Electronic Supplementary Information of 'Optical and Photophysical Properties of Anisole- and Cyanobenzene-Substituted Perylene Diimides'

Hückel-Molecular–Orbital (HMO) analysis of higher-energy transitions

Let us consider the intermediate band systems that occur at ca. 370 nm for compound **2**, 390-500 nm for **7** and 350-430 nm for **8**. These bands are characterized by a marked increase in relative intensity in the anisole di-substituted derivatives relative to the bay-unsubstituted PDI, **2**. With reference to the HMO diagrams of the three model chromophores (Figure 4 of the main text), this absorption region corresponds to transitions from the quartet of perylenic orbitals that lie under the HOMO to the LUMO and transitions from the HOMO to the corresponding virtual orbitals. In Per-T and Per-C, however, this group of transitions includes additional transitions to the LUMO and from the HOMO involving four occupied orbitals and four corresponding virtual orbitals with a prevailing (>50%) anisole character. In perylene (D_{2h}) only two transitions of this group are allowed by symmetry (A_u (HOMO)$\rightarrow B_{2g}$ (10$\rightarrow$13) and $B_{1u}\rightarrow B_{3g}$ (LUMO) (6$\rightarrow$11), both y-polarized). The *minus* combination of the $^1\Phi_{10\rightarrow13}$ and $^1\Phi_{6\rightarrow11}$ configurations provides the well-known alternant-hydrocarbon expression of the excited state involved in the $\alpha/^1L_b$ transition that appears at 325 nm in the spectrum of perylene. The single, weak band at 370 nm in the spectrum of compound **2**, that shares D_{2h} symmetry with perylene, can be assigned as the equivalent of this band. On the other hand, in Per-T, eight of the sixteen transitions belonging to the above said group are allowed with (x,y) polarization, while all of them become allowed with either x or z polarization in Per-C, due to loss of the centre of symmetry. This may well account for the marked increase in the intensity of the bands of compounds **7** and **8** in the 350-500 nm range, relative to compound **2**. Interestingly, the quite intense band with maximum at about 430 nm in the spectrum of compound **7** and of that around 410 nm in the spectrum of compound **3**, that are both characterized by the *cis* arrangement of the substituents, may be traced back to the so-called *cis*-peak appearing in the *cis* forms of polyenic compounds, e.g. α,ω-diphenylpolyenes.[1]

The spectrum of perylene at higher frequencies consists of two complex absorption bands. The first one, with maximum at 252 nm, can be assigned to the $\beta/^1B_b$ transition, that involves excitation to state $1/\sqrt{2}(^1\Phi_{10\rightarrow13}+^1\Phi_{6\rightarrow11})$. The second one is a very intense band with maximum at 206 nm, extending from 220 to <180nm. Inspection of the HMO diagram in Figure 4 suggests that this broad band, peculiar to perylene, involves excitations from the four degenerate MOs lying under the HOMO to the four MOs lying above the LUMO. It is a matter of sixteen transitions, ten of which are allowed by symmetry, six x-polarized and four y-polarized. Thus, following the same considerations made

above for the $\alpha/^1L_b$ transition, the peak in the spectrum of compound **2** at about 260 nm should be assigned as the equivalent of the perylenic $\beta/^1B_b$ band. Similarly, the intense absorption growing below 250 nm may be identified as the equivalent of the perylenic band centred at 206 nm. As emphasized in Figure 3, the intense bands that appear in the 250-360 nm region of the spectrum of the anisole-substituted compounds correspond to a substantial intensity increase relative to the absorption of perylene and of the unsubstituted diimide, **2**, in the same region. As previously pointed out, Per-T and Per-C show grouping of orbitals similar to those of perylene with additional orbitals of anisolic character. According to our modelling depicted in Figure 4, the number of individual transitions involved in the bands between, roughly, 200 and 350 nm, change from 16 to 36 on moving from the parent compound, perylene, to its derivatives Per-C and Per-T. Half of them are allowed for Per-T, all for Per-C. Thus, the observed marked enhancement of intensity in the spectra of compounds **7** and **8** relative to compound **2** in the 250-350 nm region can be explained by the same considerations made above regarding the analogous intensity effects occurring in the intermediate (350-500 nm) spectral region.

1 F. Momicchioli, I. Baraldi and M.C. Bruni, *J.C.S. Faraday II* 1972, **68**, 1556; I. Baraldi, F.Momicchioli and M.C. Bruni, *J.C.S. Faraday II* 1972, **68**, 1571.

