Supplementary Materials

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Overview of Calculations of Electron Transfer Integral

The electron transfer (ET) module implemented in NWChem quantum chemistry package utilizes the method of *Corresponding Orbital Transformation*[1-3] to calculate electron transfer integral t (also called the electron transfer matrix element). The calculation proceeded in the following steps:

(i) Optimization of geometry of nMPSi chain on energy potential surface constructed by DFT (CAM-B3LYP/6-31G*) method in the neutral electronic ground state.

(ii) Optimization of geometry of nMPSi chain on energy potential surface constructed by DFT (CAM-B3LYP/6-31G*) method in the cationic doublet electronic state. Here the geometry obtained for the neutral electronic ground state was used as the starting point in the optimization process.

(iii) The nMPSi chain in the configuration optimized for the cationic doublet electronic state is divided into two parts of the same length (n/2).

(iv) Using *Corresponding Orbital Transformation Method*[1–3] within unrestricted Hartree-Fock approximation we calculated orbital energies and expansion coefficients for the individual parts of the n-MPSi chain. The reactant (R) and product (P) states were localized on the left- and right-hand part of the n-MPSi chain, respectively (Fig. S3). Wave functions for the state R (reactant state within the electronic doublet state) and for the state P (product state within the electronic doublet state) were then used for the calculation of the transfer integral [cf. equation (2) in the main article] (Tab. S1). Alternatively, it is possible to calculate the transfer integral from the splitting of the highest occupied orbitals. In such a case, $t^{+} = (E_{\mathrm{HOMO}} - E_{\mathrm{HOMO\text{-}1}})/2$ where E_{HOMO} and $E_{\mathrm{HOMO\text{-}1}}$ are highest occupied orbital energies of n-MPSi in the neutral electronic state.

(v) Evaluation of the transfer integral is possible only for rather short n-MPSi oligomers ($n \leq 20$). Since the transfer integral typically exponentially decreases with increasing transfer distance, we fitted the calculated values by an exponential function (Figs. S1 and S2) and estimated the transfer integral for a 40mer on the basis of this fit.

Calculations of Reorganization Energy

States involved in the calculations of the reorganization energy are schematically shown in Fig. S4. The results obtained for various oligomer lengths are summarized in Tab. S2. Note that the reorganization energy is calculated for the individual parts of the n-MPSi oligomer, i.e., for the chains consisting of n/2 units.

Fig. S1. Transfer integral calculated using Corresponding Orbital Transformation Method as a function of the oligomer MPSi length. The best fit was achieved with the function $t(n) = 6157.8\ e^{-0.1876n}$ meV ($R^2 = 0.9700$).

