Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

A joint experimental/theoretical study of the ultrafast excited state deactivation of deadenosine and 9-methyladenine in water and acetonitrile

Supplementary Information

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Figure S1. Fluorescence decays curves of dA in water recorded at 330 nm after excitation at 267 nm recorded with the present and the former fluorescence upconversion setups.

Figure S2. Normalized steady-state absorption and corrected fluorescence spectra (λ_{exc} =255 nm) of dA and 9Me-Ade in water and acetonitrile on a wavelength scale.

Figure S3. Lognorm fitted steady-state absorption spectra of dA and 9Me-Ade in water and acetonitrile.

Figure S4. Lognorm fitted steady-state corrected fluorescence spectra of dA and 9Me-Ade in water and acetonitrile.

Figure S5. Total UV fluorescence decays of 9Me-Ade in acetonitrile and of dA in water after excitation at 267 nm**.**

Figure S6. Total VIS fluorescence decays of dA and 9Me-Ade in water after excitation at 267 nm**.**

Table S1. Characteristic times (in ps) and corresponding normalized amplitudes of the fluorescence decays of dA and 9Me-Ade in H_2O and CH_3CN after excitation at 267 nm.

Table S2. Main features of the lowest energy excited states of 9Me-Ade in water solution, according to LR-PCM/CAM-B3LYP and M052X calculations on the 9Me-Ade·4H2O model. PCM/ 6-31G(d) geometry optimizations.

Table S3. Main features of the lowest energy excited states of 9Me-Ade in CH_3CN solution, according to LR-PCM/CAM-B3LYP and M052X calculations. PCM/ 6-31G(d) geometry optimizations.

Table S4. Cartesian coordinates of the S_0 minimum of 9Me-Ade•$4H_2O$ according to PCM/PBE0/6-31G(d) calculations

Table S5. Cartesian coordinates of the L_a-min^{C2} of 9Me-Ade•$4H_2O$ according to PCM/TD-PBE0/6-31G(d) calculations

Table S6. Cartesian coordinates of the planar pseudo-minimum for L_a state minimum of 9Me-Ade•$4H_2O$ according to PCM/TD-PBE0/6-31G(d) calculations.

Figure S1. Fluorescence decays curves of dA in water recorded at 330 nm after excitation at 267 nm. The left curve (with fitted curve in blue) was recorded with the present experimental setup, characterized by an apparatus function of 350 fs fwhm (pink). The right curve (with fitted curve in red) was recorded with the former experimental setup, characterized by an apparatus function of 450 fs fwhm (brown).

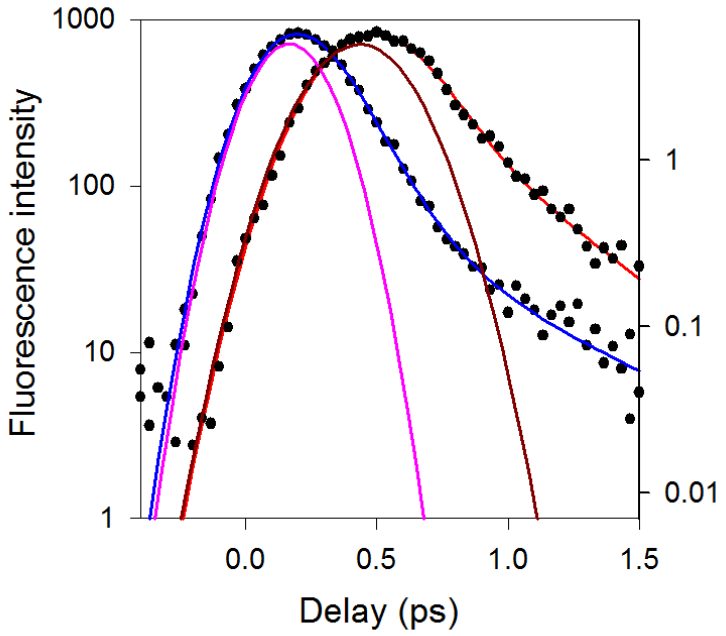

Figure S2. Normalized steady-state absorption and corrected fluorescence spectra (λ_{exc} =255 nm) of dA and 9Me-Ade in water and acetonitrile on a wavelength scale. Fluorescence spectra were truncated at 290 nm in order to suppress the scattered Raman light and smoothed over a few data points.

