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

Supporting Information

Cross-over from pyrene to acene optical and electronic properties, a theoretical investigation of a series of pyrene derivatives fused with N-, S, and O-containing heterocycles

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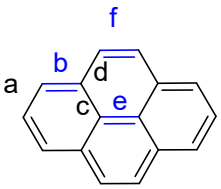
Table S1. Value of Ω to predict ordering of states in TD-DFT computations in pyrene.



$\Omega = \frac{4(a+c+d)/12}{(4b+e+2f)/7}$ (1)[1]

	a	b	c	d	e	f
Pyrene, DFT-optimized at tuned wB97X-D/cc-pvtz level of theory (this study)						
Length (Å)	1.37981	1.3875	1.40731	1.43628	1.42274	1.33894
Calculated according to equation 1: Ω=1.0211						
Pyrene[2]						
Length (Å)	1.386	1.400	1.422	1.436	1.428	1.344
Calculated according to equation 1: Ω=1.019212						

a,c,d= transversal bonds to central bond e; b,f= paralell bonds to central bond e.

Table S2. Optimized geometries of **1a**-**d** as assessed at the tuned ωB97X-D/cc-pvtz level of theory in the ground state.

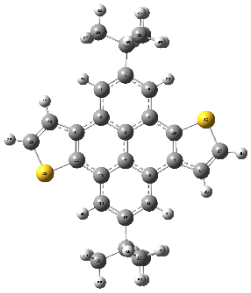
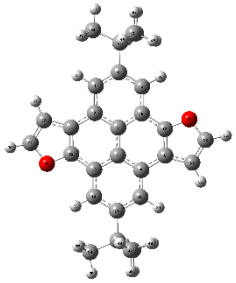
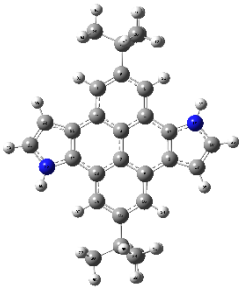
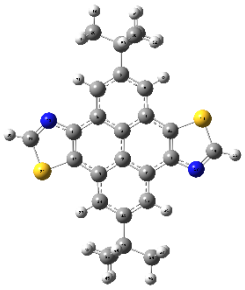
	1a	1b	1c	1d
Optimized Geometry				

Table S3. Optimized geometries of **1e**, **PY**, **2**, and **TC** as assessed at the tuned ωB97X-D/cc-pvtz level of theory in the ground state.

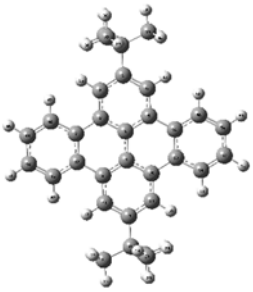
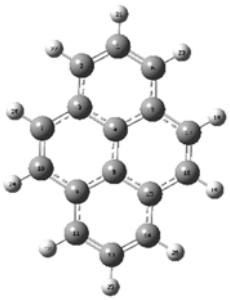
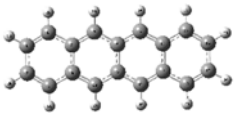
	1e	PY	2	TC
Optimized Geometry				

Table S4. Gas Phase Vertical transition energies, wavelengths, oscillator strength, transition dipole moments, electronic configurations and populations of **1a** as computed using time-dependent DFT (TD-DFT) at the ωB97X-D/cc-pVTC level of theory.

	Transition	E_{vert}	λ_{vert}	f	μ_{ge}	Electronic config.			%CB
1a	$S_0 \rightarrow S_1$	3.81	326	0.1531	1.6419	H-1	→	LUMO	25
						HOMO	→	LUMO	52
						HOMO	→	L+1	14
	$S_0 \rightarrow S_2$	3.86	321	0.1168	1.235	H-1	→	LUMO	32
						HOMO	→	LUMO	36
						HOMO	→	L+1	24
	$S_0 \rightarrow S_3$	4.43	280	0.0019	0.0176	H-3	→	LUMO	20
						H-2	→	LUMO	16
						HOMO	→	L+2	54
	$S_0 \rightarrow S_4$	4.63	268	0.5497	4.8487	H-1	→	LUMO	33
						HOMO	→	L+1	50
	$S_0 \rightarrow S_5$	4.65	267	0.074	0.6493	H-2	→	LUMO	41
						H-1	→	L+2	11
						HOMO	→	L+2	28
	$S_0 \rightarrow S_6$	4.81	258	0.0014	0.012	H-3	→	LUMO	67
						H-2	→	LUMO	15
	$S_0 \rightarrow S_7$	5.06	245	0.8306	6.7032	H-1	→	L+1	76
	$S_0 \rightarrow S_8$	5.09	244	0.167	1.3398	H-2	→	L+1	18
						H-1	→	L+2	43
	$S_0 \rightarrow S_9$	5.20	239	0.0028	0.0221	H-3	→	L+1	20
						H-1	→	L+2	10
						HOMO	→	L+3	48
	$S_0 \rightarrow S_{10}$	5.29	234	0.0111	0.0854	H-4	→	LUMO	38
						H-3	→	L+2	17
						H-2	→	L+2	14
						HOMO	→	L+4	14

E_{vert} = gas phase vertical transition energy (e.V.); λ_{vert} = wavelength of vertical transition (nm); f = oscillator strength; μ_{ge} = transition dipole moment (Debye); %CB = percent of major contributions (≥10%); H = HOMO; L = LUMO.

Table S5. Gas Phase Vertical transition energies, wavelengths, oscillator strength, transition dipole moments, electronic configurations and populations of **1b** as computed using time-dependent DFT (TD-DFT) at the ωB97X-D/cc-pVTC level of theory.

	Transition	E_{vert}	λ_{vert}	f	μ_{ge}	Electronic config.			%CB
1b	$S_0 \rightarrow S_1$	3.88	320	0.004	0.0422	H-1	→	LUMO	40
						HOMO	→	L+1	57
	$S_0 \rightarrow S_2$	3.90	318	0.2925	3.0639	H-1	→	L+1	10
						HOMO	→	LUMO	88
	$S_0 \rightarrow S_3$	4.54	273	0.0004	0.0039	H-2	→	LUMO	79
						HOMO	→	L+2	10
	$S_0 \rightarrow S_4$	4.75	261	0.4732	4.0643	H-1	→	LUMO	53
						HOMO	→	L+1	38
	$S_0 \rightarrow S_5$	4.80	259	0.0381	0.3239	HOMO	→	L+2	68
	$S_0 \rightarrow S_6$	5.19	239	0.1469	1.1543	H-2	→	L+1	53
						H-1	→	L+2	20
	$S_0 \rightarrow S_7$	5.20	238	1.1709	9.1828	H-1	→	L+1	73
	$S_0 \rightarrow S_8$	5.25	236	0.033	0.2564	H-3	→	LUMO	19
						H-3	→	L+1	11
						HOMO	→	L+3	43
	$S_0 \rightarrow S_9$	5.52	225	0.0007	0.0049	H-3	→	LUMO	66
						HOMO	→	L+3	16
	$S_0 \rightarrow S_{10}$	5.64	220	0.022	0.159	H-2	→	L+2	18
						H-1	→	L+2	45
						HOMO	→	L+3	19

E_{vert} = gas phase vertical transition energy (e.V.); λ_{vert} = wavelength of vertical transition (nm); f = oscillator strength; μ_{ge} = transition dipole moment (Debye); %CB = percent of major contributions (≥10%); H = HOMO; L = LUMO.

Table S6. Gas Phase Vertical transition energies, wavelengths, oscillator strength, transition dipole moments, electronic configurations and populations of **1c** as computed using time-dependent DFT (TD-DFT) at the ωB97X-D/cc-pVTC level of theory.

	Transition	E_{vert}	λ_{vert}	f	μ_{ge}	Electronic config.			%CB
1c	$S_0 \rightarrow S_1$	4.04	307	0.0055	0.0557	H-1	→	LUMO	38
						HOMO	→	L+1	56
	$S_0 \rightarrow S_2$	4.13	300	0.2547	2.5188	H-1	→	L+1	14
						HOMO	→	LUMO	81
	$S_0 \rightarrow S_3$	4.76	260	0.0011	0.0091	H-3	→	LUMO	10
						H-2	→	LUMO	70
	$S_0 \rightarrow S_4$	5.01	247	0.7008	5.7078	H-1	→	LUMO	57
						HOMO	→	L+1	39
	$S_0 \rightarrow S_5$	5.16	240	0.0086	0.0679	H-2	→	L+1	17
						H-1	→	L+2	11
						HOMO	→	L+2	43
						HOMO	→	L+5	11
	$S_0 \rightarrow S_6$	5.28	235	1.426	11.017	H-1	→	L+1	79
						HOMO	→	LUMO	15
	$S_0 \rightarrow S_7$	5.36	231	0.002	0.0149	H-3	→	L+1	26
						HOMO	→	L+2	27
						HOMO	→	L+5	29
	$S_0 \rightarrow S_8$	5.42	229	0.0049	0.0372	H-3	→	LUMO	59
						H-2	→	L+1	19
	$S_0 \rightarrow S_9$	5.63	220	0.0039	0.0286	H-3	→	LUMO	14
						H-2	→	LUMO	14
						H-2	→	L+1	37
						HOMO	→	L+2	13
	$S_0 \rightarrow S_{10}$	5.94	209	0.0243	0.1674	H-2	→	L+1	10
						H-1	→	L+2	55
						HOMO	→	L+5	17

E_{vert} = gas phase vertical transition energy (e.V.); λ_{vert} = wavelength of vertical transition (nm); f = oscillator strength; μ_{ge} = transition dipole moment (Debye); %CB = percent of major contributions (≥10%); H = HOMO; L = LUMO.

