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

Ultrafast intersystem crossing for nitrophenols: Ab initio nonadiabatic molecular dynamic simulation

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Supplementary information

Table S1. Vertical excitation/de-excitation energies calculated at 6SA-CASSCF(12,9) /6-31G(d,p) level for all four minima, five intersystem crossings and one conical intersection for both PNP and MNP system with including correction by MRCI and CASPT2 methods at CASSCF optimized geometries.

Geometry	S0			S1			T1			T2		
	CAS SCF	MRCI	PT2	CAS SCF	MRCI	PT2	CAS SCF	MRCI	PT2	CAS SCF	MRCI	PT2
MNP-S0	0.00	0.00	0.00	3.81	4.20	4.13	2.94	3.64	3.62	3.65	3.93	3.89
MNP-S1	1.51	1.89	1.93	2.75	3.39	3.37	2.21	2.99	3.01	2.65	3.23	3.24
MNP-T1	1.19	1.54	1.57	2.82	3.46	3.43	2.08	2.89	2.90	2.71	3.27	3.26
MNP-T2	1.38	1.52	1.55	2.75	3.37	3.36	2.20	3.06	3.07	2.65	3.20	3.22
MNP-S0S1	3.22	3.84	3.85	3.22	3.86	3.84	2.95	3.59	3.61	3.35	4.04	4.04
MNP-S0T1	2.54	3.10	3.12	3.02	3.66	3.64	2.55	3.24	3.26	3.03	3.66	3.66
MNP-S0T2	3.35	4.02	4.04	3.37	4.05	4.05	3.22	3.88	3.90	3.38	4.10	4.11
MNP-S1T1	2.59	2.80	2.84	3.35	3.70	3.73	3.24	3.58	3.72	3.27	3.68	3.63
MNP-S1T2-1	2.48	3.01	3.02	2.98	3.58	3.56	2.55	3.23	3.27	2.98	3.58	3.58
MNP-S1T2-2	2.40	2.86	2.88	2.99	3.57	3.55	2.53	3.17	3.20	2.99	3.58	3.56
PNP-S0	0.00	0.00	0.00	3.89	4.28	4.02	3.02	3.73	3.71	3.72	4.01	3.96
PNP-S1	1.89	1.85	1.88	2.79	3.45	3.42	2.31	3.05	3.08	2.70	3.28	3.28
PNP-T1	1.26	1.62	1.66	2.88	3.54	3.50	2.15	2.96	2.98	2.77	3.34	3.34
PNP-T2	1.62	2.30	2.32	2.80	3.48	3.47	2.28	3.14	3.16	2.69	3.32	3.34
PNP-S0S1	3.23	3.86	3.85	3.23	3.84	3.85	2.97	3.60	3.63	3.36	4.03	4.04
PNP-S0T1	2.60	3.16	3.19	3.08	3.73	3.71	2.60	3.30	3.33	3.09	3.73	3.73
PNP-S0T2	3.19	3.93	3.94	3.22	3.98	4.00	3.06	3.83	3.86	3.23	4.01	4.03
PNP-S1T1	3.01	3.43	3.49	3.70	4.30	4.35	3.53	4.24	4.31	3.66	4.23	4.30
PNP-S1T2-1	2.53	3.06	3.08	3.00	3.60	3.59	2.60	3.28	3.31	3.00	3.62	3.61
PNP-S1T2-2	2.43	3.08	3.09	2.89	3.87	3.58	2.48	3.27	3.31	2.89	3.61	3.60

