Supplementary Material

Deposited as separate files:

bipydiol.35.mp4: Movie of the bipydiol photoisomerization. Shown is the HOMO.

bipydiol.36.mp4: Movie of the bipydiol photoisomerization. Shown is the LUMO.

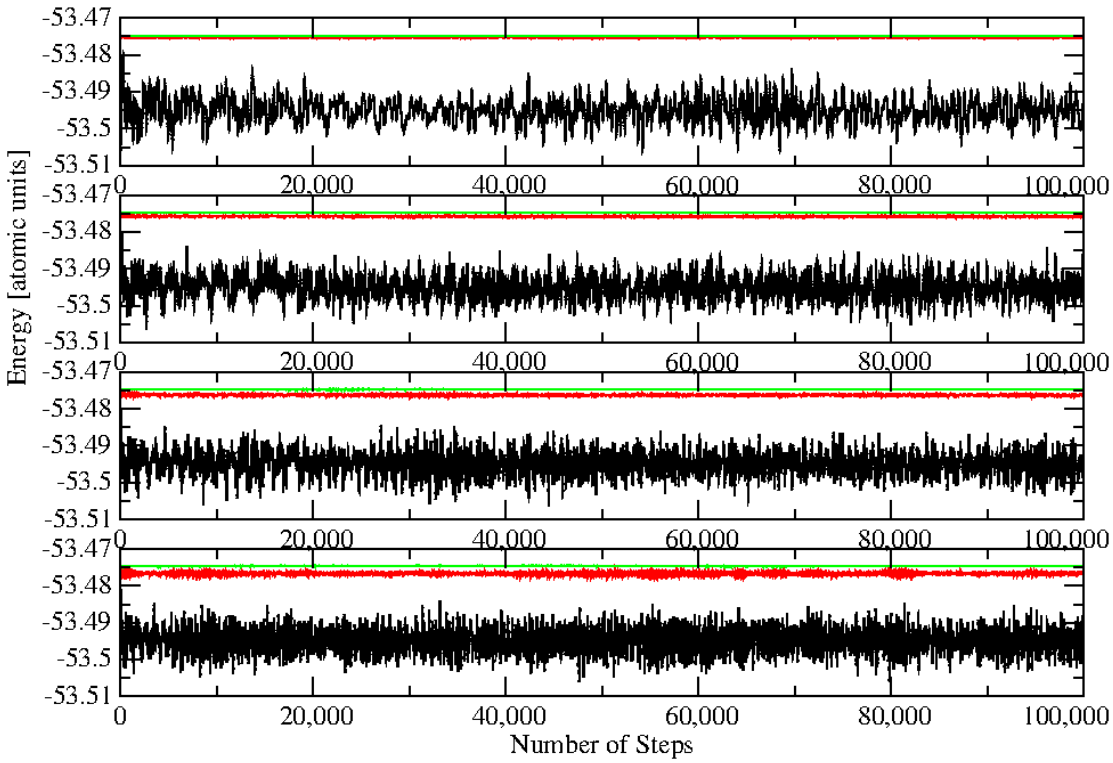

Figure S1. Stability test: Ground state CPMD simulations of phenol for 100000 steps using timesteps of 1, 2, 3, and 4 atomic units, respectively. Unit cell: 18 atomic units, plane-wave cutoff: 70 Rydberg. Simulation times: 2, 5, 7, and 10 ps. Total CPU times: 200, 192, 187, and 188 minutes on 16 cores. Plotted are the Kohn-Sham energy (black), the total energy (red), and the CPMD energy (green). The difference between the Kohn-Sham energy and the total energy corresponds to the kinetic energy of the nuclei. The difference between the total energy and the CPMD energy corresponds to the fictitious kinetic energy of the electrons. The simulations are perfectly stable. For a timestep of 8 atomic units (not shown), CPMD fails completely. This is a frequently observed pattern: CPMD is either perfectly stable or fails completely.

