Supplementary Information

Theoretical study on excited-state intermolecular proton transfer reactions of 1*H*-pyrrolo[3,2-*h*]quinoline with water and methanol

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TABLE S1: Cartesian coordinates of ground-state optimized structures of $PQ(H_2O)_{n=1,2}$ and $PQ(MeOH)_{n=1,2}$ complexes at RI-MP2/SVP level (in Å).

1. $PQ(H_2O)$

C	0.0360720	1.2314735	2.5278182
C	0.0282944	0.0537676	0.5368212
C	-0.0261479	-1.2086393	1.2208959
C	-0.0093444	-1.1719288	2.6337179
C	0.0126661	0.0480040	3.2925082
C	-0.0286859	0.0113166	-0.8857876
C	0.0075611	-1.2130818	-1.6077759
C	-0.0330693	-2.4449345	-0.8962393
C	-0.0185531	-2.4376019	0.4826203
C	0.0315020	0.5162310	-3.0552963
C	0.0234865	-0.8697983	-2.9918173
H	0.0525878	2.2083381	3.0234713
H	-0.0295414	-2.1109717	3.1950075
H	0.0183540	0.1032559	4.3828642
H	-0.0328922	-3.3933461	-1.4411472
H	-0.0435466	-3.3771926	1.0417318
H	0.0483748	1.1761420	-3.9210613
H	0.0363420	-1.5509381	-3.8404767
N	0.0315905	1.2432093	1.1978659
N	0.0091642	1.0340944	-1.7864674
H	0.0087457	2.0320747	-1.5243341
H	0.0675725	2.8450522	0.2416771
O	-0.0045371	3.5136274	-0.4782757
H	-0.9036893	3.8457380	-0.3711181

2. $PQ(H_2O)_2$

C	-0.0928086	2.6430962	0.5633971
C	-0.0066211	0.3278090	0.5578257
C	-0.0516933	0.2755554	1.9943784
C	-0.1021613	1.5092044	2.6822030
C	-0.1427950	2.6977825	1.9694839
C	-0.0310340	-0.9196895	-0.1289223
C	0.0921418	-2.1574789	0.5643650
C	0.0838536	-2.1699028	1.9868757
C	0.0363233	-0.9795099	2.6804498
C	0.0441076	-2.5412617	-1.6543528
C	0.1215316	-3.1814105	-0.4267294
H	-0.1000433	3.5616985	-0.0336766
H	-0.1235353	1.5112369	3.7761987
H	-0.1922683	3.6631309	2.4770085
H	0.1492155	-3.1192084	2.5263763
H	0.0230315	-0.9744019	3.7739897
H	0.0308073	-2.9527124	-2.6623040
H	0.1931803	-4.2550587	-0.2638955
N	-0.0384230	1.5040838	-0.1234283
N	-0.0326949	-1.1852752	-1.4660430
H	-0.1713659	-0.5212314	-2.2467716
H	0.3224278	2.0912754	-1.7799771
O	0.5289899	2.5541600	-2.6282648
H	1.4895852	2.6348740	-2.6063325
H	-1.3725534	0.5486031	-3.9238357
O	-0.4428772	0.3284894	-3.7937997
H	-0.0413437	1.1984826	-3.5761630

3. PQ(MeOH)

C	0.2380480	2.3495641	1.3814058
C	0.0792577	0.1845687	0.5788947
C	-0.0672966	-0.3537312	1.9028404
C	-0.0891211	0.5722259	2.9704947
C	0.0724397	1.9256868	2.7148738
C	0.1451799	-0.7555688	-0.4886679
C	-0.0683888	-2.1463812	-0.2860538
C	-0.2260361	-2.6424662	1.0385330
C	-0.2554009	-1.7613011	2.0990484
C	0.2069524	-1.7385713	-2.4873383
C	-0.0053981	-2.7595709	-1.5722123
H	0.3723745	3.4121451	1.1514371
H	-0.2181345	0.2078249	3.9941184
H	0.0699347	2.6591362	3.5235579
H	-0.3652594	-3.7137261	1.2100297
H	-0.3828586	-2.1292809	3.1209750
H	0.3141034	-1.7816964	-3.5699534
H	-0.1065323	-3.8179502	-1.8045088
N	0.2513088	1.5141974	0.3462507
N	0.2875392	-0.5394949	-1.8274600
H	0.4237795	0.3947731	-2.2478725
H	0.4446535	2.1101121	-1.3625786
O	0.3969809	2.1854972	-2.3458722
C	-0.9129708	2.6128436	-2.6455641
H	-1.1187785	3.6227967	-2.2530368
H	-1.0228027	2.6480006	-3.7374837
H	-1.6806963	1.9274413	-2.2447501

