Supporting material for:

Charge assisted assembly of zwitterionic pyridone hydrates

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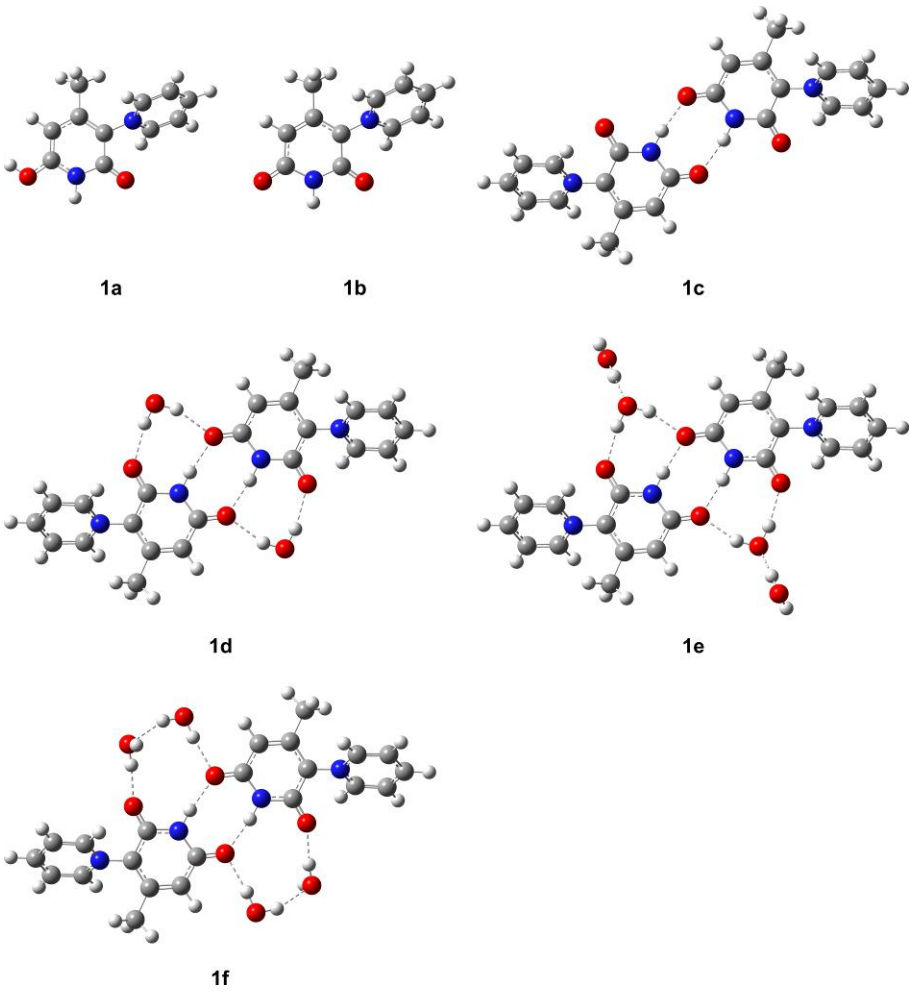


Fig. S1 Optimized geometry forms of compound **1** without (**1a**, **1b**, **1c**) and with water molecules (**1d** ,**1e**, **1f**).

Table S1 Optimized geometry forms of compound **1·2H$_2$O** in comparison with experimental data