Table S7. Gas Phase Vertical transition energies, wavelengths, oscillator strength, transition dipole moments, electronic configurations and populations of **1d** and **1e** as computed using time-dependent DFT (TD-DFT) at the ωB97X-D/cc-pVTC level of theory.

CP	Transition	E_{vert}	λ_{vert}	f	μ_{ge}	Electronic config.	%CB
1d	$S_0 \rightarrow S_1$	3.84	323	0.2527	2.6877	HOMO → LUMO	85
	$S_0 \rightarrow S_2$	3.87	320	0.0132	0.1393	H-1 → LUMO	52
						HOMO → L+2	39
	$S_0 \rightarrow S_4$	4.69	264	0.5884	5.1214	H-1 → LUMO	42
						HOMO → L+2	56
	$S_0 \rightarrow S_7$	5.13	242	0.7506	5.9766	H-1 → L+2	61
						HOMO → L+3	21
	$S_0 \rightarrow S_9$	5.29	234	0.5107	3.9382	H-2 → L+1	26
						H-1 → L+2	25
						HOMO → L+3	39
1e	$S_0 \rightarrow S_1$	3.93	315	0.0124	0.1291	H-1 → LUMO	59
						HOMO → L+2	36
	$S_0 \rightarrow S_2$	4.10	302	0.0993	0.9888	H-1 → L+2	21
						HOMO → LUMO	73
	$S_0 \rightarrow S_5$	4.77	260	0.9181	7.854	H-1 → LUMO	37
						HOMO → L+2	58
	$S_0 \rightarrow S_8$	4.95	250	0.6485	5.3428	H-3 → L+1	11
						H-1 → L+2	42
						HOMO → LUMO	14
						HOMO → L+4	14
	$S_0 \rightarrow S_9$	4.97	250	0.4958	4.0738	H-3 → L+1	16
						H-2 → L+3	10
						H-1 → L+2	28
						HOMO → LUMO	10
						HOMO → L+4	20

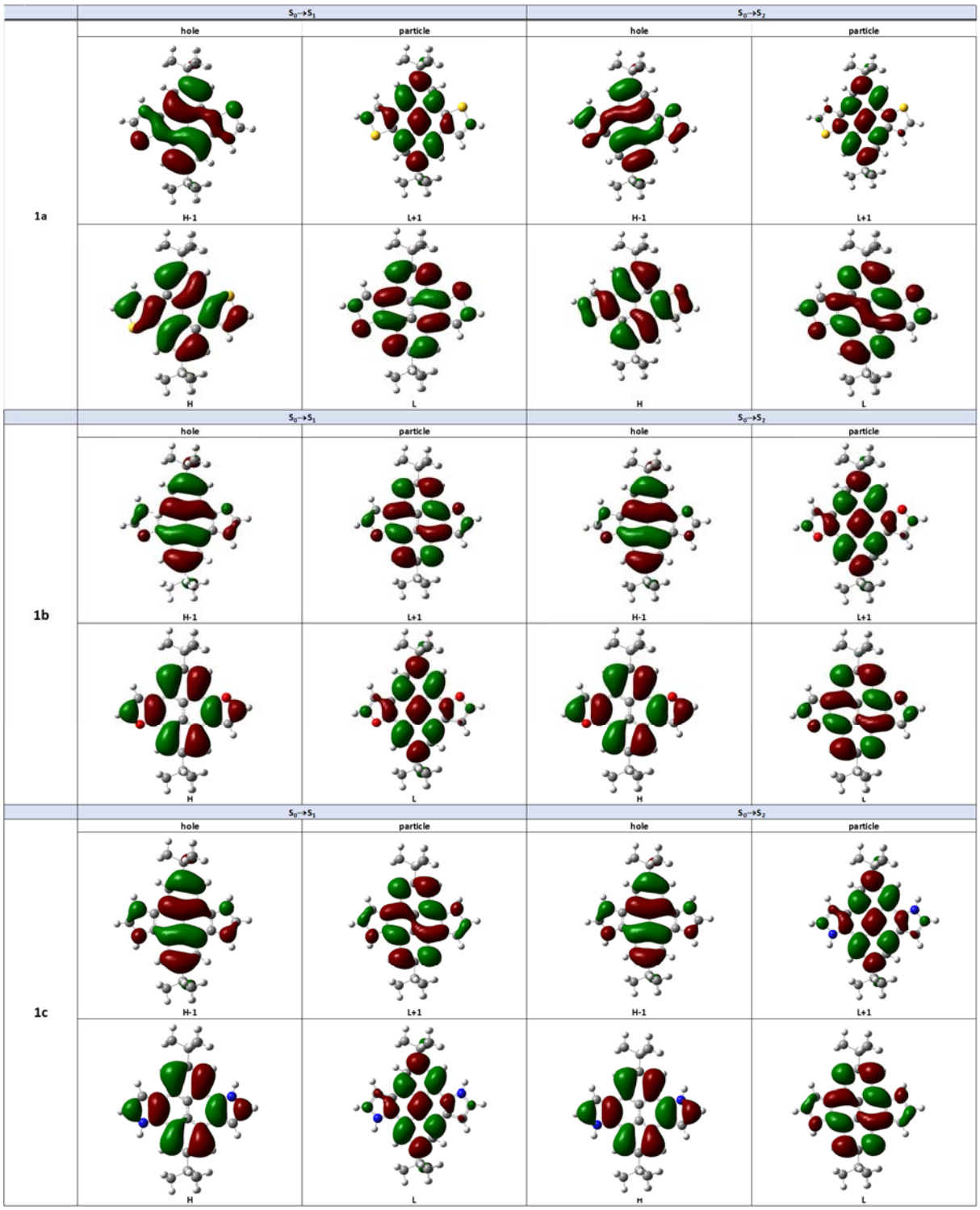
E_{vert} = gas phase vertical transition energy (e.V.); λ_{vert} = wavelength of vertical transition (nm); f = oscillator strength; μ_{ge} = transition dipole moment (Debye); %CB = percent of major contributions (≥10%); H = HOMO; L = LUMO.

Table S8. Gas Phase Vertical transition energies, wavelengths, oscillator strength, transition dipole moments, electronic configurations and populations of **PY**, **2**, and **TC** as computed using time-dependent DFT (TD-DFT) at the ωB97X-D/cc-pVTC level of theory.

CP	Transition	E_{vert}	λ_{vert}	f	μ_{ge}	Electronic config.	%CB
PY	$S_0 \rightarrow S_1$	4.24	293	0.0003	0.0031	H-1 → LUMO	44
						HOMO → L+1	53
	$S_0 \rightarrow S_2$	4.32	287	0.3247	3.0654	H-1 → L+1	13
						HOMO → LUMO	87
	$S_0 \rightarrow S_4$	5.52	225	0.5279	3.9024	H-1 → LUMO	54
						HOMO → L+1	46
	$S_0 \rightarrow S_6$	5.96	208	1.209	8.2819	H-1 → L+1	80
						HOMO → LUMO	14
2	$S_0 \rightarrow S_1$	3.91	317	0.0043	0.0448	H-1 → LUMO	56
						HOMO → L+1	42
	$S_0 \rightarrow S_2$	3.92	316	0.3776	3.9274	HOMO → LUMO	90
	$S_0 \rightarrow S_4$	4.89	253	0.308	2.569	H-1 → LUMO	41
						HOMO → L+1	56
	$S_0 \rightarrow S_7$	5.46	227	1.6238	12.1455	H-1 → L+1	86
TC	$S_0 \rightarrow S_1$	2.82	440	0.0701	1.0157	HOMO → LUMO	99
	$S_0 \rightarrow S_2$	3.72	333	0.0035	0.0388	H-1 → LUMO	52
						HOMO → L+1	45
	$S_0 \rightarrow S_5$	4.97	250	2.8788	23.6598	H-1 → LUMO	45
						HOMO → L+1	53
	$S_0 \rightarrow S_7$	5.40	230	0.0123	0.0927	H-3 → LUMO	32
						H-2 → L+2	22
						HOMO → L+3	44
	$S_0 \rightarrow S_8$	5.45	227	0.0003	0.0021	H-3 → LUMO	53
						HOMO → L+3	41

