222309

¹ Our electromers have been discovered casually by one of us (W.G.) during theoretical studies on reversible absorption and desorption of dihydrogen by certain molecular species. In a sense, molecular switching reported here is analogue of the process of H_2 liberation from the Kubas complex [30]. The latter reaction, however, proceeds with entire separation of products, in contrast to our system.

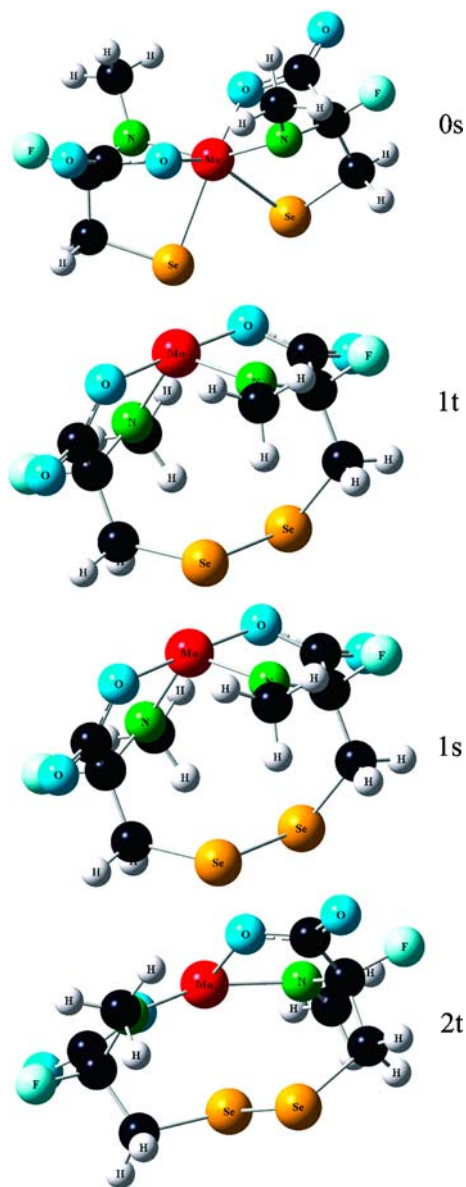


Fig. 1 Complex of Mo with the derivative of triply deprotonated selenocysteine ($^- \text{Se}-\text{CH}_2-\text{CF}(\text{NMe})-\text{COO}^-$) is shown in this figure. Optimized molecular geometries of states **0s**, **1t**, **1s** and **2t**. The coordination of Mo(VI) by Se, N and O in state **0s** is a distorted octahedron, of Mo(IV) in states **1t** and **1s**—a butterfly, while of Mo(V) in state **2t**—a distorted tetragonal pyramid. The Se–Se contact is 3.04 Å in **0s**, 2.38 Å in **1t**, 2.37 Å in **1s**, and 2.43 Å in **2t**

freezing them within C_2 symmetry, with the exception of state **2t** (see next section). Frequency calculations have shown that the optimized states **0s**, **1s** and **1t** (see next section) are true minima on the potential energy surface; state **2t**, however, shows no genuine symmetry elements.

Calculations were performed using Becke's three-parameter hybrid functional combined with the Lee–Yang–Parr correlation functional (B3LYP). We used the LANL relativistic pseudopotential followed by a double zeta valence basis set for heavier elements (W, Mo, Te; for U we used SDDAll pseudopotential), and Pople's 6–

Table 1 Total electronic energy difference for the states **0s** and **1t** for complexes of $M = \text{Mo}$, W, U and Te with triply deprotonated CyS, CySe and CyTe. Positive value of ΔE^{01} corresponds to the preference of state **0s**

ΔE^{01}	W	Mo	U	Te
CyS	+1.55	+0.60	+0.11	–2.15
CySe	+1.23	+0.38	–0.33	Not computed
CyTe	+1.20	+0.05	–0.68	Not computed

311 + $+G^{**}$ basis set for the light atoms (C, H, N, O, F, Cl, S) and 6–311 G^{**} for Se. Our calculations were done with the Gaussian 03 package [31].

Results and discussion

To obtain memory effects [32] we need to design a molecule that preferably has two stable electronic states (electromers) with negligible difference of free energies,² analogous to 0 and 1 in binary code. Electromers should be distinguished by molecular geometry and/or electronic structure,³ and show significant differences in their electronic and vibrational spectra (so that each state could be specifically read and written). To avoid spontaneous (thermal) mutual transformation of the 0 to 1 states the energy minima corresponding to both electromers should be also separated by a sufficiently large barrier.

Our research was initially focused on metals that occur in at least two stable oxidation states differing by two electrons (0/2, 1/3, 2/4, 3/5, 4/6, 5/7, 6/8). We have chosen heavy transition and post-transition metals able to form hexa- and tetravalent complexes, namely W, Mo, Te and U. As a ligand we used triply deprotonated cysteine, CyS—an amino acid with a terminal–SH group. Alternatively, we used the Se–analogue of cysteine (selenocysteine or 2-selenoalanine, CySe).⁴ The sulphide (or selenide) group may be involved in a $2e^-$ oxidation reaction leading to disulphide (diselenide)

² If memory is meant to operate at ambient temperatures ($kT = 2.57 \times 10^{-2}$ eV/molecule at $T = 298$ K), and the lifetime of each electromer is to be longer than 10^{11} s ($> 3,170$ years), the activation barrier for the 0/1 interconversion needs to be at least 0.65 eV, as determined from the Arrhenius equation. Simultaneously—if the entropies of both electromers are similar—the zero-point corrected difference of internal energies of two electromers should not be larger than kT (ca 0.03 eV) to avoid strong thermodynamic preference for one isomer only.

³ “Mnemon” is an interesting kind of memory, first postulated over 20 years ago, where two distinct electronic states differ rather little in nuclear coordinates [33, 34]. Analogous phenomenon has been observed for narrow family of solids, as well [35].

