Supporting Information

tt1   *tt2*
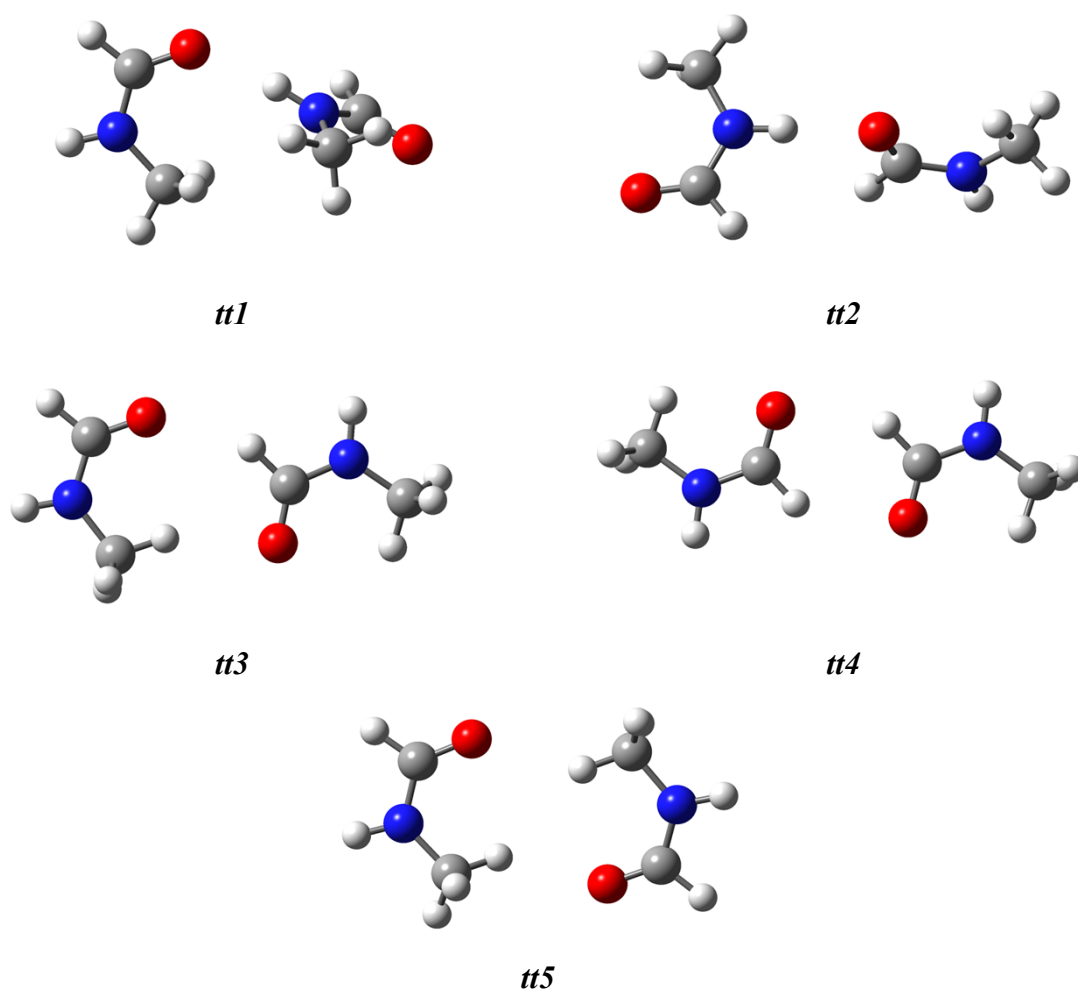
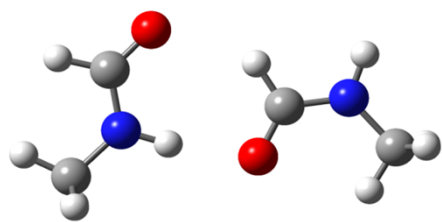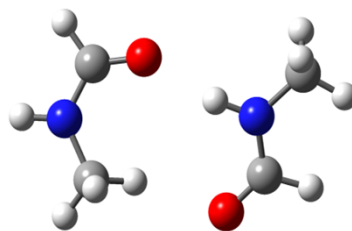*tt3*   *tt4*

tt5

Figure 1S. *trans-trans* NMF dimers

1

tc1

tc2
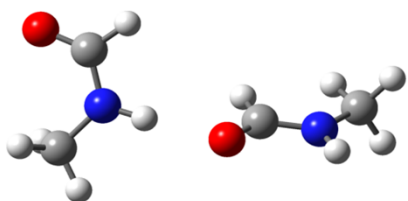
tc3
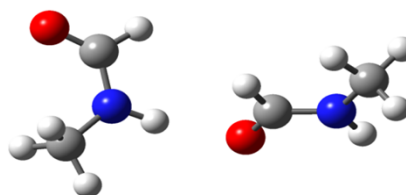
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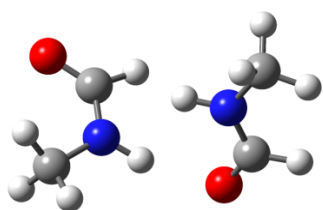
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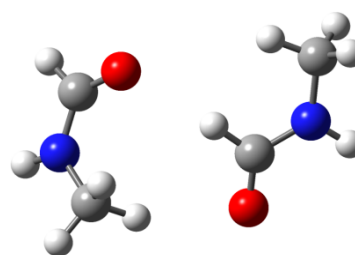
tc6
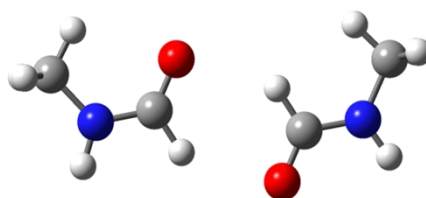
tc7