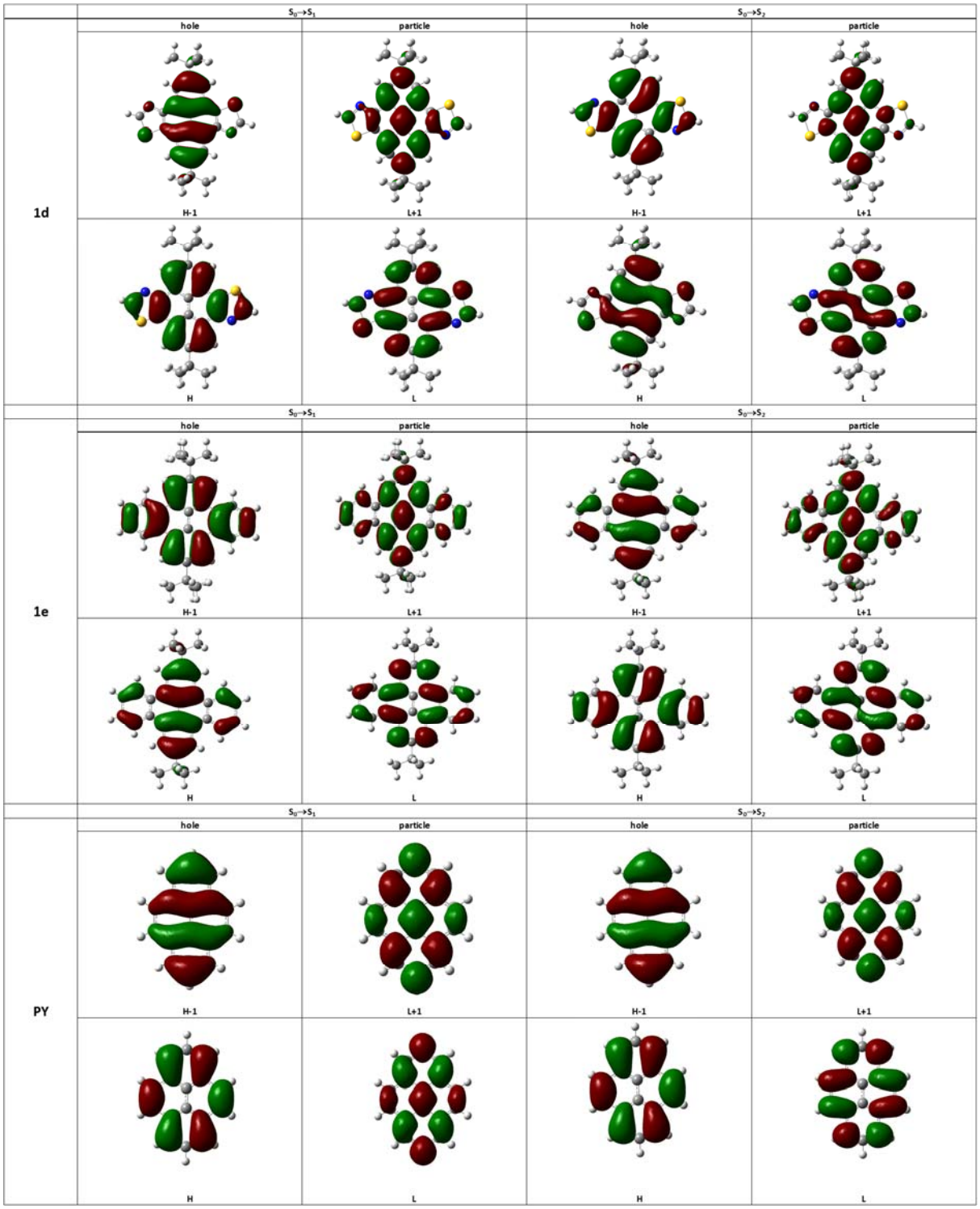
E_{vert} = gas phase vertical transition energy (e.V.); λ_{vert} = wavelength of vertical transition (nm); f = oscillator strength; μ_{ge} = transition dipole moment (Debye); %CB = percent of major contributions (≥10%); H = HOMO; L = LUMO.

Table S 9. Pairs of Natural Transition orbitals (isovalue surface 0.02 a.u.) for $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions at the ωB97X-D[3]/cc-pVTZ[4] level of theory for **1a**-**c**.



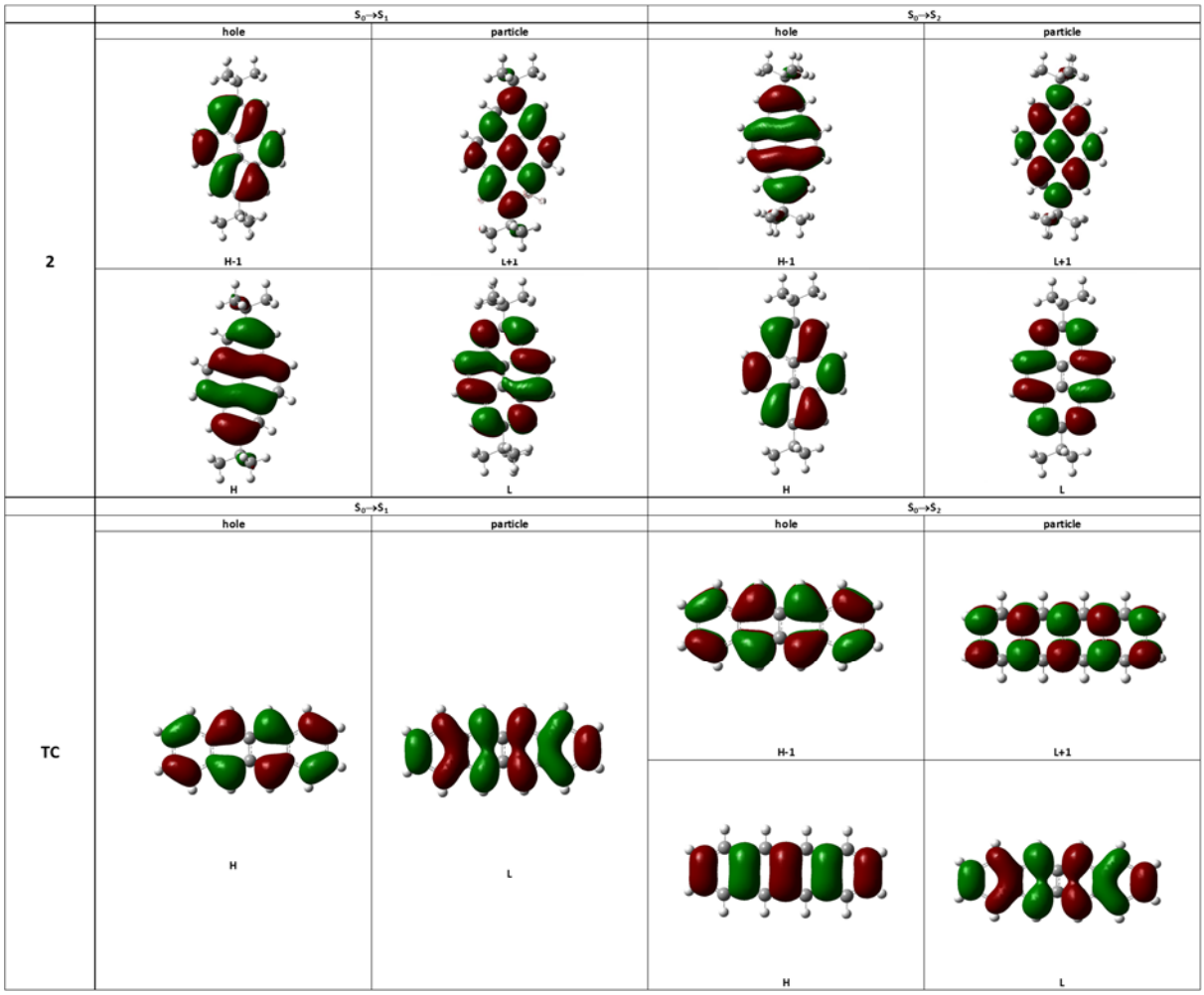
H = Highest occupied transition orbital (HOTO); L = lowest unoccupied transition orbital (LUTO).

Table S 10. Pairs of Natural Transition orbitals (isovalue surface 0.02 a.u.) for $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions at the ωB97X-D[3]/cc-pVTZ[4] level of theory for **1d**, **1e,** and **PY**.



H = Highest occupied transition orbital (HOTO); L = lowest unoccupied transition orbital (LUTO).

Table S 11. Pairs of Natural Transition orbitals (isovalue surface 0.02 a.u.) for $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions at the ωB97X-D[3]/cc-pVTZ[4] level of theory for **2** and **TC**.



H = Highest occupied transition orbital (HOTO); L = lowest unoccupied transition orbital (LUTO).

Table S12. Frequency, ω (cm^{-1}), Huang-Rhys factors, S, and relaxation energies, λ_{rel} (meV), for the totally symmetric vibrations of **1a** in its neutral and anionic state as computed at ω-tuned ωB97X-D/cc-pVTZ level of theory. Values are unscaled.