⁴ Both cysteine and selenocysteine occur frequently in Nature; for instance, methyl derivative of selenocysteine is found in garlic, onion and broccoli. Selenocysteine—called also as “the 21st amino acid”—is also present in various enzymes where it plays important role in many biological processes. Some believe it is an anticancer agent.

Table 2 Total electronic energy difference for the states **0s** and **1t** for various derivatives of the complex of Mo^{VI} with triply deprotonated **CySe**

Mo/CySe	$\text{C}_\beta(\text{Me}_2)$	NF	Unsub.	$\text{C}_\beta(\text{F}_2)$	$\text{C}_\alpha(\text{F})$	$\text{C}_\alpha(\text{Cl})$	NMe	NMe $\text{C}_\alpha(\text{F})$	NMe $\text{C}_\alpha(\text{Cl})$
ΔE^{01}	+55	+0.49	+0.38	+0.30	+0.25	+0.22	+0.16	+0.05	-0.14

Positive value of ΔE^{01} corresponds to the preference of **0s** state. NF and NMe correspond to substitutions of amine H for F and methyl, respectively. $\text{C}_\alpha(\text{F})$ and $\text{C}_\alpha(\text{Cl})$ refer to substitution of H at C_α for respective halogens. $\text{C}_\beta(\text{Me}_2)$ and $\text{C}_\beta(\text{F}_2)$ denote substitutions of

two H's at C_β for methyl groups and F, respectively. Isomers of a molecule with the simultaneous NMe and $\text{C}_\alpha(\text{F})$ substitutions have been shown in the Fig. 1.

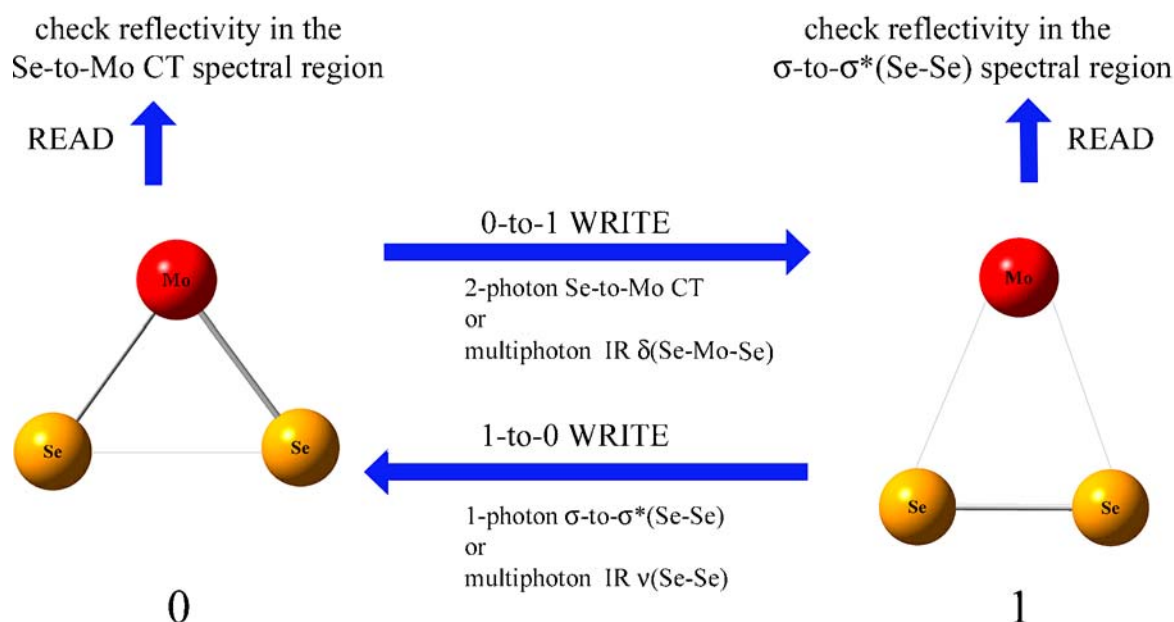


Fig. 2 Scheme of writing and reading processes for states **0s** and **1t**. State **1s** could be used as mediator of writing, due to feasibility of the spin-allowed $0s \rightarrow 1s$ transformation. *CT* stands for “charge-transfer”, δ for bending mode, ν for stretching vibrational mode

bond formation (S–S, Se–Se⁵). In the case of cysteine, this reaction yields cystine.

While screening various geometries of complexes of triply deprotonated **CyS** and **CySe** with the (formally hexavalent) metals $M = \text{Mo}, \text{W}, \text{U}, \text{Te}$, we detected four important isomers. They are shown in Fig. 1.

One true minimum on the potential energy surface corresponds to the approximate description $\text{Mo}^{VI}(\text{Se-CH}_2\text{-CF}(\text{NMe})\text{-COO}^-)_2$. There are two equivalent Mo–Se bonds of 2.57 Å, Mo–N bonds of 2.02 Å, Mo–O bonds of 2.00 Å; the Se–Se separation is large (3.04 Å), the electronic configuration of a metal is d^0 and the ground state of the molecule is a singlet. This electromer is one of two lowest energy states that we wish to use as analogues of 0 and 1 in binary code. Therefore we will call this state **0s**.

