Unraveling the acid-base characterization and solvent effects on structural and electronic properties of a bis-bidentated bridging ligand

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Supplementary Information

CONTENT

1. Studied Systems

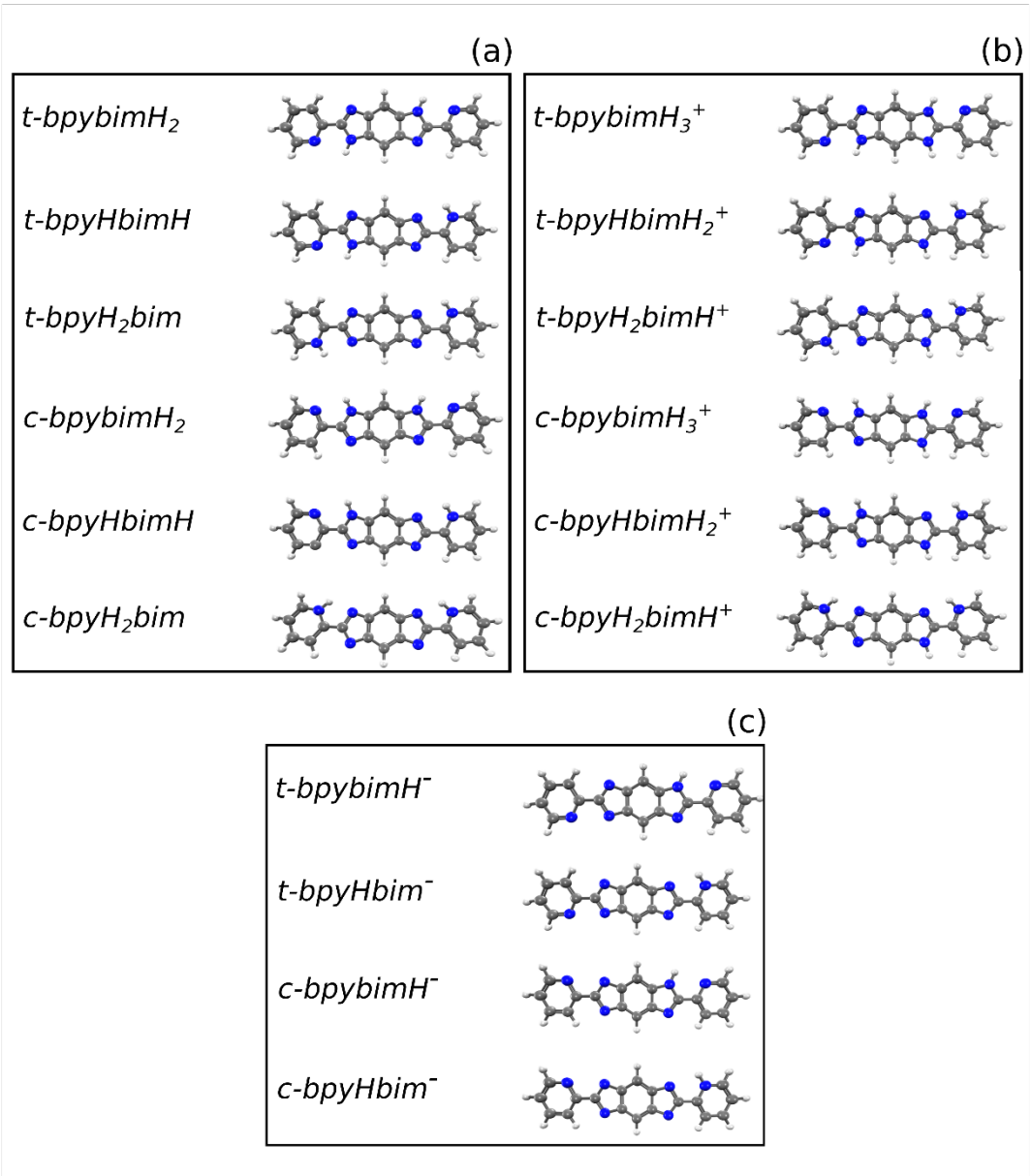


Figure S1: Illustration of the 16 studied isomers: (a) 6 neutral species (t-*bpybimH$_2$, t-bpyHbimH, t-bpyH$_2$bim, c-bpybimH$_2$, c-bpyHbimH and c-bpyH$_2$bim*; (b) 6 monocationic species (*t-bpybimH$_3^+$, t-bpyHbimH$_2^+$, t-bpyH$_2$bimH$^+$, c-bpybimH$_3^+$, c-bpyHbimH$_2^+$ and c-bpyH$_2$bimH$^+$*); (c) 4 mono-anionic species (*t-bpybimH$^-$, t-bpyHbim$^-$, c-bpybimH$^-$ and c-bpyHbim$^-$*).

2. Optimized Geometries

Table S1: Optimized geometries of the neutral trans isomers of bis(2-pyridyl)-benzo-bis(imidazole) (*t-bpybimH$_2$*, t-bpyHbimH and *t-bpyH$_2$bim*) in vacuum, using the B3LYP functional and the basis set aug-cc-pVDZ.

t-bpybimH$_2$			
Atomic Number	Coordinates		
	X	Y	Z
7	-2.506	-1.060	0.001
7	-5.266	-1.161	-0.001
7	-2.491	1.188	0.000
7	2.506	1.060	0.000
7	2.491	-1.188	0.000
7	5.266	1.161	0.000
6	-7.437	-0.117	0.000
6	-6.847	1.152	0.000
6	-5.458	1.250	0.000
6	-4.706	0.064	0.000
6	-6.601	-1.237	-0.001
6	-3.241	0.101	0.000
6	-1.169	-0.707	0.000
6	-1.186	0.730	0.000
6	0.004	1.470	0.000
6	-0.004	-1.470	0.000
6	1.169	0.707	0.000
6	1.186	-0.730	0.000
6	3.241	-0.101	0.000
6	4.706	-0.064	0.000
6	5.458	-1.250	0.000
6	6.601	1.237	0.000
6	6.847	-1.152	0.000
6	7.437	0.117	0.000
1	-7.027	-2.244	-0.001
1	-8.520	-0.239	-0.001
1	-4.941	2.208	0.001
1	-7.464	2.052	0.000
1	4.941	-2.208	0.000
1	7.027	2.244	-0.001
1	7.464	-2.052	0.000
1	8.520	0.239	0.000
1	-0.004	2.559	0.000
1	0.004	-2.559	0.001
1	2.924	1.981	0.000
1	-2.924	-1.981	0.000

t-bpyHbimH			
Atomic Number	Coordinates		
	X	Y	Z
7	2.518	-1.084	0.000
7	5.284	-1.124	0.000
7	2.463	1.167	0.000
7	-2.512	1.040	0.000
7	-2.458	-1.292	0.000
7	-5.188	1.116	0.000
6	7.430	-0.029	0.000
6	6.810	1.226	0.000
6	5.420	1.291	0.000
6	4.694	0.088	0.000
6	6.620	-1.168	0.000
6	3.229	0.095	0.000
6	1.171	-0.760	0.000
6	1.160	0.689	0.000
6	-0.032	1.407	0.000
6	0.032	-1.546	0.000
6	-1.211	0.639	0.000
6	-1.183	-0.824	0.000
6	-3.183	-0.143	0.000
6	-4.609	-0.123	0.000
6	-5.471	-1.244	0.000
6	-6.524	1.329	0.000
6	-6.838	-1.053	0.000
6	-7.387	0.256	0.000
1	7.069	-2.165	0.000
1	8.516	-0.126	0.000
1	4.879	2.236	0.000
1	7.405	2.140	0.000
1	-5.012	-2.231	0.000
1	-6.851	2.367	0.000
1	-7.506	-1.915	0.000
1	-8.462	0.422	0.000
1	-0.044	2.496	0.000
1	0.052	-2.636	0.000
1	2.952	-1.996	0.000
1	-4.500	1.877	0.000

t-bpyH$_2$bim			
Atomic Number	Coordinates		
	X	Y	Z
7	2.531	-1.058	0.001
7	5.197	-1.076	0.000
7	2.425	1.275	0.000
7	-2.531	1.058	0.000
7	-2.425	-1.275	0.000
7	-5.197	1.076	0.000
6	7.379	-0.176	0.000
6	6.808	1.123	0.000
6	5.436	1.289	0.000
6	4.597	0.153	0.000
6	6.536	-1.265	0.000
6	3.170	0.142	0.000
6	1.215	-0.689	0.000
6	1.154	0.784	0.000
6	-0.064	1.481	0.000
6	0.064	-1.481	0.000
6	-1.215	0.689	0.000
6	-1.154	-0.784	0.000
6	-3.170	-0.142	0.000
6	-4.597	-0.153	0.000
6	-5.436	-1.289	0.000
6	-6.536	1.265	0.000
6	-6.808	-1.123	0.000
6	-7.379	0.176	0.000
1	6.882	-2.297	0.000
1	8.457	-0.323	0.000
1	4.958	2.267	0.000
1	7.461	1.997	0.000
1	-4.958	-2.267	0.000
1	-6.882	2.297	0.000
1	-7.461	-1.997	0.000
1	-8.457	0.323	0.000
1	-0.104	2.570	0.000
1	0.104	-2.570	0.000
1	-4.516	1.846	0.000
1	4.516	-1.846	0.000

Table S2: Optimized geometries of the neutral cis isomers of bis(2-pyridyl)-benzo-bis(imidazole) (*c-bpybimH*$_2$, *c-bpyHbimH* and *c-bpyH*$_2$*bim*) in vacuum, using the B3LYP functional and the basis set aug-cc-pVDZ.

c-bpybimH$_2$			
Atomic Number	Coordinates		
	X	Y	Z
7	-2.497	1.195	0.000
7	-5.261	-1.165	0.000
7	-2.502	-1.053	0.000
7	2.502	-1.054	0.000
7	2.497	1.195	0.000
7	5.261	-1.165	0.000
6	-7.437	-0.131	0.000
6	-6.854	1.140	0.000
6	-5.466	1.245	0.000
6	-4.707	0.064	0.000
6	-6.596	-1.248	0.000
6	-3.242	0.109	0.000
6	-1.187	0.741	0.000
6	-1.169	-0.696	0.000
6	0.000	-1.460	0.000
6	0.000	1.480	0.000
6	1.169	-0.696	0.000
6	1.186	0.741	0.000
6	3.242	0.109	0.000
6	4.707	0.064	0.000
6	5.466	1.245	0.000
6	6.596	-1.248	0.000
6	6.854	1.140	0.000
6	7.437	-0.131	0.000
1	-7.016	-2.257	0.000
1	-8.520	-0.260	0.000
1	-4.954	2.207	0.000
1	-7.475	2.037	0.000
1	4.954	2.207	0.000
1	7.016	-2.256	0.000
1	7.475	2.037	0.000
1	8.520	-0.260	0.000
1	-2.917	-1.975	0.000
1	0.000	-2.549	0.000
1	0.000	2.569	0.000
1	2.916	-1.976	0.000

c-bpyHbimH			
Atomic Number	Coordinates		
	X	Y	Z
7	-2.513	1.207	0.000
7	-5.234	-1.200	0.000
7	-2.472	-1.044	0.000
7	2.509	-1.042	0.000
7	2.461	1.290	0.000
7	5.188	-1.115	0.000
6	-7.425	-0.196	0.000
6	-6.859	1.083	0.000
6	-5.473	1.208	0.000
6	-4.697	0.037	0.000
6	-6.568	-1.301	0.000
6	-3.233	0.106	0.000
6	-1.190	0.782	0.000
6	-1.142	-0.666	0.000
6	0.029	-1.408	0.000
6	-0.029	1.545	0.000
6	1.212	-0.639	0.000
6	1.182	0.824	0.000
6	3.184	0.144	0.000
6	4.609	0.124	0.000
6	5.470	1.245	0.000
6	6.525	-1.326	0.000
6	6.837	1.056	0.000
6	7.387	-0.253	0.000
1	-6.974	-2.315	0.000
1	-8.506	-0.340	0.000
1	-4.973	2.175	0.000
1	-7.493	1.972	0.000
1	5.010	2.232	0.000
1	6.853	-2.364	0.000
1	7.504	1.919	0.000
1	8.462	-0.419	0.000
1	0.048	-2.498	0.000
1	-0.055	2.634	0.000
1	4.501	-1.877	0.000
1	-2.870	-1.974	0.000

c-bpyH$_2$*bim*			
Atomic Number	Coordinates		
	X	Y	Z
7	-2.479	1.318	0.000
7	-5.142	-1.151	0.000
7	-2.482	-1.017	0.000
7	2.483	-1.017	0.000
7	2.479	1.319	0.000
7	5.141	-1.150	0.000
6	-7.363	-0.352	0.000
6	-6.852	0.972	0.000
6	-5.490	1.201	0.000
6	-4.599	0.104	0.000
6	-6.471	-1.401	0.000
6	-3.173	0.157	0.000
6	-1.186	0.880	0.000
6	-1.185	-0.594	0.000
6	0.000	-1.340	0.000
6	0.000	1.626	0.000
6	1.185	-0.594	0.000
6	1.186	0.881	0.000
6	3.173	0.157	0.000
6	4.600	0.105	0.000
6	5.491	1.201	0.000
6	6.470	-1.401	0.000
6	6.853	0.972	0.000
6	7.363	-0.353	0.000
1	-6.770	-2.447	0.000
1	-8.433	-0.549	0.000
1	-5.058	2.200	0.000
1	-7.545	1.815	0.000
1	5.059	2.200	0.000
1	6.768	-2.448	0.000
1	7.546	1.814	0.000
1	8.433	-0.550	0.000
1	0.000	-2.429	0.000
1	0.000	2.716	0.000
1	4.424	-1.886	0.000
1	-4.425	-1.887	0.000

3. Atomic Charges

Table S3: Calculated CHELPG atomic charges of the isomer *t-bpybim*H_2 in solution, using the B3LYP functional and the basis set aug-cc-pVDZ, with solvent effects treated under the PCM approximation.

Atom num.	Atom type	Toluene (Tol)	Acetone	DMSO	Methanol	Water (Wat)	ΔQ Tol/Wat
1	N	-0.254	-0.250	-0.250	-0.250	-0.250	0.004
2	N	-0.640	-0.660	-0.662	-0.661	-0.663	-0.023
3	N	-0.612	-0.646	-0.649	-0.648	-0.650	-0.039
4	N	-0.253	-0.250	-0.250	-0.250	-0.250	0.004
5	N	-0.612	-0.646	-0.649	-0.648	-0.650	-0.039
6	N	-0.640	-0.660	-0.662	-0.661	-0.663	-0.023
7	C	-0.297	-0.299	-0.299	-0.299	-0.299	-0.002
8	C	0.125	0.128	0.129	0.129	0.129	0.003
9	C	-0.259	-0.260	-0.260	-0.260	-0.260	-0.001
10	C	0.468	0.463	0.463	0.463	0.462	-0.006
11	C	0.367	0.377	0.378	0.378	0.379	0.011
12	C	0.252	0.267	0.268	0.268	0.269	0.016
13	C	0.087	0.092	0.093	0.093	0.093	0.006
14	C	0.353	0.347	0.347	0.347	0.347	-0.006
15	C	-0.348	-0.356	-0.357	-0.356	-0.357	-0.009
16	C	-0.348	-0.356	-0.357	-0.356	-0.357	-0.009
17	C	0.087	0.092	0.093	0.093	0.093	0.006
18	C	0.353	0.348	0.347	0.347	0.347	-0.006
19	C	0.252	0.267	0.268	0.268	0.269	0.016
20	C	0.468	0.463	0.463	0.463	0.462	-0.006
21	C	-0.259	-0.260	-0.260	-0.260	-0.260	-0.001
22	C	0.367	0.377	0.378	0.378	0.379	0.011
23	C	0.125	0.128	0.129	0.129	0.129	0.003
24	C	-0.297	-0.299	-0.299	-0.299	-0.299	-0.002
25	H	0.019	0.023	0.023	0.023	0.024	0.005
26	H	0.116	0.126	0.127	0.127	0.127	0.011
27	H	0.099	0.097	0.097	0.097	0.097	-0.002
28	H	0.071	0.080	0.081	0.080	0.081	0.010
29	H	0.099	0.097	0.097	0.097	0.097	-0.002
30	H	0.019	0.023	0.023	0.023	0.024	0.005
31	H	0.071	0.080	0.081	0.080	0.081	0.010
32	H	0.116	0.126	0.127	0.127	0.127	0.011
33	H	0.184	0.193	0.193	0.193	0.194	0.010
34	H	0.184	0.193	0.193	0.193	0.194	0.010
35	H	0.267	0.277	0.278	0.278	0.279	0.011
36	H	0.267	0.277	0.278	0.278	0.279	0.011

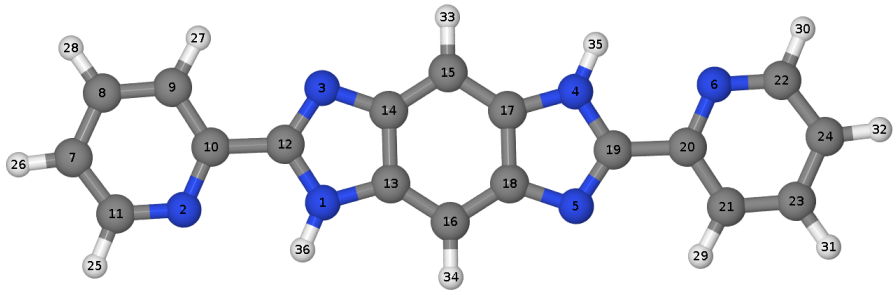


Table S4: Calculated CHELPG atomic charges of the isomer *t-bpyHbimH* in solution, using the B3LYP functional and the basis set aug-cc-pVDZ, with solvent effects treated under the PCM approximation.

