

Supplementary Information

Effect of Number and Different types of Proton Donors on Excited-State Intramolecular Single and Double Proton Transfers of Bipyridine Derivatives: Theoretical Insights

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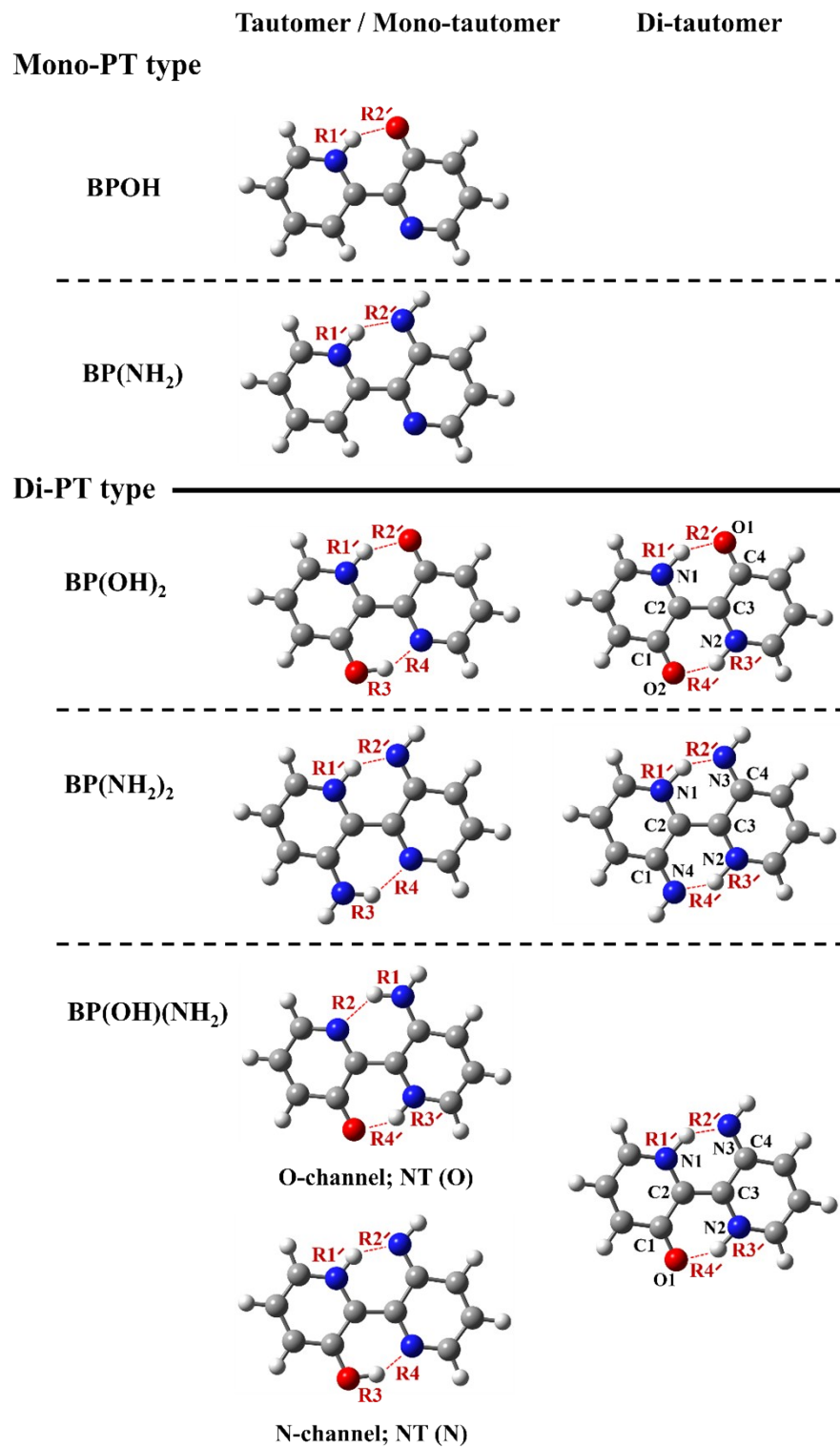


Figure S1. Optimized structures of tautomer (T), mono-tautomer (NT), and di-tautomer (TT) forms computed at B3LYP/TZVP level of theory in gas phase.

