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

Aggregation-caused quenching versus Crystallization Induced Emission in thiazolo[5,4-b]thieno[3,2-e]pyridine (TTP) derivatives: theoretical insights.

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Impact of the XC functionals on the structural parameters and the absorption spectra for solvated systems

For isolated molecules in solution, optimization of the ground state has been carried out with three different functionals, namely PBE0, CAM-B3LYP and B3LYP. Key structural parameters have been carefully inspected and are gathered in Table SI. It shows that the structures are not impacted by the choice of the XC functionals, the variations being trifling when modifying the computational scheme used in the course of the geometry optimizations.

Table SI: Relevant structural parameters for the three tested functionals. See Figure 1 for the atom numbering.

	0			**1**		
	PBE0	CAM-B3LYP	B3LYP	PBE0	CAM-B3LYP	B3LYP
Dihedral(°))						
ϕ	2	3	-19	0	0	0
ψ	-73	-76	-103	72	75	-101
Bond (Å)						
C_a - C_b	1.403	1.399	1.408	1.420	1.414	1.424
C_b - C_c	1.461	1.467	1.466	1.452	1.459	1.457
C_c - N_d	1.300	1.294	1.303	1.309	1.303	1.312
N_d - C_e	1.372	1.380	1.380	1.372	1.380	1.380
C_e - C_f	1.400	1.396	1.404	1.399	1.395	1.403
C_f - C_g	1.482	1.487	1.491	1.482	1.486	1.491
O - H				0.993	0.990	0.994
N_d...H				1.735	1.758	1.761
Angle (°))						
N_d-O-H				146	145	146

The first excitation energy was then calculated with 9 different combinations of TD//optimization computational schemes and compared to experimental data.[1,2] Results are shown on Figure S1 where the benchmark calculations have been carried out for the molecules **0** and **1**. First, the energy difference $|\Delta\mathrm{E}_{exp-calc}|$ between calculated and experimental values are very similar for **0** and **1**. Second, the geometry optimizations carried out with the CAM-B3LYP functional systematically lead to a large $|\Delta\mathrm{E}_{exp-calc}|$ value and this functional can thus be ruled out in the course of the geometry optimization. Thirdly, the calculation of the excitation energy with the same CAM-B3LYP functional also leads to larger $|\Delta\mathrm{E}_{exp-calc}|$ value compared to excited-sate calculations carried out with the PBE0 and B3LYP functionals for the same structure. For instance, the $|\Delta\mathrm{E}_{exp-calc}|$ values are respectively 0.12 eV and 0.19 eV for the B3LYP//B3LYP and CAM-B3LYP//B3LYP schemes for the molecule **0**. At that stage, one can conclude that the B3LYP//B3LYP and PBE0//B3LYP strategies provide the same $|\Delta\mathrm{E}_{exp-calc}|$ values. For the sake of simplicity, we have thus decided to carry out geometry optimizations and TD-DFT calculations with the same XC functional, namely B3LYP. Indeed, with the B3LYP//B3LYP strategy, the $|\Delta\mathrm{E}_{exp-calc}|$ value is equal to 0.12 eV for both **0** and **1**.

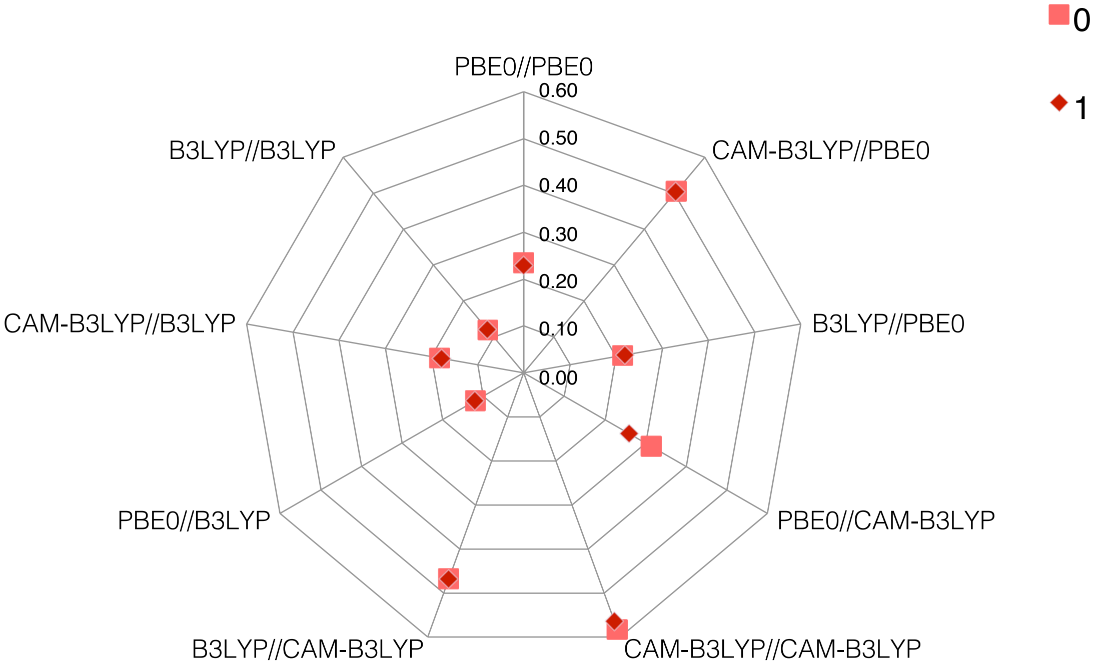

Figure S1: Representation of the energy difference between the experimental and calculated excitation energies $|\Delta E_{exp-calc}|$ in eV as a function of the TD//Optimization calculation scheme for **0** and **1**.

Computed absorption spectra for solvated systems: molecules 0 and 1.

Table SII: Calculated absorption wavelength (λ in nm) along with oscillator strength (f) and electronic transition assignments for **0** and **1** in solution H and L denote HOMO and LUMO, respectively. .

	0			**1**		
	λ	f	Assignment	λ	f	Assignment
Exp.[1]	360			373		
S_1	349	0.983	H → L	360	0.740	H → L
S_2	335	0.084	H-1 → L	344	0.029	H-1 → L
S_3	295	0.213	H → L+1	314	0.144	H-2 → L
S_4	285	0.050	H-2 → L	298	0.116	H → L+1
S_5	284	0.394	H-1 → L+1	292	0.006	H-3 → L
S_6	280	0.003	H-2 → L	286	0.615	H-1 → L+1