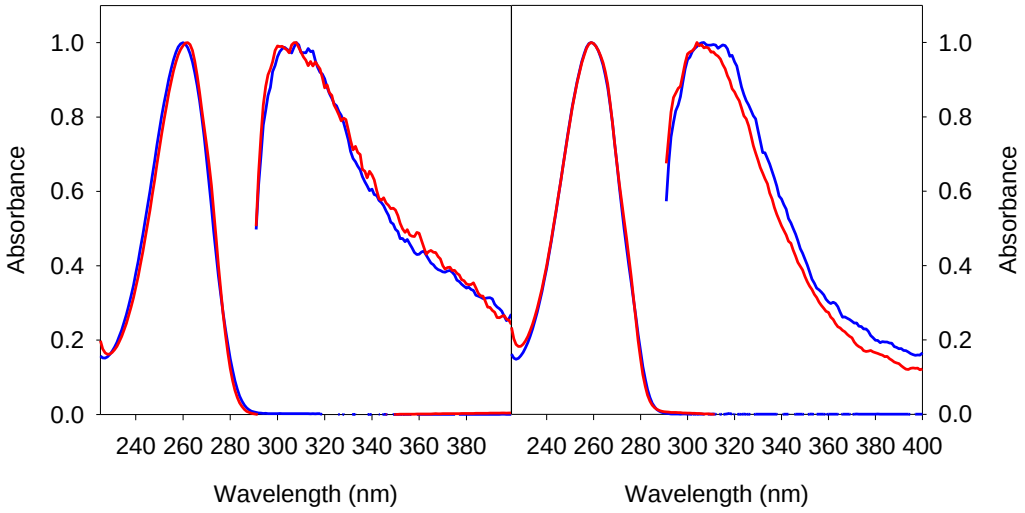

Figure S3. Lognorm fitted steady-state absorption spectra of dA and 9Me-Ade in water and acetonitrile. Deviations are shown with (green) and without (red) additional Gaussian bands used to correct for the "oscillating" artefacts.