1a						
Neutral				Anion		
	ω	S	λ_{rel}	ω	S	λ_{rel}
	cm^{-1}		meV	cm^{-1}		meV
	210	0.694	50.6	197	0.003	0
	220	-0.004	0	209	-0.692	50.1
	266	-0.09	1.1	256	-0.003	0
	299	0.233	8.1	295	0.001	0
	305	-0.008	0	298	-0.238	8.5
	375	-0.105	2	373	-0.124	2.8
	394	-0.315	19.6	393	-0.309	18.7
	493	-0.213	11.1	489	-0.036	0.3
	494	0.114	3.2	492	0.237	13.8
	620	-0.2	12.4	602	-0.001	0
	623	0.003	0	603	0.237	17
	646	0.069	1.5	621	0.003	0
	648	-0.446	64.4	640	-0.003	0
	655	-0.041	0.6	645	-0.428	59.1
	690	0.072	1.8	669	0	0
	699	0	0	687	0.074	1.9
	744	-0.256	24.3	720	-0.002	0
	765	0	0	735	0.271	26.9
	810	0.171	11.8	773	0	0
	850	0.118	5.9	796	0	0
	872	0	0	807	-0.162	10.6
	908	0	0	832	-0.087	3.2
	949	-0.123	7.2	945	-0.211	20.9
	960	0.376	68	953	0.314	46.8
	1052	0.052	1.4	1049	0.064	2.1
	1077	-0.096	5	1058	-0.011	0.1
	1080	0.014	0.1	1068	0.095	4.9
	1159	-0.068	2.7	1148	-0.037	0.8
	1239	0.051	1.6	1237	0.036	0.8
	1259	0.068	2.9	1239	0.088	4.8
	1265	-0.122	9.5	1263	-0.056	2
	1279	-0.109	7.6	1272	-0.206	26.9
	1320	-0.271	48.4	1289	-0.111	7.9
	1322	-0.118	9.2	1293	-0.319	65.7
	1333	-0.41	111.7	1299	-0.101	6.6
	1342	-0.039	1	1334	-0.171	19.4
	1368	0.03	0.6	1347	0.07	3.3
	1404	0.007	0	1375	0.045	1.4
	1407	0.002	0	1397	0.151	15.8
	1439	-0.221	35.3	1404	-0.339	80.8
	1443	-0.362	94.4	1425	-0.031	0.7
	1445	-0.121	10.7	1427	-0.198	28.1
	1489	-0.001	0	1434	-0.126	11.3
	1530	0.066	3.4	1527	0.07	3.8
	1537	-0.107	8.7	1537	-0.069	3.7
	1552	0.016	0.2	1541	0.134	13.7
	1599	-0.094	7.1	1567	-0.037	1.1
	1643	0.045	1.7	1583	0.015	0.2
	1680	-0.64	343.6	1652	-0.681	382.9
	3044	-0.027	1.1	3033	-0.028	1.2
	3116	0.007	0.1	3101	0.029	1.3
	3117	-0.035	1.9	3115	-0.001	0

Table S13. Frequency, ω (cm^{-1}), Huang-Rhys factors, S, and relaxation energies, λ_{rel} (meV), for the totally symmetric vibrations of **1b** in its neutral and anionic state as computed at ω-tuned ωB97X-D/cc-pVTZ level of theory. Values are unscaled.

1b						
Neutral				Anion		
	ω	S	λ_{rel}	ω	S	λ_{rel}
	cm^{-1}		meV	cm^{-1}		meV
	136	-0.127	1.1	136	-0.123	0
	164	-0.002	0	166	0	32.4
	187	0.001	0	190	0.001	32.1
	210	0.403	17.1	210	0.555	0
	211	0.669	47.3	211	0.551	0
	268	-0.095	1.2	260	-0.003	0
	279	0.024	0.1	267	0.076	8.1
	297	0.238	8.4	278	0.016	0.1
	326	-0.088	1.3	325	-0.059	0.1
	349	-0.008	0	342	-0.02	2.8
	355	0.126	2.8	356	0.126	1.2
	389	0.004	0	387	0.001	18.7
	423	-0.306	19.8	419	-0.298	0
	479	-0.035	0.3	474	-0.014	16
	498	0.253	15.9	497	0.254	0
	617	0	0	607	0	72
	651	-0.462	69.6	630	-0.002	0
	681	0	0	672	0.001	4.9
	709	-0.115	4.7	695	-0.002	0
	813	-0.191	14.8	764	0	0
	866	0.005	0	798	0.001	10.9
	871	0	0	811	0.013	2.7
	898	0.345	53.6	846	0	0
	918	0	0	858	-0.002	45.3
	924	-0.001	0	891	-0.319	3
	1018	0	0	988	-0.005	19.6
	1050	-0.074	2.9	1034	-0.195	8
	1066	-0.187	18.6	1055	-0.004	5
	1090	-0.022	0.3	1069	-0.002	7
	1092	0.093	4.7	1070	0.097	0.1
	1108	0.122	8.3	1101	0.112	1.3
	1156	-0.09	4.6	1144	-0.048	0.1
	1237	0.01	0.1	1235	0.003	2.5
	1241	-0.041	1.1	1235	-0.035	43.2
	1285	-0.039	1	1248	-0.064	13.8
	1287	0.038	0.9	1277	0.26	79.1
	1288	-0.043	1.2	1285	-0.147	3
	1326	-0.476	150.2	1311	-0.068	0.8
	1329	0.055	2	1312	0.019	0.8
	1358	-0.06	2.5	1314	-0.036	0
	1365	0.011	0.1	1339	0.035	14.6
	1391	-0.151	15.8	1355	-0.007	6.9
	1402	0.343	82.2	1384	0.145	8.8
	1406	-0.065	3	1390	-0.1	0.1
	1407	0.161	18.1	1397	0.01	12.3
	1408	0.047	1.6	1398	0.011	73.1
	1439	0.003	0	1408	0.132	4
	1440	0.047	1.6	1410	0.322	3.7
	1442	0.026	0.5	1426	0.075	1.3
	1450	0.263	50.2	1428	0.072	5.7
	1464	0.104	7.9	1432	0.043	0.6
	1510	0.033	0.8	1495	0.005	1.3
	1566	0.016	0.2	1562	0.01	3.7
	1569	0.037	1.1	1570	0.024	12.6
	1572	-0.062	3	1578	-0.069	0
	1622	-0.088	6.3	1587	-0.126	2.4
	1648	-0.007	0	1595	-0.007	0.1
	1651	0.039	1.3	1600	0.055	486.2
	1704	-0.742	468.9	1690	-0.759	0
	3038	0.007	0.1	3023	0.021	1.5
	3043	0.03	1.3	3032	0.031	0
	3110	-0.006	0	3093	-0.001	1.5
	3116	-0.036	2	3113	0	0

Table S14. Frequency, ω (cm^{-1}), Huang-Rhys factors, S, and relaxation energies, λ_{rel} (meV), for the totally symmetric vibrations of **1c** in its neutral and anionic state as computed at ω-tuned ωB97X-D/cc-pVTZ level of theory. Values are unscaled.

1c						
Neutral				Anion		
	ω	S	λ_{rel}	ω	S	λ_{rel}
	cm^{-1}		meV	cm^{-1}		meV
	213	0.816	70.9	195	0.001	0
	215	-0.07	0.5	212	-0.811	69.9
	300	0.254	9.7	270	0.048	0.3
	330	0.026	0.1	298	0.253	9.5
	356	0.134	3.2	336	0.001	0
	361	-0.056	0.6	356	-0.108	2.1
	383	-0.063	0.8	361	-0.119	2.6
	424	-0.148	4.7	393	0	0
	453	-0.003	0	419	-0.149	4.7
	503	0.245	15.1	502	0.244	15
	655	-0.442	63.8	630	-0.001	0
	660	0.003	0	654	0.448	65.6
	822	-0.201	16.6	752	0	0
	884	0	0	820	-0.134	7.4
	885	0	0	822	0.147	8.9
	908	-0.309	43.4	864	0	0
	928	0	0	902	-0.277	34.7
	938	-0.118	6.5	921	-0.002	0
	940	0	0	930	0.145	9.8
	1057	-0.027	0.4	1046	-0.06	1.9
	1079	-0.145	11.4	1066	-0.134	9.5
	1090	0.036	0.7	1069	0.079	3.4
	1151	-0.143	11.7	1141	-0.173	17.2
	1167	-0.087	4.4	1155	-0.046	1.2
	1252	0	0	1247	-0.048	1.5
	1284	0.029	0.5	1262	0.054	1.8
	1290	-0.033	0.7	1281	-0.453	131.6
	1303	0.127	10.5	1296	0.176	20.1
	1329	0.067	3	1297	0.004	0
	1332	0.536	191.2	1302	0.232	35.1
	1371	0.034	0.8	1328	0.067	3
	1383	-0.012	0.1	1346	-0.014	0.1
	1391	0.08	4.4	1375	0.005	0
	1412	0.122	10.5	1392	0.034	0.8
	1413	0.007	0	1397	0.081	4.6
	1413	-0.146	15.1	1399	-0.073	3.7
	1420	-0.394	110.2	1405	-0.019	0.3
	1445	-0.062	2.7	1418	-0.039	1.1
	1450	-0.185	24.8	1424	-0.426	129.3
	1486	0.029	0.6	1440	0.102	7.6
	1490	-0.058	2.5	1444	-0.099	7.1
	1492	-0.001	0	1463	-0.171	21.4
	1496	-0.242	43.9	1493	0	0
	1502	0.075	4.2	1494	0	0
	1521	-0.002	0	1509	-0.039	1.2
	1557	0.039	1.2	1532	0.017	0.2
	1567	-0.059	2.7	1562	-0.013	0.1
	1579	0.005	0	1570	0.057	2.6
	1629	0.005	0	1601	0.075	4.5
	1673	0.017	0.2	1623	0.159	20.4
	1719	-0.801	552	1700	-0.789	528.8
	3056	0.025	1	3045	0.029	1.3
	3129	0.024	0.9	3113	0.03	1.4
	3130	0.034	1.8	3125	0.001	0
	3730	0.023	1	3747	0.03	1.7

Table S15. Frequency, ω (cm^{-1}), Huang-Rhys factors, S, and relaxation energies, λ_{rel} (meV), for the totally symmetric vibrations of **1d** in its neutral and anionic state as computed at ω-tuned ωB97X-D/cc-pVTZ level of theory. Values are unscaled.

