Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

A Combined Spectroscopic and Computational Investigation on the Solvent-to-Chromophore Excited-State Proton Transfer in the 2,2'-Pyridylbenzimidazole-Methanol complex

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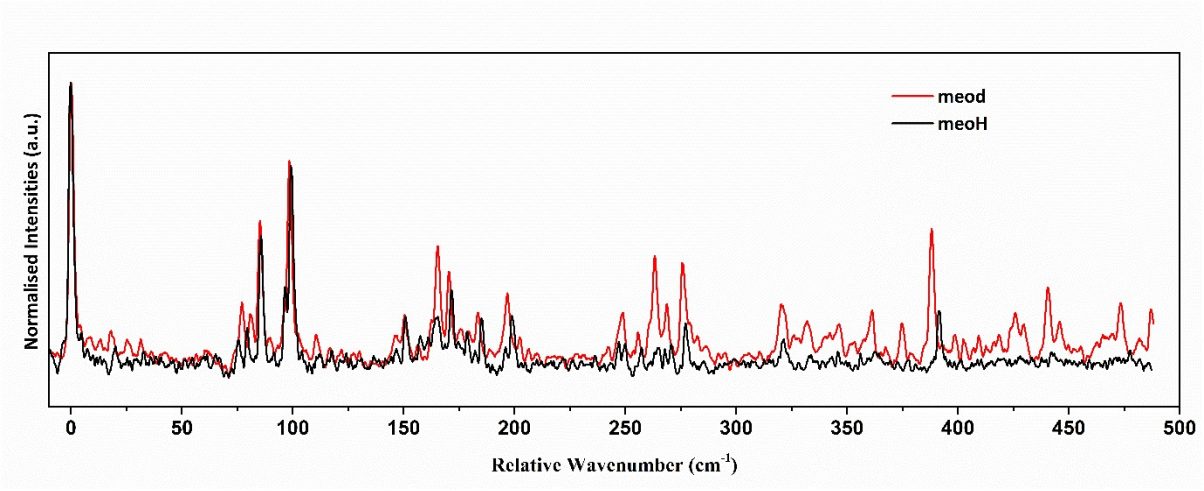
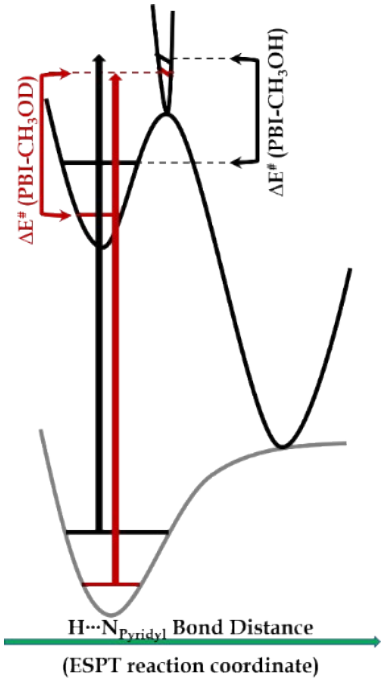


Figure S1. To compare the kinetic isotope effect, the baseline corrected normalized R2PI spectra of PBI–CH_3OD and PBI–CH_3OH of all the vibrational modes. The ID/IH values are given in Table 2 of the article, calculated by integrating each peak. Both the spectra were recorded using identical experimental conditions (including the identical set of lasers). The normalization was done at the band origin transitions only. The band origin and transition to ν_{45} band at 97 cm^{-1} have shown nearly identical intensity patterns in both the systems, which confirms the correctness of the normalization methods.



Scheme S1: The effect of isotopic substitution on the zero-point energy and energy barriers of a reaction. The ZPE corrected energy barrier in PBI-CH_3OD, i.e., the $\Delta E^{\#}$(PBI-CH_3OD) is higher than the same in PBI-CH_3OH complex.

Table S1: Charges on H(4), H(2) and CH_3O species in each structure along the ESPT and ESHT pathways.

	ESHT pathway			
Sr. no (Str.)	**d(N(5)-H(4)) (Å)**	**H(2)**	**H(4)**	**CH_3O**
1 (str-a)	1.619	0	0	0
2	1.576	0.002	0.001	0.016
3	1.533	0.002	0.002	0.038
4 (TS_{HT})	1.490	0.004	0.001	0.063
5	1.447	0.011	-0.003	0.081
6	1.404	0.034	0.01	0.09
7	1.361	0.032	-0.013	0.09
8	1.318	0.042	-0.017	0.08
9	1.275	0.05	-0.019	0.065
10	1.232	0.056	-0.017	0.046
11	1.189	0.06	-0.014	0.026
12	1.146	0.062	-0.011	0.01
13	1.103	0.062	-0.011	-0.001
14	1.060	0.062	-0.015	-0.008
15 (str-b)	1.017	0.062	-0.021	-0.012
	ESPT pathway			
1 (str-a)	1.619	0	0	0
2	1.532	0	-0.008	-0.011
3	1.445	0.001	-0.018	-0.026
4 (TS_{PT})	1.358	0.001	-0.029	-0.047
5	1.271	-0.006	-0.022	-0.228
6 (str-d)	1.184	0.005	-0.008	-0.299
7	1.097	0.028	-0.003	-0.328
8 (str-e)	1.010	0.026	-0.016	-0.343