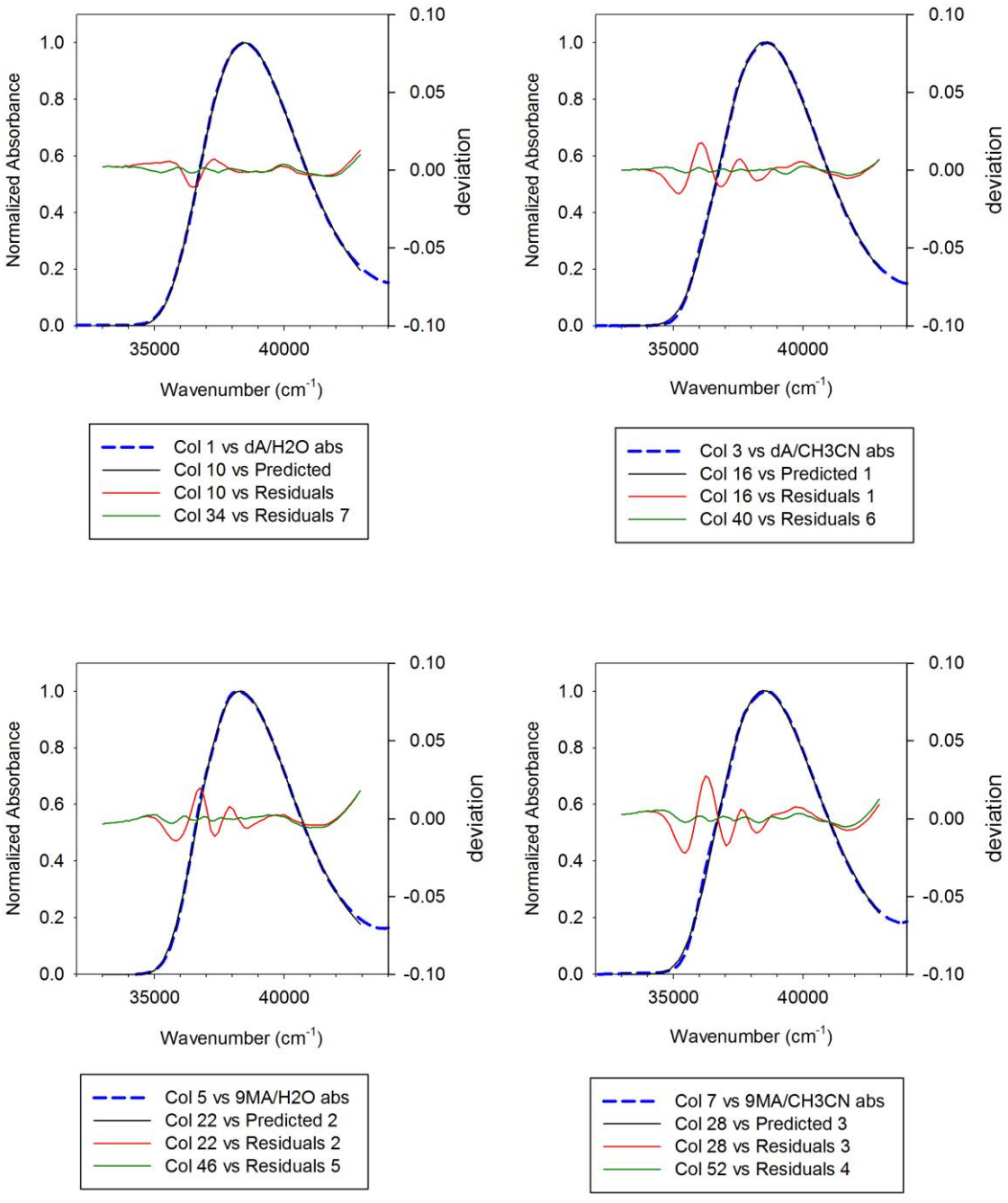

Figure S4. Lognorm fitted steady-state corrected fluorescence spectra of dA and 9Me-Ade in water and acetonitrile. In addition to the main band around $32x10^3$ cm^{-1}, a low-intensity broad Gaussian distribution was added in order to account for the red wing. The shape of the latter is too uncertain for any attempt of assignment.

