Supporting Information

Mechanistic Analysis of Fluorescence Quenching of Reduced Nicotinamide Adenine Dinucleotide by Oxamate in Lactate Dehydrogenase Ternary Complexes

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Table S1. Electronic transition energies of dihydronicotinamide related compounds obtained by computations at td-B3LYP/6-31g(d) level and from experimental. Numbers in parentheses are oscillator strength and extinction coefficients ($M^{-1}cm^{-1}$) respectively.

Compound	Electronic State	Energy (eV)	Energy (nm)	Experimental UV-vis Maximum
1-methyl-1,4-dihydronicotinamide	S_1 (π-π*)	3.747	331 (0.113)	356, Acetone(1)
	S_2 (n-π*)	4.514	275 (0.001)	
Twisted 1-methyl-1,4-dihydronicotinamide	S_1 (π-π*)	3.652	340 (0.07)	
	S_2 (n-π*)	4.489	276 (0.002)	
1-methyl-1,4-dihydropyridine	S_1 (π-π*)	4.417	281 (0.034)	a. 270 (3000), MeOH(2) b. 278 (2500), c-hexane(3)
1-methyl-3-acetyl-1,4-dihydropyridine	S_1 (π-π*)	3.671	338 (0.138)	c. 371 (10400), EtOH(2, 4) 374, Acetonitrile(1)
1-methyl-1,4,5,6-tetrahydronicotinamide	S_1 (n-π*)	4.701	264 (0)	d. 287 (19500), 95% EtOH(5)
	S_2 (π-π*)	4.883	253 (0.365)	295, EtOH(6)
	S_1 (n-π*)	4.277	290 (0.067)†	
	S_2 (π-π*)	4.475	277 (0.179)†	

Compounds measured in experimental:

a. 1-methyl-4,4-dimethyl-1,4-dihydropyridine(2)
b. 1,4-dihydropyridine(3)
c. 1-benzyl-3-acetyl-1,4-dihydropyridine(2, 4)
d. 1,4,5,6-tetrahydronicotinamide(5)
† At 6-311++g(d,p) level.

Table S2. Energies (eV) of locally excited sates (LE) and charge transfer (CT) states in vacuum and in water with polarizable continuum model (PCM) at selected dielectric constant (ε).

State	ε	case 1	case 2	case 3	case 4	case 5	case 6	case 7	case 8
LE	vacuum	3.087	3.209	3.271	3.261	3.186	3.18	3.276	3.265
	4	3.103	3.149	3.21	3.203	3.177	3.178	3.246	3.265
	78	3.122	3.156	3.196	3.191	3.186	3.189	3.245	
CT	vacuum	5.658	3.094	5.297	4.827	4.333	4.008	3.74	3.167
	4	4.989	3.284	4.814	4.5	4.27	4.032	3.851	3.167
	78	4.737	3.336	4.611	4.339	4.238	4.034	3.889	

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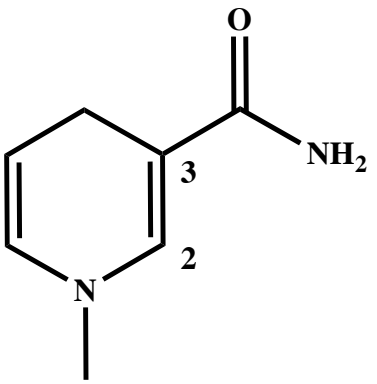
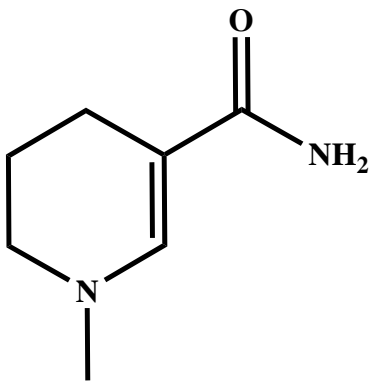


1-methyl-1,4-dihydronicotinamide



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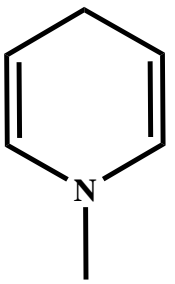

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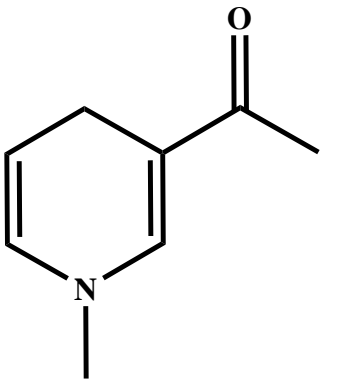

1-methyl-3-acetyl-1,4-dihydropyridine

Figure S1. Structures of dihydronicotinamide and related compounds.

