Supporting Information for "Direct Evidence of Torsional Motion in an Aggregation-Induced Emissive Chromophore"

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Details on quantum chemical calculations

Geometry optimization for the ground state (S_0) has been performed at the PBE0/6-311++G** in different solvents ($CHCl_3$ Chloroform, CH_2Cl_2 Dichloromethane, and CH_3CN Acetonitrile), characterized by different polarities, to reproduce the experimentally observed independence of both absorption and emission spectra on solvent polarity. The PBE0 functional has been previously demonstrated to be appropriate to describe the electronic and optical features of a series of organic dyes [S1, S2]. The S_0 minimum has been confirmed by calculation of the vibrational frequencies. Vertical transition energies have been then computed in the different solvents at the corresponding

geometries by the Time Dependent DFT (TDDFT) approach, solving for up to 10 singlet excited states. To overcome the well-known failure of some commonly used functionals in describing long-range charge-transfer (CT) states [S3], other two exchange-correlation functionals, besides PBE0, have been considered for TDDFT calculations, that is, LC-BLYP [S4] and CAM-B3LYP [S5], which have been shown to provide a better performance for treating excited states [S6]. In all cases, the largest oscillator strength was found to be associated to the transition to the first excited state (S_1), having $\pi \rightarrow \pi^*$ character and arising essentially from a HOMO→LUMO excitation. S_1 was then submitted to geometry optimization in all the considered solvents. In one case (LC-BLYP/6-311++G in chloroform), all 10 first excited states were included in the optimization of S_1 to check for the occurrence of root-flipping events. Analytic frequency calculations for excited states are not currently available, so frequencies have been computed numerically, to check the attainment of the minimum, only for the LC-BLYP/6-311++G excited state optimized in chloroform, owing to the highly demanding computational costs. The S_1 optimized geometries were found very similar for all the considered functionals in the different solvents. In the paper we make reference to the geometry obtained with what we conclude to be, by comparison with the experimental results, the best performing functional, CAM-B3LYP.

Bulk solvent effects on the ground and the excited state geometries and on the transition energies have been taken into account by means of the conductor-like polarizable continuum model, CPCM [S7], according to two different approaches: the linear-response (LR) method and the state-specific (SS) method. The former is based on the direct determination of the excitation energies, avoiding explicit calculation of the excited-state electron density [S8]. The latter instead solves the Schrödinger equation for the states of interest (ground and excited states) through an iterative mutual optimization of the electron density in the specific excited state with solvent degrees of freedom [S9-S10]. The differences between the two approaches have been widely discussed in the literature [S11-S12]. In both frameworks, the vertical excitation/emission energies have been computed within the non equilibrium approach, where only the solvent electronic distribution is equilibrated with the new (excited) electronic structure of the solute, while molecular motions of the solvent are frozen. The excited-state optimizations in solution have been instead performed within the standard LR approach using the equilibrium approximation, i.e., considering a full solvent relaxation. For the presently investigated molecule, the LR formalism gave always excitation energies lower that those obtained by the SS method. Differences were however quite small in absorption spectra, independently on the functional and on the solvent considered, and became somewhat larger in emission spectra, in particular when LC-BLYP and CAM-B3LYP functionals were used. The better agreement with the experimental emission spectra has been obtained with the

LR approach and in the paper we report the results obtained within this method. As far as the performance of the different functionals used is concerned, as evaluated by comparison with the experimental results obtained in CH_2Cl_2, we found that PBE0 worked very well in determining the excitation energies, confirming previous results reported in the literature [S13], but strongly overestimated the emission energies. On the other hand, emission energies obtained by LC-BLYP and CAM-B3LYP were very similar and closer to the experimental values. Only the latter functional, however, provides excitation energies in acceptable agreement with the experimental results.

Table S1. LR-PCM TD-CAM-B3LYP/6-311++G**//PBE0/6-311++G** Maximum Absorption ($\lambda_{\mathrm{max}}^{\mathrm{abs}}$, nm) and Emission ($\lambda_{\mathrm{max}}^{\mathrm{em}}$, nm) Wavelengths, Oscillator Strength (f) and Excited State Dipole Moment (μ_1, Debye), and PBE0/6-311++G** Ground State Dipole Moment (μ_0, Debye) for the Title Compound.