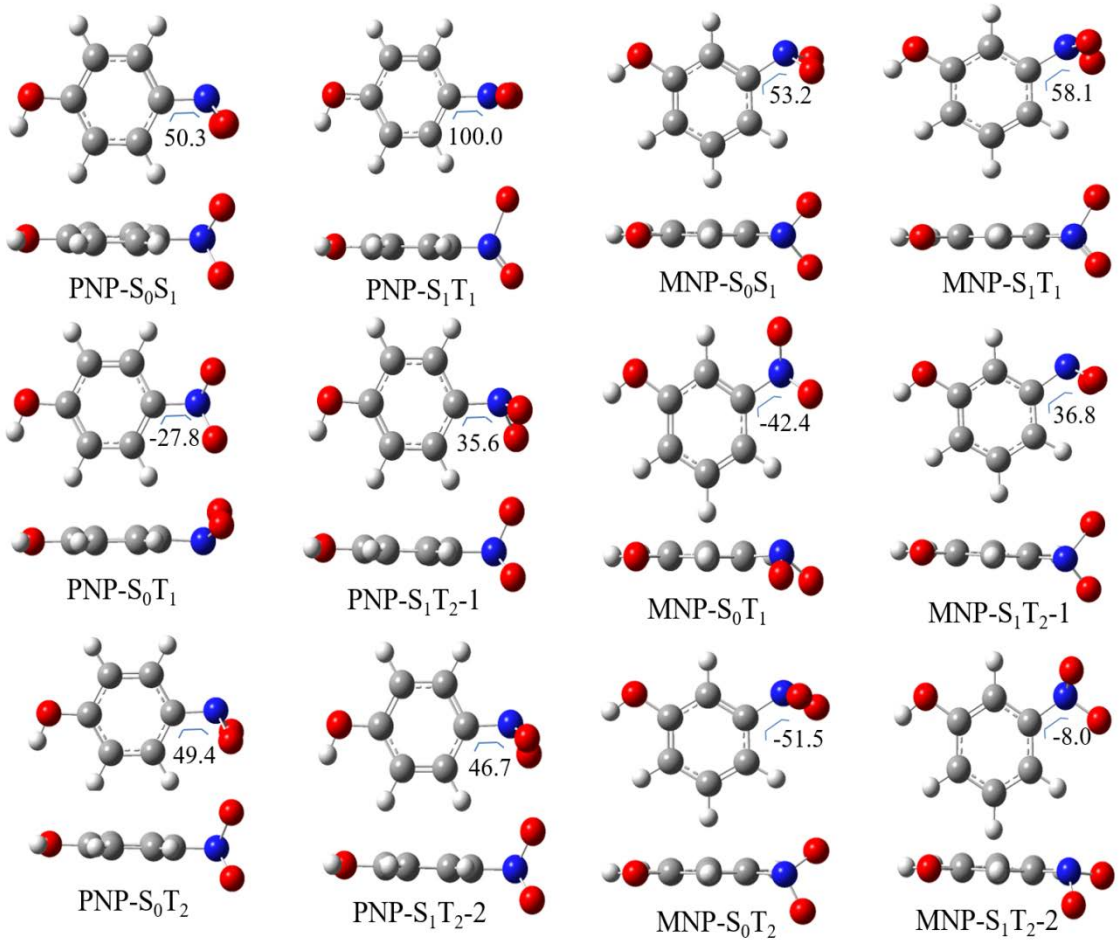

Fig. S1 Electronic structures corresponding to the five intersystem crossings and one conical intersection among S_0, S_1, T_1 and T_2 potential energy surfaces associated with torsion dihedral angle $C_2C_3N_{13}O_{14}$, respectively for PNP and MNP systems.