Figure 2S. *trans-cis* NMF dimers

cc1

cc2

cc3
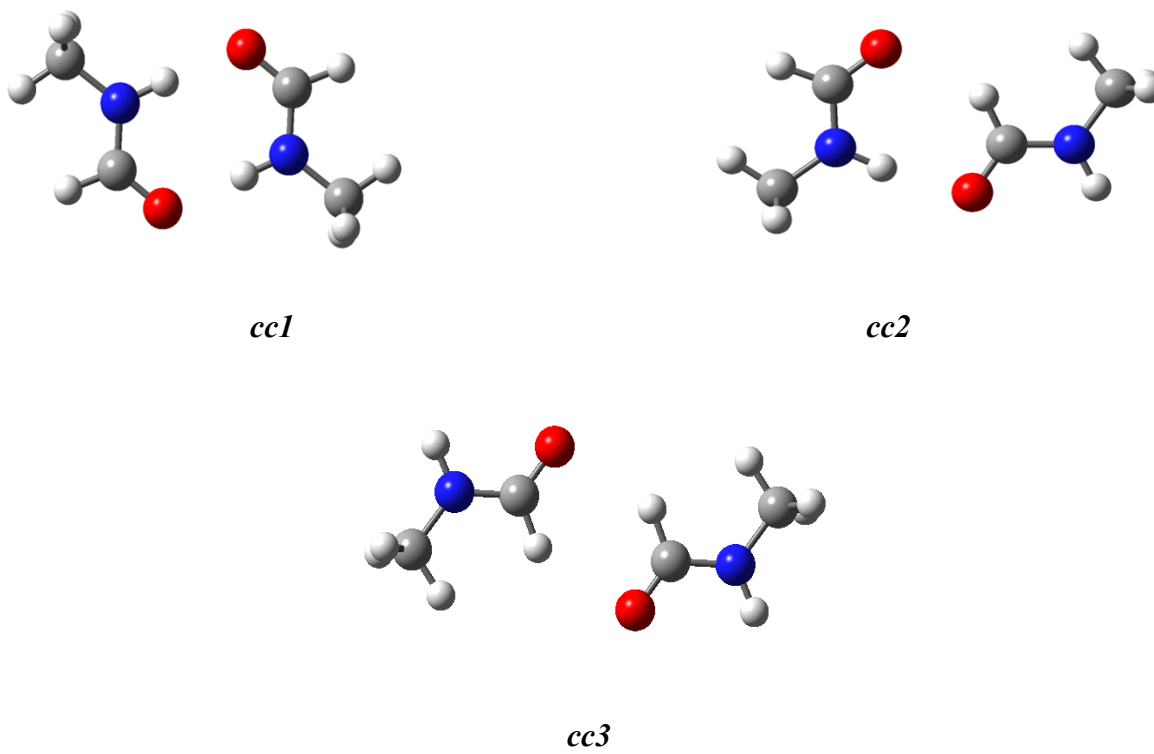
Figure 3S. *cis-cis* NMF dimers
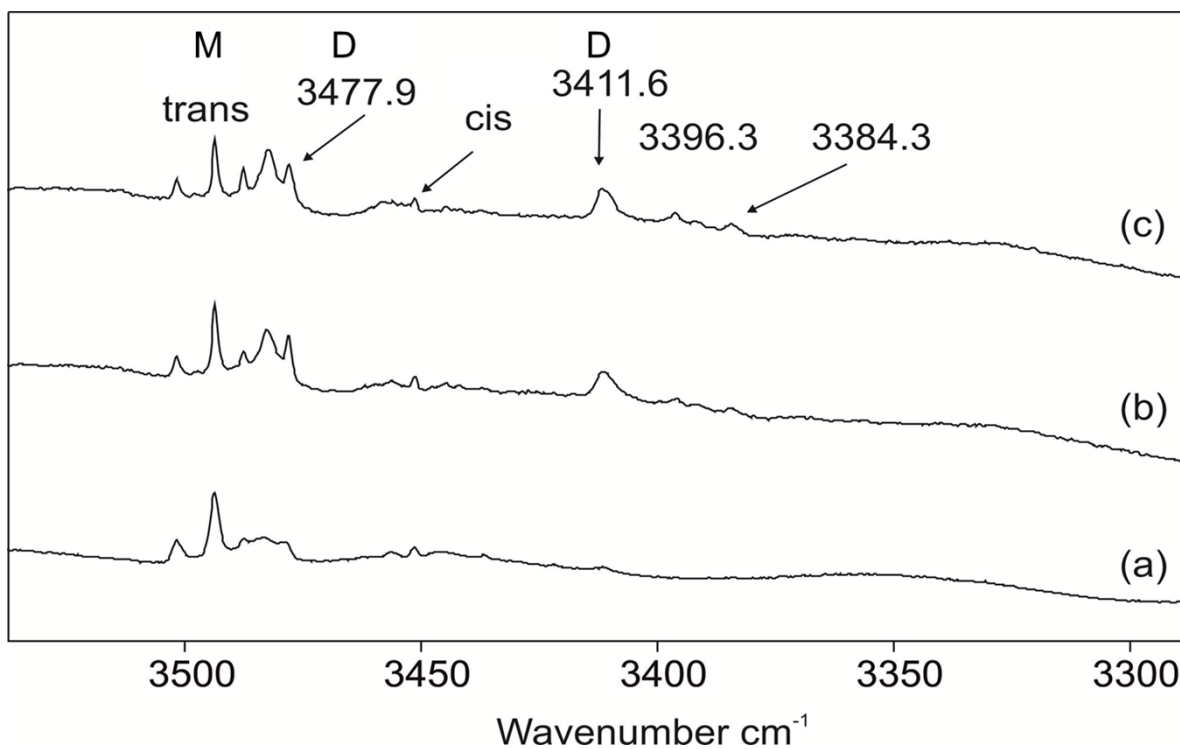
Figure 4S. Matrix-isolated IR spectra of NMF in the N−H stretching region. (a) IR spectrum of NMF in argon matrix at 10 K, temperature of the sample during deposition was kept at −35 °C. (b) After annealing at 30 