Electronic Supplementary Information (ESI)

A fast redox-induced switching mechanism in a conformationally controllable molecular thread in solution

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Computational Setup

A. Classical Molecular Dynamics Simulations (MD) of 1 and 1⁻

We have performed forty classical MD simulations for **1** and **1⁻** species at 298K in NVT ensemble and in acetonitrile (CH_3CN) infinite dilute solution: twenty MD simulations of 2 ns for neutral (**1**) species and twenty MD simulations of 80 ns for reduced (**1⁻**) species, respectively. Thus, the total length of the current classical sampling is 1.64 µs. It is worth noting that **1/1⁻** MD simulations were initiated taking into account not correlated molecular structures, as obtained by equilibrium simulations (Zazza, C.; Amadei, A.; Sanna, N.; Aschi, M. *Chem. Commun*. 2008, 29,3399-3401), at the centre of the simulating box (see **ESI-Figure 1** reported below) of 720 nm³ filled with CH_3CN (Grabuleda, X.; Jaime, C; Kollman, P.A. *J. Comp. Chem*. 2000, **21**, 901-908.) at its typical liquid density of 782.2 kg/m³. The redox-induced conformational relaxation profiles, as a function of the intramolecular distance between the geometrical centre of *succ* and *ni* moieties (see Fig. 2 and Fig. 3 reported in the manuscript), were fitted using a kinetic model (see below) with the main goal to estimate the rate constants (k_1 and k_{-1}) characterizing the observed mechanical response upon selective oxidation/reduction of the *ni* moiety in such a synthetic thread.
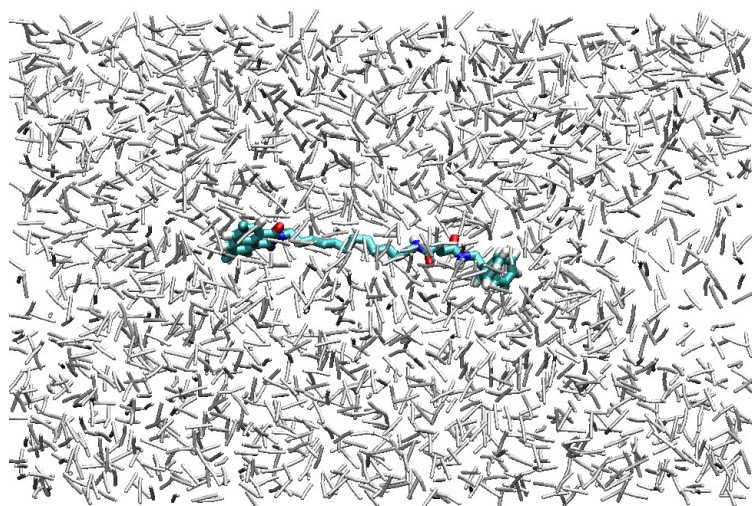
ESI-Figure 1: A pictorial representation of the classical simulation box.

For **1** and **1⁻** we used Gromos96 bond parameters and Lennard-Jones, respectively (van Gunsteren, W. F.; Billeter, S. R.; Eising, A. A.; Hunemberger, P. H.; Kruger, P.; Mark, A. E.; Scott, V. R. P.; Tironi, I. G. Biomolecular simulation: The GROMOS96 manual and user guide. vdf Hochschlverlag AG an der ETH Zurich, Zurich **1996**.). An integration step of 2.0 fs was used and the temperature was kept constant by the isokinetic temperature coupling (Berendsen, H. J. C.; Postma, J. P. M.; van Gunsteren, W. F.; Di Nola, A. *J. Chem. Phys*. 1994 **81**, 3684-3690.). Long range electrostatics was computed by the Particle Mesh Ewald (PME) method, with 34 wave vectors in each dimension and a 4th order cubic interpolation. A cut-off of 1.1 nm was used and pair list was updated every 5 integration steps.