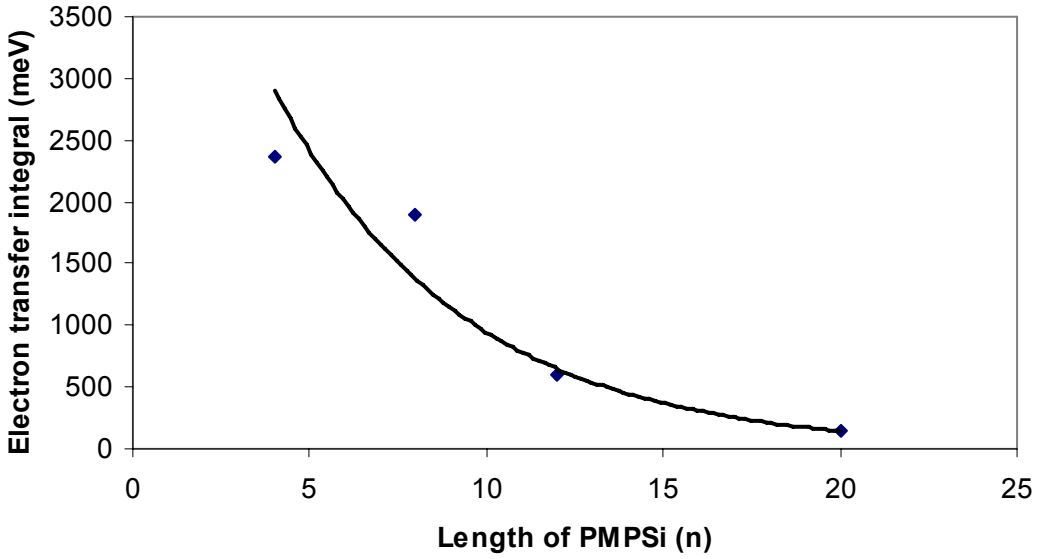
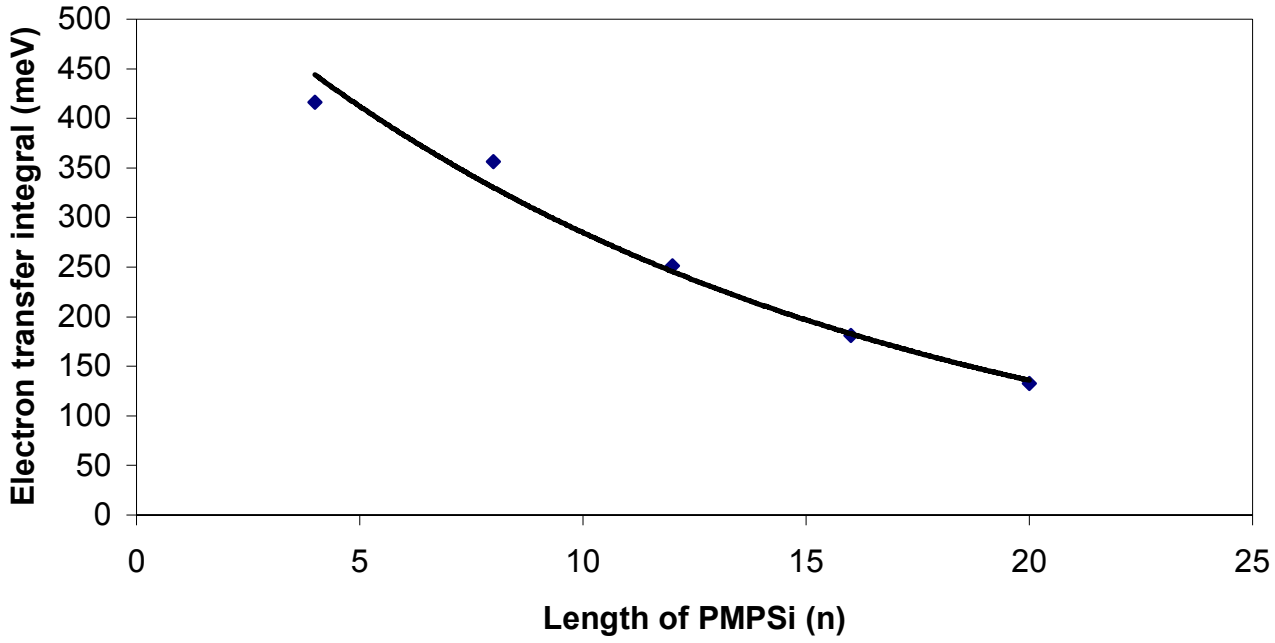


Fig. S2. Transfer integral calculated from the splitting of HOMOs orbitals as a function of the oligomer MPSi length. The best fit was achieved with the function $t(n) = 596.52\ e^{-0.0739n}$ meV ($R^2 = 0.9877$).



Tab. S1. Values of reorganization energy λ^+, effective length of hole transfer L, transfer integral t^+ and charge carrier mobility μ calculated for oligomers of different length. Superscripts denote the method employed as specified in the Table.

nMPSi	λ^+	L	t^+ (HF)[a]	t^+(DFT)[b]	μ^a	μ^b
n	(eV)	(Å)	(meV)		($cm^2V^{-1}s^{-1}$)	
32	0.560	28.91	15.2	56.1	7.4×10^{-2}	10.0×10^{-1}
34	0.563	30.76	10.5	48.4	3.9×10^{-2}	8.3×10^{-1}
36	0.551	32.80	7.2	41.7	2.4×10^{-2}	7.9×10^{-1}
40	0.548	36.71	3.4	31.0	6.8×10^{-3}	5.7×10^{-1}
[a] Calculated using Corresponding Orbital Transformation Method						
[b] Calculated from splitting of HOMOs						

Tab. S2. Results of calculations of reorganization energies λ^+ and transfer integrals for n/2-MPSi oligomers.

n/2-MPSi	B3LYP/6-31G*			CAM-B3LYP/6-31G*				
	λ^+_1	λ^+_2	λ^+	λ^+_1	λ^+_2	λ^+	t^{+a}	t^{+b}
n/2	(eV)	(eV)	(eV)	(eV)	(eV)	(eV)	(meV)	(meV)
4 mer	0.263	0.343	0.606	0.389	0.470	0.858	2377	416
8 mer	0.216	0.244	0.460	0.328	0.356	0.684	1984	356
12 mer	0.174	0.191	0.365	0.286	0.317	0.603	605	251
16 mer	0.136	0.148	0.285	0.261	0.300	0.560	c	181
20 mer	0.106	0.116	0.223	0.249	0.299	0.548	138	133

[a] Calculated using Corresponding Orbital Transformation Method

[b] Calculated from splitting of HOMOs

[c] Not converged

Fig. S3. Charge transport over PMPSi oligomer.