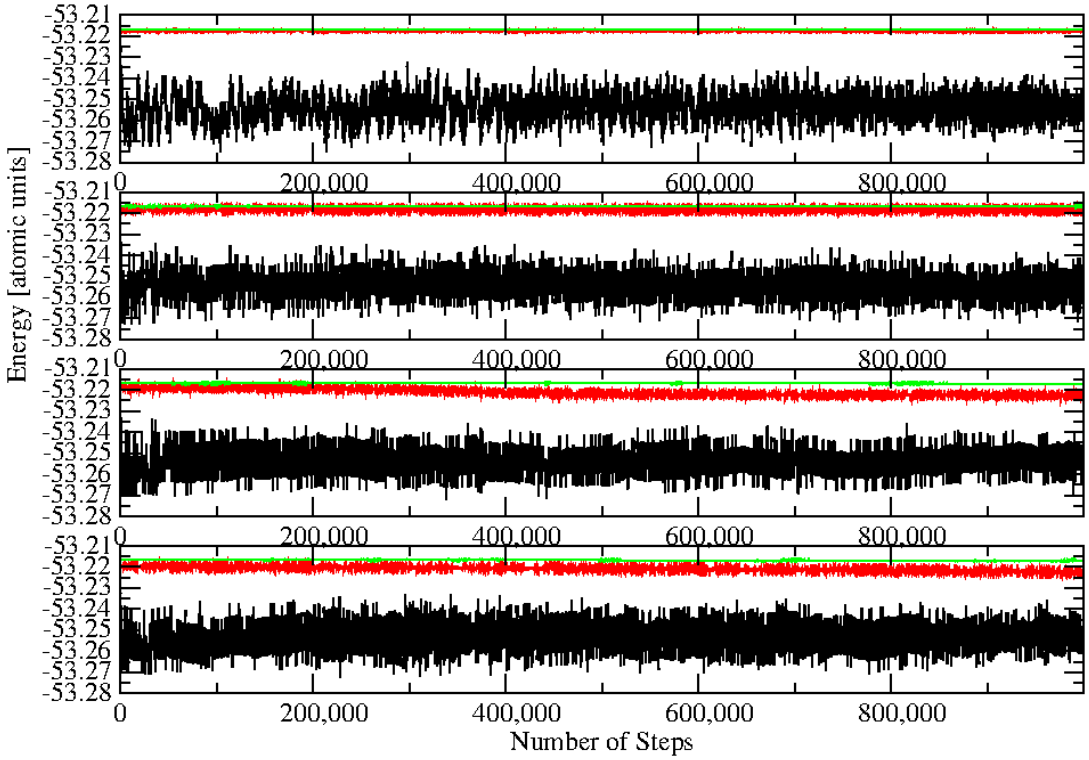

Figure S2. Stability test: Ground state CPMD simulations of phenol for 1000000 steps using timesteps of 1, 2, 3, and 4 atomic units, respectively. Unit cell: 12 atomic units, plane-wave cutoff: 50 Rydberg. Simulation times: 24, 48, 73, and 97 ps. Total CPU times: 355, 363, 338, and 343 minutes on 16 cores. Plotted are the Kohn-Sham energy (black), the total energy (red), and the CPMD energy (green). Also in these longer calculations, the energies are conserved. A slight drift starts for timesteps larger than 2 atomic units (0.05 fs).