Table S1. Covalent bonds, intra-HBs, distances between heavy atoms and torsion angles of tautomer (T), mono-tautomer (NT), and di-tautomer (TT) forms for all molecules computed at B3LYP/TZVP (in S_0) and TD-B3LYP/TZVP (in S_1) levels of theory.

Molecule	Form	R1/R1□		R2/R2□		R3/R3□		R4/R4□		O···N or N···N		N1C2C3C4 /N2C3C2C1			
		S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1		
<i>Mono-PT type</i>															
BPOH	K	1.032	1.027	1.797	1.792	—	—	—	—	2.534	2.677	0.0	0.0		
BP(NH₂)	K	1.037	1.037	1.814	1.775	—	—	—	—	2.667	2.673	0.0	0.0		
<i>Di-PT type</i>															
BP(OH)₂	MK	1.110	1.033	1.441	1.764	1.009	0.989	1.684	1.779	2.602	2.655	0.0	12.0		
	DK	1.063	1.038	1.607	1.722	1.063	1.038	1.607	1.722	2.552	2.610	0.0	0.0		
BP(NH₂)₂	MK	1.047	1.070	1.715	1.632	1.020	1.014	1.841	1.958	2.651	2.739	0.2	15.0		
	DK	1.113	1.052	1.504	1.685	1.113	1.052	1.504	1.684	2.511	2.598	0.0	0.0		
BP(OH)(NH₂)	MK (O)	N···N/O···N										2.663/	2.768/	0.0	14.0
		2.609	2.601	0.0	28.0										
		2.678/	2.616/												
MK (N)	1.037	1.061	1.815			1.715	1.020	0.990	1.596	1.786	2.534	2.666	0.0	0.0	
	DK	1.092	1.038	1.566	1.777	1.072	1.047	1.561	1.631	2.539/	2.650/				
		2.529	2.555												

Table S2. Vibrational frequencies corresponding to O-H stretching and symmetric and asymmetric N-H stretching in S_0 and S_1 states of N form (mono-PT type) and NN form (di-PT type).

Vibrational mode	State	Wavenumber (cm ⁻¹)				
		Mono-PT type			Di-PT type	
		BPOH	BP(NH ₂)	BP(OH) ₂	BP(NH ₂) ₂	BP(OH)(NH ₂)
O-H stretching	S_0	3134	—	3071	—	2984
	S_1	2419	—	2338	—	2523
$\Delta\nu$		715	—	733	—	461
Symmetric N-H stretching	S_0	—	3458	—	3435	3434
	S_1	—	2850	—	3104	3066
$\Delta\nu$		—	608	—	331	368
Asymmetric N-H stretching	S_0	—	3674	—	3678	3681
	S_1	—	3602	—	3629	3633
$\Delta\nu$		—	72	—	49	48

*positive (+) value of $\Delta\nu$ corresponded to red-shift.