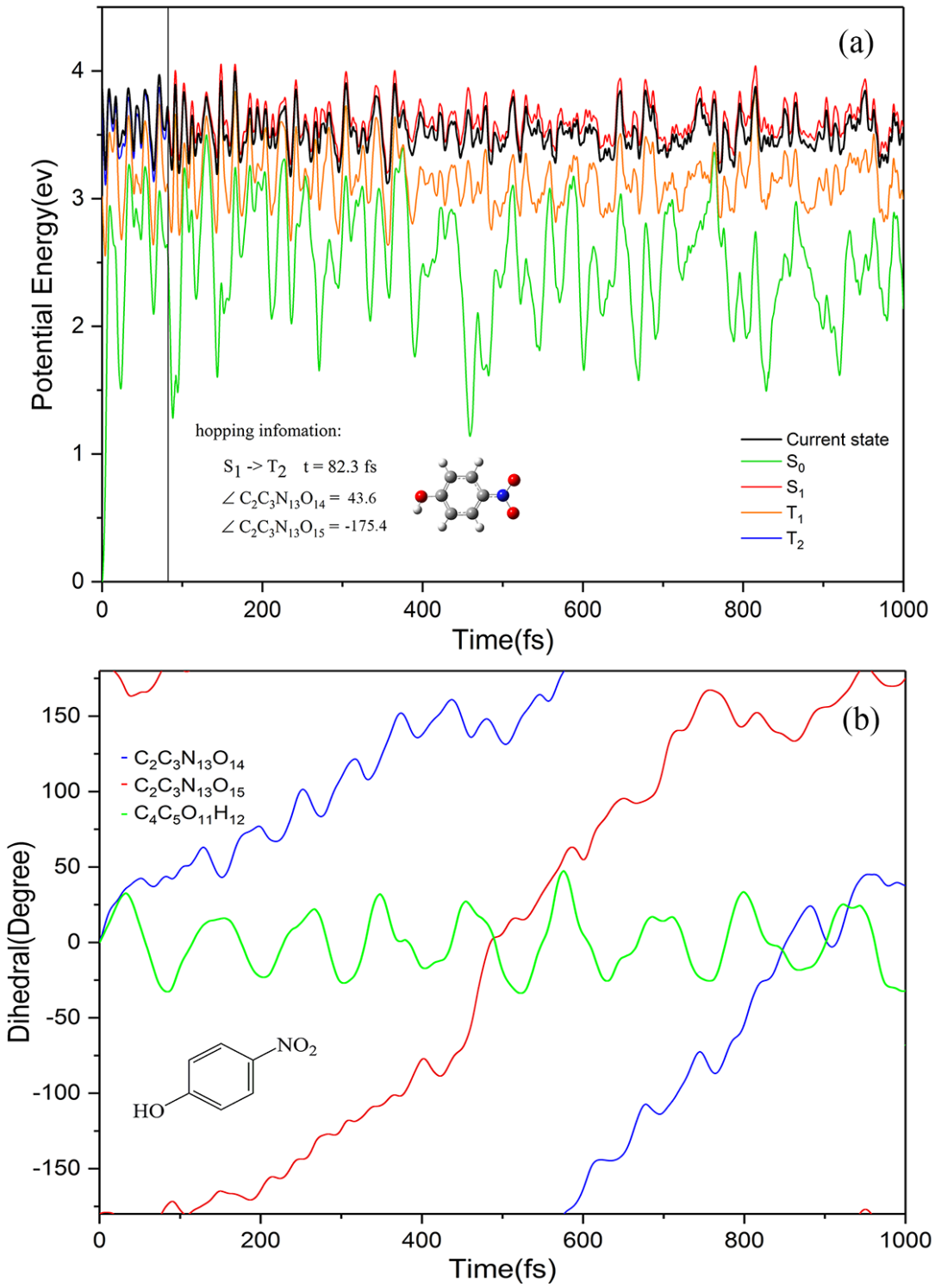

Fig. S2 A typical trajectory for $S_1 \rightarrow T_2$ relaxation pathway in terms of evolution time for PNP system. (a) Potential energy profile with one-step intersystem crossing via S1T2-1 and then stays on T2 as resonance trajectory, and (b) oscillatory motion of the three torsion dihedral angles.

