

Butterfly Molecules: How Cross-Stacking Determines Bulk Physical Properties

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Table S1. Values calculated for some relevant dihedral angles (in degrees) in the electronic ground state, S_0 (shown in **Figure 1**). Calculations were carried out both in gas phase and in solution at the B3LYP/6-31G**, B3LYP/6-31+G**, PBE0/6-31G** and PBE0/6-31+G** levels of theory. Compounds **1** and **2** were calculated in tetrahydrofuran (THF) solution and compounds **3** and **4** in dichloromethane (DCM) solution.

Method	Compound	Gas phase				solvent	Solution phase			
		θ_1	θ_2	θ_3	θ_4		θ_1	θ_2	θ_3	θ_4
B3LYP/6-31G**	1	-7.5	-26.5	50.5		THF	-6.2	-25.7	50.4	
	2	-38.2	-66.2	-46.7			-37.7	-66.2	-48.2	
	3	55.8	-55.8	-56.5	56.4	DCM	55.4	-55.2	-56.1	56.1
	4	54.3	55.8	-55.2	58.3		53.5	55.5	-54.8	57.8
B3LYP/6-31+G**	1	-6.0	-24.5	54.6		THF	-5.5	-23.8	54.4	
	2	-39.4	-66.4	-46.6			-38.9	-66.5	-48.0	
	3	58.6	-60.0	-61.4	61.3	DCM	58.0	-59.1	-60.5	60.5
	4	58.1	60.0	-59.9	62.1		57.0	57.7	-59.0	61.4
PBE0/6-31G**	1	-10.9	-28.3	49.0		THF	-9.4	-27.5	48.6	
	2	-37.5	-64.6	-44.7			-36.9	-64.8	-46.5	
	3	54.4	-54.6	-54.2	54.8	DCM	53.8	-54.0	-54.0	54.4
	4	53.2	55.1	-53.7	56.7		52.2	54.8	-53.2	56.1
PBE0/6-31+G**	1	-7.2	-26.9	51.9		THF	-6.0	-25.8	51.7	
	2	-38.6	-64.6	-44.6			-38.0	-64.7	-46.2	
	3	56.6	-58.0	-58.1	58.5	DCM	55.9	-57.0	-57.4	57.7
	4	56.0	56.7	-56.9	59.7		54.8	56.4	-56.1	58.9

Table S2. Selected structural parameters (bond lengths in Å and inter-ring dihedral angles in degrees) calculated for the S₀ and S₁ states in solution at the B3LYP/6-31G**, PBE0/6-31G**, TD-B3LYP/6-31G** and TD-PBE0/6-31G** levels of theory (atom numbering shown in **Figure 1**).

B3LYP/6-31G**									PBE0/6-31G**							
Compound ^a		BOND LENGTH			DIHEDRAL ANGLE			BOND DISTANCE			DIHEDRAL ANGLE					
		S ₀	S ₁	Δ (S ₁ -S ₀)	S ₀	S ₁	Δ(S ₁ -S ₀)	S ₀	S ₁	Δ (S ₁ -S ₀)	S ₀	S ₁	Δ(S ₁ -S ₀)			
1	C19-C20	1.490	1.489	0.001	θ ₁	-6.2	-1.2	5.0	C19-C20	1.483	1.482	0.001	θ ₁	-9.4	-1.1	8.3
	C49-C50	1.490	1.489	0.001	θ ₂	-25.7	-7.3	18.4	C49-C50	1.483	1.482	0.001	θ ₂	-27.6	-7.6	20.0
	C48-C46	1.467	1.418	0.049	θ ₃	50.4	53.1	2.7*	C48-C46	1.463	1.413	0.050	θ ₃	48.6	51.9	3.3*
	C46=C44	1.350	1.392	0.042					C46=C44	1.347	1.388	0.041				
	C44-C43	1.466	1.431	0.035					C44-C43	1.462	1.428	0.034				
	C19-C1	1.397	1.377	0.020					C19-C1	1.394	1.373	0.021				
	C1-C48	1.405	1.435	0.030					C1-C48	1.401	1.430	0.029				
2	C1-C2	1.416	1.450	0.034	θ ₁	-37.7	-34.6	3.1	C1-C2	1.412	1.446	0.034	θ ₁	-36.9	-34.0	2.9
	C2-C4	1.484	1.437	0.047	θ ₂	-66.2	-43.8	22.4	C2-C4	1.478	1.430	0.048	θ ₂	-64.8	-43.0	21.8
	C4=C8	1.354	1.392	0.038	θ ₃	-48.2	-34.5	13.7	C4=C8	1.352	1.388	0.036	θ ₃	-46.5	-33.5	13.0
	C8-C16	1.492	1.475	0.017					C8-C16	1.484	1.468	0.016				
	C8-C9	1.493	1.478	0.015					C8-C9	1.485	1.471	0.014				
	C16-C25	1.406	1.414	0.008					C16-C25	1.402	1.409	0.007				
	C9-C35	1.405	1.411	0.006					C9-C35	1.401	1.406	0.005				
3	C14-C46	1.490	1.468	0.022	θ ₁	55.4	41.2	14.2	C14-C46	1.483	1.462	0.021	θ ₁	53.8	40.5	13.3
	C13-C14	1.418	1.462	0.044	θ ₂	-55.2	-40.4	14.8	C13-C14	1.413	1.456	0.043	θ ₂	-54.0	-39.5	14.5
	C17-C57	1.490	1.467	0.023	θ ₃	-56.1	-45.0	11.1	C17-C57	1.483	1.461	0.022	θ ₃	-54.0	-44.4	9.6
	C17-C18	1.419	1.461	0.042	θ ₄	56.1	46.6	9.5	C17-C18	1.415	1.455	0.040	θ ₄	54.4	46.0	8.4
	C21-C68	1.492	1.480	0.012					C21-C68	1.484	1.474	0.010				
	C21-C3	1.452	1.432	0.020					C21-C3	1.447	1.427	0.020				
	C10-C35	1.491	1.478	0.013					C10-C35	1.484	1.472	0.012				
	C9-C10	1.453	1.435	0.018					C9-C10	1.448	1.429	0.019				
	C6-C22	1.541	1.541	0.000					C6-C22	1.531	1.531	0.000				
4	C4-C22	1.488	1.466	0.022	θ ₁	53.5	41.0	12.5	C4-C22	1.481	1.459	0.022	θ ₁	52.2	40.1	12.1
	C3-C4	1.420	1.461	0.041	θ ₂	55.5	42.5	13.0	C3-C4	1.415	1.455	0.040	θ ₂	54.8	41.9	12.9
	C7-C37	1.489	1.468	0.021	θ ₃	-54.8	-44.8	10.0	C7-C37	1.482	1.461	0.021	θ ₃	-53.3	-44.0	9.3
	C7-C8	1.419	1.463	0.044	θ ₄	57.8	47.7	10.1	C7-C8	1.415	1.457	0.042	θ ₄	56.1	46.7	9.4
	C19-C67	1.490	1.477	0.013					C19-C67	1.483	1.471	0.012				
	C18-C19	1.453	1.434	0.019					C18-C19	1.448	1.429	0.019				
	C11-C52	1.491	1.479	0.012					C11-C52	1.483	1.472	0.011				
	C11-C12	1.454	1.435	0.019					C11-C12	1.449	1.430	0.019				

^a THF was the solvent employed for the calculations of compounds 1 and 2 according with the previous experimental studies. DCM was the solvent used for compounds 3 and 4.

* The dihedral angle increases after excitation.

Table S3. Selected structural parameters (bond lengths in Å and inter-ring dihedral angles in degrees) calculated for the S₀ and S₁ states in solid phase calculated at the B3LYP/6-31G**//UFF and TD-B3LYP/6-31G**//UFF levels of theory (atom numbering is shown in Figure 1).

Compound		BOND LENGTH				DIHEDRAL ANGLE			Crystal ^a
		S ₀	S ₁	Δ (S ₁ -S ₀)		S ₀	S ₁	Δ (S ₁ -S ₀)	
1	C19-C20	1.486	1.482	0.004	θ ₁	-6.4	-1.0	5.4	-24.1(-0.5)
	C49-C50	1.486	1.482	0.004	θ ₂	-18.8	-10.1	8.7	-19.5(18.7)
	C48-C46	1.465	1.426	0.039	θ ₃	46.9	45.3	1.6	55.7(-48.7)
	C46=C44	1.350	1.385	0.035					
	C44-C43	1.464	1.435	0.029					
	C19-C1	1.395	1.380	0.015					
	C1-C48	1.403	1.426	0.023					
2	C1-C2	1.415	1.443	0.028	θ ₁	-28.5	-29.3	0.8*	-31.4(-26.6)
	C2-C4	1.482	1.447	0.035	θ ₂	-65.7	-52.8	12.9	-65.9(-66.7)
	C4=C8	1.354	1.380	0.026	θ ₃	-55.9	-48.2	7.7	-60.3(-53.6)
	C8-C16	1.489	1.473	0.016					
	C8-C9	1.496	1.487	0.009					
	C16-C25	1.408	1.413	0.005					
	C9-C35	1.404	1.409	0.005					
3	C14-C6	1.487	1.472	0.015	θ ₁	55.8	32.5	23.3	53.1(64.0)
	C13-C14	1.417	1.453	0.036	θ ₂	-56.6	-50.8	5.8	-54.5(-61.6)
	C17-C57	1.488	1.462	0.026	θ ₃	60.1	52.4	7.7	-59.8(67.7)
	C17-C18	1.420	1.460	0.040	θ ₄	72.6	69.6	3.0	52.5(70.5)
	C21-C68	1.494	1.481	0.013					
	C21-C3	1.450	1.429	0.021					
	C10-C35	1.498	1.493	0.005					
	C9-C10	1.453	1.433	0.020					
4	C6-C22	1.543	1.543	0.000					
	C4-C22	1.488	1.469	0.019	θ ₁	46.2	43.5	2.7	48.1(-56.2)
	C3-C4	1.425	1.458	0.033	θ ₂	51.2	46.8	4.4	56.2(-48.1)
	C7-C37	1.488	1.470	0.018	θ ₃	-55.7	-49.8	5.9	-58.0(52.9)
	C7-C8	1.420	1.455	0.035	θ ₄	43.1	37.6	5.5	52.9(58.0)
	C19-C67	1.487	1.479	0.008					
	C18-C19	1.448	1.431	0.017					
	C11-C52	1.482	1.468	0.014					
	C11-C12	1.454	1.438	0.016					

^a Refs.19, 21, 22. Experimental crystallographic parameters are also included.