Atom num.	Atom type	Toluene (Tol)	Acetone	DMSO	Methanol	Water (Wat)	ΔQ Tol/Wat
1	N	-0.236	-0.232	-0.232	-0.232	-0.232	0.004
2	N	-0.633	-0.655	-0.657	-0.656	-0.658	-0.025
3	N	-0.608	-0.644	-0.647	-0.646	-0.648	-0.040
4	N	-0.693	-0.712	-0.714	-0.713	-0.714	-0.021
5	N	-0.694	-0.739	-0.744	-0.742	-0.745	-0.051
6	N	-0.070	-0.068	-0.067	-0.067	-0.067	0.003
7	C	-0.302	-0.304	-0.304	-0.304	-0.304	-0.002
8	C	0.132	0.135	0.136	0.135	0.136	0.004
9	C	-0.267	-0.270	-0.270	-0.270	-0.270	-0.004
10	C	0.475	0.472	0.472	0.472	0.472	-0.003
11	C	0.362	0.372	0.373	0.372	0.373	0.012
12	C	0.237	0.246	0.247	0.246	0.247	0.010
13	C	0.032	0.033	0.033	0.033	0.033	0.001
14	C	0.381	0.378	0.378	0.378	0.378	-0.003
15	C	-0.416	-0.432	-0.434	-0.433	-0.434	-0.018
16	C	-0.315	-0.324	-0.325	-0.325	-0.326	-0.010
17	C	0.336	0.325	0.324	0.324	0.323	-0.013
18	C	0.277	0.270	0.269	0.269	0.269	-0.008
19	C	0.508	0.550	0.555	0.553	0.556	0.048
20	C	0.101	0.078	0.076	0.077	0.075	-0.027
21	C	-0.074	-0.069	-0.069	-0.069	-0.069	0.005
22	C	0.012	0.036	0.038	0.037	0.039	0.027
23	C	0.032	0.042	0.043	0.043	0.043	0.011
24	C	-0.135	-0.130	-0.130	-0.130	-0.130	0.006
25	H	0.017	0.022	0.022	0.022	0.023	0.005
26	H	0.115	0.126	0.127	0.126	0.127	0.012
27	H	0.099	0.097	0.097	0.097	0.097	-0.002
28	H	0.067	0.077	0.078	0.078	0.078	0.011
29	H	0.084	0.081	0.081	0.081	0.081	-0.003
30	H	0.143	0.153	0.154	0.154	0.154	0.011
31	H	0.101	0.111	0.112	0.112	0.112	0.012
32	H	0.110	0.122	0.124	0.123	0.124	0.014
33	H	0.175	0.177	0.177	0.177	0.177	0.002
34	H	0.172	0.181	0.182	0.181	0.182	0.010
35	H	0.255	0.266	0.267	0.266	0.267	0.012
36	H	0.221	0.230	0.231	0.230	0.231	0.009

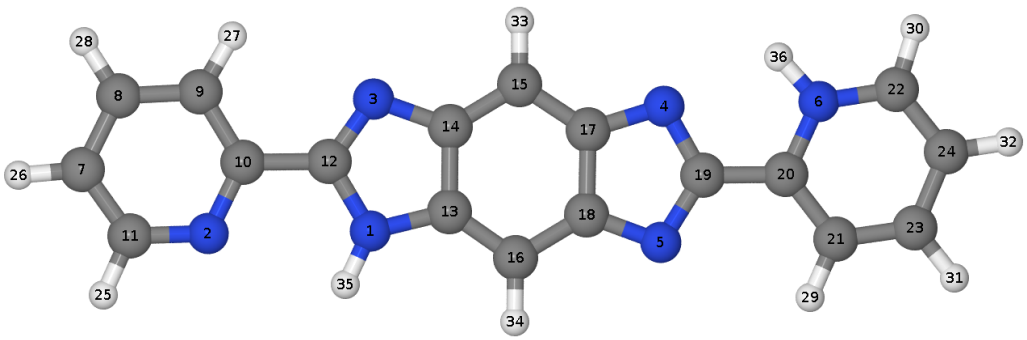


Table S5: Calculated CHELPG atomic charges of the isomer *t-bpyH$_2$bim* in solution, using the B3LYP functional and the basis set aug-cc-pVDZ, with solvent effects treated under the PCM approximation.

Atom num.	Atom type	Toluene (Tol)	Acetone	DMSO	Methanol	Water (Wat)	ΔQ Tol/Wat
1	N	-0.673	-0.690	-0.691	-0.690	-0.691	-0.018
2	N	-0.064	-0.064	-0.064	-0.064	-0.064	0.000
3	N	-0.697	-0.743	-0.748	-0.746	-0.749	-0.053
4	N	-0.673	-0.690	-0.691	-0.690	-0.691	-0.018
5	N	-0.697	-0.743	-0.748	-0.746	-0.749	-0.053
6	N	-0.064	-0.064	-0.064	-0.064	-0.064	0.000
7	C	-0.166	-0.162	-0.161	-0.161	-0.161	0.006
8	C	0.036	0.048	0.049	0.049	0.050	0.013
9	C	-0.058	-0.057	-0.057	-0.057	-0.057	0.001
10	C	0.091	0.073	0.071	0.071	0.070	-0.021
11	C	0.037	0.061	0.063	0.062	0.064	0.027
12	C	0.497	0.531	0.534	0.533	0.535	0.038
13	C	0.272	0.256	0.254	0.255	0.254	-0.018
14	C	0.330	0.327	0.327	0.327	0.326	-0.004
15	C	-0.401	-0.420	-0.422	-0.421	-0.422	-0.021
16	C	-0.401	-0.420	-0.422	-0.421	-0.422	-0.021
17	C	0.272	0.256	0.254	0.255	0.254	-0.018
18	C	0.330	0.327	0.327	0.327	0.326	-0.004
19	C	0.497	0.531	0.534	0.533	0.535	0.038
20	C	0.091	0.073	0.071	0.071	0.070	-0.021
21	C	-0.058	-0.057	-0.057	-0.057	-0.057	0.001
22	C	0.037	0.061	0.063	0.062	0.064	0.027
23	C	0.036	0.048	0.049	0.049	0.050	0.013
24	C	-0.166	-0.162	-0.161	-0.161	-0.161	0.006
25	H	0.133	0.144	0.145	0.144	0.145	0.012
26	H	0.117	0.131	0.132	0.131	0.132	0.015
27	H	0.075	0.073	0.073	0.073	0.073	-0.002
28	H	0.097	0.108	0.109	0.108	0.109	0.012
29	H	0.075	0.073	0.073	0.073	0.073	-0.002
30	H	0.133	0.144	0.145	0.144	0.145	0.012
31	H	0.097	0.108	0.109	0.108	0.109	0.012
32	H	0.117	0.131	0.132	0.131	0.132	0.015
33	H	0.166	0.168	0.168	0.168	0.168	0.002
34	H	0.166	0.168	0.168	0.168	0.168	0.002
35	H	0.209	0.218	0.218	0.218	0.219	0.010
36	H	0.209	0.218	0.218	0.218	0.219	0.010

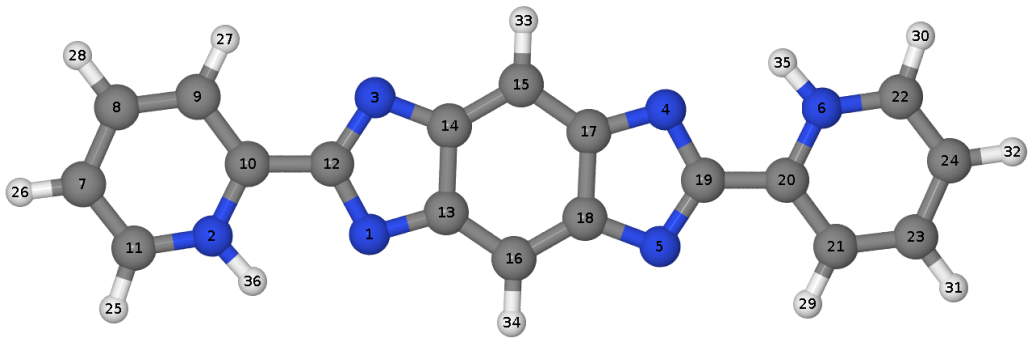


Table S6: Calculated CHELPG atomic charges of the isomer *c-bpybimH*$_2$ in solution, using the B3LYP functional and the basis set aug-cc-pVDZ, with solvent effects treated under the PCM approximation.

Atom num.	Atom type	Toluene (Tol)	Acetone	DMSO	Methanol	Water (Wat)	ΔQ Tol/Wat
1	N	-0.604	-0.643	-0.647	-0.645	-0.648	-0.044
2	N	-0.634	-0.652	-0.653	-0.653	-0.654	-0.019
3	N	-0.232	-0.222	-0.221	-0.221	-0.221	0.012
4	N	-0.233	-0.223	-0.222	-0.222	-0.222	0.012
5	N	-0.604	-0.643	-0.647	-0.645	-0.648	-0.044
6	N	-0.634	-0.652	-0.653	-0.653	-0.654	-0.019
7	C	-0.298	-0.298	-0.298	-0.298	-0.298	-0.001
8	C	0.119	0.121	0.121	0.121	0.121	0.002
9	C	-0.251	-0.251	-0.251	-0.251	-0.251	0.000
10	C	0.465	0.459	0.459	0.459	0.458	-0.007
11	C	0.365	0.373	0.374	0.374	0.374	0.009
12	C	0.238	0.251	0.252	0.252	0.253	0.015
13	C	0.390	0.402	0.403	0.403	0.404	0.013
14	C	0.040	0.029	0.027	0.028	0.027	-0.014
15	C	-0.295	-0.284	-0.283	-0.283	-0.282	0.013
16	C	-0.392	-0.420	-0.422	-0.421	-0.423	-0.031
17	C	0.041	0.029	0.028	0.028	0.028	-0.014
18	C	0.390	0.402	0.403	0.403	0.404	0.013
19	C	0.239	0.252	0.253	0.253	0.254	0.015
20	C	0.465	0.459	0.458	0.459	0.458	-0.007
21	C	-0.251	-0.251	-0.251	-0.251	-0.251	0.000
22	C	0.365	0.373	0.374	0.374	0.374	0.009
23	C	0.119	0.121	0.121	0.121	0.121	0.002
24	C	-0.298	-0.298	-0.298	-0.298	-0.298	-0.001
25	H	0.018	0.023	0.024	0.024	0.024	0.006
26	H	0.117	0.127	0.128	0.127	0.128	0.011
27	H	0.097	0.095	0.094	0.094	0.094	-0.003
28	H	0.073	0.082	0.083	0.082	0.083	0.010
29	H	0.097	0.095	0.094	0.094	0.094	-0.003
30	H	0.018	0.023	0.024	0.024	0.024	0.006
31	H	0.073	0.082	0.083	0.082	0.083	0.010
32	H	0.117	0.127	0.128	0.127	0.128	0.011
33	H	0.256	0.265	0.265	0.265	0.266	0.010
34	H	0.190	0.206	0.207	0.207	0.208	0.018
35	H	0.177	0.178	0.178	0.178	0.178	0.001
36	H	0.256	0.265	0.266	0.265	0.266	0.010

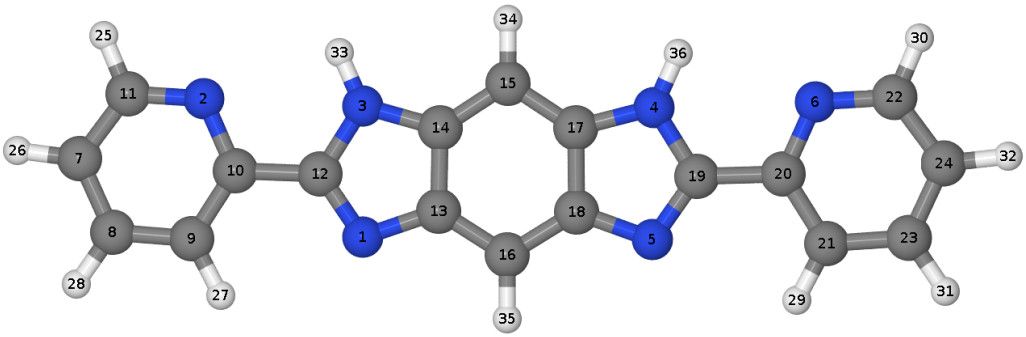


Table S7: Calculated CHELPG atomic charges of the isomer *c-bpyHbimH* in solution, using the B3LYP functional and the basis set aug-cc-pVDZ, with solvent effects treated under the PCM approximation.

Atom num.	Atom type	Toluene (Tol)	Acetone	DMSO	Methanol	Water (Wat)	ΔQ Tol/Wat
1	N	-0.606	-0.643	-0.647	-0.646	-0.649	-0.042
2	N	-0.627	-0.649	-0.651	-0.650	-0.651	-0.024
3	N	-0.259	-0.255	-0.254	-0.254	-0.254	0.005
4	N	-0.694	-0.709	-0.710	-0.709	-0.710	-0.016
5	N	-0.688	-0.738	-0.743	-0.741	-0.744	-0.056
6	N	-0.057	-0.054	-0.054	-0.054	-0.054	0.003
7	C	-0.291	-0.292	-0.292	-0.292	-0.292	-0.002
8	C	0.119	0.122	0.123	0.122	0.123	0.004
9	C	-0.234	-0.236	-0.236	-0.236	-0.236	-0.003
10	C	0.431	0.428	0.428	0.428	0.427	-0.004
11	C	0.358	0.368	0.369	0.369	0.370	0.011
12	C	0.274	0.284	0.285	0.284	0.285	0.011
13	C	0.340	0.345	0.345	0.345	0.345	0.005
14	C	0.076	0.069	0.068	0.069	0.068	-0.008
15	C	-0.369	-0.367	-0.366	-0.366	-0.366	0.003
16	C	-0.364	-0.392	-0.395	-0.394	-0.396	-0.032
17	C	0.290	0.264	0.261	0.262	0.260	-0.030
18	C	0.321	0.329	0.330	0.330	0.330	0.010
19	C	0.505	0.548	0.552	0.551	0.553	0.048
20	C	0.097	0.074	0.072	0.073	0.071	-0.026
21	C	-0.075	-0.071	-0.071	-0.071	-0.071	0.005
22	C	0.003	0.027	0.030	0.029	0.031	0.027
23	C	0.032	0.042	0.043	0.043	0.043	0.012
24	C	-0.132	-0.128	-0.127	-0.127	-0.127	0.005
25	H	0.018	0.023	0.024	0.023	0.024	0.006
26	H	0.111	0.122	0.123	0.123	0.123	0.012
27	H	0.090	0.087	0.087	0.087	0.087	-0.003
28	H	0.068	0.078	0.079	0.078	0.079	0.011
29	H	0.085	0.082	0.081	0.082	0.081	-0.004
30	H	0.144	0.154	0.155	0.155	0.155	0.012
31	H	0.101	0.111	0.112	0.112	0.112	0.011
32	H	0.109	0.122	0.123	0.123	0.123	0.014
33	H	0.182	0.191	0.193	0.192	0.193	0.011
34	H	0.166	0.167	0.167	0.167	0.167	0.001
35	H	0.216	0.225	0.226	0.226	0.226	0.010
36	H	0.260	0.271	0.272	0.271	0.272	0.012

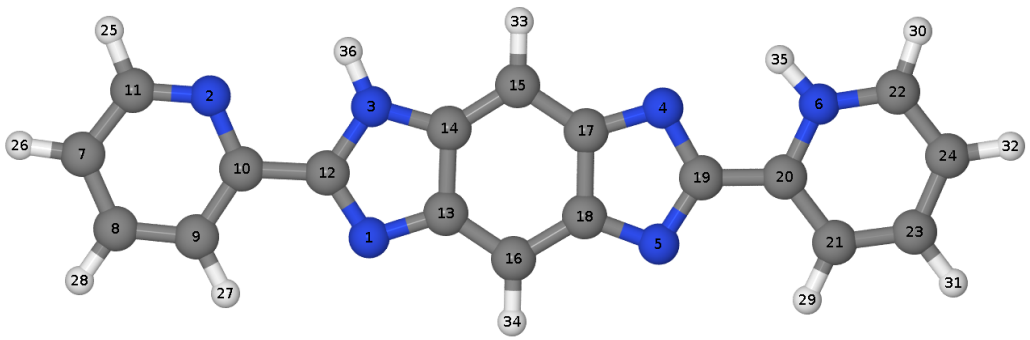
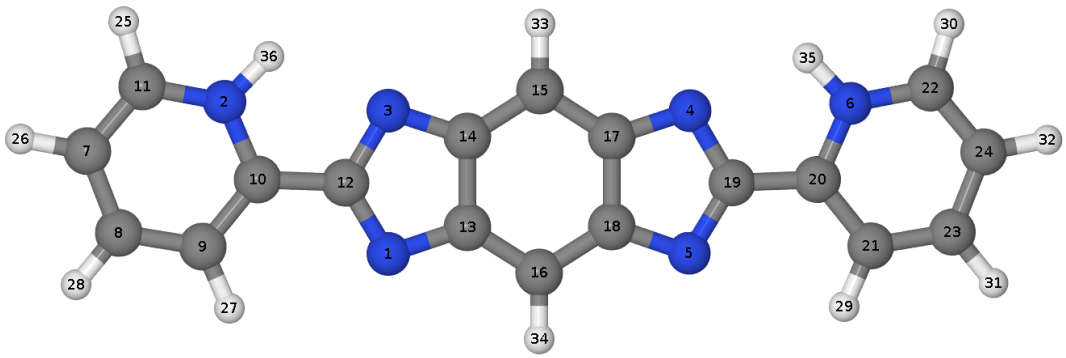


Table S8: Calculated CHELPG atomic charges of the isomer *c-bpyH$_2$bim* in solution, using the B3LYP functional and the basis set aug-cc-pVDZ, with solvent effects treated under the PCM approximation.

Atom num.	Atom type	Toluene (Tol)	Acetone	DMSO	Methanol	Water (Wat)	ΔQ Tol/Wat
1	N	-0.687	-0.736	-0.741	-0.739	-0.743	-0.06
2	N	-0.052	-0.053	-0.053	-0.053	-0.053	0.00
3	N	-0.697	-0.713	-0.714	-0.714	-0.715	-0.02
4	N	-0.697	-0.713	-0.714	-0.714	-0.715	-0.02
5	N	-0.688	-0.737	-0.741	-0.740	-0.743	-0.06
6	N	-0.049	-0.050	-0.050	-0.050	-0.050	0.00
7	C	-0.144	-0.139	-0.138	-0.139	-0.138	0.01
8	C	0.019	0.030	0.031	0.031	0.032	0.01
9	C	-0.041	-0.039	-0.039	-0.039	-0.039	0.00
10	C	0.074	0.055	0.053	0.054	0.052	-0.02
11	C	0.010	0.035	0.037	0.036	0.038	0.03
12	C	0.516	0.551	0.555	0.554	0.556	0.04
13	C	0.287	0.290	0.291	0.291	0.291	0.00
14	C	0.292	0.270	0.267	0.268	0.267	-0.03
15	C	-0.391	-0.396	-0.396	-0.396	-0.396	0.00
16	C	-0.360	-0.391	-0.394	-0.393	-0.395	-0.04
17	C	0.292	0.270	0.267	0.268	0.266	-0.03
18	C	0.287	0.290	0.291	0.291	0.291	0.00
19	C	0.517	0.552	0.556	0.554	0.557	0.04
20	C	0.073	0.054	0.051	0.052	0.051	-0.02
21	C	-0.040	-0.038	-0.038	-0.038	-0.038	0.00
22	C	0.005	0.030	0.032	0.031	0.033	0.03
23	C	0.017	0.029	0.030	0.030	0.030	0.01
24	C	-0.139	-0.134	-0.134	-0.134	-0.133	0.01
25	H	0.139	0.150	0.151	0.151	0.151	0.01
26	H	0.113	0.126	0.127	0.127	0.128	0.01
27	H	0.071	0.068	0.068	0.068	0.068	0.00
28	H	0.100	0.111	0.112	0.112	0.112	0.01
29	H	0.071	0.069	0.068	0.068	0.068	0.00
30	H	0.140	0.151	0.152	0.152	0.152	0.01
31	H	0.100	0.111	0.112	0.112	0.112	0.01
32	H	0.112	0.125	0.126	0.126	0.127	0.01
33	H	0.160	0.162	0.162	0.162	0.163	0.00
34	H	0.163	0.163	0.164	0.164	0.164	0.00
35	H	0.213	0.223	0.224	0.223	0.224	0.01
36	H	0.213	0.223	0.224	0.224	0.225	0.01



4. Molecular Mechanic Parameters

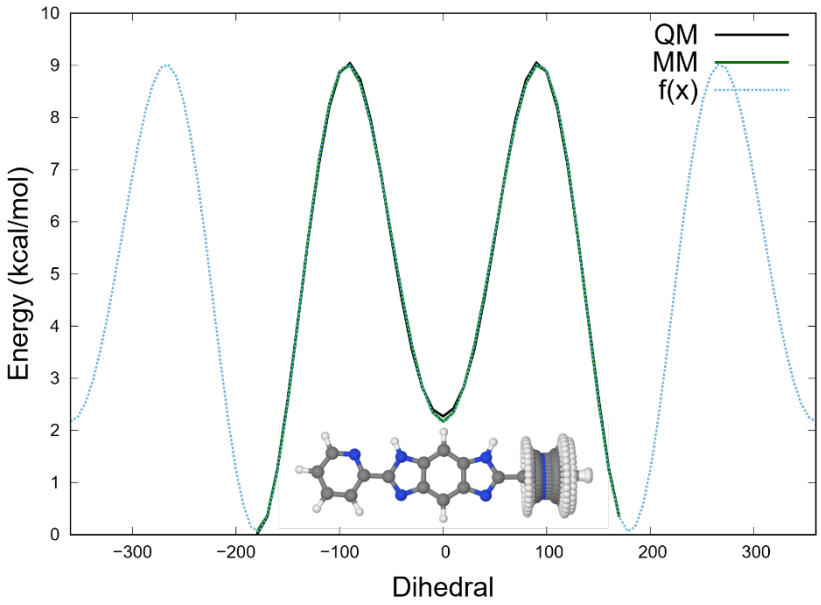


Figure S2: Quantum Mechanics (QM) fit of the N-C-C-N dihedral distribution and the Molecule Mechanics (MM) curve obtained from the parameters shown in Table S9.