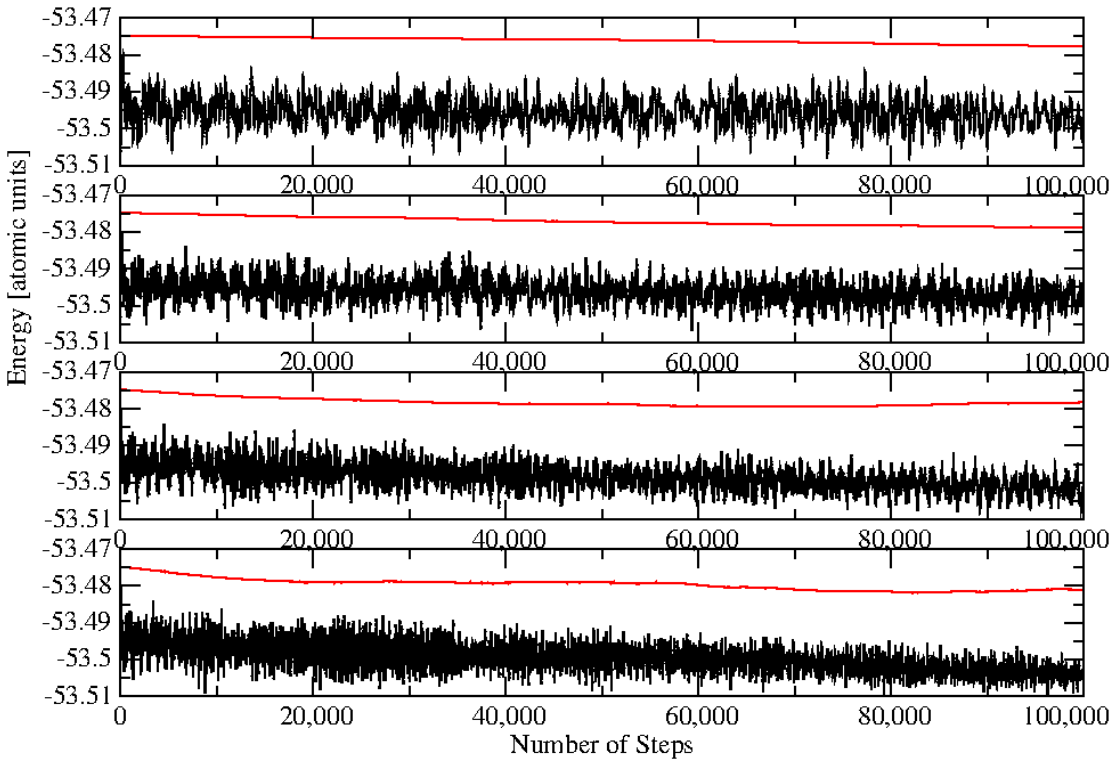

Figure S3. Stability test: Ground state BOMD simulations of phenol for 100000 steps using timesteps of 1, 2, 3, and 4 atomic units, respectively. Unit cell: 18 atomic units, plane-wave cutoff: 70 Rydberg. Simulation times: 2, 5, 7, and 10 ps. Total CPU times: 1339, 1373, 1432, and 1535 minutes on 16 cores. Plotted are the Kohn-Sham energy (black) and the total energy (red). There is a drift in total energy which forbids to use timesteps much larger than 4 atomic units (0.10 fs).

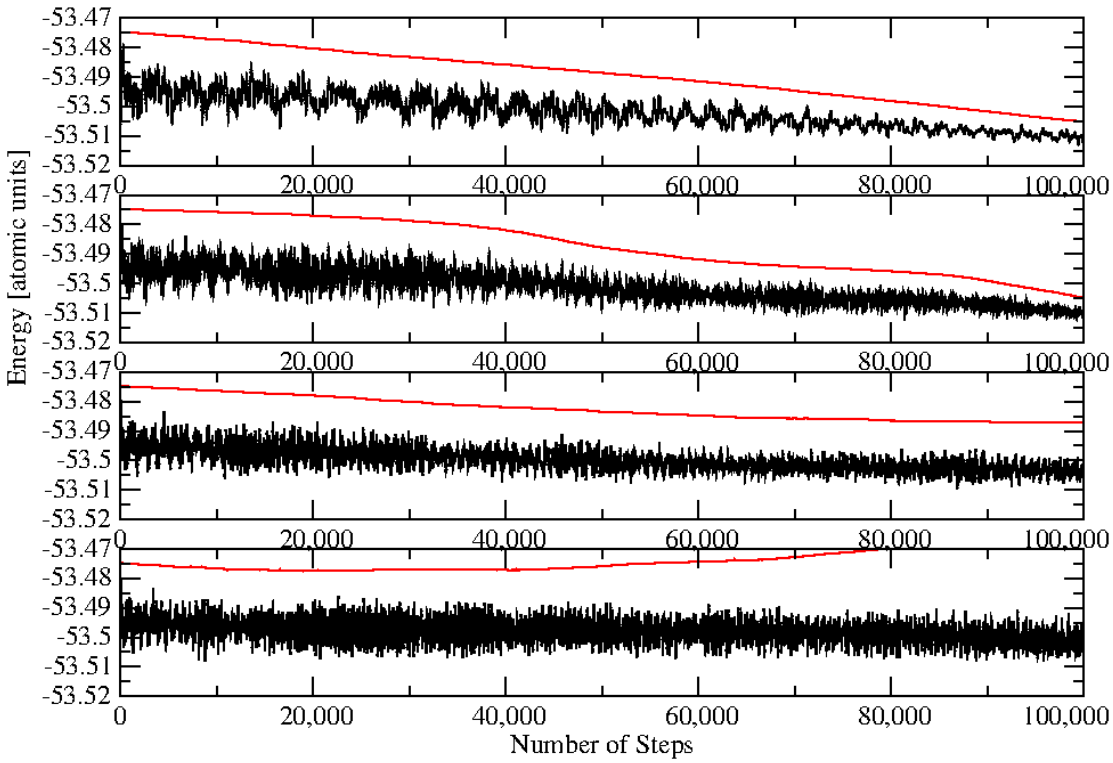

Figure S4. Stability test: Ground state BOMD simulations of phenol for 100000 steps using timesteps of 1, 2, 3, and 4 atomic units, respectively. Unit cell: 18 atomic units, plane-wave cutoff: 70 Rydberg. Simulation times: 2, 5, 7, and 10 ps. The convergence criterion for the wavefunction was loosened from 0.00001 to 0.00002 atomic units. Total CPU times: 1007, 1189, 1344, and 1416 minutes on 16 cores. Plotted are the Kohn-Sham energy (black) and the total energy (red). A clear drift is observed. Obviously, saving CPU time by changing the convergence criterion is not an option.

