Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information
(ESI)

Can a synthetic thread act as an electrochemically switchable molecular device?

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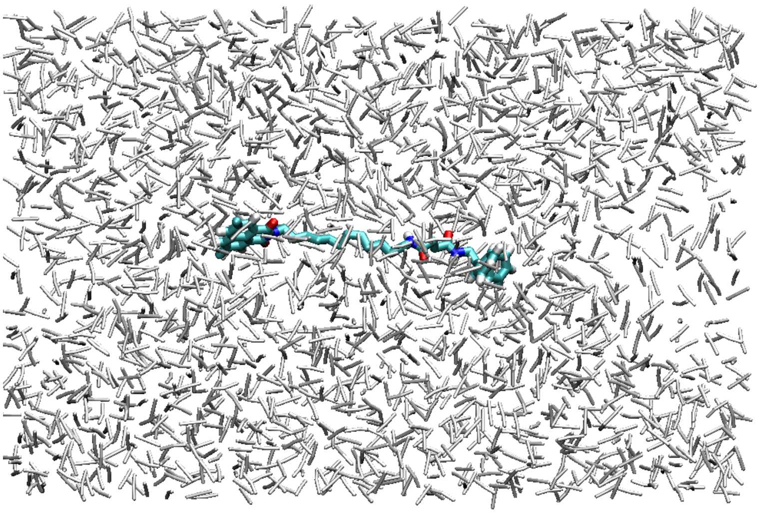
Computational Setup

A. Classical Molecular Dynamics Simulations of **1** and **1**$^-$

We have performed two MD simulations of 20 ns of **1** and **1**$^-$ at 300 K in NVT ensemble in acetonitrile (CH_3CN) with the rototranslational constrain algorithm applied to the solute molecule (Amadei A, Chillemi G, Ceruso M A, Grottesi A, Di Nola A. *J Chem Phys.* 2000, **112**, 9-23.). Both simulations were initiated with the structure fully elongated at the centre of a box (see **ESI-Figure 1** reported below) of 720 nm^3 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/m^3. 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**.).

The trajectories were then propagated for 20 ns using an integration step of 2.0 fs 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 simulations were carried out using the Gromacs software, version 3.0.3 (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) Point charges (see data below) were recalculated on the two terminals succ and ni sites by mimicking the solvent with a Conductor-like Polarizable Continuum Model (CPCM, V. Barone and M. Cossi, *J. Phys. Chem. A* 1998, **102**, 1995.) by adopting a Merz-Kollman (MK) scheme and 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.)



ESI-Figure 1: A pictorial representation of the classical simulation box.

B. Perturbed Matrix Method (PMM) calculations and Redox Potential of 1/1-

The *ni/ni*$^-$ site was used as quantum centre, 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.), with the rest of **1**$^-$ and the solvent acting as an electrostatic perturbation. *ni/ni*$^-$ unperturbed Hamiltonian matrix, of dimension [13x13], was constructed using Time Dependent Density Functional Theory (TD-DFT) calculations adopting the same functionals, in the unrestricted formalism, and basis sets previously cited.

These quantum chemical calculations, carried out on *ni/ni*$^-$ site, provided the 13-dimensional *unperturbed* basis set to be used for constructing and diagonalizing, at each step of MD simulation, the perturbed electronic Hamiltonian matrix according to PMM computational procedure. The use of TD-DFT was imposed by the lack of convergence experienced using CASSCF wavefunctions for high-energy electronic eigenstates.

For a detailed description of PMM for calculating electronic spectra see, for example, Zazza, C.; Amadei, A.; Sanna, N.; Grandi, A.; Chillemi, G.; Di Nola, A.; D'Abramo, M.; Aschi, M. *Phys. Chem. Chem. Phys.* 2006 **8**, 1385-1393.

By means of PMM, with the same theoretical/computational level adopted for UV spectrum, we evaluated the perturbed ground state electronic energy of **1**$^-$ (U_1^-) and **1** (U_1) within the **1**$^-$ free energy minimum ensemble. The obtained perturbed energies were then used for calculating ΔA_{ox} using the equation (II) providing a value of 136.0 kJ/mol (see for example: A. Amadei, M. D'Alessandro, M. Aschi, *J. Phys. Chem. B* 2004, ***108***, 16250-16254; C. Zazza, A. Amadei, A. Palma, N. Sanna, S. Tatoli, M. Aschi, *J. Phys. Chem. B,* 2008, **112**, 3184-3192)

$$\Delta A_{ox} = -k_B T \ln \left\langle e^{-\beta(U_{\mathbf{1}} - U_{\mathbf{1}^-})} \right\rangle_{\mathbf{1}^-, R^*_{s-n,\mathbf{1}^-}} \qquad \text{(II)}$$

The overall free energy associated to the oxidation of **1**$^-$ (ΔA_{redox}) was finally calculated by using equation (**III**) For the derivation of equation (**III**) see Theoretical appendix reported at the end of this section.

$$\Delta A_{redox} = \Delta A_{ox} - k_B T \ln \frac{\int e^{-\beta \Delta A_{c,\mathbf{1}}(R_{s-n})} dR_{s-n}}{\int e^{-\beta \Delta A_{c,\mathbf{1}^-}(R_{s-n})} dR_{s-n}} \qquad \text{(III)}$$

where $\Delta A_{c,1-}$ is the conformational free energy of **1**$^-$.