Molecular orbitals of the solvated systems

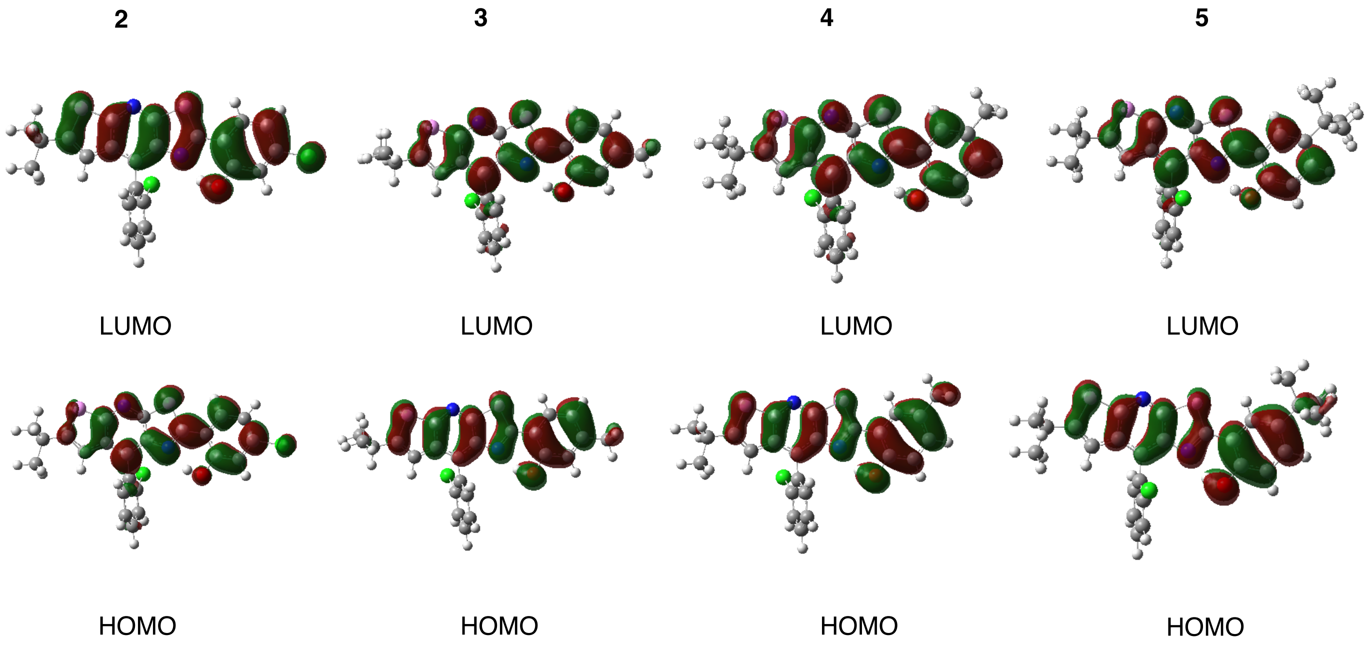

Figure S2: Molecular Orbitals (MO) of **2**, **3**, **4** and **5** calculated at the PCM(benzene)-B3LYP level (isodensity = 0.025 au).

Solvated systems: Structural parameters for the ground and first excited states.

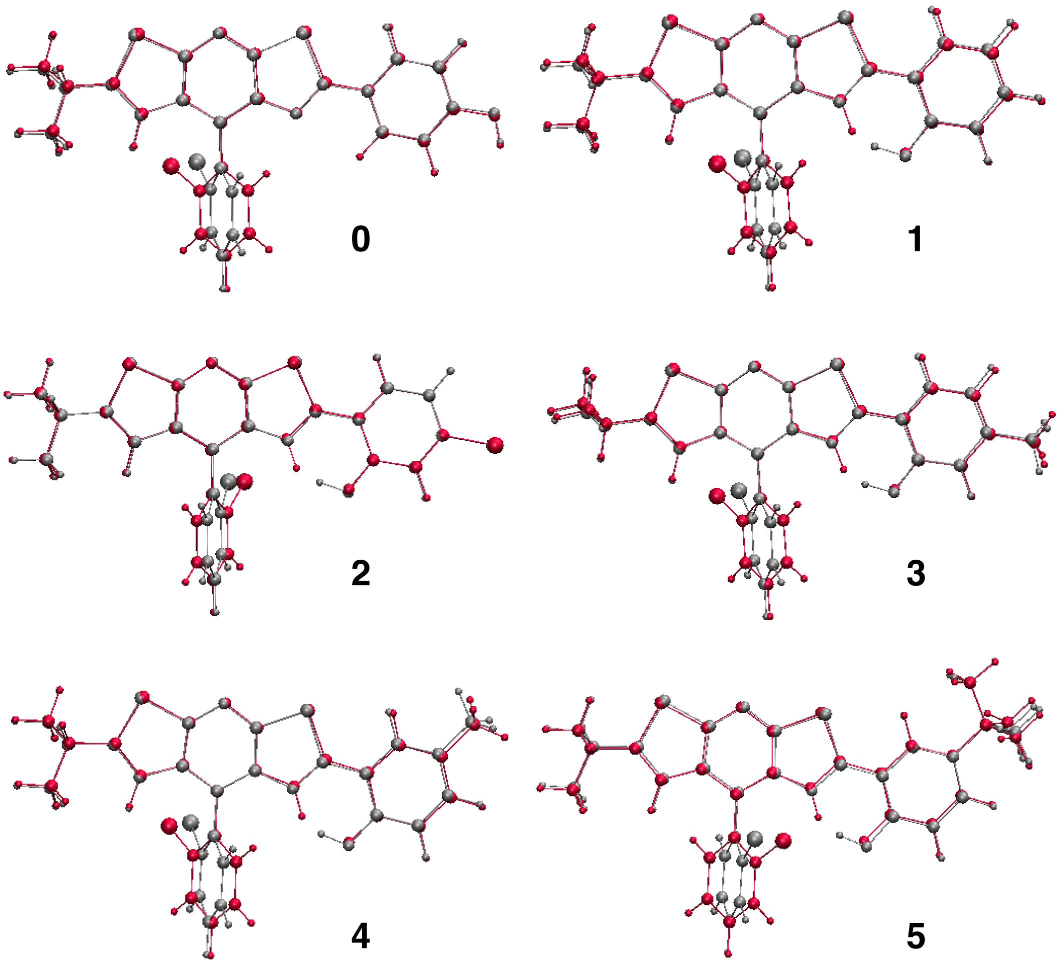

Figure S3: Structure superposition of the optimized ground (S_0) and first excited state (S_1^*(E) for **0** and S_1^*(K) for **1**, **2**, **3**, **4** and **5**) of the molecules in solution. Ground and excited states are represented in grey and red respectively.

Solvated systems: Frequencies and HR factors.

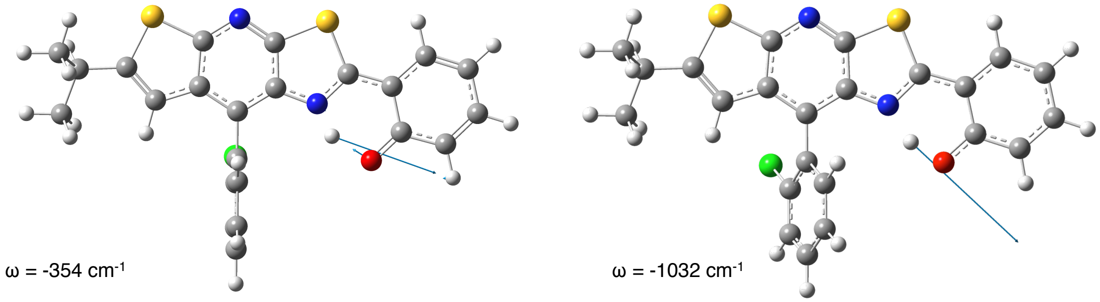

Figure S4: Representation of the imaginary frequencies of the TS_{E-K} (left) and TS^{*}_{E-K} (right) for **1**.

Table SIII: Selected Huang-Rhys factors ($HR_j \geq 1$) with the corresponding reorganization energies $E_{reorg,j}$ and normal mode frequencies ω_j both in cm^{-1} for **0**, **1**, **2**, **3**, **4** and **5** in the first excited state.

	mode	ω	HR	E_{reorg}		mode	ω	HR	E_{reorg}
0					**3**				
	1	20	5	105		1	18	12	218
	26	377	1	215		4	35	1	27
	28	392	1	296		10	95	1	56
	29	410	1	217		12	139	1	115
	32	432	1	522		13	144	3	498
	33	434	1	378		16	189	1	110
	44	634	1	1244		31	400	1	428
1					**4**				
	1	23	13	275		1	13	12	152
	4	34	2	66		10	108	1	86
	10	124	1	98		12	133	1	149
	16	221	1	237		14	149	2	338
	28	406	1	260		15	168	2	322
	29	422	1	537		17	194	1	111
	34	478	1	405		27	338	1	187
						31	404	1	343
						75	1040	1	656
2					**5**				
	2	20	7	134		1	15	23	356
	4	30	6	188		3	23	3	60
	5	36	3	123		13	130	1	110
	6	52	2	90		19	221	1	223
	7	59	1	52		33	351	1	243
	8	61	1	77		36	391	1	236
	9	89	1	61		37	408	1	522
	40	539	1	698		41	442	1	432
	49	695	1	671		53	628	1	607
	50	702	1	535		55	644	1	356
	51	704	1	757		60	722	1	401
	59	808	2	1255		69	839	1	787