K during 15 minutes. (c) After annealing at 35 K during 15 minutes. Bands of monomeric NMF are marked as **M**, dimers as **D. D** signals are assigned to ***tt-1 and tt-2*** dimers.
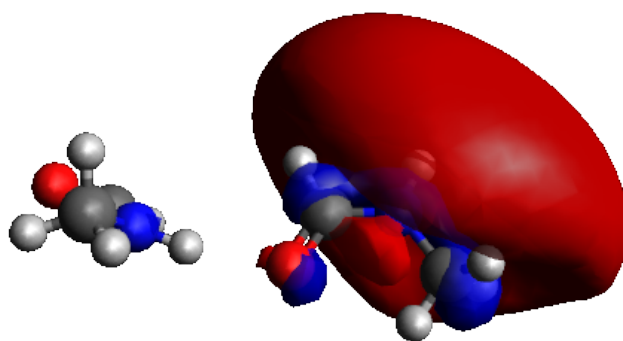
Figure 5S. The LUMO orbital is a Rydberg orbital located on B.
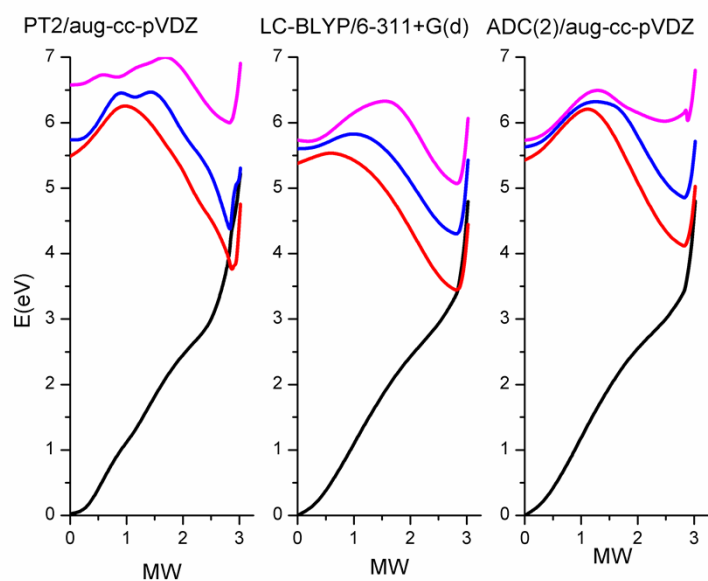
a.)
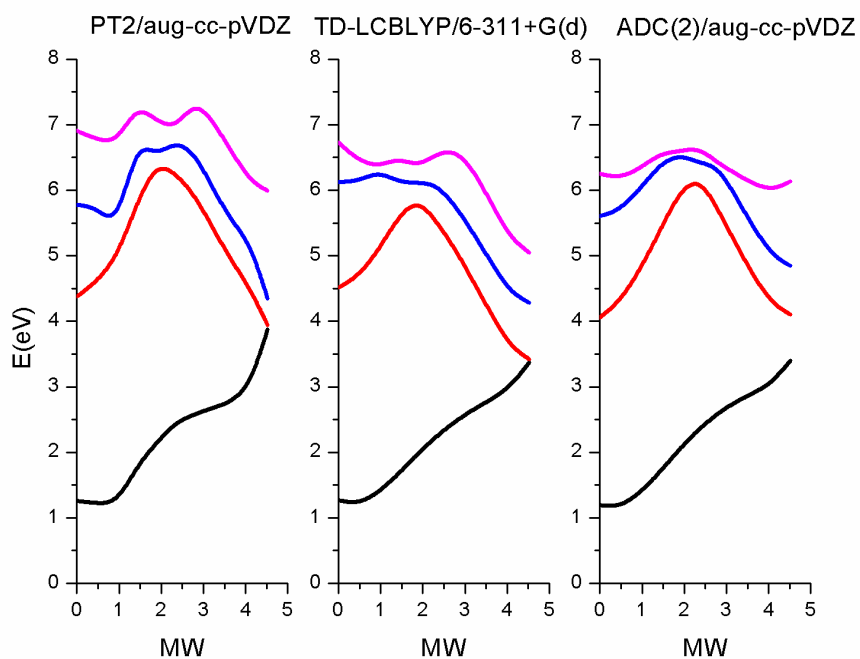
b.)