4. PQ(MeOH)$_2$

C	-0.3309564	2.6102028	-0.0901010
C	-0.0707731	0.4753580	0.7760259
C	-0.1518415	0.9608463	2.1270122
C	-0.3178941	2.3535975	2.3000691
C	-0.4284862	3.1816706	1.1928557
C	0.0209589	-0.9347968	0.6056910
C	0.2282975	-1.8091704	1.7097257
C	0.1830949	-1.2899852	3.0336249
C	0.0189234	0.0645898	3.2321327
C	0.2585710	-2.9948423	-0.2057018
C	0.3623233	-3.1223915	1.1712874
H	-0.3816496	3.2357885	-0.9882322
H	-0.3709207	2.7643079	3.3129120
H	-0.5656632	4.2592716	1.3015968
H	0.3114913	-1.9596050	3.8889654
H	-0.0246925	0.4757381	4.2445822
H	0.2943125	-3.7538939	-0.9855794
H	0.5164718	-4.0484163	1.7219045
N	-0.1721616	1.3042284	-0.2969643
N	0.0710315	-1.6769208	-0.5372991
H	-0.1349072	-1.3591994	-1.5040939
H	0.3792965	1.1845567	-1.9586109
O	0.7467590	1.2204733	-2.8773251
O	-0.6362663	-1.0311751	-3.1413550
H	-0.0938423	-0.2230544	-3.2890995
C	2.1490336	1.1194756	-2.7524722
H	2.4577504	0.1952868	-2.2337291
H	2.5859317	1.1096042	-3.7594526
H	2.5729148	1.9773515	-2.2045429
C	-1.9883780	-0.6231879	-3.1208003
H	-2.3227371	-0.2647326	-4.1078698
H	-2.6029810	-1.4907985	-2.8471439
H	-2.1694199	0.1748790	-2.3805612

TABLE S2: Relative ground (S_0) and excited states ($\pi\pi^*$, $\pi\sigma^*$) energies (kcal.mol^{-1}) for characteristic points of normal (N), intermediary structure (IS), and tautomer (T) along the reaction pathways for one selected trajectory of each complex.

State	Form	Complex			
		PQ(H_2O)	PQ(H_2O)$_2$	PQ(MeOH)	PQ(MeOH)$_2$
S_0	N	0	0	0	0
	IS1	58	38	53	74
	IS2	50	20	83	102
	IS3	-	33	-	87
	T	34	25	33	51
$\pi\pi^*$	N	100	89	110	100
	IS1	141	123	137	138
	IS2	133	105	163	176
	IS3	-	122	-	167
	T	102	102	112	115
$\pi\sigma^*$	N	175	186	184	176
	IS1	232	217	233	249
	IS2	226	201	216	266
	IS3	-	204	-	240
	T	162	203	167	213

TABLE S3: Average relative ground (S_0) and excited states ($\pi\pi^*$) energies (kcal.mol^{-1}) of all ESPT trajectories for each complex for characteristic points.

State	Form	Complex			
		PQ(H_2O)	PQ(H_2O)$_2$	PQ(MeOH)	PQ(MeOH)$_2$
S_0	N	0	0	0	0
	IS1	34	28	32	25
	IS2	28	31	33	32
	IS3	-	34	-	34
	T	23	27	29	27
$S_1(\pi\pi^*)$	N	91	87	96	87
	IS1	94	95	93	87
	IS2	83	91	84	86
	IS3	-	88	-	82
	T	83	85	83	81