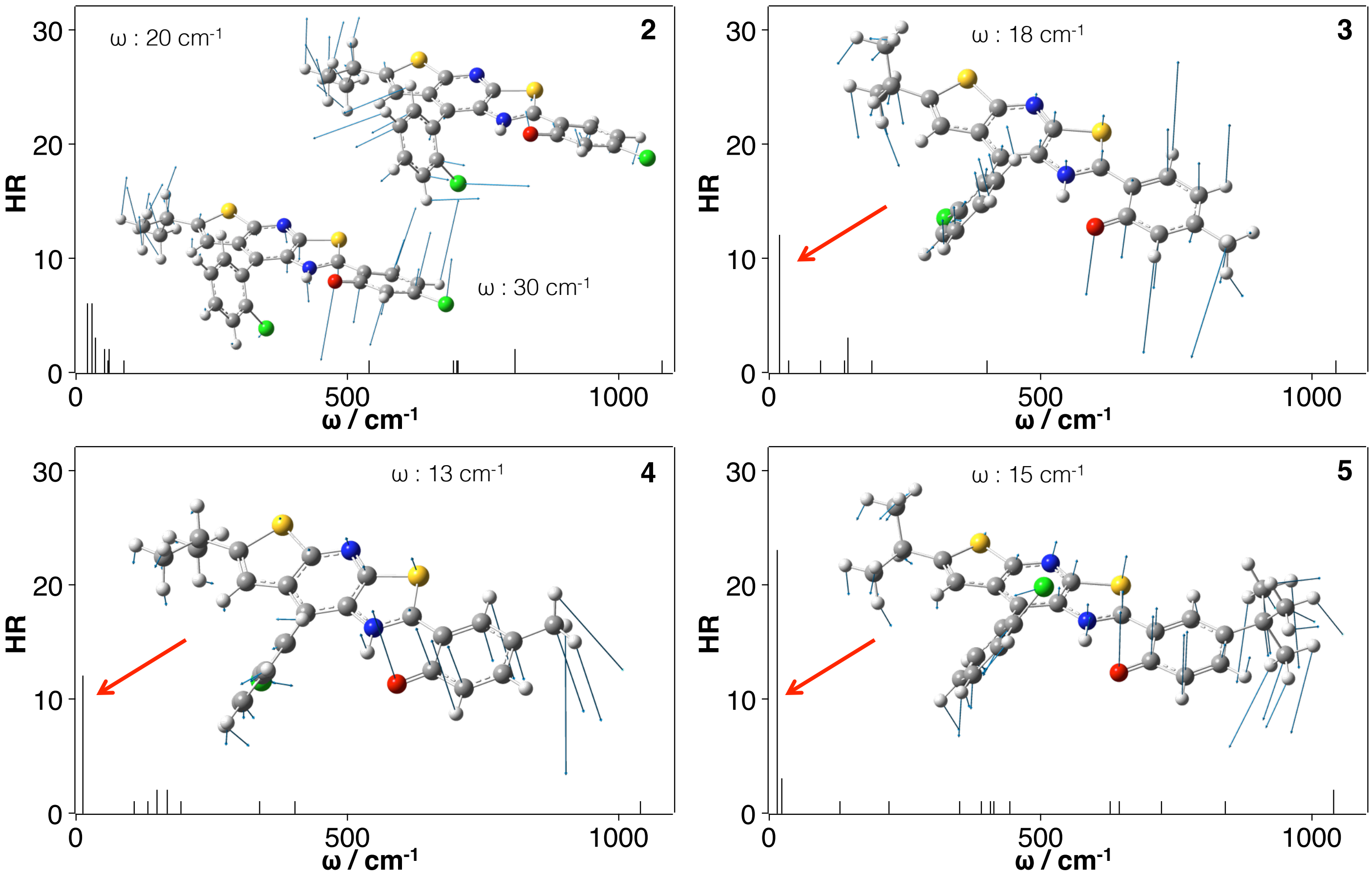

Figure S5: Calculated HR factors of **2**, **3**, **4** and **5**.

Table SIV: Calculated frequencies (cm^{-1}) for **0** in solution for the ground (top) and excited state (bottom).

29	33	49	54	64	67	69	73	110	130	147	155
166	190	195	218	263	274	281	292	310	312	316	348
373	398	416	422	426	433	439	455	461	461	470	525
528	532	581	604	617	632	636	643	660	683	695	706
711	726	747	773	780	782	806	832	834	852	854	860
873	890	944	962	968	971	975	989	1008	1024	1037	1044
1061	1078	1110	1121	1131	1135	1144	1183	1193	1199	1205	1235
1249	1262	1276	1279	1289	1294	1321	1331	1342	1343	1369	1371
1404	1423	1452	1454	1457	1488	1492	1495	1502	1505	1510	1534
1538	1572	1586	1589	1613	1619	1632	2977	2999	3004	3062	3067
3072	3072	3138	3148	3152	3157	3168	3175	3177	3185	3191	3729
20	27	39	44	47	55	65	70	95	119	142	151
160	173	184	214	232	253	264	275	284	287	311	334
350	374	381	390	408	411	418	431	434	446	454	462
500	516	539	562	579	586	618	634	646	654	671	696
704	706	732	742	760	769	790	802	814	822	843	855
867	871	935	942	945	957	963	966	988	999	1029	1038
1056	1064	1104	1108	1125	1128	1146	1168	1180	1182	1191	1197
1233	1247	1268	1279	1287	1305	1318	1327	1334	1363	1372	1379
1399	1417	1419	1441	1459	1460	1475	1482	1485	1489	1499	1500
1508	1525	1553	1571	1580	1606	1633	2998	3024	3030	3090	3094
3097	3100	3156	3171	3175	3185	3195	3197	3202	3213	3225	3804

Table SV: Calculated frequencies (cm^{-1}) for **1** in solution for the ground (top) and excited state (bottom).

29	36	50	53	57	69	76	81	123	135	153	157
172	193	205	227	262	274	274	282	298	311	321	354
358	395	403	430	432	453	462	463	477	504	526	529
543	556	605	620	622	632	643	675	680	697	707	715
747	751	773	774	779	787	806	824	838	852	860	874
877	891	944	965	968	972	976	1001	1009	1036	1044	1051
1061	1081	1110	1120	1131	1141	1145	1181	1184	1199	1231	1240
1254	1267	1280	1290	1293	1297	1328	1331	1343	1345	1369	1404
1423	1437	1452	1458	1468	1489	1492	1495	1503	1506	1510	1524
1538	1569	1586	1590	1603	1620	1644	2978	2999	3004	3062	3068
3071	3073	3144	3149	3151	3158	3168	3169	3175	3178	3192	3237
21	27	29	34	46	57	62	72	108	124	146	151
163	175	189	221	231	247	255	266	277	292	312	328
348	365	388	406	422	426	439	449	452	478	504	514
524	537	548	581	586	595	636	646	661	686	694	700
716	731	743	756	761	782	796	823	844	852	858	871
873	890	934	936	961	964	965	966	996	1037	1041	1046
1059	1064	1100	1106	1113	1128	1145	1151	1182	1192	1198	1237
1243	1261	1273	1280	1299	1318	1321	1328	1341	1364	1369	1388
1394	1398	1418	1426	1444	1450	1466	1486	1488	1493	1495	1500
1508	1532	1550	1582	1591	1597	1613	2997	3023	3028	3087	3092
3098	3100	3165	3169	3180	3180	3191	3195	3201	3205	3220	3244

Table SVI: Calculated frequencies (cm^{-1}) for **2** in solution for the ground (top) and excited state (bottom).

28	33	46	51	54	62	70	73	97	126	147	152
166	183	185	207	222	246	263	277	289	294	306	308
318	343	372	395	410	418	429	438	454	463	477	487
526	530	541	565	594	606	631	632	640	647	681	693
702	711	718	737	751	774	780	790	807	816	830	852
861	873	885	892	900	945	963	968	971	976	1010	1037
1045	1061	1080	1090	1110	1121	1131	1144	1162	1184	1199	1229
1238	1255	1262	1280	1283	1294	1294	1324	1330	1341	1345	1371
1395	1404	1423	1450	1457	1467	1488	1492	1495	1497	1503	1510
1520	1538	1568	1586	1589	1591	1619	1635	2979	3000	3005	3063
3068	3072	3073	3149	3153	3157	3169	3179	3189	3189	3193	3209

17	20	22	30	36	52	59	61	89	119	137	144
160	167	178	188	201	230	238	256	266	275	286	297
313	336	352	371	387	402	411	421	433	440	455	461
472	513	522	539	549	575	592	596	625	637	653	676
695	702	704	714	735	741	753	765	792	805	808	841
847	854	872	882	891	929	935	964	966	969	1001	1037
1047	1060	1067	1078	1107	1114	1120	1129	1147	1183	1196	1202
1235	1240	1256	1277	1283	1302	1307	1319	1326	1327	1350	1367
1386	1392	1397	1398	1418	1449	1456	1467	1485	1489	1496	1498
1500	1507	1510	1550	1575	1590	1598	1620	3001	3024	3029	3089
3093	3099	3100	3171	3173	3183	3193	3204	3210	3215	3217	3356

Table SVII: Calculated frequencies (cm^{-1}) for **3** in solution for the ground (top) and excited state (bottom).