Figure 6S. a.) Linear interpolation between the Franck-Condon geometry and the crossing for the hydrogen-transfer process, *tt-1* dimer**.** b.) Linear interpolation between the minimum in S_1 to the conical intersection for the hydrogen transfer process, *tt-1* dimer**.**

6
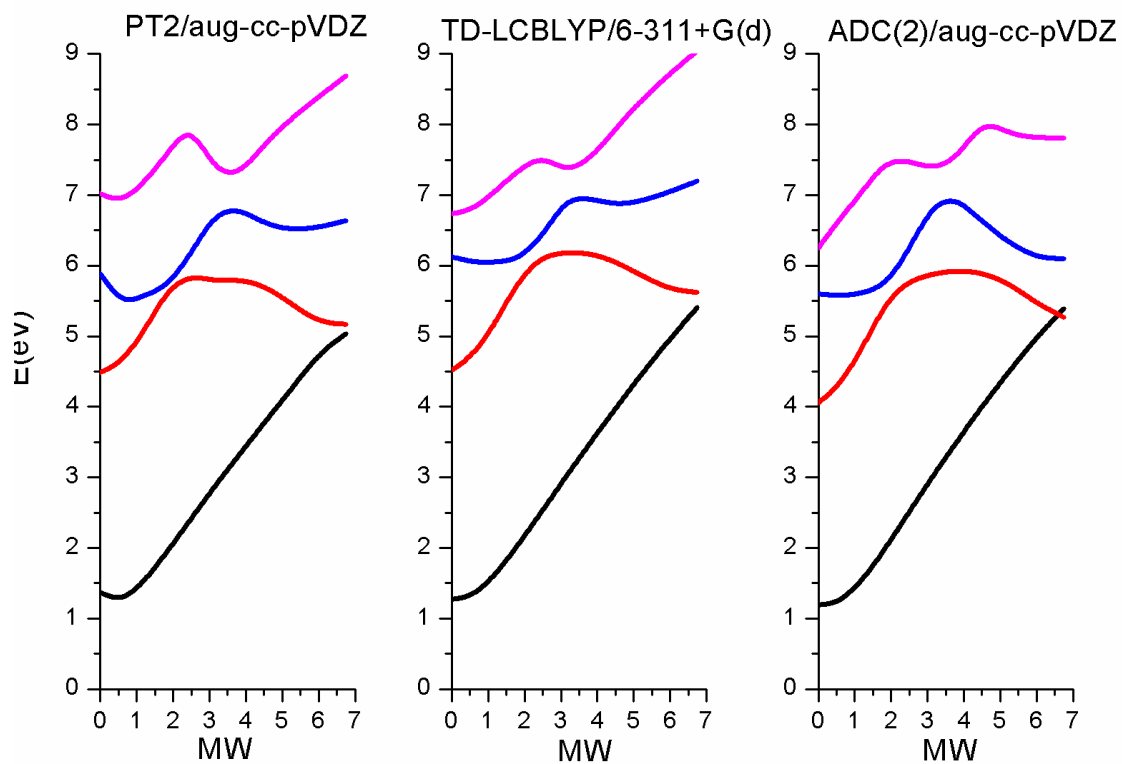
Figure 7S. Linear interpolation between the S_1 geometry and the conical intersection for the CN breaking process in monomer A (CN-A), dimer ***tt-1***
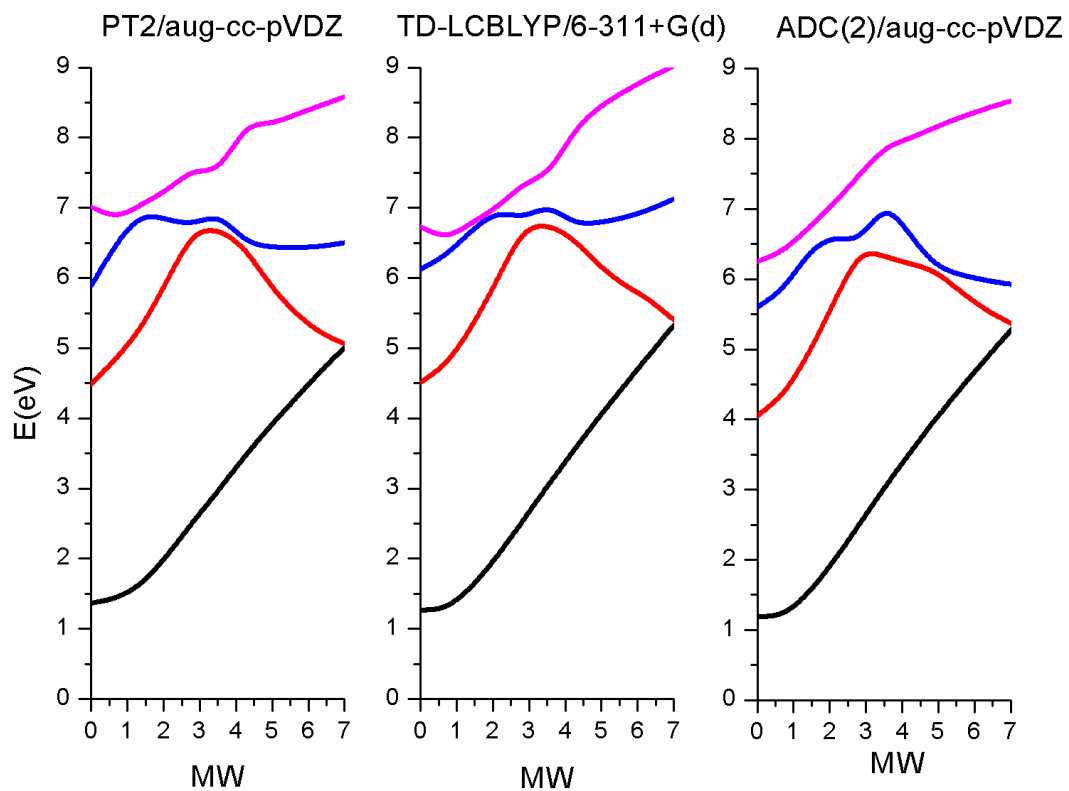
Figure 8S. Linear interpolation between the S_1 geometry and the conical intersection for the CN breaking process in monomer B (CN-B), dimer *tt-1*