Another distinct minimum corresponds to the approximate description $\text{Mo}^{IV}(\text{OOC-CF}(\text{NMe})\text{-}$

$\text{CH}_2\text{-Se-Se-CH}_2\text{-CF}(\text{NMe})\text{-COO}^-)$. It shows a very long Mo–Se separation (4.28 Å), which is beyond the sum of van-der-Waals radii of Mo and Se (ca 3.73 Å). This isomer is characterized by the presence of an Se–Se bond at 2.38 Å. The electronic configuration of the metal is d^2 , and this electromer has a high-spin (triplet) ground state in the weak ligand field of N- and O-ligands. We will call this state **1t**, as this is the second low-energy electromer, which we wish to use for the tunable 0/1 switching. State **1t** also has its low-spin (singlet) analogue denoted **1s**, lying some +0.65 eV above **1t**. **1s** has a geometry similar to that of **1t** (for example, the Se–Se bond length is of 2.37 Å for **1s**) except for the slightly longer Mo–N and shorter Mo–O distances in the former (Mo–N: 1.93 Å instead of 1.96 Å; Mo–O: 1.97 Å instead of 2.05 Å).⁶ The last important minimum will be called **2t**; it can be described approximately as $d^1 \text{Mo}^V(\text{OOC-CF}(\text{NMe})\text{-CH}_2\text{-Se-Se-CH}_2\text{-CF}(\text{NMe})\text{-COO}^-)$. This electromer has low symmetry: there are two distinct Mo–Se distances (2.62 and 3.65 Å), while the pairs of the Mo–N and Mo–O bonds are not equivalent (Mo–N: 2.00 vs 2.03 Å; Mo–O: 2.05 vs

⁵ The disulphide bridge has the utmost importance for the structure and folding of proteins.

⁶ Due to pronounced similarities in the molecular structure between **1s** and **1t**, **1s** can be used as mediator in the **0s/1t** switching via facile intersystem crossing between **1s** and **1t**.

2.08 Å). The Se–Se bond (2.43 Å) is now longer than for **1t**, due to additional electron density in the σ^* orbital of the Se–Se unit. State **2t** is higher in energy than **0s** and **1t** for the vast majority of complexes studied, and will not be involved in the 0/1 switching.

The metal oxidation states may be assigned as Mo^{VI} for **0s**, Mo^{IV} for **1t**, and Mo^V for **2t**. This rather formal description finds support in the calculated Se–Se bond lengths, and from an analysis of the electron counts and the frontier orbitals of the electromers in question (see Appendix).

In conclusion, we have proposed a novel family of electromeric molecules,⁷ their tautomerism being associated with the simplistic intramolecular $2e^-$ redox process, $\text{M}^{n+}(\text{L}^-)_2 \leftrightarrow \text{M}^{(n-2)+}(\text{L}-\text{L})$.⁸

Tuning the energy difference of states **0s** and **1t** via chemical substitutions

Importantly for the proposed use of our molecules as read/write devices, the chemically distinct **0s** and **1t** states need to be equivalent in terms of free energy.^{9,10} It turns out that the total electronic energy difference, ΔE^{01} , may be reduced to nearly zero via deliberate chemical substitutions at the metal site ($\text{Mo} \rightarrow \text{W}$, U , Te), sulphide site ($\text{S} \rightarrow \text{Se}$, Te) and in the aliphatic backbone of the **CyS** ligand, both at C_α , C_β and at the amide N (see Tables 1 and 2).

The value of ΔE^{01} for states **0s** and **1t** can be tuned in broad limits (+1.55 to –2.15 eV) via substitutions at the metal and sulphide positions (Table 1).¹¹

Obviously, these sites are of crucial importance for the $\text{M}^{VI}(\text{L}^-)_2 \leftrightarrow \text{M}^{IV}(\text{L}-\text{L})$ reaction. Further substitutions in the peripheral sites of the amino acid assure fine control over the redox reaction. This is exemplified by the complex with a Mo/Se_2 core, for which the ΔE^{01} value can successfully be manipulated in the +0.55 to

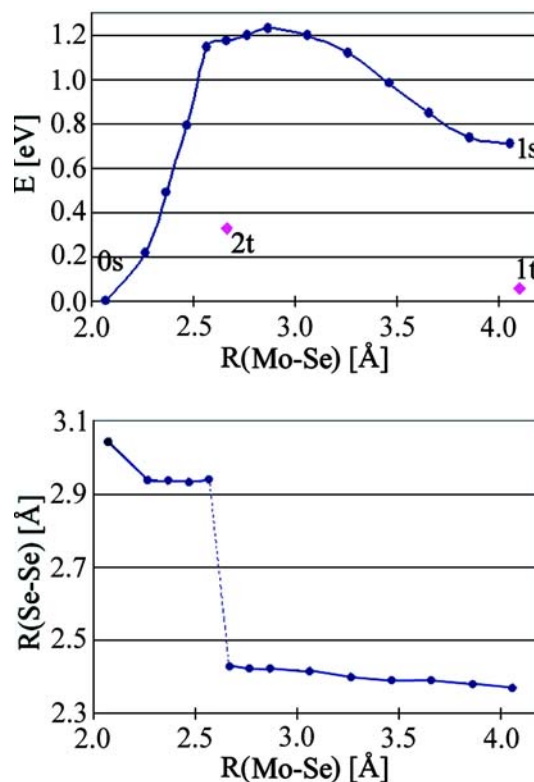


Fig. 3 The thermal switching path between state **0s** and **1s** (top) and the concomitant changes in the Se–Se separation (bottom). $R(\text{Mo}-\text{Se})$ is the distance from Mo to the middle of the Se–Se bond, $R(\text{Se}-\text{Se})$ is the Se–Se distance. States **1t** and **2t** were also introduced in the upper plot

–0.14 eV range (Table 2). The ΔE^{01} value can be brought closer to thermodynamic equilibrium (+0.05 eV, which corresponds to +0.03 eV after vibrational corrections are introduced). The small values of internal energy difference for two chemically distinct isomers is certainly below the reliability of energy determination by our preliminary calculations, and they should be probed in the future by configuration interaction methods. A realistic treatment should necessarily include interactions of isomers with the surface of a solid substrate and with molecules of solvent, and intermolecular interactions (including explicit magnetic interactions) between identical and different isomers in the 2D array. All these will substantially affect the energy landscape and their impact on the ΔE^{01} value and may exceed the accuracy of our present calculations.

Importantly, the *qualitative* impact of chemical substitutions on the shift of the ΔE^{01} value should *not* be computational method-dependent. The strong induction effects exerted by various substituents in our calculations agree well with intuition based on molecular orbital theory,¹² and the general trends seen for

¹² We note here one interesting and seemingly counterintuitive exception: in our calculations Cl shows slightly stronger inductive effects than F. It should be noted, however, that electron affinity of Cl (3.62 eV) is the largest among all chemical elements, and exceeds that of F (3.40 eV).