* The dihedral angle increases after excitation. The two conformational structures are separated by parenthesis.

Table S4. Vertical transition energy (E in eV and nm), oscillator strength (f) and main components of the $S_0 \rightarrow S_n$ transitions (% contribution) calculated in gas phase at different levels of theory.

Method	Compound	6-31G**				6-31+G**			
		E/eV(nm)	f	Transition	% contribution	E/eV(nm)	f	Transition	% contribution
TD-B3LYP	1	3.51 (353.5)	1.41	$S_0 \rightarrow S_1$	H→L (99)	3.41 (363.3)	1.34	$S_0 \rightarrow S_1$	H→L (98)
		3.93 (315.4)	0.03	$S_0 \rightarrow S_2$	H-2→L (55) H→L+1 (42)	3.856 (321.5)	0.05	$S_0 \rightarrow S_2$	H→L+1 (49) H-2→L (47)
		4.32 (286.9)	0.31	$S_0 \rightarrow S_4$	H→L +1 (54) H-2→L (43)	4.21 (294.8)	0.26	$S_0 \rightarrow S_4$	H-2→L (50) H→L+1 (47)
	2	2.89 (428.3)	0.35	$S_0 \rightarrow S_1$	H→L (98)	2.84 (436.3)	0.34	$S_0 \rightarrow S_1$	H→L (98)
		3.66 (338.9)	0.01	$S_0 \rightarrow S_2$	H→L+2 (61) H-1→L (37)	3.58 (346.4)	0.02	$S_0 \rightarrow S_2$	H→L+1 (78) H-1→L (19)
	3	3.33 (372.7)	0.50	$S_0 \rightarrow S_1$	H→L (94)	3.28 (377.7)	0.50	$S_0 \rightarrow S_1$	H→L (94)
		3.55 (349.4)	0.00	$S_0 \rightarrow S_2$	H-1→L (49) H→L+1 (48)	3.51 (353.2)	0.00	$S_0 \rightarrow S_2$	H→L+1 (49) H-1→L (47)
		3.97 (312.3)	0.15	$S_0 \rightarrow S_3$	H→L+2 (73) H→L+1 (17)	3.87 (320.1)	0.13	$S_0 \rightarrow S_3$	H→L+2 (75) H→L+1 (17)
		4.11 (301.8)	0.34	$S_0 \rightarrow S_4$	H-2→L (57) H-1→L (23) H→L+1 (14)	4.06 (305.0)	0.40	$S_0 \rightarrow S_4$	H-2→L (45) H-1→L (28) H→L+1 (17)
		4.29 (288.6)	0.23	$S_0 \rightarrow S_5$	H-2→L (38) H-1→L (19) H→L+1 (18) H→L+2(18)	4.23 (293.4)	0.17	$S_0 \rightarrow S_5$	H-2→L (48) H-1→L (14) H→L+1 (14) H→L+2 (14)
		3.13 (396.1)	0.60	$S_0 \rightarrow S_1$	H→L (96)	3.09 (400.6)	0.59	$S_0 \rightarrow S_1$	H→L (96)
	4	3.46 (358.6)	0.01	$S_0 \rightarrow S_2$	H-1→L (51) H→L+1 (40)	3.42 (362.3)	0.01	$S_0 \rightarrow S_2$	H-1→L (47) H→L+1 (44)
		3.73 (332.7)	0.19	$S_0 \rightarrow S_3$	H-2→L (53) H-1→L (25) H→L+1 (13)	3.70 (334.8)	0.27	$S_0 \rightarrow S_3$	H-2→L (42) H-1→L (32) H→L+1 (17)
		3.84 (322.5)	0.44	$S_0 \rightarrow S_4$	H-2→L (41) H→L+1 (24) H-1→L (19)	3.77 (328.5)	0.11	$S_0 \rightarrow S_4$	H→L+6 (81)
		3.87 (320.4)	0.02	$S_0 \rightarrow S_5$	H→L+2 (80)	3.82 (324.2)	0.28	$S_0 \rightarrow S_5$	H-2→L (51) H-1→L (15) H→L+1 (13) H-4→L (13)
		4.20 (295.2)	0.14	$S_0 \rightarrow S_8$	H-4→L (25) H→L+5 (18) H→L+1 (11) H→L+2 (10)	4.08 (304.1)	0.02	$S_0 \rightarrow S_8$	H→L+4 (32) H-5→L (31) H→L+5 (13) H→L+3 (12)
		3.61 (343.1)	1.47	$S_0 \rightarrow S_1$	H→L (99)	3.53 (351.6)	1.40	$S_0 \rightarrow S_1$	H→L (98)
	1	4.49 (276.3)	0.37	$S_0 \rightarrow S_4$	H→L +1 (55) H-2→L (43)	4.38 (283.1)	0.31	$S_0 \rightarrow S_4$	H-2→L (74) H→L+2 (24)
TD-PBE0	2	2.98 (416.5)	0.37	$S_0 \rightarrow S_1$	H→L (99)	2.75 (450.9)	0.37	$S_0 \rightarrow S_1$	H→L (98)
	3	3.42 (362.9)	0.53	$S_0 \rightarrow S_1$	H→L (95)	3.38 (367.3)	0.52	$S_0 \rightarrow S_1$	H→L (95)

	4.10 (302.3)	0.23	$S_0 \rightarrow S_3$	$H \rightarrow L+2$ (68) $H \rightarrow L+1$ (21)	4.01 (308.9)	0.18	$S_0 \rightarrow S_3$	$H \rightarrow L+2$ (71) $H \rightarrow L+1$ (19)
	4.24 (292.1)	0.32	$S_0 \rightarrow S_4$	$H-2 \rightarrow L$ (52) $H-1 \rightarrow L$ (23) $H \rightarrow L+2$ (11)	4.20 (295.0)	0.41	$S_0 \rightarrow S_4$	$H-2 \rightarrow L$ (42) $H-1 \rightarrow L$ (28) $H \rightarrow L+1$ (14) $H \rightarrow L+2$ (11)
	4.42 (280.6)	0.24	$S_0 \rightarrow S_5$	$H-2 \rightarrow L$ (40) $H-1 \rightarrow L$ (19) $H \rightarrow L+1$ (18) $H \rightarrow L+2$ (17)	4.36 (284.5)	0.19	$S_0 \rightarrow S_5$	$H-2 \rightarrow L$ (52) $H-1 \rightarrow L$ (15) $H \rightarrow L+1$ (15) $H \rightarrow L+2$ (12)
	3.22 (384.8)	0.64	$S_0 \rightarrow S_1$	$H \rightarrow L$ (96)	3.19 (388.7)	0.63	$S_0 \rightarrow S_1$	$H \rightarrow L$ (96)
	3.87 (320.2)	0.31	$S_0 \rightarrow S_3$	$H-2 \rightarrow L$ (41) $H-1 \rightarrow L$ (34) $H \rightarrow L+1$ (16)	3.85 (322.4)	0.40	$S_0 \rightarrow S_3$	$H-1 \rightarrow L$ (38) $H-2 \rightarrow L$ (32) $H \rightarrow L+1$ (20)
	3.99 (310.4)	0.40	$S_0 \rightarrow S_4$	$H-2 \rightarrow L$ (39) $H \rightarrow L+2$ (29) $H \rightarrow L+1$ (20)	3.92 (316.3)	0.04	$S_0 \rightarrow S_4$	$H \rightarrow L+2$ (80)
4	4.01(309.5)	0.03	$S_0 \rightarrow S_5$	$H \rightarrow L+2$ (53) $H-2 \rightarrow L$ (18) $H-5 \rightarrow L$ (16)	3.98 (311.5)	0.30	$S_0 \rightarrow S_5$	$H-2 \rightarrow L$ (61) $H-1 \rightarrow L$ (14) $H \rightarrow L+1$ (12)
	4.35 (284.8)	0.21	$S_0 \rightarrow S_8$	$H-4 \rightarrow L$ (47) $H \rightarrow L+1$ (15) $H \rightarrow L+2$ (13)	4.26 (291.1)	0.05	$S_0 \rightarrow S_8$	$H-5 \rightarrow L$ (41), $H \rightarrow L+5$ (14) $H \rightarrow L+4$ (14)

Table S5. Vertical transition energy (E in eV and nm), oscillator strength (f), and main components of the $S_0 \rightarrow S_n$ transitions (% contribution) calculated at the **TD-B3LYP** level of theory for compounds **1** and **2** in tetrahydrofuran (THF) solution and for compounds **3** and **4** in dichloromethane (DCM) solution. Results from Linear Response (LR) and State Specific (SS) approaches are compared.