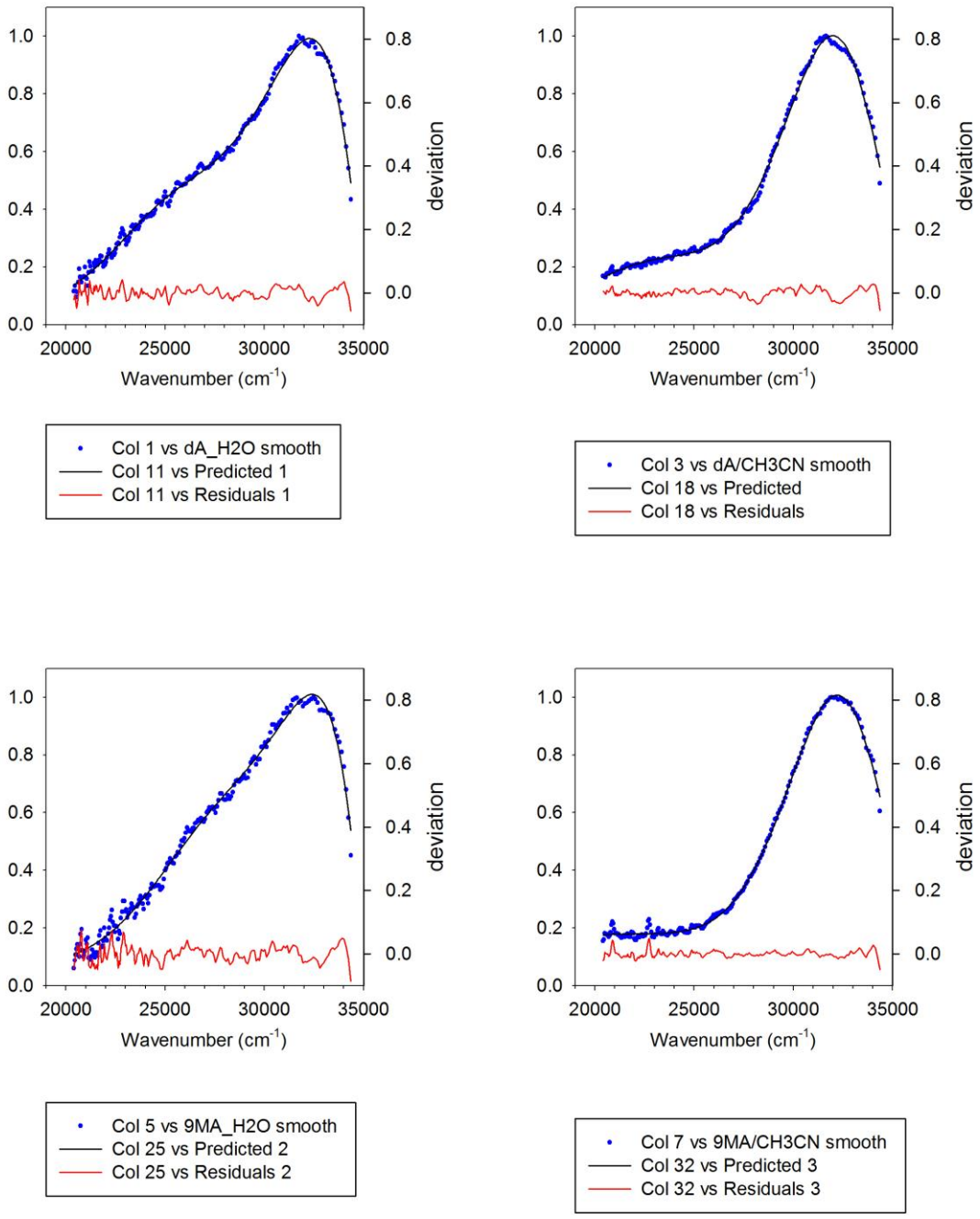

Figure S5. Total UV fluorescence decays of 9Me-Ade in acetonitrile and of dA in water after excitation at 267 nm.