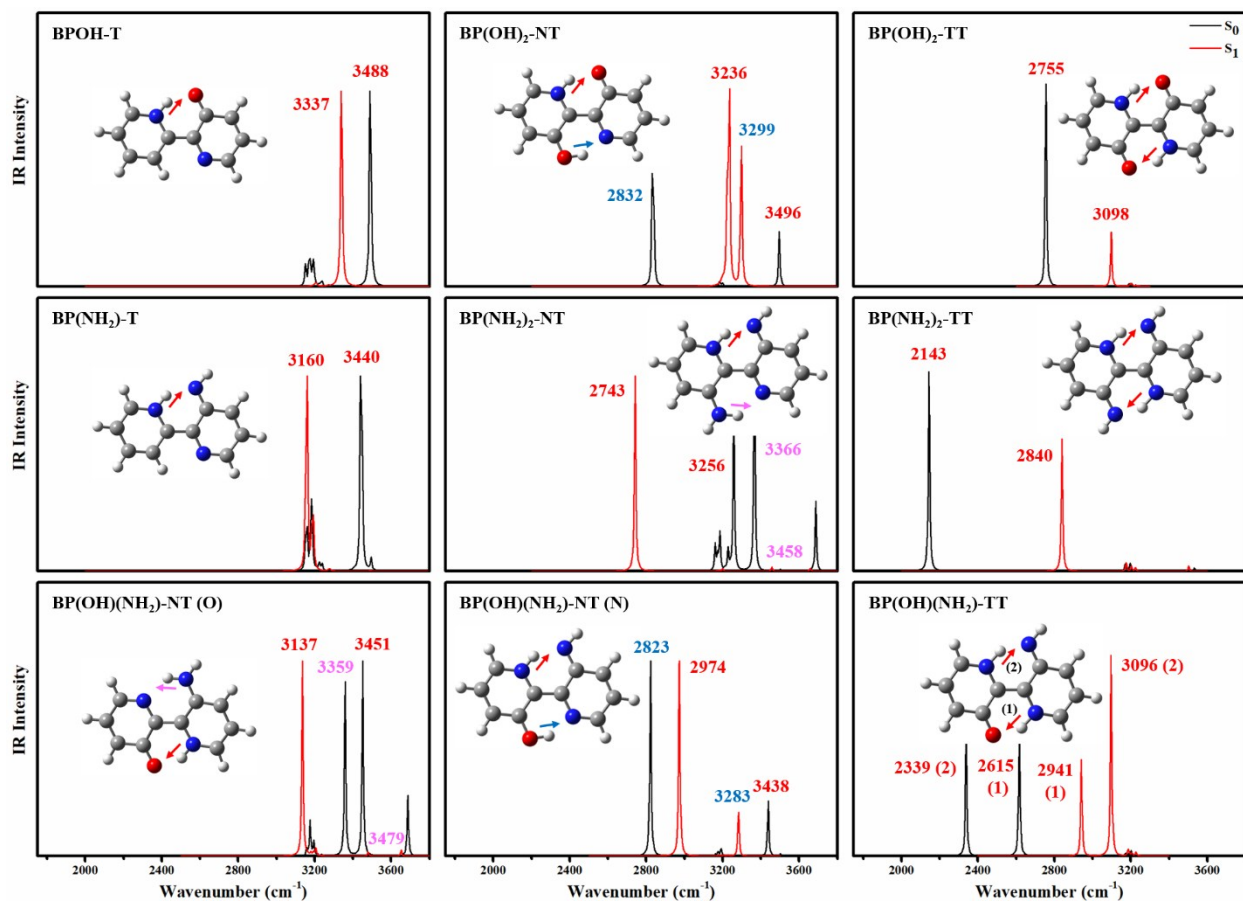


Figure S2. Calculated vibrational spectra of O-H and N-H stretching in the S_0 (black line) and S_1 (red line) states of tautomer (T), mono-tautomer (NT) and di-tautomer (TT) forms. The O-H stretching is labeled in blue. The N-H stretching for primary amine and secondary amine are labeled in pink and red, respectively.

Table S3. Vibrational frequencies corresponding to O-H stretching and N-H stretching corresponding to 2nd PT process in S_0 and S_1 states of mono-tautomer (NT) form of di-PT type.