Method	Compound	LR approximation				SS approximation			
		E/eV(nm)	f	Transition	% contribution	E/eV(nm)	f	Transition	% contribution
6-31G**	1	3.15 (393.6)	1.64	$S_0 \rightarrow S_1$	H→L (99)	3.26 (380.7)	1.45	$S_0 \rightarrow S_1$	H→L (100)
		4.01 (308.9)	0.44	$S_0 \rightarrow S_4$	H-2→L (49), H→L+1 (49)	4.05 (306.1)	0.35	$S_0 \rightarrow S_4$	H-2→L (50), H→L+1 (48)
	2	2.76 (449.5)	0.46	$S_0 \rightarrow S_1$	H→L (98)	2.80 (443.3)	0.39	$S_0 \rightarrow S_1$	H→L (98)
		3.15 (393.7)	0.71	$S_0 \rightarrow S_1$	H→L (97)	3.21 (386.1)	0.54	$S_0 \rightarrow S_1$	H→L (95)
	3	3.84 (323.2)	0.33	$S_0 \rightarrow S_3$	H→L+2 (56), H→L+1 (27) H-1→L (15)	3.82 (324.5)	0.16	$S_0 \rightarrow S_3$	H→L+2 (62), H→L+1 (25)
		3.98 (311.4)	0.37	$S_0 \rightarrow S_4$	H-2→L (52), H-1→L (23) H→L+2 (14)	3.91 (317.0)	0.54	$S_0 \rightarrow S_4$	H→L (95)
		4.17 (297.2)	0.32	$S_0 \rightarrow S_5$	H-2→L (44), H→L+2 (23) H-1→L (15), H→L+1 (11)	4.20 (295.4)	0.31	$S_0 \rightarrow S_5$	H-2→L (37), H→L+2 (20) H-1→L (20), H→L+1 (14)
		3.05 (406.4)	0.75	$S_0 \rightarrow S_1$	H→L (97)	3.08 (402.2)	0.59	$S_0 \rightarrow S_1$	H→L (96)
		3.65 (340.1)	0.30	$S_0 \rightarrow S_3$	H-2→L (46), H-1→L (29) H→L+1 (18)	3.45 (359.1)	0.13	$S_0 \rightarrow S_3$	H→L+2 (40), H-2→L (29) H→L+1 (23)
		3.74 (331.9)	0.48	$S_0 \rightarrow S_4$	H-2→L (51), H→L+1 (22) H-1→L (16)	3.46 (358.5)	0.14	$S_0 \rightarrow S_4$	H-1→L (40), H-2→L (29) H→L+1 (23)
		4.18 (296.5)	0.28	$S_0 \rightarrow S_8$	H-5→L (57), H→L+1 (14) H→L+2 (13)	3.74 (332.0)	0.02	$S_0 \rightarrow S_8$	H→L+2 (39), H→L+3 (38)
	4	3.05 (406.5)	1.65	$S_0 \rightarrow S_1$	H→L (99)	3.22 (385.3)	1.44	$S_0 \rightarrow S_1$	H→L (99)
		3.95 (314.1)	0.31	$S_0 \rightarrow S_4$	H-2→L (54), H→L+1 (44)	3.94 (314.6)	0.00	$S_0 \rightarrow S_4$	H→L+1 (49), H-1→L (42)
		3.95 (314.0)	0.00	$S_0 \rightarrow S_5$	H→L+2 (56), H-1→L (38)	4.17 (297.7)	0.24	$S_0 \rightarrow S_5$	H-2→L (52), H→L+2 (45)
	2	2.71 (457.2)	0.44	$S_0 \rightarrow S_1$	H→L (98)	2.75 (451.2)	0.37	$S_0 \rightarrow S_1$	H→L (98)
		3.41 (363.2)	0.02	$S_0 \rightarrow S_2$	H→L+1 (81), H-2→L (16)	3.19 (388.6)	0.00	$S_0 \rightarrow S_2$	H→L+1 (95)
	3	3.16 (392.7)	0.70	$S_0 \rightarrow S_1$	H→L (96)	3.22 (385.3)	0.53	$S_0 \rightarrow S_1$	H→L (95)
		3.79 (327.3)	0.18	$S_0 \rightarrow S_3$	H→L+2 (69), H→L+1 (19)	3.77 (329.3)	0.09	$S_0 \rightarrow S_3$	H→L+2 (72), H→L+1 (19)

	3.99 (310.8)	0.59	$S_0 \rightarrow S_4$	H-1 $\rightarrow$ L (35), H-2 $\rightarrow$ L (32) H $\rightarrow$ L+1 (14), H-1 $\rightarrow$ L+2(13)	3.94 (314.6)	0.29	$S_0 \rightarrow S_4$	H-2 $\rightarrow$ L (56), H-1 $\rightarrow$ L (28)
	4.14 (299.7)	0.20	$S_0 \rightarrow S_5$	H-2 $\rightarrow$ L (61), H $\rightarrow$ L+2 (12) H $\rightarrow$ L+1 (11)	4.17 (297.7)	0.24	$S_0 \rightarrow S_5$	H-2 $\rightarrow$ L (45), H-1 $\rightarrow$ L (17) H $\rightarrow$ L+2 (14), H $\rightarrow$ L+1 (13)
	3.07 (403.9)	0.74	$S_0 \rightarrow S_1$	H$\rightarrow$L (97)	3.11 (399.3)	0.57	$S_0 \rightarrow S_1$	H$\rightarrow$L (95)
	3.67 (338.1)	0.40	$S_0 \rightarrow S_3$	H-1 $\rightarrow$ L (38), H-2 $\rightarrow$ L (35) H $\rightarrow$ L+1 (20)	3.44 (360.26)	0.15	$S_0 \rightarrow S_3$	H-1 $\rightarrow$ L (49), H $\rightarrow$ L+1 (24) H-2 $\rightarrow$ L (20)
4	3.74 (331.4)	0.31	$S_0 \rightarrow S_4$	H-2 $\rightarrow$ L (63), H-1 $\rightarrow$ L (15) H $\rightarrow$ L+1 (14)	3.52 (352.8)	0.22	$S_0 \rightarrow S_4$	H-1 $\rightarrow$ L (41), H $\rightarrow$ L+1 (25) H-2 $\rightarrow$ L (17)
	4.11 (301.7)	0.23	$S_0 \rightarrow S_8$	H-5 $\rightarrow$ L (45), H $\rightarrow$ L+1 (13)	3.97 (312.8)	0.01	$S_0 \rightarrow S_8$	H-4 $\rightarrow$ L (84)

Table S6. Vertical transition energy (E in eV and nm), oscillator strength (f), and main components of the $S_0 \rightarrow S_n$ transition (% contribution) calculated at the **TD-PBE0** level of theory for compounds **1** and **2** in tetrahydrofuran (THF) solution and for compounds **3** and **4** in dichloromethane (DCM) solution. Results from Linear Response (LR) and State Specific (SS) approaches are compared.

Method	Compound	LR approximation				SS approximation			
		E/eV(nm)	f	Transition	% contribution	E/eV(nm)	f	Transition	% contribution
6-31G**	1	3.28 (377.6)	1.66	$S_0 \rightarrow S_1$	H→L (99)	3.39 (365.8)	1.46	$S_0 \rightarrow S_1$	H→L (99)
		4.17 (297.1)	0.55	$S_0 \rightarrow S_4$	H-2→L (52) H→L+1(46)	4.22 (294.1)	0.44	$S_0 \rightarrow S_4$	H-2→L (51), H→L+1 (47)
	2	2.82 (440.0)	0.50	$S_0 \rightarrow S_1$	H→L (98)	2.86 (433.7)	0.42	$S_0 \rightarrow S_1$	H→L (98)
		3.23 (384.2)	0.75	$S_0 \rightarrow S_1$		3.29 (376.6)	0.58	$S_0 \rightarrow S_1$	H→L (96)
	3	3.94 (314.4)	0.42	$S_0 \rightarrow S_3$	H→L+2 (50) H→L+1 (30) H-1→L (18)	3.94 (314.9)	0.21	$S_0 \rightarrow S_3$	H→L+2 (58), H→L+1 (28)
		4.12 (301.2)	0.37	$S_0 \rightarrow S_4$	H-2→L (45) H-1→L (24) H→L+2 (21)	4.07 (305.2)	0.20	$S_0 \rightarrow S_4$	H-2→L (57), H-1→L (23) H→L+2 (12)
		4.30 (288.5)	0.32	$S_0 \rightarrow S_5$	H-2→L (50) H→L+2 (21) H-1→L (14) H→L+1 (11)	4.33 (286.4)	0.33	$S_0 \rightarrow S_5$	H-2→L (40), H→L+2 (21) H-1→L (19), H→L+1 (14)
		3.13 (395.7)	0.80	$S_0 \rightarrow S_1$	H→L (97)	3.17 (391.4)	0.63	$S_0 \rightarrow S_1$	H→L (96)
		3.78 (328.2)	0.53	$S_0 \rightarrow S_3$	H-1→L (41) H→L+1 (28) H-2→L (23)	3.59 (354,37)	0.23	$S_0 \rightarrow S_3$	H-1→L (50), H→L+1 (22) H-2→L (20)
	4	3.89 (319.0)	0.42	$S_0 \rightarrow S_4$	H-2→L (69) H→L+1 (16) H-1→L (10)	3.65 (339.8)	0.26	$S_0 \rightarrow S_4$	H-1→L (42), H-2→L (27) H→L+1 (20)
		4.33 (286.4)	0.27	$S_0 \rightarrow S_8$	H-5→L (62) H→L+1 (13) H→L+2 (12)	4.35 (285.4)	0.25	$S_0 \rightarrow S_8$	H-5→L (56), H→L+1 (15) H→L+2 (12)
	1	3.19 (389.1)	1.67	$S_0 \rightarrow S_1$	H→L (99)	3.30 (376.4)	1.47	$S_0 \rightarrow S_1$	H→L (99)
		4.10 (302.1)	0.42	$S_0 \rightarrow S_5$	H-2→L (58) H→L+2 (40)	4.14 (299.6)	0.32	$S_0 \rightarrow S_5$	H-2→L (54), H→L+2 (43)
	2	2.77 (447.5)	0.48	$S_0 \rightarrow S_1$	H→L (98)	2.84 (437.4)	0.39	$S_0 \rightarrow S_1$	H→L (98)
	3	3.23 (384.4)	0.75	$S_0 \rightarrow S_1$	H→L (97)	3.29 (376.8)	0.57	$S_0 \rightarrow S_1$	H→L (95)
		3.90 (318.3)	0.27	$S_0 \rightarrow S_3$	H→L+2 (61) H→L+1 (24) H-1→L (12)	3.88 (319.4)	0.14	$S_0 \rightarrow S_3$	H→L+2 (65), H→L+1 (24)
		4.11 (301.8)	0.59	$S_0 \rightarrow S_4$	H-1→L (35) H-2→L (30)	4.08 (304.3)	0.31	$S_0 \rightarrow S_4$	H-2→L (50), H-1→L (30)

6-31+G**	H→L+2 (20) H→L+1 (10)							
	4.27 (290.6)	0.22	$S_0 \rightarrow S_5$	H-2→L (64) H→L+2 (12) H-1→L (10)	4.30 (288.6)	0.28	$S_0 \rightarrow S_5$	H-2→L (46), H-1→L (18) H→L+2 (16), H→L+1 (13)
4	3.14 (394.8)	0.79	$S_0 \rightarrow S_1$	H→L (97)	3.18 (390.0)	0.62	$S_0 \rightarrow S_1$	H→L (96)
	3.79 (327.3)	0.60	$S_0 \rightarrow S_3$	H-1→L (47) H→L+1 (23) H-2→L (21)	3.55 (349.3)	0.22	$S_0 \rightarrow S_3$	H-1→L (60) H→L+1 (20) H-2→L (13)
	3.89 (318.5)	0.30	$S_0 \rightarrow S_4$	H-2→L (75) H→L+1 (10) H-1→L (9)	3.65 (340.0)	0.36	$S_0 \rightarrow S_4$	H-1→L (54), H-1→L (25) H-5→L (10)
	4.07 (304.6)	0.01	$S_0 \rightarrow S_6$	H-3→L (98)	3.65 (340.0)	0.36	$S_0 \rightarrow S_6$	H-1→L (54), H-1→L (25) H-5→L (10)
	4.27 (290.3)	0.22	$S_0 \rightarrow S_8$	H-6→L (58), H→L+1 (12)	4.15 (298.9)	0.01	$S_0 \rightarrow S_8$	H-4→L (83)

Table S7. Vertical transition energy (E in eV and nm), oscillator strength (f), and main components of the transitions (% contribution) calculated with ONIOM at the TD-B3LYP/6-31G**//UFF level in a molecular cluster mimicking the solid state.