Table S9: Fitted Fourier parameters (kcal/mol) for the rotation of the pyridine group.

Dihedral	V_1	V_2	V_3
N_5-C-C-N_6	0.586	1.972	0.501
N_4-C-C-C	0.586	1.972	0.501
N_5-C-C-C	-0.028	1.972	0.057
N_4-C-C-N_6	-0.028	1.972	0.057

Table S10: OPLS-AA Lennard Jones parameters adopted for bis(2-pyridyl)-benzo-bis(imidazole).

Atom	ε (kcal/mol)	σ (Å)
N	0.17	3.25
C	0.07	3.55
H	0.03	2.42

Table S11: Geometry, atomic charges and Lennard Jones parameters adopted for toluene.[1]

Atom type	X	Y	Z	q(e)	ε (kcal/mol)	σ (Å)
C	0.672	-2.823	0.003	-0.115	0.070	3.55
C	2.072	-2.823	0.003	-0.115	0.070	3.55
C	2.768	-1.618	0.003	-0.115	0.070	3.55
C	2.068	-0.405	0.003	-0.115	0.070	3.55
C	0.676	-0.405	0.003	-0.115	0.070	3.55
C	-0.024	-1.618	0.003	-0.115	0.070	3.55
H	0.132	-3.759	0.003	0.115	0.030	2.42
H	2.612	-3.759	0.003	0.115	0.030	2.42
H	3.848	-1.618	0.003	0.115	0.030	2.42
H	2.608	0.530	0.003	0.115	0.030	2.42
H	-1.104	-1.618	0.003	0.115	0.030	2.42
C	-0.079	0.903	0.003	0.115	0.170	3.80
H	-1.006	0.778	-0.521	0.000	0.000	0.00
H	-0.274	1.203	1.008	0.000	0.000	0.00
H	0.507	1.652	-0.489	0.000	0.000	0.00

Table S12: Geometry, atomic charges and Lennard Jones parameters adopted for acetone.[2]

Atom type	X	Y	Z	q(e)	ε (kcal/mol)	σ (Å)
C	-2.052	-0.068	0.001	-0.180	0.066	3.50
C	-0.530	-0.087	0.002	0.470	0.105	3.75
H	-2.402	0.965	0.000	0.060	0.030	2.50
H	-2.422	-0.577	-0.889	0.060	0.030	2.50
H	-2.423	-0.576	0.891	0.060	0.030	2.50
C	0.120	-1.464	0.003	-0.180	0.066	3.50
H	1.204	-1.355	0.004	0.060	0.030	2.50
H	-0.190	-2.012	0.893	0.060	0.030	2.50
H	-0.189	-2.013	-0.886	0.060	0.030	2.50
O	0.106	0.964	0.002	-0.470	0.210	2.96

Table S13: Geometry, atomic charges and Lennard Jones parameters adopted for methanol.[3]

Atom type	X	Y	Z	q(e)	ε (kcal/mol)	σ (Å)
H	2.663	0.800	0.667	0.418	0.000	0.00
O	2.853	1.320	1.437	-0.683	0.170	3.12
C	1.794	1.040	2.327	0.145	0.066	3.50
H	0.864	1.060	1.747	0.040	0.030	2.50
H	1.984	0.030	2.667	0.040	0.030	2.50
H	1.844	1.750	3.157	0.040	0.030	2.50

Table S14: Geometry, atomic charges and Lennard Jones parameters adopted for DMSO.[4]

Atom type	X	Y	Z	q(e)	ε (kcal/mol)	σ (Å)
S	0.000	0.000	0.000	0.139	0.395	3.56
O	1.045	-0.033	-1.117	-0.459	0.280	2.93
C	-1.612	-0.099	-0.794	0.160	0.160	3.81
C	0.002	-1.631	0.761	0.160	0.160	3.81
H	-2.384	-0.226	-0.035	0.000	0.000	0.00
H	-1.799	0.819	-1.352	0.000	0.000	0.00
H	-1.630	-0.949	-1.476	0.000	0.000	0.00
H	-0.786	-1.683	1.512	0.000	0.000	0.00
H	-0.175	-2.389	-0.003	0.000	0.000	0.00
H	0.967	-1.811	1.234	0.000	0.000	0.00

Table S15: Geometry, atomic charges and Lennard Jones parameters adopted for water.[5]

Atom type	X	Y	Z	q(e)	ε (kcal/mol)	σ (Å)
O	0.621	-1.467	-2.346	-0.834	0.152	3.15
H	0.794	-2.381	-2.072	0.417	0.000	0.00
H	1.219	-1.204	-3.063	0.417	0.000	0.00

5. Dihedrals Distributions

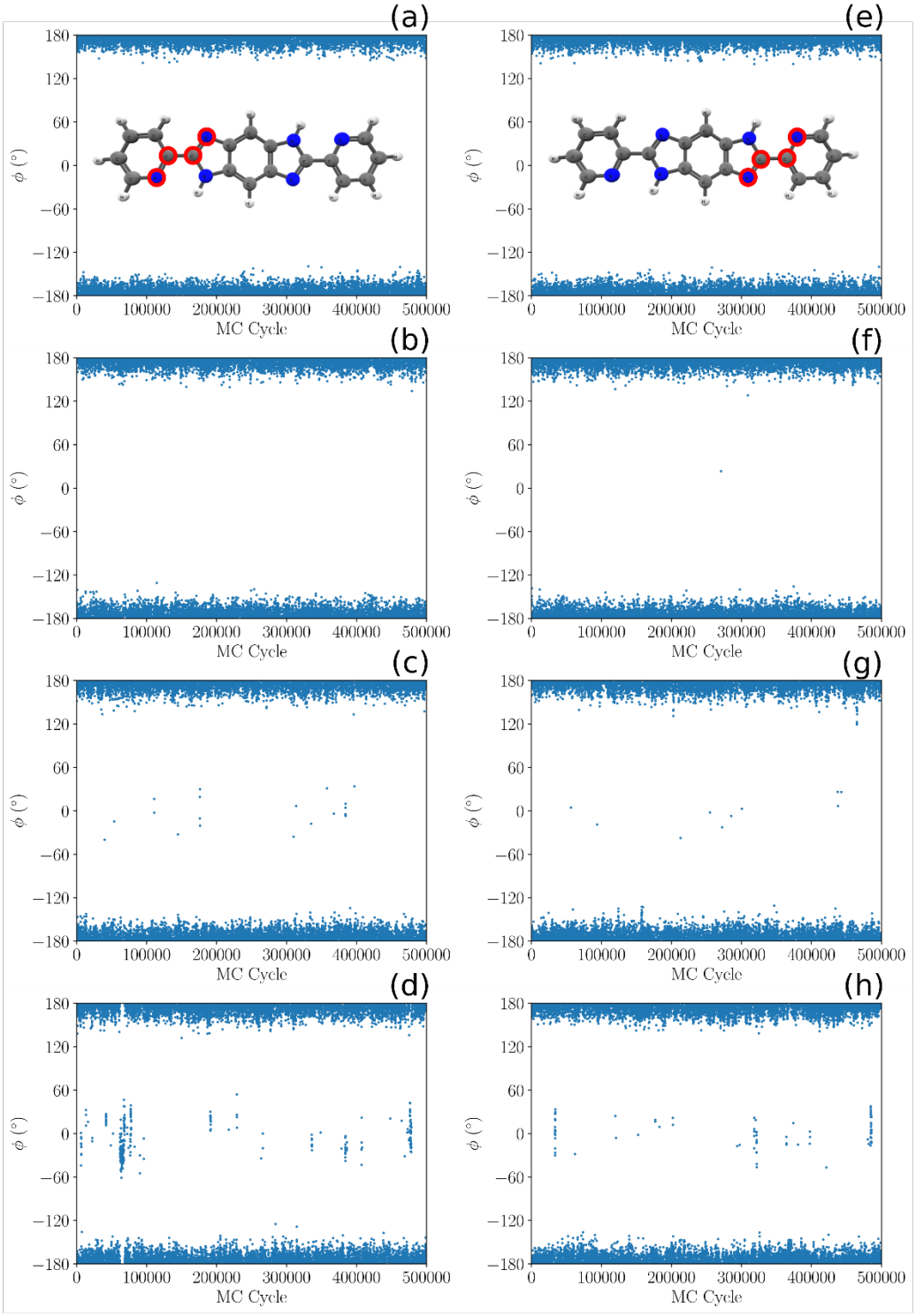


Figure S3: N_{im}-C-C-N_{py} dihedrals distributions of *t-bpybimH₂* in toluene (a,e), acetone (b,f), methanol (c,g) and water (d,h).

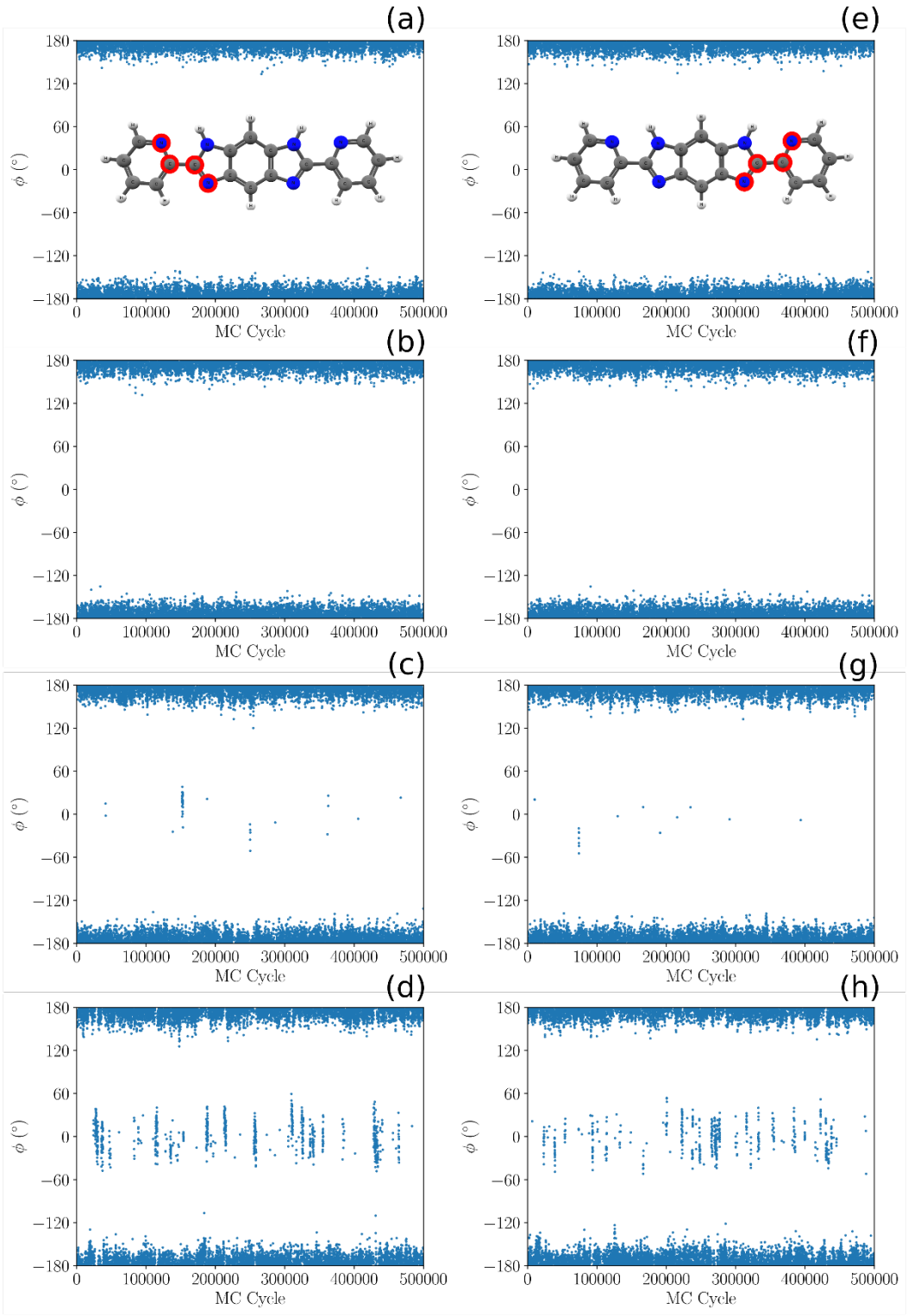


Figure S4: N_{im}-C-C-N_{py} dihedrals distributions of c-*bpybimH*$_2$ in toluene (a,e), acetone (b,f), methanol (c,g) and water (d,h).

6. Mass Spectrum

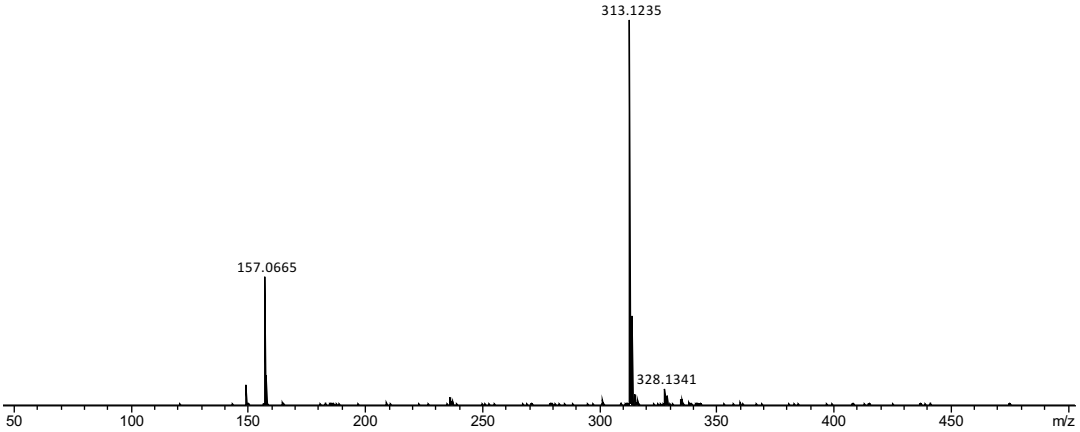


Figure S5: Mass spectrum of the bis(2-pyridyl)-benzo-bis(imidazole) ligand.

7. Experimental UV-Vis Absorption Spectra

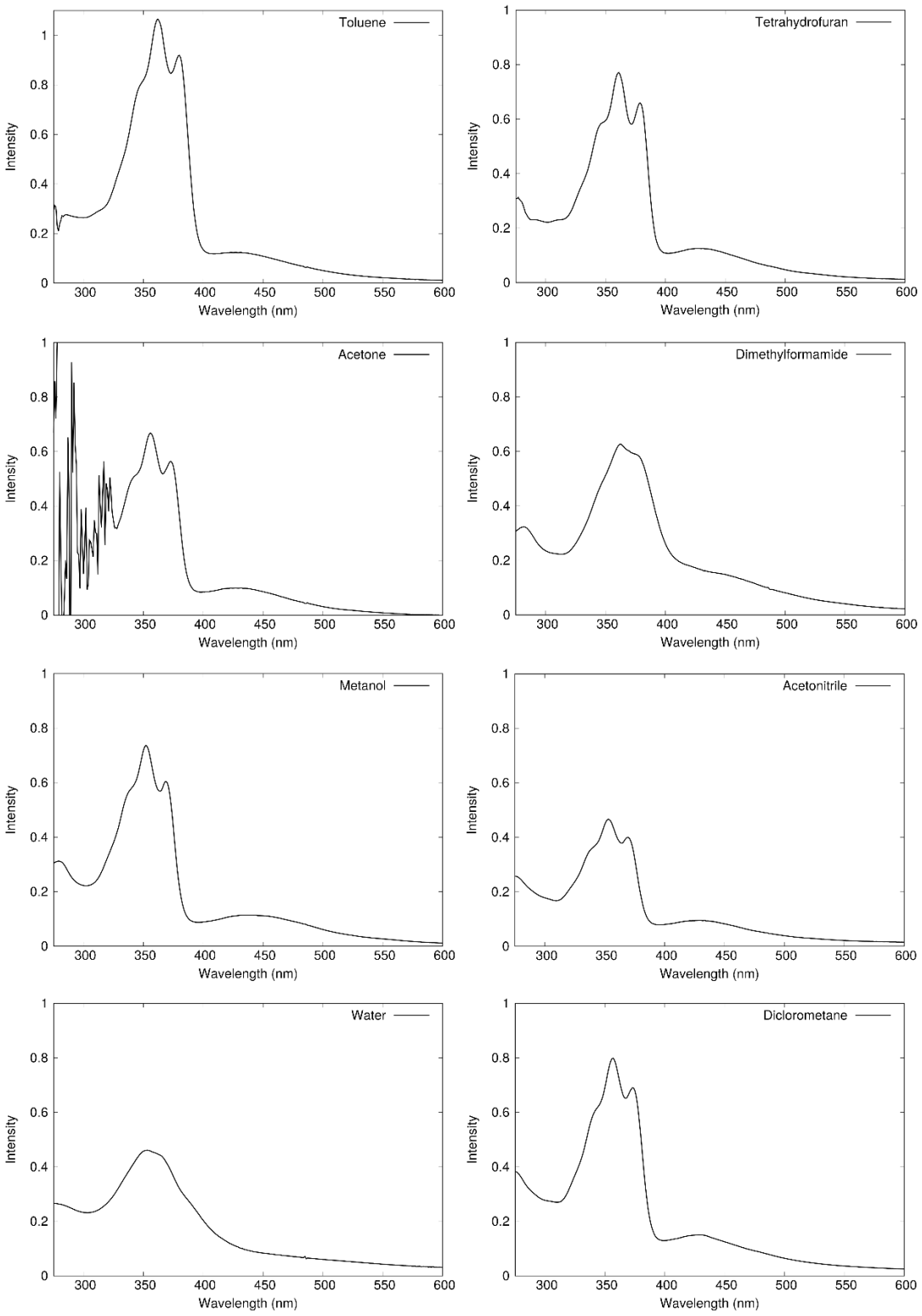


Figure S6: Experimental UV-Vis absorption spectra of the bis(2-pyridyl)-benzo-bis(imidazole) ligand in different solvents measured in a quartz cuvette with 10.0 mm optical path.