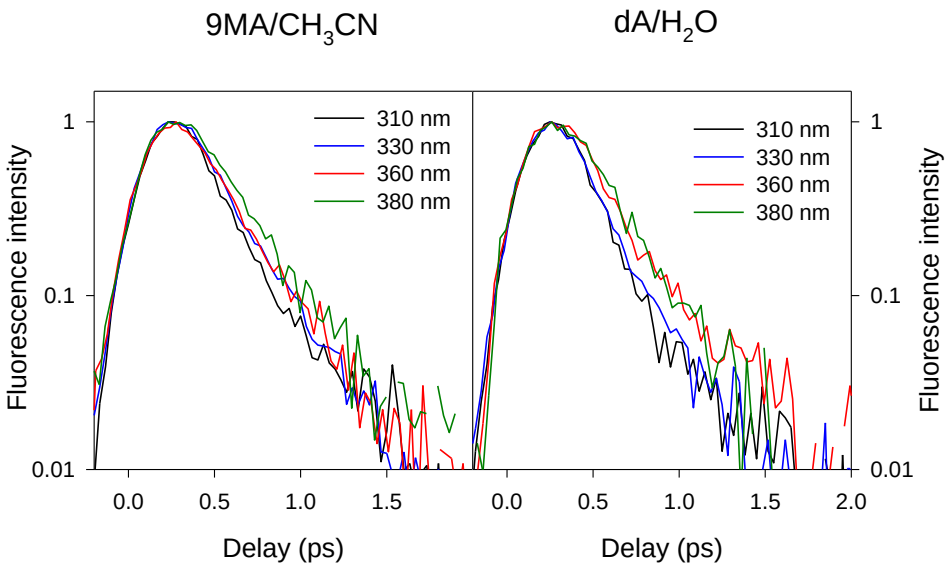

Figure S6. Total VIS fluorescence decays of dA and 9Me-Ade in water after excitation at 267 nm.

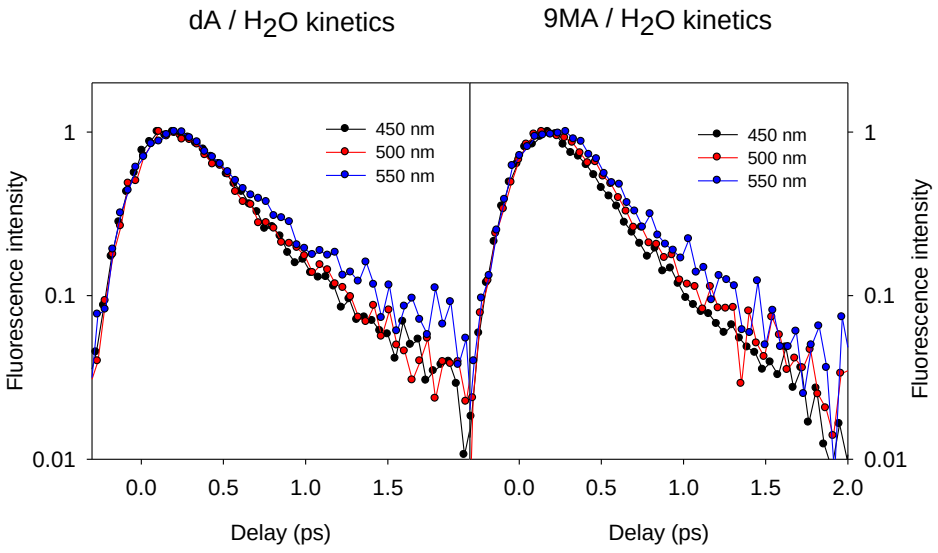

Table S1. Characteristic times (in ps) and corresponding normalized amplitudes (α_2 =1-α_1) of the fluorescence decays of dA and 9MA in H_2O and CH_3CN after excitation at 267 nm. For the fluorescence decays a bi-exponential model function was used; $\alpha\exp(-t/\tau_1) + (1-\alpha)\exp(-t/\tau_2)$, while for the fluorescence anisotropy a mono-exponential function was used; $r_0\exp(-t/\tau_R)$ with τ_R fixed to 50 ps.