Compound	E/eV(nm)	f	Transition	% contribution
1	3.19 (388.5)	1.48	$S_0 \rightarrow S_1$	H $\rightarrow$ L (100)
	3.97 (312.2)	0.34	$S_0 \rightarrow S_4$	H-2 $\rightarrow$ L (56) H $\rightarrow$ L+1 (43)
2	2.79 (444.3)	0.41	$S_0 \rightarrow S_1$	H $\rightarrow$ L (98)
	3.26 (380.3)	0.56	$S_0 \rightarrow S_1$	H $\rightarrow$ L (95)
3	3.95 (313.6)	0.10	$S_0 \rightarrow S_3$	H $\rightarrow$ L+2 (79) H $\rightarrow$ L+1 (11)
	4.12 (301.0)	0.35	$S_0 \rightarrow S_4$	H-2 $\rightarrow$ L (59)
				H-1 $\rightarrow$ L (21)
				H $\rightarrow$ L+1 (14)
	4.23 (293.3)	0.29	$S_0 \rightarrow S_5$	H-2 $\rightarrow$ L (34) H $\rightarrow$ L+1 (20)
				H-1 $\rightarrow$ L (23) H $\rightarrow$ L+2 (14)
4	3.02 (410.0)	0.63	$S_0 \rightarrow S_1$	H $\rightarrow$ L (96)
	3.65 (339.8)	0.28	$S_0 \rightarrow S_3$	H-2 $\rightarrow$ L (44) H-1 $\rightarrow$ L (32)
				H $\rightarrow$ L+1 (17)
	3.74 (331.2)	0.31	$S_0 \rightarrow S_4$	H $\rightarrow$ L+2 (54) H $\rightarrow$ L+1 (21)
				H-2 $\rightarrow$ L (17)
	3.81 (325.5)	0.18	$S_0 \rightarrow S_5$	H-2 $\rightarrow$ L (35) H $\rightarrow$ L+2 (28)
				H-2 $\rightarrow$ L (19)
	4.15 (298.5)	0.13	$S_0 \rightarrow S_8$	H-3 $\rightarrow$ L (97)

Table S8. The vertical transition energies (E in eV and nm), oscillator strength (f), and main components of the $S_1 \rightarrow S_0$ transition (% contribution) calculated in solution with Linear Response (LR-PCM) and State Specific (SS-PCM) approaches at different levels of theory. Experimental results also shown for comparison.

Compound	Appr.	TD-B3LYP/6-31G**			TD-PBE0/6-31G**			Exp. Solution	
		E/eV(nm)	f	% contribution	E/eV(nm)	f	% contribution	λ_{max} (nm)	Φ_F
1	LR-PCM	2.41 (515.4)	2.12	H $\rightarrow$ L (100)	2.48 (500.3)	2.14	H $\rightarrow$ L (100)	400, 423 ^a	0.95
	SS-PCM	2.71 (457.8)	1.76	H $\rightarrow$ L (100)	2.78 (446.1)	1.78	H $\rightarrow$ L (100)		
2	LR-PCM	1.90 (654.2)	0.91	H $\rightarrow$ L (100)	1.93 (642.3)	0.94	H $\rightarrow$ L (100)	528 ^b	0.17
	SS-PCM	2.06 (601.4)	0.68	H $\rightarrow$ L (100)	2.10 (590.3)	0.70	H $\rightarrow$ L (100)		
3	LR-PCM	2.54 (488.2)	1.01	H $\rightarrow$ L (99)	2.61 (475.3)	1.06	H $\rightarrow$ L (99)	412 ^c	0.92
	SS-PCM	2.72 (455.9)	0.63	H $\rightarrow$ L (98)	2.79 (443.8)	0.66	H $\rightarrow$ L (98)		
4	LR-PCM	2.47 (501.5)	1.04	H $\rightarrow$ L (99)	2.54 (488.2)	1.08	H $\rightarrow$ L (99)	421 ^c	0.90
	SS-PCM	2.64 (470.2)	0.67	H $\rightarrow$ L (98)	2.71 (457.4)	0.70	H $\rightarrow$ L (98)		

^aRef.20; ^bRef.21; ^cRef.22.

Table S9. The vertical transition energies (E in eV and nm), oscillator strength (f), and main components of the $S_1 \rightarrow S_0$ transition (% contribution) for solid-phase calculated with ONIOM at the TD-B3LYP/6-31G**//UFF level in a molecular cluster mimicking the solid state. Experimental results also shown for comparison.

Compound	E / eV(nm) <i>calc.</i>	f	Transition	% contribution	E / eV(nm) <i>exp.</i>	Φ_F
1	2.76 (449.9)	1.66	$S_1 \rightarrow S_0$	H $\rightarrow$ L (100)	2.79 (444) ^a	-
2	2.22 (559.3)	0.59	$S_1 \rightarrow S_0$	H $\rightarrow$ L (100)	2.39 (518) ^b	0.60 (crystal)
3	2.79 (445.1)	0.64	$S_1 \rightarrow S_0$	H $\rightarrow$ L (98)	3.02 (410) ^c	0.75 (film)
4	2.69 (461.4)	0.67	$S_1 \rightarrow S_0$	H $\rightarrow$ L (98)	2.80 (443) ^c	0.72 (film)

^aRef.20; ^bRef.21; ^cRef.22.

Table S10. Selected normal modes ν_i (in cm^{-1}) of the ground state with reorganization energy λ_i (≥ 5 meV) for the S_0 - S_1 relaxation in solution at different levels of theory.

1		2		3		4	
B3LYP/6-31G**		PBE0/6-31G**		B3LYP/6-31G**		PBE0/6-31G**	
ν_i	λ_i	ν_i	λ_i	ν_i	λ_i	ν_i	λ_i
19	18	13	13	28	43	26	38
43	7	46	12	46	41	45	21
95	14	74	5	51	18	49	34
143	6	94	16	62	16	62	14
158	18	143	9	109	7	108	7
257	5	162	19	242	8	241	7
1191	11	261	8	381	6	382	5
1208	5	1209	15	399	15	402	16
1313	8	1321	6	491	15	490	18
1326	10	1344	15	633	5	631	5
1351	12	1368	12	657	13	659	14
1370	8	1592	5	877	5	891	11
1622	44	1649	29	888	10	1481	6
1635	53	1665	77	1305	40	1543	5
1692	40	1717	50	1528	9	1632	46
				1603	46	1651	6
				1625	6	1688	14
				1651	9	1695	35
				1654	6		
				1662	22		
				1667	15		
λ_1 (eV)	0.304	0.328		0.404	0.403	0.245	0.247
λ_2 (eV)	0.376	0.426		0.509	0.524	0.301	0.305
λ_{total} (eV)*	0.680	0.754		0.913	0.927	0.546	0.552

* $\lambda_{\text{total}} = \lambda_1$ (ground state) + λ_2 (excited state)

Table S11. The ground molecular orbital energies (E_{HOMO} and E_{LUMO} in eV) and energy gap (E_{H-L} in eV) calculated in gas phase, tetrahydrofuran (THF) for compounds **1** and **2**, and dichloromethane (DCM) for compounds **3** and **4** at different levels of theory.

Method	Compound	Gas phase			Solution		
		E_{HOMO}	E_{LUMO}	E_{H-L}	E_{HOMO}	E_{LUMO}	E_{H-L}
B3LYP/6-31G**	1	-5.207	-1.698	3.51	-5.320	-1.822	3.50
	2	-4.928	-1.769	3.16	-5.099	-1.933	3.17
	3	-5.030	-1.605	3.42	-5.204	-1.784	3.42
	4	-4.762	-1.401	3.36	-5.013	-1.672	3.34
PBE0/6-31G**	1	-5.474	-1.612	3.86	-5.609	-1.761	3.85
	2	-5.142	-1.716	3.43	-5.344	-1.908	3.44
	3	-5.262	-1.558	3.70	-5.469	-1.771	3.70
	4	-4.982	-1.342	3.64	-5.266	-1.651	3.61
B3LYP/6-31+G**	1	-5.465	-2.041	3.42	-5.547	-2.131	3.42
	2	-5.220	-2.101	3.12	-5.351	-2.223	3.13
	3	-5.319	-1.867	3.45	-5.456	-2.013	3.44
	4	-5.067	-1.675	3.39	-5.285	-1.912	3.37
PBE0/6-31+G**	1	-5.675	-1.896	3.78	-5.782	-2.017	3.76
	2	-5.379	-1.995	3.38	-5.544	-2.149	3.39
	3	-5.491	-1.768	3.72	-5.664	-1.952	3.71
	4	-5.224	-1.564	3.66	-5.476	-1.841	3.63

Table S12. Optimized structural parameters, bond length (in Å) and inter-ring dihedral angle (θ_i in degrees), for the neutral, anion and cation structures of compounds **1**, **2**, **3** and **4**, estimated in gas phase at the B3LYP/6-31G** level of theory. The absolute value differences between the Neutral and Anion $|\Delta(\text{N-A})|$ and Neutral and Cation $|\Delta(\text{N-C})|$ have been included for comparison.