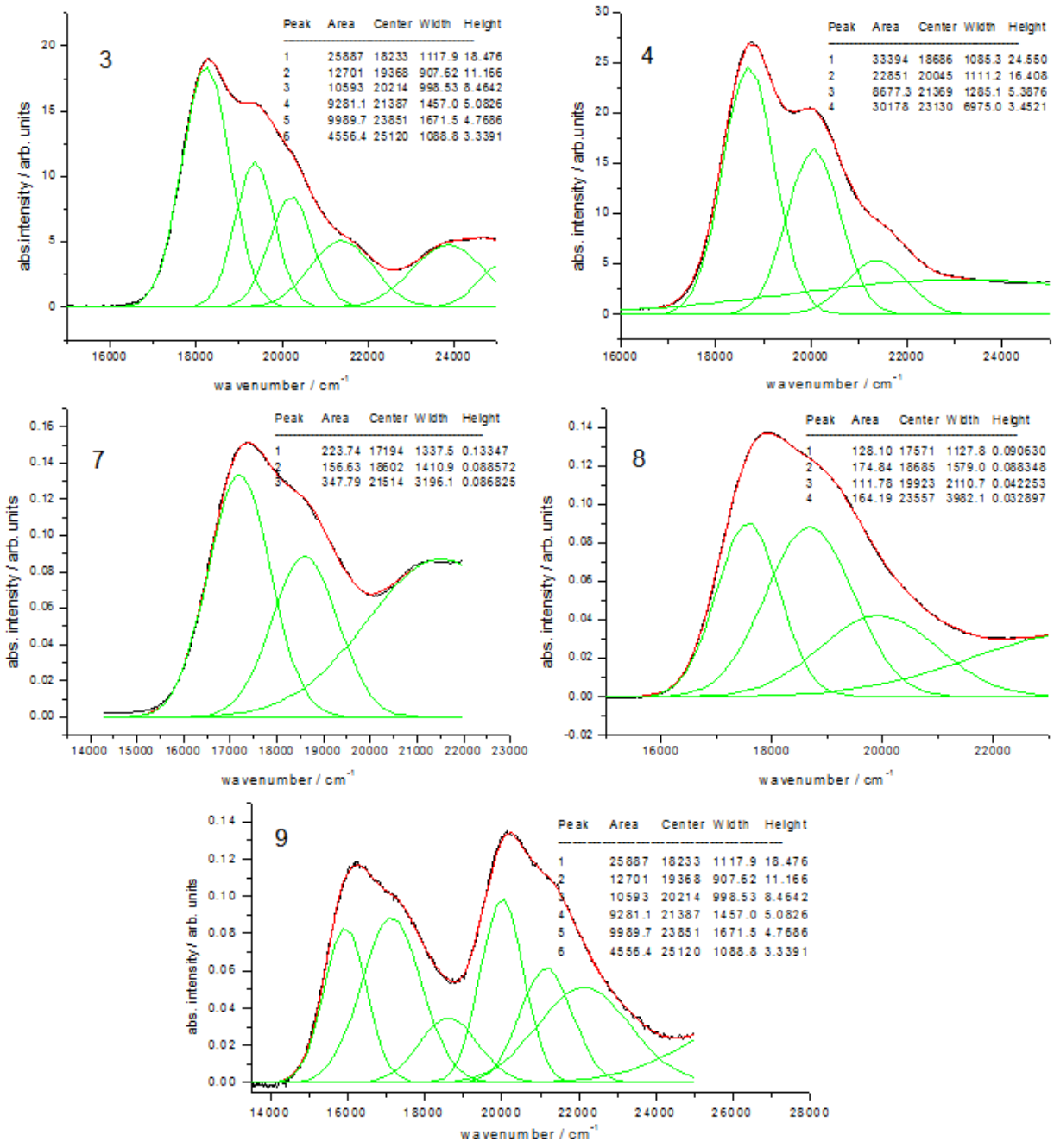

Figure SI1. Decomposition of the lowest-energy absorption bands of compounds **3**, **4**, **7** and **8** and of the two lowest-energy bands of compound **9** in cyclohexane as superpositions of Gaussian bands. Best fitting band parameters are reported. All maximum absorbances were lower than 0.2.

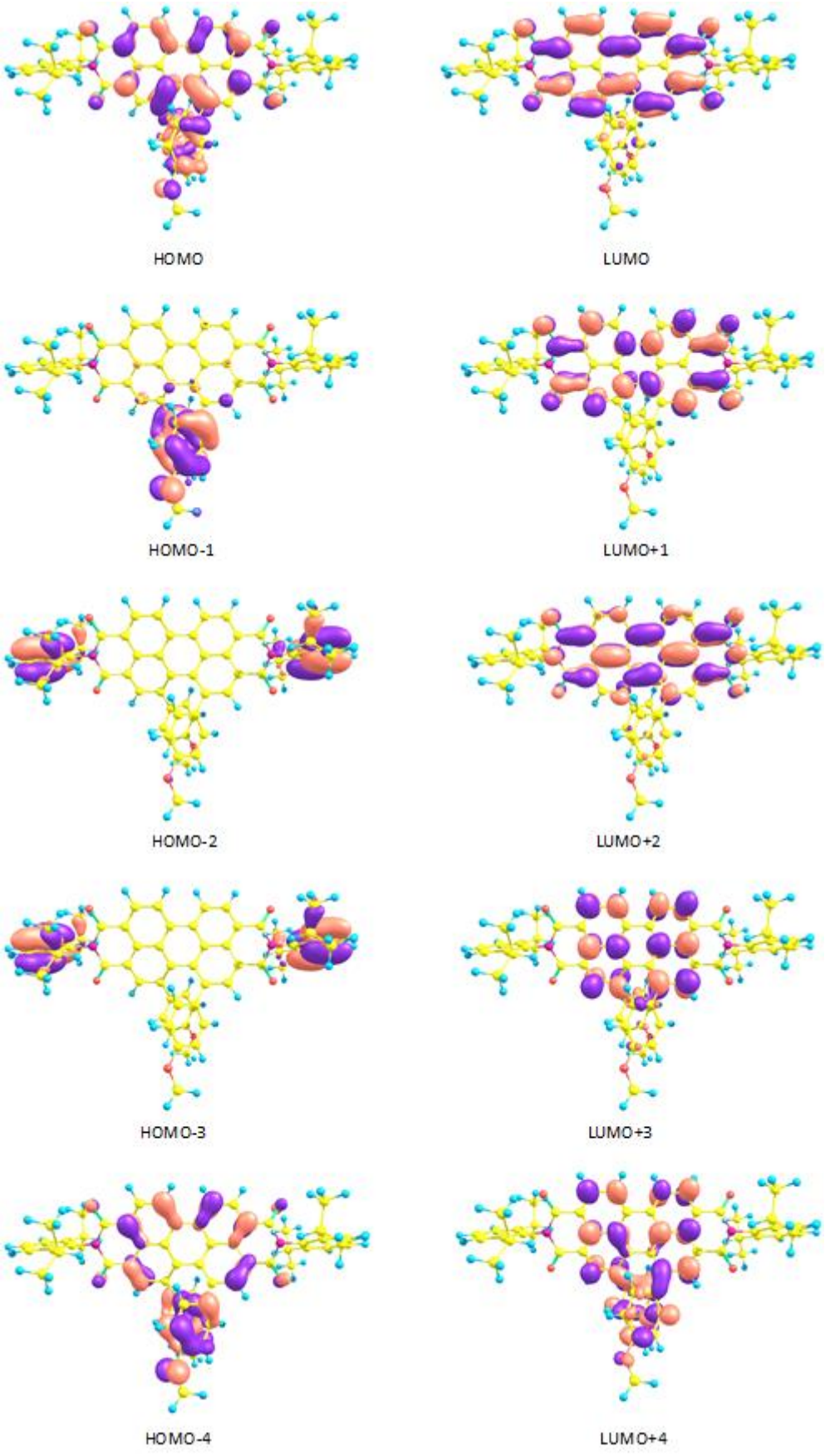

Figure SI2. KS DFT molecular orbital pictorial representation for compound **7** in the gas phase.