⁷ The term “electromers” was recently used in relation to the radical cation of tetramethyleneethane [36]. The word “tautomerism” is used instead to describe more subtle reorganizations of the electronic structure and concomitant changes of molecular geometry, as in the case of the croconate dianion [37].

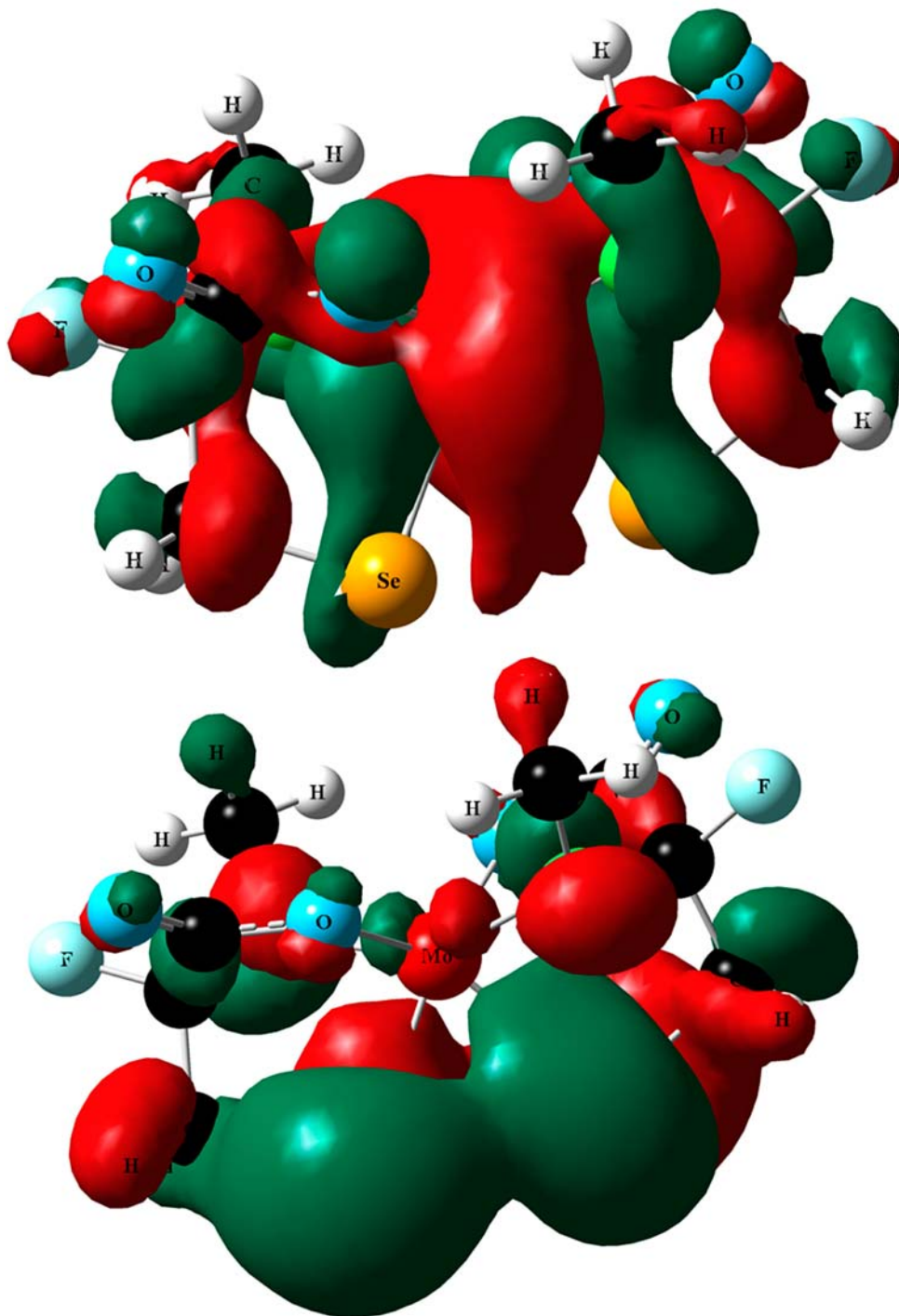
⁸ The basis of the switching process for our family of compounds is very different from that for the *dinuclear* Mo/S cluster complexes, which are known to exhibit photochromic behavior [38].

⁹ At $T=0$ and $p=0$, equality of internal energies (U) corresponds to equality of the thermodynamic Gibbs free enthalpies (G).

¹⁰ Vibrational corrections to the *difference* of total energy of the two electromers were computed to be small (of the order of 0.01 eV). Apparently, the formation of the Se–Se bond in the **1t** state is connected with the weakening of the Mo–Se bonds, and the sum of oscillation energies is nearly conserved.

¹¹ The ranking of the ΔE^{01} values in the order: $\text{W} > \text{Mo} > \text{U} > \text{Te}$ can be understood on the basis of the values of standard redox potentials for the $\text{M}^{VI}/\text{M}^{IV}$ redox pairs of metals and for these elements, Te^{VI} being the most oxidizing, W^{VI} the least. Qualitative discrepancy seen for U may come from use of SDD pseudopotential for this element only. Obviously, RTe^- is easier to oxidize than its selenium analogue, and RSe^- , in turn, than the sulphur species.

Fig. 4 The HOMO (*bottom*) and LUMO (*top*) frontier orbitals of the singlet state **0s**. Note, the donor function is Se-centred (lone pairs), while the acceptor function is Mo-centred (essentially one of d orbitals). HOMO has B, while LUMO-A symmetry. *Red* and *green* colours stand for opposite signs of the orbital wavefunction



isoelectronic species (W, Mo, U, Te; CyTe, CySe, CyS) find confirmation in the established redox behaviour of hexavalent transition metals and of pnictide-containing ligands.