Quantum Chemical (QC) calculations were carried out using Gaussian03 package (Gaussian 03, Revision C.02, Frisch, M. J. et. al. and Pople, J. A.; Gaussian, Inc., Wallingford CT, **2004**.). PMM simulations were accomplished with a development version of the PMM toolkit. All the computations were performed at CASPUR (Rome) running on a four-way HP-Proliant DL-585 server.

Theoretical Appendix: derivation of equation (III)

Let's consider the two free energy curves reported in Figure 3 (see manuscript).

We have that:

$A_{c,1} = A_{c,1}(R^*_{s-n}) + \Delta A_{c,1}$ and $A_{c,1-} = A_{c,1-}(R^*_{s-n}) + \Delta A_{c,1-}$

Oxidation free energy, i.e. $\Delta A_{redox} = A_{c,1} - A_{c,1-}$ can be also expressed as:

$$\Delta A_{redox} = -k_B T \ln \frac{\int e^{-\beta A c,\mathbf{1}} dR_{s-n}}{\int e^{-\beta \Delta A_{c,\mathbf{1}^-}} dR_{s-n}}$$

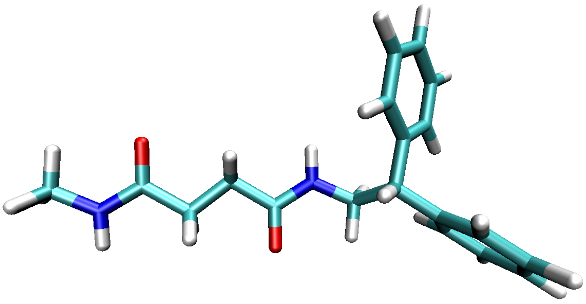
hence

$$\Delta A_{redox} = -k_B T \ln \frac{\int e^{-\beta A_{c,\mathbf{1}}(R^{*}_{s-n})} e^{-\beta \Delta A_{c,\mathbf{1}}} dR_{s-n}}{\int e^{-\beta A_{c,\mathbf{1}^{-}}(R^{*}_{s-n})} e^{-\beta \Delta A_{c,\mathbf{1}^{-}}} dR_{s-n}} =$$

$$= \Delta A_{redox} = \Delta A_{ox} - k_B T \ln \frac{\int e^{-\beta \Delta A_{c,\mathbf{1}}(R_{s-n})} dR_{s-n}}{\int e^{-\beta \Delta A_{c,\mathbf{1}^{-}}(R_{s-n})} dR_{s-n}}$$

which is equation (III) as reported above.

C. Succinimide Site *(succ):* Molecular Coordinates and ESP Charges



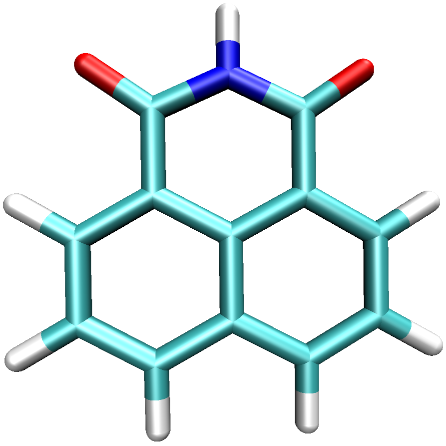
ESI-Figure 2: Succinimide station; oxygen atoms are in red, nitrogen in blue, carbon in cyan and hydrogen in white.

Charge from ESP fit (VSXC/6-311++G**/CPCM/Acetonitrile) :

C	-1.665910	-0.772872	-0.513254	.698931
O	-1.640269	-2.018964	-0.446343	-.578664
N	-0.526241	-0.042561	-0.792547	-.711218
C	-2.951735	0.014045	-0.338001	-.118306
C	-4.124822	-0.922426	-0.151495	-.200154
C	-5.398141	-0.136572	0.100419	.613901
O	-5.398856	1.107265	0.206631	-.580140
N	-6.564700	-0.864627	0.212237	-.476456
C	-7.836947	-0.266222	0.456364	-.071597