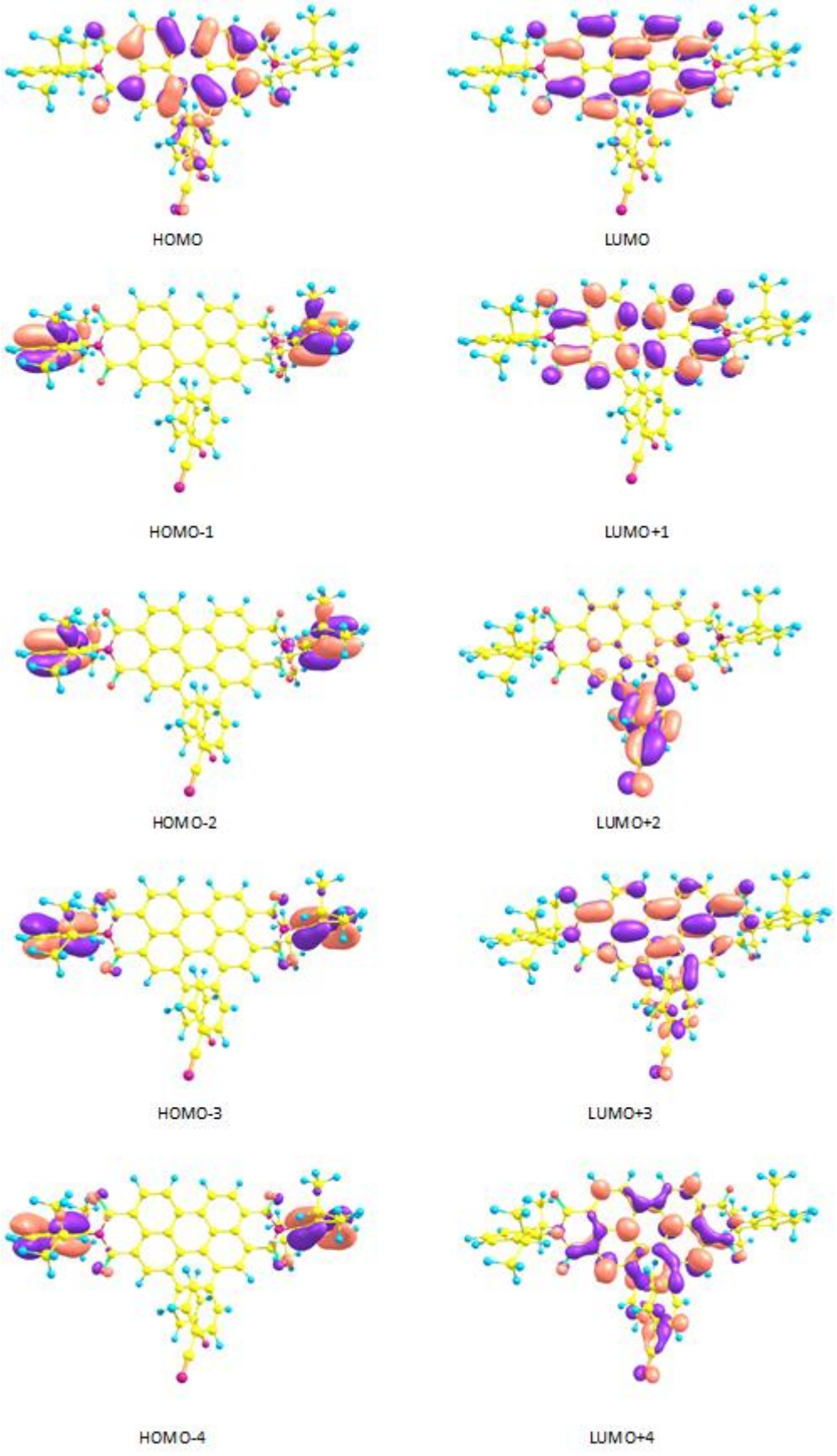

Figure SI3. KS DFT molecular orbital pictorial representation for compound **3** in the gas phase.

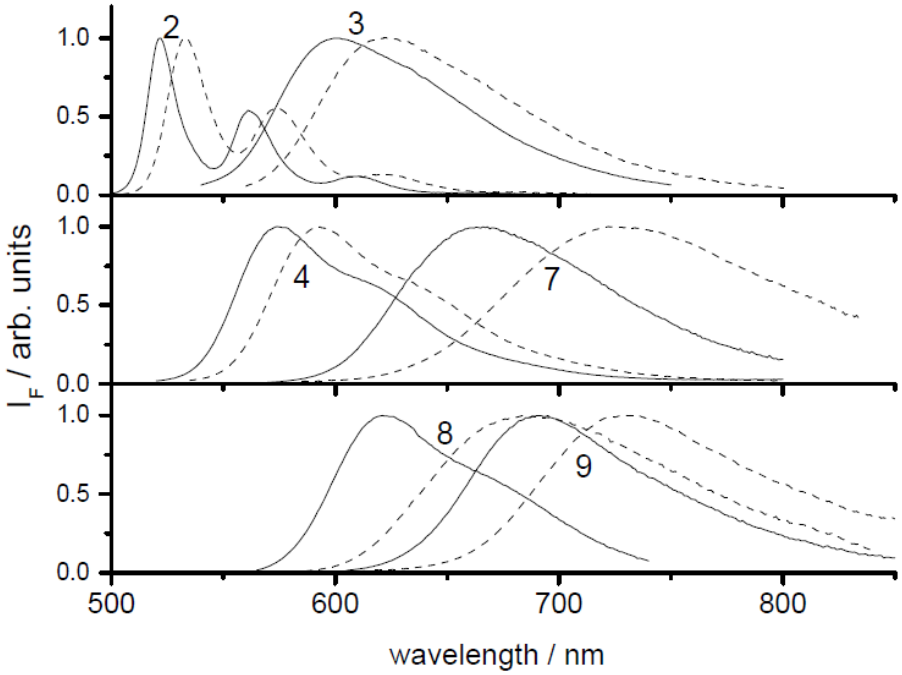

Figure SI4. Corrected and normalized fluorescence emission spectra of the indicated PDI in cyclohexane (C, solid lines) and acetonitrile (A, dashed lines). All spectra were measured on samples with maximum absorbances lower than 0.2. Excitation wavelengths were 450 and 490 nm (**2** in C and A, respectively), 535 and 550 nm (**3**), 515 and 530 nm (**4**), 560 and 570 nm (**7**), 560 and 580 nm (**8**), 570 and 600 nm (**9**).

Table SI1. TDDFT spectra for compound **2** in cyclohexane.