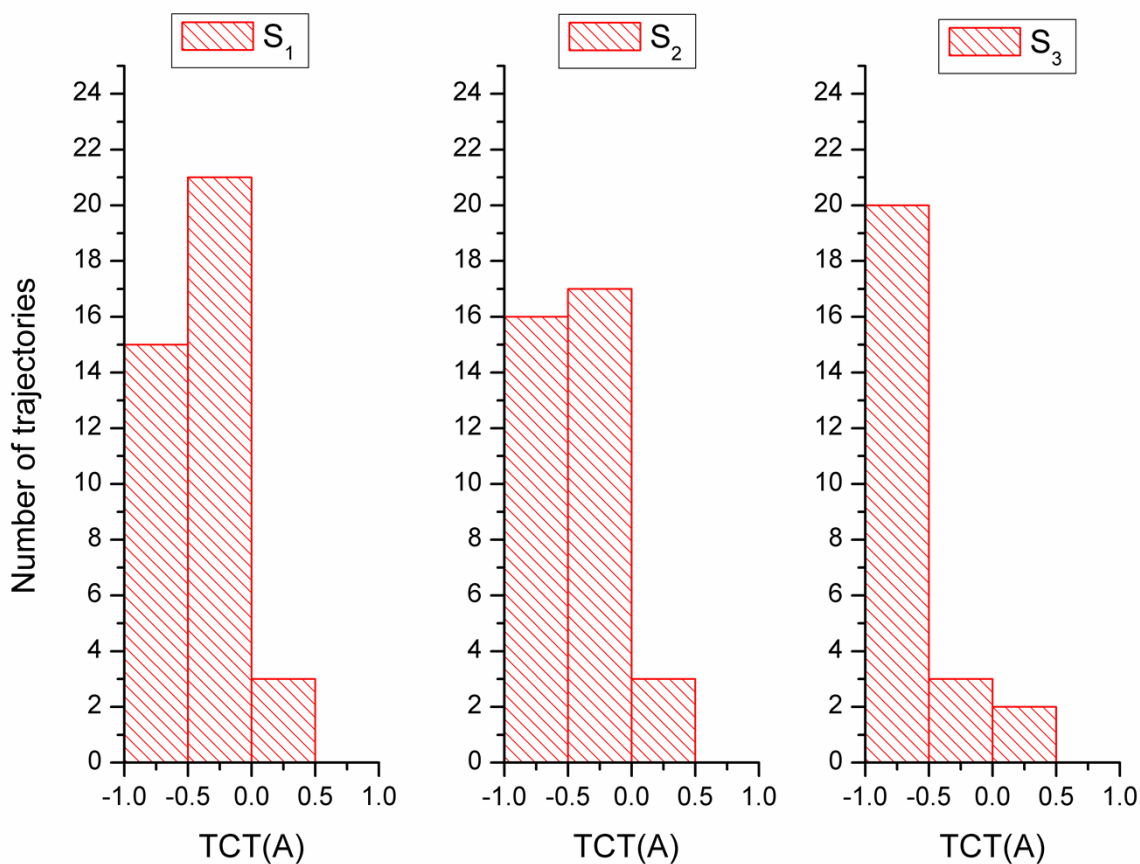
Figure 9S. Histograms showing the charge transfer TCT(A) parameter for all the initial conditions (all *tt-1* and *tt-2* trajectories were considered). The TCT(A) parameter (-1<TCTA<1), which provides a characterization of the excited state according to charge transferred, was computed for every initial condition geometry. High negative values mean that the electron density is transferred from A to B, high positive values mean electron transfer from B to A. Intermediate values correspond to delocalized and highly localized excitations.