1d						
Neutral				Anion		
	ω	S	λ_{rel}	ω	S	λ_{rel}
	cm^{-1}		meV	cm^{-1}		meV
	123	-0.184	2.1	124	-0.19	2.2
	208	0.703	51.5	208	0.698	50.8
	349	0	0	352	0.153	4.1
	350	-0.14	3.4	357	0	0
	394	0.211	8.8	391	0.214	9
	472	-0.114	3.1	453	0	0
	494	0.241	14.3	469	0.1	2.3
	495	0	0	492	-0.24	14.2
	624	0.211	13.9	608	0.249	18.8
	651	0.477	73.9	632	0	0
	653	0	0	649	0.444	64.1
	693	-0.153	8.1	689	-0.178	10.9
	747	0.209	16.3	729	0	0
	759	0	0	738	-0.208	15.9
	813	0.187	14.3	784	0	0
	849	0.003	0	812	0.179	13
	888	-0.104	4.8	843	0	0
	941	0	0	881	0.071	2.2
	966	-0.319	49.2	955	-0.309	45.5
	1053	-0.044	1	1050	-0.05	1.3
	1091	0.082	3.7	1080	0.103	5.8
	1158	0.099	5.6	1149	0.051	1.5
	1237	0	0	1227	0.042	1.1
	1264	0	0	1251	-0.098	6
	1271	-0.169	18.1	1267	0	0
	1279	-0.045	1.3	1271	-0.147	13.7
	1319	0.185	22.5	1294	0.355	81.8
	1332	0.435	126	1301	0.127	10.4
	1341	0	0	1328	0.079	4.2
	1382	-0.068	3.2	1354	-0.076	3.9
	1420	-0.06	2.6	1400	0	0
	1440	0	0	1407	0.447	140.4
	1440	-0.208	31.3	1425	0	0
	1445	0.39	110.2	1431	0	0
	1491	0	0	1484	-0.074	4.1
	1493	0.041	1.2	1490	0.001	0
	1503	-0.051	2	1495	0	0
	1513	-0.043	1.4	1505	0	0
	1516	0	0	1507	0.05	1.9
	1521	-0.09	6.1	1509	0	0
	1526	0	0	1523	0.078	4.7
	1588	0.169	22.6	1564	0.142	15.7
	1649	0.032	0.9	1584	0.089	6.2
	1681	0.637	341.2	1653	0.672	373.8
	3044	0.031	1.5	3034	0.034	1.7
	3117	0.037	2.2	3101	0.035	1.9

Table S16. Frequency, ω (cm^{-1}), Huang-Rhys factors, S, and relaxation energies, λ_{rel} (meV), for the totally symmetric vibrations of **1e** in its neutral and anionic state as computed at ω-tuned ωB97X-D/cc-pVTZ level of theory. Values are unscaled.

1e						
Neutral				Anion		
	ω	S	λ_{rel}	ω	S	λ_{rel}
	cm^{-1}		meV	cm^{-1}		meV
	210	0.707	52.5	210	0.7	51.4
	262	0.156	3.2	262	0.145	2.7
	289	0.212	6.5	289	0.232	7.8
	327	-0.132	2.8	328	-0.12	2.4
	357	0.12	2.6	357	0.127	2.9
	488	-0.252	15.5	489	-0.242	14.4
	637	0.335	35.9	624	0	0
	639	0.084	2.3	624	0.036	0.4
	642	0	0	638	-0.335	35.8
	679	-0.27	24.8	674	-0.288	28
	813	-0.184	13.8	794	0	0
	879	0.023	0.2	812	0.18	13.1
	904	-0.215	20.9	840	0	0
	928	0	0	899	-0.184	15.2
	1049	0	0	1047	-0.279	40.8
	1056	0	0	1049	-0.242	30.8
	1063	-0.373	74.2	1055	0	0
	1093	0.071	2.7	1071	0.035	0.7
	1120	-0.005	0	1103	-0.054	1.6
	1168	0.065	2.4	1158	0.112	7.3
	1214	0.148	13.3	1193	0.011	0.1
	1224	0.035	0.7	1204	0.077	3.6
	1273	-0.36	82.4	1259	-0.124	9.7
	1303	-0.021	0.3	1275	-0.415	109.7
	1311	-0.459	138.1	1290	-0.281	50.8
	1322	0.061	2.5	1293	0.127	10.5
	1349	0.131	11.6	1334	0.003	0
	1365	0	0	1344	-0.263	46.7
	1379	0.418	120.6	1372	0.122	10.2
	1388	0.051	1.8	1372	0.002	0
	1389	0	0	1396	-0.267	49.6
	1407	0	0	1400	0.327	75
	1476	0.222	36.5	1453	0.043	1.4
	1528	0.041	1.3	1520	0	0
	1531	0	0	1526	0.084	5.4
	1549	0.11	9.3	1529	0.135	13.8
	1581	0	0	1539	0.058	2.6
	1637	-0.052	2.2	1543	0	0
	1648	0.128	13.5	1603	0	0
	1676	0.092	7.1	1645	0.202	33.6
	1679	0.582	284	1646	0	0
	1679	0	0	1650	0.582	279.8
	3043	-0.032	1.5	3033	-0.033	1.7
	3114	0	0	3100	-0.035	1.9
	3116	0.041	2.6	3113	0	0

Table S17. Frequency, ω (cm^{-1}), Huang-Rhys factors, S, and relaxation energies, λ_{rel} (meV), for the totally symmetric vibrations of **PY** in its neutral and anionic state as computed at ω-tuned ωB97X-D/cc-pVTZ level of theory. Values are unscaled.

PY						
Neutral				Anion		
	ω	S	λ_{rel}	ω	S	λ_{rel}
	cm^{-1}		meV	cm^{-1}		meV
	422	-0.932	183.3	419	-0.925	179.4
	615	-0.306	28.8	614	-0.349	37.4
	835	0.475	94.1	762	0	0
	901	0	0	834	-0.438	80
	1125	0.092	4.7	1114	0.104	6.1
	1201	-0.246	36.4	1175	-0.342	68.8
	1294	-0.801	415.3	1255	-0.001	0
	1295	0.139	12.6	1275	0	0
	1297	0	0	1278	0.595	226.2
	1390	0.101	7.1	1354	0.001	0
	1415	0	0	1385	0.426	126
	1488	0.586	255.4	1425	0.578	237.9
	1667	-0.149	18.6	1601	-0.161	20.8
	1763	0.776	531.2	1722	0.779	522.4
	3219	0.001	0	3179	0.041	2.6
	3221	0.035	1.9	3182	0	0
	3239	0	0	3205	0.029	1.4
	3248	-0.037	2.3	3218	-0.029	1.3

Table S18. Frequency, ω (cm^{-1}), Huang-Rhys factors, S, and relaxation energies, λ_{rel} (meV), for the totally symmetric vibrations of **2** in its neutral and anionic state as computed at ω-tuned ωB97X-D/cc-pVTZ level of theory. Values are unscaled Values are unscaled.

2						
Neutral				Anion		
	ω	S	λ_{rel}	ω	S	λ_{rel}
	cm^{-1}		meV	cm^{-1}		meV
	184	0.247	5.6	188	0.295	8.2
	216	-0.815	71.7	217	-0.795	68.5
	320	-0.254	10.4	320	-0.271	11.7
	468	-0.336	26.5	467	-0.315	23.2
	487	-0.073	1.3	482	-0.071	1.2
	665	-0.51	86.6	664	-0.518	89
	822	-0.161	10.6	774	0	0
	919	0	0	822	0.144	8.5
	939	-0.323	49	866	0	0
	952	0.125	7.4	938	0.269	34
	969	0	0	949	-0.151	10.8
	1145	0.008	0	1135	0.112	7.1
	1147	-0.011	0.1	1160	-0.122	8.6
	1173	0	0	1168	0.28	45.8
	1187	0.285	48.3	1181	0	0
	1261	0.301	57.1	1256	0.128	10.3
	1296	-0.076	3.8	1274	-0.217	30.1
	1321	0	0	1305	0.42	114.9
	1329	-0.59	231	1306	0	0
	1378	-0.066	3	1364	-0.048	1.6
	1401	0.018	0.2	1371	0.347	82.5
	1403	0	0	1384	0.061	2.6
	1420	0.028	0.6	1404	0.061	2.6
	1439	-0.033	0.8	1413	-0.429	130.2
	1470	-0.424	132.5	1428	0	0
	1488	0	0	1428	-0.043	1.3
	1635	-0.138	15.6	1585	-0.098	7.6
	1655	0.089	6.5	1594	0	0
	1664	0	0	1596	0.079	5
	1709	-0.675	389.9	1677	-0.695	405
	3038	0	0	3022	0.029	1.2
	3043	-0.038	2.3	3031	-0.04	2.4
	3115	0	0	3098	-0.039	2.4
	3116	-0.047	3.4	3113	0	0
	3197	-0.03	1.4	3166	-0.031	1.5

Table S19. Frequency, ω (cm^{-1}), Huang-Rhys factors, S, and relaxation energies, λ_{rel} (meV), for the totally symmetric vibrations of **TC** in its neutral and anionic state as computed at ω-tuned ωB97X-D/cc-pVTZ level of theory. Values are unscaled.