		B3LYP						B3LYP-D3			
	Exp.	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1b**	**1c**	**1d**	**1e**
C1–C2	1.409(3)	1.4524	1.4488	1.4557	1.4475	1.4445	1.4429	1.4485	1.4556	1.4471	1.4441
C1–N1	1.374(3)	1.4028	1.3856	1.3845	1.3821	1.3813	1.3796	1.3859	1.3841	1.3813	1.3805
C1–O2	1.254(2)	1.2200	1.2377	1.2363	1.2413	1.2434	1.2458	1.2375	1.2361	1.2412	1.2433
C2–C3	1.392(3)	1.3814	1.4239	1.4204	1.4173	1.4163	1.4187	1.4226	1.4189	1.4158	1.4148
C2–N2	1.447(3)	1.4480	1.4185	1.4162	1.4227	1.4252	1.4245	1.4180	1.4158	1.4224	1.4248
C3–C11	1.509(3)	1.5074	1.5162	1.5162	1.5149	1.5145	1.5146	1.5157	1.5157	1.5144	1.5138
C4–C3	1.378(3)	1.4156	1.3725	1.3729	1.3758	1.3769	1.3745	1.3722	1.3727	1.3757	1.3768
C4–C5	1.399(3)	1.3756	1.4438	1.4407	1.4336	1.4310	1.4328	1.4442	1.4405	1.4329	1.4302
C5–N1	1.371(2)	1.3550	1.4049	1.3912	1.3881	1.3872	1.3885	1.4057	1.3905	1.3872	1.3861
C5–O1	1.267(2)	1.3337	1.2262	1.2381	1.2449	1.2474	1.2471	1.2262	1.2389	1.2455	1.2480
C6–C7	1.366(3)	1.3797	1.3798	1.3781	1.3785	1.3786	1.3785	1.3797	1.3782	1.3786	1.3787
C6–N2	1.342(3)	1.3563	1.3687	1.3698	1.3663	1.3649	1.3652	1.3681	1.3692	1.3656	1.3643
C7–C8	1.368(4)	1.3948	1.3934	1.3944	1.3943	1.3942	1.3943	1.3938	1.3947	1.3946	1.3945
C8–C9	1.369(4)	1.3924	1.3942	1.3937	1.3927	1.3925	1.3926	1.3945	1.3939	1.3930	1.3928
C9–C10	1.365(3)	1.3816	1.3783	1.3798	1.3805	1.3807	1.3805	1.3784	1.3798	1.3805	1.3807
C10–N2	1.346(3)	1.3574	1.3680	1.3690	1.3657	1.3645	1.3651	1.3676	1.3686	1.3652	1.3640
R^2	-	**0.8245**	**0.8923**	**0.8983**	**0.9249**	**0.9341**	**0.9308**	**0.8911**	**0.8985**	**0.9256**	**0.9345**
SD	-	0.0268	0.0241	0.0229	0.0189	0.0175	0.0179	0.0242	0.0228	0.0188	0.0174
Δ_{Max}	-	0.0667	0.0448	0.0467	0.0385	0.0355	0.0339	0.0452	0.0466	0.0381	0.0351
C1–C2–N2–C6		–59.74	44.21	43.54	45.43	46.28	46.43	45.96	45.17	46.95	47.78
Dipole moment		13.62	10.65	-	-	-	-	10.72	-	-	-

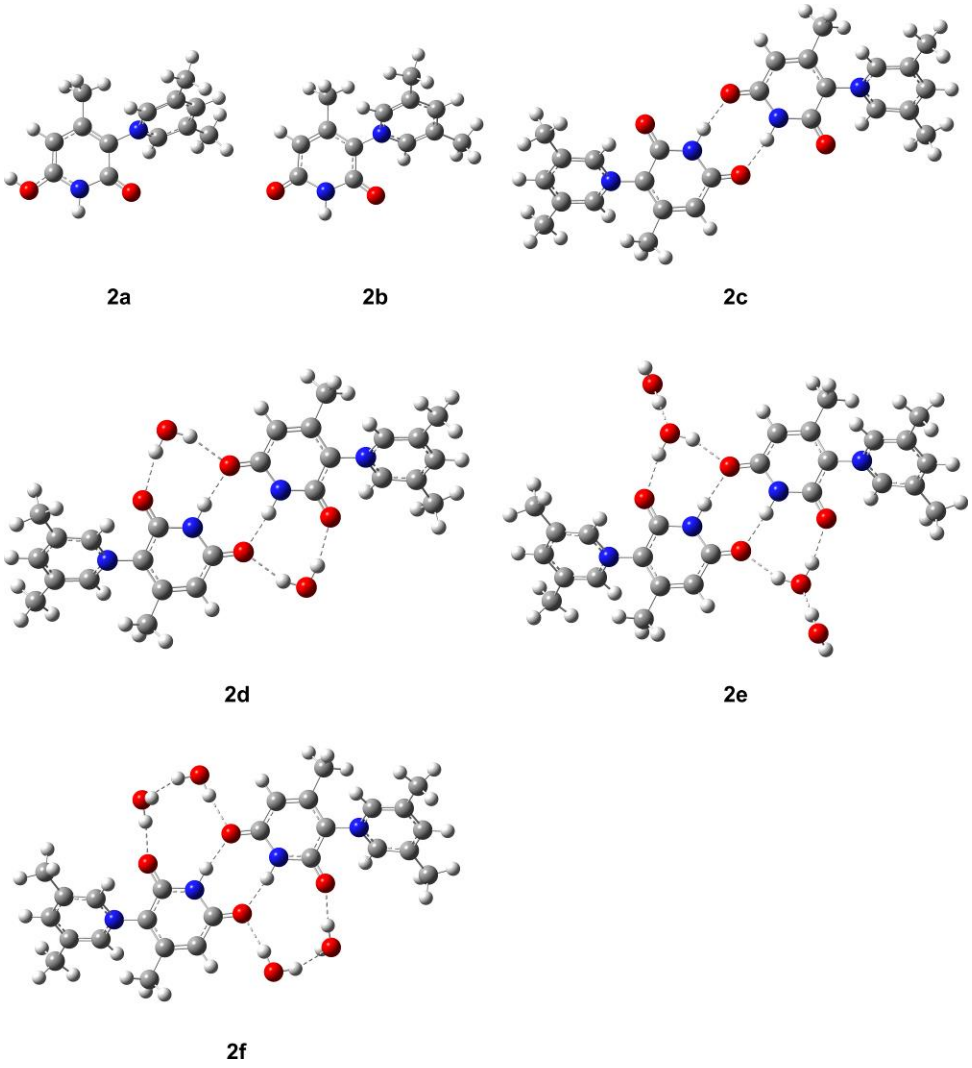
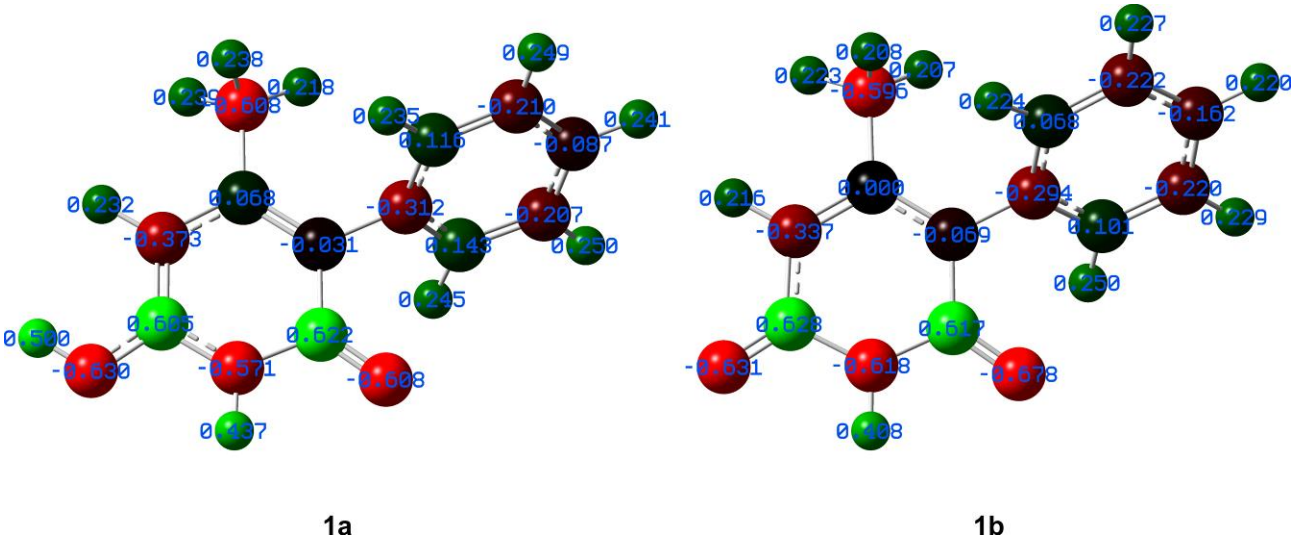