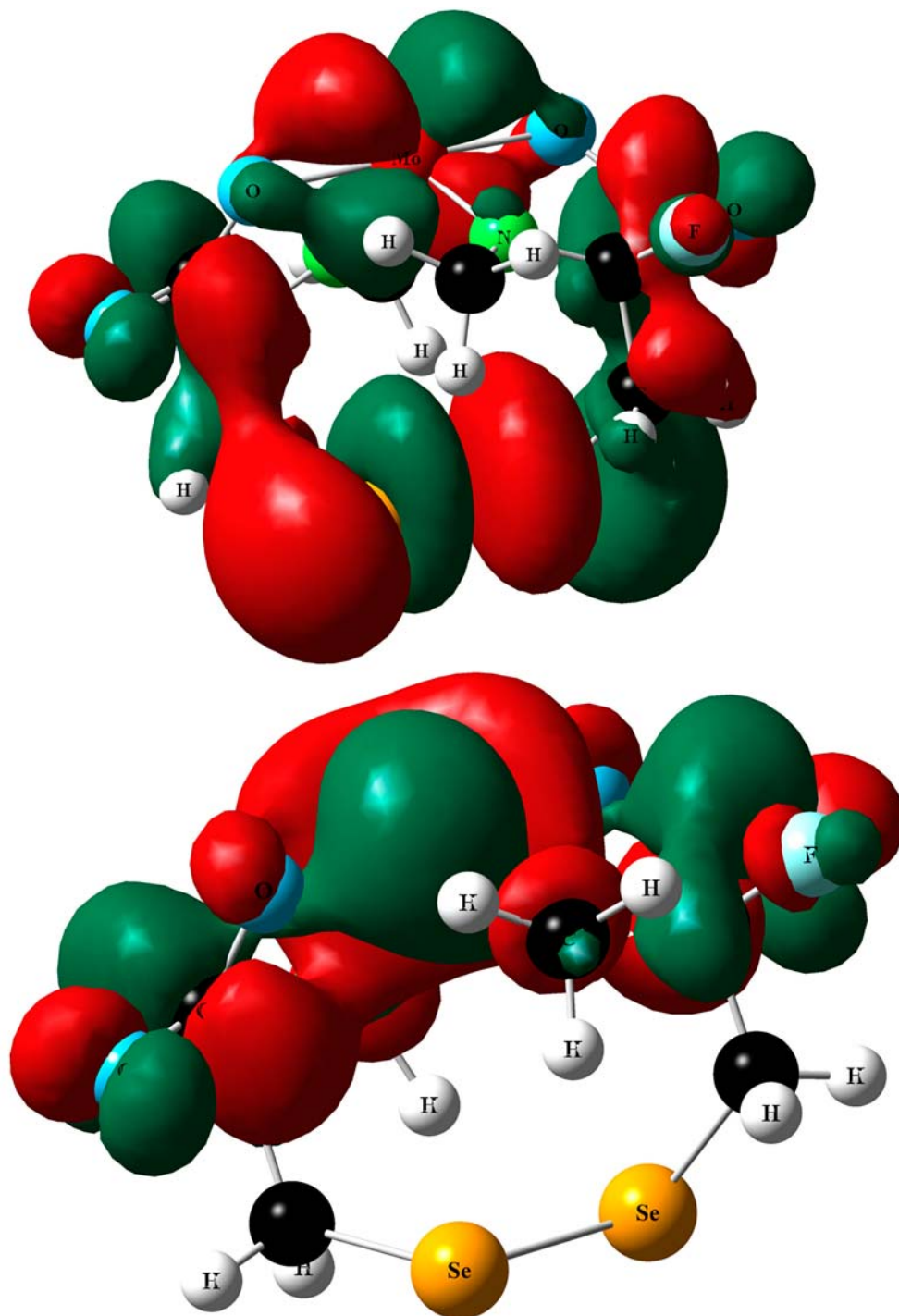
At this stage we leave the calculations in order to analyse the feasibility of the read-write processes and diversity of accessible methods of 0/1 switching.

The 0/1 switching and read–write processes

State **1t** can be obtained from **0s** via an *intramolecular* $2e^-$ redox process¹³ and concomitant geometry defor-

¹³ Unfortunately, a spin-forbidden two-photon process is required to achieve this. Presence of heavy atoms in the molecule (strong spin–orbit coupling) allows bend this unfavourable selection rule.

Fig. 5 The SOMO-1 (*bottom*) and SOMO (*top*) orbitals of the triplet state **1t**. Note, both singly-occupied orbitals are Mo-centred, and there is also a Se–Se σ^* component in the upper orbital. SOMO-1 has A, while SOMO-B symmetry. *Red* and *green* colours stand for opposite signs of the orbital wavefunction



