Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Gating the Conductance of Extended Metal Atom Chains: a Computational Analysis of $Ru_3(dpa)_4(NCS)_2$ and $[Ru_3(npa)_4(NCS)_2]$

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Supporting Information

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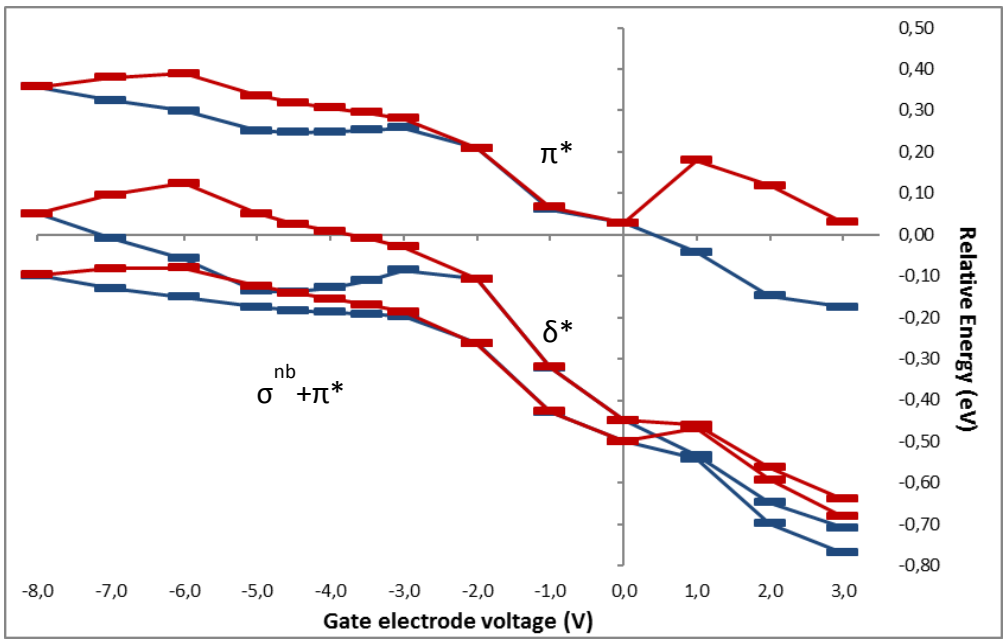
Table S1. Effect of the relativistic effects —scalar or spin-orbit coupling— on the electronic structure of the EMAC system $\mathbf{2}^{+}$. Listed are the computed LUMO and HOMO–*n* energies (in eV, higher energies first) for $Ru_3(npa)_4(NCS)_2^{+}$ ($\mathbf{2}^{+}$) and for a model system composed of one Ru center and its environment based on the real EMAC system, i.e. $RuCa(Py)_4(NCS)^{3+}$. The absolute energies of the latter case must not be compared to the full system because of the molecular charge difference.

Calculation details: B3LYP functional, all-electron TZP basis set, single point runs.

System	Scalar effects	Spin-orbit coupling	Orbital
$Ru_3(npa)_4(NCS)_2^{+}$ (S = 1/2)	–6.712	–6.502	LUMO
	–7.755	–7.836	HOMO
	–7.825	–7.862	HOMO–1
	–7.849	–7.912	HOMO–2
	–7.874	–7.975	HOMO–3
$RuCa(Py)_4(NCS)^{3+}$ (S = 1)	–13.968	–13.986	LUMO
	–15.036	–15.082	HOMO
	–15.322	–15.336	HOMO–1
	–15.487	–15.468	HOMO–2
	–15.554	–15.595	HOMO–3

A)



B)