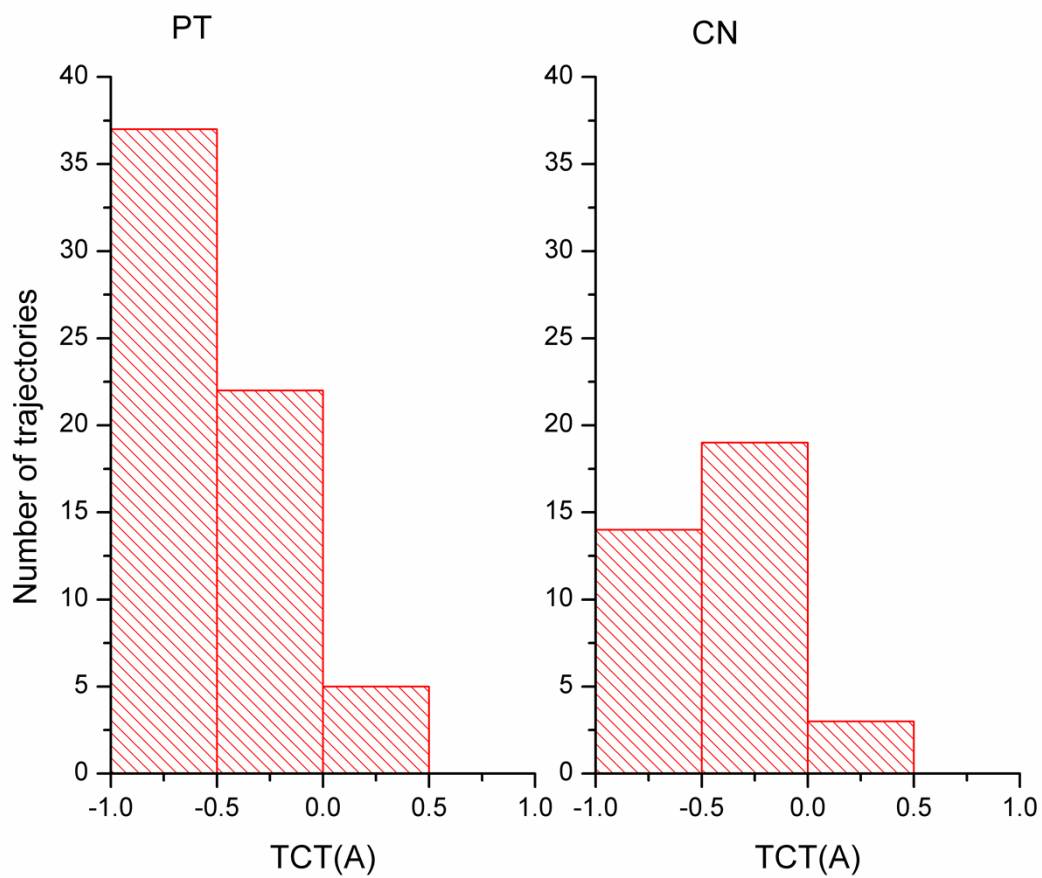
Figure 10S. Histograms showing the distribution of the charge transfer parameter for the initial conditions related to the hydrogen transfer and the dissociative trajectories (*tt-1* and *tt-2* together).
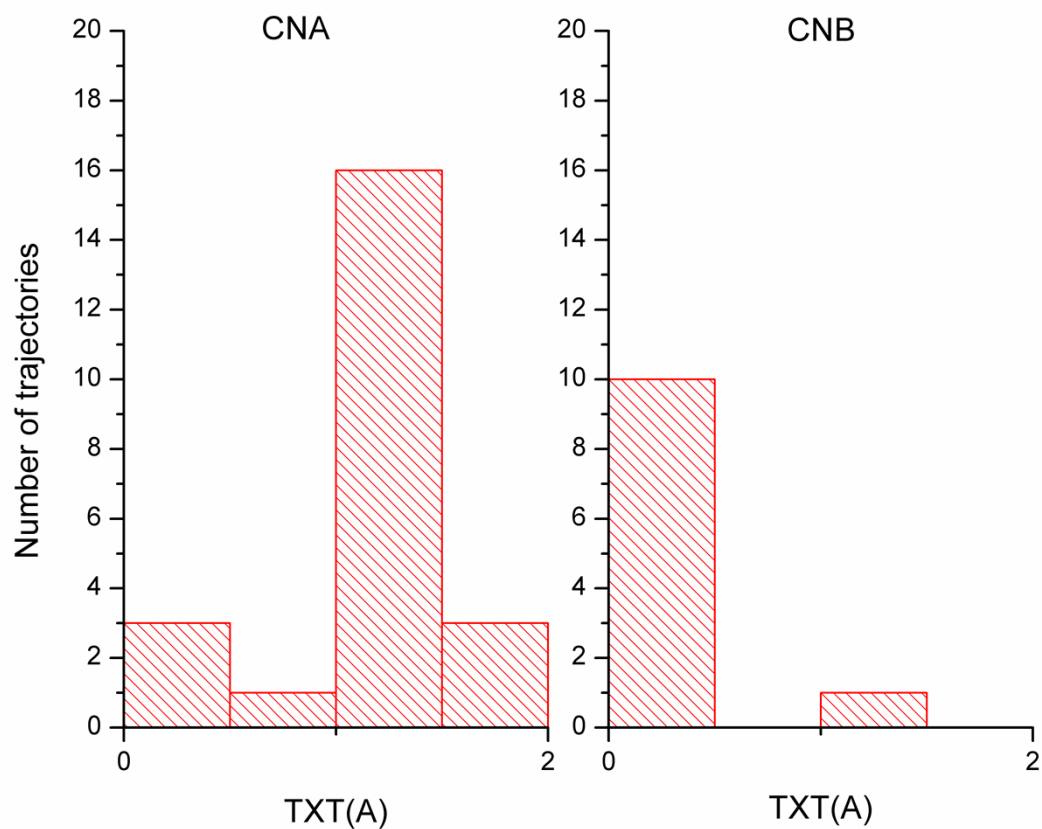
Figure 11S. Histograms showing the distribution of the TXT(A) parameter for the initial conditions related to the hydrogen transfer and the dissociative trajectories (***tt-1*** and ***tt-2*** together). The TXT(A) parameter (0<TXT<2) provides a