Journal Name

ARTICLE TYPE

Cite this: DOI: 10.1039/xxxxxxxxxx

Rationalisation of the Optical Signatures of *nor*-Dihydroxanthene-Hemicyanine Fused Near-Infrared Fluorophores By First Principle Tools: ESI

Received Date
Accepted Date

DOI: 10.1039/xxxxxxxxxx

www.rsc.org/journalname

Table S1 Vertical absorption energies determined at various levels of theory. ADZ and ATZ stand for *aug*-cc-pVDZ and *aug*-cc-pVTZ, respectively. All values are in eV.

	TD-CAM-B3LYP/6-311++G(2df,2pd)					ADC(2)		CC2	
	Gas	LR-PCM(eq)	LR-PCM(neq)	cLR-PCM(eq)	cLR-PCM(neq)	Gas (ADZ)	Gas (ATZ)	Gas (ADZ)	Gas (ATZ)
1a	2.362	2.098	2.211	2.369	2.374	1.807	1.794	2.031	2.018
2a	2.312	2.064	2.172	2.324	2.329	1.763	1.749	1.987	1.974
1b	2.293	2.039	2.145	2.291	2.297	1.701	1.692	1.943	1.932
2b	2.245	2.006	2.108	2.249	2.255	1.659	1.649	1.899	1.887
1c	2.273	2.025	2.132	2.281	2.287	1.681	1.671	1.920	1.908
2c	2.227	1.991	2.094	2.238	2.244	1.640	1.630	1.878	1.866
1d	2.372	2.099	2.213	2.374	2.379	1.824	1.811	2.048	2.035
2d	2.321	2.067	2.176	2.330	2.334	1.779	1.765	2.003	1.990
1e	2.357	2.088	2.201	2.361	2.366	1.805	1.792	2.031	2.018
2e	2.309	2.056	2.165	2.318	2.323	1.762	1.748	1.987	1.974
1f	2.345	2.100	2.209	2.362	2.367	1.768	1.758	1.989	1.978
2f	2.298	2.068	2.172	2.319	2.323	1.731	1.720	1.951	1.939
1g	2.346	2.081	2.193	2.349	2.354	1.782	1.769	2.008	1.995
2g	2.297	2.047	2.155	2.305	2.310	1.739	1.726	1.965	1.952

Table S2 Vertical emission energies determined at various levels of theory. ADZ and ATZ stand for *aug*-cc-pVDZ and *aug*-cc-pVTZ, respectively. All values are in eV.

	TD-CAM-B3LYP/6-311++G(2df,2pd)				ADC(2)		CC2	
	Gas	LR-PCM(eq)	cLR-PCM(eq)	cLR-PCM(neq)	Gas (ADZ)	Gas (ATZ)	Gas (ADZ)	Gas (ATZ)
1a	2.244	1.964	2.248	2.244	1.695	1.682	1.941	1.928
2a	2.182	1.923	2.195	2.190	1.629	1.615	1.879	1.865
1b	2.190	1.921	2.188	2.183	1.609	1.599	1.870	1.859
2b	2.137	1.886	2.142	2.137	1.558	1.548	1.818	1.807
1c	2.164	1.901	2.170	2.165	1.580	1.570	1.840	1.829
2c	2.113	1.865	2.124	2.118	1.531	1.520	1.789	1.778
1d	2.252	1.964	2.252	2.248	1.707	1.694	1.952	1.939
2d	2.189	1.924	2.199	2.195	1.639	1.625	1.889	1.875
1e	2.234	1.947	2.232	2.228	1.686	1.673	1.932	1.920
2e	2.175	1.909	2.181	2.177	1.622	1.609	1.871	1.858
1f	2.223	1.960	2.235	2.230	1.660	1.649	1.905	1.894
2f	2.163	1.919	2.181	2.177	1.598	1.586	1.847	1.834
1g	2.233	1.953	2.234	2.230	1.677	1.665	1.923	1.911
2g	2.174	1.913	2.183	2.178	1.615	1.602	1.865	1.852

Table S3 Adiabatic energies determined at various levels of theory. ADZ and ATZ stand for *aug*-cc-pVDZ and *aug*-cc-pVTZ, respectively. All values are in eV.

	TD-CAM-B3LYP/6-311++G(2df,2pd)			ADC(2)		CC2	
	Gas	LR-PCM(eq)	cLR-PCM(eq)	Gas (ADZ)	Gas (ATZ)	Gas (ADZ)	Gas (ATZ)
1a	2.309	2.030	2.313	1.668	1.708	1.883	1.921
2a	2.254	1.991	2.263	1.603	1.643	1.818	1.855
1b	2.249	1.980	2.247	1.579	1.623	1.813	1.853
2b	2.199	1.946	2.202	1.528	1.571	1.759	1.797
1c	2.226	1.962	2.231	1.543	1.585	1.774	1.812
2c	2.178	1.927	2.186	1.495	1.535	1.721	1.758
1d	2.319	2.030	2.318	1.680	1.721	1.895	1.934
2d	2.261	1.993	2.268	1.613	1.651	1.828	1.864
1e	2.293	2.008	2.294	1.668	1.695	1.883	1.907
2e	2.239	1.972	2.245	1.609	1.634	1.821	1.844
1f	2.288	2.027	2.302	1.625	1.670	1.838	1.879
2f	2.234	1.990	2.252	1.566	1.610	1.778	1.817
1g	2.296	2.015	2.296	1.648	1.690	1.865	1.904
2g	2.242	1.979	2.248	1.588	1.629	1.803	1.842