TC						
Neutral				Anion		
	ω	S	λ_{rel}	ω	S	λ_{rel}
	cm^{-1}		meV	cm^{-1}		meV
	321	-1.061	180.5	304	-0.001	0
	322	0	0	319	1.062	180.1
	637	0.377	45.3	636	0.371	43.7
	776	-0.094	3.4	762	-0.089	3
	883	-0.125	6.9	827	0	0
	941	0	0	881	-0.09	3.6
	1031	0.112	6.5	1051	0.055	1.6
	1197	0.28	46.9	1178	0.293	50.7
	1235	-0.421	109.6	1237	-0.369	84.4
	1429	0	0	1406	-0.438	134.7
	1434	0.583	243.5	1412	0	0
	1453	-0.352	90.1	1423	0	0
	1467	0	0	1428	0.58	240.2
	1496	0.259	50.2	1477	0	0
	1498	0.002	0	1483	0.067	3.4
	1584	0.041	1.3	1528	0.001	0
	1613	0.335	90.3	1551	0.288	64.2
	1685	0	0	1598	-0.24	45.9
	3187	0.026	1.1	3155	0.03	1.5
	3215	0.04	2.6	3188	0.046	3.4

Table S20. Frequency, ω (cm^{-1}), Huang-Rhys factors, S, and relaxation energies, λ_{rel} (meV), for the totally symmetric vibrations of **1a** in its neutral and cationic state as computed at ω-tuned ωB97X-D/cc-pVTZ level of theory. Values are unscaled.

1a						
	Neutral			Cation		
	ω	S	λ_{rel}	ω	S	λ_{rel}
	cm^{-1}		meV	cm^{-1}		meV
	210	0.36	13.6	209	0.354	13
	246	-0.231	6.6	242	-0.231	6.5
	287	0.258	9.5	282	0	0
	293	0.011	0	287	0.275	10.8
	299	-0.1	1.5	295	-0.026	0.1
	305	0.002	0	299	0.128	2.4
	320	-0.09	1.3	319	-0.071	0.8
	351	0.101	1.8	348	0.002	0
	353	0.112	2.2	351	0.03	0.2
	354	-0.039	0.3	353	-0.119	2.5
	394	-0.34	22.7	389	-0.374	27.2
	472	-0.07	1.2	470	-0.05	0.6
	493	-0.08	1.6	484	-0.007	0
	504	0	0	494	-0.099	2.4
	620	-0.281	24.5	614	-0.029	0.3
	623	0.005	0	616	0.279	23.9
	648	0.156	7.9	634	0.002	0
	655	0.002	0	649	0.136	6
	671	0	0	650	0.07	1.6
	690	0.081	2.3	691	0.085	2.5
	744	-0.184	12.6	739	-0.192	13.7
	810	-0.116	5.4	809	-0.109	4.8
	850	-0.226	21.7	831	-0.228	21.6
	942	-0.001	0	951	-0.109	5.6
	949	0.077	2.8	953	0.019	0.2
	960	-0.234	26.3	958	-0.221	23.4
	1077	0.126	8.5	1078	0.131	9.2
	1129	0.072	2.9	1133	0.093	4.9
	1159	0.12	8.3	1158	0.138	11.1
	1239	0.043	1.1	1244	0.056	1.9
	1259	0.072	3.3	1260	0.045	1.3
	1265	-0.082	4.2	1273	-0.044	1.2
	1279	-0.227	33	1282	-0.12	9.2
	1285	-0.01	0.1	1286	-0.155	15.4
	1320	-0.134	11.9	1302	-0.103	6.9
	1322	-0.103	7	1312	-0.202	26.8
	1333	-0.267	47.3	1350	-0.197	26.3
	1342	0.214	30.8	1354	0.023	0.4
	1368	0.047	1.5	1366	0.201	27.5
	1388	-0.112	8.7	1368	-0.221	33.5
	1407	0	0	1413	0.107	8.2
	1408	-0.006	0	1415	-0.063	2.8
	1426	0.053	2	1415	0.026	0.5
	1439	-0.113	9.1	1423	-0.189	25.3
	1439	0.016	0.2	1429	0.348	86.7
	1443	-0.356	91.3	1446	-0.041	1.2
	1445	-0.104	7.8	1447	-0.001	0
	1452	-0.005	0	1453	-0.22	35.1
	1490	-0.045	1.5	1489	0	0
	1497	-0.038	1.1	1493	-0.001	0
	1509	-0.047	1.7	1510	-0.03	0.7
	1530	0.05	1.9	1527	0.067	3.5
	1537	-0.229	40.5	1531	-0.065	3.3
	1599	-0.296	70.1	1562	-0.15	17.5
	1612	-0.057	2.7	1567	-0.212	35.4
	1643	0.106	9.3	1596	0.09	6.4
	1680	-0.508	216.3	1661	-0.473	185.9
	3117	0.028	1.2	3126	0.001	0
	3124	-0.01	0.2	3131	-0.03	1.4

Table S21. Frequency, ω (cm^{-1}), Huang-Rhys factors, S, and relaxation energies, λ_{rel} (meV), for the totally symmetric vibrations of **1b** in its neutral and cationic state as computed at ω-tuned ωB97X-D/cc-pVTZ level of theory. Values are unscaled.

1b						
Neutral				Cation		
	ω	S	λ_{rel}	ω	S	λ_{rel}
	cm^{-1}		meV	cm^{-1}		meV
	210	0.154	2.5	209	0.318	10.6
	211	0.289	8.8	212	0.081	0.7
	255	-0.116	1.7	250	-0.041	0.2
	258	-0.006	0	251	-0.111	1.6
	297	0.133	2.6	290	0.009	0
	300	0.006	0	294	0.123	2.2
	349	0.369	23.8	346	0.009	0
	352	-0.265	12.3	351	-0.032	0.2
	355	0.212	7.9	352	0.229	9.2
	358	-0.039	0.3	358	-0.468	39.2
	423	-0.074	1.1	416	-0.091	1.7
	498	0.076	1.4	499	0.074	1.4
	651	0.187	11.3	627	0.001	0
	681	0	0	652	-0.172	9.6
	709	0.039	0.5	708	0.056	1.1
	751	-0.057	1.2	748	-0.049	0.9
	792	0	0	812	-0.077	2.4
	813	0.082	2.7	822	0	0
	886	0	0	895	-0.183	15
	898	0.138	8.5	919	0.343	53.9
	923	0.341	53.8	932	0.002	0
	924	-0.056	1.4	935	-0.002	0
	1050	0.056	1.7	1049	0.042	0.9
	1066	0.132	9.3	1058	0.045	1.1
	1090	-0.015	0.1	1091	-0.111	6.7
	1108	-0.151	12.6	1106	-0.137	10.4
	1149	0.017	0.2	1151	0.091	4.8
	1156	0.21	25.5	1153	0.14	11.3
	1174	0.013	0.1	1160	0.051	1.5
	1195	-0.027	0.4	1179	-0.206	25.1
	1196	0.154	14.1	1192	0.015	0.1
	1285	-0.09	5.2	1284	-0.131	11
	1287	-0.014	0.1	1285	-0.098	6.1
	1288	-0.143	13.3	1291	-0.033	0.7
	1290	0.002	0	1313	0.227	33.9
	1326	-0.37	90.9	1319	-0.147	14.2
	1358	-0.087	5.1	1357	-0.139	13
	1365	0.008	0	1365	0.117	9.3
	1391	-0.081	4.6	1389	-0.043	1.3
	1402	-0.093	6.1	1400	-0.06	2.5
	1406	0.017	0.2	1408	0.336	79.7
	1407	0.002	0	1414	0.055	2.1
	1407	-0.039	1.1	1414	-0.033	0.7
	1408	-0.001	0	1415	-0.049	1.7
	1439	0	0	1418	-0.027	0.5
	1440	-0.015	0.2	1441	-0.07	3.5
	1442	0.045	1.5	1447	0.005	0
	1450	0.196	27.9	1447	0.001	0
	1464	0.076	4.2	1450	0.02	0.3
	1469	0.009	0.1	1467	0.189	26.3
	1526	-0.061	2.8	1522	-0.037	1
	1569	0.114	10.1	1557	0.083	5.3
	1572	-0.164	21.1	1571	-0.038	1.2
	1622	0.194	30.5	1586	0.225	40.3
	1651	0.074	4.5	1615	0.019	0.3
	1704	-0.604	311.3	1686	-0.552	257.2
	3116	0.028	1.2	3126	0.002	0
	3125	0.01	0.2	3131	0.03	1.4

Table S22. Frequency, ω (cm^{-1}), Huang-Rhys factors, S, and relaxation energies, λ_{rel} (meV), for the totally symmetric vibrations of **1c** in its neutral and cationic state as computed at ω-tuned ωB97X-D/cc-pVTZ level of theory. Values are unscaled.