	TDDFT EXCITATION ENERGIES						
STATE*	HARTREE	EV	KCAL/MOL	CM-1	NANOMETERS	OSC. STR.	STATE COMPOSITION**
1A	0.0876170419	2.3842	54.9805	19229.72	520.03	0.8640553	0.988[HL]
1A	0.0934669642	2.5434	58.6514	20513.63	487.48	0.0000357	0.991[(H-1)L]
1A	0.0936914538	2.5495	58.7923	20562.90	486.31	0.0192667	0.980[(H-2)L]
1A	0.1007845593	2.7425	63.2433	22119.65	452.09	0.0000000	
1A	0.1008442043	2.7441	63.2807	22132.74	451.82	0.0000000	
1A	0.1193365714	3.2473	74.8848	26191.35	381.81	0.0000409	
1A	0.1194300053	3.2499	74.9435	26211.86	381.51	0.0000001	
1A	0.1223486652	3.3293	76.7750	26852.43	372.41	0.0000159	
1A	0.1273658706	3.4658	79.9233	27953.58	357.74	0.0000364	
1A	0.1285562195	3.4982	80.6703	28214.83	354.42	0.0001738	
1A	0.1296056769	3.5267	81.3288	28445.16	351.55	0.0190869	0.885[(H-8)L]
1A	0.1329078245	3.6166	83.4009	29169.90	342.82	0.0000012	
1A	0.1350066748	3.6737	84.7180	29630.54	337.49	0.0000433	
1A	0.1353081863	3.6819	84.9072	29696.71	336.74	0.0000000	
1A	0.1395134957	3.7964	87.5461	30619.67	326.59	0.0624020	0.865[(H-11)L]; 0.059|H(L+4)]
1A	0.1417739025	3.8579	88.9645	31115.77	321.38	0.0001817	
1A	0.1421999358	3.8695	89.2318	31209.28	320.42	0.0006670	
1A	0.1500234387	4.0823	94.1411	32926.34	303.71	0.0000075	
1A	0.1501319862	4.0853	94.2093	32950.16	303.49	0.0000328	
1A	0.1570589796	4.2738	98.5560	34470.46	290.10	0.0003036	
1A	0.1571666748	4.2767	98.6236	34494.10	289.90	0.0000028	
1A	0.1572910749	4.2801	98.7017	34521.40	289.68	0.0000016	
1A	0.1573446438	4.2816	98.7353	34533.16	289.58	0.0000429	
1A	0.1580298481	4.3002	99.1652	34683.54	288.32	0.0000788	
1A	0.1640292917	4.4635	102.9299	36000.27	277.78	0.0000111	
1A	0.1641027914	4.4655	102.9761	36016.40	277.65	0.0000000	
1A	0.1695732952	4.6143	106.4089	37217.04	268.69	0.0000395	
1A	0.1700917027	4.6284	106.7342	37330.81	267.88	0.0004359	
1A	0.1732519777	4.7144	108.7173	38024.41	262.99	0.0599468	0.542[H(L+4)]; 0.277[(H-5)(L+1)]; 0.085[(H-9)(L+1)]
1A	0.1753686007	4.7720	110.0455	38488.96	259.81	0.0000015	

Table SI2. TDDFT spectra for compound **2** in acetonitrile.

	TDDFT EXCITATION ENERGIES						
STATE*	HARTREE	EV	KCAL/MOL	CM-1	NANOMETERS	OSC. STR.	STATE COMPOSITION**
1A	0.0872641922	2.3746	54.7591	19152.28	522.13	0.8951122	0.9996[HL]
1A	0.1006520347	2.7389	63.1601	22090.57	452.68	0.0000386	0.990[(H-1)L]
1A	0.1007640585	2.7419	63.2304	22115.15	452.18	0.0017802	0.988[(H-2)L]
1A	0.1081585675	2.9431	67.8705	23738.06	421.26	0.0000000	
1A	0.1082281062	2.9450	67.9142	23753.32	420.99	0.0000000	
1A	0.1209585713	3.2915	75.9027	26547.34	376.69	0.0000054	
1A	0.1259811301	3.4281	79.0544	27649.66	361.67	0.0000424	
1A	0.1260456580	3.4299	79.0949	27663.82	361.48	0.0000002	
1A	0.1268411787	3.4515	79.5941	27838.42	359.22	0.0000176	
1A	0.1276801459	3.4744	80.1205	28022.55	356.86	0.0001670	
1A	0.1289773655	3.5097	80.9345	28307.26	353.27	0.0410366	0.906[(H-6)L]
1A	0.1332934735	3.6271	83.6429	29254.54	341.83	0.0000296	
1A	0.1408129766	3.8317	88.3615	30904.88	323.57	0.0000503	
1A	0.1413218577	3.8456	88.6808	31016.56	322.41	0.0000008	
1A	0.1413452764	3.8462	88.6955	31021.70	322.35	0.0020503	
1A	0.1440755884	3.9205	90.4088	31620.94	316.25	0.0442292	0.927[(H-11)L]
1A	0.1459313359	3.9710	91.5733	32028.23	312.22	0.0001686	
1A	0.1560945588	4.2475	97.9508	34258.80	291.90	0.0000147	
1A	0.1561862174	4.2500	98.0083	34278.91	291.72	0.0000230	
1A	0.1590200345	4.3272	99.7866	34900.86	286.53	0.0003148	
1A	0.1635995130	4.4518	102.6603	35905.94	278.51	0.0000051	
1A	0.1636668971	4.4536	102.7025	35920.73	278.39	0.0000534	
1A	0.1643212762	4.4714	103.1132	36064.35	277.28	0.0000352	
1A	0.1644389243	4.4746	103.1870	36090.17	277.08	0.0002098	
1A	0.1712986879	4.6613	107.4916	37595.72	265.99	0.0000123	
1A	0.1714002493	4.6640	107.5553	37618.01	265.83	0.0000000	
1A	0.1725845114	4.6963	108.2984	37877.92	264.01	0.0265486	0.501[(H-5)(L+1)]; 0.391[H(L+4)]
1A	0.1741933490	4.7400	109.3080	38231.02	261.57	0.0005612	
1A	0.1748755991	4.7586	109.7361	38380.76	260.55	0.0001929	
1A	0.1774864372	4.8297	111.3744	38953.77	256.71	0.0422441	0.453[H(L+6)]; 0.192[(H-5)(L+1)]; 0.175[H(L+4)]

Table SI3. TDDFT spectra for compound **3** in cyclohexane.