H	-8.546622	-0.514090	-0.379069	.072072
H	-8.268719	-0.654336	1.418680	.072809
H	-7.733010	0.849823	0.527502	.076122
C	0.777221	-0.637966	-0.869295	.266324
C	1.734980	-0.190916	0.258909	-.306502
C	2.986222	-1.013679	0.259848	.251278
C	3.592176	-1.314652	1.488041	-.271241
C	4.754800	-2.080750	1.534443	-.076568
C	5.326148	-2.558899	0.355238	-.194172
C	4.728972	-2.265557	-0.869539	-.090894
C	3.566565	-1.496339	-0.918480	-.258527
H	3.146796	-0.942030	2.422880	.152035
H	5.221179	-2.309270	2.504048	.133604
H	6.242557	-3.165369	0.392037	.145312
H	5.173525	-2.641850	-1.802653	.140662
H	3.108831	-1.276905	-1.894620	.130123
C	2.017595	1.275945	0.140903	.203225
C	1.351850	2.177935	0.980579	-.249288
C	1.586254	3.547680	0.870246	-.100952
C	2.486769	4.029959	-0.079070	-.158292
C	3.153616	3.136963	-0.917716	-.123260
C	2.920129	1.767296	-0.809398	-.188460
H	0.644993	1.804858	1.736936	.148244
H	1.060308	4.248097	1.535677	.139246
H	2.672057	5.110493	-0.164510	.139388
H	3.867409	3.512663	-1.665561	.140297
H	3.452775	1.062175	-1.466644	.128908
H	1.213294	-0.373271	1.246185	.116944
H	0.677422	-1.760495	-0.834990	.022464
H	1.229121	-0.344275	-1.860866	.033418
H	-0.560032	0.946759	-0.708654	.350614
H	-2.861487	0.689695	0.554352	.050550
H	-3.128604	0.668207	-1.232828	.062084
H	-4.241754	-1.566285	-1.063314	.057114
H	-3.927844	-1.607711	0.716184	.060102
H	-6.527062	-1.850815	0.126628	.348921

D. Naphtalimide Site *($ni^{\cdot-}$, radical anion):* Molecular Coordinates and ESP Charges



ESI-Figure 3: Naphtalimide station; oxygen atoms are in red, nitrogen in blue, carbon in cyan and hydrogen in white.

Charge from ESP fit (VSXC/6-311++G**/CPCM/Acetonitrile) :

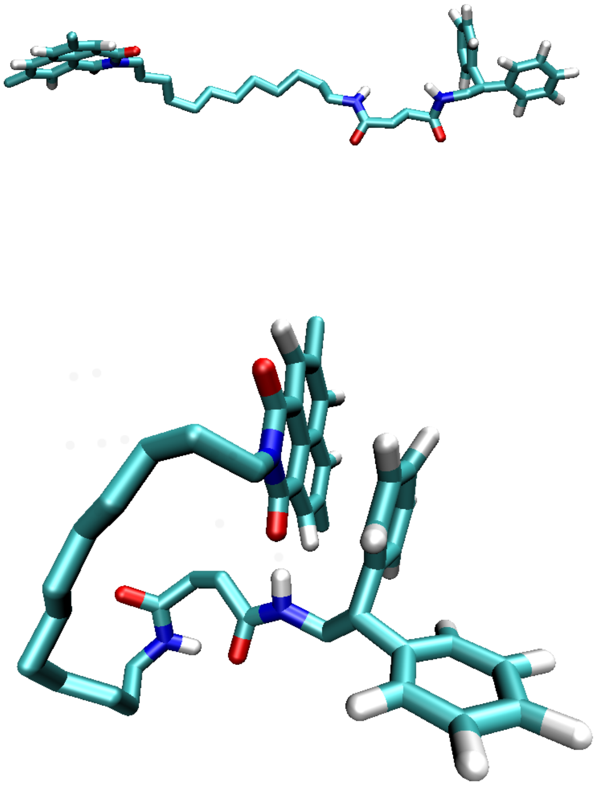
C	0.000000	1.247661	-2.541550	-0.296954
C	0.000000	0.000000	-1.854003	0.141352
C	0.000000	0.000000	-0.409043	0.239546
C	0.000000	1.250821	0.282390	-0.292755
C	0.000000	2.475728	-0.437849	-0.174909
C	0.000000	2.463640	-1.839062	-0.161898
C	0.000000	-1.250821	0.282390	-0.292755
C	0.000000	-1.256484	1.731331	0.693092
N	0.000000	0.000000	2.336728	-0.636724
C	0.000000	1.256484	1.731331	0.693092
C	0.000000	-1.247661	-2.541550	-0.296954
C	0.000000	-2.463640	-1.839062	-0.161898
C	0.000000	-2.475728	-0.437849	-0.174909
O	0.000000	2.291052	2.456212	-0.762576
O	0.000000	-2.291052	2.456212	-0.762576
H	0.000000	0.000000	3.365596	0.382494
H	0.000000	-3.404192	-2.389289	0.146976
H	0.000000	3.404192	-2.389289	0.146976
H	0.000000	3.406179	0.129595	0.131120
H	0.000000	1.230002	-3.633774	0.154570
H	0.000000	-1.230002	-3.633774	0.154570
H	0.000000	-3.406179	0.129595	0.131120