Neutral and Cation $ \Delta(\text{N-C}) $ have been included for comparison.												
Compound		BOND DISTANCE					DIHEDRAL ANGLE					
		Neutral	Anion	Cation	$ \Delta(\text{N-A}) $	$ \Delta(\text{N-C}) $		Neutral	Anion	Cation	$ \Delta(\text{N-A}) $	$ \Delta(\text{N-C}) $
1	<i>C19-C20</i>	1.490	1.489	1.487	0.001	0.003	θ_1	-7.5	-2.1	-1.5	5.4	6.0
	<i>C49-C50</i>	1.490	1.489	1.487	0.001	0.003	θ_2	-26.5	-10.38	-11.3	16.1	15.2
	<i>C48-C46</i>	1.467	1.432	1.433	0.035	0.034	θ_3	50.5	50.7	53.5	0.2*	3.0*
	<i>C46=C44</i>	1.350	1.377	1.374	0.027	0.024						
	<i>C44-C43</i>	1.466	1.444	1.442	0.022	0.024						
	<i>C19-C1</i>	1.397	1.385	1.382	0.012	0.015						
	<i>C1-C48</i>	1.405	1.424	1.420	0.019	0.015						
2	<i>C1-C2</i>	1.416	1.442	1.437	0.026	0.021	θ_1	-38.2	-35.8	-36.3	2.4	1.9
	<i>C2-C4</i>	1.484	1.447	1.455	0.037	0.029	θ_2	-66.2	-45.5	-52.8	20.7	13.4
	<i>C4=C8</i>	1.355	1.384	1.375	0.029	0.020	θ_3	-46.7	-33.3	-40.6	13.4	6.1
	<i>C8-C16</i>	1.492	1.481	1.480	0.011	0.012						
	<i>C8-C9</i>	1.492	1.484	1.483	0.008	0.009						
	<i>C16-C25</i>	1.406	1.413	1.410	0.007	0.004						
	<i>C9-C35</i>	1.404	1.409	1.407	0.005	0.003						
3	<i>C14-C46</i>	1.490	1.477	1.477	0.013	0.013	θ_1	55.8	43.7	49.4	12.1	6.4
	<i>C13-C14</i>	1.418	1.447	1.442	0.029	0.024	θ_2	-55.8	-43.3	-48.8	12.5	7.0
	<i>C17-C57</i>	1.490	1.476	1.477	0.014	0.013	θ_3	-56.5	-46.7	-49.5	9.8	7.0
	<i>C17-C18</i>	1.419	1.447	1.442	0.028	0.023	θ_4	56.4	47.7	50.5	8.7	5.9
	<i>C21-C68</i>	1.491	1.484	1.482	0.007	0.009						
	<i>C21-C3</i>	1.451	1.438	1.438	0.013	0.013						
	<i>C10-C35</i>	1.491	1.483	1.482	0.008	0.009						
	<i>C9-C10</i>	1.452	1.440	1.439	0.012	0.013						
4	<i>C6-C22</i>	1.541	1.543	1.539	0.002	0.002						
	<i>C4-C22</i>	1.488	1.477	1.472	0.011	0.016	θ_1	54.3	45.4	46.1	8.9	8.2
	<i>C3-C4</i>	1.420	1.466	1.442	0.046	0.022	θ_2	55.8	46.6	48.1	9.2	7.7
	<i>C7-C37</i>	1.489	1.479	1.473	0.010	0.016	θ_3	-55.2	-49.2	-46.7	6.0	8.5
	<i>C7-C8</i>	1.419	1.447	1.443	0.028	0.024	θ_4	58.3	51.8	49.8	6.5	8.5
	<i>C19-C67</i>	1.490	1.485	1.477	0.005	0.013						
	<i>C18-C19</i>	1.452	1.437	1.443	0.015	0.009						
	<i>C11-C52</i>	1.490	1.486	1.479	0.004	0.011						
	<i>C11-C12</i>	1.453	1.438	1.443	0.015	0.010						

*The dihedral angle increases from neutral to charged state.

Table S13. Selected normal modes ν_i (in cm^{-1}) of the ground state with reorganization energy (≥ 5 meV) for holes (λ_+) and electrons (λ_-) at the B3LYP/6-31G** level in gas phase.

1				2				3				4			
ν_i	λ_-	ν_i	λ_+	ν_i	λ_-	ν_i	λ_+	ν_i	λ_-	ν_i	λ_+	ν_i	λ_-	ν_i	λ_+
17	11	17	12	27	65	27	10	47	9	1325	6	11	5	11	8
94	21	45	7	46	47	35	5	50	17	1384	9	49	10	49	8
159	10	94	5	63	17	46	11	140	5	1656	5	64	5	1384	8
213	0	143	13	146	5	51	6	210	10	1664	21	173	7	1661	25
1192	9	159	12	382	6	109	6	1325	8			1295	6		
1328	5	213	0	400	14	140	5	1384	7			1322	8		
1625	26	215	0	491	6	242	5	1656	8			1384	7		
1638	28	240	5	657	7	491	11	1658	5			1559	5		
1694	14	673	5	1307	19	889	7	1664	13			1661	20		
		1351	6	1606	18	1307	16								
		1563	5	1627	5	1530	5								
		1625	12	1654	10	1606	23								
		1638	13	1657	5	1663	8								
		1694	20	1663	9										
				1669	5										
$\lambda_1(\text{eV})$	0.175		0.162		0.292		0.163		0.144		0.099		0.138		0.133
$\lambda_2(\text{eV})$	0.196		0.159		0.349		0.181		0.174		0.107		0.149		0.150
$\lambda_{\text{total}}(\text{eV})^*$	0.371		0.321		0.641		0.344		0.318		0.206		0.287		0.283

* $\lambda_{\text{total}} = \lambda_1$ (ground state) + λ_2 (charged state)

Table S14. Selected normal modes ν_i (in cm^{-1}) of the ground state with reorganization energy (≥ 5 meV) for holes (λ_+) and electrons (λ_-) at the PBE0/6-31G** level in gas phase.

1				2				3				4			
ν_i	λ_-	ν_i	λ_+	ν_i	λ_-	ν_i	λ_+	ν_i	λ_-	ν_i	λ_+	ν_i	λ_-	ν_i	λ_+
15	13	15	14	26	68	26	7	50	7	1402	9	11	5	11	7
46	6	46	11	46	51	34	6	51	19	1696	26	51	7	51	5
94	23	143	16	64	15	46	8	141	5			65	7	65	5
163	13	163	10	147	5	50	5	212	10			174	8	1403	8
262	6	243	8	241	5	109	5	1352	6			1353	8	1665	5
1209	6	262	6	383	6	490	12	1402	6			1403	5	1692	28
1368	7	672	5	403	14	659	5	1685	6			1576	5		
1652	17	1212	5	490	8	892	7	1696	19			1692	20		
1668	42	1345	7	659	8	1329	13								
1719	7	1368	5	1329	16	1545	5								
1719	12	1594	6	1635	18	1635	24								
		1652	8	1654	5	1691	6								
		1668	21	1681	5	1697	8								
		1719	9	1691	9										
		1719	16	1697	13										
$\lambda_1(\text{eV})$	0.192		0.181		0.300		0.161		0.146		0.103		0.141		0.138
$\lambda_2(\text{eV})$	0.218		0.180		0.373		0.175		0.174		0.108		0.151		0.149
$\lambda_{\text{total}}(\text{eV})^*$	0.410		0.361		0.673		0.336		0.320		0.211		0.292		0.287

* $\lambda_{\text{total}} = \lambda_1$ (ground state) + λ_2 (charged state)

Table S15. Harmonic vibrational wavenumbers (cm⁻¹) for the isolated molecule (B3LYP/6-31G**) in solution and the molecule in the cluster ONIOM(B3LYP/6-31G**):UFF) for the ground S₀ and excited S₁ states.

Compound 1				Compound 2				Compound 3				Compound 4			
Isolated molecule		Cluster		Isolated molecule		Cluster		Isolated		Cluster		Isolated		Cluster	
S ₀	S ₁	S ₀	S ₁	S ₀	S ₁	S ₀	S ₁	S ₀	S ₁	S ₀	S ₁	S ₀	S ₁	S ₀	S ₁
14	12	74	74	14	8	56	57	17	15	70	69	11	10	62	61
19	28	80	79	17	16	63	66	18	21	71	71	14	13	65	63
19	29	85	85	27	28	71	72	28	35	74	78	23	23	65	64
28	35	91	91	28	30	72	73	37	36	82	81	24	27	67	65
34	36	95	96	35	33	78	75	43	49	83	82	27	29	71	66
37	38	95	97	46	49	86	87	43	51	87	92	28	30	74	70
43	46	99	101	46	54	88	89	48	54	96	97	32	34	77	75
48	49	104	105	51	57	96	97	50	60	98	103	41	43	80	84
57	59	108	115	62	61	104	100	55	61	99	107	46	50	91	87
71	69	117	117	62	66	112	110	59	64	110	115	49	51	103	100
95	97	134	136	64	70	120	114	61	69	118	117	53	58	105	103
95	107	142	147	72	84	121	123	71	73	123	122	55	61	111	104
111	119	146	149	79	87	124	125	78	89	133	131	65	71	116	112
143	147	154	155	109	96	132	127	86	92	135	134	73	78	120	118
149	159	176	178	115	105	141	139	136	138	145	148	87	88	122	122
158	165	182	181	126	133	147	146	140	151	156	154	91	90	133	131
213	208	228	224	145	157	155	158	153	157	173	167	92	95	135	134
214	224	230	235	151	158	169	167	191	188	197	195	97	101	140	137
239	230	243	242	159	161	176	171	198	193	203	203	125	125	149	149
247	230	259	247	193	202	204	206	206	209	215	213	125	126	152	151
254	268	266	272	226	231	235	236	210	213	223	219	132	138	157	156
257	268	266	277	226	235	236	237	221	223	227	222	154	150	165	160
296	279	296	288	242	253	258	262	223	225	234	232	160	160	171	169
313	289	332	309	249	257	260	263	226	231	240	235	161	164	180	182
365	362	374	375	251	261	265	268	235	237	249	244	163	165	184	184
381	378	386	388	291	292	297	297	246	247	255	252	173	174	191	194
403	381	397	391	293	301	300	306	254	262	265	259	175	182	198	199
414	412	420	417	325	332	333	335	264	270	283	284	197	194	209	210
414	412	420	417	340	334	348	347	276	282	287	288	207	204	220	215
419	419	438	438	381	370	382	386	287	290	295	294	213	210	231	225
419	420	443	443	393	383	396	387	311	309	304	305	224	222	239	234
444	466	459	463	399	399	405	397	327	328	329	325	231	226	248	246
472	466	482	468	415	407	417	402	331	337	339	334	233	235	248	249
495	494	494	495	418	418	423	422	351	342	341	340	239	236	257	252
516	495	519	500	418	418	424	422	360	359	366	358	241	239	263	261
516	506	519	508	423	424	435	433	364	362	380	372	247	246	265	264