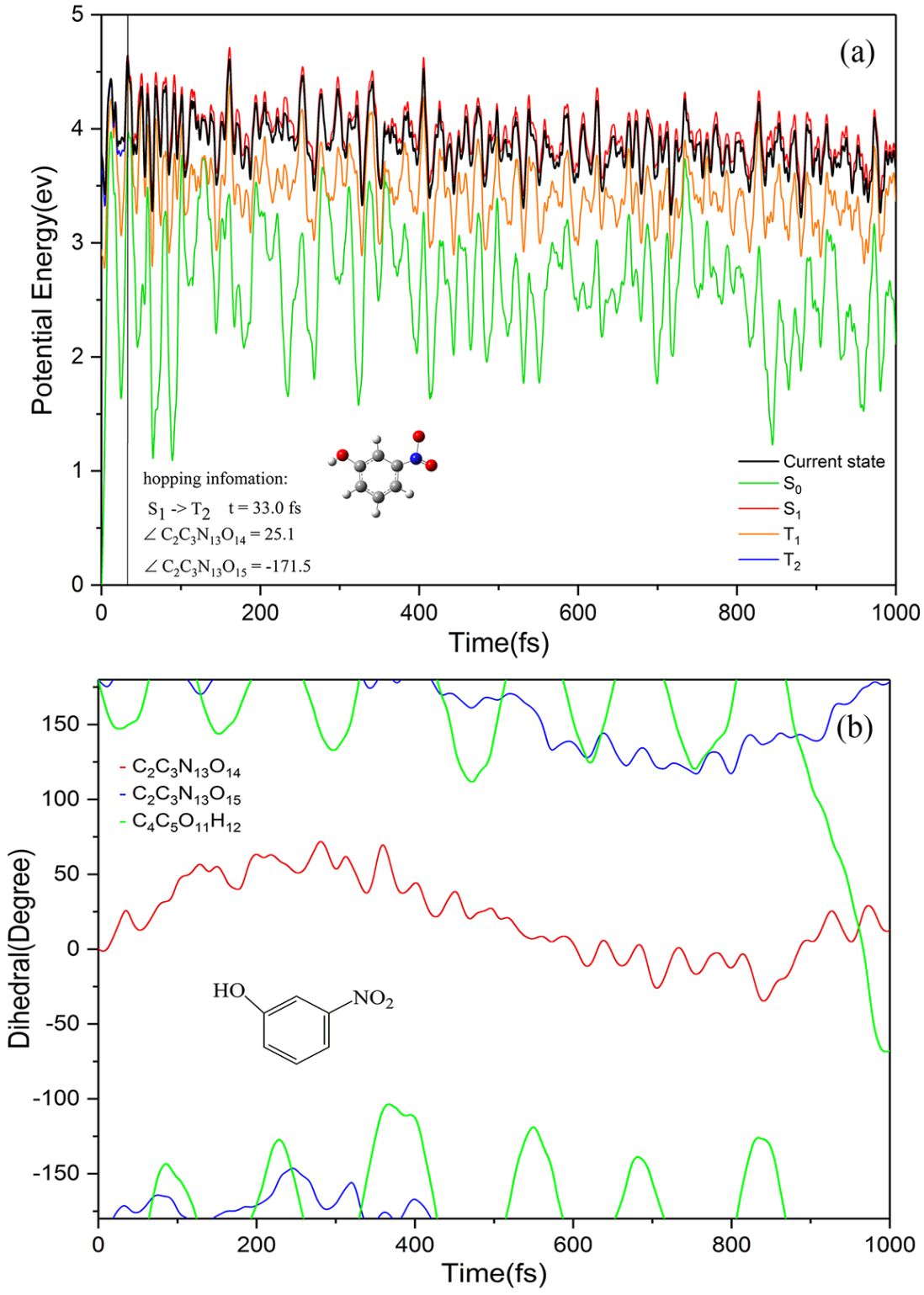

Fig. S3 The same as Fig. S2, but for MNP system.