measure of the localization of the excitation over one particular monomer. A value close to 2 means that the excitation is localized on A, a value close to 0 means that the excitation is localized on B; charge transfer states and delocalized states have intermediate values.
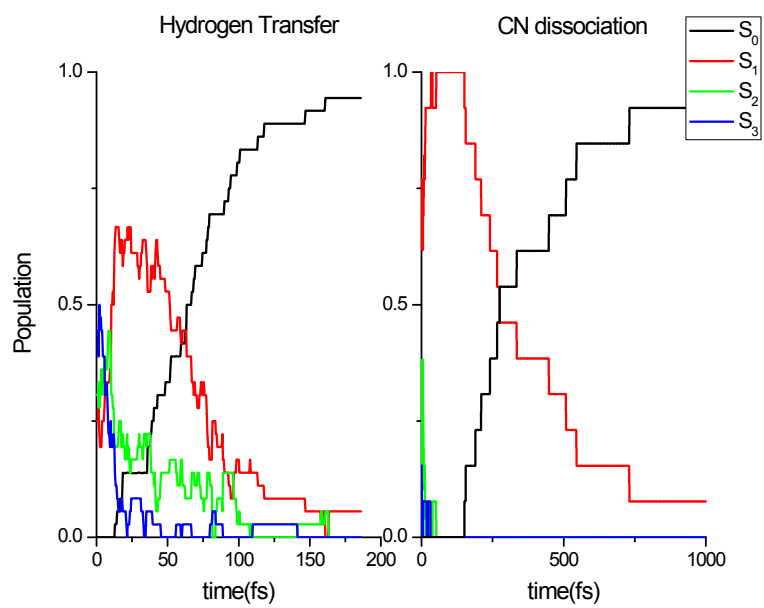
Figure 12S. Population of the different excited states vs. time for the hydrogen transfer trajectories.
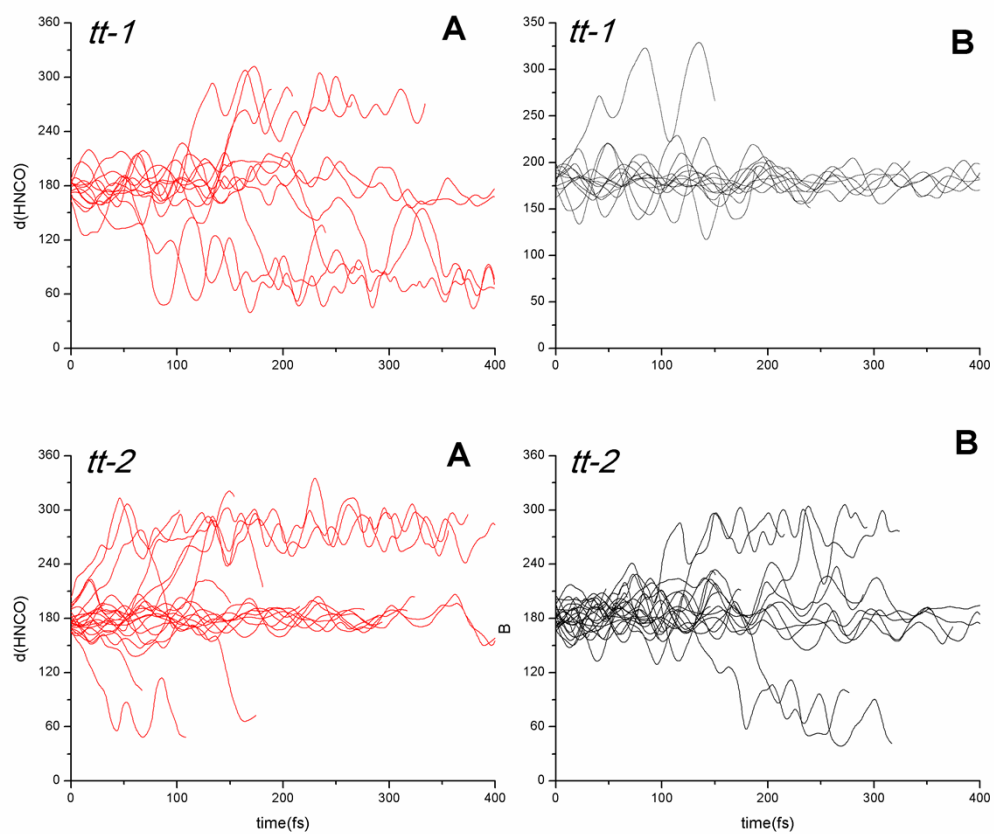
Figure 13S. Evolution of the HNCO angles in monomers A and B for the *tt-1* and *tt-2* isomers. Only CN trajectories are shown here.