All the MD simulations were carried out using the Gromacs software, version 3.3 (E. Lindahl, B. Hess and D. van der Spoel: *GROMACS 3.0: A package for molecular simulation and trajectory analysis. J. Mol. Model.* 2001, **7**, 306-317). Atomic point charges were recalculated by mimicking the solvent with a Conductor-like

Polarizable Continuum Model (CPCM, V. Barone and M. Cossi, *J. Phys. Chem. A* 1998, **102**, 1995.) and adopting a Merz-Kollman (MK) scheme with ESP fitting procedure (Besler, B. H.; Merz Jr. B. K. M.;, and Kollman, P. A., *J. Comp. Chem.* 1990, **11**, 431.) on different functionals, namely B3LYP, VSXC and PW91 with the 6-311++G(d,p) atomic basis set on all atoms. B3LYP, VSXC, and PW91 provided similar results in terms of atomic point charges and electronic excitations. Before doing any classical/statistical sampling in dilute solution, CPCM represents a reasonable and well-known computational tool for evaluating the polarization of the surrounding environment on a solute molecule in its own electronic ground state. (see for example, Ludwig, V.; Coutinho, K.; and Canuto, S., *Phys. Chem. Chem. Phys*. 2007, **9**, 4907.)

B. The Kinetic Model and the corresponding fitting procedure

The conformational changes accompanying **1** and **1⁻** relaxation processes at room temperature, were investigated considering the molecular geometry of the molecular thread as divided between two different conformational "states": the elongated molecular structures were characterized having a $R_{s-n} \geq 8.0$ Å, whilst the basically folded ones showing $R_{s-n} < 8.0$ Å (see text into the manuscript). In so doing, we model the classical trajectory of the molecular thread in MeCN dilute solution into a sort of two different "covalent" species which are directly related to the conformational shaping along the sampling (see Scheme 1 reported below).
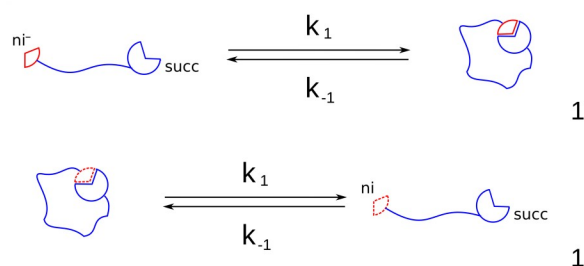
Scheme 1. Dotted line represents radical anion species; *ni* is reported in red, *succ* in blue.

Therefore, taking into account the **1⁻** species (upper panel in Scheme 1) and using standard relations as arising from kinetic theory we can write that:

$$dP_e(t)/dt = -k_1 P_e(t) + k_{-1} P_f(t) \qquad \text{(I)}$$

$$dP_f(t)/dt = k_1 P_e(t) - k_{-1} P_f(t) \qquad \text{(II)}$$

in which $P_e(t)$ and $P_f(t)$ represent the probability (i.e., occurrence frequency) of the elongated and folded/closed conformations, respectively. Therefore, having at any instant of time that $P_e(t) + P_f(t)=1$ we can re-write the equation (I) as follows:

$$dP_e(t)/dt = -k_1 P_e(t) + k_{-1}[1 - P_e(t)] = -k_1 P_e(t) + k_{-1} - k_{-1} P_e(t) \qquad \text{(III)}$$

$$dP_e(t)/dt = -(k_1 + k_{-1}) P_e(t) + k_{-1} \qquad \text{(IV)}$$

hence, according to equation (IV), $P_e(t)$ probability can be obtained via the ordinary solution of the first-order differential equations:

$$P_e(t) = P_e(0) e^{-(k_1 + k_{-1})t} + e^{-(k_1 + k_{-1})} k_{-1} \int_0^t e^{(k_1 + k_{-1})t} \, dt \qquad \text{(V)}$$

$$P_e(t) = P_e(0) e^{-(k_1 + k_{-1})t} + e^{-(k_1 + k_{-1})} k_{-1} \left\{ \frac{[e^{(k_1 + k_{-1})t} - 1]}{(k_1 + k_{-1})} \right\} \qquad \text{(VI)}$$