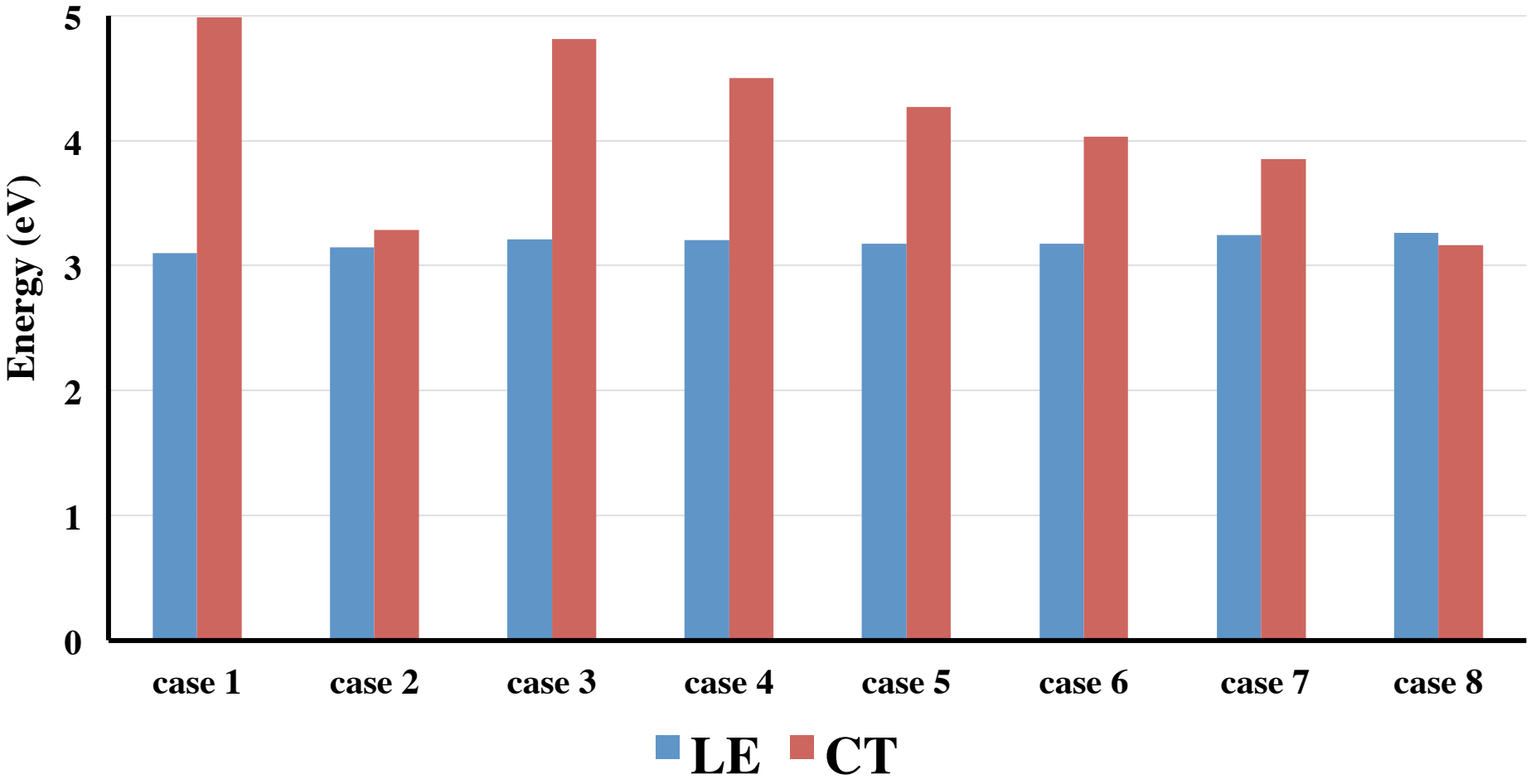

Figure S2. Energetic comparison of LE and CT states in selected cases in water (PCM, ε=4).