1c						
Neutral				Cation		
	ω	S	λ_{rel}	ω	S	λ_{rel}
	cm^{-1}		meV	cm^{-1}		meV
	137	-0.012	0	138	-0.145	1.5
	138	-0.148	1.5	149	-0.002	0
	213	0.298	9.4	212	0.303	9.7
	215	-0.028	0.1	216	-0.031	0.1
	300	0.101	1.5	299	0.103	1.6
	356	0.368	24.1	357	0.03	0.2
	358	-0.174	5.4	359	-0.042	0.3
	360	-0.073	1	362	-0.045	0.4
	361	-0.227	9.3	364	-0.48	42
	424	-0.115	2.8	416	-0.135	3.8
	655	0.214	15.1	631	0	0
	686	0.001	0	658	0.196	12.7
	731	0	0	748	0.073	2
	753	0.073	2	749	0	0
	822	0.091	3.4	821	0.085	2.9
	884	0	0	904	-0.26	30.5
	908	-0.193	16.9	931	-0.425	84
	938	0.441	91.3	952	0.001	0
	1079	0.064	2.2	1070	0.013	0.1
	1090	-0.069	2.6	1095	-0.079	3.4
	1151	0.092	4.8	1128	0.052	1.5
	1167	0.14	11.5	1159	0.063	2.3
	1171	0.003	0	1171	0.22	28.4
	1179	0.161	15.4	1175	0	0
	1290	-0.046	1.3	1294	-0.082	4.4
	1300	0.052	1.7	1300	0.001	0
	1303	0.195	24.7	1306	0.115	8.6
	1329	0.051	1.7	1315	0.061	2.4
	1332	0.368	90.1	1324	0.307	62.3
	1371	0.057	2.2	1364	0.066	2.9
	1391	0.111	8.6	1390	0.011	0.1
	1412	-0.016	0.2	1417	-0.309	67.8
	1413	-0.001	0	1418	-0.041	1.2
	1414	0.001	0	1420	0.114	9.2
	1420	0.014	0.1	1422	0.161	18.4
	1445	-0.025	0.5	1423	-0.221	34.9
	1445	-0.033	0.8	1437	-0.307	67.7
	1450	-0.392	111.3	1442	-0.091	6
	1452	0.043	1.3	1452	0.019	0.3
	1468	0.003	0	1453	0.04	1.2
	1490	-0.035	0.9	1466	-0.134	13.1
	1504	0.005	0	1508	0.075	4.3
	1514	0.044	1.5	1516	0.038	1.1
	1553	-0.076	4.5	1534	-0.007	0
	1557	0.212	34.9	1541	0.059	2.7
	1567	0.129	12.9	1565	0.141	15.6
	1579	-0.001	0	1568	-0.151	17.9
	1629	0.275	61.5	1605	0.209	34.9
	1673	0.06	3	1632	0.023	0.4
	1719	-0.575	284	1699	-0.513	223.4
	3130	-0.027	1.1	3137	-0.004	0
	3139	0.012	0.2	3144	0.031	1.5

Table S23. Frequency, ω (cm^{-1}), Huang-Rhys factors, S, and relaxation energies, λ_{rel} (meV), for the totally symmetric vibrations of **1d** in its neutral and cationic state as computed at ω-tuned ωB97X-D/cc-pVTZ level of theory. Values are unscaled.

1d						
	Neutral			Cation		
	ω	S	λ_{rel}	ω	S	λ_{rel}
	cm^{-1}		meV	cm^{-1}		meV
	208	0.382	15.2	207	0.38	14.9
	253	0.065	0.5	250	0.094	1.1
	294	0.408	24.4	286	0.001	0
	298	-0.001	0	296	-0.403	24
	350	0.272	13	351	0.259	11.8
	394	0.282	15.7	388	0.327	20.8
	494	0.107	2.8	487	0	0
	495	0	0	495	0.11	3
	624	0.349	37.9	620	0.346	37.1
	651	-0.111	4	633	-0.002	0
	675	0.002	0	651	0.114	4.2
	693	-0.066	1.5	689	-0.065	1.5
	742	0	0	738	0.139	7.1
	747	0.147	8.1	739	0.007	0
	813	-0.1	4	811	-0.118	5.7
	835	0	0	831	-0.116	5.6
	849	0.098	4.1	875	0	0
	955	0	0	965	0.258	32
	966	0.261	32.8	974	0	0
	1053	0.06	1.9	1052	0.047	1.2
	1091	-0.147	11.8	1094	-0.159	13.8
	1158	-0.183	19.3	1154	-0.187	20.3
	1237	-0.003	0	1227	-0.047	1.3
	1239	-0.059	2.2	1238	0	0
	1264	0	0	1258	-0.103	6.6
	1271	-0.187	22.3	1263	0	0
	1279	0.037	0.9	1276	0.107	7.3
	1311	0	0	1303	-0.045	1.3
	1319	0.001	0	1314	0.203	27
	1332	0.353	83.1	1336	0	0
	1341	0	0	1339	-0.21	29.4
	1350	0.221	32.9	1356	0	0
	1382	0.099	6.8	1363	0.323	70.9
	1407	0.005	0	1409	0.213	32
	1431	0	0	1421	-0.206	30.3
	1440	-0.104	7.7	1438	-0.349	87.3
	1445	0.349	87.9	1448	0	0
	1461	0	0	1450	-0.14	14.1
	1493	0.045	1.5	1494	0.001	0
	1513	0.029	0.7	1511	0.079	4.7
	1516	-0.001	0	1516	-0.045	1.6
	1521	-0.124	11.7	1521	0	0
	1530	0.053	2.1	1529	0	0
	1588	0.379	113.9	1572	0.248	48.4
	1681	0.544	248.8	1660	0.517	222.2
	3117	-0.031	1.5	3123	-0.016	0.4
	3123	0.012	0.2	3132	0.035	1.9

Table S24. Frequency, ω (cm^{-1}), Huang-Rhys factors, S, and relaxation energies, λ_{rel} (meV), for the totally symmetric vibrations of **1e** in its neutral and cationic state as computed at ω-tuned ωB97X-D/cc-pVTZ level of theory. Values are unscaled.

1e						
Neutral				Cation		
	ω	S	λ_{rel}	ω	S	λ_{rel}
	cm^{-1}		meV	cm^{-1}		meV
	210	0.227	5.4	202	0.203	4.2
	262	0.182	4.3	253	0.214	5.8
	289	0.242	8.4	283	0	0
	299	-0.004	0	285	-0.189	5.1
	327	-0.53	45.8	325	-0.002	0
	331	0	0	326	0.525	45
	357	-0.065	0.8	355	-0.149	3.9
	384	0	0	380	-0.243	11.2
	393	0.196	7.6	383	0	0
	478	0.085	1.7	473	0.07	1.2
	483	0	0	478	0	0
	488	-0.061	0.9	489	-0.067	1.1
	637	-0.277	24.4	617	0	0
	639	-0.166	8.8	624	0	0
	665	0	0	637	0.331	34.9
	679	-0.264	23.6	675	-0.258	22.5
	696	0.074	1.9	686	0.058	1.2
	813	0.12	5.9	806	0.001	0
	828	0	0	806	0.121	5.9
	879	-0.057	1.4	870	-0.022	0.2
	902	0	0	898	-0.226	22.9
	904	0.221	22	901	0	0
	1051	0.052	1.4	1048	0	0
	1056	0	0	1052	0.07	2.6
	1063	-0.076	3.1	1055	0	0
	1120	-0.054	1.7	1099	-0.107	6.2
	1168	0	0	1155	0.196	22.2
	1168	0.265	41.1	1170	0	0
	1208	0	0	1197	0.193	22.3
	1214	0.107	6.9	1219	0	0
	1224	0	0	1227	0.046	1.3
	1273	-0.496	156.4	1271	-0.4	101.8
	1303	-0.039	1	1279	-0.259	42.9
	1311	-0.334	73.1	1296	-0.169	18.4
	1322	-0.014	0.1	1313	-0.319	66.9
	1349	-0.031	0.7	1361	-0.133	12.1
	1379	0.363	90.6	1369	0.095	6.1
	1389	0	0	1407	0.347	84.6
	1406	-0.011	0.1	1414	-0.105	7.8
	1439	0.062	2.8	1441	0	0
	1452	0	0	1447	0.077	4.3
	1476	0.112	9.2	1450	0.009	0.1
	1485	0.038	1.1	1481	0.145	15.6
	1503	0.046	1.6	1495	0.015	0.2
	1528	-0.016	0.2	1528	-0.05	1.9
	1540	0	0	1530	0.113	9.8
	1549	0.178	24.5	1552	0	0
	1637	-0.161	21.3	1556	-0.056	2.5
	1648	0.192	30.5	1603	0	0
	1672	0	0	1614	-0.091	6.6
	1676	0.104	9	1662	0.364	109.9
	1679	0.439	162.1	1670	0.001	0
	1679	0	0	1672	0.295	72.5
	3116	-0.033	1.7	3125	-0.001	0
	3123	0.001	0		0.034	1.8

Table S25. Frequency, ω (cm^{-1}), Huang-Rhys factors, S, and relaxation energies, λ_{rel} (meV), for the totally symmetric vibrations of **PY** in its neutral and cationic state as computed at ω-tuned ωB97X-D/cc-pVTZ level of theory. Values are unscaled.