$$P_e(t) = P_e(0) e^{-(k_1 + k_{-1})t} + \frac{k_{-1}}{(k_1 + k_{-1})} \left\{ 1 - e^{-(k_1 + k_{-1})t} \right\} \qquad \text{(VII)}$$

$$P_e(t) = P_e(0) e^{-(k_1 + k_{-1})t} + \frac{k_{-1}}{(k_1 + k_{-1})} - \frac{k_{-1}}{(k_1 + k_{-1})} e^{-(k_1 + k_{-1})t} \qquad \text{(VIII)}$$

$$P_e(t) = e^{-(k_1 + k_{-1})t} \left\{ P_e(0) - \left[\frac{k_{-1}}{(k_1 + k_{-1})} \right] \right\} + \frac{k_{-1}}{(k_1 + k_{-1})} \qquad \text{(IX)}$$

thus, starting our MD simulations from the elongated conformation, we have that $P_e(0) = 1$ and so:

$$P_e(t) = e^{-(k_1 + k_{-1})t} \left\{ 1 - \left[\frac{k_{-1}}{(k_1 + k_{-1})} \right] \right\} + \frac{k_{-1}}{(k_1 + k_{-1})} = e^{-(k_1 + k_{-1})t} (1 - \chi) + \chi \qquad \text{(X)}$$

where:

$$\chi = \frac{k_{-1}}{k_1 + k_{-1}}$$

In turn, according to such a kinetic model here reported, the equation (X) was applied as mathematical functional form to evaluate the rate constants k_{-1} and k_1 (see the upper panel in Scheme I) characterizing the electrochemically-driven elongation-like conformational transition observed in our MD simulations of **1$^-$** system upon reduction of the napthalimide chemical group (see Figure 2 into the manuscript). Note that the same model was also applied for the mechanical response in **1** neutral species in MeCN dilute solution (see the bottom panel in Scheme I) at 298K.

Furthermore, we also addressed the spectroscopic changes mainly related to the electrochemically induced elongation---folding process observed in **1$^-$** ensemble (see upper panel in Scheme 1). To this end, we compared the UV absorption spectra of **1$^-$** at the equilibrium (folded conformation) with non-equilibrium MD simulations in which the **1$^-$** system in MeCN is in the elongated conformation. Therefore, the difference in absorption maximum in the two different conformations, at PMM/PW91/6-311++G(d,p) level of theory, is calculated (see text). It is worth noting that the error bar is also reported; in this respect, PMM calculations were performed on the two halves of the equilibrium and non-equilibrium trajectories.

C. The *succ-ni$^-$* supramolecular assembly model system in 1$^-$ species: PMM calculations

In order to further refine the theoretical investigation regarding the electronic properties of the synthetic

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thread in MeCN, we investigated the possibility of observing an electron transfer process between ni^- and *succ* supramolecular assembly model in **1**⁻ ensemble at 298K. In this context, we have explicitly taken into account only a portion of the *succ* moiety which is found to be rather rigid during the MD simulation (see ESI-Figure2). Therefore, the *succ/ni*⁻ interacting model was then selected as quantum centre (QC), with the rest of **1**⁻ and the surrounding solvent molecules acting as an electrostatic perturbation according to standard PMM procedure. Afterwards, the molecular structure of the QC reported in ESI-Figure 2 was optimized at PW91/6-311++G** level in CPCM model[§], and an unperturbed Hamiltonian matrix, of dimension [4x4], was constructed using Time Dependent Density Functional Theory (TD-DFT) calculations (i.e. TD-PW91/6-311++G**). In this context, as suggested by experimental literature (Brouwer, A.M.; Frochot, C.; Gatti, F.G.; Leigh, D.A.; Mottier, L.; Paolucci, F.; Roffia, S.; Wurpel, W.H. *Science* 2001, **291**, 2124-2128.) both unperturbed (gas-phase) and perturbed (via CPCM in acetonitrile dilute solution) spin densities, clearly indicates that, in **1**⁻ species, the *ni* station appears as radical anion (see for example the data reported below).