30	33	49	52	57	68	72	76	102	130	147	151
154	170	190	193	205	232	257	269	273	279	295	299
305	327	345	366	395	415	427	447	452	462	477	480
515	526	558	563	583	590	604	628	631	639	642	673
680	705	716	739	744	751	773	779	787	806	818	825
852	860	877	891	893	940	944	966	967	975	979	1009
1015	1031	1044	1059	1062	1083	1112	1119	1144	1155	1159	1184
1188	1204	1235	1244	1253	1266	1280	1289	1292	1298	1330	1334
1335	1347	1370	1402	1404	1416	1423	1452	1458	1467	1483	1486
1487	1489	1495	1500	1504	1506	1535	1541	1571	1586	1590	1591
1619	1651	2997	2998	3001	3002	3047	3059	3066	3070	3072	3081
3140	3149	3156	3158	3160	3169	3175	3178	3236			
18	23	27	35	43	52	61	66	76	95	120	139
44	156	175	189	191	201	228	246	257	262	268	287
297	320	344	351	373	388	400	415	433	435	451	471
488	509	523	544	554	559	576	578	590	635	640	648
660	699	705	714	723	731	744	759	782	795	809	843
851	860	870	877	890	920	934	937	960	961	985	994
1012	1015	1044	1055	1056	1062	1108	1112	1120	1143	1154	1181
1182	1191	1206	1236	1248	1264	1272	1277	1298	1315	1323	1331
1333	1342	1358	1384	1389	1397	1403	1416	1416	1439	1448	1464
1478	1484	1485	1486	1494	1495	1497	1503	1546	1562	1580	1593
1597	1611	3019	3021	3025	3025	3074	3083	3089	3096	3098	3109
3163	3168	3179	3180	3189	3190	3200	3203	3251			

Table SVIII: Calculated frequencies (cm^{-1}) for **4** in solution for the ground (top) and excited state (bottom).

31	35	44	50	56	69	75	76	121	131	147	152
155	170	172	190	208	226	257	274	282	291	309	314
333	344	356	368	398	404	423	436	451	461	463	473
479	521	527	532	549	605	618	629	632	643	679	682
695	706	713	746	750	773	773	779	796	807	817	851
852	859	868	880	891	892	945	971	975	983	990	1009
1033	1038	1044	1061	1069	1081	1110	1120	1130	1144	1154	1184
1199	1199	1232	1239	1254	1268	1280	1292	1293	1301	1331	1334
1341	1344	1371	1404	1410	1422	1424	1447	1457	1463	1485	1486
1488	1491	1495	1502	1510	1514	1519	1538	1569	1586	1590	1609
1619	1652	2979	2997	3000	3004	3042	3063	3068	3072	3073	3073
3137	3138	3149	3158	3169	3170	3178	3192	3247			
13	24	26	34	45	56	62	67	85	108	121	133
139	149	168	186	194	205	231	253	262	268	288	303
308	328	338	359	374	390	404	411	429	436	449	451
468	488	509	519	549	559	577	592	600	635	644	666
695	698	703	714	729	742	759	780	791	795	824	837
851	852	872	874	890	908	934	945	961	965	990	994
1010	1037	1040	1044	1057	1060	1104	1111	1126	1131	1145	1154
1181	1196	1227	1234	1244	1264	1275	1280	1299	1306	1321	1329
1336	1362	1367	1386	1397	1402	1406	1417	1431	1442	1445	1460
1465	1468	1485	1489	1491	1494	1499	1508	1535	1551	1578	1597
1608	1614	2998	3006	3022	3028	3046	3087	3092	3098	3099	3115
3151	3169	3171	3180	3191	3195	3200	3201	3220			

Table SIX: Calculated frequencies (cm^{-1}) for **5** in solution for the ground (top) and excited state (bottom).

29	30	38	46	52	53	65	69	77	108	113	130
140	150	172	184	192	214	226	253	257	275	283	285
291	303	308	314	323	344	350	355	366	371	396	405
423	436	444	449	453	462	468	478	516	526	530	539
580	606	616	632	642	655	665	680	690	703	711	734
751	752	773	779	792	807	815	827	852	859	860	869
880	892	900	929	942	944	969	971	975	988	994	1009
1037	1044	1047	1053	1061	1081	1110	1120	1129	1132	1144	1159
1184	1199	1215	1220	1229	1237	1255	1273	1276	1281	1292	1293
1308	1331	1333	1340	1345	1370	1398	1402	1404	1414	1423	1434
1448	1457	1464	1484	1487	1488	1490	1492	1495	1498	1502	1506
1509	1510	1518	1522	1538	1569	1586	1589	1608	1619	1647	2978
2994	2995	3000	3002	3004	3055	3056	3060	3063	3063	3066	3068
3068	3072	3073	3148	3152	3157	3169	3170	3172	3179	3192	3249
15	22	23	30	39	41	57	59	68	87	110	119
130	139	169	182	188	190	221	226	230	244	253	265
272	282	283	309	318	326	331	341	351	356	372	391
408	413	419	427	442	445	448	460	499	512	514	524
558	570	589	604	628	634	644	652	688	697	707	722
732	736	749	757	782	791	826	835	839	850	853	867
874	879	908	927	934	939	957	962	965	967	990	991
1035	1040	1040	1041	1053	1060	1102	1107	1118	1127	1136	1144
1166	1180	1196	1207	1211	1234	1242	1263	1268	1278	1293	1300
1306	1319	1328	1337	1363	1365	1393	1396	1397	1400	1411	1417
1424	1430	1434	1441	1459	1477	1481	1484	1485	1488	1488	1489
1499	1501	1507	1509	1518	1532	1549	1569	1598	1603	1608	2994
3022	3023	3024	3028	3030	3086	3088	3090	3091	3092	3096	3097
3098	3101	3104	3169	3180	3183	3190	3193	3197	3201	3217	3252

Crystalline systems: molecule 0

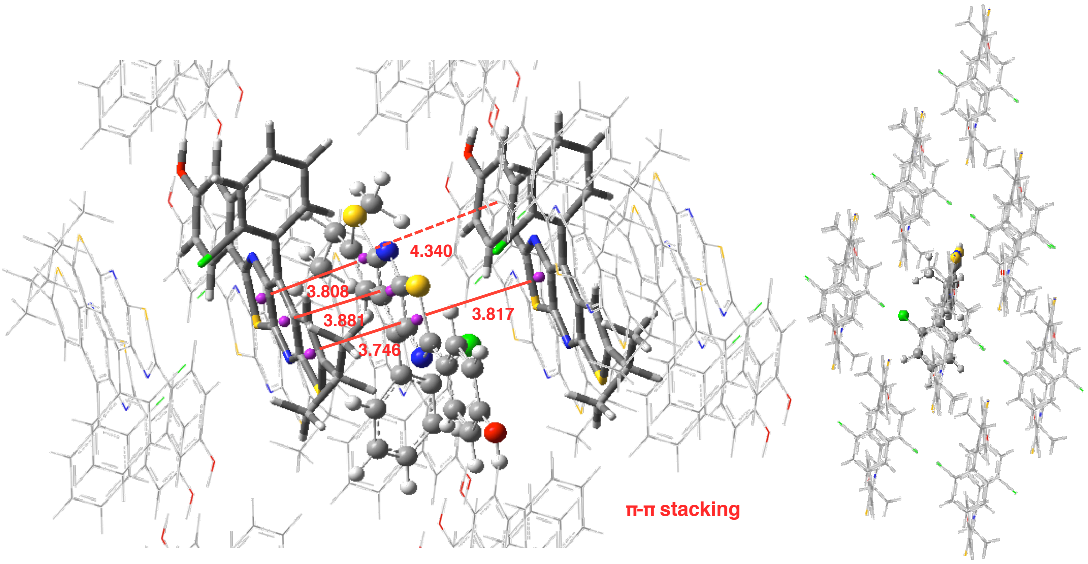

Figure S6: Left: Representation of the packing of system **0**. Distances (in angstroms) between the two (three) monomers that are involved in the dimer (trimer) are also indicated. Right: Representation of the cluster of 26 molecules used in the QM/QM' calculations.