529	526	535	531	424	425	438	437	395	380	401	388	250	249	268	267
539	527	550	536	441	434	447	441	409	406	418	416	264	264	280	279
541	536	552	544	467	457	476	469	418	418	426	423	270	269	284	283
611	606	616	610	469	459	477	470	419	419	435	428	277	276	296	291
611	609	616	612	474	475	484	473	419	420	438	432	279	281	297	296
631	625	636	629	485	489	490	487	420	422	440	435	284	284	309	308
631	626	637	630	491	490	493	488	445	432	449	444	303	304	318	317
632	630	641	636	507	517	522	531	457	449	466	454	307	306	320	317
633	630	641	639	540	520	548	531	467	468	472	470	324	323	331	327
636	632	641	640	551	557	555	553	485	472	480	474	331	331	341	340
672	658	675	664	594	589	595	590	495	487	507	498	338	334	347	344
682	670	686	669	611	608	615	611	515	512	511	506	347	343	358	350
704	684	708	689	612	615	618	611	527	515	530	518	358	350	363	359
704	687	709	692	622	618	624	621	528	516	540	526	367	359	380	370
708	703	713	709	623	619	628	622	543	537	543	537	381	377	394	387
717	717	728	725	626	625	630	625	561	559	565	562	392	380	395	391
717	718	728	725	627	625	633	627	586	578	589	583	403	388	414	394
742	723	746	728	632	628	637	631	588	588	591	590	428	425	438	433
760	747	766	749	633	631	638	637	611	607	614	607	428	425	439	435
768	761	777	766	633	631	640	638	621	612	623	616	429	427	444	438
778	765	783	770	657	638	659	643	624	621	629	621	429	429	448	443
784	778	792	788	657	641	659	646	629	627	632	629	443	433	450	444
793	787	799	794	673	671	678	671	631	627	638	633	452	450	459	455
838	826	844	829	689	678	694	685	632	630	639	636	459	451	465	459
852	826	856	829	713	709	717	711	634	632	641	637	461	457	466	460
852	842	856	845	715	710	718	712	637	632	647	640	470	461	475	468
863	861	872	860	716	710	723	716	645	634	653	644	474	472	480	478
863	862	883	862	716	711	723	718	677	655	681	657	492	481	497	485
868	866	883	866	720	720	725	724	682	662	687	661	495	491	501	495
881	866	889	880	741	733	744	729	689	675	690	679	512	505	519	510
883	867	890	882	741	736	745	742	707	697	708	702	520	510	523	515
895	877	899	884	754	748	756	746	717	705	719	703	532	528	539	533
918	880	920	885	771	759	780	768	718	709	727	715	534	531	541	538
924	896	924	898	778	768	787	773	718	712	729	716	546	543	549	546
930	904	931	904	785	772	791	777	721	715	734	726	556	549	562	556
930	904	932	904	786	780	792	781	724	717	738	735	561	555	566	560
939	932	943	937	792	784	797	790	734	731	750	742	562	558	568	562
941	933	945	937	796	792	799	794	759	743	765	743	581	577	584	580
958	938	965	945	807	794	810	795	776	771	781	775	586	583	590	589
975	943	975	951	820	817	827	820	785	778	787	781	595	591	602	596
975	944	975	952	860	857	863	841	787	782	792	788	597	592	604	599
980	971	998	971	863	858	864	857	791	784	800	790	603	601	607	605
980	971	999	971	864	858	864	857	800	786	807	792	625	609	631	615

997	983	1001	994	864	861	875	866	804	800	810	804	631	630	634	633
998	983	1001	994	865	863	876	867	814	806	820	814	643	639	652	644
1004	992	1015	1000	876	871	878	868	854	842	858	845	647	643	653	650
1004	992	1015	1000	877	872	878	871	860	854	863	859	653	648	660	654
1010	993	1016	1000	888	886	891	876	864	856	869	865	659	654	666	662
1011	1000	1016	1005	925	920	928	924	865	857	877	867	675	662	679	668
1012	1004	1022	1019	929	927	929	924	866	860	877	867	691	668	692	669
1013	1005	1022	1020	932	933	931	931	867	862	879	869	693	677	695	679
1014	1013	1024	1023	940	935	946	936	908	885	902	872	715	705	717	706
1014	1013	1025	1023	942	937	947	937	911	902	912	882	727	718	731	719
1045	1036	1058	1049	948	940	950	940	923	905	918	906	740	733	744	738
1054	1043	1062	1052	960	948	963	948	924	914	922	910	741	734	746	740
1054	1043	1062	1052	963	949	965	949	926	917	927	911	744	738	749	741
1057	1056	1070	1069	975	964	977	965	931	923	928	924	746	740	750	744
1077	1066	1084	1075	976	966	978	966	934	931	935	932	758	748	761	752
1107	1106	1117	1118	981	978	979	976	939	932	940	933	768	754	772	754
1107	1106	1118	1118	981	979	979	976	941	939	945	939	782	776	785	779
1109	1110	1118	1120	982	982	986	979	943	941	947	944	799	787	804	789
1110	1110	1119	1120	982	982	992	984	945	944	948	946	803	799	807	802
1183	1168	1186	1175	1000	983	1001	985	946	945	965	958	808	805	811	808
1183	1180	1194	1197	1001	984	1001	986	966	965	971	966	816	814	813	811
1183	1181	1201	1198	1004	1001	1006	999	968	967	976	968	830	823	823	816
1184	1183	1201	1207	1004	1001	1007	999	981	982	978	979	831	825	831	824
1185	1183	1207	1207	1004	1002	1016	1011	982	983	982	982	832	826	834	828
1191	1197	1207	1208	1004	1002	1017	1011	982	983	988	983	832	828	843	836
1206	1205	1214	1212	1013	1008	1020	1015	983	984	994	985	840	833	846	840
1206	1205	1214	1212	1013	1008	1020	1015	1004	998	1005	1006	848	844	856	849
1208	1206	1216	1213	1014	1010	1021	1019	1004	999	1010	1006	851	847	859	852
1208	1207	1216	1215	1014	1011	1021	1019	1005	1001	1013	1009	851	848	864	859
1240	1245	1245	1251	1050	1051	1055	1057	1005	1002	1014	1012	853	850	866	862
1245	1254	1250	1258	1052	1051	1056	1057	1013	1003	1018	1013	861	851	875	873
1268	1269	1274	1273	1053	1055	1058	1074	1013	1004	1018	1014	867	864	888	881
1291	1275	1296	1288	1056	1055	1059	1074	1014	1009	1025	1017	909	875	914	892
1296	1296	1303	1294	1057	1077	1071	1080	1014	1010	1025	1017	910	886	918	899
1313	1299	1318	1303	1057	1081	1074	1080	1015	1011	1032	1021	924	905	924	902
1323	1321	1328	1325	1065	1092	1077	1091	1022	1014	1039	1035	925	912	927	909
1326	1323	1334	1330	1095	1105	1105	1108	1049	1049	1050	1049	930	916	930	918
1332	1338	1338	1340	1108	1110	1108	1109	1053	1050	1060	1058	933	926	938	925
1338	1346	1347	1347	1109	1111	1109	1114	1053	1053	1062	1060	934	933	939	927
1351	1356	1357	1356	1110	1114	1118	1119	1056	1054	1064	1061	944	944	940	938
1355	1358	1360	1367	1112	1120	1120	1126	1060	1054	1070	1064	957	957	949	949
1360	1359	1368	1369	1135	1131	1141	1132	1061	1057	1105	1100	958	958	959	954
1361	1372	1368	1372	1176	1168	1177	1171	1105	1108	1107	1108	959	960	968	965