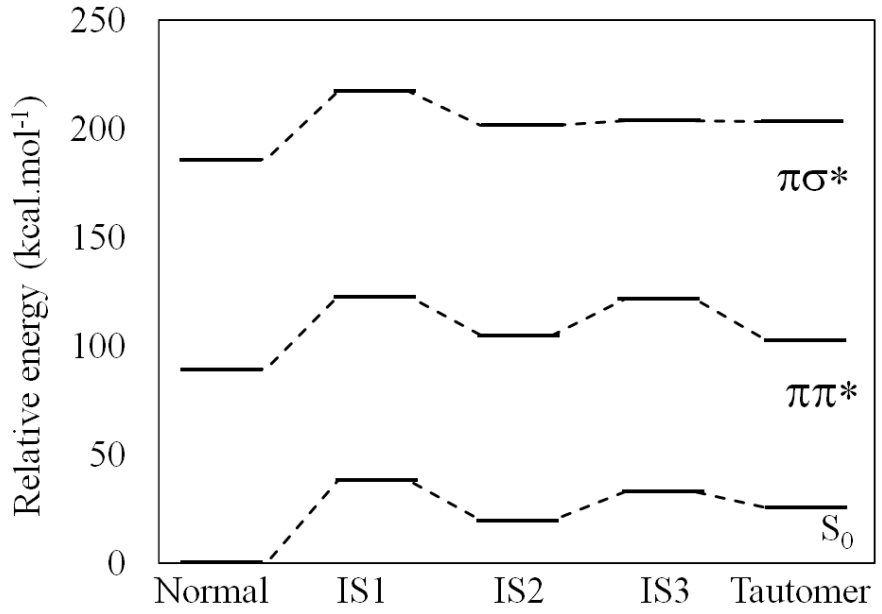

Fig S1. Potential energy diagram of a selected trajectory for $PQ(H_2O)_2$ complex at ground state (S_0) and excited states ($\pi\pi^*$, $\pi\sigma^*$) computed at RI-ADC(2)/SVP-SV(P) level.

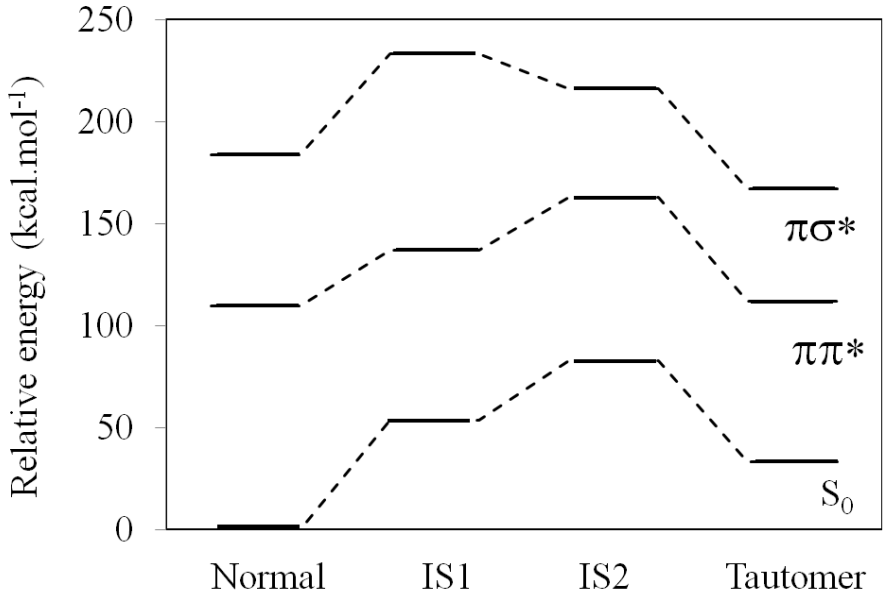

Fig S2. Potential energy diagram of a selected trajectory for PQ(MeOH) complex at ground state (S_0) and excited states ($\pi\pi^*$, $\pi\sigma^*$) computed at RI-ADC(2)/SVP-SV(P) level.