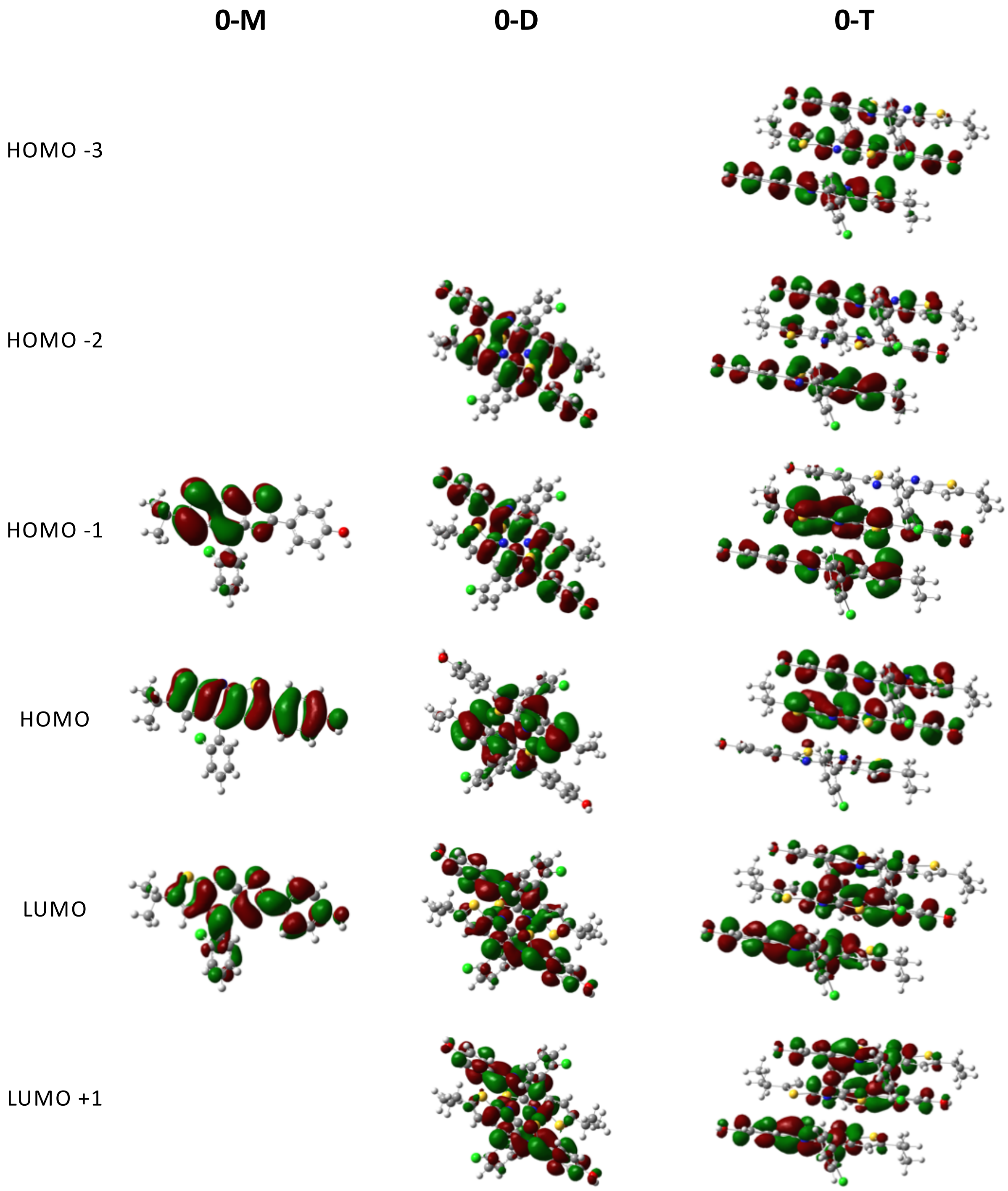

Figure S7: Molecular orbitals calculated for the **0-M**, **0-D** and **0-T** models (isodensity = 0.025 au).

Crystalline systems: molecule 1

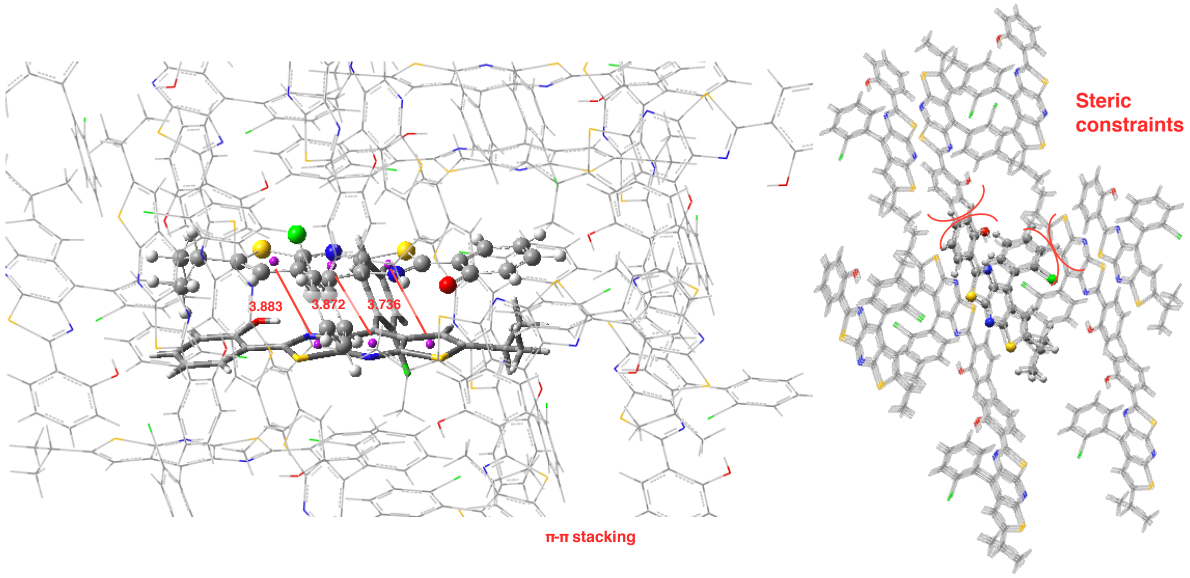

Figure S8: Left: Representation of the packing of system **1**. Distances (in angstroms) between the two monomers that are involved in the dimer are also indicated. Right: Representation of the cluster of 27 molecules used in the QM/QM' calculations.