Vibrational mode	State	Wavenumber (cm ⁻¹)			
		BP(OH) ₂	BP(NH ₂) ₂	BP(OH)(NH ₂)	
				NT (O)	NT (N)
O-H stretching	S_0	2832	—	—	2823
	S_1	3299	—	—	3283
$\Delta\nu$		-467	—	—	-460
N-H stretching	S_0	—	3366	3359	—
	S_1	—	3458	3479	—
$\Delta\nu$		—	-92	-120	—

*negative (-) value of $\Delta\nu$ corresponded to blue-shift.

Table S4. Bond critical point parameters (in a.u.) in S_1 state corresponding to the intra-HBs of N and NN forms for all molecules.

Molecule	Bonds	$\rho(\mathbf{r})$	$\mathbf{G}(\mathbf{r})$	$\mathbf{V}(\mathbf{r})$	$\mathbf{H}(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	E_{HB}
<i>Mono-PT type</i>							
BPOH	R2	0.065	0.048	-0.066	-0.018	0.118	0.033
BP(NH₂)	R2	0.054	0.042	-0.052	-0.011	0.124	0.026
<i>Di-PT type</i>							
BP(OH₂)	R2, R4	0.058	0.042	-0.056	-0.014	0.109	0.028
BP(NH₂)₂	R2, R4	0.047	0.037	-0.044	-0.007	0.121	0.022
BP(OH)(NH₂)	R2 (N-H \cdots N)	0.047	0.036	-0.043	-0.007	0.118	0.022
	R4 (O-H \cdots N)	0.075	0.052	-0.078	-0.026	0.107	0.039

Table S5. Bond critical point parameters (in a.u.) in S_1 state corresponding to the 2nd PT process of NT form of di-PT type.

Molecule	Form	Bonds	$\rho(\mathbf{r})$	$\mathbf{G}(\mathbf{r})$	$\mathbf{V}(\mathbf{r})$	$\mathbf{H}(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	E_{HB}
BP(OH₂)	MK	R4	0.047	0.033	-0.042	-0.009	0.098	0.021
BP(NH₂)₂	MK	R4	0.032	0.025	-0.026	-0.001	0.096	0.013
BP(OH)(NH₂)	MK (N)	R4 (O-H \cdots N)	0.046	0.033	-0.041	-0.008	0.097	0.021
	MK (O)	R2 (N-H \cdots N)	0.030	0.023	-0.023	-0.0003	0.091	0.012

Table S6. Calculated maxima wavelengths of absorption (λ_{abs}) and emission (λ_{emis}) spectra with their oscillator strengths (f) and molecular orbitals (MOs) contribution as well as Stokes shifts of all molecules computed at TD-B3LYP/TZVP level of theory.

Molecule	Form	Absorption			Emission		Stokes shift (nm)
		$\lambda_{\text{abs, nm}}$	f	MOs contribution	$\lambda_{\text{emis, nm}}$	f	
<i>Mono-PT type</i>							
BPOH	N	313	0.315	HOMO→LUMO (96%)	336	0.300	23
	T				692	0.024	379
BP(NH₂)	N	340	0.263	HOMO→LUMO (97%)	384	0.230	44
	T				743	0.017	403
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<i>Di-PT type</i>							
BP(OH)₂	NN	329	0.370	HOMO→LUMO (97%)	361	0.398	32
	NT				530	1.37	201
	TT				460	0.400	131
BP(NH₂)₂	NN	362	0.334	HOMO→LUMO (98%)	403	0.321	41
	NT				623	0.111	261
	TT				532	0.308	170
BP(OH)(NH₂)	NN	350	0.331	HOMO→LUMO (98%)	383	0.342	33
	NT (O)				539	0.139	189
	NT (N)				727	0.065	377
	TT				547	0.223	197