E. Naphtalimide Site *(ni, neutral):* Molecular Coordinates and ESP Charges

Charge from ESP fit (VSXC/6-311++G**/CPCM/Acetonitrile) :

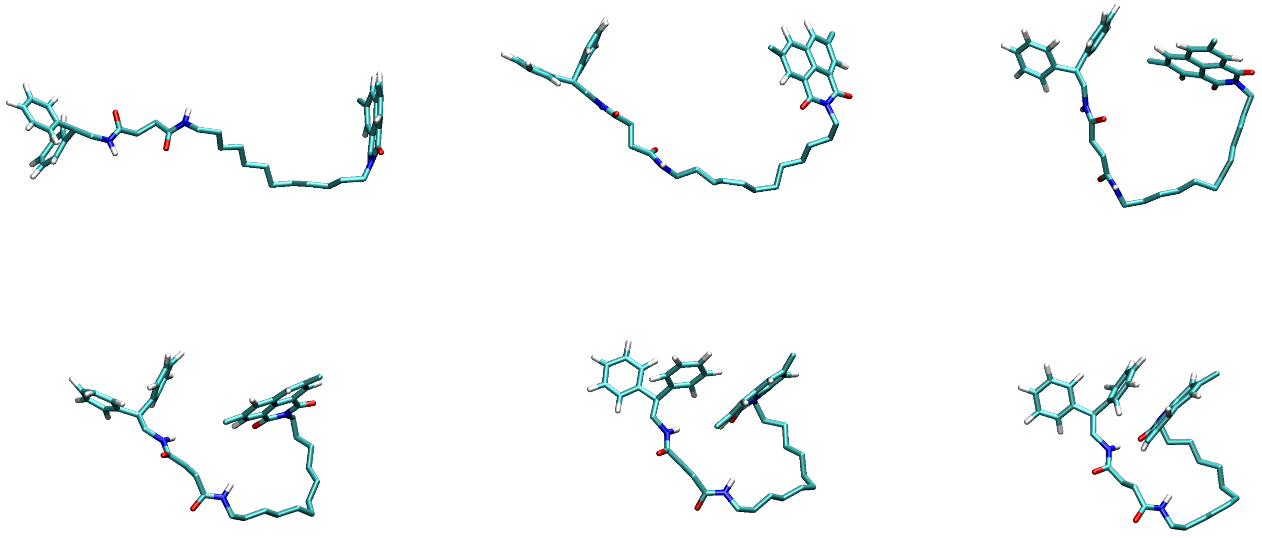
C	0.000000	1.250327	-2.541074	-.204924
C	0.000000	0.000000	-1.857889	.131816
C	0.000000	0.000000	-0.411173	.256513
C	0.000000	1.251008	0.277967	-.295858
C	0.000000	2.475691	-0.433895	-.038584
C	0.000000	2.465570	-1.834853	-.142837
C	0.000000	-1.251008	0.277967	-.295858
C	0.000000	-1.263783	1.734192	.766468
N	0.000000	0.000000	2.333636	-.636604
C	0.000000	1.263783	1.734192	.766468
C	0.000000	-1.250327	-2.541074	-.204924
C	0.000000	-2.465570	-1.834853	-.142837
C	0.000000	-2.475691	-0.433895	-.038584
O	0.000000	2.290894	2.453031	-.642984
O	0.000000	-2.290894	2.453031	-.642984
H	0.000000	0.000000	3.347757	.398327
H	0.000000	-3.405878	-2.384027	.166182
H	0.000000	3.405878	-2.384027	.166182
H	0.000000	3.397391	0.143606	.140509
H	0.000000	1.232842	-3.632260	.177002
H	0.000000	-1.232842	-3.632260	.177002
H	0.000000	-3.397391	0.143606	.140509

F. Representative configurations of the two free energy minima of $1/1^-$.



ESI-Figure 4: Helmoltz (300K) Free energy minima: neutral (upper) and radical anion (bottom), respectively. Oxygen atoms are in red, nitrogen in blue, carbon in cyan and hydrogen in white.

G. Spring-like conformational transition of $\mathbf{1}^-$



ESI-Figure 5: Snapshots of the spring-like conformational transition of $\mathbf{1}^-$ after the reduction of *ni*-site. Oxygen atoms are in red, nitrogen in blue, carbon in cyan and hydrogen in white.