	TDDFT EXCITATION ENERGIES						
STATE	HARTREE	EV	KCAL/MOL	CM-1	NANOMETERS	OSC. STR.	STATE COMPOSITION**
1A	0.0786207317	2.1394	49.3353	17255.26	579.53	0.4841960	0.989[HL]
1A	0.0882145093	2.4004	55.3554	19360.85	516.51	0.0000847	
1A	0.0883169412	2.4032	55.4197	19383.33	515.91	0.0004465	
1A	0.0961411303	2.6161	60.3295	21100.54	473.92	0.0005773	
1A	0.0962061753	2.6179	60.3703	21114.81	473.60	0.0002373	
1A	0.1056293520	2.8743	66.2834	23182.96	431.35	0.1128862	0.946[(H-5)L]
1A	0.1100737606	2.9953	69.0723	24158.40	413.93	0.1169591	0.940[(H-6)L]
1A	0.1170242446	3.1844	73.4338	25683.85	389.35	0.0000835	
1A	0.1173170571	3.1924	73.6176	25748.12	388.38	0.0005769	
1A	0.1207864189	3.2868	75.7946	26509.55	377.22	0.0009971	
1A	0.1210684372	3.2944	75.9716	26571.45	376.34	0.0000851	
1A	0.1227989714	3.3415	77.0575	26951.26	371.04	0.0017936	
1A	0.1268917021	3.4529	79.6258	27849.51	359.07	0.0528742	
1A	0.1285569486	3.4982	80.6707	28214.99	354.42	0.1471787	0.564[H(L+2)]; 0.205[(H-11)L]; 0.111[(H-15)L]
1A	0.1297475487	3.5306	81.4178	28476.30	351.17	0.0032428	
1A	0.1303035623	3.5457	81.7667	28598.33	349.67	0.0584913	
1A	0.1326775360	3.6103	83.2564	29119.35	343.41	0.0226035	
1A	0.1333963771	3.6299	83.7075	29277.12	341.56	0.0016737	
1A	0.1346312922	3.6635	84.4824	29548.15	338.43	0.0342032	
1A	0.1361718597	3.7054	85.4491	29886.27	334.60	0.0067547	
1A	0.1384515400	3.7675	86.8797	30386.60	329.09	0.1437876	0.729[(H-15)L]
1A	0.1414001701	3.8477	88.7300	31033.75	322.23	0.0853793	
1A	0.1421768570	3.8688	89.2173	31204.21	320.47	0.0001914	
1A	0.1422641641	3.8712	89.2721	31223.37	320.27	0.0003600	
1A	0.1486592295	4.0452	93.2851	32626.93	306.50	0.0046791	
1A	0.1487587810	4.0479	93.3476	32648.78	306.29	0.0006883	
1A	0.1488957327	4.0517	93.4335	32678.84	306.01	0.0037114	
1A	0.1498644359	4.0780	94.0414	32891.44	304.03	0.0000106	
1A	0.1499230446	4.0796	94.0781	32904.30	303.91	0.0000730	
1A	0.1504743071	4.0946	94.4241	33025.29	302.80	0.0002154	

Table SI4. TDDFT spectra for compound **3** in acetonitrile.

	TDDFT EXCITATION ENERGIES						
STATE	HARTREE	EV	KCAL/MOL	CM-1	NANOMETERS	OSC. STR.	STATE COMPOSITION**
1A	0.0782854346	2.1303	49.1249	17181.67	582.02	0.4962314	0.989[HL]
1A	0.0966934058	2.6312	60.6760	21221.75	471.21	0.0002542	
1A	0.0968463883	2.6353	60.7720	21255.33	470.47	0.0003568	
1A	0.1046089016	2.8466	65.6431	22959.00	435.56	0.0120209	
1A	0.1047051087	2.8492	65.7035	22980.12	435.16	0.0093685	
1A	0.1055849662	2.8731	66.2556	23173.22	431.53	0.0967286	
1A	0.1092817502	2.9737	68.5753	23984.57	416.93	0.1112914	0.941[(H-6)L]
1A	0.1193843101	3.2486	74.9148	26201.83	381.65	0.0010656	
1A	0.1196288012	3.2553	75.0682	26255.49	380.87	0.0002813	
1A	0.1215094849	3.3064	76.2484	26668.25	374.98	0.0041488	
1A	0.1240249625	3.3749	77.8268	27220.33	367.37	0.0005305	
1A	0.1242625807	3.3814	77.9760	27272.48	366.67	0.0000024	
1A	0.1270449077	3.4571	79.7219	27883.13	358.64	0.0731169	
1A	0.1278795006	3.4798	80.2456	28066.31	356.30	0.1736925	0.692[H(L+2)]; 0.120[(H-13)L]
1A	0.1281729748	3.4878	80.4298	28130.72	355.48	0.0040244	
1A	0.1314641747	3.5773	82.4950	28853.05	346.58	0.0848392	
1A	0.1354653674	3.6862	85.0058	29731.21	336.35	0.0021682	
1A	0.1377553968	3.7485	86.4428	30233.81	330.76	0.0437870	
1A	0.1397669883	3.8033	87.7051	30675.31	326.00	0.0000899	
1A	0.1400566599	3.8111	87.8869	30738.88	325.32	0.0319363	
1A	0.1417386490	3.8569	88.9424	31108.04	321.46	0.0873315	
1A	0.1419828342	3.8635	89.0956	31161.63	320.91	0.0563374	
1A	0.1492564719	4.0615	93.6599	32758.01	305.27	0.0060537	
1A	0.1496156706	4.0712	93.8853	32836.84	304.54	0.0004395	
1A	0.1497587410	4.0751	93.9750	32868.24	304.25	0.0002614	
1A	0.1565708701	4.2605	98.2497	34363.33	291.01	0.0127437	
1A	0.1572645105	4.2794	98.6850	34515.57	289.72	0.0002149	
1A	0.1573377250	4.2814	98.7309	34531.64	289.59	0.0000734	
1A	0.1574740017	4.2851	98.8164	34561.55	289.34	0.0002391	
1A	0.1576165893	4.2890	98.9059	34592.84	289.08	0.0017335	

Table SI5. TDDFT spectra for compound **4** in cyclohexane.