	dA		9Me-Ade	
	H_2O	CH_3CN	H_2O	CH_3CN
		310 nm		
τ_1	0.08 ± 0.02	0.12 ± 0.02	0.09 ± 0.02	0.08 ± 0.02
α_1	0.92 ± 0.02	0.76 ± 0.04	0.96 ± 0.03	0.85 ± 0.02
τ_2	0.41 ± 0.06	0.34 ± 0.04	0.42 ± 0.13	0.35 ± 0.03
$<\tau>$	0.11 ± 0.02	0.18 ± 0.02	0.10 ± 0.02	0.12 ± 0.02
r_0	0.32 ± 0.01	0.31 ± 0.01	0.31 ± 0.01	0.32 ± 0.01
		330 nm		
τ_1	0.08 ± 0.03	0.15 ± 0.03	0.11 ± 0.01	0.07 ± 0.03
α_1	0.82 ± 0.04	0.58 ± 0.09	0.96 ± 0.02	0.66 ± 0.06
τ_2	0.33 ± 0.05	0.37 ± 0.03	0.50 ± 0.09	0.31 ± 0.02
$<\tau>$	0.12 ± 0.03	0.24 ± 0.03	0.13 ± 0.01	0.15 ± 0.03
r_0	0.29 ± 0.01	0.29 ± 0.01	0.29 ± 0.01	0.30 ± 0.01
		360 nm		
τ_1	0.15 ± 0.03	0.26 ± 0.05	0.11 ± 0.02	0.13 ± 0.05
α_1	0.87 ± 0.06	0.82 ± 0.25	0.86 ± 0.05	0.66 ± 0.10
τ_2	0.54 ± 0.11	0.54 ± 0.22	0.37 ± 0.06	0.35 ± 0.05
$<\tau>$	0.20 ± 0.03	0.31 ± 0.09	0.15 ± 0.02	0.21 ± 0.04
r_0	0.28 ± 0.01	0.29 ± 0.01	0.28 ± 0.01	0.27 ± 0.01
		380 nm		
τ	0.27 ± 0.01	0.33 ± 0.01	0.24 ± 0.01	0.30 ± 0.01
r_0	0.28 ± 0.01	0.29 ± 0.01	0.27 ± 0.01	0.29 ± 0.01
		450 nm		
τ_1	0.36 ± 0.02		0.28 ± 0.02	
α_1	0.98 ± 0.01		0.95 ± 0.03	
τ_2	3.3 ± 1.8		1.2 ± 0.3	
$<\tau>$	0.41 ± 0.05		0.32 ± 0.03	
r_0	0.17 ± 0.03		0.18 ± 0.01	

Table S2. Main features of the lowest energy excited states of 9Me-Ade in water solution, according to LR-PCM/CAM-B3LYP and M052X calculations on the 9Me-Ade·4H_2O model. PCM/ 6-31G(d) geometry optimizations.

	L_a	L_b	$S_{n\pi^*}$
CAM-B3LYP			
6-31G(d)	5.36(0.30)	5.49(0.11)	5.92(0.00)
6-31+G(d,p)	5.21(0.40)	5.31(0.04)	5.90(0.00)
6-311+G(2d,2p)	5.15(0.39)	5.33(0.04)	5.87(0.00)
M052X			
6-31G(d)	5.48(037)	5.63(0.08)	5.96(0.00)
6-31+G(d,p)	5.32(0.43)	5.54(0.04)	5.94(0.00)
6-311+G(2d,2p)	5.26(0.42)	5.48(0.04)	5.94(0.00)

Table S3. Main features of the lowest energy excited states of 9Me-Ade in CH_3CN solution, according to LR-PCM/CAM-B3LYP and M052X calculations. PCM/ 6-31G(d) geometry optimizations.

	L_a	L_b	$S_{n\pi^*}$
CAM-B3LYP			
6-31G(d)	5.46(0.30)	5.53(0.04)	5.53(0.01)*
6-31+G(d,p)	5.28(0.36)	5.45(0.01)	5.55(0.00)
6-311+G(2d,2p)	5.22(0.35)	5.39(0.01)	5.53(0.00)
M052X			
6-31G(d)	5.55(0.34)	5.68(0.03)	5.61(0.02)*
6-31+G(d,p)	5.39(0.40)	5.60(0.02)	5.61(0.00)
6-311+G(2d,2p)	5.33(0.38)	5.55(0.02)	5.62(0.00)

Table S4. Cartesian coordinates of the S_0 minimum of 9Me-Ade·4H_2O according to PCM/PBE0/6-31G(d) calculations