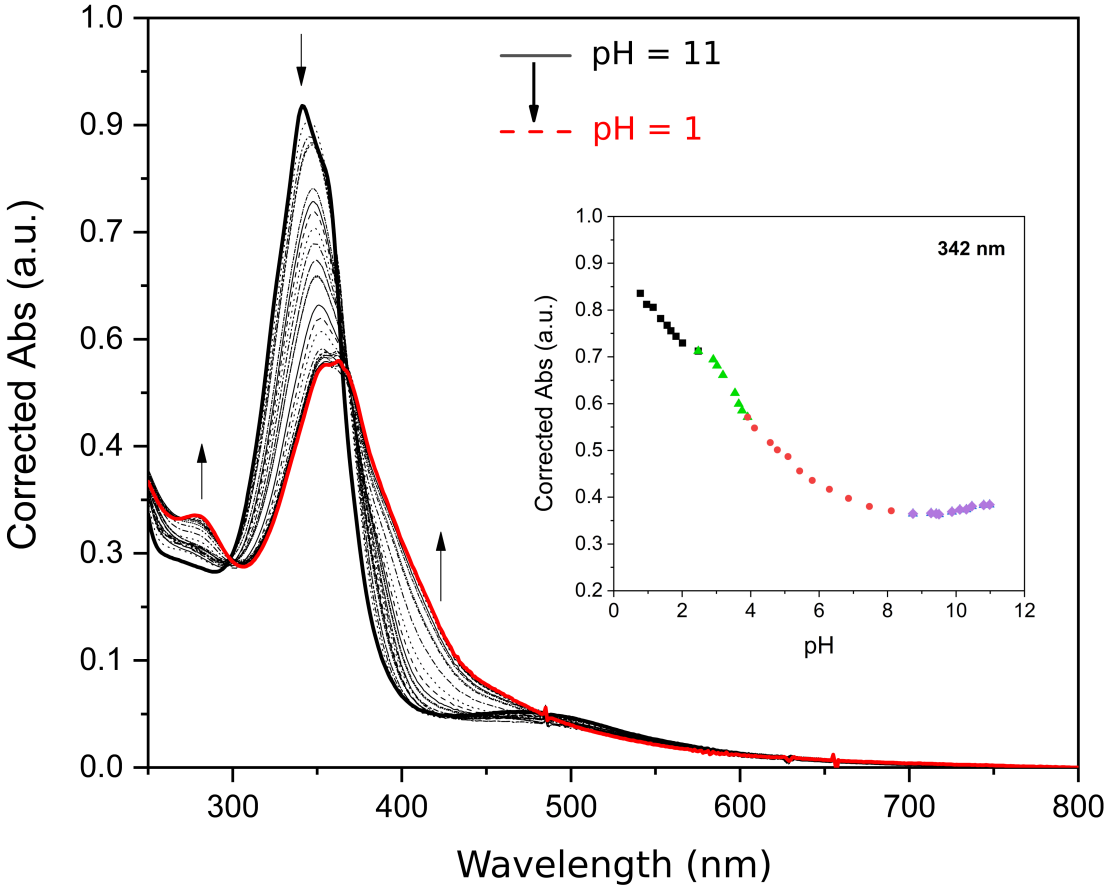


Figure S7: Evolution of the UV-Vis absorption spectra of the bis(2-pyridyl)-benzo-bis(imidazole) ligand as a function of the solution pH in the 1.0 to 11.0 range. Inset show the absorbance at 350 nm versus the pH variation.

8. Electronic Excitations

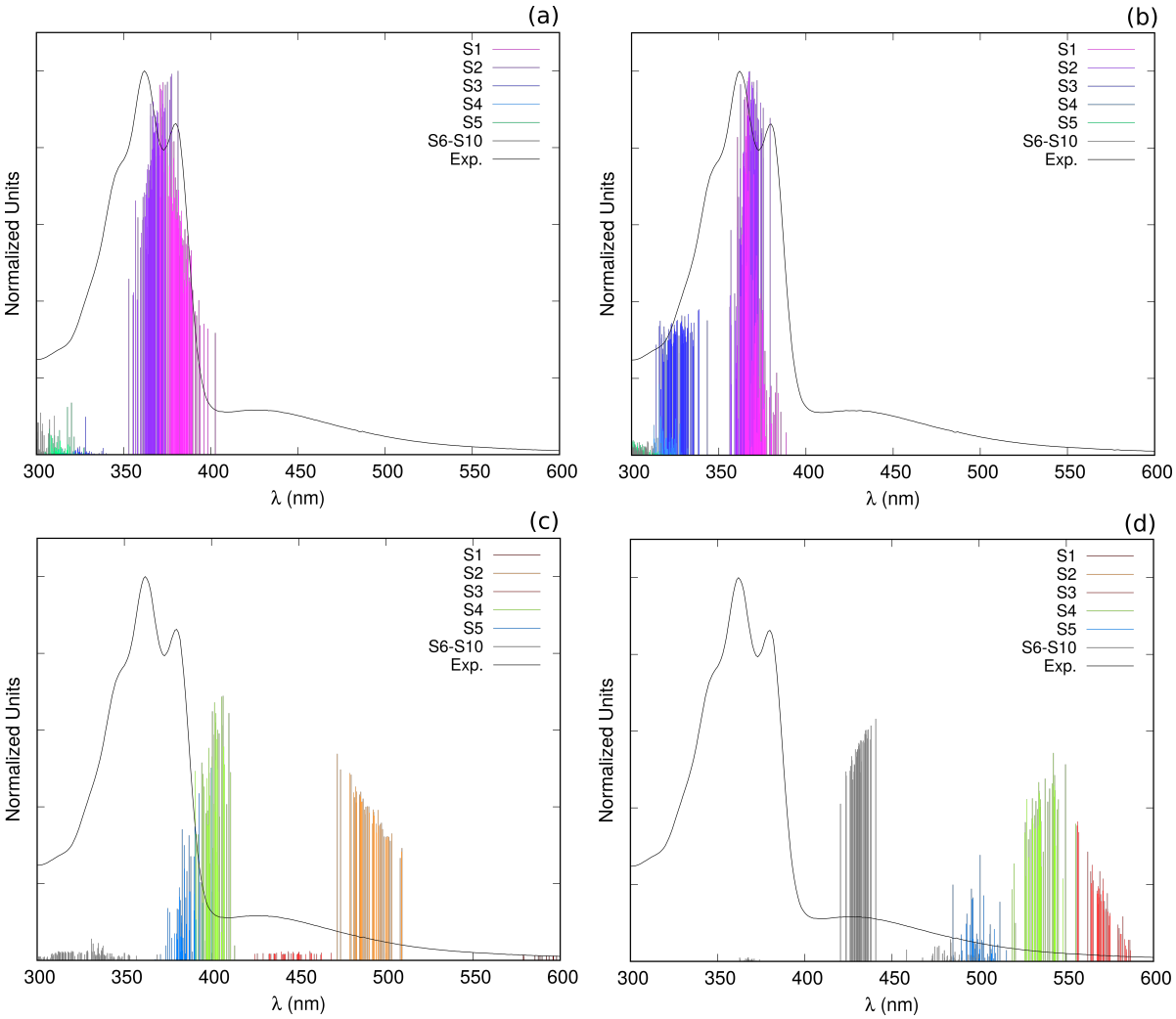


Figure S8: Electronic excitations (colored vertical lines) of the isomers *t-bpybimH*$_2$ (a), *c-bpybimH*$_2$ (b), *t-bpyHbimH* (c) and *t-bpyH*$_2$*bim* (d) in a solution of toluene. For each case, a total of 100 of statiscally uncorrelated configurations of the system solute/solvent were extracted from the MC simulations and used in the calculation of the first 10 electronic excitations. The excitations were calculated using the TD-DFT theory with B3LYP/aug-cc-pVDZ and solvent effects were considered by treating the solvent as point charges. Excitations in (a) and (b) are normalized accordingly to the most intense experimental absorption band, and excitations in (c) and (d) follows the same normalization factor. Experimental UV-Vis absorption spectra of bis(2-pyridyl)-benzo-bis(imidazole) in toluene (solid black line) measured in a quartz cuvette with 10.0 mm optical path.

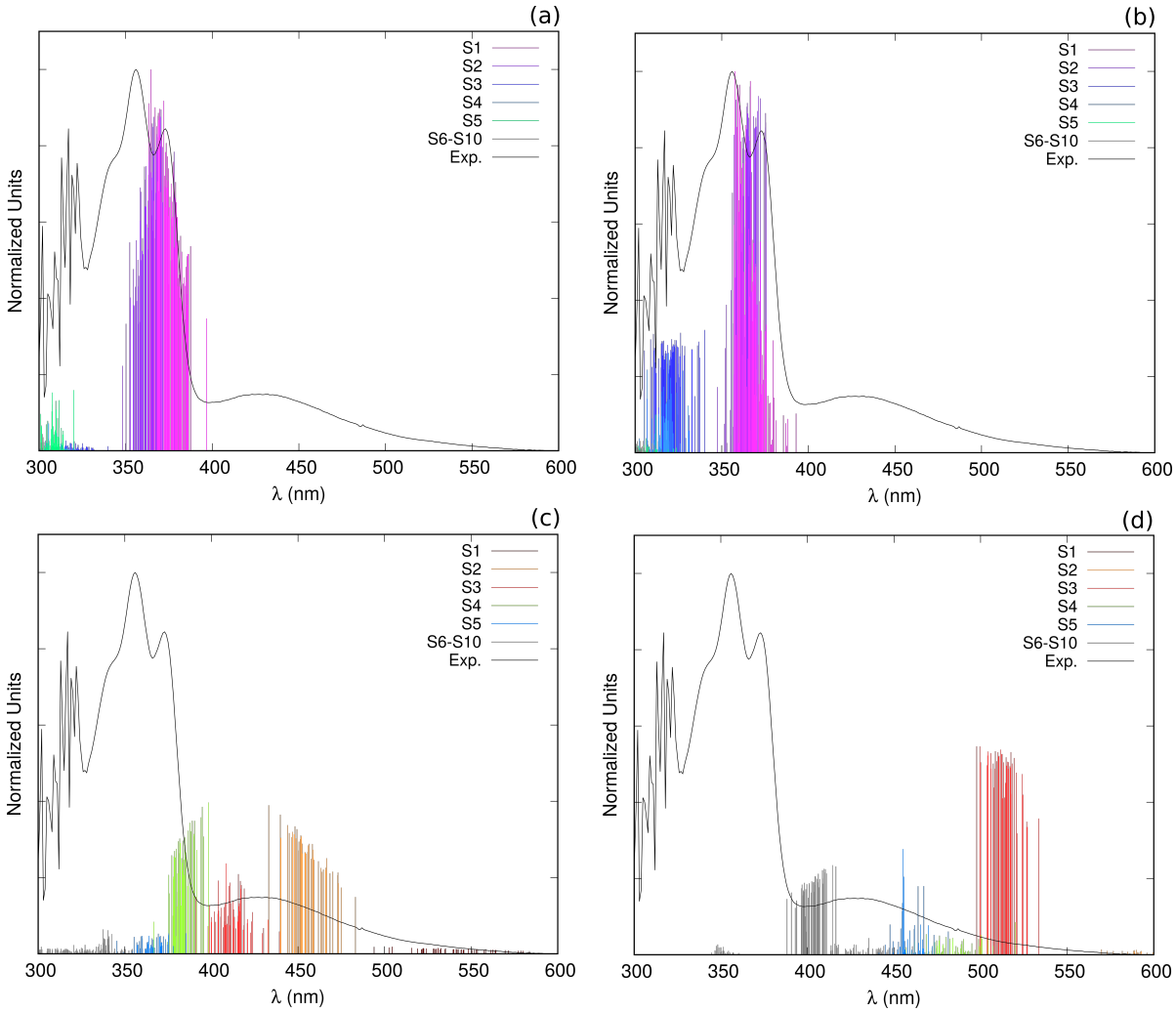


Figure S9: Electronic excitations (colored vertical lines) of the isomers *t-bpybimH*$_2$ (a), *c-bpybimH*$_2$ (b), c-*bpyHbimH* (c) and c-*bpyH*$_2$*bim* (d) in a solution of acetone. For each case, a total of 100 of statiscally uncorrelated configurations of the system solute/solvent were extracted from the MC simulations and used in the calculation of the first 10 electronic excitations. The excitations were calculated using the TD-DFT theory with B3LYP/aug-cc-pVDZ and solvent effects were considered by treating the solvent as point charges. Excitations in (a) and (b) are normalized accordingly to the most intense experimental absorption band, and excitations in (c) and (d) follows the same normalization factor. Experimental UV-Vis absorption spectra of bis(2-pyridyl)-benzo-bis(imidazole) in acetone (solid black line) measured in a quartz cuvette with 10.0 mm optical path.

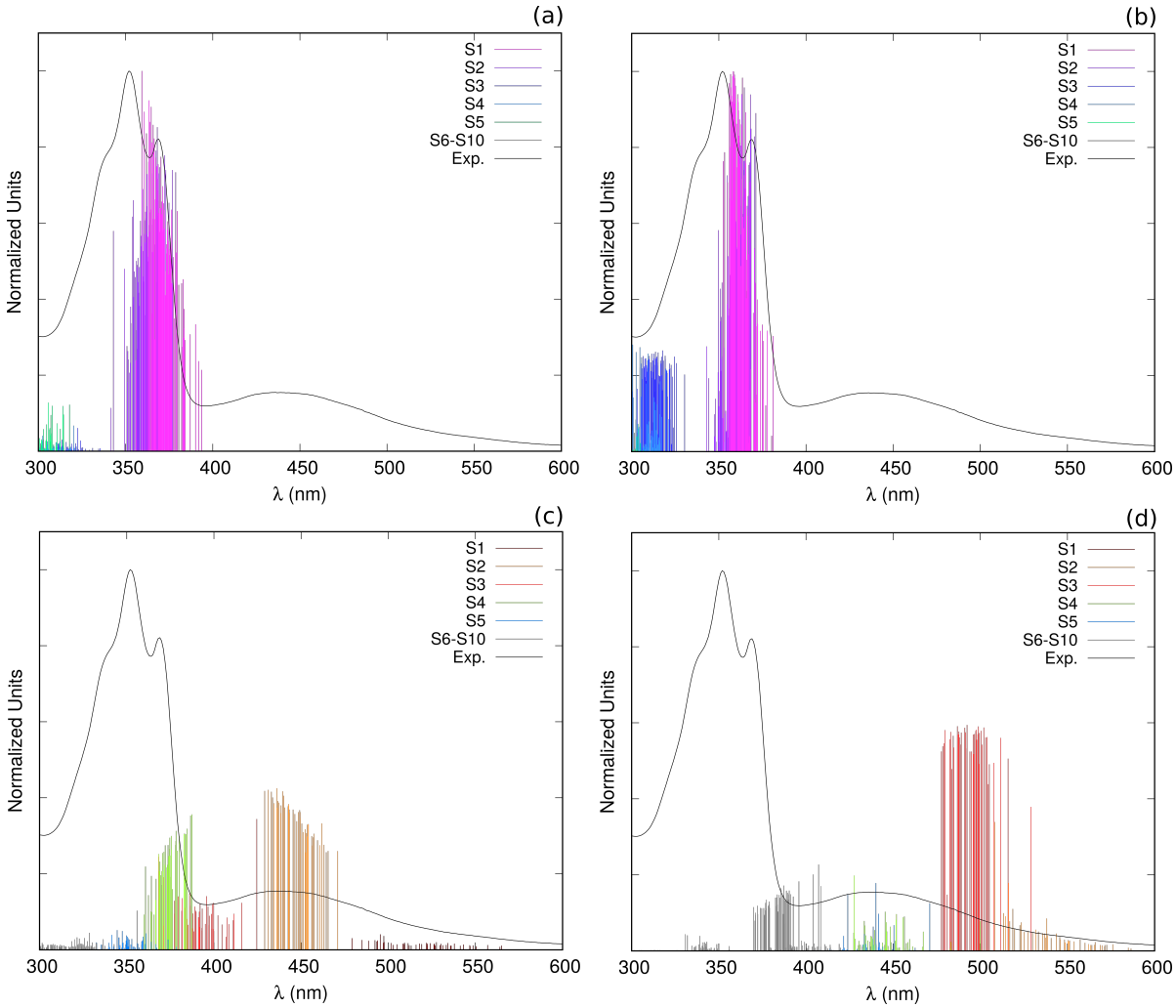


Figure S10: Electronic excitations (colored vertical lines) of the isomers *t-bpybimH*$_2$ (a), *c-bpybimH*$_2$ (b), c-*bpyHbimH* (c) and c-*bpyH*$_2$*bim* (d) in a solution of methanol. For each case, a total of 100 of statiscally uncorrelated configurations of the system solute/solvent were extracted from the MC simulations and used in the calculation of the first 10 electronic excitations. The excitations were calculated using the TD-DFT theory with B3LYP/aug-cc-pVDZ and solvent effects were considered by treating the solvent as point charges. Excitations in (a) and (b) are normalized accordingly to the most intense experimental absorption band, and excitations in (c) and (d) follows the same normalization factor. Experimental UV-Vis absorption spectra of bis(2-pyridyl)-benzo-bis(imidazole) in methanol (solid black line) measured in a quartz cuvette with 10.0 mm optical path.

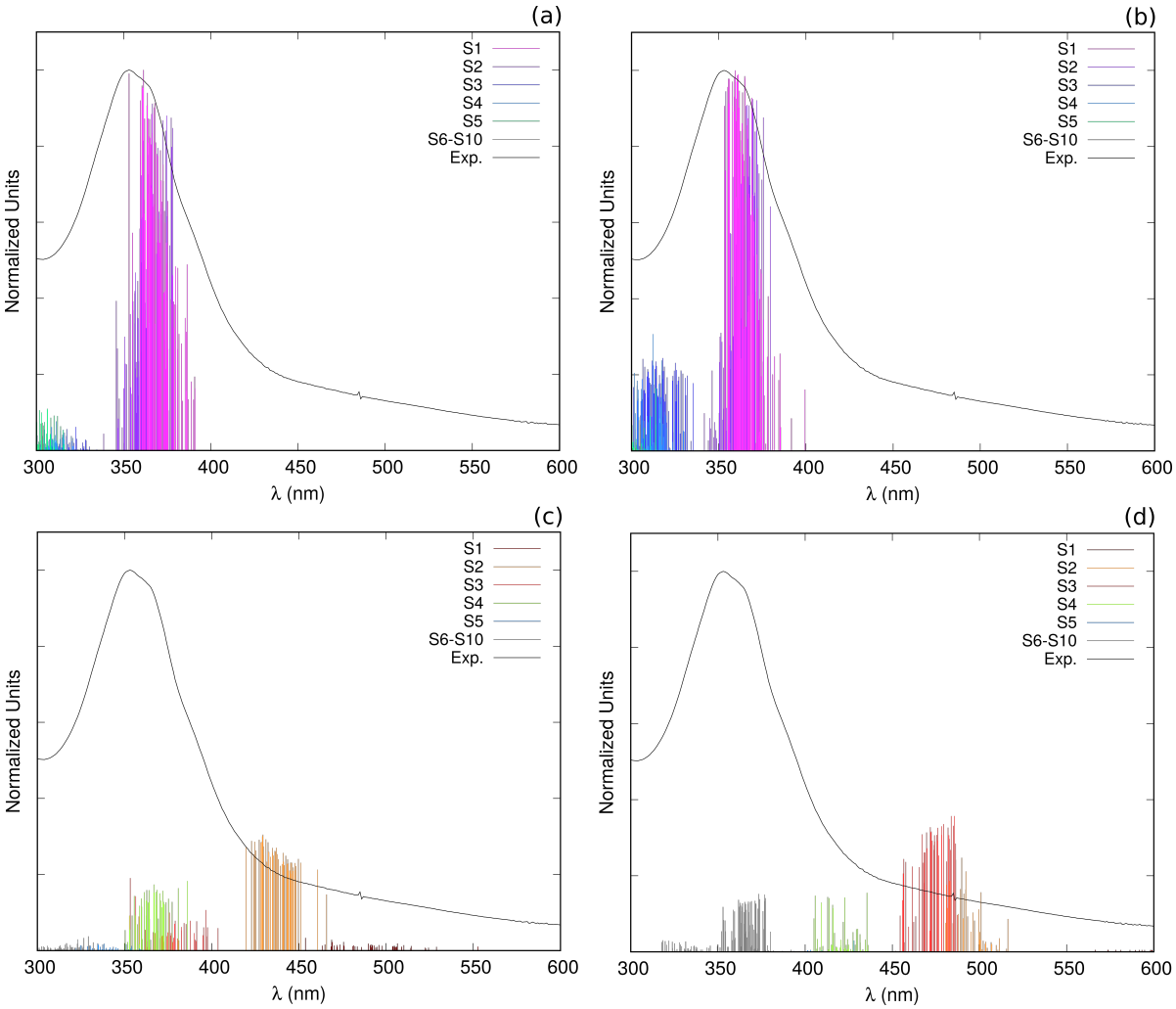


Figure S11: Electronic excitations (colored vertical lines) of the isomers *t-bpybimH*$_2$ (a), *c-bpybimH*$_2$ (b), c-*bpyHbimH* (c) and c-*bpyH*$_2$*bim* (d) in a solution of water. For each case, a total of 100 of statiscally uncorrelated configurations of the system solute/solvent were extracted from the MC simulations and used in the calculation of the first 10 electronic excitations. The excitations were calculated using the TD-DFT theory with B3LYP/aug-cc-pVDZ and solvent effects were considered by treating the solvent as point charges. Excitations in (a) and (b) are normalized accordingly to the most intense experimental absorption band, and excitations in (c) and (d) follows the same normalization factor. Experimental UV-Vis absorption spectra of bis(2-pyridyl)-benzo-bis(imidazole) in water (solid black line) measured in a quartz cuvette with 10.0 mm optical path.