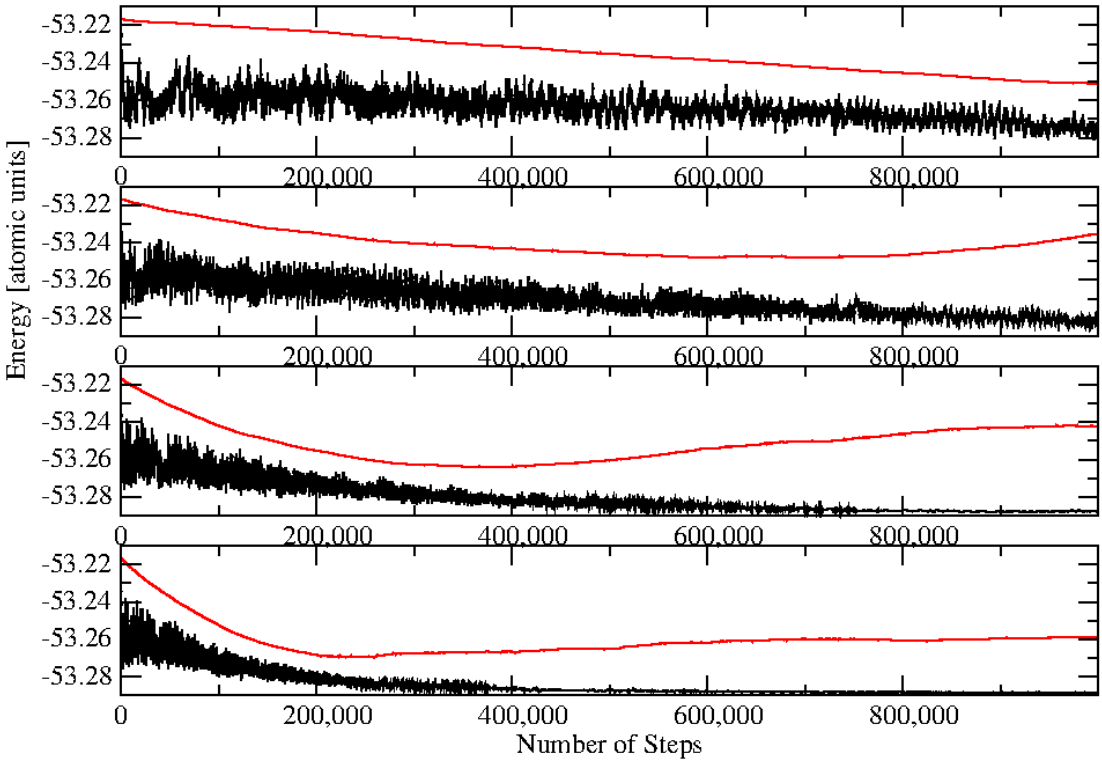

Figure S5. Stability test: Ground state BOMD simulations of phenol for 1000000 steps using timesteps of 1, 2, 3, and 4 atomic units, respectively. Unit cell: 12 atomic units, plane-wave cutoff: 50 Rydberg. Simulation times: 24, 48, 73, and 97 ps. Total CPU times: 2383, 2696, 2856, and 2976 minutes on 16 cores. Plotted are the Kohn-Sham energy (black) and the total energy (red). The drift in long-time simulations is stronger than for CPMD.