1366	1377	1369	1380	1177	1183	1182	1184	1105	1108	1110	1111	963	965	969	968
1368	1377	1373	1381	1182	1183	1186	1188	1106	1109	1120	1118	965	965	973	970
1370	1397	1373	1389	1183	1183	1188	1188	1106	1109	1126	1127	968	969	976	976
1379	1400	1382	1400	1184	1183	1188	1193	1133	1123	1138	1130	970	973	979	979
1429	1450	1437	1446	1184	1188	1196	1197	1146	1140	1155	1148	972	976	987	980
1478	1455	1489	1448	1184	1189	1199	1197	1183	1182	1188	1186	973	976	991	1000
1486	1483	1496	1489	1197	1194	1208	1199	1183	1182	1190	1189	975	977	1005	1011
1489	1483	1496	1494	1202	1198	1211	1201	1183	1183	1192	1192	1011	1006	1019	1016
1489	1487	1498	1497	1206	1204	1212	1211	1183	1183	1204	1202	1015	1009	1021	1018
1519	1492	1525	1498	1206	1204	1212	1211	1187	1186	1208	1203	1026	1018	1033	1026
1534	1518	1540	1515	1207	1208	1229	1228	1203	1198	1208	1208	1029	1022	1039	1029
1537	1527	1541	1530	1208	1209	1232	1229	1205	1200	1211	1212	1033	1023	1046	1035
1538	1527	1542	1532	1247	1258	1255	1263	1205	1202	1213	1213	1037	1026	1052	1048
1544	1534	1550	1537	1263	1259	1266	1265	1205	1207	1214	1216	1050	1051	1057	1057
1561	1540	1566	1544	1273	1282	1274	1279	1206	1207	1220	1223	1053	1053	1060	1059
1622	1548	1627	1555	1297	1295	1303	1300	1210	1228	1233	1232	1061	1058	1076	1074
1626	1588	1631	1594	1303	1303	1308	1318	1228	1229	1235	1234	1062	1060	1078	1076
1627	1589	1635	1596	1305	1311	1314	1325	1232	1231	1263	1239	1064	1061	1082	1078
1628	1621	1638	1625	1324	1321	1329	1328	1262	1238	1277	1266	1065	1061	1082	1079
1635	1625	1643	1633	1324	1325	1329	1335	1276	1258	1281	1278	1133	1122	1136	1129
1652	1627	1658	1635	1334	1335	1339	1337	1280	1265	1288	1281	1135	1135	1141	1138
1654	1641	1661	1646	1335	1339	1340	1342	1295	1281	1303	1286	1137	1138	1147	1145
1654	1642	1665	1647	1360	1350	1361	1361	1304	1295	1305	1297	1137	1140	1151	1150
1654	1650	1665	1653	1361	1360	1361	1361	1306	1303	1311	1306	1139	1143	1156	1152
1691	1651	1694	1660	1361	1363	1370	1363	1317	1310	1320	1324	1149	1145	1159	1159
1692	1654	1695	1665	1361	1363	1372	1365	1324	1319	1328	1328	1175	1174	1181	1180
3157	3167	3173	3173	1384	1364	1382	1372	1325	1321	1334	1334	1176	1174	1189	1187
3157	3167	3173	3173	1388	1365	1387	1374	1326	1335	1336	1343	1177	1175	1189	1187
3177	3177	3184	3182	1394	1376	1402	1375	1334	1352	1358	1355	1177	1176	1191	1190
3177	3177	3184	3182	1407	1384	1415	1387	1358	1358	1358	1358	1188	1186	1195	1193
3182	3182	3186	3189	1414	1397	1417	1400	1359	1360	1361	1359	1200	1190	1207	1199
3182	3182	3186	3189	1449	1408	1457	1402	1359	1361	1368	1362	1200	1191	1211	1205
3183	3183	3196	3196	1482	1470	1484	1475	1360	1364	1385	1364	1201	1196	1211	1208
3183	3183	3196	3196	1482	1475	1485	1478	1383	1365	1393	1369	1203	1203	1212	1211
3187	3188	3202	3203	1483	1478	1487	1482	1392	1369	1394	1376	1205	1205	1212	1213
3187	3188	3202	3204	1484	1481	1488	1484	1394	1371	1404	1383	1208	1208	1214	1214
3188	3193	3206	3213	1484	1482	1492	1489	1400	1381	1408	1400	1209	1209	1216	1215
3188	3193	3206	3214	1485	1487	1494	1493	1408	1400	1415	1405	1210	1209	1220	1220
3193	3197	3211	3219	1528	1488	1532	1494	1409	1409	1435	1407	1210	1210	1223	1224
3193	3197	3213	3220	1532	1513	1536	1528	1434	1418	1445	1421	1212	1227	1228	1226
3197	3202	3217	3221	1533	1526	1537	1530	1438	1434	1447	1443	1229	1230	1229	1229
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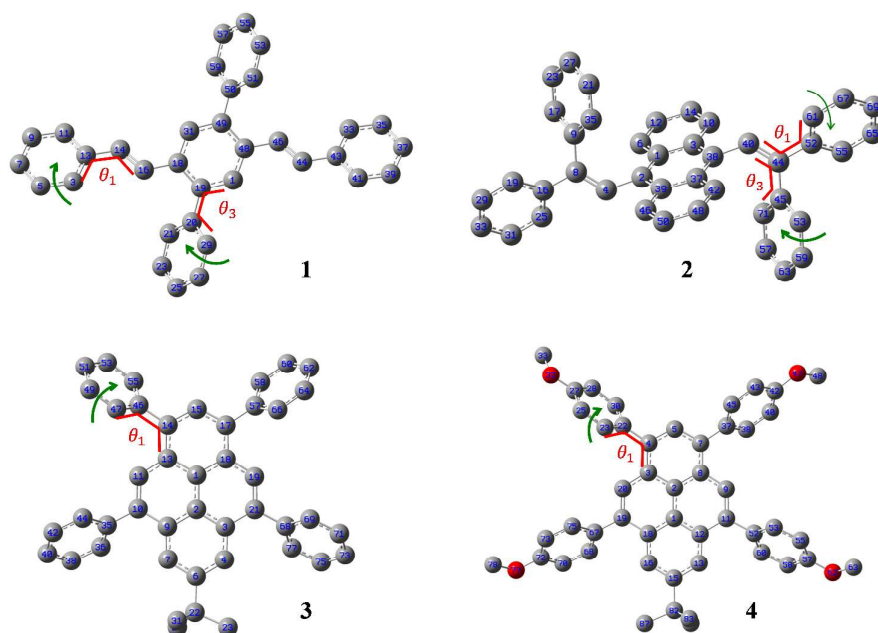


Figure S1. Molecular representation indicating the torsional angles involved in the rotation.

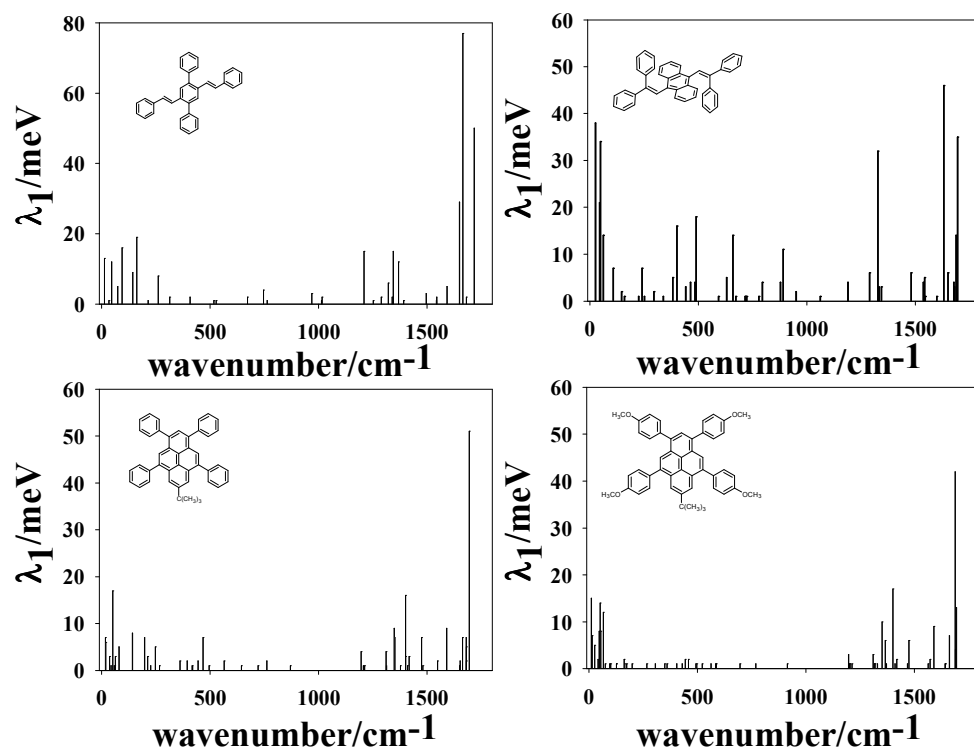


Figure S2. Reorganization energy (in meV) *versus* normal mode wavenumbers (in cm^{-1}) of the ground state calculated for compounds **1**, **2**, **3** and **4** in solution at the PBE0/6-31G** level of theory.