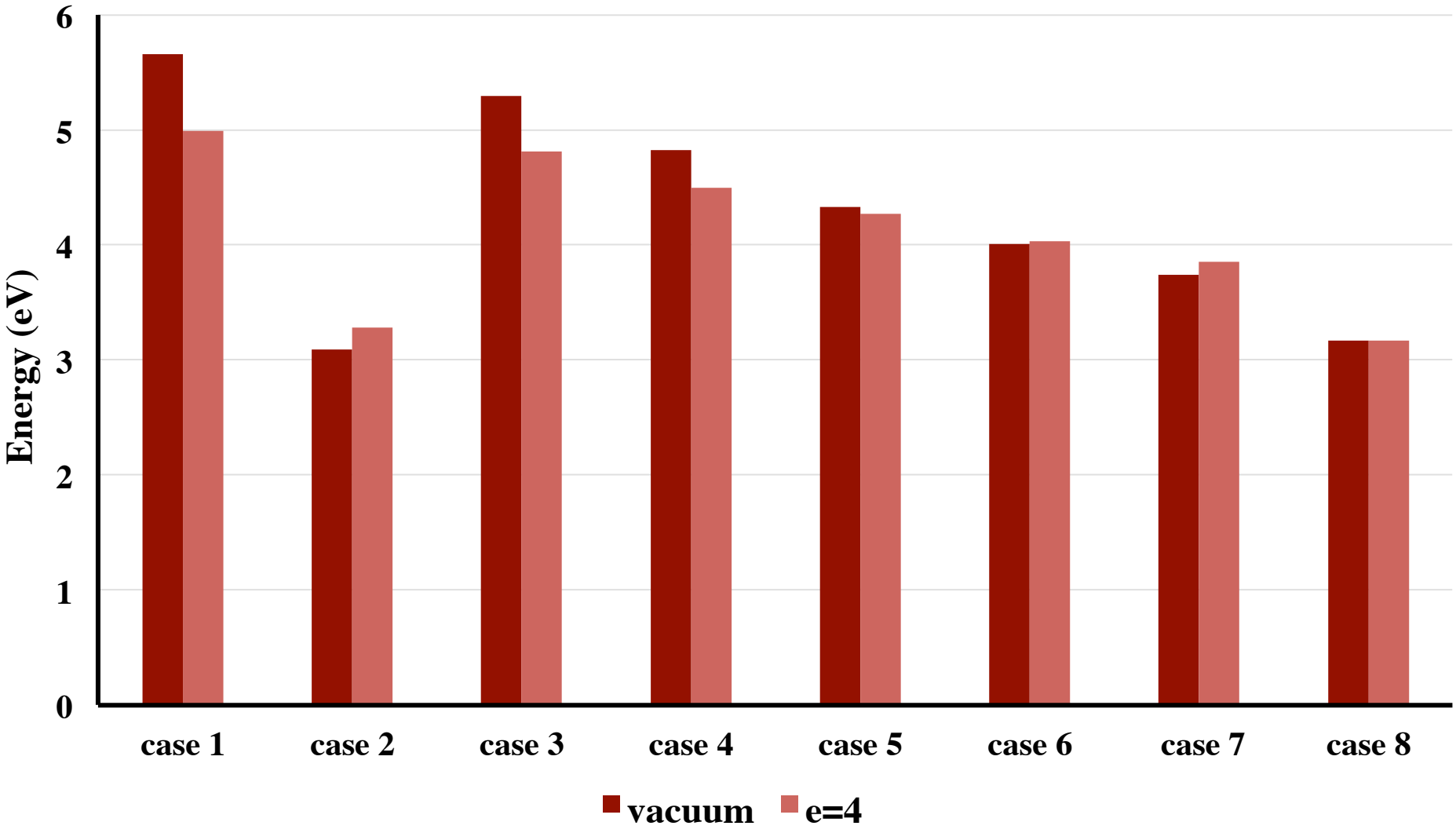

Figure S3. Comparison of Energies of CT states in selected cases in vacuum and water (PCM, ε=4).