Table 1S. Calculated stabilization energies and ZPE corrections for the NMF dimers at the B3LYP-D3/aug-cc-pVTZ level of theory.

	B3LYP-D3/aug-cc-pVTZ (kcal/mol)		
	ΔE	ZPE	ΔE+ ZPE
trans-trans			
*tt*1	-7.9	1.0	-6.9
*tt*2	-7.6	1.0	-6.6
*tt*3	-5.4	0.8	-4.6
*tt*4	-5.5	0.9	-4.6
*tt*5	-5.0	0.7	-4.3
trans-cis			
*tc*1	-10.8	1.4	-9.4
*tc*2	-10.2	1.3	-8.9
*tc*3	-7.7	1.1	-6.6
*tc*4	-7.7	1.0	-6.7
*tc*5	-8.6	1.2	-7.4
tc6	-6.6	1.1	-5.5
tc7	-5.8	0.9	-4.9
cis-cis			
*cc*1	-16.5	1.8	-14.7
*cc*2	-11.1	1.4	-9.7
*cc*3	-6.0	0.9	-5.1

Table 2S. Experimental (argon matrix) and calculated vibrational wavenumbers κ and shifts Δκ (in cm^{-1}) of the *tt-3* and *tt-4* dimers. All the calculated wavenumbers were scaled using the factors shown in **Table 1**.

| Experimental Argon (cm^{-1}) | | B3LYP-D3/aug-cc-pVTZ | | | | Assignment |
| | | *tt-3* | | *tt-4* | | |
κ	Δκ	κ	Δκ	κ	Δκ	
946.6	−1.7	936.1	-8.7	944.5	-0.3	C^m–N str.
951.5	+3.8	949.2	+4.4	951.6	+6.8	
1209.2	+3.7	1211.3	+3.4	1206.4	-1.5	C–N str.
		1220.0	+12.0	1215.9	+8.0	
1688.9	−36.5	1690.9	-33.4	1678.6	-46.2	C=O str.
		1720.3	-4.5	1708.6	-16.2	
		3487.9	-5.3	3493.5	+0.3	N–H str.
		3495.4	+2.2	3495.5	+2.2	

Table 3S. Experimental (argon matrix) and calculated vibrational wavenumbers κ and shifts Δκ (in cm^{-1}) of the **tc-1** and **tc-2** dimers (the shifts were computed with respect to the *cis* monomer). All the calculated wavenumbers were scaled using the factors shown in **Table 1.**

Experimental Argon (cm^{-1})		B3LYP-D3/aug-cc-pVTZ				Assignment
		tc-1		*tc-2*		
κ	Δκ	κ	Δκ	κ	Δκ	
946.6	-54.3	949.9	-53.1	941.3	-61.7	
1019.0 [a]	+18.1	1028.4	+25.4	1024.9	+22.0	C^m–N str.
		1221.3	-69.1	1232.1	-58.3	
1320.2 [a]	+27.3	1338.0	+47.6	1331.5	+41.1	C–N str.
1688.9	-41.7	1668.4	-62.4	1691.1	-39.7	
		1717.6	-13.2	1721.3	-9.5	C=O str.
		3202.3	-255.7	3295.3	-162.6	
		3492.5	+34.5	3494.0	+36.1	N–H str.

[a] Vibrational modes of the *cis*– conformer of NMF.

Table 4S. Vertical excitations (E) and oscillator strengths (f) calculated at the TD/LC-BLYP(μ=0.2)/6-311+G(d) level of theory for the ***tt-1*** and ***tt-2*** isomers in gas phase and considering the matrix as a contimum model (PCM, Argon as solvent).

tt-1	*E* (eV)		*f*	
	Gas Phase	*PCM (Argon)*	*Gas Phase*	*PCM (Argon)*
S_1	5.43	5.49	0.002	0.002
S_2	5.61	5.65	0.002	0.002
S_3	5.80	5.90	0.003	0.004
S_4	5.83	5.90	0.004	0.004
S_5	6.07	6.14	0.002	0.002
tt-2	*E* (eV)		*f*	
	Gas Phase	*PCM (Argon)*	*Gas Phase*	*PCM (Argon)*
S_1	5.46	5.51	0.004	0.004
S_2	5.70	5.73	0.001	0.001
S_3	5.74	5.86	0.003	0.003
S_4	5.81	5.93	0.013	0.013
S_5	6.04	6.10	0.007	0.006