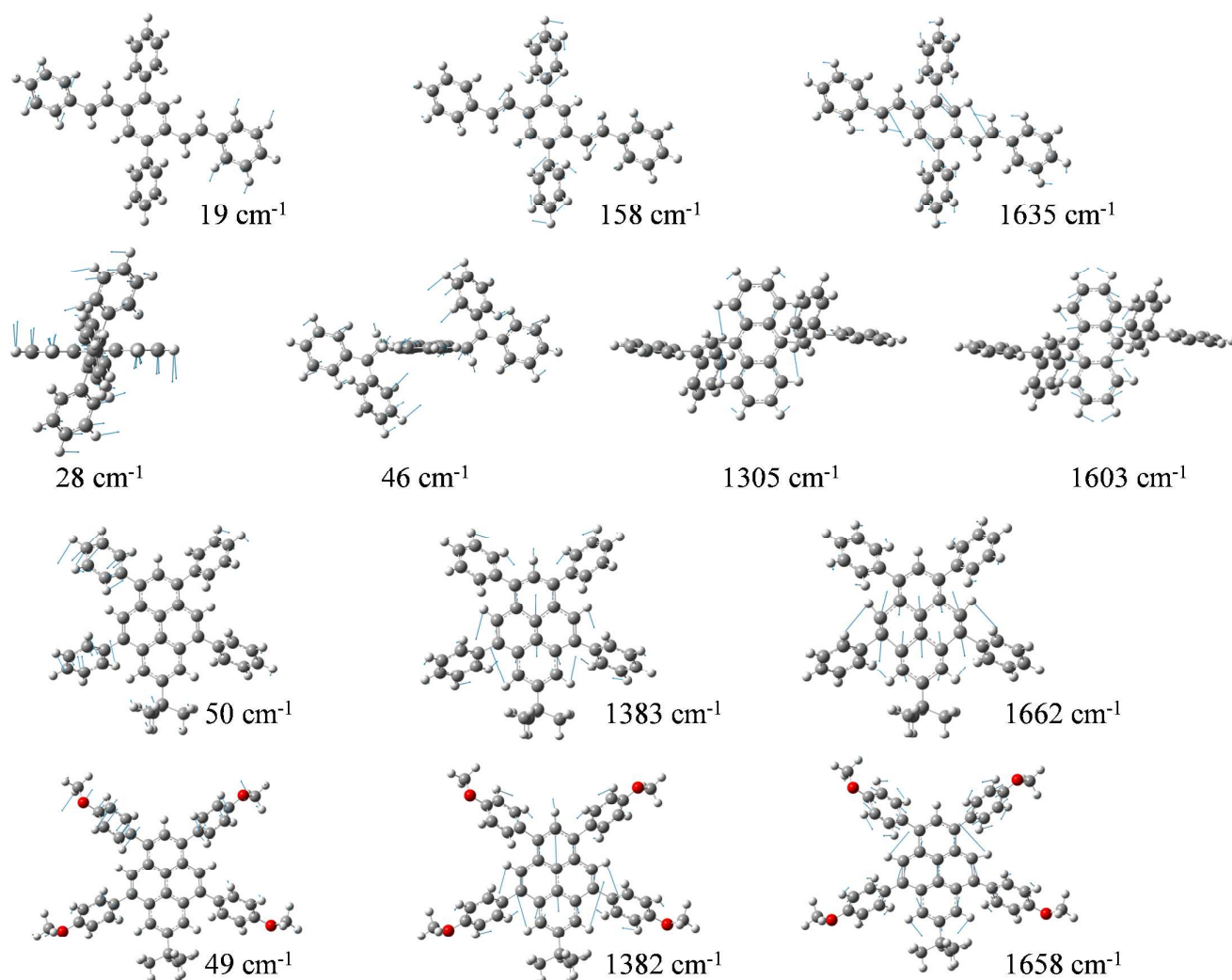


Figure S3. Atomic displacements for the selected normal modes calculated for compounds **1**, **2**, **3** and **4** at the B3LYP/6-31G** level of theory.

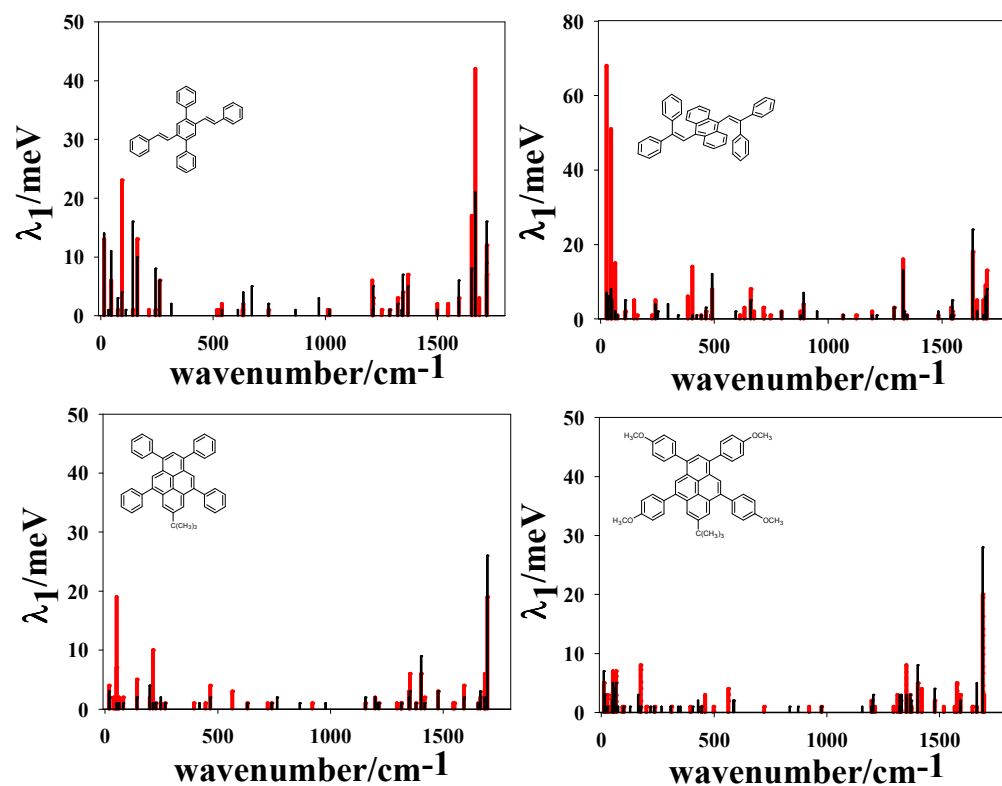


Figure S4. Reorganization energy (in meV) *versus* normal mode wavenumbers (in cm^{-1}) for holes (black bar) and electron (red bar) of the ground state for compounds **1-4**, calculated at the PBE0/6-31G** level of theory in gas phase.

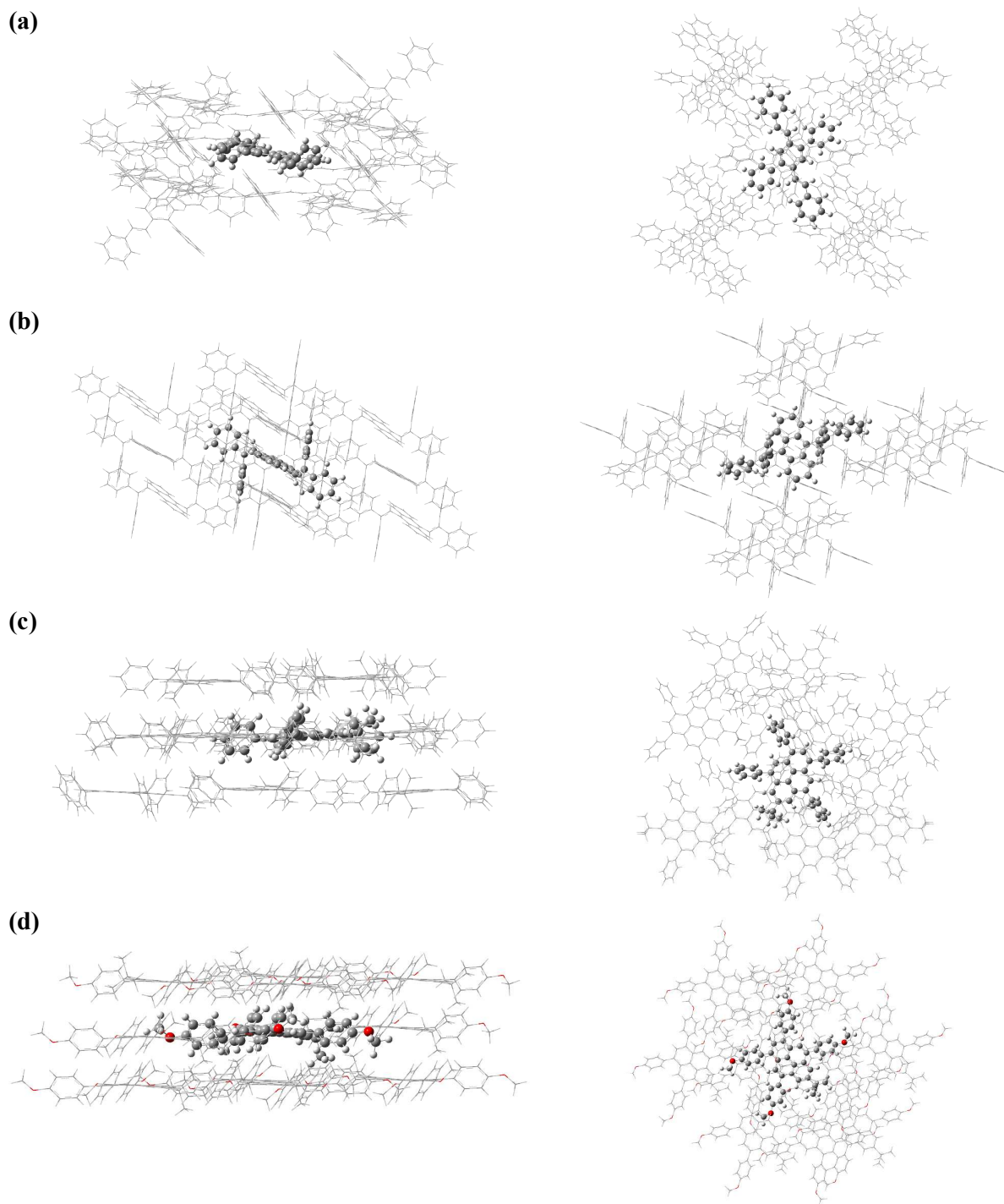


Figure S5. QM/MM model cluster for compounds **1-4** (which correspond to a-d, respectively). The centered molecule, treated as high level, is highlighted with respect to the surrounding molecules, treated as low level.

Computational Details

The intramolecular reorganization energy λ is the sum of two terms $\lambda = \lambda_1 + \lambda_2$ which reflect the geometric changes in the molecule when going from the neutral to the excited/charged molecular state (λ_1) or vice versa (λ_2). The reorganization energy was calculated using two approaches, the adiabatic potential energy surfaces approach (AP) and a normal-mode (NM) analysis using the program DUSHIN developed by Reimers.⁴⁸

In the AP approach, these terms can be calculated from the adiabatic potential energy surface as: $\lambda_1 = E_n(G_*) - E_n(G_n)$ and $\lambda_2 = E_*(G_n) - E_*(G_*)$ where n denotes neutral state, and $*$ is the excited state (+ or – specifically for the cationic or anionic states). $E_n(G_n)$ and $E_*(G_*)$ are the ground-state energies and excited/charged states, respectively; $E_n(G_*)$ and $E_*(G_n)$ are the energy of the neutral molecule at the optimal excited/charged geometry and the energy of the excited/charged state at the optimal geometry of the neutral molecule. The adiabatic electron affinity (AEA) and adiabatic ionization potential (AIP) are calculated according to: $AEA = E_n(G_n) - E_-(G_-)$ and $AIP = E_+(G_+) - E_n(G_n)$.

In the NM approach, λ can be calculated according to equation:

$$\lambda = \sum_i \lambda_i = \sum_i \hbar \omega_i S_i$$

where λ_i is the reorganization energy associated to the i -th vibrational mode, ω_i is the corresponding wavenumber and S_i is the Huang-Rhys factor which accounts the displacement of the equilibrium positions of the nuclei upon a photoexcitation.