Table S16: Averages of the energy, E(eV), and oscillator strength, f, of the electronic excitations of monomers of bis(2-pyridyl)-benzo-bis(imidazole) in solution (monomers of *t-bpybimH$_2$ for toluene and monomers of c-bpybimH$_2$ for other solvents*). Character of states obtained by analyses of the transition density matrices using the Theodore[6] program: LC refers to Local Centered contributions, *bim-bpy* refers to charge transfer contributions from benzo-bis(imidazole) to bis(2-pyridyl).

				Character of monomer states		
	State	E(eV)	f	LC	bim-bpy	Others
Toluene	1	3.24 ± 0.05	0.589	0.389	0.488	0.124
	2	3.38 ± 0.04	0.780	0.380	0.456	0.164
	3	3.79 ± 0.06	0.005	0.211	0.649	0.139
	4	3.93 ± 0.07	0.003	0.176	0.684	0.140
	5	3.98 ± 0.06	0.017	0.184	0.654	0.162
	6	4.08 ± 0.07	0.002	0.127	0.706	0.167
	7	4.22 ± 0.08	0.071	0.076	0.810	0.113
	8	4.35 ± 0.08	0.023	0.106	0.754	0.139
	9	4.53 ± 0.03	0.003	0.438	0.159	0.404
	10	4.59 ± 0.03	0.001	0.459	0.151	0.390
Acetone	1	3.36 ± 0.06	0.420	0.381	0.458	0.160
	2	3.41 ± 0.05	0.731	0.389	0.445	0.165
	3	3.87 ± 0.08	0.272	0.235	0.664	0.101
	4	3.94 ± 0.07	0.061	0.218	0.576	0.206
	5	4.10 ± 0.09	0.012	0.143	0.720	0.137
	6	4.16 ± 0.09	0.010	0.114	0.732	0.154
	7	4.29 ± 0.09	0.007	0.141	0.697	0.162
	8	4.38 ± 0.10	0.024	0.130	0.655	0.215
	9	4.56 ± 0.04	0.004	0.403	0.194	0.403
	10	4.63 ± 0.04	0.003	0.459	0.142	0.399
Methanol	1	3.41 ± 0.06	0.719	0.401	0.431	0.168
	2	3.47 ± 0.06	0.480	0.429	0.475	0.095
	3	3.96 ± 0.08	0.234	0.264	0.663	0.073
	4	4.02 ± 0.06	0.057	0.256	0.572	0.173
	5	4.21 ± 0.09	0.011	0.163	0.688	0.149
	6	4.28 ± 0.10	0.010	0.140	0.714	0.146
	7	4.39 ± 0.07	0.006	0.173	0.637	0.189
	8	4.46 ± 0.07	0.015	0.254	0.472	0.275
	9	4.54 ± 0.06	0.008	0.357	0.327	0.317
	10	4.62 ± 0.08	0.011	0.365	0.312	0.324
Water	1	3.37 ± 0.07	0.691	0.383	0.420	0.197
	2	3.45 ± 0.08	0.513	0.409	0.458	0.134
	3	3.94 ± 0.10	0.173	0.256	0.609	0.135
	4	3.99 ± 0.09	0.075	0.251	0.571	0.178
	5	4.20 ± 0.10	0.015	0.163	0.628	0.208
	6	4.27 ± 0.12	0.014	0.137	0.688	0.175
	7	4.40 ± 0.09	0.007	0.208	0.527	0.265
	8	4.48 ± 0.10	0.017	0.214	0.511	0.275
	9	4.60 ± 0.07	0.013	0.329	0.321	0.349
	10	4.72 ± 0.09	0.009	0.329	0.309	0.361

9. Kohn Sham Molecular Orbitals

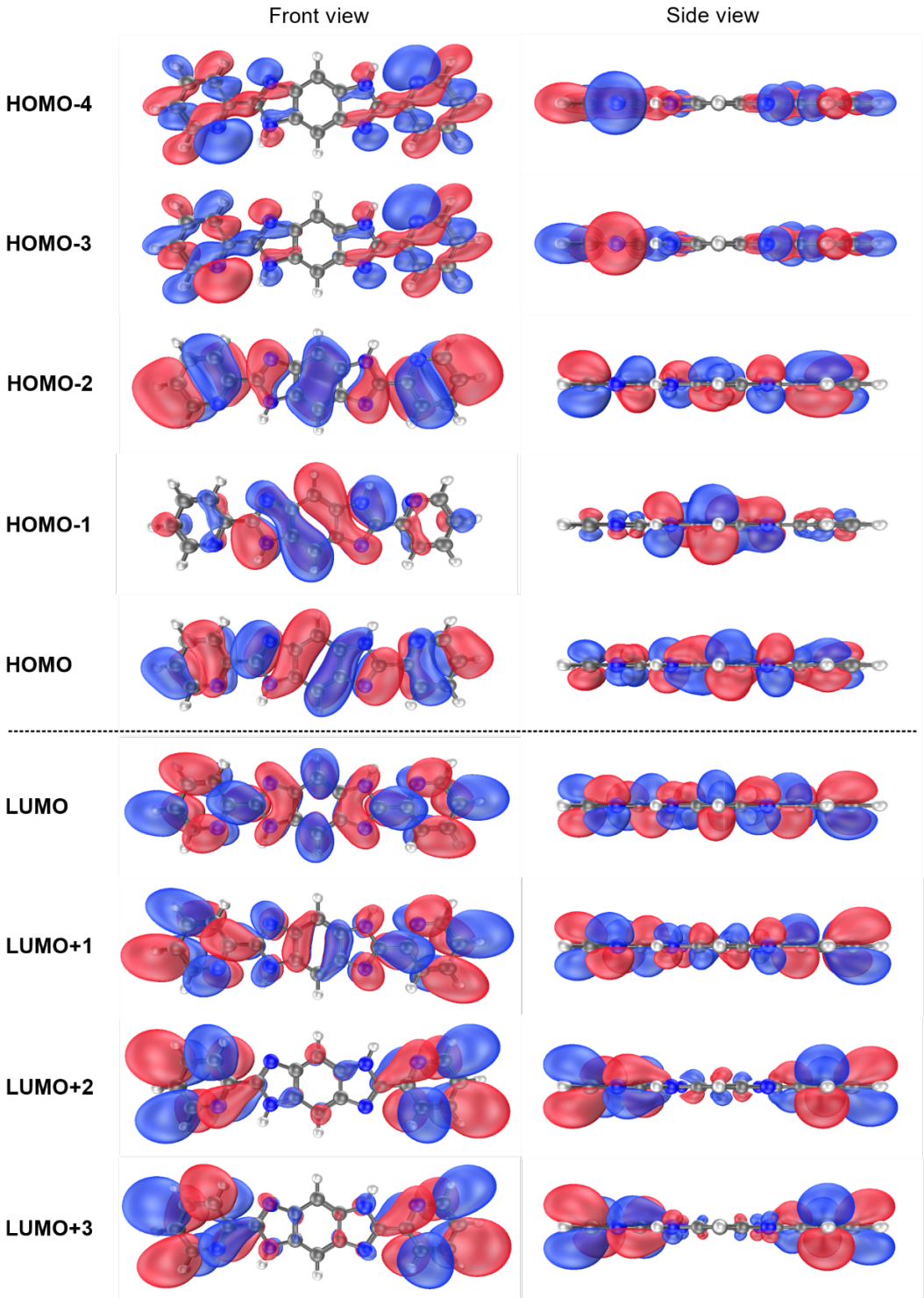


Figure S12: Kohn Sham molecular orbitals (isovalue = 0.04) of the isomer *t-bpybimH*$_2$ in vacuum.

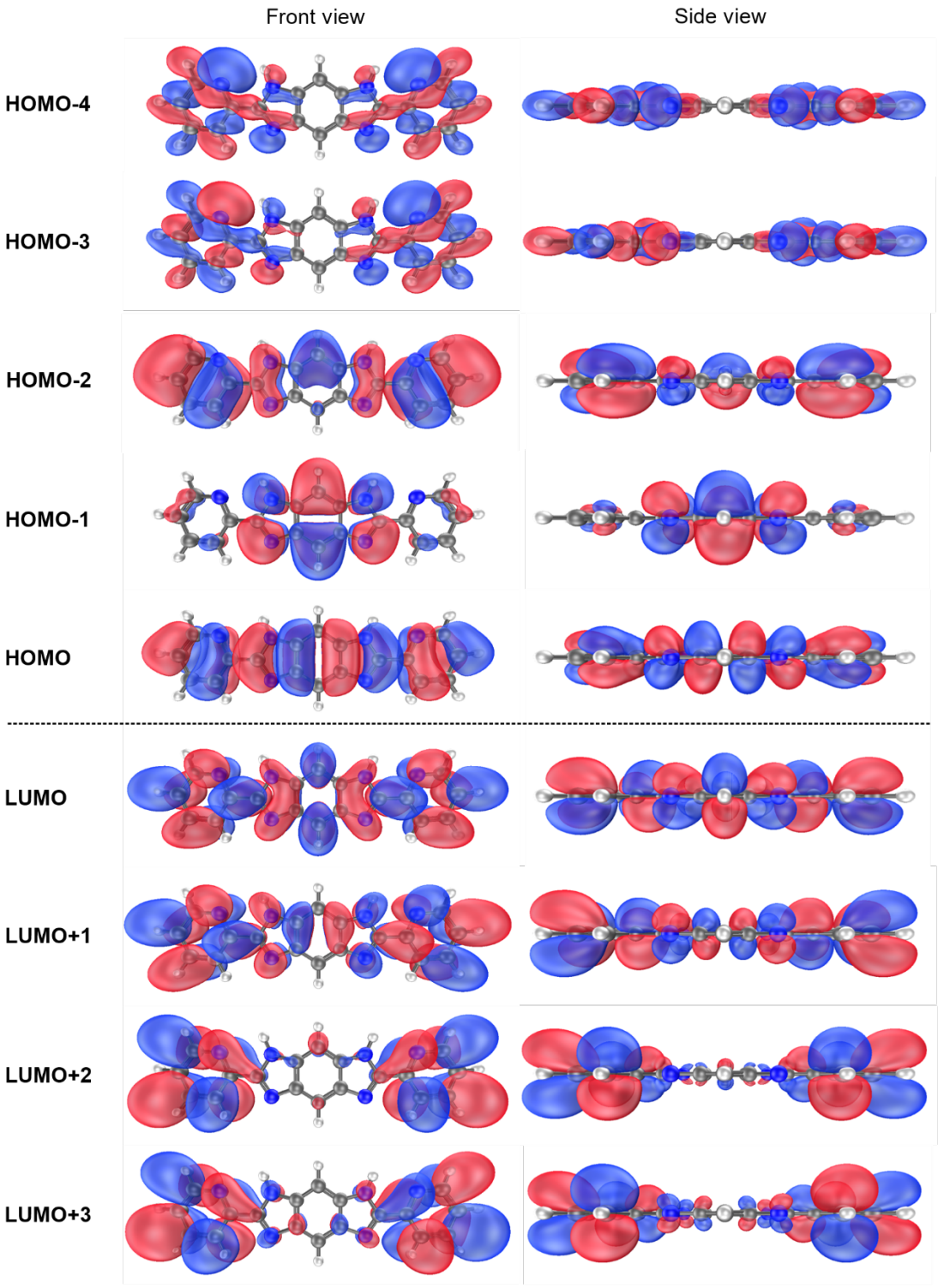


Figure S13: Kohn Sham molecular orbitals (isovalue = 0.04) of the isomer c-*bpybimH*$_2$ in vacuum.

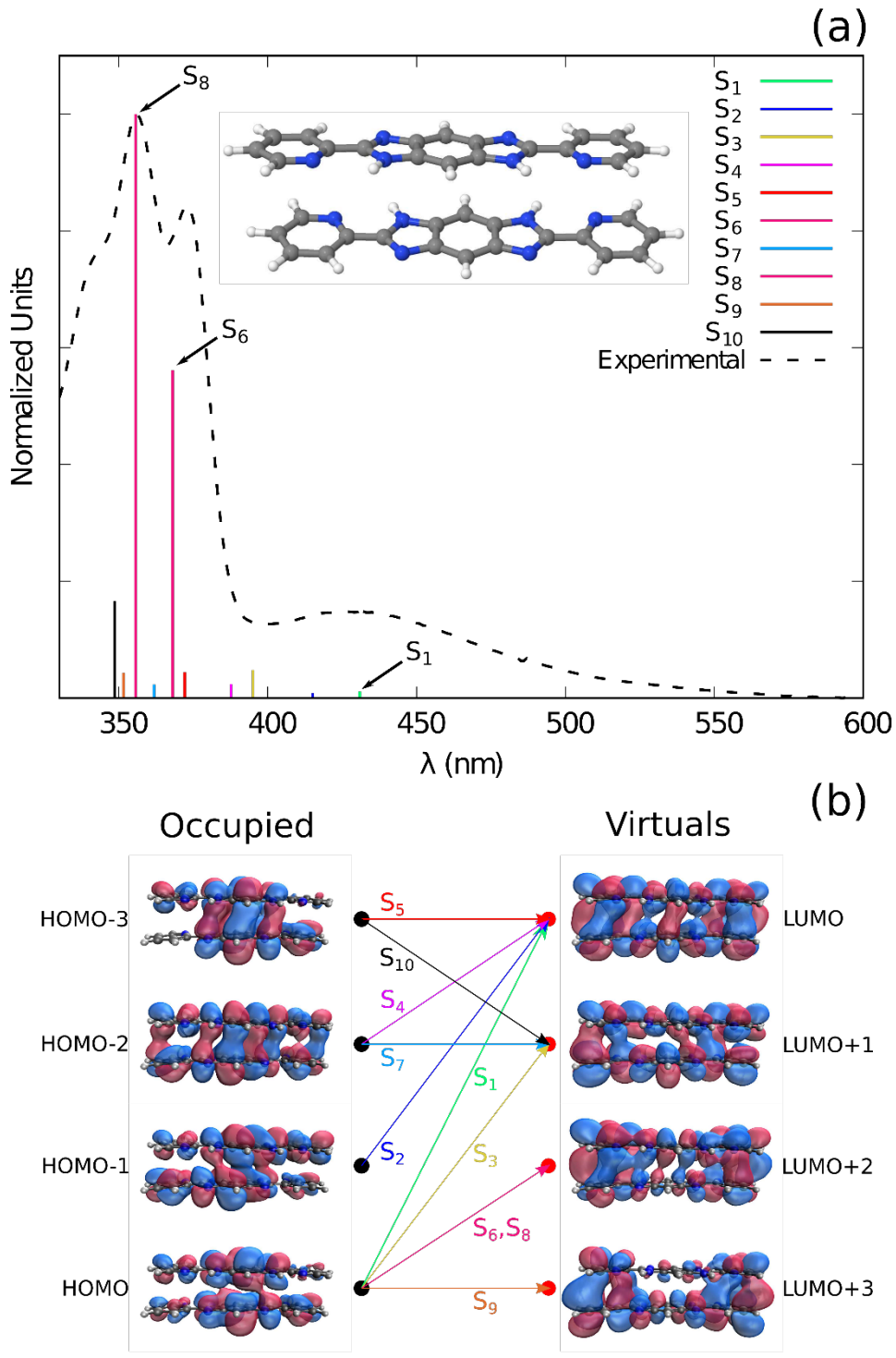


Figure S14: (a) Electronic excitations (colored vertical lines) of a dimer of *c-bpybim*H_2 in acetone, obtained from a specific dimer MC configuration in a solution of acetone. Excitations calculated using the TD-DFT theory with B3LYP/(aug-cc-pVDZ for C,N and cc-pVDZ for H) and solvent effects considered by treating the solvent as point charges. Excitations normalized accordingly to the most intense experimental absorption band. Experimental UV-Vis absorption spectra of bis(2-pyridyl)-benzo-bis(imidazole) in toluene (dashed black line) measured in a quartz cuvette with 10.0 mm optical path. (b) Occupied and virtual molecular orbitals that most contribute to each electronic excitation (isovalue 0.04).

Table S17: Averages of the energy, E(eV), and oscillator strength, f, of the calculated electronic excitations of dimers of bis(2-pyridyl)-benzo-bis(imidazole) in solution (dimers of *t-bpybimH$_2$ for toluene and dimers of c-bpybimH$_2$ for other solvents*). Character of states obtained by analyses of the transition density matrices using the Theodore[6] program: LC refers to Local Centered contributions; *bim-bpy* refers to charge transfer contributions from benzo-bis(imidazole) to bis(2-pyridyl); (*bim-bpy)** refers to charge transfer contributions from benzo-bis(imidazole) to bis(2-pyridyl) of different monomers; (*bim-bim)** refers to charge transfer contributions between benzo-bis(imidazole) groups of different monomers.