Fig. S2 Optimized geometry forms of compound **2** without (**2a**, **2b**, **2c**) and with water molecules (**2d**, **2e**, **2f**).

Table S2 Optimized geometry forms of compound **2·4H$_2$O** in comparison with experimental data

		B3LYP						B3LYP-D3			
	Exp.	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**	**2b**	**2c**	**2d**	**2e**
C1–C2	1.404(3)	1.4519	1.4476	1.4549	1.4463	1.4431	1.4411	1.4471	1.4547	1.4459	1.4426
C1–N1	1.376(3)	1.4042	1.3865	1.3851	1.3827	1.3819	1.3801	1.3868	1.3849	1.3819	1.3811
C1–O2	1.264(3)	1.2199	1.2383	1.2368	1.2420	1.2441	1.2465	1.2381	1.2366	1.2419	1.2441
C2–C3	1.394(2)	1.3798	1.4224	1.4190	1.4156	1.4144	1.4165	1.4211	1.4175	1.4140	1.4129
C2–N2	1.457(3)	1.4491	1.4216	1.4190	1.4259	1.4285	1.4283	1.4209	1.4183	1.4252	1.4277
C3–C4	1.376(2)	1.4169	1.3737	1.3738	1.3769	1.3781	1.3762	1.3733	1.3736	1.3768	1.3780
C3–C11	1.505(3)	1.5071	1.5160	1.5161	1.5148	1.5143	1.5143	1.5156	1.5157	1.5142	1.5137
C4–C5	1.404(3)	1.3747	1.4428	1.4398	1.4327	1.4301	1.4314	1.4431	1.4398	1.4321	1.4294
C5–N1	1.376(3)	1.3551	1.4049	1.3915	1.3885	1.3875	1.3884	1.4059	1.3908	1.3875	1.3865
C5–O1	1.266(3)	1.3352	1.2272	1.2388	1.2457	1.2483	1.2488	1.2272	1.2396	1.2464	1.2490
C6–N2	1.346(3)	1.3528	1.3635	1.3648	1.3603	1.3589	1.3580	1.3628	1.3640	1.3596	1.3582
C6–C7	1.380(2)	1.3880	1.3856	1.3854	1.3872	1.3876	1.3885	1.3854	1.3852	1.3870	1.3873
C7–C12	1.504(3)	1.5048	1.5069	1.5071	1.5066	1.5064	1.5065	1.5064	1.5066	1.5060	1.5058
C7–C8	1.385(3)	1.3973	1.3965	1.3966	1.3952	1.3950	1.3939	1.3963	1.3963	1.3950	1.3947
C8–C9	1.386(2)	1.3996	1.3989	1.3991	1.3997	1.3997	1.4008	1.3987	1.3989	1.3996	1.3996
C9–C10	1.379(2)	1.3860	1.3824	1.3819	1.3820	1.3823	1.3814	1.3819	1.3814	1.3816	1.3818
C9–C13	1.498(3)	1.5052	1.5075	1.5078	1.5073	1.5071	1.5071	1.5069	1.5072	1.5067	1.5065
C10–N2	1.344(3)	1.3553	1.3657	1.3669	1.3640	1.3629	1.3641	1.3653	1.3665	1.3636	1.3625
R^2	-	**0.8504**	**0.9195**	**0.9218**	**0.9453**	**0.9531**	**0.9531**	**0.9186**	**0.9219**	**0.9457**	**0.9536**
SD	-	0.0279	0.0226	0.0219	0.0179	0.0164	0.0163	0.0227	0.0219	0.0177	0.0162
Δ_{Max}	-	0.0692	0.0436	0.0509	0.0423	0.0391	0.0371	0.0431	0.0507	0.0419	0.0386
C1–C2–N2–C6		–64.42	45.62	44.65	46.87	47.86	47.67	47.12	46.16	48.12	49.00
Dipole moment		15.18	11.75					11.81			