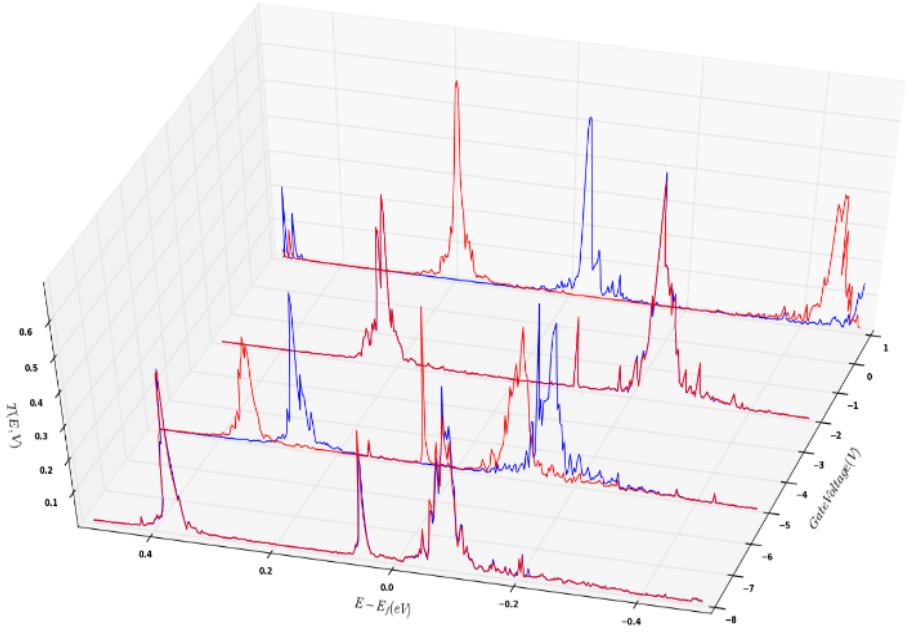


Figure S1. A) Molecular projected self-consistent Hamiltonian (MPSH) eigenvalues (left) and B) transmission spectra (right) and for $Ru_3(dpa)_4(NCS)_2$ (**1**) as a function of gate voltage.

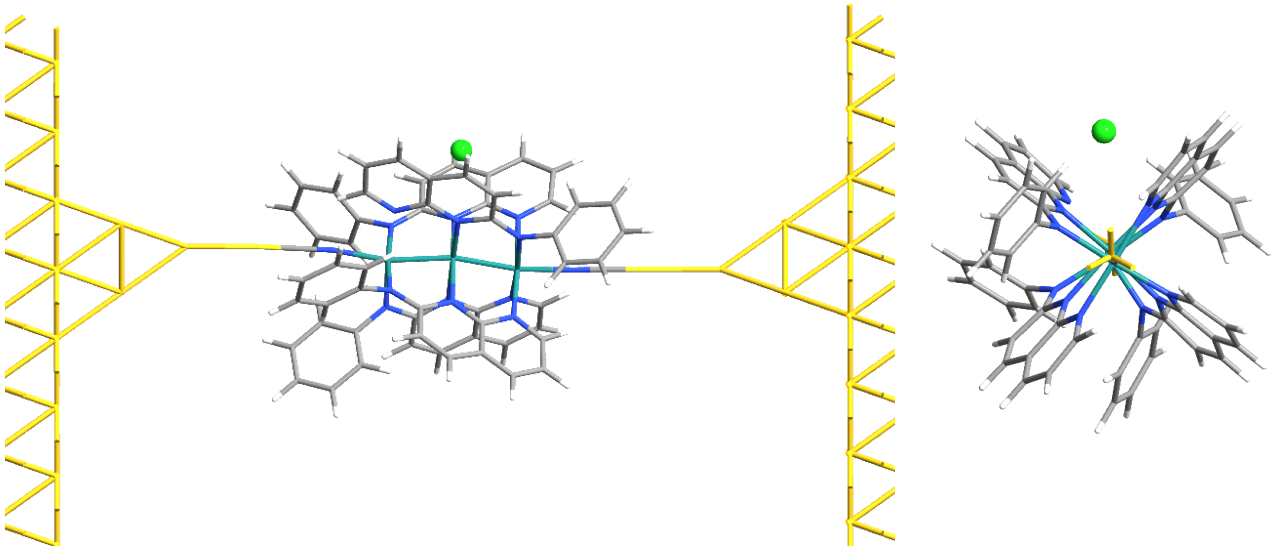


Figure S2. Device configuration with species **2** and the heteroatom (X = Na, Cl as a green sphere) with perpendicular (left) and parallel (right) views to the chain.