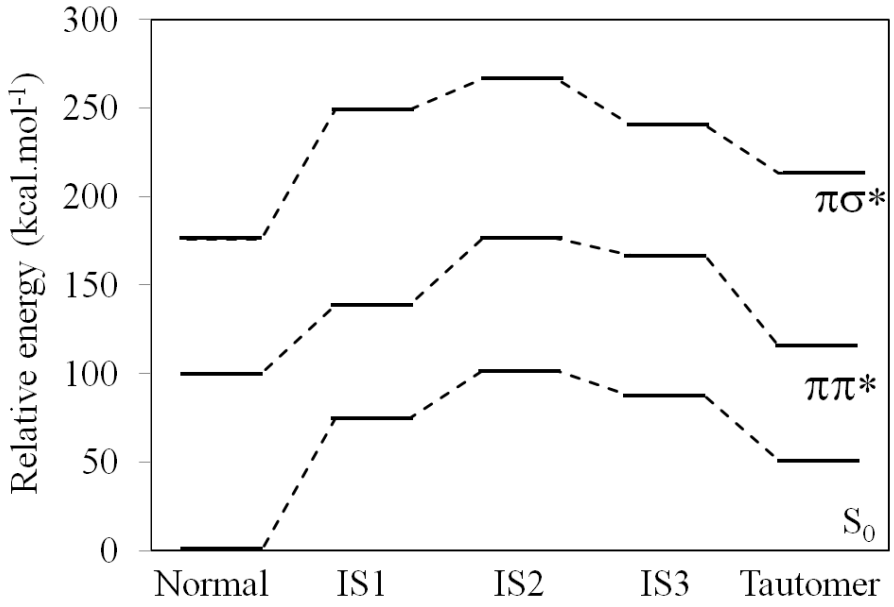

Fig S3. Potential energy diagram of a selected trajectory for $PQ(MeOH)_2$ complex at ground state (S_0) and excited states ($\pi\pi^*$, $\pi\sigma^*$) computed at RI-ADC(2)/SVP-SV(P) level.

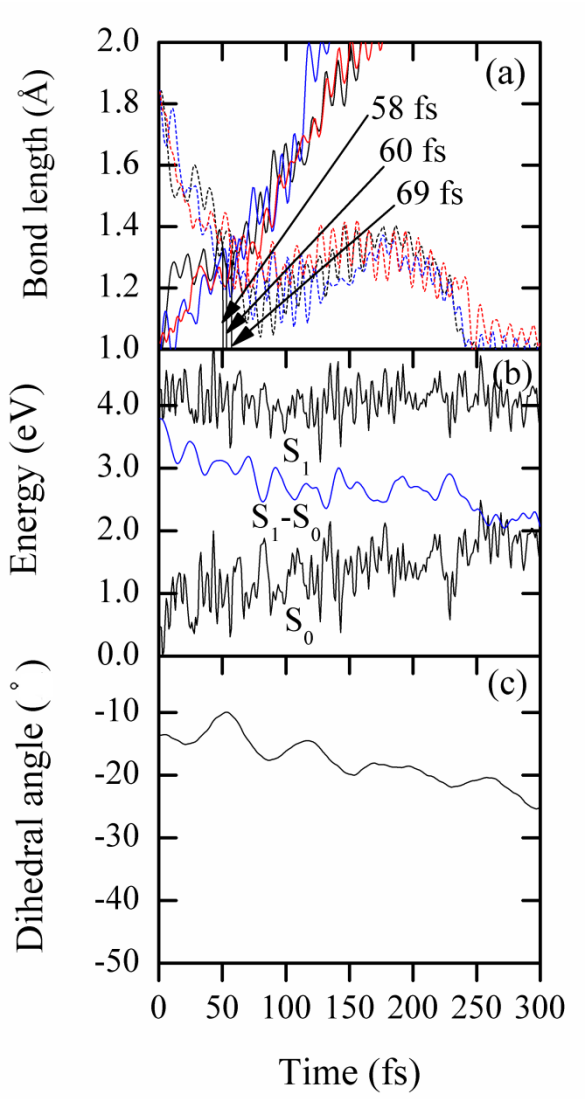

Fig S4. Average values over 3 trajectories of $PQ(H_2O)_2$ complex exhibiting excited-state triple , as a function of time: (a) Average lengths of broken and new bonds; N1–H1 and O1···H1 in black, O1–H2 and O2···H2 in blue, and O2–H3 and N2···H3 in red (b) Average relative energies of the excited state (S_1), ground state (S_0), and the S_1-S_0 energy gap and (c) Average dihedral angle of O1N1N2O2.