1a **1b**

Fig. S3 NBO charges of **1a** and **1b** forms of the compound **1**.

Table S3 NBO charge of **1a** and **1b** forms of the compound **1**

		1a		**1b**	
		Vacuum	Water	Vacuum	Water
1	C	–0.373	–0.362	–0.337	–0.389
2	C	0.068	0.084	0.000	0.039
3	C	0.605	0.603	0.628	0.619
4	N	–0.571	–0.565	–0.618	–0.615
5	C	0.622	0.628	0.617	0.612
6	C	–0.031	–0.024	–0.069	–0.084
7	C	–0.608	–0.608	–0.596	–0.604
8	O	–0.630	–0.651	–0.631	–0.750
9	O	–0.608	–0.686	–0.678	–0.747
10	N	–0.312	–0.316	–0.294	–0.302
11	C	0.143	0.137	0.101	0.132
12	C	0.116	0.131	0.068	0.117
13	C	–0.207	–0.207	–0.220	–0.215
14	C	–0.210	–0.207	–0.222	–0.213
15	C	–0.087	–0.083	–0.162	–0.103
16	H	0.218	0.225	0.207	0.219
17	H	0.238	0.242	0.208	0.224
18	H	0.239	0.233	0.223	0.223
19	H	0.245	0.245	0.250	0.241
20	H	0.235	0.246	0.224	0.239
21	H	0.250	0.252	0.229	0.246
22	H	0.249	0.252	0.227	0.247
23	H	0.437	0.436	0.408	0.409
24	H	0.232	0.242	0.216	0.216
25	H	0.500	0.513	-	-
26	H	0.241	0.242	0.220	0.237
	$\Sigma_{Pyridone}$	0.3381	0.3093	–0.4210	–0.6271
	$\Sigma_{Pyridinium}$	0.6619	0.6907	0.4210	0.6271

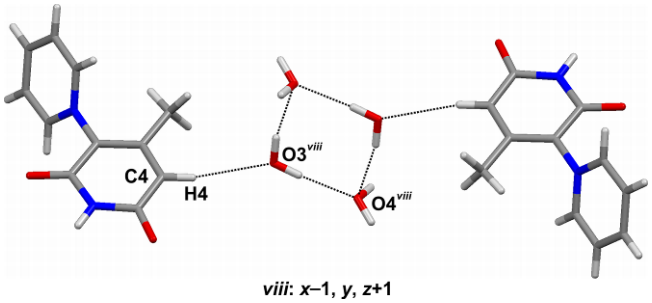
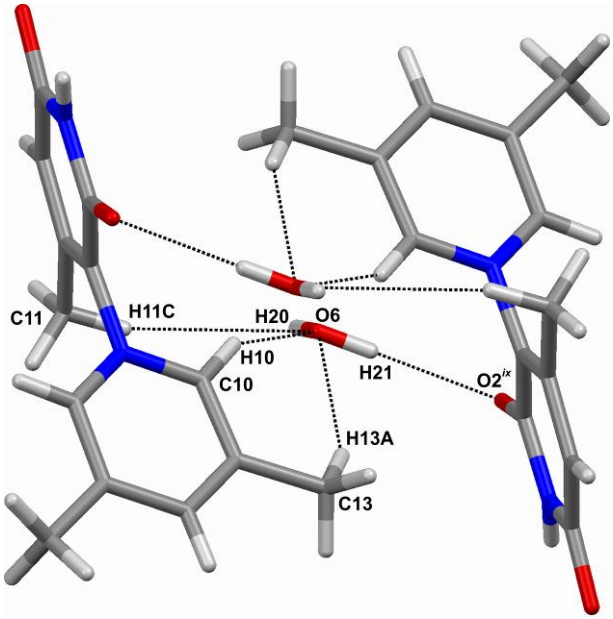


Fig. S4 The structural segment of **1·2H$_2$O** containing water molecule W2.



ix: −*x*+1, −*y*, −*z*+1

Fig. S5 The structural segment of **2·4H$_2$O** containing interlayer water molecule W4.