PY						
	Neutral			Cation		
	ω	S	λ_{rel}	ω	S	λ_{rel}
	cm^{-1}		meV	cm^{-1}		meV
	422	-0.432	39.3	424	-0.45	43
	615	0.308	29.2	624	0.29	26.2
	835	-0.196	16.1	837	-0.193	15.6
	1125	0.088	4.4	1129	0.097	5.3
	1201	-0.182	20	1200	-0.276	45.9
	1294	-0.757	370.4	1271	-0.001	0
	1295	0.131	11.2	1291	0	0
	1297	0	0	1301	0.683	303.5
	1390	-0.109	8.3	1373	-0.001	0
	1415	0	0	1412	0.189	25.3
	1488	0.453	152.9	1475	0.643	305
	1763	0.831	608.4	1742	0.72	451.6
	3248	0.034	1.9	3268	0.03	1.5

Table S26. Frequency, ω (cm^{-1}), Huang-Rhys factors, S, and relaxation energies, λ_{rel} (meV), for the totally symmetric vibrations of **2** in its neutral and cationic state as computed at ω-tuned ωB97X-D/cc-pVTZ level of theory. Values are unscaled.

2						
Neutral				Cation		
	ω	S	λ_{rel}	ω	S	λ_{rel}
	cm^{-1}		meV	cm^{-1}		meV
	216	-0.336	12.2	214	-0.342	12.5
	320	-0.092	1.3	318	-0.091	1.3
	468	-0.389	35.4	471	-0.378	33.5
	487	-0.118	3.4	482	-0.16	6.2
	579	-0.163	7.7	580	0	0
	593	0	0	587	-0.173	8.8
	665	0.229	17.5	635	0	0
	693	0	0	665	-0.211	14.8
	822	0.063	1.6	820	0.059	1.5
	929	0	0	940	-0.201	19
	939	0.18	15.3	940	0	0
	943	0	0	955	-0.068	2.2
	952	-0.074	2.6	964	0	0
	1051	-0.039	0.8	1050	-0.045	1.1
	1145	-0.167	16	1143	-0.195	21.7
	1147	0.061	2.1	1172	0	0
	1173	0	0	1180	0.015	0.1
	1182	0	0	1183	-0.147	12.8
	1187	0.07	2.9	1201	0	0
	1238	0	0	1231	-0.041	1.1
	1240	0.089	4.9	1238	0	0
	1261	0.512	165.6	1258	0	0
	1264	0	0	1261	0.297	55.6
	1296	-0.09	5.3	1266	-0.369	86.2
	1329	-0.442	130.1	1319	-0.394	102.5
	1378	0.153	16.1	1382	0	0
	1401	-0.013	0.1	1392	-0.114	9
	1407	0	0	1395	0.057	2.2
	1420	0.04	1.1	1417	0	0
	1439	0.067	3.2	1447	0	0
	1440	0	0	1448	-0.128	12
	1470	-0.306	68.8	1457	-0.498	180.8
	1509	-0.044	1.5	1511	-0.03	0.7
	1529	-0.039	1.2	1529	-0.044	1.4
	1635	0.08	5.2	1590	0	0
	1655	0.078	5	1600	0.044	1.5
	1674	0	0	1624	-0.038	1.1
	1709	-0.668	381.7	1694	-0.589	294
	3116	0.037	2.1	3127	0	0
	3124	0.018	0.5	3132	0.04	2.5
	3197	0.027	1.1	3216	0.019	0.6

Table S27. Frequency, ω (cm^{-1}), Huang-Rhys factors, S, and relaxation energies, λ_{rel} (meV), for the totally symmetric vibrations of **TC** in its neutral and cationic state as computed at ω-tuned ωB97X-D/cc-pVTZ level of theory. Values are unscaled.

TC						
Neutral				Cation		
	ω	S	λ_{rel}	ω	S	λ_{rel}
	cm^{-1}		meV	cm^{-1}		meV
	321	0.182	5.3	319	0.173	4.8
	776	-0.065	1.7	781	0	0
	869	0	0	892	0.067	2
	883	-0.1	4.4	899	0	0
	1031	0.158	12.9	1058	0.11	6.4
	1197	0.214	27.5	1207	0.001	0
	1201	0	0	1210	-0.281	47.9
	1235	-0.394	96.1	1253	-0.392	96.3
	1429	0	0	1424	-0.339	81.7
	1434	0.519	192.8	1431	0	0
	1453	-0.25	45.5	1446	0	0
	1467	0	0	1454	0.553	222.7
	1496	0.195	28.4	1498	0.01	0.1
	1584	0.193	29.5	1566	0.003	0
	1613	0.532	228.5	1568	0.35	95.9
	1685	0	0	1618	-0.383	118.6
	3215	-0.027	1.1	3231	-0.021	0.7

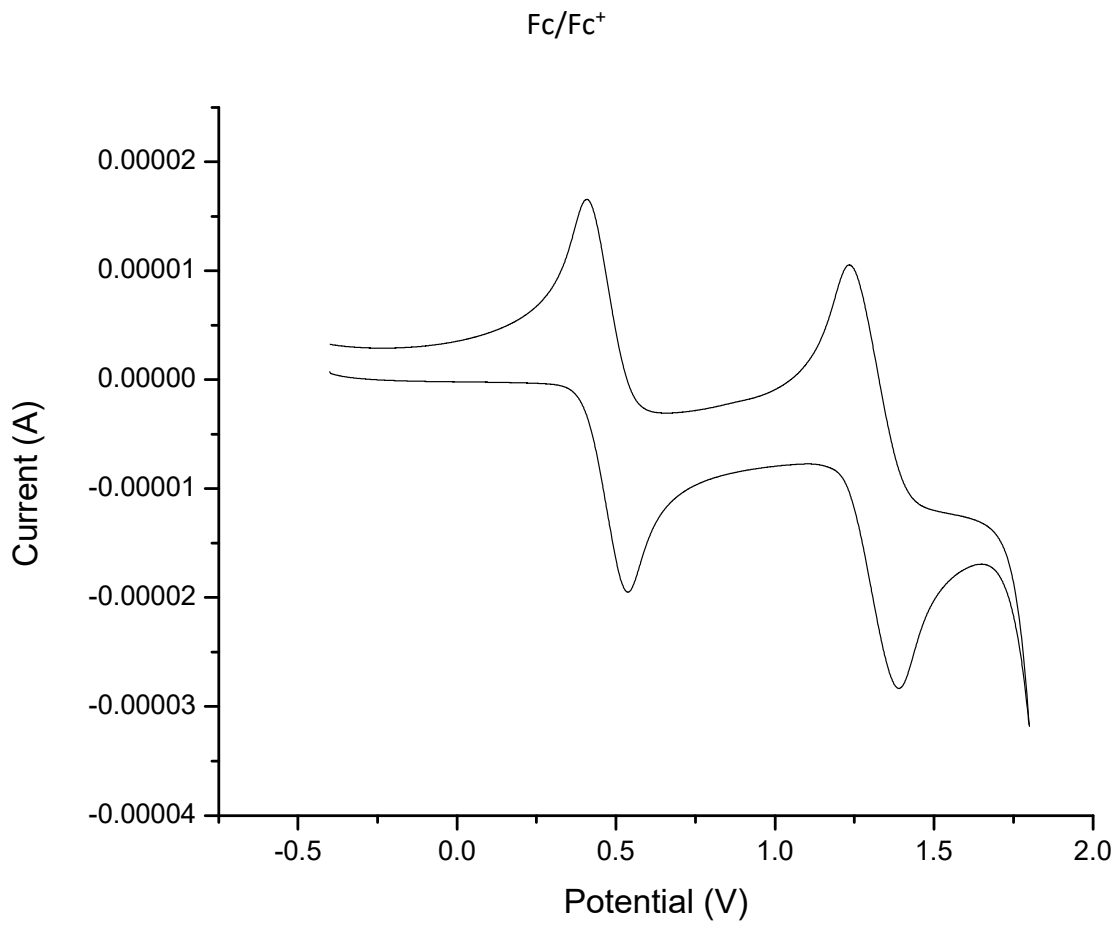


Figure S1. Cyclic voltammogram of **2** in tetra-^{n}butylammonium hexafluorophosphate (0.1 M) in dichloromethane containing ferrocene (Fc/Fc^{+}).

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