Calculated, at B3LYP/6-311++G** level of theory, spin densities of the *succ-ni*⁻ supramolecular assembly model (see ESI-Figure 2). The atoms of the *ni* moiety are reported in blue and the atoms of the *succ* model system in red, respectively.

```
 1   N   -0.029106
 2   C    0.104790
 3   O    0.070985
 4   C    0.083251
 5   O    0.082700
 6   C    0.026658
 7   C    0.035244
 8   C   -0.010429
 9   C    0.173735
10   C    0.206202
11   C   -0.058130
12   C    0.251831
13   C   -0.076671
14   C    0.226612
15   C   -0.035035
16   H    0.000080
17   H   -0.014051
18   H    0.000991
19   H   -0.016063
20   H   -0.014309
21   H    0.000501
22   H   -0.012488
```

.....sum ≈ -1.00 (alpha electron over ni moiety; see for example ESI-Figure 3 in which the HOMO of the 1⁻ species is found to be locally confined within the ni chemical group.)

```
23   H   -0.000795
24   N    0.001894
25   C    0.000010
26   O    0.000123
27   C   -0.000398
28   C    0.001537
29   H    0.000481
```

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§ The optimization procedure was carried out mimicking the acetonitrile dilute solution by means of standard CPCM approach. Moreover, it should be remarked that during the geometry relaxation procedure, the interatomic distance between the carboxylic oxygen atom (i.e., O=CNR) of the *ni* group and the nitrogen atom within the OCN-H moiety of the *succ* station was kept frozen at the value in the free energy minimum conformation for **1**⁻ system in MeCN at 298K (see Zazza C.; Amadei, A.; Sanna, N.; Aschi, M. *Chem. Commun.* 2008, **29**, 3399-3401).

30 H   -0.000139
31 H   0.000252
32 H   -0.000003
33 H   -0.000156
34 H   -0.000104

.....sum ≈ 0.00 (i.e., neutral succ)
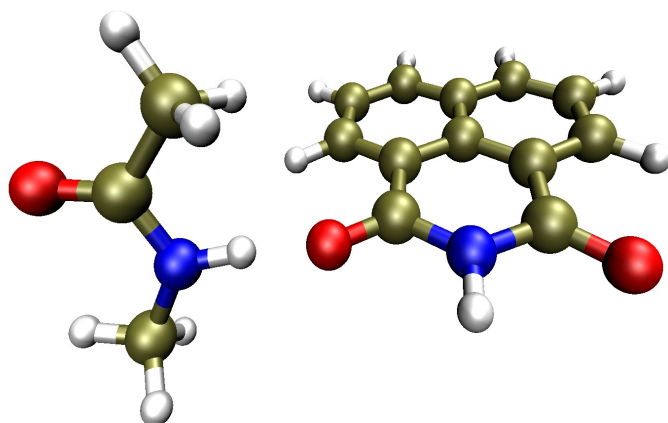
ESI-Figure 2 Quantum Mechanics subsystem of the PMM/PW91/6-311++G(d,p)MD approach. Note that for the sake of clarity the classical surrounding environment (i.e. the rest of **1⁻** system and solvent molecules are omitted.
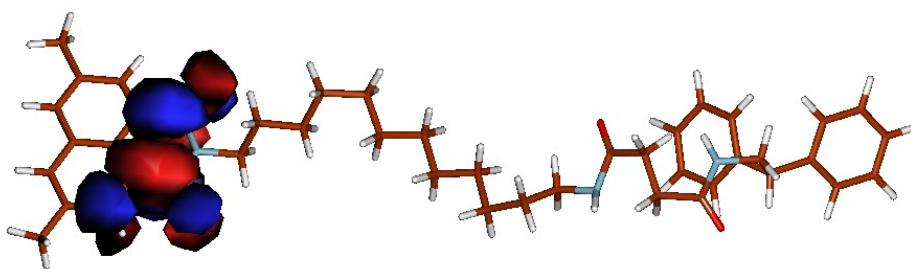

ESI-Figure 3: HOMO of the **1⁻** molecular species.