				Character of states				
	State	E (eV)	f	LC	bim-bpy	(bim-bpy)*	(bim-bim)*	Others
Toluene	1	2.87 ± 0.11	0.005	0.115	0.121	0.321	0.289	0.155
	2	2.97 ± 0.12	0.013	0.138	0.161	0.315	0.289	0.097
	3	3.15 ± 0.04	0.096	0.192	0.240	0.246	0.203	0.119
	4	3.21 ± 0.04	0.015	0.163	0.223	0.291	0.245	0.078
	5	3.32 ± 0.03	0.065	0.246	0.327	0.195	0.172	0.059
	6	3.38 ± 0.04	0.298	0.274	0.346	0.167	0.123	0.091
	7	3.43 ± 0.05	0.337	0.260	0.319	0.186	0.132	0.104
	8	3.48 ± 0.04	0.358	0.214	0.284	0.247	0.161	0.094
	9	3.53 ± 0.05	0.190	0.093	0.242	0.404	0.141	0.119
	10	3.57 ± 0.06	0.266	0.106	0.309	0.360	0.115	0.111
Acetone	1	2.92 ± 0.12	0.009	0.174	0.182	0.265	0.239	0.140
	2	3.02 ± 0.13	0.016	0.131	0.162	0.334	0.305	0.068
	3	3.19 ± 0.04	0.096	0.124	0.164	0.315	0.258	0.140
	4	3.25 ± 0.05	0.033	0.135	0.191	0.328	0.277	0.070
	5	3.36 ± 0.06	0.107	0.279	0.385	0.152	0.120	0.064
	6	3.42 ± 0.06	0.422	0.264	0.349	0.167	0.116	0.104
	7	3.48 ± 0.06	0.317	0.214	0.296	0.221	0.137	0.132
	8	3.52 ± 0.06	0.381	0.189	0.300	0.267	0.142	0.102
	9	3.60 ± 0.06	0.164	0.136	0.305	0.328	0.131	0.099
	10	3.65 ± 0.07	0.178	0.129	0.307	0.341	0.128	0.095
Methanol	1	2.92 ± 0.12	0.010	0.155	0.145	0.267	0.262	0.171
	2	3.04 ± 0.12	0.011	0.112	0.127	0.350	0.353	0.058
	3	3.23 ± 0.04	0.092	0.156	0.172	0.263	0.238	0.170
	4	3.33 ± 0.06	0.041	0.197	0.248	0.263	0.241	0.051
	5	3.43 ± 0.05	0.233	0.314	0.393	0.131	0.100	0.062
	6	3.48 ± 0.04	0.550	0.279	0.324	0.160	0.113	0.124
	7	3.53 ± 0.04	0.392	0.226	0.277	0.223	0.134	0.140
	8	3.59 ± 0.05	0.346	0.169	0.232	0.305	0.191	0.104
	9	3.67 ± 0.06	0.089	0.127	0.209	0.336	0.195	0.134
	10	3.72 ± 0.08	0.107	0.122	0.268	0.351	0.158	0.102
Water	1	3.00 ± 0.11	0.014	0.123	0.116	0.237	0.240	0.284
	2	3.10 ± 0.11	0.042	0.105	0.115	0.293	0.293	0.194
	3	3.24 ± 0.04	0.052	0.147	0.143	0.232	0.225	0.253
	4	3.34 ± 0.06	0.039	0.171	0.203	0.226	0.217	0.183
	5	3.42 ± 0.06	0.203	0.207	0.239	0.176	0.157	0.221
	6	3.48 ± 0.04	0.537	0.269	0.306	0.119	0.102	0.205
	7	3.52 ± 0.05	0.521	0.261	0.292	0.130	0.099	0.218
	8	3.61 ± 0.06	0.341	0.195	0.230	0.209	0.168	0.197
	9	3.71 ± 0.06	0.143	0.101	0.159	0.310	0.169	0.261
	10	3.78 ± 0.07	0.070	0.108	0.212	0.318	0.154	0.207

10. NMR Magnetic Shielding

Table S18: Theoretical isotropic and anisotropic magnetic shieldings (in ppm) of all atoms of bis(2-pyridyl)-benzo-bis(imidazole) (isomers *t-bpybimH$_2$*, *t-bpyHbimH* and *t-bpyH$_2$bim*) in DMSO. Values calculated at B3LYP/aug-cc-pVDZ level using the GIAO approximation and considering the PCM model of solvent. The atoms numbering follows the numbering of the structures showed in Figure S15.

Atom Number	t-*bpybimH$_2$*			*t-bpyHbimH*			*t-bpyH$_2$bim*		
	Atom type	Isotropic	Anisotropic	Atom type	Isotropic	Anisotropic	Atom type	Isotropic	Anisotropic
1	N	117.70	94.53	N	120.81	87.43	N	23.01	301.68
2	N	-45.50	492.40	N	-45.58	490.96	N	78.20	205.34
3	N	16.77	325.84	N	17.39	322.73	N	10.03	324.68
4	N	117.70	94.53	N	16.23	315.25	N	23.01	301.68
5	N	16.77	325.83	N	7.22	331.92	N	10.03	324.68
6	N	-45.50	492.40	N	78.92	205.22	N	78.20	205.34
7	C	67.48	169.16	C	67.73	168.01	C	70.96	164.53
8	C	55.02	193.47	C	55.38	193.43	C	47.29	200.42
9	C	70.41	168.97	C	70.62	169.34	C	68.55	163.27
10	C	41.46	157.60	C	41.24	158.44	C	41.97	156.79
11	C	40.85	164.01	C	41.00	163.68	C	53.01	157.77
12	C	38.36	96.97	C	38.68	95.43	C	37.62	99.18
13	C	59.31	131.81	C	57.93	129.52	C	40.69	136.96
14	C	46.23	128.64	C	45.52	123.70	C	37.44	134.91
15	C	92.99	123.20	C	86.99	120.06	C	90.44	111.81
16	C	92.99	123.20	C	95.77	115.70	C	90.44	111.81
17	C	59.31	131.81	C	42.80	138.64	C	40.69	136.96
18	C	46.23	128.64	C	39.31	138.12	C	37.44	134.91
19	C	38.36	96.97	C	38.32	98.46	C	37.62	99.18
20	C	41.46	157.60	C	41.85	157.20	C	41.97	156.79
21	C	70.41	168.97	C	68.61	163.14	C	68.55	163.27
22	C	40.85	164.01	C	52.92	158.31	C	53.01	157.77
23	C	55.02	193.47	C	46.85	201.19	C	47.29	200.42
24	C	67.48	169.16	C	70.79	165.33	C	70.96	164.53
25	H	22.48	6.28	H	22.51	6.25	H	23.28	4.96
26	H	23.78	5.05	H	23.82	5.00	H	23.96	4.06
27	H	22.69	9.36	H	22.71	9.38	H	22.86	8.13
28	H	23.29	5.55	H	23.31	5.53	H	23.17	5.33
29	H	22.69	9.36	H	22.80	8.19	H	22.86	8.13
30	H	22.48	6.28	H	23.23	5.02	H	23.28	4.96
31	H	23.29	5.55	H	23.12	5.39	H	23.17	5.33
32	H	23.78	5.05	H	23.92	4.10	H	23.96	4.06
33	H	23.48	6.69	H	23.48	6.69	H	23.67	6.67
34	H	23.48	6.69	H	23.67	6.74	H	23.67	6.67
35	H	21.01	8.78	H	21.34	8.46	H	18.57	11.53
36	H	21.01	8.78	H	18.64	11.27	H	18.57	11.53

Table S19: Theoretical isotropic and anisotropic magnetic shieldings (in ppm) of all atoms of bis(2-pyridyl)-benzo-bis(imidazole) (isomers *c-bpybimH$_2$*, *c-bpyHbimH* and *c-bpyH$_2$bim*) in DMSO. Values calculated at B3LYP/aug-cc-pVDZ level using the GIAO approximation and considering the PCM model of solvent. The atoms numbering follows the numbering of structures showed in Figure S15.

Atom Number	*c-bpybimH$_2$*			*c-bpyHbimH*			*c-bpyH$_2$bim*		
	Atom type	Isotropic	Anisotropic	Atom type	Isotropic	Anisotropic	Atom type	Isotropic	Anisotropic
1	N	15.40	328.05	N	17.27	323.13	N	9.73	326.97
2	N	-45.12	492.21	N	-44.88	492.76	N	77.94	206.15
3	N	117.24	94.87	N	120.35	88.30	N	23.48	300.32
4	N	117.25	94.85	N	18.52	311.18	N	23.54	300.13
5	N	15.37	328.06	N	4.15	337.13	N	9.79	326.90
6	N	-45.14	492.22	N	78.99	205.34	N	77.85	206.28
7	C	67.57	169.12	C	67.93	168.53	C	70.87	164.17
8	C	54.97	193.35	C	55.12	192.53	C	47.28	200.42
9	C	70.54	168.86	C	70.42	168.35	C	68.91	163.62
10	C	41.38	157.56	C	41.11	158.51	C	42.15	157.34
11	C	40.85	163.89	C	40.92	163.52	C	53.14	158.10
12	C	38.88	95.41	C	38.85	94.80	C	37.70	99.07
13	C	47.52	124.79	C	46.31	122.41	C	38.12	133.08
14	C	57.92	135.62	C	57.22	130.93	C	39.97	138.43
15	C	101.49	118.94	C	96.85	114.38	C	92.04	109.68
16	C	83.75	128.07	C	85.81	121.53	C	88.79	113.97
17	C	57.92	135.63	C	41.45	142.00	C	39.98	138.45
18	C	47.52	124.80	C	40.56	134.50	C	38.11	133.04
19	C	38.88	95.41	C	38.35	98.29	C	37.69	99.09
20	C	41.37	157.57	C	41.84	157.21	C	42.15	157.35
21	C	70.54	168.87	C	68.65	163.38	C	68.93	163.64
22	C	40.85	163.90	C	53.02	158.19	C	53.13	158.14
23	C	54.97	193.35	C	46.94	201.03	C	47.28	200.46
24	C	67.58	169.11	C	70.80	165.37	C	70.86	164.18
25	H	22.48	6.28	H	22.50	6.27	H	23.28	4.97
26	H	23.78	5.05	H	23.81	5.02	H	23.98	4.05
27	H	22.69	9.33	H	22.72	9.35	H	22.86	8.12
28	H	23.29	5.55	H	23.32	5.52	H	23.18	5.31
29	H	22.69	9.33	H	22.79	8.18	H	22.86	8.12
30	H	22.48	6.28	H	23.24	5.02	H	23.28	4.97
31	H	23.29	5.55	H	23.13	5.38	H	23.18	5.31
32	H	23.78	5.05	H	23.92	4.10	H	23.98	4.05
33	H	21.01	8.81	H	23.74	6.79	H	23.76	6.72
34	H	23.68	6.76	H	23.43	6.62	H	23.58	6.64
35	H	23.28	6.58	H	18.69	11.27	H	18.50	11.66
36	H	21.02	8.81	H	21.35	8.44	H	18.52	11.64

Table S20: Theoretical isotropic and anisotropic magnetic shieldings (in ppm) of all atoms of bis(2-pyridyl)-benzo-bis(imidazole) (conformers *t-bpybimH$_2$*, *t-bpyHbimH* and *t-bpyH$_2$bim*) in DMSO. Values calculated at B3LYP/aug-cc-pVDZ level using the GIAO approximation and considering a micro-solvated PCM model of solvent (with two explicit DMSO). The atoms numbering follows the numbering of the optimized clusters in Figure S16.

Atom Number	*t-bpybimH$_2$*			*t-bpyHbimH*			*t-bpyH$_2$bim*		
	Atom type	Isotropic	Anisotropic	Atom type	Isotropic	Anisotropic	Atom type	Isotropic	Anisotropic
1	H	22.47	8.92	H	23.18	8.23	H	23.24	8.15
2	C	41.34	164.17	C	52.51	163.81	C	52.63	163.36
3	N	-48.88	489.09	N	63.72	246.31	N	63.84	244.32
4	C	68.25	165.62	C	70.77	163.58	C	70.99	162.12
5	C	39.46	159.50	C	41.16	158.01	C	41.48	158.47
6	H	23.80	5.08	H	23.95	4.31	H	24.04	4.24
7	C	55.68	191.27	C	50.25	199.20	C	50.79	198.54
8	C	69.48	167.82	C	66.73	165.05	C	66.90	164.74
9	C	37.59	95.80	C	36.65	97.54	C	36.23	98.08
10	H	23.33	5.37	H	23.22	5.28	H	23.28	5.23
11	H	22.51	9.89	H	22.31	9.45	H	22.35	9.46
12	N	14.72	311.35	N	4.29	310.25	N	5.80	301.14
13	N	103.25	120.07	N	10.14	327.61	N	15.47	318.12
14	C	46.91	131.78	C	41.62	141.11	C	40.45	138.66
15	H	17.08	24.80	C	42.49	134.46	C	41.26	133.87
16	C	56.09	132.01	C	95.80	113.70	C	91.49	111.03
17	C	93.10	120.22	C	88.38	118.53	C	91.48	111.03
18	C	93.09	120.22	H	23.66	8.59	H	23.67	9.17
19	H	23.60	8.66	C	55.94	129.99	C	41.27	133.88
20	C	56.09	132.01	H	23.55	9.31	H	23.67	9.17
21	H	23.60	8.66	C	46.82	128.55	C	40.44	138.65
22	C	46.91	131.77	N	105.91	114.42	N	15.46	318.04
23	N	103.26	120.06	N	15.31	305.07	N	5.81	301.13
24	N	14.73	311.34	H	17.51	24.39	C	36.22	98.08
25	H	17.09	24.80	C	37.86	95.13	C	41.49	158.51
26	C	37.60	95.79	C	39.47	160.20	N	63.81	244.32
27	C	39.46	159.51	N	-49.46	491.56	C	66.91	164.76
28	N	-48.88	489.06	C	69.89	167.14	C	52.64	163.37
29	C	69.48	167.83	C	41.69	163.21	H	22.35	9.46
30	C	41.34	164.17	H	22.54	9.91	C	50.79	198.57
31	H	22.51	9.89	C	55.96	190.80	H	23.24	8.15
32	C	55.69	191.27	H	22.48	8.91	C	70.99	162.10
33	H	22.47	8.92	C	68.67	164.80	H	23.28	5.23
34	C	68.25	165.61	H	23.37	5.36	H	24.04	4.24
35	H	23.33	5.37	H	23.85	5.07	S	255.01	323.86
36	H	23.80	5.08	S	255.23	325.08	O	257.92	129.30
37	S	247.97	332.55	O	258.26	131.25	C	143.85	63.31
38	O	258.32	157.74	C	143.91	62.78	C	147.65	62.75
39	C	145.66	64.64	C	147.63	62.38	H	28.54	8.46
40	C	146.06	65.13	H	28.52	8.50	H	27.14	7.55
41	H	28.87	9.00	H	27.14	7.41	H	28.95	5.64
42	H	28.06	5.77	H	28.91	5.63	H	28.73	9.21
43	H	28.97	4.45	H	28.72	9.23	H	28.75	6.29
44	H	28.75	9.59	H	28.73	6.29	H	28.51	8.02
45	H	28.69	5.55	H	28.49	8.03	S	254.97	323.96
46	H	28.44	7.68	S	250.43	336.12	O	257.97	129.35
47	S	247.95	332.56	O	258.74	156.80	C	143.84	63.33
48	O	258.31	157.74	C	145.50	65.76	C	147.63	62.76
49	C	146.06	65.12	C	145.91	65.63	H	28.54	8.45
50	C	145.66	64.64	H	28.79	9.50	H	27.14	7.56
51	H	28.75	9.59	H	28.49	7.64	H	28.95	5.64
52	H	28.44	7.68	H	28.72	5.51	H	28.73	9.21
53	H	28.69	5.55	H	28.85	8.92	H	28.75	6.29
54	H	28.86	9.00	H	28.99	4.44	H	28.51	8.02
55	H	28.97	4.46	H	28.00	5.86	H	14.00	26.42
56	H	28.06	5.77	H	13.97	26.49	H	14.00	26.41

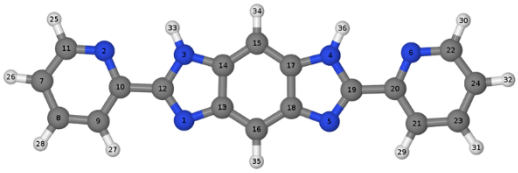
Table S21: Theoretical isotropic and anisotropic magnetic shieldings (in ppm) of all atoms of bis(2-pyridyl)-benzo-bis(imidazole) (conformers *c-bpybimH$_2$*, *c-bpyHbimH* and *c-bpyH$_2$bim*) in DMSO. Values calculated at B3LYP/aug-cc-pVDZ level using the GIAO approximation and considering a micro-solvated PCM model of solvent (with two explicit DMSO). The atoms numbering follows the numbering of the optimized clusters in Figure S16.

Atom Number	*c-bpybimH$_2$*			*c-bpyHbimH*			*c-bpyH$_2$bim*		
	Atom type	Isotropic	Anisotropic	Atom type	Isotropic	Anisotropic	Atom type	Isotropic	Anisotropic
1	H	22.53	9.19	H	23.20	8.28	H	23.29	8.19
2	C	40.59	163.57	C	51.50	159.61	C	51.75	159.90
3	N	-49.07	495.51	N	61.37	250.67	N	63.46	244.96
4	C	68.56	165.87	C	71.03	164.60	C	71.22	163.83
5	C	39.92	162.26	C	41.14	158.66	C	41.78	158.09
6	H	23.83	5.02	H	23.97	4.30	H	24.01	4.24
7	C	54.91	188.80	C	49.42	195.96	C	49.98	195.80
8	C	68.90	165.31	C	66.37	165.02	C	66.48	165.38
9	C	37.20	92.44	C	34.97	96.10	C	34.83	95.91
10	H	23.35	5.23	H	23.22	5.14	H	23.30	5.09
11	H	22.47	9.83	H	22.27	9.46	H	22.30	9.41
12	N	15.26	320.54	N	7.73	330.24	N	11.41	323.94
13	N	104.07	118.94	N	15.02	313.18	N	17.04	310.78
14	C	47.53	128.06	C	42.42	138.09	C	40.84	137.93
15	H	17.53	24.30	C	41.92	139.99	C	40.37	136.86
16	C	55.59	135.17	C	85.96	118.40	C	88.90	110.58
17	C	84.68	124.26	C	97.50	113.38	C	93.67	110.60
18	C	100.69	116.23	H	23.44	6.64	H	23.53	6.58
19	H	23.25	6.65	C	47.00	126.01	C	40.84	137.93
20	C	47.53	128.05	H	23.68	10.42	H	23.66	10.07
21	H	23.63	10.26	C	55.30	130.12	C	40.37	136.86
22	C	55.58	135.17	N	18.43	318.80	N	11.41	323.95
23	N	15.27	320.54	N	109.01	109.04	N	17.05	310.79
24	N	104.07	118.95	C	37.06	93.41	C	34.83	95.91
25	C	37.20	92.43	H	17.72	23.05	C	41.78	158.09
26	H	17.53	24.31	C	39.29	160.83	N	63.47	244.94
27	C	39.92	162.26	N	-49.94	491.31	C	66.48	165.38
28	N	-49.07	495.49	C	69.62	166.83	C	51.75	159.90
29	C	68.90	165.32	C	41.35	163.91	H	22.30	9.41
30	C	40.60	163.57	H	22.46	9.89	C	49.98	195.80
31	H	22.47	9.83	C	55.60	189.84	H	23.29	8.19
32	C	54.91	188.80	H	22.56	9.06	C	71.22	163.83
33	H	22.53	9.20	C	68.99	165.52	H	23.30	5.09
34	C	68.55	165.87	H	23.37	5.21	H	24.01	4.24
35	H	23.35	5.23	H	23.84	5.01	S	255.30	323.72
36	H	23.83	5.02	S	253.60	327.38	O	258.88	129.71
37	S	250.50	340.94	O	258.24	132.53	C	144.24	64.73
38	O	258.35	154.67	C	143.90	63.46	C	146.87	63.45
39	C	145.35	65.73	C	147.15	62.43	H	28.71	8.13
40	C	145.47	65.72	H	28.48	9.34	H	27.36	7.73
41	H	28.81	9.01	H	27.07	6.77	H	29.08	5.67
42	H	28.04	5.43	H	28.89	5.40	H	28.78	8.93
43	H	28.96	4.59	H	28.73	9.01	H	28.79	6.31
44	H	28.75	9.58	H	28.72	6.25	H	28.55	7.82
45	H	28.74	5.47	H	28.55	7.97	S	255.31	323.70
46	H	28.49	7.48	S	252.64	339.62	O	258.87	129.72
47	S	250.52	340.91	O	259.02	156.28	C	144.24	64.72
48	O	258.34	154.64	C	146.02	65.34	C	146.87	63.44
49	C	145.47	65.72	C	145.35	66.98	H	28.71	8.13
50	C	145.35	65.72	H	28.83	9.05	H	27.36	7.73
51	H	28.75	9.58	H	27.97	5.91	H	29.08	5.67
52	H	28.49	7.48	H	29.03	4.33	H	28.78	8.93
53	H	28.74	5.47	H	28.79	9.59	H	28.79	6.31
54	H	28.81	9.01	H	28.78	5.30	H	28.55	7.82
55	H	28.96	4.59	H	28.57	7.35	H	14.40	25.75
56	H	28.04	5.43	H	14.11	26.46	H	14.40	25.74

t-*bpybim*H_2

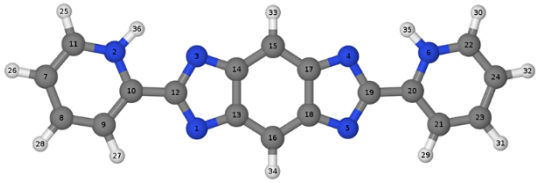
t-bpyHbimH

t-bpyH_2*bim*



c-bpybimH_2

c-bpyHbimH



c-bpyH_2*bim*

Figure S15: Atoms numbering of the neutral isomers of bis(2-pyridyl)-benzo-bis(imidazole).