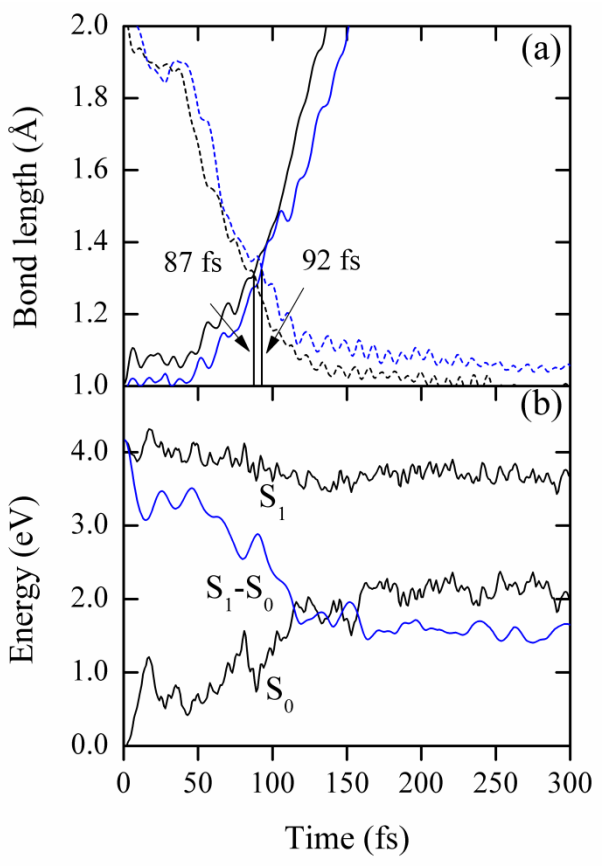

Fig S5. Average values over 36 trajectories of PQ(MeOH) complex exhibiting excted-state double proton transfer, as a function of time: (a) Average lengths of broken and new bonds; N1–H1 and O1···H1 in black and O1–H2 and N2···H2 in blue (b) Average relative energies of the excited state (S_1), ground state (S_0), and the S_1-S_0 energy gap.

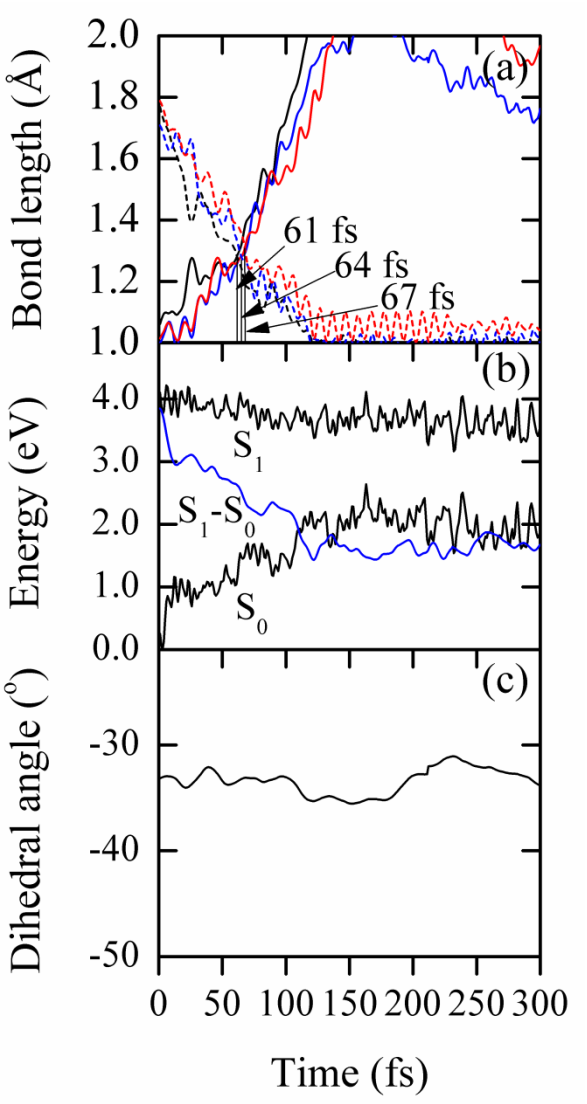

Fig S6. Average values over 14 trajectories of $PQ(MeOH)_2$ complex exhibiting excited-state triple proton transfer, as a function of time: (a) Average lengths of broken and new bonds; N1–H1 and O1···H1 in black, O1–H2 and O2···H2 in blue, and O2–H3 and N2···H3 in red (b) Average relative energies of the excited state (S_1), ground state (S_0), and the S_1-S_0 energy gap and (c) Average dihedral angle of O1N1N2O2.