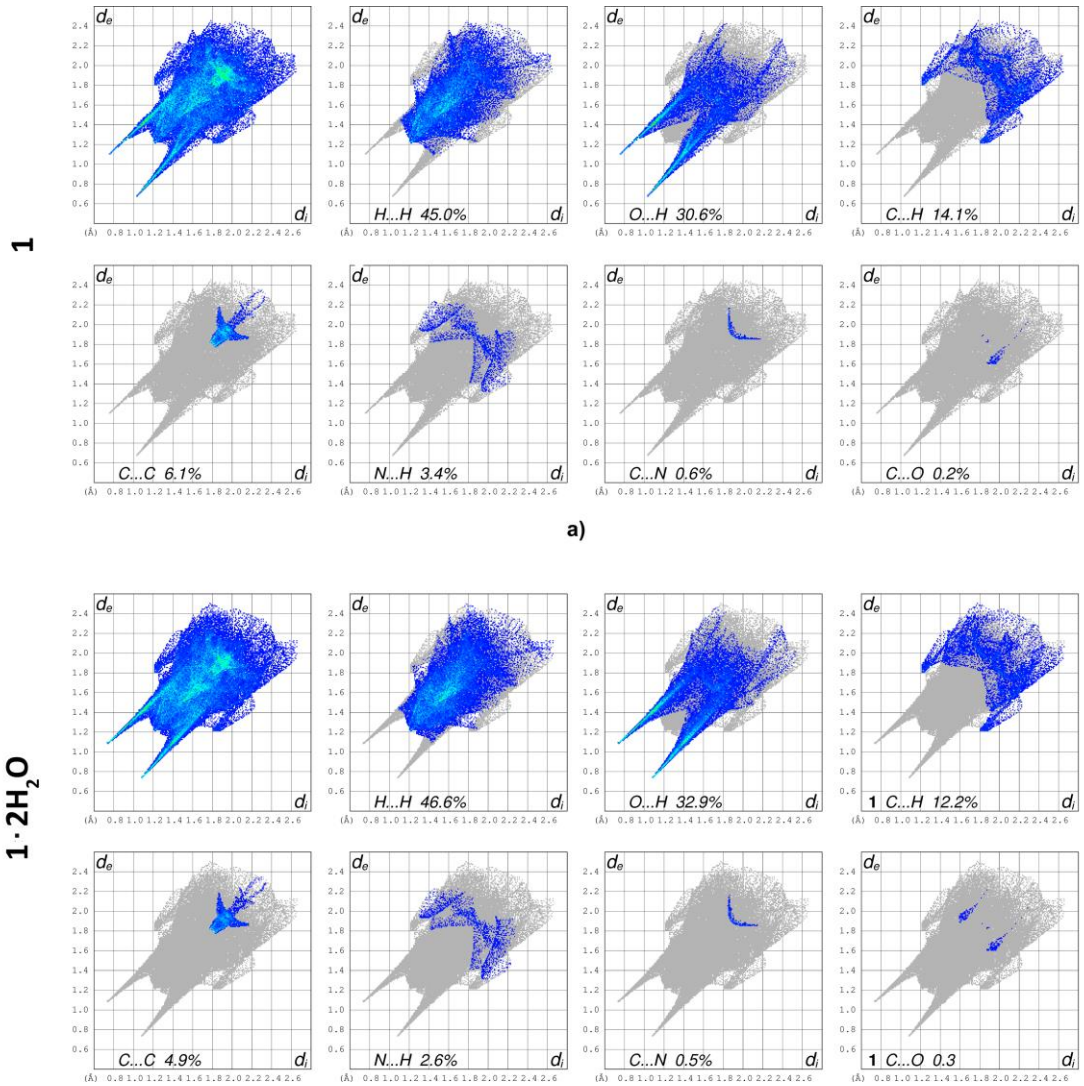


Fig. S6 Hirshfeld surface analysis of **1** without (a) and with (b) zwitterion-water interactions included.