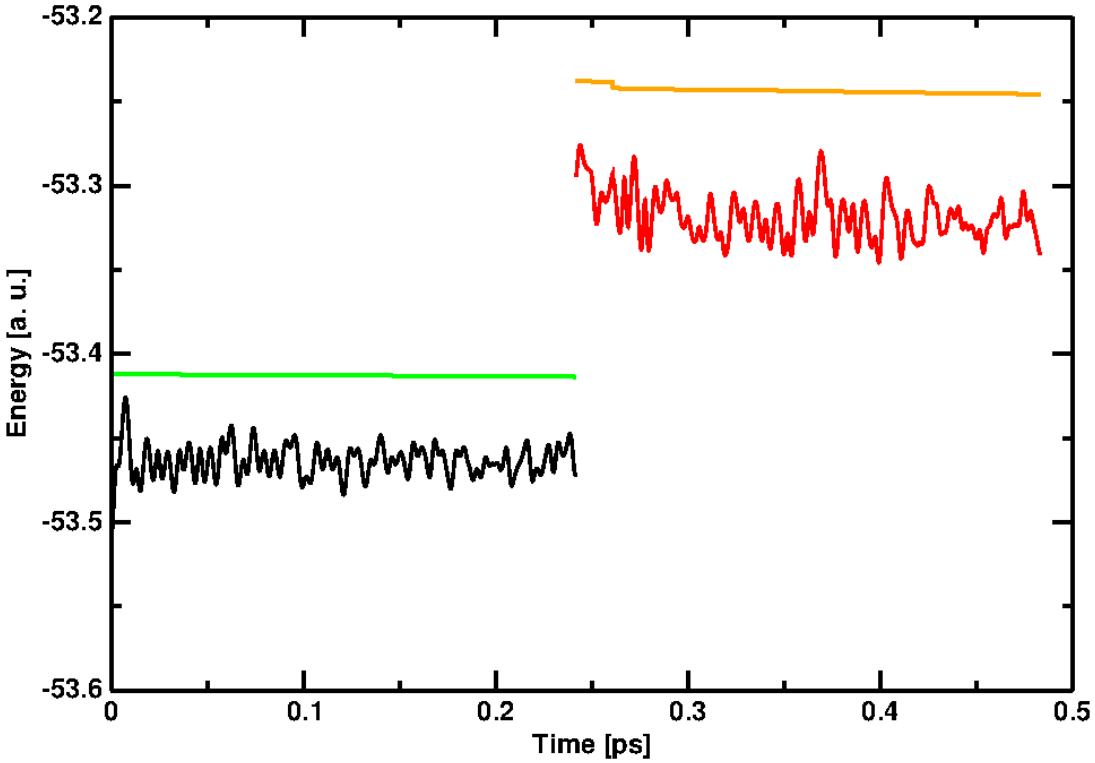

Figure S6. Energies during the photodissociation of phenol, BOMD simulation. For the simulation parameters see the Methods section. Black and green: ground state Kohn-Sham and total energy. Red and orange: excited state Kohn-Sham and total energy. The transition between ground and excited state is vertical.