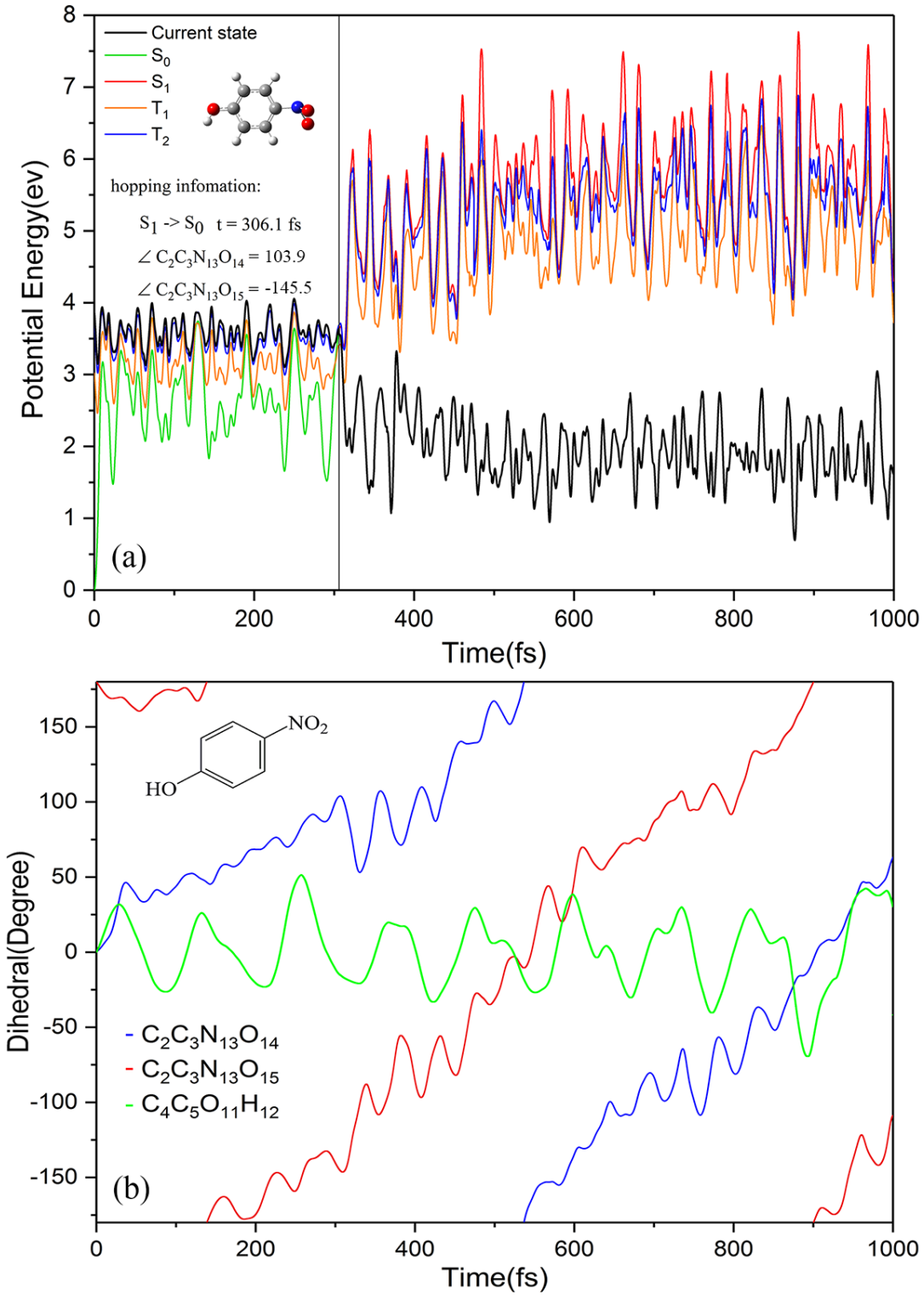

Fig. S4 A typical trajectory for $S_1 \rightarrow S_0$ relaxation pathway in terms of evolution time for PNP system in the case of only considering two singlet states (S_1 and S_0) in dynamic simulation. (a) Potential energy profile with one-step via S1S0 conical intersection, (b) oscillatory motion of the three torsion dihedral angles.