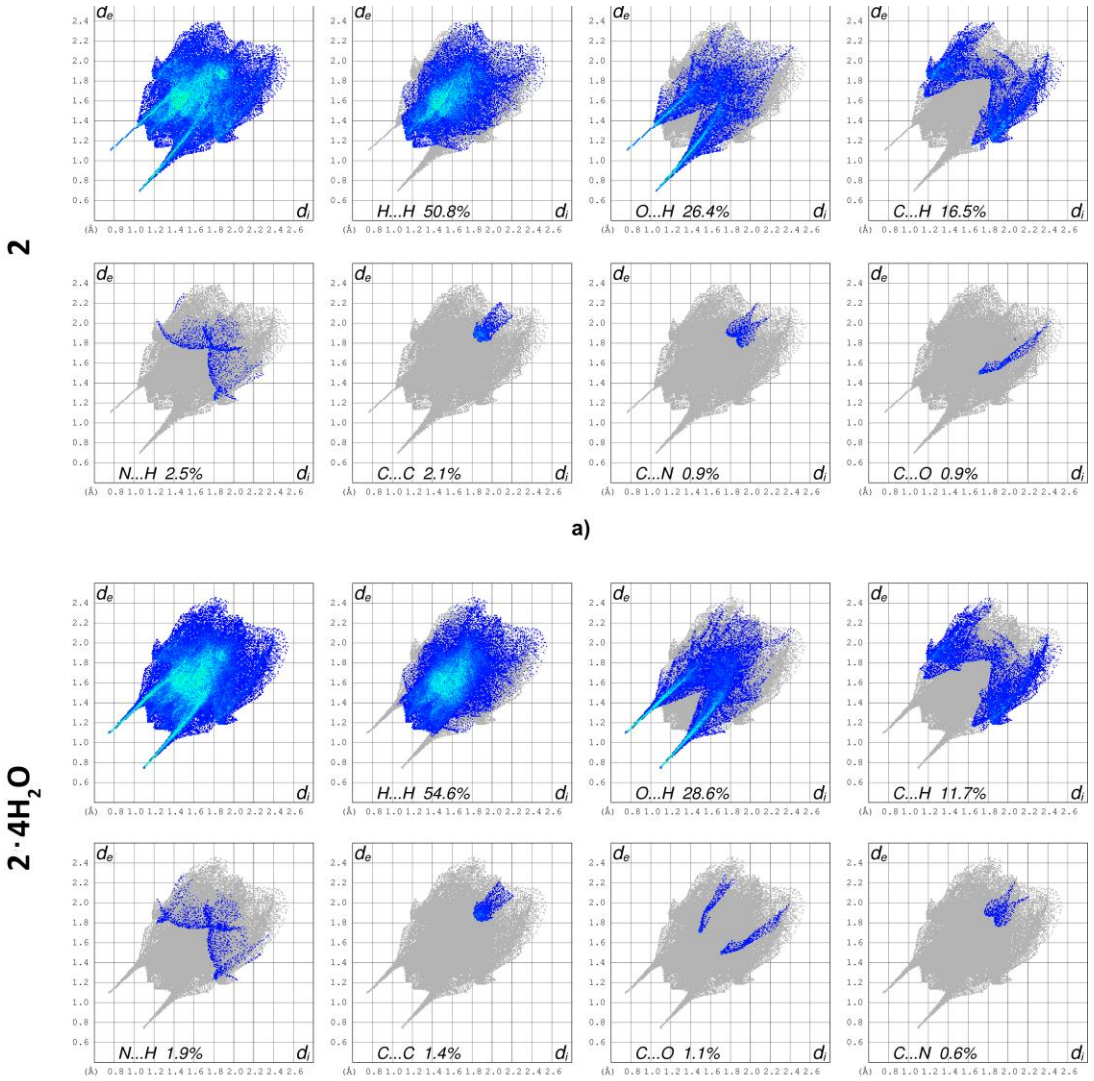


Fig. S7 Hirshfeld surface analysis of **2** without (a) and with (b) zwitterion-water interactions included.