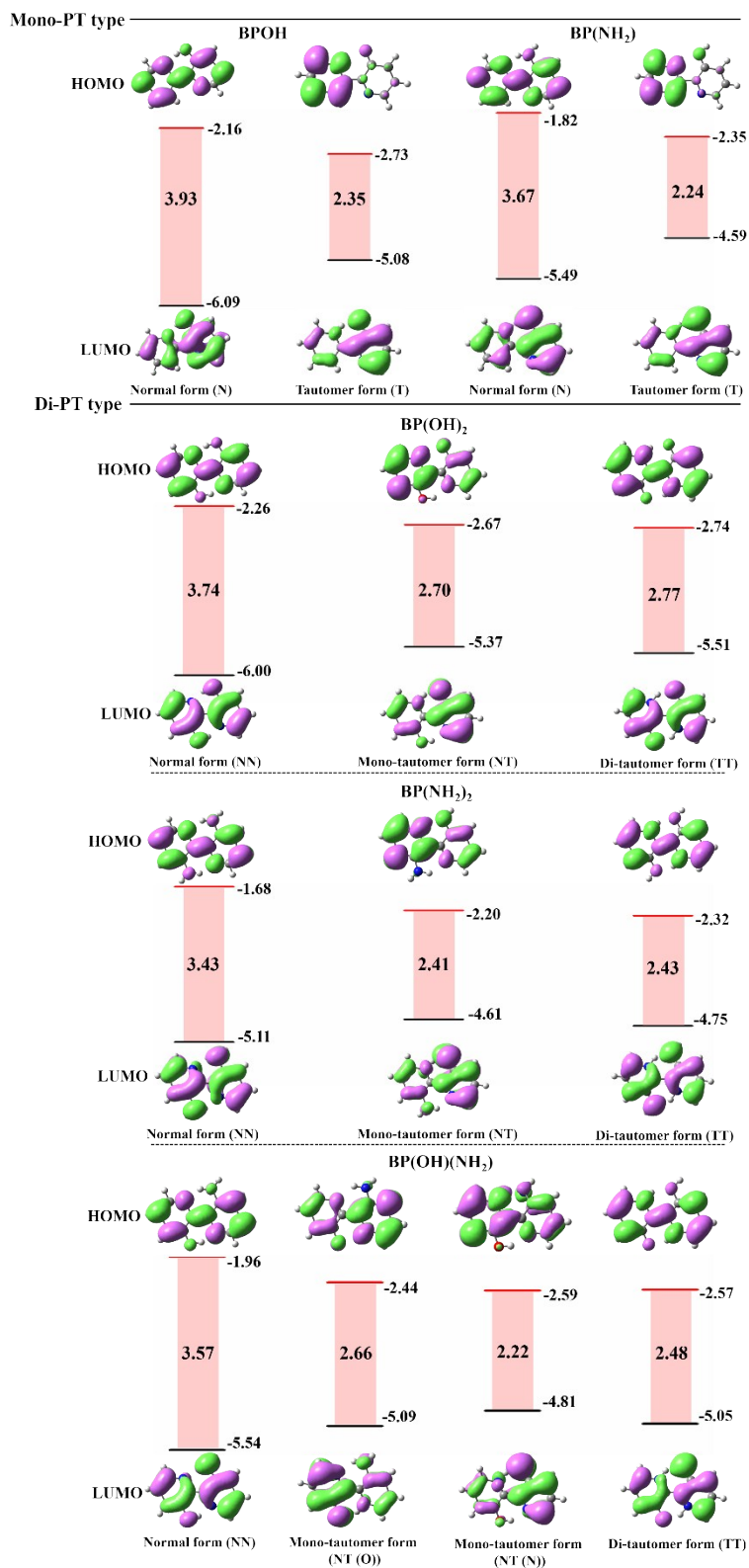


Figure S3. Schematic diagram of HOMO and LUMO energy levels as well as energy gaps (eV) corresponding to emission peaks of all molecules computed at B3LYP/TZVP level of theory.