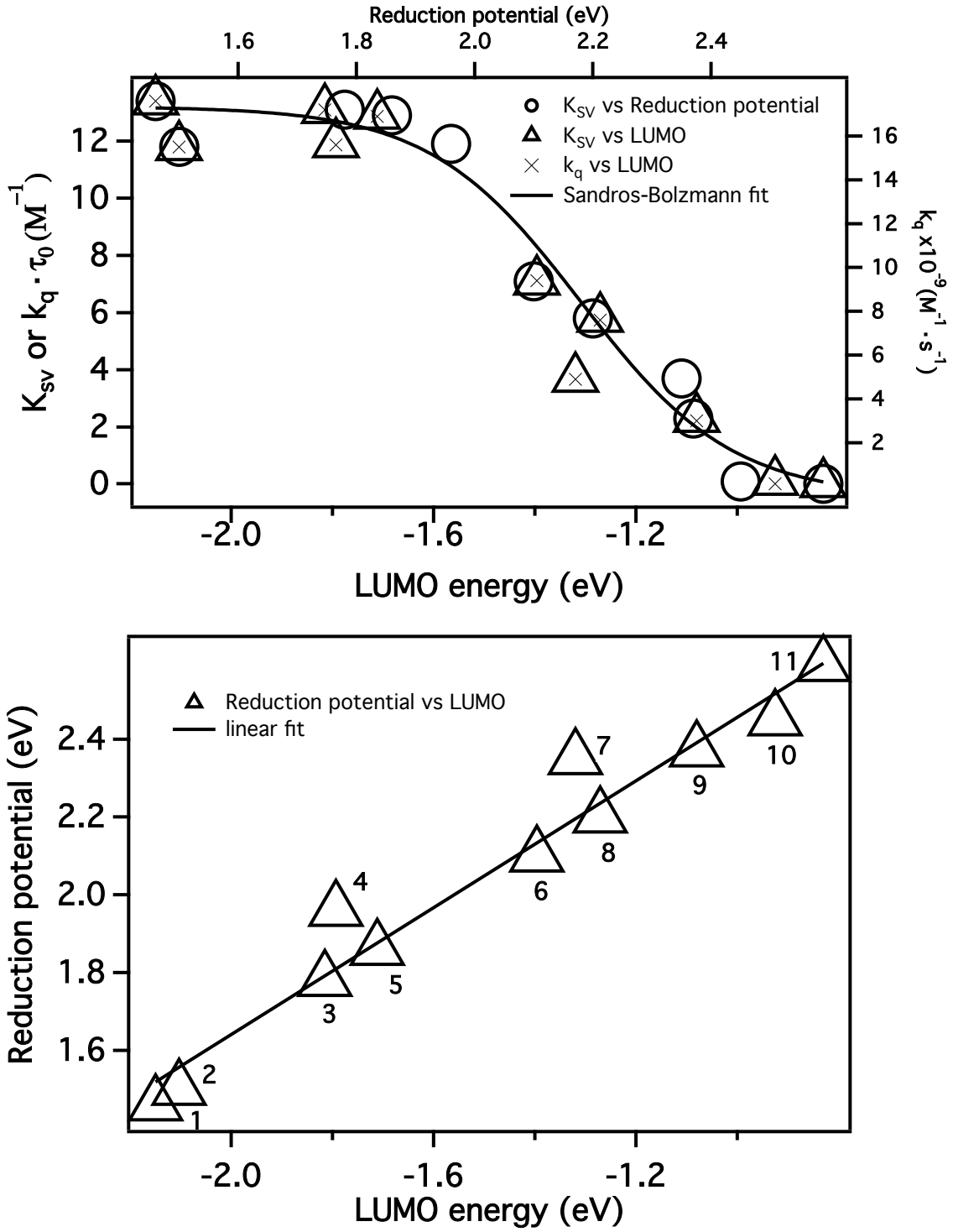

Figure S4. Correlation between LUMO energies and the reduction potentials (b) and the quenching constants (a) of selected quenchers. LUMO energies were calculated at B3LYP/6-31g(d) level. The reduction potentials and the quenching constants were from the reference (7). Quenchers in the figure are given in order of increasing LUMO energy: 1. Trifluoroacetophanone, 2. Diethylfumarate, 3. Dimethylterephthalate, 4. 1-Cyanonaphthalene, 5. Benzophenone, 6. Acetophenone, 7. Cyanobenzene, 8. E-stilbene, 9. Methylbenzoate, 10. Styrene, and 11. 1-methylnaphthalene.