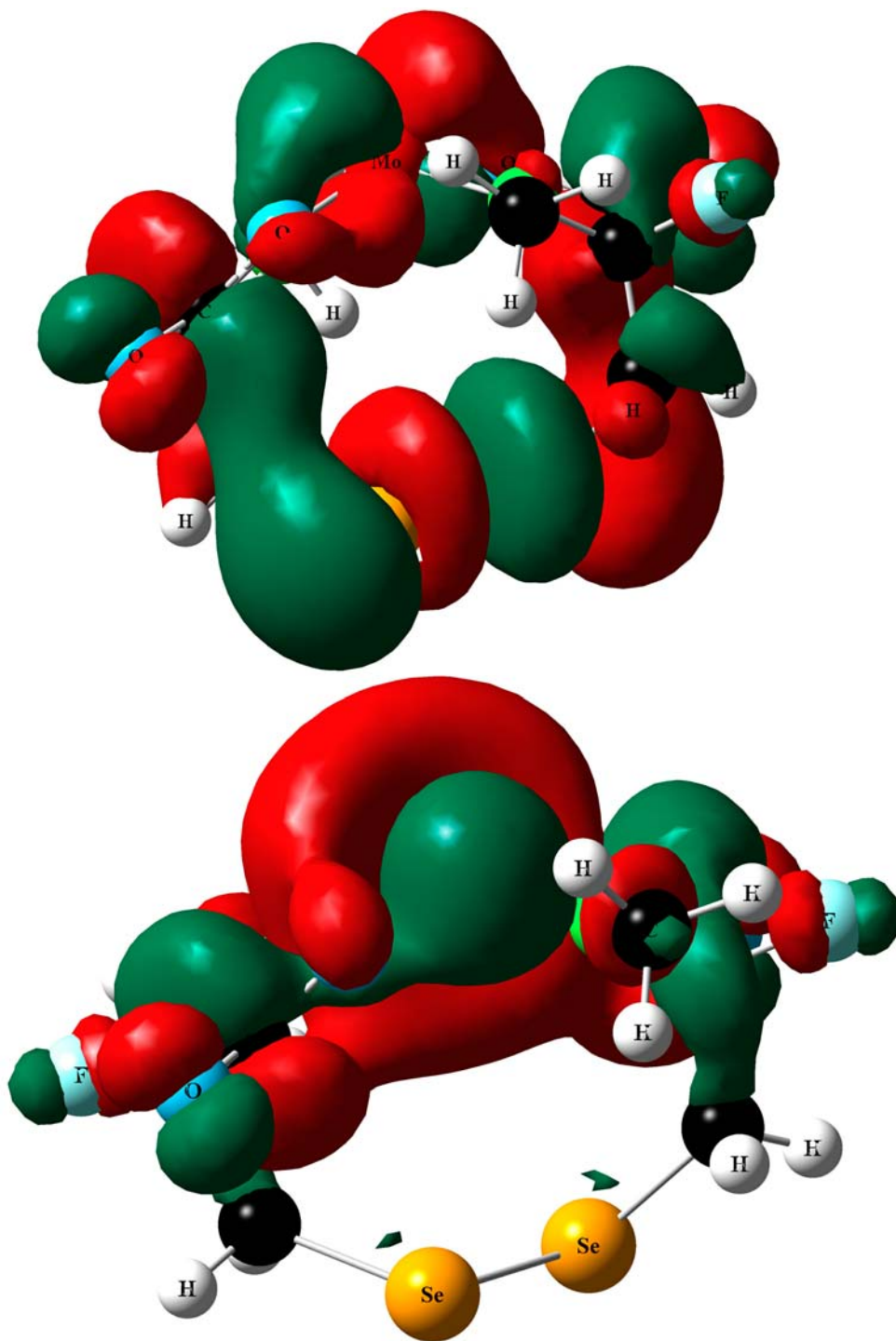
mations. Such a process could be achieved either via two simultaneous charge-transfer Se-to-Mo electronic excitations or via pumping up the Se–Mo–Se bending vibrational mode (leading to temporal shortening of the Se–Se contact, and subsequent fast changes in the electronic structure). State **1t**, instead, could be switched back into state **0s** via either UV σ -to- σ^* excitation of the diselenide subunit, or via selective multiphoton IR absorption of the Se–Se stretching mode; both would lead to Se–Se bond rupture.

The above-mentioned excitations might be used for writing and reading of the 0/1 bits, as illustrated in Fig. 2.¹⁴

States **0s** and **1t** differ in multiplicity. Therefore, direct transformation between these states is not easy to achieve via optical excitations due to their spin-forbidden character and small cross sections for radiation

¹⁴ No explicit erase function is necessary for our memory. Erase function may be supplemented if three states of comparable energy are involved in memory storage.

Fig. 6 The HOMO (*bottom*) and LUMO (*top*) orbitals of the singlet state **1s**. Note, HOMO is Mo-centred, while there is a predominant Se–Se σ^* component in the LUMO. HOMO has A, while LUMO-B symmetry. Red and green colours stand for opposite signs of the orbital wavefunction