N	-1.132334	-0.001304	0.651745
C	-1.046506	-0.002055	-0.680896
N	0.042232	0.000000	-1.439910
C	1.163810	0.002272	-0.699556
C	1.228811	0.002403	0.690548
C	0.000000	0.000000	1.400000
N	2.541085	0.002514	1.107174
C	3.235982	0.003316	-0.005596
N	2.463466	0.001729	-1.131269
H	-1.998026	-0.004445	-1.208485
N	-0.077369	0.000065	2.725653
H	-0.987656	-0.002583	3.207381
H	0.786534	0.002729	3.278424
H	4.316376	0.003358	-0.066181
C	2.934293	0.030389	-2.504655
H	3.679368	-0.753670	-2.654717
H	2.086841	-0.142771	-3.171160
H	3.377964	1.003294	-2.731445
H	-3.730291	0.004956	1.668760
O	-4.061494	-0.887354	1.497547
H	-2.818294	0.004618	1.273142
O	-2.583989	-0.017889	4.110670
H	-2.656653	-0.929091	4.425397
H	-3.145663	-0.001087	3.294295
H	-0.066190	-0.143114	-3.321614
O	0.005859	-0.213920	-4.298763
H	0.065092	0.707981	-4.581906
H	2.811857	0.006137	2.945000
O	2.563601	0.026495	3.899255
H	2.704658	0.948520	4.154261

Table S5. Cartesian coordinates of the L_a-min^{C2} of 9Me-Ade·4H_2O according to PCM/TD-PBE0/6-31G(d) calculations

N	-1.178510	0.378239	0.675103
C	-1.038715	0.845787	-0.613099
N	0.058205	0.442248	-1.423676
C	1.164762	0.408995	-0.737955
C	1.229183	0.475249	0.691315
C	-0.030767	0.269890	1.366483
N	2.505697	0.223099	1.104596
C	3.206495	0.059694	-0.000618
N	2.453193	0.106890	-1.138495
H	-1.944352	1.114114	-1.144915
N	-0.056044	-0.050361	2.656501
H	-0.959182	-0.220828	3.146419
H	0.826374	-0.092173	3.196431
H	4.276052	-0.099646	-0.037934
C	2.915053	-0.008991	-2.506073
H	3.836223	-0.593797	-2.520812
H	2.146569	-0.516161	-3.096096
H	3.106356	0.979457	-2.935812
O	-3.723669	0.027975	1.695190
H	-4.027788	-0.810165	1.320720
H	-2.826799	0.167690	1.280415
O	-2.463745	-0.511691	3.996707
H	-2.509703	-1.469782	4.119255
H	-3.070453	-0.333872	3.229756
H	-0.102031	-0.500053	-3.063505
O	-0.035373	-0.978939	-3.918766
H	0.012630	-0.264090	-4.567081
H	2.794639	-0.006038	2.928224
O	2.497063	-0.127729	3.860522
H	2.642001	0.736481	4.270300

Table S6. Cartesian coordinates of the planar pseudo-minimum for L_a state minimum of 9Me-Ade·4H_2O according to PCM/TD-PBE0/6-31G(d) calculations.

N	-1.18213	0.01127	0.66574
C	-1.1142	0.05387	-0.69645
N	0.06594	0.01957	-1.46356
C	1.14736	0.02601	-0.74539
C	1.21534	0.03594	0.68981
C	-0.0506	0.00911	1.37359
N	2.49651	0.01677	1.1103
C	3.23062	0.00307	-0.00349
N	2.47723	-0.00858	-1.15267
H	-2.04622	0.05987	-1.2444
N	-0.07984	-0.01038	2.7124
H	-0.98618	-0.02408	3.23099
H	0.81318	-0.00252	3.24115
H	4.31142	-0.00526	-0.03038
C	2.97021	0.01611	-2.51015
H	3.71872	-0.76902	-2.64979
H	2.13244	-0.15921	-3.18912
H	3.42122	0.98736	-2.74176
O	-3.74507	-0.00315	1.74501
H	-4.0829	-0.89373	1.57715
H	-2.84979	0.0034	1.30926
O	-2.48364	-0.04355	4.10521
H	-2.57185	-0.94328	4.4487
H	-3.09249	-0.02014	3.31948
H	-0.02855	-0.1467	-3.33103
O	0.04095	-0.23112	-4.30909
H	0.10954	0.68642	-4.60391
H	2.76917	0.01569	2.93592
O	2.47327	0.02741	3.87849
H	2.62371	0.94035	4.1611