	TDDFT EXCITATION ENERGIES						
STATE*	HARTREE	EV	KCAL/MOL	CM-1	NANOMETERS	OSC. STR.	STATE COMPOSITION**
1A	0.0876979945	2.3864	55.0313	19247.49	519.55	0.7727612	0.972[HL]
1A	0.0918425084	2.4992	57.6321	20157.10	496.10	0.0000387	0.990[(H-1)L]
1A	0.0921360063	2.5071	57.8162	20221.52	494.52	0.0361436	0.964[(H-2)L]
1A	0.0995717702	2.7095	62.4822	21853.48	457.59	0.0000001	
1A	0.0996535735	2.7117	62.5336	21871.43	457.22	0.0000000	
1A	0.1173508614	3.1933	73.6388	25755.54	388.27	0.0000438	
1A	0.1181580047	3.2152	74.1453	25932.68	385.61	0.0000001	
1A	0.1195175693	3.2522	74.9984	26231.07	381.23	0.0000000	
1A	0.1213325416	3.3016	76.1373	26629.41	375.52	0.0000001	
1A	0.1226544342	3.3376	76.9668	26919.54	371.48	0.0000006	
1A	0.1271484137	3.4599	79.7868	27905.85	358.35	0.0000009	
1A	0.1276658634	3.4740	80.1115	28019.42	356.90	0.0696264	0.925[(H-10)L]
1A	0.1286032921	3.4995	80.6998	28225.16	354.29	0.0000006	
1A	0.1317597439	3.5854	82.6805	28917.92	345.81	0.0000012	
1A	0.1351890874	3.6787	84.8324	29670.58	337.03	0.0094543	0.982[(H-13)L]
1A	0.1355087650	3.6874	85.0330	29740.74	336.24	0.0000400	
1A	0.1360525373	3.7022	85.3743	29860.08	334.90	0.0000007	
1A	0.1361823390	3.7057	85.4557	29888.57	334.58	0.0000005	
1A	0.1389599653	3.7813	87.1987	30498.19	327.89	0.0763650	0.910[(H-14)L]
1A	0.1406140092	3.8263	88.2366	30861.21	324.03	0.0000066	
1A	0.1419096485	3.8616	89.0497	31145.57	321.07	0.0000013	
1A	0.1419684061	3.8632	89.0865	31158.46	320.94	0.0000733	
1A	0.1435666487	3.9066	90.0894	31509.24	317.37	0.0000002	
1A	0.1467508709	3.9933	92.0876	32208.09	310.48	0.0001395	0.984[(H-1)(L+1)]
1A	0.1468705233	3.9966	92.1627	32234.35	310.23	0.0000007	
1A	0.1537187507	4.1829	96.4600	33737.37	296.41	0.0000636	
1A	0.1537501495	4.1838	96.4797	33744.26	296.35	0.0000054	
1A	0.1544911737	4.2039	96.9447	33906.89	294.93	0.0000008	
1A	0.1545665225	4.2060	96.9920	33923.43	294.78	0.0000472	
1A	0.1554137556	4.2290	97.5236	34109.38	293.17	0.0000002	

Table SI6. TDDFT spectra for compound **4** in acetonitrile.

	TDDFT EXCITATION ENERGIES						
STATE*	HARTREE	EV	KCAL/MOL	CM-1	NANOMETERS	OSC. STR.	STATE COMPOSITION**
1A	0.0872672036	2.3747	54.7610	19152.94	522.11	0.8175876	0.998[HL]
1A	0.0996804774	2.7124	62.5505	21877.34	457.09	0.0000157	0.992[(H-1)L]
1A	0.0997937730	2.7155	62.6215	21902.20	456.58	0.0018513	0.990[(H-2)L]
1A	0.1075073227	2.9254	67.4619	23595.13	423.82	0.0000006	
1A	0.1076166618	2.9284	67.5305	23619.13	423.39	0.0000000	
1A	0.1175688962	3.1992	73.7756	25803.39	387.55	0.0000001	
1A	0.1190463370	3.2394	74.7027	26127.65	382.74	0.0000274	0.953[(H-6)L]
1A	0.1196119419	3.2548	75.0576	26251.79	380.93	0.0000012	
1A	0.1261074982	3.4316	79.1337	27677.40	361.31	0.0000088	
1A	0.1261947711	3.4339	79.1884	27696.55	361.06	0.0000001	
1A	0.1266529836	3.4464	79.4760	27797.12	359.75	0.1008569	0.922[(H-8)L]
1A	0.1269930709	3.4557	79.6894	27871.76	358.79	0.0000274	0.891[(H-13)L]
1A	0.1277381124	3.4759	80.1569	28035.28	356.69	0.0000067	
1A	0.1312282385	3.5709	82.3470	28801.27	347.21	0.0123089	0.994[(H-10)L]
1A	0.1320880921	3.5943	82.8865	28989.99	344.95	0.0000027	
1A	0.1331867608	3.6242	83.5760	29231.12	342.10	0.0000003	
1A	0.1415991665	3.8531	88.8548	31077.42	321.78	0.0000243	0.859[(H-18)L]
1A	0.1417058310	3.8560	88.9218	31100.84	321.53	0.0000043	
1A	0.1417855144	3.8582	88.9718	31118.32	321.35	0.0001067	0.935[H(L+4)]
1A	0.1417888685	3.8583	88.9739	31119.06	321.35	0.0000035	
1A	0.1417992434	3.8586	88.9804	31121.34	321.32	0.0000032	
1A	0.1438207429	3.9136	90.2489	31565.00	316.81	0.0503100	0.943[(H-15)L]
1A	0.1455299425	3.9601	91.3214	31940.13	313.09	0.0000296	0.677[(H-16)L]; 0.238[H(L+5)]
1A	0.1537816231	4.1846	96.4994	33751.17	296.29	0.0001135	0.984[(H-1)(L+1)]
1A	0.1538499042	4.1865	96.5423	33766.15	296.15	0.0000017	
1A	0.1566099263	4.2616	98.2742	34371.91	290.94	0.0000010	
1A	0.1616381093	4.3984	101.4295	35475.46	281.88	0.0000007	
1A	0.1617122508	4.4004	101.4760	35491.74	281.76	0.0001812	0.981[(H-1)(L+2)]
1A	0.1617399330	4.4012	101.4934	35497.81	281.71	0.0000608	0.953[(H-4)L+1)]
1A	0.1618153678	4.4032	101.5407	35514.37	281.58	0.0000022	

Table SI7. TDDFT spectra for compound **7** in cyclohexane.