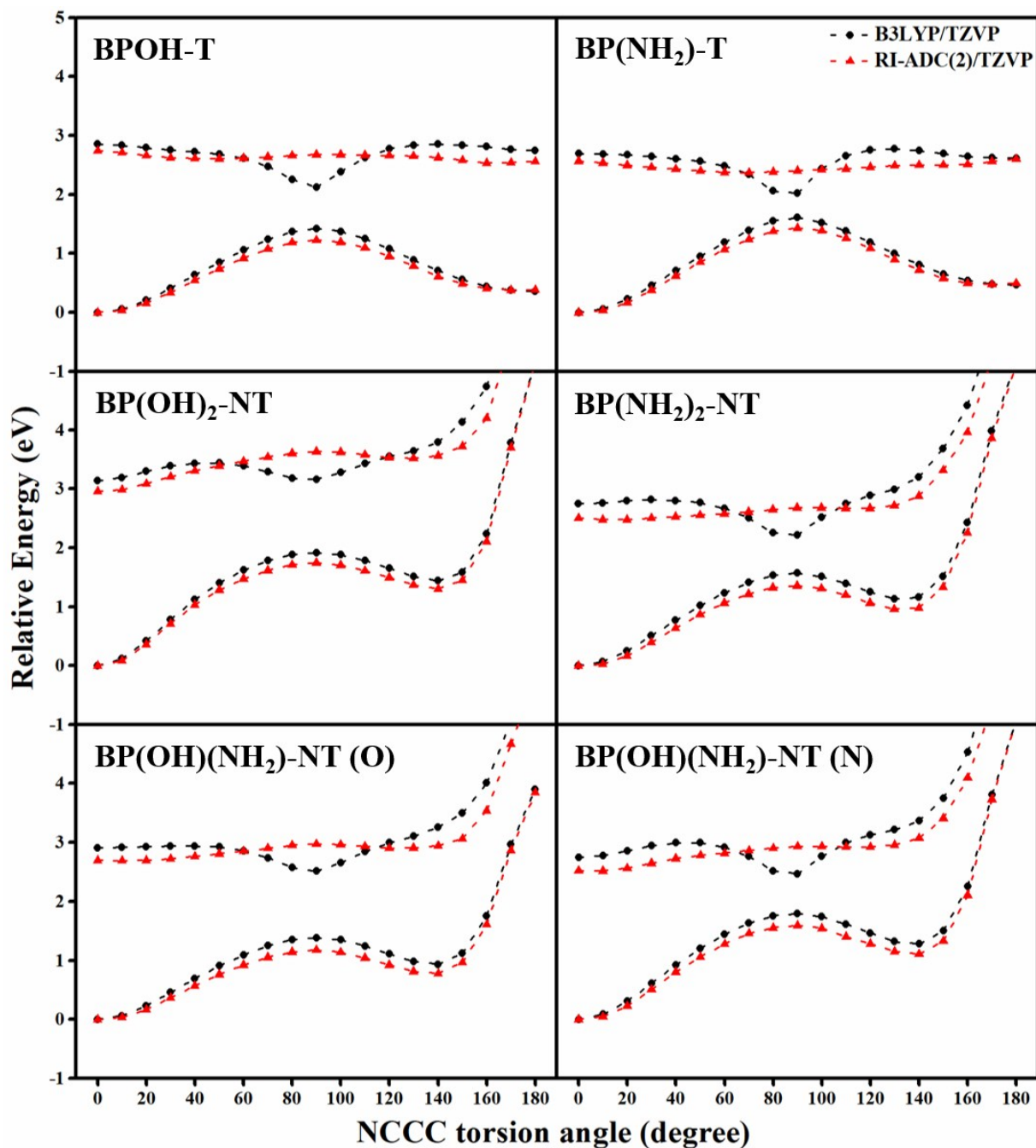


Figure S4. Potential energy curves corresponding to scanned NCCC torsion of tautomer (T) and mono-tautomer (NT) species of all molecules calculated at TD-B3LYP (black lines) and RI-ADC(2) (red lines) with TZVP basis set.