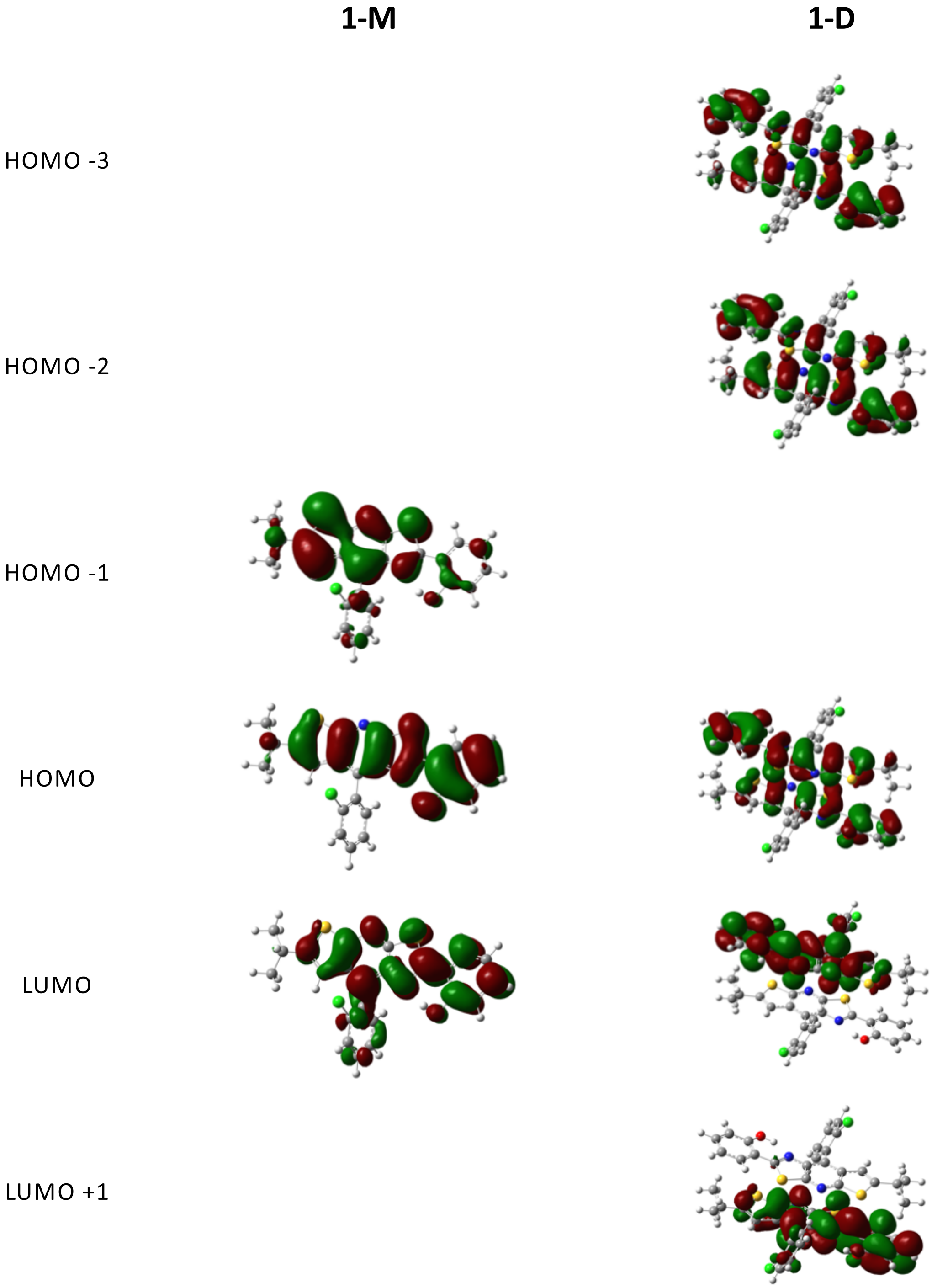

Figure S9: Relevant molecular orbitals calculated for the **1-M** and **1-D** models (isodensity = 0.025 au).

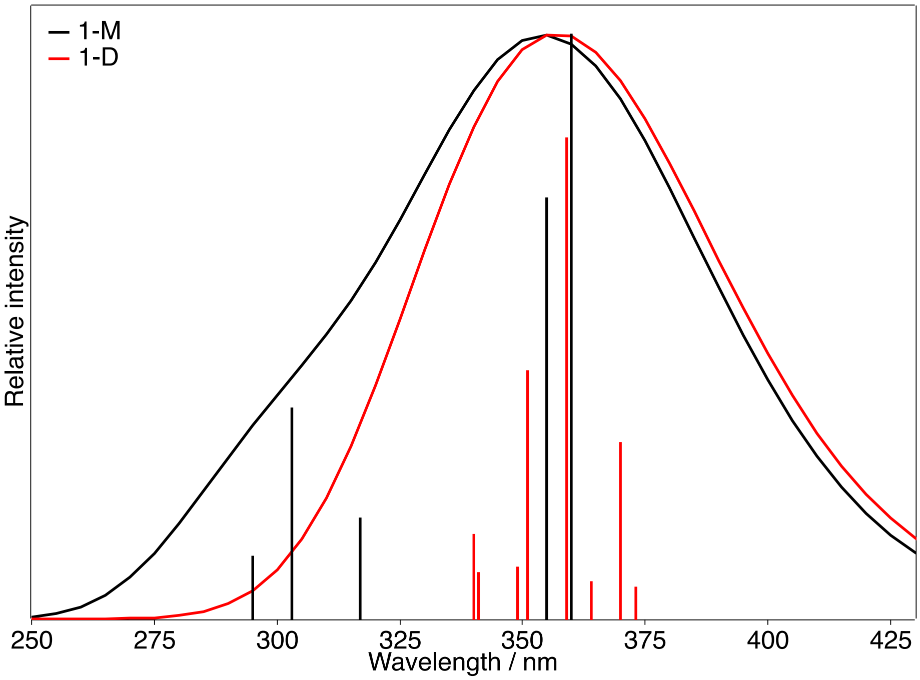

Figure S10: Absorption spectra of the **1-M** (black) and **1-D** (red) models. The sticks have been convoluted with a Gaussian presenting a FWHM of 0.3 eV.

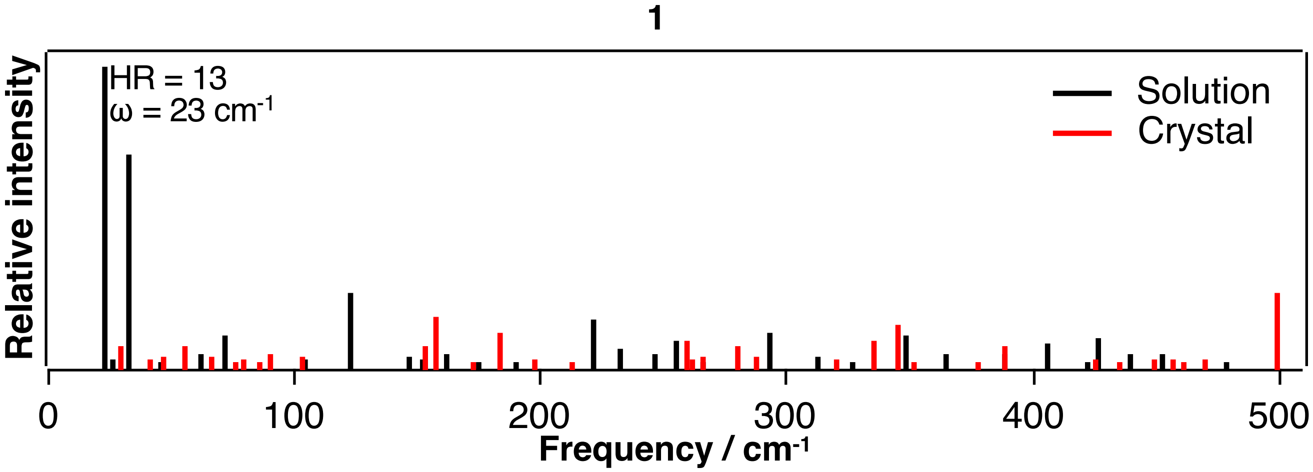

Figure S11: Low-frequency vibrational spectrum (0-500 cm^{-1}) calculated for the S_1*(K) structure for **1** in the crystalline phase. The vibrational mode corresponding to a large HR value in solution is given..

Crystalline systems: molecules 2 to 5.