TDDFT EXCITATION ENERGIES							
STATE	HARTREE	EV	KCAL/MOL	CM-1	NANOMETERS	OSC. STR.	STATE COMPOSITION**
1A	0.0709507151	1.9307	44.5223	15571.88	642.18	0.3093191	0.979[HL]
1A	0.0807808028	2.1982	50.6907	17729.34	564.04	0.1294924	0.990[(H-1)L]
1A	0.0965866212	2.6283	60.6090	21198.31	471.74	0.0294983	0.989[(H-2)L]
1A	0.0967949683	2.6339	60.7398	21244.04	470.72	0.0000208	
1A	0.1002940439	2.7291	62.9355	22012.00	454.30	0.3065756	0.961[(H-4)L]
1A	0.1037769796	2.8239	65.1210	22776.41	439.05	0.0025121	
1A	0.1038089403	2.8248	65.1411	22783.43	438.92	0.0000208	
1A	0.1132101323	3.0806	71.0404	24846.75	402.47	0.0036781	
1A	0.1160960974	3.1591	72.8514	25480.15	392.46	0.0008294	
1A	0.1175823502	3.1996	73.7840	25806.34	387.50	0.0100708	
1A	0.1209282688	3.2906	75.8836	26540.69	376.78	0.0008894	
1A	0.1213649251	3.3025	76.1577	26636.52	375.42	0.0002906	
1A	0.1217437826	3.3128	76.3954	26719.67	374.26	0.0058470	
1A	0.1222985185	3.3279	76.7435	26841.42	372.56	0.0104609	
1A	0.1283146355	3.4916	80.5187	28161.81	355.09	0.0040762	
1A	0.1298369273	3.5330	81.4739	28495.91	350.93	0.0250312	
1A	0.1331471793	3.6231	83.5511	29222.43	342.20	0.0277617	
1A	0.1341520189	3.6505	84.1817	29442.96	339.64	0.0188467	
1A	0.1368704138	3.7244	85.8875	30039.58	332.89	0.0003131	
1A	0.1372092399	3.7337	86.1001	30113.95	332.07	0.0001735	
1A	0.1390739057	3.7844	87.2702	30523.19	327.62	0.0095159	
1A	0.1407401469	3.8297	88.3158	30888.89	323.74	0.0003423	
1A	0.1408813927	3.8336	88.4044	30919.89	323.42	0.0380883	
1A	0.1468184118	3.9951	92.1300	32222.92	310.34	0.0477361	
1A	0.1476598068	4.0180	92.6579	32407.58	308.57	0.0033433	
1A	0.1488192725	4.0496	93.3855	32662.05	306.17	0.0000918	
1A	0.1493426796	4.0638	93.7140	32776.93	305.09	0.0109992	
1A	0.1526369579	4.1535	95.7812	33499.94	298.51	0.4652017	0.702[H(L+4)]
1A	0.1557748413	4.2388	97.7502	34188.63	292.49	0.0011746	
1A	0.1557989343	4.2395	97.7653	34193.91	292.45	0.0002365	

Table SI8. TDDFT spectra for compound **7** in acetonitrile.

TDDFT EXCITATION ENERGIES							
STATE	HARTREE	EV	KCAL/MOL	CM-1	NANOMETERS	OSC. STR.	STATE COMPOSITION**
1A	0.0695945426	1.8938	43.6712	15274.24	654.70	0.2955742	0.978[HL]
1A	0.0783044934	2.1308	49.1368	17185.85	581.87	0.1282319	0.990[(H-1)L]
1A	0.0983651476	2.6767	61.7251	21588.65	463.21	0.3437480	0.959[(H-2)L]
1A	0.1020246717	2.7762	64.0215	22391.83	446.59	0.0000089	
1A	0.1022866021	2.7834	64.1858	22449.31	445.45	0.0135443	
1A	0.1094082670	2.9772	68.6547	24012.34	416.45	0.0000771	
1A	0.1094729737	2.9789	68.6953	24026.54	416.21	0.0000002	
1A	0.1104275691	3.0049	69.2944	24236.05	412.61	0.0043159	
1A	0.1142542398	3.1090	71.6956	25075.91	398.79	0.0016741	
1A	0.1154175438	3.1407	72.4256	25331.22	394.77	0.0146525	
1A	0.1201635250	3.2698	75.4038	26372.85	379.18	0.0041724	
1A	0.1214828117	3.3057	76.2316	26662.40	375.06	0.0102933	
1A	0.1263669998	3.4386	79.2965	27734.35	360.56	0.0322986	
1A	0.1270637841	3.4576	79.7337	27887.28	358.59	0.0010061	
1A	0.1271588583	3.4602	79.7934	27908.14	358.32	0.0028121	
1A	0.1273598015	3.4656	79.9195	27952.25	357.75	0.0085198	
1A	0.1326463388	3.6095	83.2368	29112.51	343.49	0.0225470	
1A	0.1334435086	3.6312	83.7371	29287.46	341.44	0.0200025	
1A	0.1377480106	3.7483	86.4382	30232.19	330.77	0.0064281	
1A	0.1418169490	3.8590	88.9915	31125.22	321.28	0.0040107	
1A	0.1425255084	3.8783	89.4361	31280.73	319.69	0.0000133	
1A	0.1428207031	3.8863	89.6214	31345.52	319.02	0.0537089	
1A	0.1437038943	3.9104	90.1756	31539.36	317.06	0.0000335	
1A	0.1458941381	3.9700	91.5500	32020.06	312.30	0.0000007	
1A	0.1478686693	4.0237	92.7890	32453.42	308.13	0.0261340	
1A	0.1527926188	4.1577	95.8788	33534.10	298.20	0.3652007	0.628[H(L+4)]; 0.130[(H-4)(L+1)]
1A	0.1531454384	4.1673	96.1002	33611.54	297.52	0.0006113	
1A	0.1533719490	4.1735	96.2424	33661.25	297.08	0.0633623	
1A	0.1556453933	4.2353	97.6690	34160.22	292.74	0.0862935	
1A	0.1577521034	4.2927	98.9910	34622.58	288.83	0.1341349	0.930[(H-1)(L+3)]

Table SI9. TDDFT spectra for compound **8** in cyclohexane.