In this section, by applying a recent extension of the PMM methodology we evaluated the effects of the perturbing and fluctuating classical surrounding environment on the spin densities of the *succ/ni⁻* interacting model. In this respect, using PMM we can directly follow the position of the electron in excess during the 20 ns of MD simulation in equilibrium ensemble for the **1⁻** species in acetonitrile at 298 K. The theoretical framework is essentially based on the definition of an unperturbed spin density matrix operator for each *l*-th

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chemical group (termed as $\tilde{\rho}\,^o_{s,l}$ and corresponding to a pseudo-diagonal matrix formed by unperturbed spin densities previously collected) and on the computation of its expectation value:

$$[\tilde{\rho}\,^o_{s,l}]_{i,i} = \vec{C}_i^{\,T*}\,\tilde{\rho}\,^o_{s,l}\,\vec{C}_i$$

where $\vec{C}_i$ indicates the *i*-th perturbed electronic Hamiltonian eigenvector which is calculated at each step during the classical sampling according to standard PMM procedure. In the current case we are considering the ground state and the first third doublet electronic excited states of the model system reported in ESI-Figure 2 at TD-PW91/6-311++G(d,p) level of theory.[#] From Figure ESI-Figure 4 it is evident that excess of electronic spin density in **1**⁻ molecular thread remains basically localized onto the *ni*⁻ moiety (see text into the manuscript).

succ-------ni⁻

PMM/PW91 spin density over the ni moiety
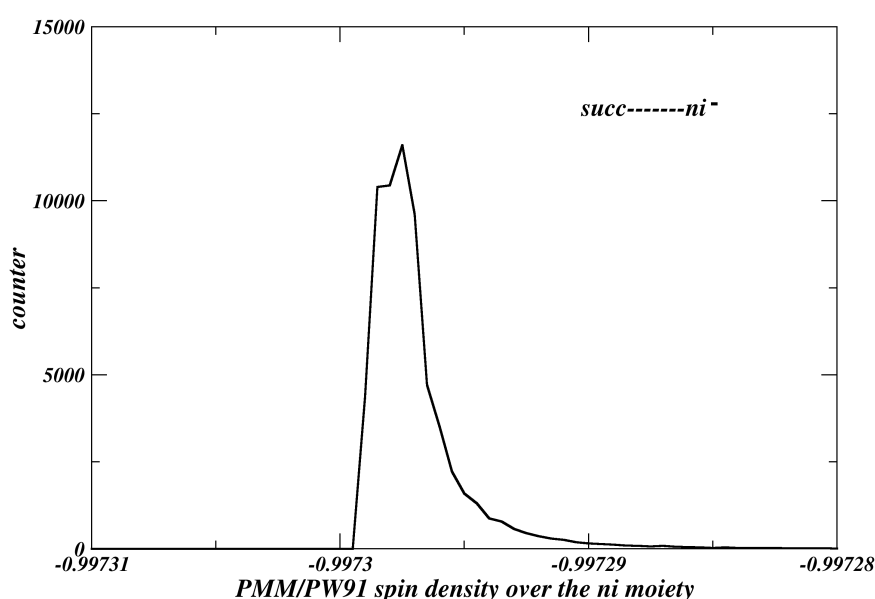
ESI-Figure 4: Calculated distribution, at PMM/PW91/6-311++G(d,p) level of theory, of the perturbed spin density over the *ni* moiety in the **1**⁻ synthetic molecular thread in MeCN as obtained by means of classical MD sampling (20 ns, equilibrium conditions) at room temperature (298K).

[#] It means that, a [4x4] perturbed electronic Hamiltonian matrix is diagonalized at each step of the classical MD sampling (equilibrium conditions) in order to evaluate a predefined set of "perturbed" electronic degrees of freedom along the *ni—succ* interacting couple.