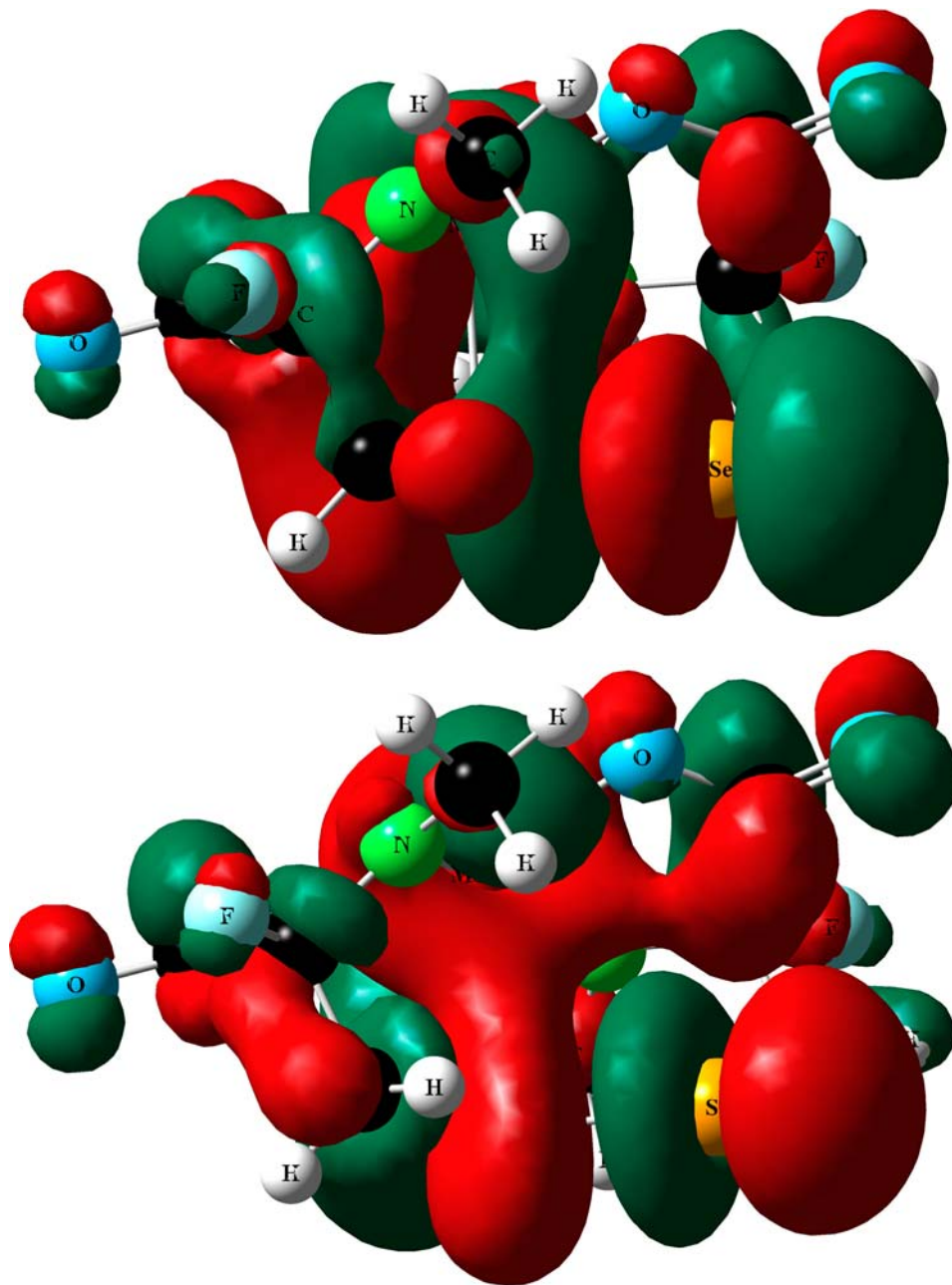


absorption connected with multiphoton processes. The spin restriction does not apply, however, if the **0s**–to–**1s** switching is operative. Because of the pronounced similarities in the molecular geometry for **1s** and **1t**, state **1s** can be used as a mediator in the **0s/1t** switching via the **0s**–to–**1s** excitation and subsequent intersystem crossing between **1s** and **1t**.

Thermal switching path and thermal stability of electromers

We have traced the thermal reaction path for the **0s** to **1s** conversion (Fig. 3) while progressively elongating the Mo–Se distances and optimizing the remaining coordinates (the C_2 symmetry was preserved).

Fig. 7 The SOMO-1 (*bottom*) and SOMO (*top*) orbitals of the triplet state **2t**. Note, there is a Se–Se σ^* component in both orbitals. *Red* and *green* colours stand for opposite signs of the orbital wavefunction



The transition state is about 0.55 eV above **1s** and 1.25 eV above **0s**. The Se–Se bond length decreases along the reaction path, and a dramatic drop in the Se–Se distance from 2.9 to 2.4 Å is seen at a Mo–Se separation of 2.5–2.6 Å, indicating the avoided crossing of the potential energy surfaces of the two singlet electronic states.

The barriers for the thermal interconversions between singlet states are close to or larger than the value of +0.65 eV, postulated earlier to guarantee sufficient thermal stability of electromers.² State **1t** is about 0.7 eV below **1s** in energy and supposedly it should be even more stable than **1s**, as soon as the conversion to **0s** is taken into account. Unfortunately,

as mutual transformations between singlet and triplet states are considered, the thermal stability of **0s** and **1t** decreases because of the presence of the low-lying **2t** state. This seems to be the most serious deficiency of our memory-exhibiting molecules, and we are currently trying to remove the asymmetric **2t** state from the low-energy landscape via diverse chemical substitutions.¹⁵

¹⁵ **2t** shows significant dipole moment (5.9 D), in contrast to **0s** and **1t**; it is thus supposed that **2t** will not be stabilized in nonpolar solvents with respect to **0s** and **1t**.

Table 3 Optimized geometry of state **0s** and **1t** in Cartesian coordinates (rounded to the second decimal place)

Atom	0s			1t		
	<i>x</i>	<i>y</i>	<i>Z</i>	<i>x</i>	<i>y</i>	<i>z</i>
Mo	0.00	0.20	0.00	0.00	-0.92	0.00
Se	1.46	-1.87	-0.42	-1.00	2.17	-0.64
Se	-1.46	-1.87	0.42	1.00	2.17	0.64
F	3.85	1.15	1.05	-3.41	-0.61	1.42
F	-3.85	1.15	-1.05	3.41	-0.61	-1.42
O	1.24	1.07	-1.30	-1.72	-1.89	-1.11
O	-1.24	1.07	1.30	1.72	-1.89	1.11
O	-3.36	1.82	1.59	3.57	-0.64	1.46
O	3.36	1.82	-1.59	-3.57	-0.64	-1.46
N	1.55	0.72	1.18	-1.14	-0.89	1.17
N	-1.55	0.72	-1.18	1.14	-0.89	-1.17
C	-3.10	-0.94	-0.23	2.61	-0.97	0.80
C	3.10	-0.94	0.23	-2.61	-0.97	-0.80
C	-2.78	0.53	-0.44	0.84	-0.56	-2.57
C	2.78	0.53	0.44	-0.84	-0.56	2.57
C	2.53	1.25	-0.96	-2.32	-0.29	0.58
C	-2.53	1.25	0.96	2.32	-0.29	-0.58
C	1.50	1.94	2.00	-2.33	1.24	0.51
C	-1.50	1.94	-2.00	2.33	1.24	-0.51
H	-3.91	-1.06	0.48	0.58	0.50	-2.68
H	3.91	-1.06	-0.48	-0.58	0.50	2.68
H	3.37	-1.38	1.19	-0.02	-1.15	-2.89
H	-3.37	-1.38	-1.19	0.02	-1.15	2.89
H	1.61	2.85	1.40	1.70	-0.79	-3.19
H	-1.61	2.85	-1.40	-1.70	-0.79	3.19
H	0.55	1.96	2.53	-2.27	1.66	151
H	-0.55	1.96	-2.53	2.27	1.66	-1.51
H	2.33	1.92	2.71	-3.28	1.54	0.06
H	-2.33	1.92	-2.71	3.28	1.54	-0.06