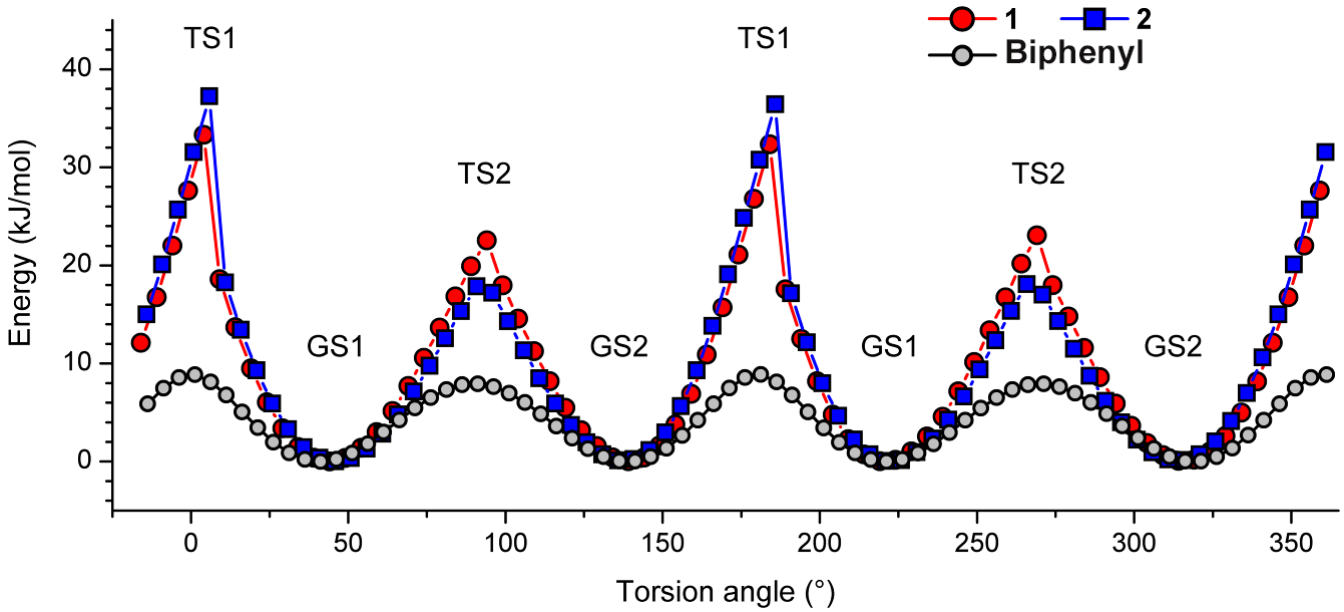


Fig. S8 Comparable PES study of **1** and **2** with biphenyl.

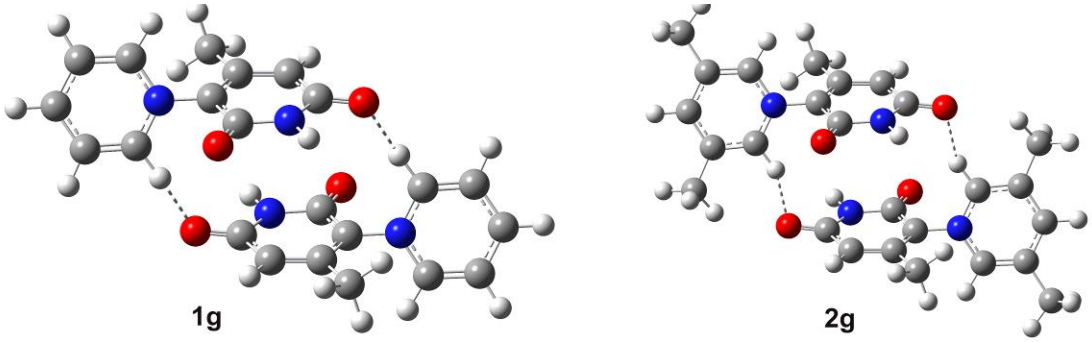


Fig S9. Optimized geometry forms affected by crystal network of compounds **1·2H$_2$O** and **2·4H$_2$O**.

Table S4 Optimized geometry forms of compound **1·2H$_2$O** in comparison with experimental data

	Exp.	**1g**	ε = 1.8819	ε = 4.7113	ε = 9.8629	ε = 17.332	ε = 24.852	ε = 46.826	ε = 78.3553	**1e**
C1–C2	1.409(2)	1.4410	1.4407	1.4334	1.4305	1.4294	1.4288	1.4283	1.4281	1.4237
C1–N1	1.374(3)	1.3920	1.3871	1.3892	1.3903	1.3908	1.3910	1.3912	1.3913	1.3854
C1–O2	1.254(2)	1.2360	1.2418	1.2452	1.2465	1.2469	1.2473	1.2475	1.2476	1.2556
C2–C3	1.392(3)	1.4110	1.4178	1.4119	1.4095	1.4085	1.4082	1.4079	1.4077	1.4033
C2–N2	1.447(3)	1.4310	1.4283	1.4376	1.4415	1.4431	1.4436	1.4442	1.4445	1.4484
C3–C11	1.509(3)	1.5130	1.5144	1.5126	1.5118	1.5114	1.5113	1.5111	1.5111	1.5094
C4–C3	1.378(3)	1.3800	1.3771	1.3818	1.3839	1.3847	1.3850	1.3854	1.3855	1.3880
C4–C5	1.399(3)	1.4330	1.4375	1.4314	1.4289	1.4280	1.4275	1.4271	1.4269	1.4176
C5–N1	1.371(2)	1.3970	1.4026	1.4005	1.3996	1.3993	1.3990	1.3988	1.3987	1.3868
C5–O1	1.267(2)	1.2420	1.2337	1.2413	1.2446	1.2459	1.2466	1.2472	1.2475	1.2634
C6–C7	1.366(3)	1.3840	1.3806	1.3809	1.3808	1.3808	1.3808	1.3808	1.3808	1.3809
C6–N2	1.342(3)	1.3610	1.3630	1.3590	1.3576	1.3570	1.3569	1.3567	1.3565	1.3552
C7–C8	1.368(4)	1.3910	1.3929	1.3929	1.3930	1.3930	1.3930	1.3930	1.3931	1.3932
C8–C9	1.369(4)	1.3960	1.3939	1.3935	1.3933	1.3933	1.3932	1.3932	1.3932	1.3931
C9–C10	1.365(3)	1.3780	1.3793	1.3802	1.3805	1.3806	1.3807	1.3807	1.3807	1.3808
C10–N2	1.346(3)	1.3610	1.3631	1.3589	1.3574	1.3569	1.3568	1.3566	1.3566	1.3552
R^2	-	**0.9373**	**0.9242**	**0.9488**	**0.9570**	**0.9598**	**0.9611**	**0.9622**	**0.9628**	**0.9819**
SD	-	0.0176	0.0195	0.0156	0.0141	0.0136	0.0133	0.0131	0.0130	0.0085
Δ_{Max}	-	0.0340	0.0385	0.0324	0.0299	0.0290	0.0285	0.0281	0.0279	0.0252
C1–C2–N2–C6		53.65	48.86	54.77	58.32	60.10	60.76	61.48	61.81	68.08
Dipole moment		-	13.29	15.86	16.94	17.39	17.57	17.76	17.84	-