TDDFT EXCITATION ENERGIES							
STATE*	HARTREE	EV	KCAL/MOL	CM-1	NANOMETERS	OSC. STR.	STATE COMPOSITION**
1A	0.0734094723	1.9976	46.0651	16111.52	620.67	0.3579239	0.941[HL]
1A	0.0844186685	2.2971	52.9735	18527.76	539.73	0.0088885	0.994[(H-1)L]
1A	0.0965838927	2.6282	60.6073	21197.71	471.75	0.1047650	0.885[(H-2)L]; 0.096[(H-4)L]
1A	0.0969767581	2.6389	60.8538	21283.94	469.84	0.0000290	
1A	0.0985957539	2.6829	61.8698	21639.27	462.12	0.3215427	0.874[(H-4)L]; 0.083[(H-2)L]
1A	0.1038350801	2.8255	65.1575	22789.17	438.81	0.0000064	
1A	0.1038963199	2.8272	65.1959	22802.61	438.55	0.0000045	
1A	0.1186212355	3.2278	74.4360	26034.35	384.11	0.0000728	
1A	0.1200121823	3.2657	75.3088	26339.63	379.66	0.0009522	
1A	0.1209013383	3.2899	75.8667	26534.78	376.86	0.0235464	0.964[(H-8)L]
1A	0.1211203281	3.2959	76.0042	26582.84	376.18	0.0000146	
1A	0.1213008417	3.3008	76.1174	26622.46	375.62	0.0007689	
1A	0.1227146702	3.3392	77.0046	26932.76	371.30	0.0000074	
1A	0.1256627740	3.4195	78.8546	27579.79	362.58	0.0026939	0.904[H(L+2)]
1A	0.1280480305	3.4844	80.3514	28103.29	355.83	0.0233015	0.762[(H-12)L]; 0.148[(H-11)L];
1A	0.1290849369	3.5126	81.0020	28330.87	352.97	0.0000004	
1A	0.1364950842	3.7142	85.6520	29957.21	333.81	0.0020198	0.635[(H-13)L]; 0.122[(H-18)L]; 0.081[H(L+1)]; 0.054[(H-14)L]
1A	0.1366433005	3.7183	85.7450	29989.74	333.45	0.0035383	0.759[(H-17)L]; 0.169[(H-1)(L+1)]
1A	0.1370555025	3.7295	86.0036	30080.21	332.44	0.0023150	0.803[(H-1)(L+1)]; 0.160[(H-17)L]
1A	0.1372615194	3.7351	86.1329	30125.42	331.95	0.0008324	
1A	0.1402450454	3.8163	88.0051	30780.23	324.88	0.0304767	0.906[(H-15)L]; 0.054[H(L+4)]
1A	0.1410291746	3.8376	88.4972	30952.33	323.08	0.0006620	
1A	0.1468704307	3.9965	92.1626	32234.33	310.23	0.0483259	0.980[(H-1)(L+2)]
1A	0.1472381265	4.0066	92.3933	32315.03	309.45	0.0043351	0.424[(H-2)(L+1)]; 0.187[H(L+3)]; 0.167[(H-16)L]; 0.128[(H-4)(L+1)]
1A	0.1479208948	4.0251	92.8218	32464.88	308.03	0.0214641	0.274[(H-2)(L+1)]; 0.255[H(L+3)]; 0.246[(H-16)L]; 0.053[(H-4)(L+1)]
1A	0.1501103830	4.0847	94.1957	32945.42	303.53	0.0001324	
1A	0.1503439047	4.0911	94.3422	32996.67	303.06	0.0000568	
1A	0.1565369911	4.2596	98.2285	34355.90	291.07	0.0011260	
1A	0.1570131082	4.2725	98.5272	34460.39	290.19	0.0000088	
1A	0.1570660761	4.2740	98.5605	34472.02	290.09	0.0000016	

Table SI10. TDDFT spectra for compound **8** in acetonitrile.

TDDFT EXCITATION ENERGIES							
STATE*	HARTREE	EV	KCAL/MOL	CM-1	NANOMETERS	OSC. STR.	STATE COMPOSITION**
1A	0.0715750022	1.9477	44.9140	15708.90	636.58	0.3300328	0.960[HL];
1A	0.0814779092	2.2171	51.1282	17882.33	559.21	0.0086628	0.994[(H-1)L]
1A	0.0962768185	2.6198	60.4146	21130.32	473.25	0.4520938	0.941[(H-2)L]
1A	0.1016221837	2.7653	63.7689	22303.49	448.36	0.0000487	0.990[(H-3)L]
1A	0.1017982980	2.7701	63.8794	22342.14	447.58	0.0061648	0.980[(H-4)L]
1A	0.1089797383	2.9655	68.3858	23918.29	418.09	0.0000062	0.902[(H-5)L]; 0.063[(H-6)L]
1A	0.1090497346	2.9674	68.4298	23933.65	417.82	0.0000082	0.903[(H-6)L]; 0.063[(H-5)L]
1A	0.1160606838	3.1582	72.8292	25472.38	392.58	0.0000018	0.774[(H-7)L]; 0.203[H(L+1)]
1A	0.1175924199	3.1999	73.7904	25808.55	387.47	0.0231878	0.980[(H-8)L]
1A	0.1180001678	3.2109	74.0462	25898.04	386.13	0.0013452	0.672[H(L+1)]; 0.185[(H-7)L]
1A	0.1207197973	3.2850	75.7528	26494.93	377.43	0.0000672	
1A	0.1245864383	3.3902	78.1792	27343.56	365.72	0.0023183	
1A	0.1265592245	3.4439	79.4171	27776.54	360.02	0.0022790	
1A	0.1265831557	3.4445	79.4321	27781.79	359.95	0.0257028	
1A	0.1269601489	3.4548	79.6687	27864.53	358.88	0.0113970	
1A	0.1284658673	3.4957	80.6136	28195.00	354.67	0.0001307	
1A	0.1333629559	3.6290	83.6865	29269.79	341.65	0.0076647	
1A	0.1355626171	3.6888	85.0668	29752.56	336.11	0.0023194	
1A	0.1414977729	3.8504	88.7912	31055.17	322.01	0.0007183	
1A	0.1422498437	3.8708	89.2631	31220.23	320.31	0.0001457	
1A	0.1433300861	3.9002	89.9410	31457.32	317.89	0.0045640	
1A	0.1436869087	3.9099	90.1649	31535.63	317.10	0.0541515	
1A	0.1444031841	3.9294	90.6144	31692.84	315.53	0.0106753	
1A	0.1452027698	3.9512	91.1161	31868.32	313.79	0.0017895	
1A	0.1485350166	4.0418	93.2071	32599.67	306.75	0.0177363	
1A	0.1540508361	4.1919	96.6684	33810.25	295.77	0.0001216	
1A	0.1541607026	4.1949	96.7373	33834.36	295.56	0.0000085	
1A	0.1549444652	4.2163	97.2291	34006.38	294.06	0.0031017	
1A	0.1588009272	4.3212	99.6491	34852.77	286.92	0.5220325	0.792[H(L+4)]; 0.063[(H-1)(L+3)]
1A	0.1614753029	4.3940	101.3273	35439.73	282.17	0.0000573	

*It is worthwhile to remember that the symmetry was automatically switched off by the software during the TD-DFT calculation in the presence of a solvent.

**The state composition is defined by reporting the squared coefficients of the excitations from occupied to virtual KS DFT orbitals.