SI Table S2: Cartesian Coordinates of the optimized structures of PBI monomer, PBI–CH_3OH complex in the ground state S_0 and excited state S_1, calculated using B3LYP-D4/def2-TZVPP level of theory.

PBI-monomer (normal form)

Ground State S_0					**Excited State S_1**				
	Atom	X	Y	Z		Atom	X	Y	Z
1	C	-2.4372	1.3494	0	1	C	-2.4595	1.3664	0
2	H	5.1449	1.0002	0	2	H	5.1897	0.9625	0
3	N	-2.3468	-1.0533	0	3	N	-2.319	-1.0845	0
4	H	5.0267	-1.4533	0	4	H	5.0159	-1.4909	0
5	H	-5.5373	-0.0026	0	5	H	-5.528	-0.0703	0
6	C	-3.8205	1.3083	0	6	C	-3.8364	1.3068	0
7	C	1.7457	-0.7672	0	7	C	1.7305	-0.754	0
8	H	2.8487	-2.6322	0	8	H	2.7912	-2.6215	0
9	N	0.4043	-1.0687	0	9	N	0.3713	-1.0261	0
10	C	3.0297	1.2998	0	10	C	3.0678	1.2962	0
11	C	4.1082	-0.8821	0	11	C	4.1212	-0.8852	0
12	N	0.5151	1.1647	0	12	N	0.5697	1.219	0
13	C	-1.739	0.141	0	13	C	-1.7258	0.1676	0
14	C	-4.4591	0.0732	0	14	C	-4.4528	0.035	0
15	C	2.8943	-1.5516	0	15	C	2.8461	-1.5416	0
16	C	-0.28	0.1192	0	16	C	-0.3004	0.1526	0
17	H	-0.0484	-1.967	0	17	H	-0.1273	-1.9047	0
18	H	-4.1395	-2.0554	0	18	H	-4.1025	-2.0853	0
19	C	1.7951	0.6484	0	19	C	1.7974	0.6708	0
20	H	-4.3948	2.225	0	20	H	-4.4281	2.2114	0
21	H	-1.8851	2.2774	0	21	H	-1.9284	2.3082	0
22	C	4.1749	0.5218	0	22	C	4.2155	0.4947	0
23	H	3.077	2.3798	0	23	H	3.1325	2.3751	0
24	C	-3.6767	-1.0751	0	24	C	-3.6406	-1.1022	0

PBI-CH_3OH (initial structure normal form)

Ground State S_0					**Excited State S_1**				
	Atom	X	Y	Z		Atom	X	Y	Z
1	C	2.9817	1.3315	-0.1908	1	C	3.0113	1.3049	-0.1349
2	H	-5.5799	0.3101	0.1433	2	H	-5.5775	0.13	0.1616
3	H	5.0228	-1.362	0.1905	3	H	5.0177	-1.4769	0.1898
4	C	-3.8	-0.8799	0.2617	4	C	-3.7467	-0.9459	0.2534
5	C	-1.7664	0.18	0.0813	5	C	-1.7637	0.2409	0.0454
6	C	4.138	0.5784	-0.0965	6	C	4.1932	0.4817	-0.0438
7	N	-2.4688	-0.9521	0.243	7	N	-2.399	-0.9866	0.2206
8	C	-4.4997	0.3078	0.1205	8	C	-4.4995	0.1959	0.1217