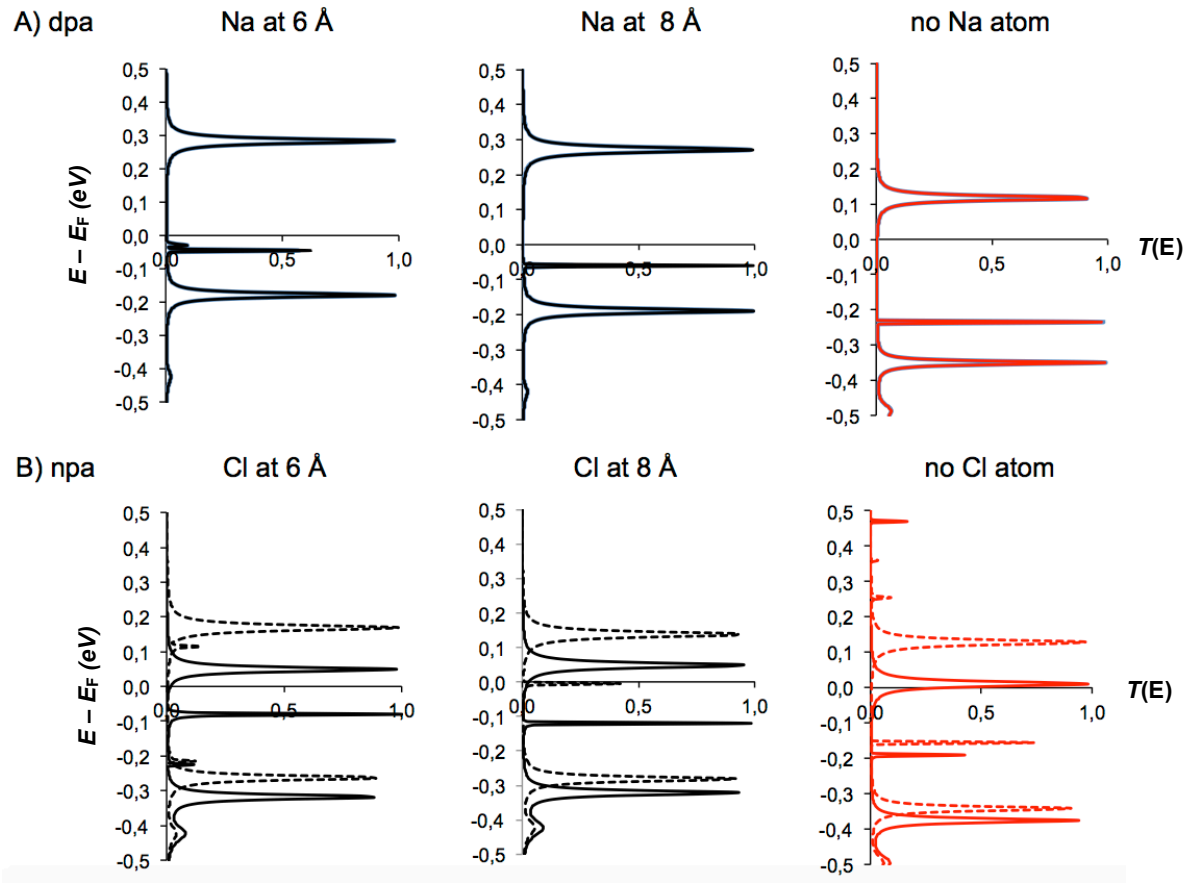


Figure S3. Calculated transmission spectra for A) the dpa and B) the npa systems with additional Na or Cl atoms located in the unit cell at different distances from the EMAC molecule (black curves). The red curves to the right represent the situation without the extra atoms in the cell.

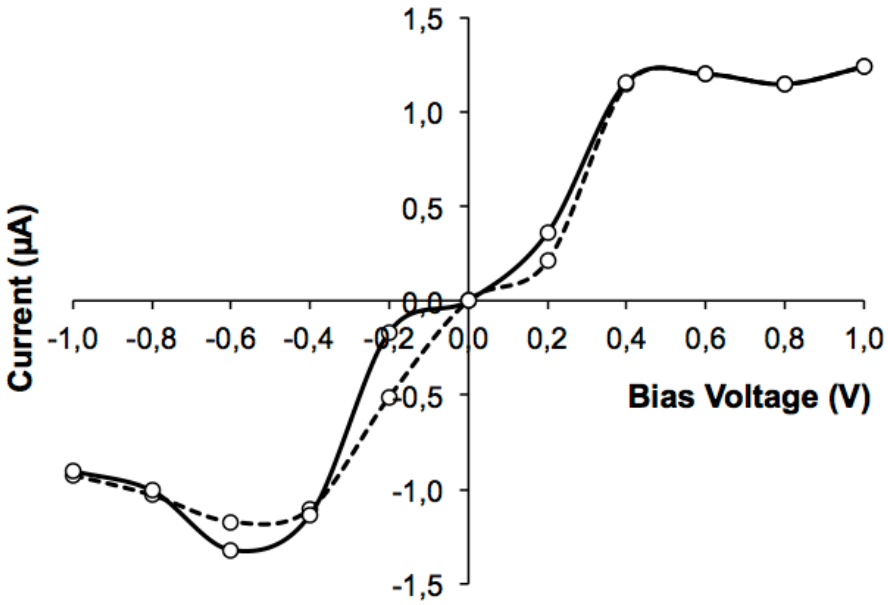


Figure S4. Calculated current (µA) as a function of the applied voltage (V) for compound **2***, the 2:2 isomer of **2**. Solid and blue lines denote spin-α and spin-β contributions.