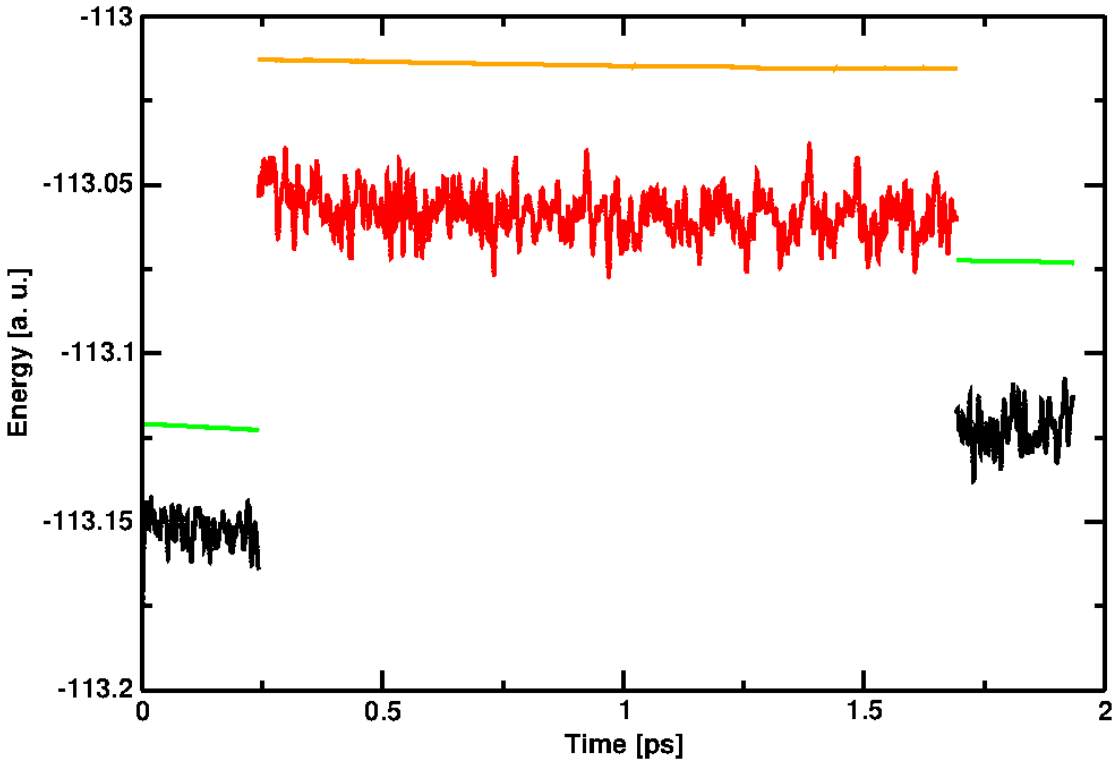

Figure S7. Energies during the photoisomerization of [2,2'-bipyridyl]-3,3'-diol, BOMD simulation. For the simulation parameters see the Methods section. Black and green: ground state Kohn-Sham and total energy. Red and orange: excited state Kohn-Sham and total energy. The transitions between ground and excited state are vertical.

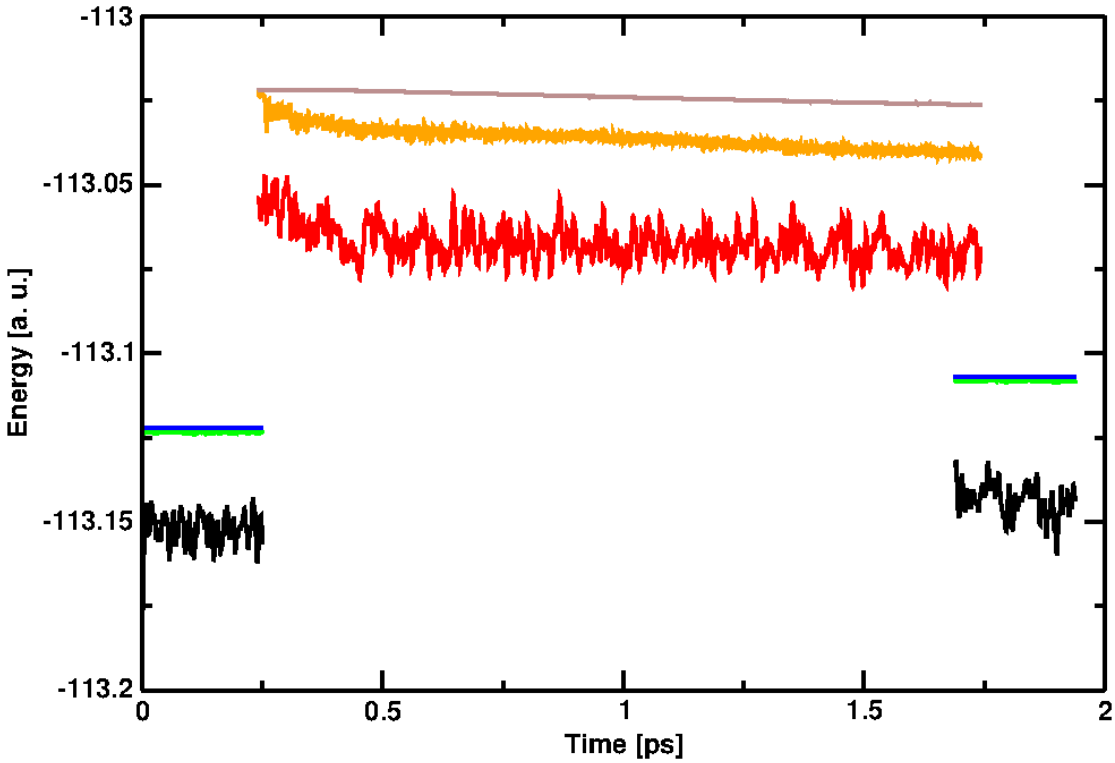

Figure S8. Energies during the photodissociation of [2,2'-bipyridyl]-3,3'-diol, CPMD simulation. For the simulation parameters see the Methods section. Black, green, and blue: ground state Kohn-Sham energy, total energy, and CPMD energy. Red, orange, and brown: excited state Kohn-Sham, total energy, and CPMD energy. The transition between ground and excited state is vertical. The kinetic energy of the electrons should be small. This is not fulfilled in the excited state simulation. Here, BOMD is the method of choice.