Table S4 Difference between the ZPVE energies of the first ES and the GS, calculated at the LR(eq)-TD-CAM-B3LYP/6-311G(2d,p) level. All values are in eV

Compound	ΔE^{ZPVE}
1a	-0.051
2a	-0.036
1b	-0.046
2b	-0.042
1c	-0.049
2c	-0.032
1d	-0.039
2d	-0.040
1e	-0.059
2e	-0.062
1f	-0.040
2f	-0.034
1g	-0.047
2g	-0.037

Table S5 Computed oscillator strengths for all compounds using different theoretical levels.

	Absorption				Emission		
	TD-CAM-B3LYP/6-311++G(2df,2pd)			CC2	TD-CAM-B3LYP/6-311++G(2df,2pd)		CC2
	Gas	LR-PCM(eq)	LR-PCM(neq)	Gas (ADZ)	Gas	LR-PCM(eq)	Gas (ADZ)
1a	1.29	1.57	1.47	1.37	1.30	1.57	1.43
2a	1.28	1.55	1.46	1.39	1.30	1.56	1.45
1b	1.25	1.53	1.42	1.31	1.27	1.55	1.36
2b	1.24	1.51	1.41	1.33	1.27	1.53	1.38
1c	1.37	1.64	1.54	1.44	1.38	1.64	1.49
2c	1.37	1.62	1.53	1.46	1.38	1.62	1.51
1d	1.28	1.56	1.46	1.37	1.30	1.56	1.43
2d	1.27	1.54	1.44	1.38	1.29	1.54	1.44
1e	1.29	1.57	1.47	1.38	1.31	1.57	1.44
2e	1.28	1.54	1.45	1.39	1.30	1.55	1.45
1f	1.31	1.59	1.49	1.35	1.33	1.59	1.44
2f	1.29	1.56	1.47	1.36	1.32	1.57	1.45
1g	1.28	1.56	1.46	1.36	1.30	1.56	1.42
2g	1.28	1.54	1.45	1.37	1.30	1.55	1.44

Table S6 Computed GS and ES dipoles on the GS geometries. Note that, as the molecules are charged, the dipole moment are gauge-dependent which is $\Delta\mu$ are also listed. All values in D. The TD-DFT stands for TD-CAM-B3LYP/6-311++G(2df,2pd) and CC2 for CC2/*aug*-cc-pVDZ.

	TD-DFT						CC2		
	Gas			$CHCl_3$			Gas		
	GS	ES	Δ	GS	ES	Δ	GS	ES	Δ
1a	1.62	1.75	0.13	2.54	2.29	-0.25	1.62	3.94	2.32
2a	3.74	3.44	-0.30	5.08	4.81	-0.26	3.44	5.00	1.56
1b	1.56	1.77	0.21	2.38	2.16	-0.22	1.45	2.70	1.25
2b	3.89	3.38	-0.52	5.20	4.50	-0.69	3.26	3.78	0.52
1c	1.72	0.38	-1.34	2.48	0.77	-1.71	1.93	1.12	-0.81
2c	2.75	2.26	-0.49	4.04	3.25	-0.79	2.27	2.40	0.13
1d	1.95	3.01	1.06	2.49	3.40	0.91	1.91	4.73	2.82
2d	4.37	4.43	0.06	5.47	5.71	0.24	3.75	4.93	1.18
1e	1.74	2.53	0.80	2.43	2.92	0.49	1.85	4.32	2.46
2e	4.10	4.03	-0.07	5.28	5.29	0.01	3.69	5.29	1.60
1f	3.16	1.54	-1.62	4.45	2.92	-1.53	3.14	2.25	-0.88
2f	3.74	2.73	-1.01	5.54	4.56	-0.99	3.49	3.51	0.02
1g	1.47	1.93	0.46	2.31	2.34	0.03	1.55	3.45	1.90
2g	3.75	3.58	-0.18	4.36	4.83	0.47	3.49	4.10	0.62

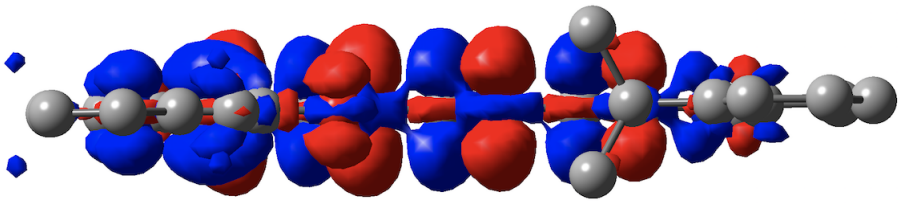

Fig. S1 Side view of the electron density difference (EDD) between the ES and GS for compounds for **1a**, showing the clear $\pi \rightarrow \pi^*$ character and the C_s like symmetry of the density changes (cut-off = 0.008 a.u.). Hydrogen atoms omitted for clarity.