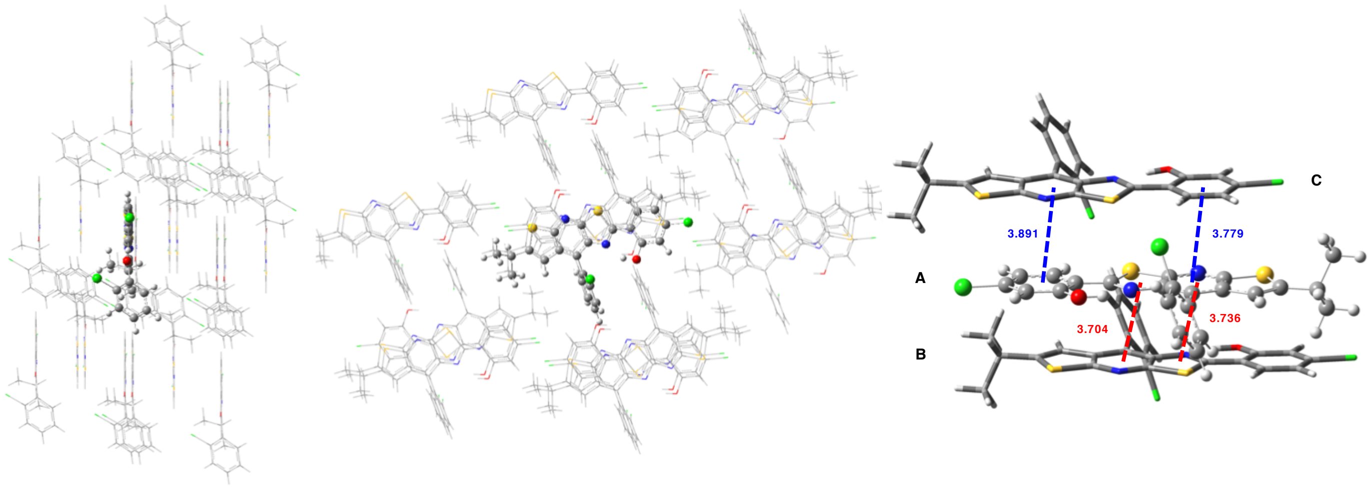

Figure S12: Representation of the packing structure of **2**. Distances (in angstroms) between the monomers that are involved in the trimer are also indicated.

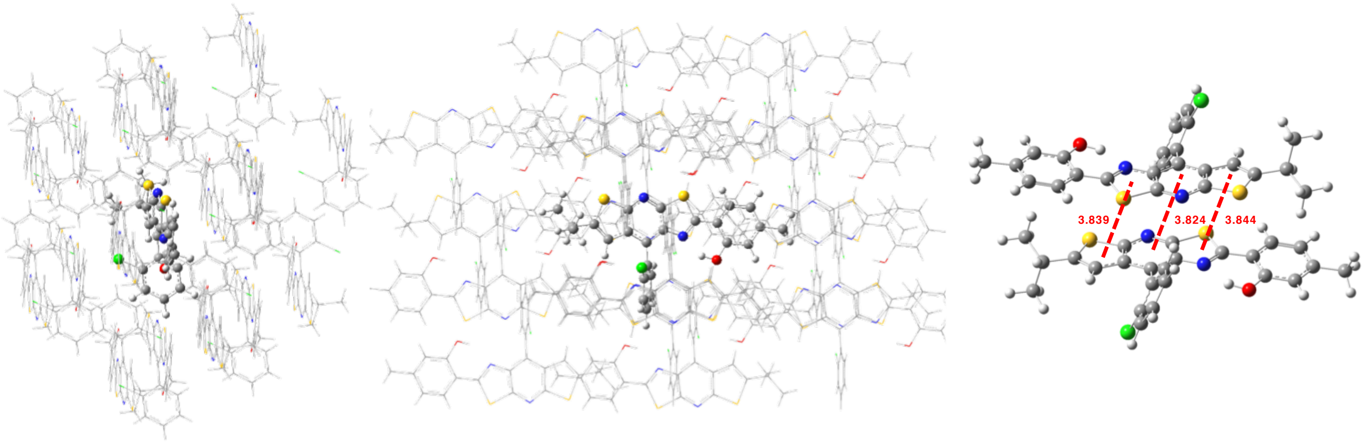

Figure S13: Representation of the packing structure of **3**. Distances (in angstroms) between the two monomers that are involved in the dimer are also indicated.

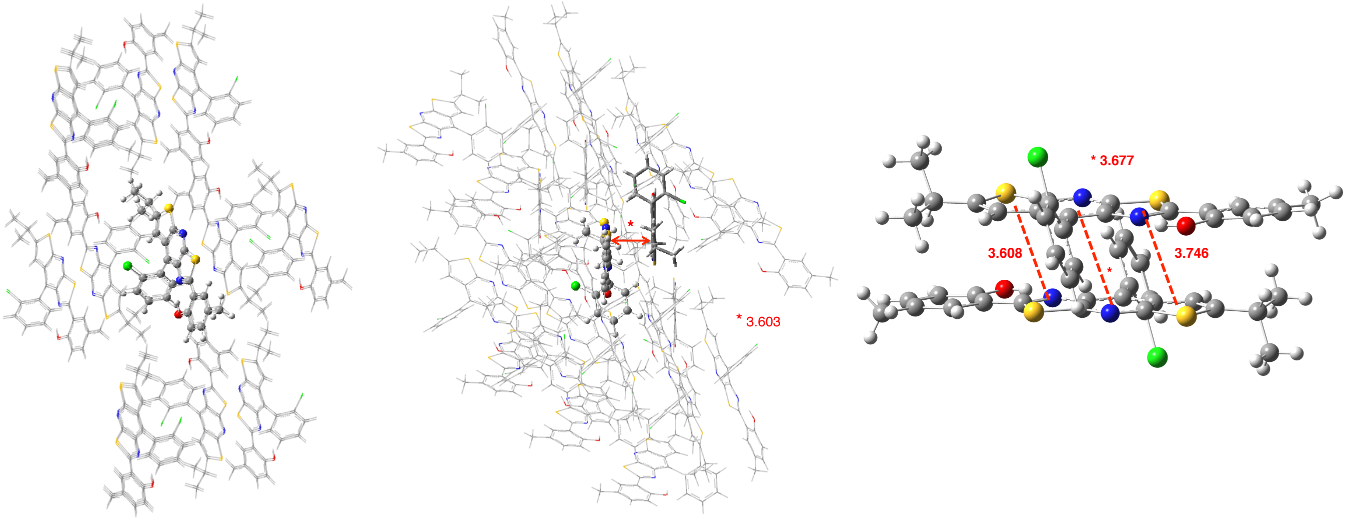

Figure S14: Representation of the packing structure of **4**. Distances (in angstroms) between the two monomers that are involved in the dimer are also indicated.

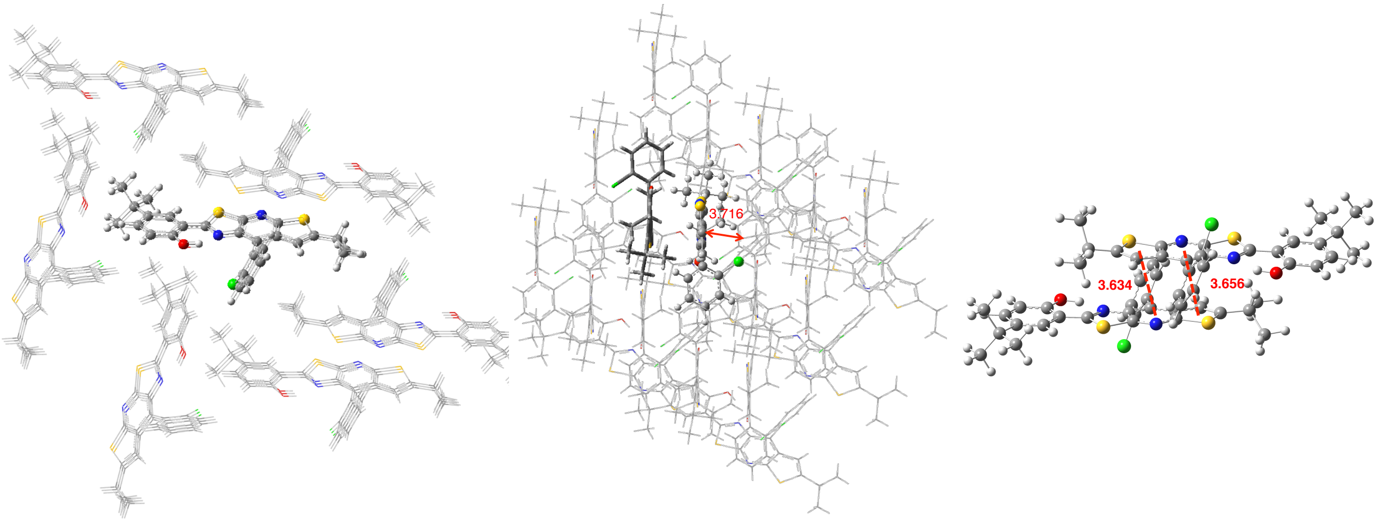

Figure S15: Representation of the packing structure of **5**. Distances (in angstroms) between the two monomers that are involved in the dimer are also indicated.