Table S22: Theoretical and experimental (EXP) chemical shifts (in ppm) of ^{1}H atoms of the bis(2-pyridyl)-benzo-bis(imidazole) isomers in a DMSO solution. Theoretical values calculated at B3LYP/aug-cc-pVDZ level using the GIAO approximation and the PCM model of solvent. Values in the standard tetramethylsilane (TMS) reference (δ ^{1}H = 31.03 ppm). Imidazole hydrogens highlighted in boldface.

	t-*bpybimH$_2$*	*c-bpybimH$_2$*	EXP	t-bpyHbimH	*t-bpyH$_2$bim*	*c-bpyHbimH*	*c-bpyH$_2$bim*
Ha	8.6	8.5	8.7	8.5	7.8	8.5	7.7
Hb	7.3	7.3	7.5	7.2	7.1	7.2	7.1
Hc	7.7	7.7	8.0	7.7	7.9	7.7	7.8
Hd	8.3	8.3	8.3	8.3	8.2	8.3	8.2
Ha’	8.6	8.5	8.7	7.8	7.8	7.8	7.7
Hb’	7.3	7.3	7.5	7.1	7.1	7.1	7.1
Hc’	7.7	7.7	8.0	7.9	7.9	7.9	7.8
Hd’	8.3	8.3	8.3	8.2	8.2	8.2	8.2
Hg	**10.0**	**10.0**	12.9	**9.7**	12.5	**9.7**	12.5
Hg’	**10.0**	**10.0**	12.9	12.4	12.5	12.3	12.5
He	7.5	7.4	(7.7) (7.6) (8.0)	7.5	7.4	7.3	7.3
Hf	7.5	7.8		7.4	7.4	7.6	7.4

Table S23: Theoretical and experimental (EXP) chemical shifts (in ppm) of ^{1}H atoms of the bis(2-pyridyl)-benzo-bis(imidazole) isomers in a DMSO solution. Theoretical values calculated at B3LYP/aug-cc-pVDZ level using the GIAO approximation and using a micro-solvated PCM model of solvent (with two DMSO molecules explicitly, see Figure S16). Values in the standard tetramethylsilane (TMS) reference (δ^{1}H = 31.03 ppm). Imidazole hydrogens highlighted in boldface.

	t-*bpybimH$_2$*	*c-bpybimH$_2$*	EXP	t-bpyHbimH	*t-bpyH$_2$bim*	*c-bpyHbimH*	*c-bpyH$_2$bim*
Ha	8.6	8.5	8.7	8.6	7.8	8.5	7.7
Hb	7.2	7.2	7.5	7.2	7.0	7.2	7.0
Hc	7.7	7.7	8.0	7.7	7.8	7.7	7.7
Hd	8.5	8.6	8.3	8.5	8.7	8.6	8.7
Ha’	8.6	8.5	8.7	7.9	7.8	7.8	7.7
Hb’	7.2	7.2	7.5	7.1	7.0	7.1	7.0
Hc’	7.7	7.7	8.0	7.8	7.8	7.8	7.7
Hd’	8.5	8.6	8.3	8.7	8.7	8.8	8.7
Hg	**13.9**	**13.5**	12.9	**13.5**	17.0	**13.3**	16.6
Hg’	**14.0**	**13.5**	12.9	17.1	17.0	16.9	16.6
He	7.4	7.4	(7.7) (7.6) (8.0)	7.5	7.4	7.4	7.4
Hf	7.4	7.8		7.4	7.4	7.6	7.5

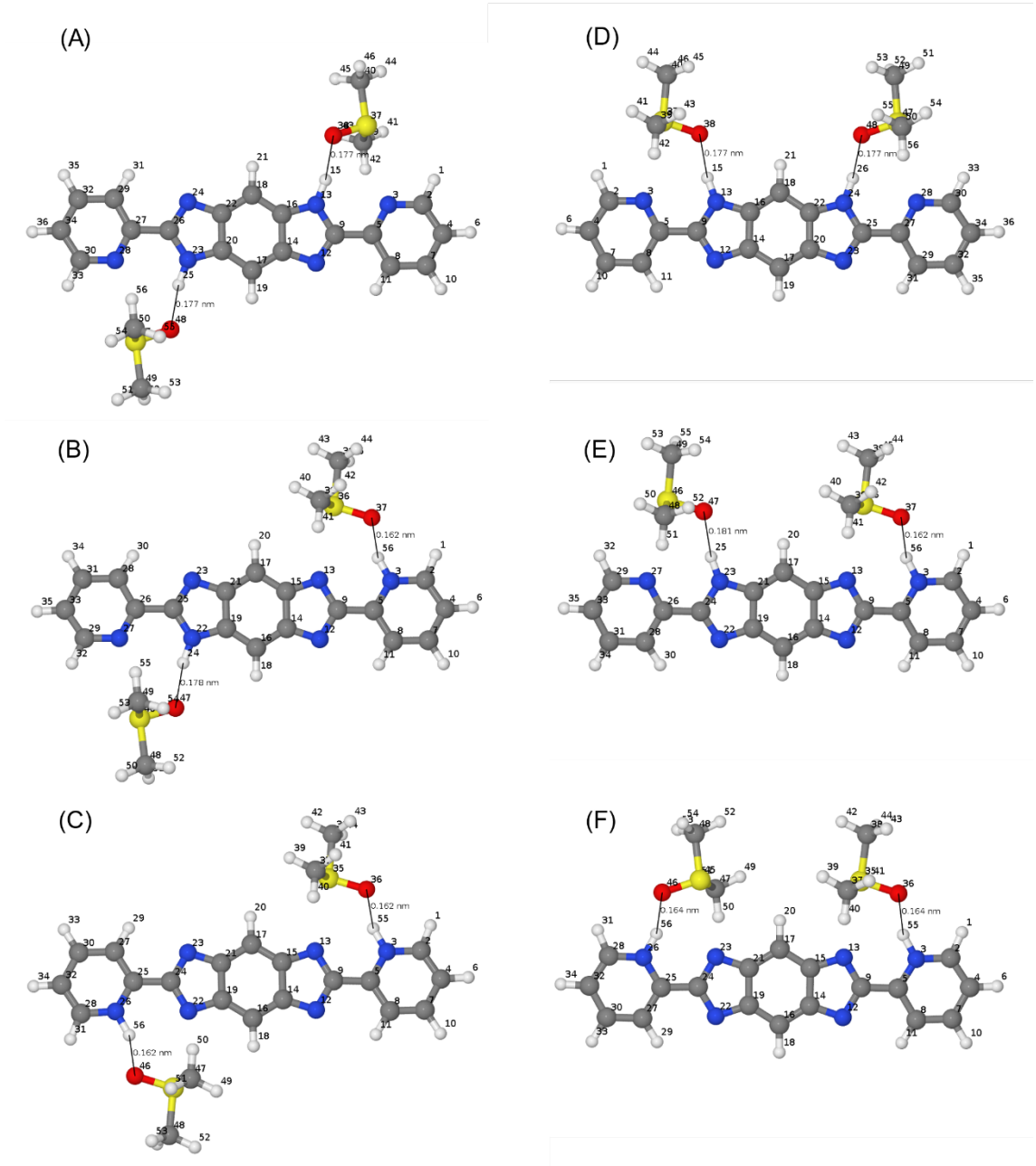
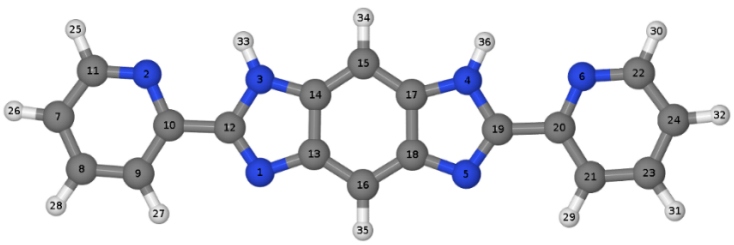


Figure S16: Optimized clusters of bis(2-pyridyl)-benzo-bis(imidazole) with two DMSO solvent molecules making hydrogen bonds for the isomers *t-bpybimH*$_2$, *t-bpyHbimH*, *t-bpyH*$_2$*bim*, *c-bpybimH*$_2$, *c-bpyHbimH* and *c-bpyH*$_2$*bim*. The geometries were optimized combining the B3LYP functional and the basis set aug-cc-pVDZ in a DMSO solution (using the PCM model).

Table S24: Comparison between the theoretical chemical shifts (in ppm) of all atoms in a monomer and in a dimer of *c-bpybimH_2 in a DMSO solution.* Theoretical values calculated at B3LYP level with the basis set aug-cc-pVDZ for C and N and cc-pVDZ for H atoms, using the GIAO approximation and the PCM model of solvent. Values in the standard tetramethylsilane (TMS) reference (δ ^{1}H = 31.03 ppm). For dimer, values were obtained from the average over 5 statistically uncorrelated configurations of the dimer in a DMSO solution obtained from MC simulation (*see illustration in Figure S17)*.

Atom Number	Atom type	S(dimer)	S(monomer)	ΔS	ΔS average
1	N	13.5±2.4	17.3	3.8	2.3±1.6
2	N	-47.2±1.5	-45.1	2.1	
3	N	116.8±2.4	117.5	0.7	
4	N	117.2±1.0	117.5	0.3	
5	N	12.9±1.1	17.2	4.3	
6	N	-47.4±2.2	-45.1	2.3	
7	C	64.3±1.0	68.2	3.9	1.2±0.9
8	C	54.4±1.5	55.5	1.1	
9	C	70.9±2.1	70.6	0.3	
10	C	42.6±1.2	41.9	0.7	
11	C	40.0±1.6	40.9	0.8	
12	C	39.6±0.7	38.2	1.4	
13	C	45.4±0.9	48.1	2.7	
14	C	58.0±0.5	59.0	1.0	
15	C	100.0±0.8	100.1	0.1	
16	C	81.7±0.8	82.0	0.4	
17	C	57.2±0.9	59.0	1.8	
18	C	45.3±1.2	48.1	2.8	
19	C	39.7±0.8	38.2	1.5	
20	C	40.9±0.5	41.9	1.0	
21	C	71.2±0.8	70.6	0.6	
22	C	40.1±0.4	40.9	0.8	
23	C	55.0±0.6	55.5	0.5	
24	C	67.3±1.0	68.2	0.8	
25	Ha	23.0±0.4	22.4	0.6	0.5±0.4
26	Hb	24.0±0.2	23.8	0.2	
27	Hd	22.9±0.2	22.7	0.3	
28	Hc	23.4±0.2	23.3	0.1	
29	Hd’	22.6±0.1	22.7	0.0	
30	Ha’	23.1±0.1	22.4	0.7	
31	Hc’	23.3±0.1	23.3	0.0	
32	Hb’	24.0±0.1	23.8	0.2	
33	Hg	21.8±0.2	20.9	0.9	
34	He	24.8±0.1	23.6	1.2	
35	Hf	23.5±0.1	23.2	0.2	
36	Hg	22.0±0.1	20.9	1.1	



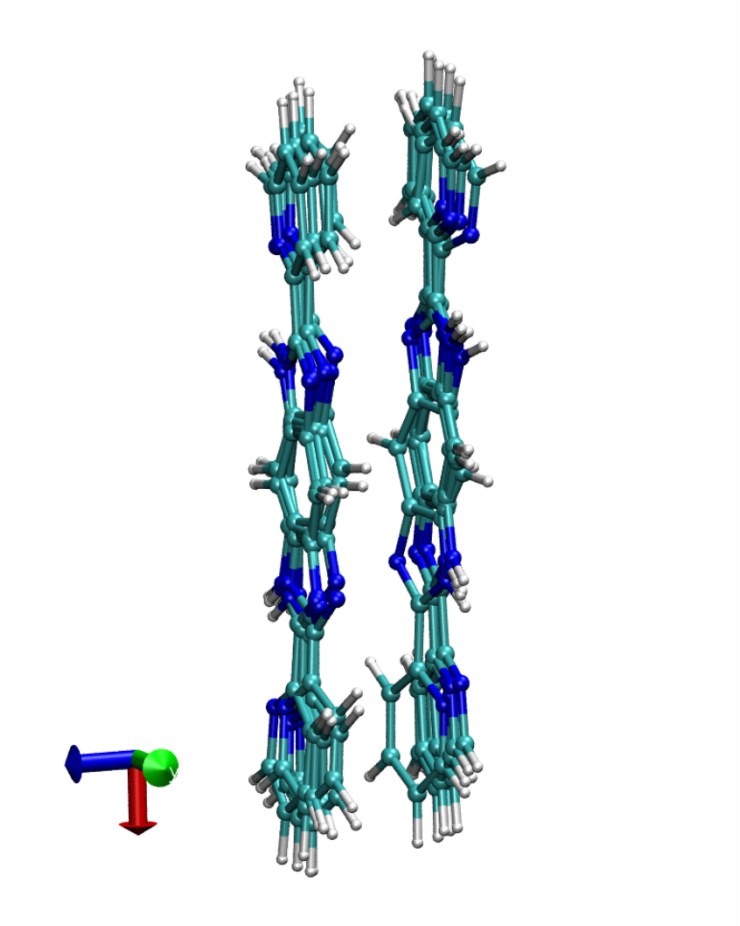


Figure S17: Dimer of *c-bpybimH_2*. Superposition of 5 configurations of a dimer of *c-bpybimH_2* obtained from MC simulations in a DMSO solution.

11. Solvation Free Energies

Table S25: Gas (G_{gas}) and solvation (G_{sol}) free energies (in kcal/mol) of 16 isomers of bis(2-pyridyl)-benzo-bis(imidazole) in water solution. G_{gas} values obtained as the sum of the electronic energies (U) and the thermal corrections (ΔU_{corr}) to the electronic and Gibbs Free Energies, $G_{gas}=U+\Delta U_{corr}$, at DFT(B3LYP/aug-cc-pVDZ) level. Solvation free energies (ΔG_{solv}) obtained from MC simulations, as the half part of the solute/solvent interaction energies. Values of G_{gas} and G_{sol} written in the reference values presented for each group of charge (E_{ref}). Dipole moments (Dip) in vacuum and in water solution, in units of Debye.

Charge	Isomers	G_{gas}	ΔG_{solv}	G_{sol}	Dip (vacuum)	Dip (water)
0	*t-bpybimH*$_2$	0.0	-32.6	-32.7	0.0	0.0
	t-bpyHbimH	20.3	-46.3	-25.9	5.6	9.0
	t-bpyH$_2$*bim*	43.2	-62.7	-19.5	0.0	0.0
	c-bpybimH$_2$	0.6	-35.0	-34.4	2.5	4.1
	c-bpyHbimH	20.4	-46.4	-25.9	6.3	10.1
	c-bpyH$_2$*bim*	43.2	-59.8	-16.6	3.4	5.4
	E_{ref} (kcal/mol)	-641057.6				
+1	*t-bpybimH*$_3^+$	0.2	-61.3	-61.1	8.6	11.8
	t-bpyHbimH$_2^+$	6.5	-65.4	-59.0	14.3	20.3
	t-bpyH$_2$*bimH*$^+$	15.8	-61.1	-45.3	5.9	10.2
	c-bpybimH$_3^+$	0.0	-59.3	-59.3	8.2	10.9
	c-bpyHbimH$_2^+$	5.8	-66.9	-61.1	13.9	20.0
	c-bpyH$_2$*bimH*$^+$	15.8	-60.1	-44.3	5.6	9.7
	E_{ref} (kcal/mol)	-641295.0				
-1	*t-bpybimH-*	0.1	-91.3	-91.2	7.5	11.6
	t-bpyHbim-	24.6	-110.0	-85.3	9.3	18.2
	c-bpybimH-	0.0	-88.7	-88.7	6.9	10.7
	c-bpyHbim-	24.7	-108.7	-84.0	8.7	17.4
	E_{ref} (kcal/mol)	-640718.5				

Table S26: Non-electrostatic (ΔG_{nele}), electrostatic (ΔG_{ele}) and polarization (ΔE_{pol}) contributions to the solvation free energy (ΔG_{solv}) of some isomers of bis(2-pyridyl)-benzo-bis(imidazole) in water solution, calculated with different methods.

Isomer	Method	ΔG_{nele}	ΔG_{ele}	ΔE_{pol}	ΔG_{solv}
c-bpybimH$_2$	FEP-MC	-16.3	-16.3	3.9	-28.7
	PCM (HF/SCFVAC 6-31+G(d))	3.8	-23.5	3.9	-15.8
	SMD (B3LYP/6-31G*)	0.7	-21.2	3.9	-16.6
t-bpybimH$_3^+$	FEP-MC	-16.4	-53.2	4.4	-65.2
	PCM (HF/SCFVAC 6-31+G(d))	3.5	-60.8	4.4	-52.9
	SMD (B3LYP/6-31G*)	2.4	-61.3	5.1	-53.8
c-bpyHbimH$_2^+$	FEP-MC	-17.2	-57.7	5.5	-69.4
	PCM (HF/SCFVAC 6-31+G(d))	3.7	-64.8	5.5	-55.5
	SMD (B3LYP/6-31G*)	2.2	-66.6	7.0	-57.3
t-bpybimH$^-$	FEP-MC	-17.5	-75.4	12.3	-80.6
	PCM (HF/SCFVAC 6-31+G(d))	3.7	-80.9	12.3	-64.9
	SMD (B3LYP/6-31G*)	-1.0	-74.5	12.1	-63.4

Table S27: Calculated energies in the protonation and deprotonation thermodynamic cycles and the obtained pKa values for different methods.

Method	Reactions	G_{gas} (X)	G_{gas} (Y)	ΔG_{gas}	ΔG_{solv} (X)	ΔG_{solv} (Y)	$\Delta\Delta G_{solv}$	ΔG_{sol}	pKa
FEP-MC	1	-641056.96	-640718.39	333.17	-28.7	-80.6	-51.9	15.4	11.3
	2	-641056.96	-641294.81	-232.45	-28.7	-65.2	-36.5	3.0	2.2
	3	-641056.96	-641289.18	-226.82	-28.7	-69.4	-40.7	1.6	1.2
PCM	1	-641056.96	-640718.39	333.17	-15.8	-64.9	-49.1	18.2	13.3
	2	-641056.96	-641294.81	-232.45	-15.8	-52.9	-37.1	3.6	2.7
	3	-641056.96	-641289.18	-226.82	-15.8	-55.5	-39.7	0.6	0.5
SMD	1	-641056.96	-640718.39	333.17	-16.6	-63.4	-46.8	20.5	15.0
	2	-641056.96	-641294.81	-232.45	-16.6	-53.8	-37.2	3.7	2.8
	3	-641056.96	-641289.18	-226.82	-16.6	-57.3	-40.7	1.6	1.2

Reaction 1: *(c-bpybimH2) → (t-bpybimH-) + H+*

Reaction 2: *(c-bpybimH$_2$) + H$^+$ → (t-bpybimH$_3^+$)*

Reaction 3: *(c-bpybimH$_2$) + H$^+$ → (c-bpyHbimH$_2^+$)*

12. pKa determination

The pKa values were determined by using the Albert and Serjeant's approach[7] based on a graphical method and direct application of the Henderson-Hasselbalch equation, Eq. (1), for the absorbance changes in a specific wavelength, in a pH range characteristic of an acid-base equilibrium.

$$\mathrm{pH} = \mathrm{pKa} + \log\left(\frac{\mathrm{Abs_i} - \mathrm{Abs_{pH}}}{\mathrm{Abs_{pH}} - \mathrm{Abs_f}}\right) \qquad \text{Eq. (1)}$$

where Absi, Absf and AbspH are the absorbance of an isolated pair of conjugated species involved in their acid-base equilibrium, defined as the absorbance at the beginning, at the end and intermediate points of the analyzed pH range.