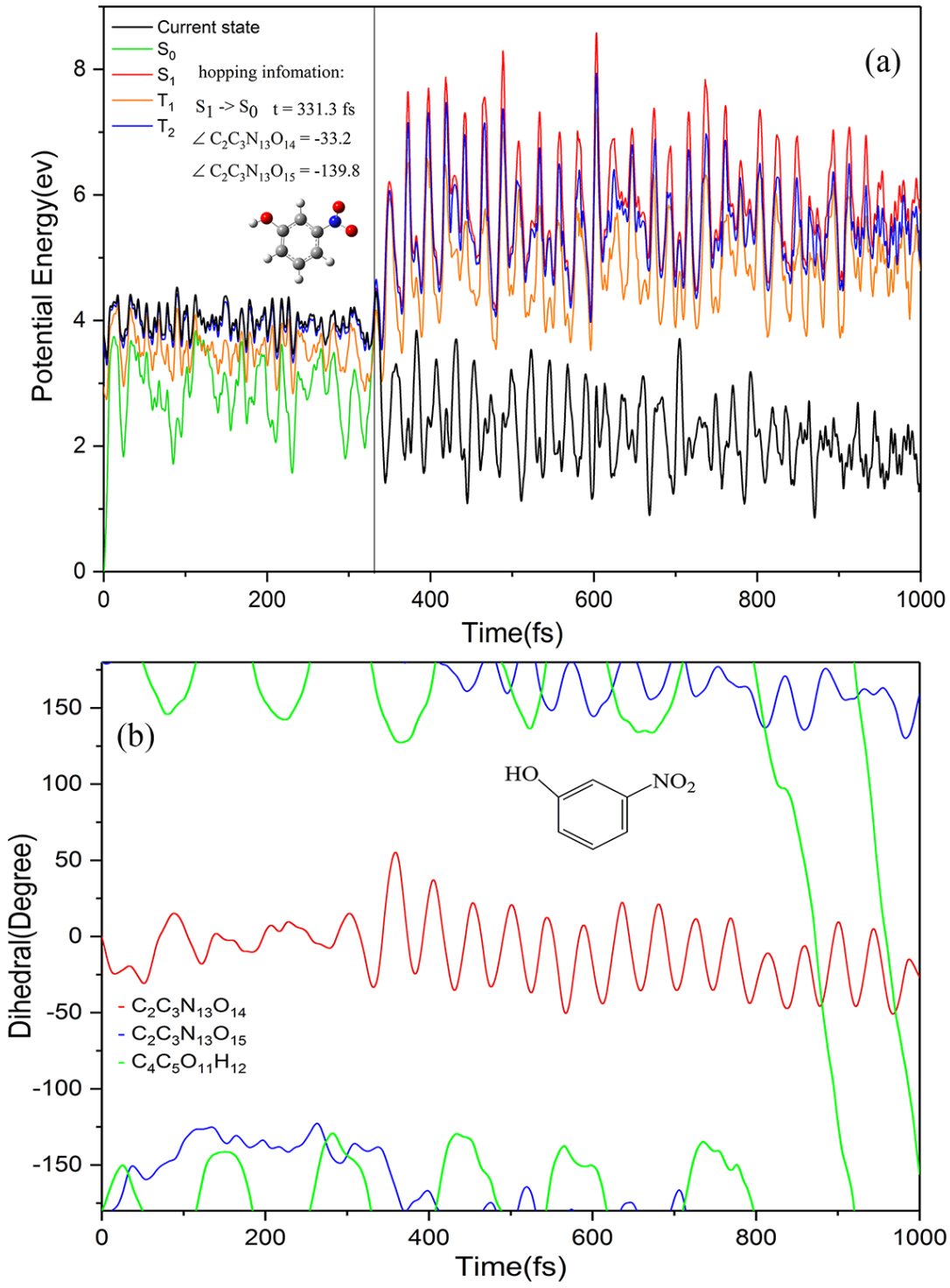

Fig. S5 The same as Fig. S4, but for MNP system.