Crystalline systems: Structural and spectral parameters.

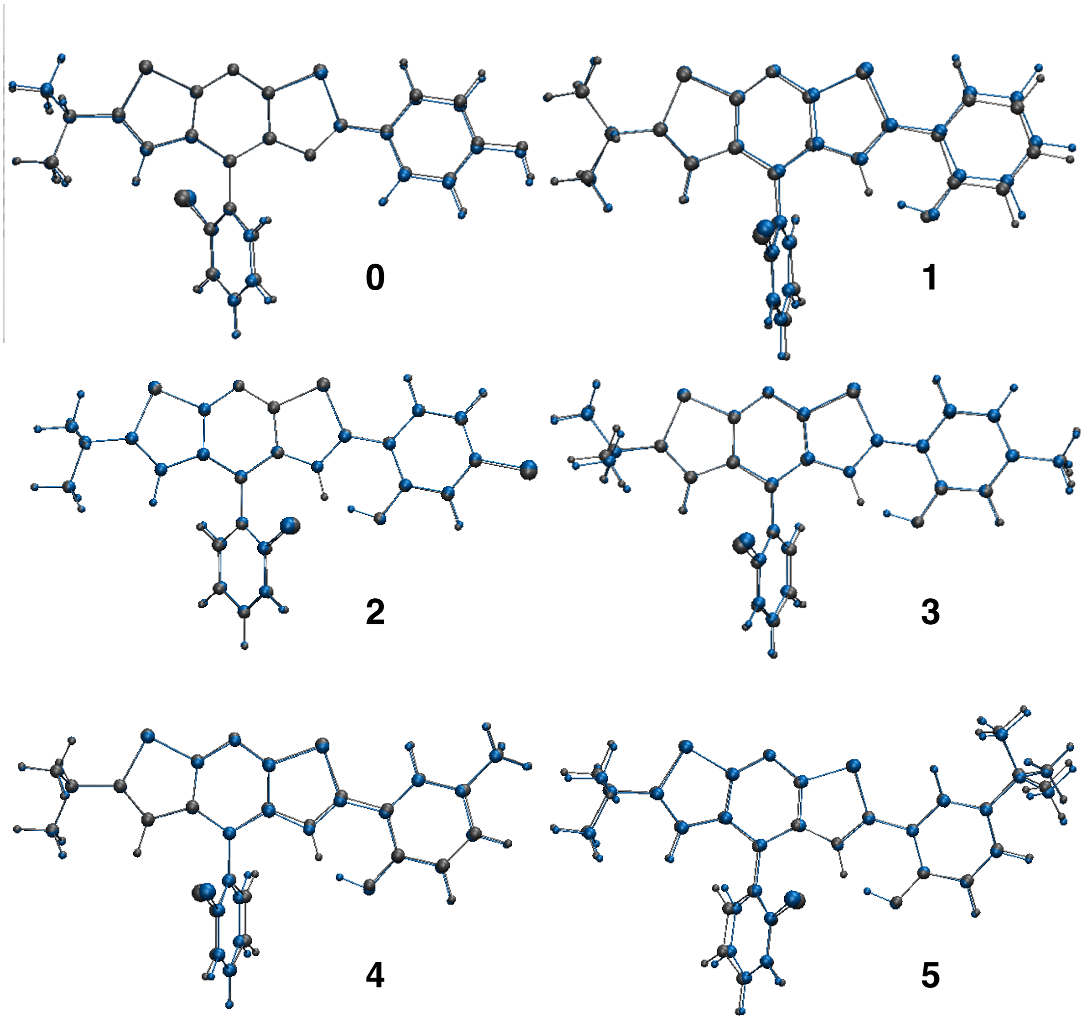

Figure S16: Structure superposition of the optimized ground (S_0) and first excited state (S_1^*(E) for **0** and S_1^*(K) for **1**, **2**, **3**, **4** and **5**) of the molecules in the crystal. One monomer is represented only. Ground and excited states are represented in blue and dark grey respectively.

Table SX: Absorption wavelength (λ in nm), oscillator strengths (f) and dominant molecular contributions in $S_0 \rightarrow S_n$ transitions for the different models for the compounds **2**, **3**, **4** and **5**. Only transitions with $f \geq 0.15$ are given. H and L denote HOMO and LUMO respectively.

Models	State	λ_{calc} (nm)	f	Assignment)
2-M	S_1	360	0.626	H → L
	S_4	303	0.181	H → L+1
2-D	S_2	370	0.188	H-1 → L
	S_4	363	0.179	H → L+1
2-T	S_6	364	0.120	H-1 → L+1
	S_7	360	0.103	H-2 → L+1
3-M	S_1	361	0.558	H → L
	S_5	295	0.244	H-1 → L+1
3-D	S_3	368	0.296	H → L+1
	S_6	356	0.562	H-2 → L
4-M	S_1	366	0.434	H → L
4-D	S_2	363	0.273	H → L+1
5-M	S_1	365	0.482	H → L
5-D	S_2	367	0.885	H-1 → L

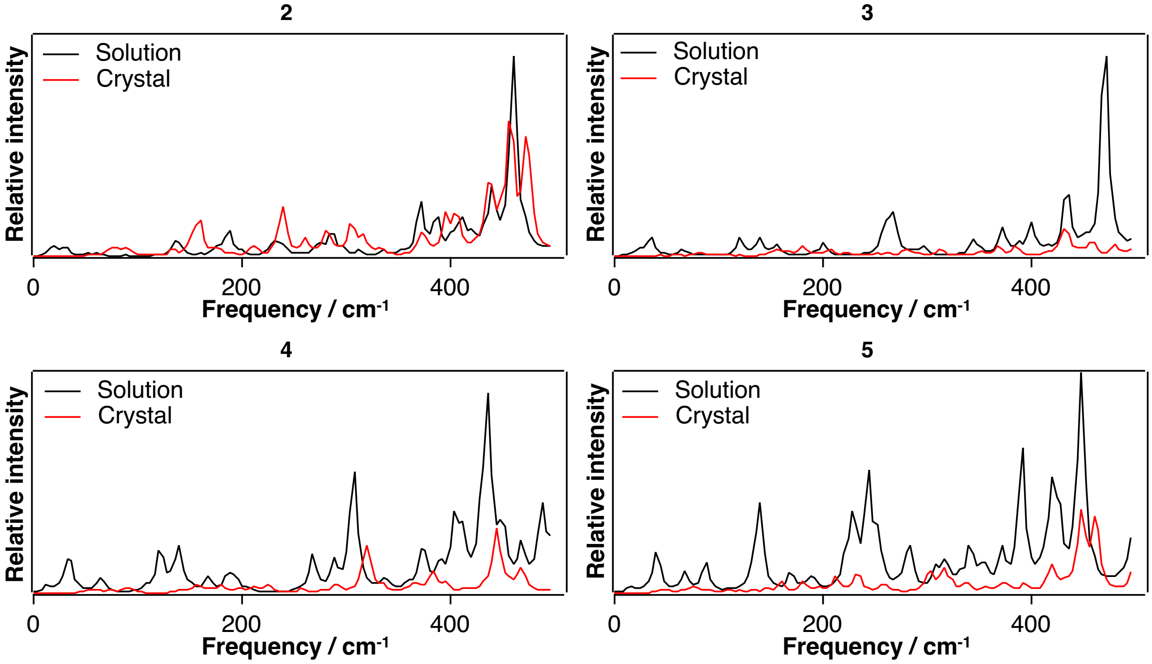

Figure S17: Low-frequency vibrational spectrum (0-500 cm^{-1}) calculated for the S_1*(K) structure for **2**-**4** in solution and in the crystalline environment.

References

(1) Huang, M.; Yu, R.; Xu, K.; Ye, S.; Kuang, S.; Zhu, X.; Wan, Y. *Chem. Sci.* **2016**, *7*, 4485–4491.

(2) Huang, M.; Ye, S.; Xu, K.; Zhou, J.; Liu, J.; Zhu, X.; Wan, Y. *J. Mater. Chem. C* **2017**, *5*, 3456–3460.