Due to the presence of sequential acid-base equilibrium processes involving several pairs of conjugated species of bis(2-pyridyl)-benzo-bis(imidazole), suitable pH regions defined by the absorbance of an isolated pair of acid-base species were previously identified. Then, the pKa values were determined by considering that each equilibrium involving a conjugated pair of acid-base species is characterized by a specific isosbestic point on these pre-defined regions in the spectrophotometric titration curve. The initial and final absorbance (Absi and Absf) in the Henderson-Hasselbalch equation were estimated by adjusting the best sigmoid to the titration curve in a specific pH range. Then, the pH vs log((Absi-AbspH)/(AbspH-Absf)) were plotted and the corresponding pKa values were determined by linear fitting. A significant number of experimental points were considered for each interval and the pKas were obtained with excellent linear correlations. We have employed the analysis of the spectrophotometric titration in the three wavelengths with the most pronounced spectral changes under pH variations: 279, 342 (the absorption maxima in water) and 420 nm. The results obtained for each analyzed wavelength are shown in Table S28.

Analyzing the evolution of the UV-Vis absorption spectra in the 1.0 to 11 pH range (Figure S18), a first acid-base equilibrium was found in the pH region 0.78 to 3.19 with isosbestic points at 299 nm, 359 nm and 417 nm. A second acid-base equilibrium was found in the pH region 3.19 to 4.57 with isosbestic points at 297 nm and 370 nm. A third acid-base equilibrium with characteristic isosbestic point values at 295 nm and 373 nm was found between 4.6 to 7.5. In this last range of pHs, the intensity of the absorption band at 347 nm decreases while a new band appears around 410 nm, indicating a possible influence of the dimerization phenomenon. Finally, a small but consistent absorbance change around 400 nm was observed in the pH 7.5 to 11.0 with isosbestic points at 295 nm and 486 nm. At the wavelength of 342 nm, these 4 regions were distinguished in the titration curve, shown in the inset of Figure 8, and treated separated by using the Eq. (1). From this treatment, 4 different pKa values were obtained: 1.3, 3.6, 5.6 and 10.2.

The next most significant change in absorbance was found at 420 nm, but no relevant spectral variation could be observed up to pH=2, as shown in Figure S20, and two equilibrium processes could be determined with pKa values of 6.7 and 10.3 based on the graphical method using equation (1) and an additional pKa of 3.8 was assigned graphically. The third most relevant change in absorbance as a function of pH was observed at 279 nm, where the titration curve (Figure S21) shows 3 distinct regions, from pH 1.0 to 2.0 (pKa = 1.5), from pH 2.0 to 4.3 (pKa = 1.9), and from 4.3 to 9.0 (pKa = 6.0).

Due to the proximity of the pKa values, it is very difficult to separate each acid-base equilibrium processes especially in the lowest pH region, but consistent results were obtained using different wavelengths (Table S28).

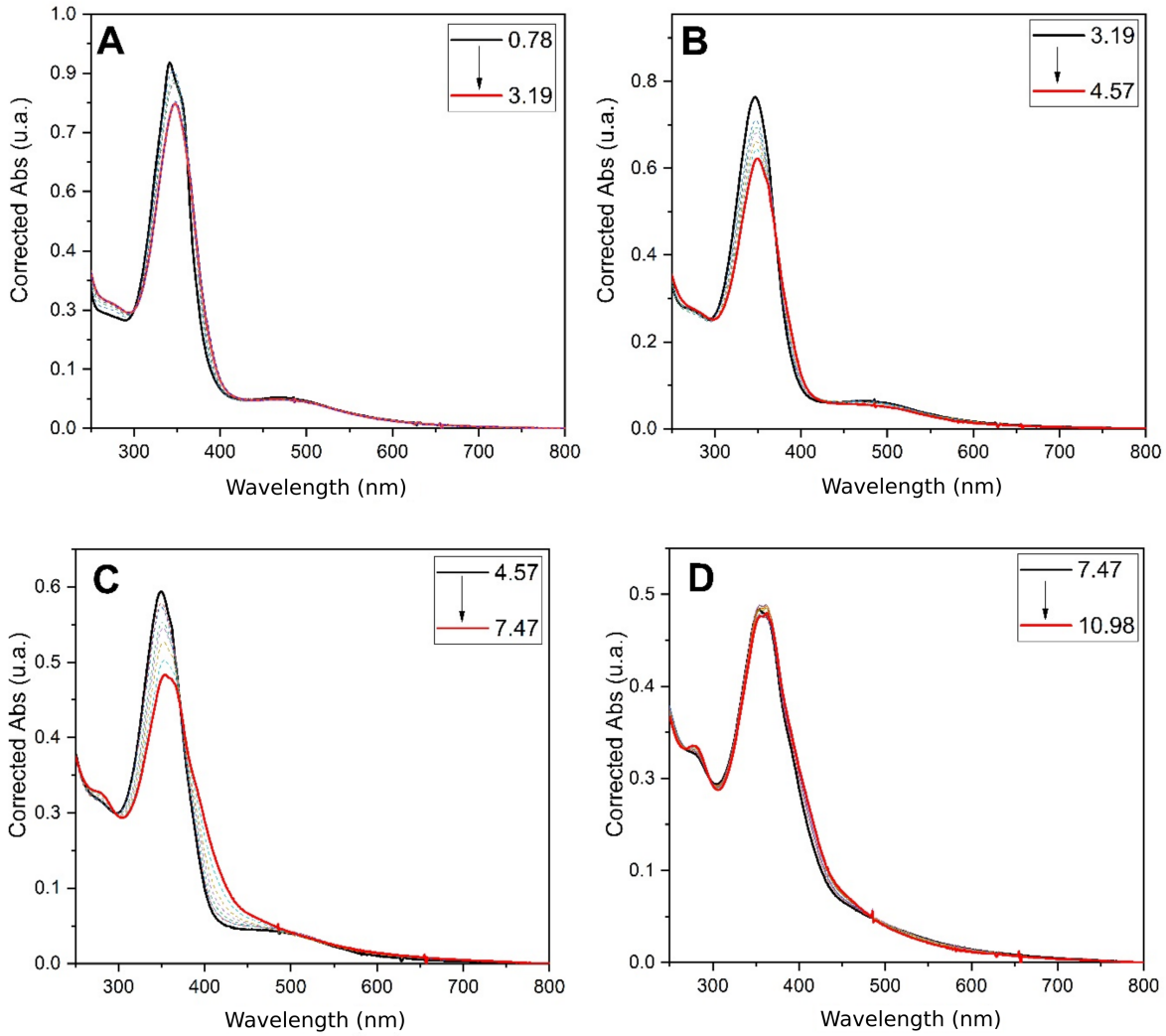


Figure S18: Evolution of the UV-Vis absorption spectra of the *bpybimH*$_2$ ligand as a function of the solution pH in the ranges of 0.8 to 3.2 (A), 3.2 to 4.6 (B), 4.6 to 7.5 (C) and 7.5 to 11.0 (D).

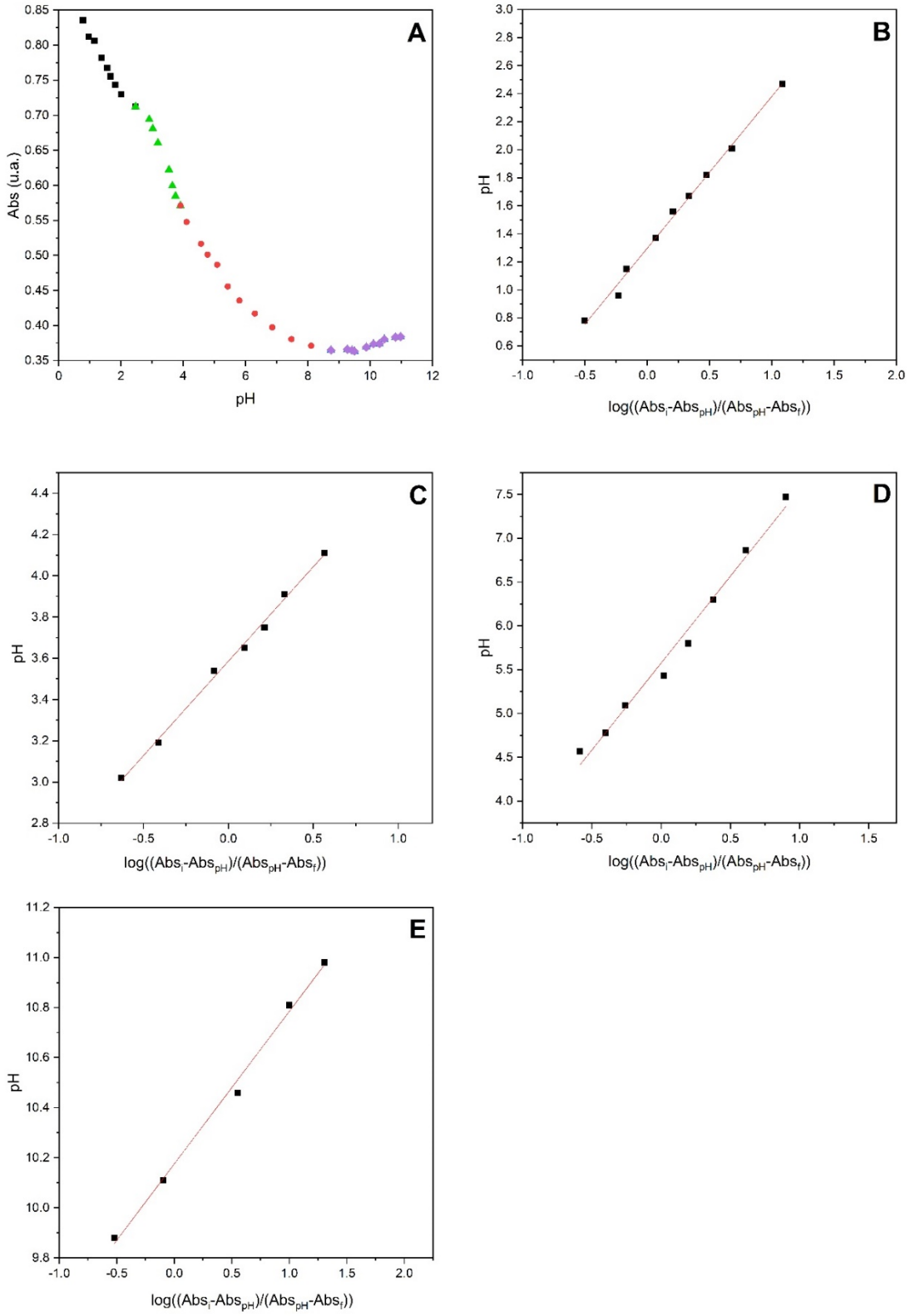


Figure S19: (A) Absorbance of *bpybimH$_2$* at 342 nm versus the pH. Estimation of the pKa values of *bpybimH$_2$* through graphical representation of pH as a function of log ((Absi- AbspH)/(AbspH- Absf)) in the pH ranges of 0.7 to 3.2 (B), 3.2 to 4.8 (C), 4.8 to 7.5 (D) and 9.1 to 11.0 (D).

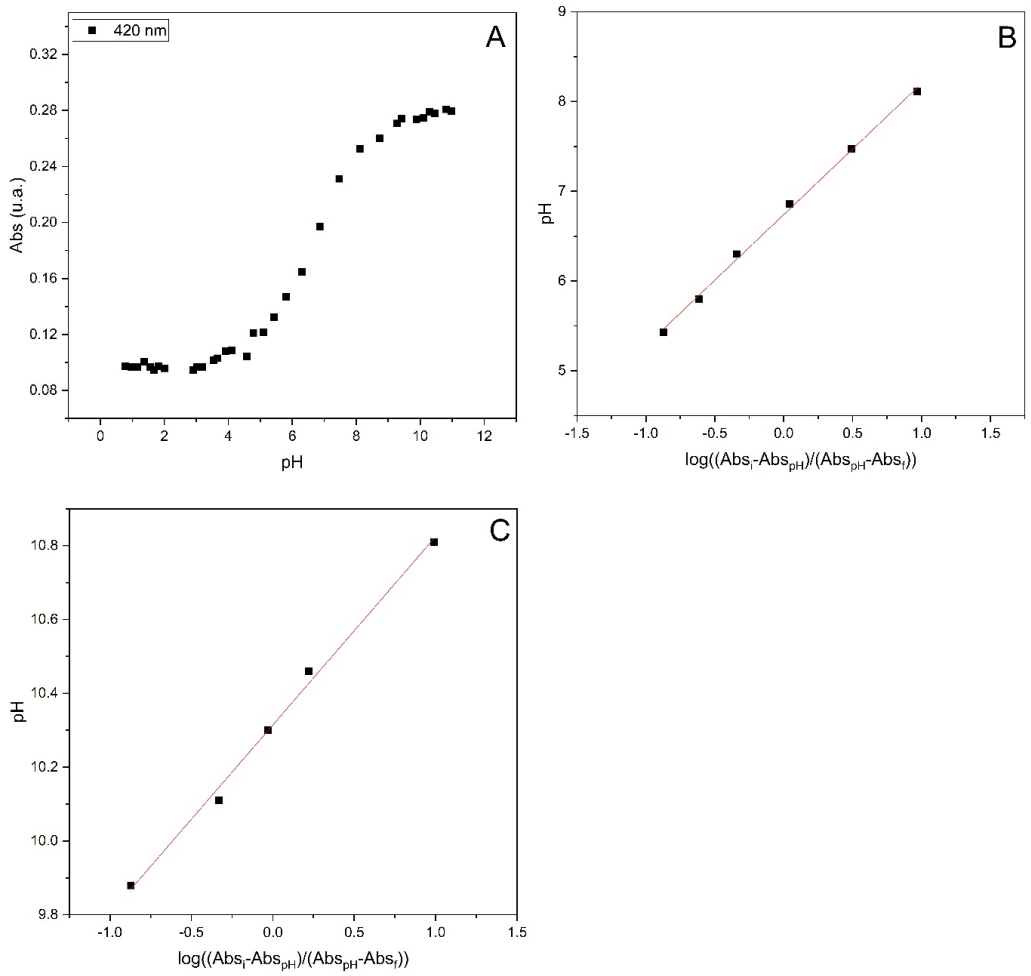


Figure S20: (A) Absorbance of *bpybimH$_2$* at 420 nm versus the pH. Estimation of the pKa values of *bpybimH$_2$* through graphical representation of pH as a function of log ((Absi- AbspH)/(AbspH- Absf)) in the pH ranges of 4.8 to 9.1 (B), 9.0 to 11.0 (C).

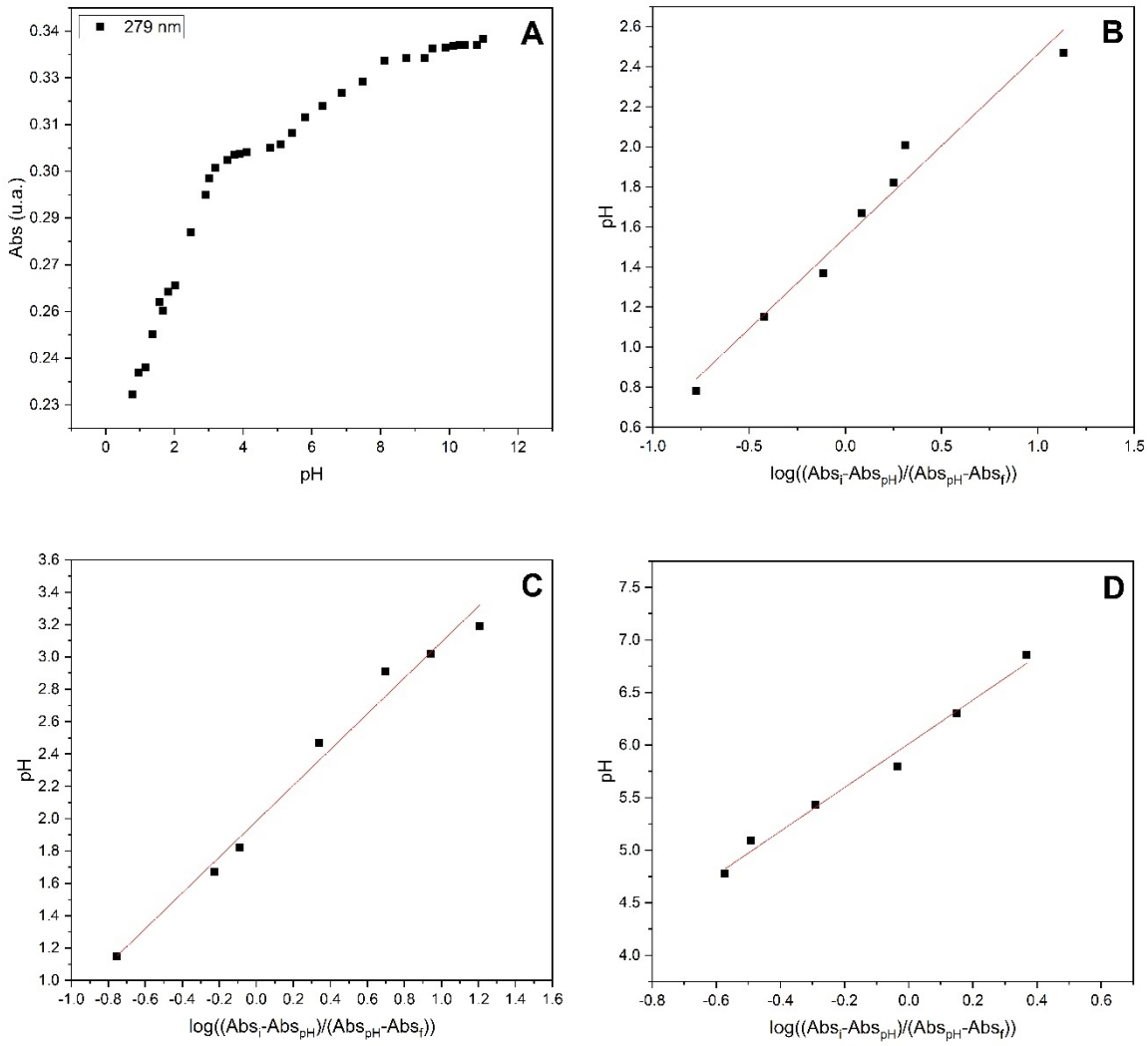


Figure S21: (A) Absorbance of *bpybimH$_2$* at 279 nm versus the pH. Estimation of the pKa values of *bpybimH$_2$* through graphical representation of pH as a function of log ((Absi- AbspH)/(AbspH- Absf)) in the pH ranges of 0.7 to 3.2 (B), 3.2 to 4.8 (C), 4.8 to 9.1 (D).

Table S28: Experimental pKas obtained for different wavelengths.

	342 nm	420 nm	279 nm	Average
pKa$_1$	1.3 ± 0.02		1.5 ± 0.04	1.3 ± 0.02
pKa$_2$			1.9 ± 0.05	1.9 ± 0.05
pKa$_3$	3.6 ± 0.02	3.8		3.7 ± 0.02
pKa$_4$	5.6 ± 0.05	6.7 ± 0.02	6.0 ± 0.04	6.0 ± 0.07
pKa$_5$	10.2 ± 0.02	10.3 ± 0.01		10.1 ± 0.04

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