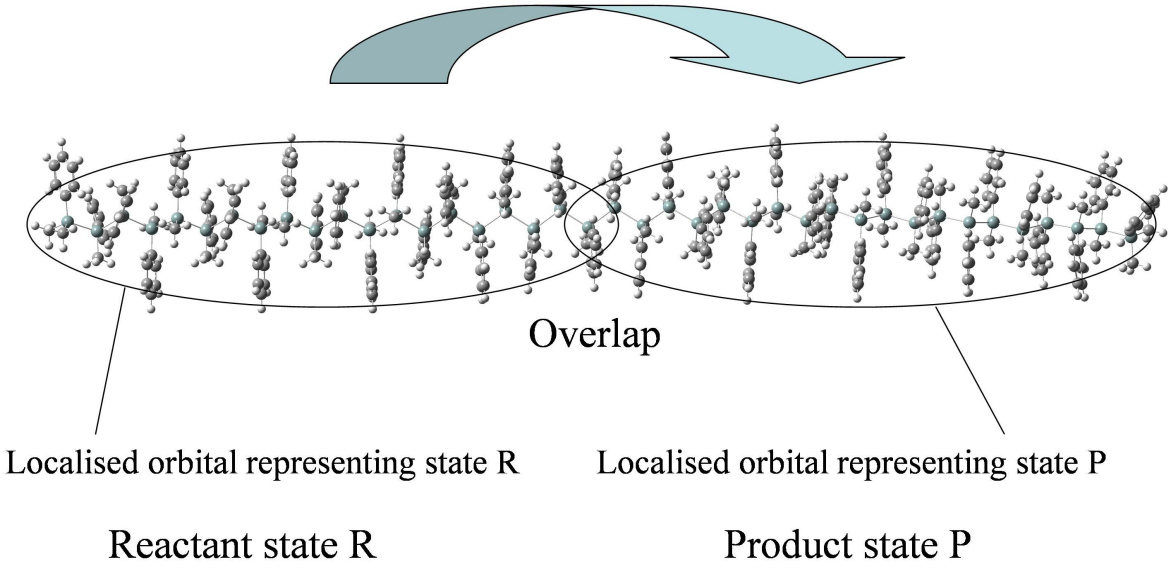
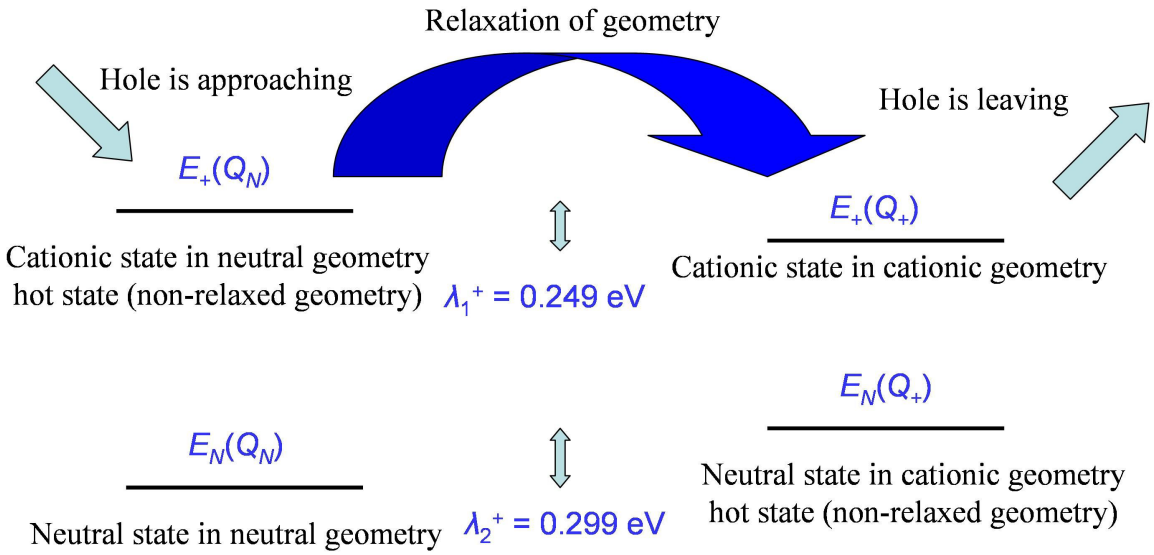


Fig. S4. Electronic states and scheme of reorganization energy calculations for PMPSi oligomer (the values are provided for n/2 = 20).



References:

1. R.A. Marcus, N. Sutin, Biochimica Biophysica Acta **35**, 437, (1985).
2. J.R. Bolton, N. Mataga, and G. McLendon in ”Electron Transfer in Inorganic, Organic and Biological Systems“ (American Chemical Society, Washington, D.C., 1991).
3. A. Farazdel, M. Dupuis, E. Clementi, and A. Aviram, J. Am. Chem. Soc. **112**, 4206 (1990).