Table S5 Optimized geometry forms of compound **2·4H$_2$O** in comparison with experimental data

	Exp.	**2g**	ε = 1.8819	ε = 4.7113	ε = 9.8629	ε = 17.332	ε = 24.852	ε = 46.826	ε = 78.3553	**2f**
C1–C2	1.404(3)	1.4385	1.4392	1.4316	1.4285	1.4272	1.4267	1.4262	1.4260	1.4189
C1–N1	1.376(3)	1.3941	1.3882	1.3907	1.3917	1.3922	1.3924	1.3927	1.3927	1.3863
C1–O2	1.264(3)	1.2363	1.2423	1.2456	1.2471	1.2477	1.2479	1.2481	1.2482	1.2577
C2–C3	1.394(2)	1.4092	1.4162	1.4102	1.4079	1.4070	1.4067	1.4064	1.4062	1.4023
C2–N2	1.457(3)	1.4372	1.4318	1.4415	1.4450	1.4467	1.4472	1.4478	1.4480	1.4525
N2–C6	1.346(3)	1.3530	1.3606	1.3560	1.3548	1.3543	1.3541	1.3540	1.3539	1.3520
C3–C4	1.376(2)	1.3822	1.3783	1.3829	1.3849	1.3857	1.3860	1.3863	1.3864	1.3873
C3–C11	1.505(3)	1.5130	1.5142	1.5122	1.5114	1.5110	1.5108	1.5106	1.5106	1.5085
C4–C5	1.404(3)	1.4305	1.4365	1.4308	1.4283	1.4273	1.4270	1.4265	1.4263	1.4191
C5–N1	1.376(3)	1.3977	1.4027	1.4005	1.3994	1.3989	1.3987	1.3984	1.3983	1.3866
C5–O1	1.266(3)	1.2437	1.2348	1.2423	1.2458	1.2472	1.2477	1.2484	1.2487	1.2651
C6–C7	1.380(2)	1.3908	1.3839	1.3857	1.3862	1.3864	1.3865	1.3865	1.3866	1.3869
C7–C8	1.385(3)	1.3935	1.3985	1.3976	1.3975	1.3975	1.3975	1.3974	1.3974	1.3975
C7–C12	1.504(3)	1.5058	1.5066	1.5057	1.5053	1.5051	1.5051	1.5050	1.5049	1.5047
C8–C9	1.386(2)	1.4013	1.3963	1.3970	1.3970	1.3971	1.3972	1.3972	1.3973	1.3975
C9–C10	1.379(2)	1.3822	1.3866	1.3865	1.3867	1.3867	1.3868	1.3868	1.3868	1.3872
C9–C13	1.498(3)	1.5073	1.5062	1.5055	1.5052	1.5051	1.5051	1.5050	1.5050	1.5047
C10–N2	1.344(3)	1.3595	1.3583	1.3549	1.3538	1.3534	1.3533	1.3532	1.3532	1.3522
R^2	-	**0.9570**	**0.9462**	**0.9657**	**0.9720**	**0.9744**	**0.9751**	**0.9760**	**0.9764**	**0.9921**
SD	-	0.0160	0.0180	0.0141	0.0126	0.0120	0.0118	0.0116	0.0115	0.0063
Δ_{Max}	-	0.0345	0.0352	0.0276	0.0245	0.0233	0.0230	0.0225	0.0223	0.0151
C1–C2–N2–C6		56.76	50.89	58.30	62.68	65.18	66.12	67.10	67.56	81.74
Dipole moment		-	14.53	17.22	18.31	18.77	18.95	19.14	19.23	-