9	C	2.8938	-1.4894	0.2514	9	C	2.8659	-1.5143	0.2085
10	H	3.0111	2.3993	-0.3576	10	H	3.1019	2.3739	-0.2653
11	H	5.1002	1.0632	-0.1912	11	H	5.1591	0.9617	-0.1085
12	H	-4.3257	-1.8178	0.3973	12	H	-4.2375	-1.9026	0.397
13	H	-1.7764	2.2994	-0.1957	13	H	-1.8893	2.344	-0.2261
14	C	-2.3916	1.4218	-0.069	14	C	-2.4543	1.4318	-0.0947
15	C	1.7309	-0.7295	0.155	15	C	1.7171	-0.7037	0.1175
16	N	0.3998	-1.0573	0.2315	16	N	0.4086	-0.9982	0.163
17	C	4.0944	-0.8113	0.1217	17	C	4.116	-0.8869	0.1232
18	H	0.0029	-1.9877	0.3761	18	H	-0.0261	-1.9463	0.2626
19	H	-4.2782	2.4308	-0.1627	19	H	-4.3958	2.3663	-0.1711
20	H	2.8638	-2.5568	0.4218	20	H	2.7814	-2.5833	0.3429
21	C	-0.3065	0.1062	0.0635	21	C	-0.3092	0.2211	0.0257
22	C	-3.772	1.4816	-0.049	22	C	-3.8422	1.4468	-0.0635
23	C	1.758	0.6689	-0.0631	23	C	1.7901	0.7035	-0.0521
24	N	0.472	1.1553	-0.1139	24	N	0.5036	1.2351	-0.1037
25	O	-1.1688	-3.4146	0.4339	25	O	-1.0568	-3.2316	0.3998
26	H	-1.7737	-2.6406	0.4113	26	H	-1.7009	-2.4387	0.3819
27	C	-1.251	-4.088	-0.8139	27	C	-1.2718	-4.0135	-0.7618
28	H	-0.4894	-4.8665	-0.8228	28	H	-0.4589	-4.7352	-0.8531
29	H	-2.2283	-4.5606	-0.9528	29	H	-2.2134	-4.5673	-0.6986
30	H	-1.0674	-3.4118	-1.6558	30	H	-1.2976	-3.3983	-1.6684

PBI-CH_3OH Transition state along ESHT and ESPT

S_1 TS-ESHT					**S_1 TS-ESPT**				
	Atom	X	Y	Z		Atom	X	Y	Z
1	C	2.9923	1.2678	-0.1377	1	C	3.2774	1.6149	-0.1777
2	H	-5.6092	0.1698	0.1463	2	H	-5.3564	0.7282	0.1245
3	H	4.9917	-1.5191	0.1538	3	H	5.1788	-1.2319	0.2005
4	C	-3.8121	-0.9398	0.2631	4	C	-3.5716	-0.405	0.2398
5	C	-1.7957	0.2148	0.0561	5	C	-1.5408	0.7223	0.0109
6	C	4.1674	0.4424	-0.0607	6	C	4.4269	0.7502	-0.0707
7	N	-2.4449	-0.9974	0.2377	7	N	-2.2141	-0.4789	0.2063
8	C	-4.5288	0.2178	0.1133	8	C	-4.2764	0.7587	0.0843
9	C	2.8429	-1.5578	0.1901	9	C	3.0281	-1.1911	0.2233
10	H	3.0829	2.3375	-0.2617	10	H	3.4071	2.677	-0.3292
11	H	5.1357	0.9173	-0.1291	11	H	5.4101	1.1919	-0.1462
12	H	-4.3168	-1.8855	0.4147	12	H	-4.0824	-1.3459	0.4013
13	H	-1.8647	2.2996	-0.2335	13	H	-1.5921	2.8112	-0.2955
14	C	-2.4496	1.4017	-0.0985	14	C	-2.1866	1.9205	-0.1508
15	C	1.6926	-0.7473	0.1127	15	C	1.9105	-0.34	0.1166
16	N	0.3897	-1.0529	0.1657	16	N	0.5929	-0.5872	0.1699
17	C	4.0883	-0.9303	0.0988	17	C	4.2991	-0.6108	0.1238

18	H	-0.1536	-2.135	0.2881	18	H	0.1054	-1.5087	0.2733
19	H	-4.3981	2.3781	-0.1985	19	H	-4.111	2.9165	-0.2512
20	H	2.761	-2.6276	0.3197	20	H	2.9039	-2.2533	0.3777
21	C	-0.3133	0.1698	0.0383	21	C	-0.0731	0.6484	4.00E-04
22	C	-3.8634	1.4505	-0.0796	22	C	-3.5872	1.9832	-0.1248
23	C	1.7763	0.663	-0.0494	23	C	2.0371	1.0581	-0.0829
24	N	0.4802	1.1905	-0.0889	24	N	0.7653	1.6328	-0.1482
25	O	-1.0148	-3.0992	0.4216	25	O	-0.9813	-2.618	0.391
26	H	-1.7535	-2.3076	0.397	26	H	-1.6229	-1.6952	0.3301
27	C	-1.1461	-3.8991	-0.7488	27	C	-1.1989	-3.4254	-0.7415
28	H	-0.2596	-4.525	-0.8542	28	H	-0.3884	-4.1531	-0.8447
29	H	-2.0198	-4.5463	-0.6608	29	H	-2.1373	-3.986	-0.6599
30	H	-1.2572	-3.2796	-1.6435	30	H	-1.2452	-2.8364	-1.6684