Table 4 Optimized geometry of state **1s** and **2t** in Cartesian coordinates (rounded to the second decimal place)

Atom	1s			2t		
	<i>x</i>	<i>y</i>	<i>Z</i>	<i>x</i>	<i>y</i>	<i>z</i>
Mo	0.00	0.00	1.88	0.28	-1.23	0.03
Se	1.18	0.05	-2.18	0.51	1.14	-1.07
Se	-1.18	-0.05	-2.18	-1.25	2.07	0.32
F	2.74	-2.65	0.61	3.79	0.45	1.29
F	-2.74	2.65	0.61	-3.79	-1.14	-0.64
O	-3.81	0.04	0.48	2.03	-1.51	-1.04
O	3.81	-0.04	0.48	-1.11	-1.39	1.53
O	1.85	0.53	1.45	4.18	-0.83	-1.11
O	-1.85	-0.53	1.45	-3.26	-0.99	2.08
N	-0.73	1.66	1.12	-1.48	-1.16	-0.98
N	0.73	-1.66	1.12	1.64	-0.48	1.29
C	2.66	-0.27	0.75	-2.74	0.91	-0.32
C	-2.66	0.27	0.75	2.18	1.52	-0.04
C	0.00	2.93	1.09	2.68	0.16	0.52
C	0.00	-2.93	1.09	1.45	-0.02	2.67
C	1.91	-1.56	0.31	3.07	-0.81	-0.64
C	-1.91	1.56	0.31	-2.36	-1.05	1.29
C	1.74	-1.61	-1.22	-2.56	-0.62	-0.20
C	-1.74	1.61	-1.22	-1.65	-1.10	-2.44
H	0.52	3.06	0.14	-1.83	-0.08	-2.82
H	-0.52	-3.06	0.14	-2.50	-1.72	-2.74
H	0.69	-3.76	1.25	-0.75	-1.49	-2.92
H	-0.69	3.76	1.25	1.29	1.07	2.73
H	0.75	2.93	1.88	2.34	-0.26	3.26
H	-0.75	-2.93	1.88	0.58	-0.52	3.08
H	2.72	-1.80	-1.65	2.89	1.97	-0.74
H	-2.72	1.80	-1.65	1.95	2.21	0.77
H	1.07	-2.42	-1.50	-3.56	1.21	0.34
H	-1.07	2.42	-1.50	-2.99	1.19	-1.34

Pros and cons of novel memory

What are the overall benefits and limitations associated with our memory? The fundamental strength of our memory is that its general principle can be applied to many isoelectronic systems. Thus, the desired control of the energy difference of states **0s** and **1t** can be achieved via judicious choice of elements and deliberate atom-by-atom and group-by-group substitutions in related molecules [39]. In addition, the electric dipole moment of both electromers is not large given the size of the molecule (1.00 D for the **0s** state, 0.16 D for **1t**). This essentially prevents intermolecular association. This in turn assures that large information storage densities might be achieved. The memory unit is small (it easily fits into the $(10 \text{ \AA})^3$ cube) and it is built of cheap chemical constituents.¹⁶

At present, our memory suffers from the presence of the low lying **2t** state (+0.33 eV vs **0s**, +0.28 eV vs **1t**,

for the compound shown in Fig. 1), which might complicate the read-write processes, and decrease the thermal stability of the **0s** and **1t** states. In consequence, information lifetime might become insufficiently short due to spontaneous interconversion of the electromers at ambient temperatures.² Thus, **2t** should either be completely eliminated via appropriate chemical substitutions, or, less easily, conditions should be provided for its energetic equivalency with **0s** and **1t**, so that **2t** becomes an independent memory carrier, thus increasing the storage capacity of each single molecule by 50%.

The large exposure of the metal centre to the environment in states **1s** and **1t** (recollect, Mo is in a butterfly ligand field) is another deficiency of our system. Any interaction of the molecule with molecules of solvent will drastically influence the energy difference of the electromers involved in the 0/1 switching.

State **0s** is composed of a very strong acid (hexavalent metal), and a very strong base (triply deprotonated cysteine derivatives). Thus, it will be somewhat difficult to find a proper reaction environment to bring these components together. It seems reasonable to first synthesize electromer **1t** (composed of milder acid and base constituents), while using deprotonated cystine.

In conclusion, our prototypical memory carrier requires further modifications, so that it might be applied

¹⁶ The price of 1 mol of 99.95% Mo is now about \$15 (the use of uranium is discouraged), and of 99% l-cysteine-\$35. Substitution of S by Se, and auxiliary substitutions will increase the price of ligand. Let's assume that the final price of 1 mol of memory carrier attached to a 2D surface is 1,000,000 times larger than the cost of the molecular components, i.e., \$50,000,000. If each molecule is effectively used for 0/1 switching, then fabrication of an analogue of the BlueRay disk would cost about 2×10^{-6} \$, instead of about \$10 (a commercial disc costs \$40)

in practice for electronic data storage. We hope to improve these shortcomings in related molecules.¹⁷

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Appendix

Frontier orbitals of state 0s are shown in Fig. 4, frontier orbitals of state 1t are shown in Fig. 5, frontier orbitals of state 1s are shown in Fig. 6 and frontier orbitals of state 2t are shown in Fig. 7 (Tables 3 and 4).

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¹⁷ We now extend our investigations to the derivatives of cysteine and demethylated methionine. Our preliminary results for molecules containing soft semimetal-based ligands ($-\text{GeH}_2^-$, $-\text{AsH}^-$, isoelectronic with $-\text{Se}^-$) and longer aliphatic chains (derivatives of methionine) indicate that the metal centre may achieve reasonable protection for states **1s** and **1t**, as the coordination of Mo by an N_2O_2 ligand is a distorted tetrahedron for these ligands.