PBI-CH_3OH ESHT and ESPT Products

S_1 ESHT Product (Structure-b)					**S_1 ESPT Product (Structure-e)**				
	Atom	X	Y	Z		Atom	X	Y	Z
1	C	3.0078	1.2896	-0.147	1	C	3.2619	1.6696	-0.1577
2	H	-5.6322	0.2645	0.2044	2	H	-5.3796	0.9875	0.1535
3	H	4.9621	-1.5132	0.1699	3	H	5.1779	-1.1199	0.1865
4	C	-3.8566	-0.8785	0.3084	4	C	-3.6911	-0.2703	0.2087
5	C	-1.7888	0.3027	0.0591	5	C	-1.5185	0.7448	-0.0245
6	C	4.1723	0.454	-0.0636	6	C	4.3865	0.8636	-0.0527
7	N	-2.4734	-0.8687	0.2584	7	N	-2.3273	-0.384	0.1149
8	C	-4.5522	0.299	0.1562	8	C	-4.3024	0.9371	0.1168
9	C	2.8051	-1.521	0.2049	9	C	3.0397	-1.1535	0.1625
10	H	3.1081	2.358	-0.2788	10	H	3.3414	2.7395	-0.2913
11	H	5.1473	0.915	-0.1364	11	H	5.3698	1.3135	-0.0817
12	H	-4.3184	-1.8364	0.4757	12	H	-4.2302	-1.1907	0.3611
13	H	-1.8724	2.3656	-0.252	13	H	-1.4896	2.8429	-0.2024
14	C	-2.448	1.4675	-0.0979	14	C	-2.1356	1.983	-0.1119
15	C	1.6718	-0.7069	0.1195	15	C	1.9174	-0.3424	0.0618
16	N	0.3538	-1.0262	0.1762	16	N	0.5643	-0.6106	0.0764
17	C	4.0696	-0.9076	0.1078	17	C	4.2783	-0.5252	0.1049
18	H	-0.363	-2.708	0.3458	18	H	0.1197	-1.5364	0.283
19	H	-4.426	2.426	-0.172	19	H	-3.9789	3.0795	-0.132
20	H	2.7131	-2.5894	0.3453	20	H	2.9611	-2.2256	0.2802
21	C	-0.2876	0.1934	0.0402	21	C	-0.0889	0.6007	-0.0327
22	C	-3.8902	1.499	-0.0518	22	C	-3.5127	2.1095	-0.0562
23	C	1.7869	0.6919	-0.0536	23	C	2.0088	1.0599	-0.0958
24	N	0.4861	1.2311	-0.0984	24	N	0.7492	1.6127	-0.1499
25	O	-1.0531	-3.4014	0.4096	25	O	-1.0395	-3.0639	0.4362
26	H	-1.9832	-1.753	0.3672	26	H	-1.9031	-1.2931	0.2325

27	C	-1.0842	-4.1249	-0.8106	27	C	-1.0912	-3.7679	-0.7162
28	H	-0.1899	-4.7437	-0.9364	28	H	-0.3383	-4.5706	-0.7466
29	H	-1.953	-4.7816	-0.7881	29	H	-2.0571	-4.3137	-0.7504
30	H	-1.1731	-3.4617	-1.6779	30	H	-1.0336	-3.156	-1.6275

PBI-CH_3OH ESPT Product (Structure-d)

S1 ESPT Product (Structure-d)				
	Atom	X	Y	Z
1	C	3.3071	1.7394	-0.3776
2	H	-5.293	0.9199	0.3116
3	H	5.3238	-0.8795	0.4313
4	C	-3.598	-0.3297	0.2052
5	C	-1.434	0.6908	-0.0197
6	C	4.4603	1.0048	-0.1381
7	N	-2.2464	-0.4434	0.0485
8	C	-4.2206	0.8754	0.2034
9	C	3.1866	-0.9953	0.4114
10	H	3.3477	2.7775	-0.6767
11	H	5.4263	1.4785	-0.2507
12	H	-4.1394	-1.2568	0.3007
13	H	-1.4224	2.8002	-0.1006
14	C	-2.0673	1.9367	-0.0381
15	C	2.0395	-0.2555	0.1724
16	N	0.6918	-0.5757	0.2245
17	C	4.4042	-0.3393	0.2527
18	H	0.3191	-1.3671	0.8008
19	H	-3.9022	3.0304	0.0222
20	H	3.1478	-2.0338	0.7116
21	C	-0.0113	0.59	-0.0568
22	C	-3.4335	2.0587	0.0512
23	C	2.0754	1.1037	-0.2127
24	N	0.7992	1.5954	-0.3505
25	O	-1.5352	-3.268	0.2371
26	H	-1.8117	-1.5416	0.1313
27	C	-1.5232	-3.9625	-0.9197
28	H	-1.0674	-4.9563	-0.8454
29	H	-2.5876	-4.1291	-1.1987
30	H	-1.1182	-3.3843	-1.765