	$CHCl_3$	CH_2Cl_2	CH_3CN
absorption			
$\lambda_{\mathrm{max}}^{\mathrm{abs}}$	350	357	363
f	1.26	1.31	1.35
μ_1	15.09	15.80	16.54
Emission			
$\lambda_{\mathrm{max}}^{\mathrm{em}}$	475	478	483
f	0.90	0.96	1.01
μ_1	11.52	12.28	12.97
μ_0	7.86	8.31	8.72

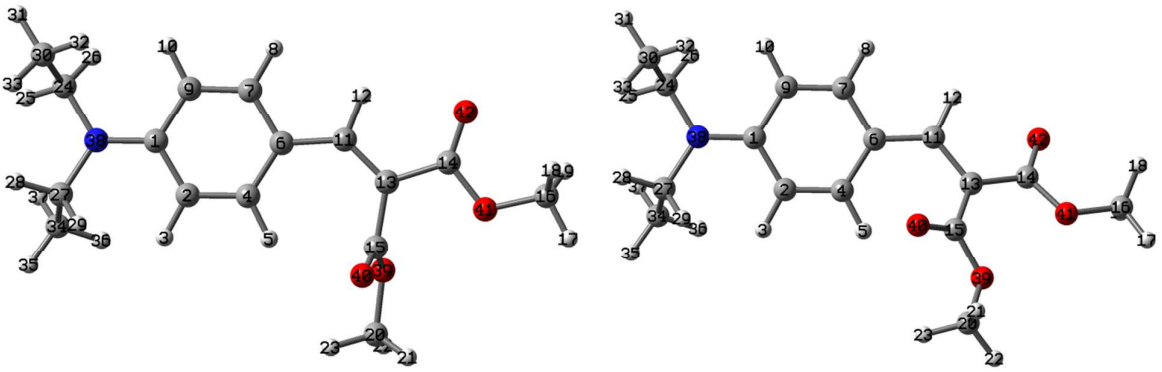

Figure S1. Optimized structures of the ground state at the PBE0/6-311++G** level of theory (left) and of the first excited singlet state at the CAM-B3LYP/6-311++G** level of theory (right) of the compound in CH_2Cl_2 with atom labeling scheme.

Table S2. Selected distances (Å) in the optimized PBE0/6-311++G** ground state (S_0) and CAM-B3LYP/6-311++G** excited singlet state (S_1) of compound **1** in CH_2Cl_2

	S_0	S_1
C1-N38	1.360	1.352
C1-C2	1.419	1.424
C1-C9	1.416	1.434
C2-C4	1.376	1.366
C9-C7	1.377	1.359
C4-C6	1.408	1.436
C7-C6	1.408	1.432
C6-C11	1.439	1.404
C11-C13	1.354	1.427
C13-C14	1.471	1.460
C13-C15	1.493	1.456
C14-O42	1.213	1.224
C15-O40	1.208	1.225
C14-O41	1.342	1.344
C15-O39	1.333	1.347
O41-C16	1.428	1.429
O39-C20	1.433	1.429

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Optimized geometry of the PBE0/6-311++G** ground state (S_0) of compound **1** in dichloromethane

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.807013	-0.246270	-0.033926
2	6	0	1.846457	0.758624	0.251747
3	1	0	2.165578	1.766479	0.483292
4	6	0	0.496577	0.492493	0.226897
5	1	0	-0.177045	1.307750	0.462289
6	6	0	-0.005202	-0.785437	-0.085739
7	6	0	0.950774	-1.779489	-0.367510
8	1	0	0.608155	-2.782693	-0.605788
9	6	0	2.305726	-1.533603	-0.346073
10	1	0	2.982933	-2.351747	-0.553942
11	6	0	-1.394826	-1.153731	-0.140153
12	1	0	-1.575360	-2.201706	-0.376146
13	6	0	-2.530753	-0.439756	0.042030
14	6	0	-3.816778	-1.139709	-0.097327
15	6	0	-2.592235	1.008131	0.401473
16	6	0	-6.152657	-0.877573	0.004299
17	1	0	-6.846523	-0.064095	0.205716
18	1	0	-6.280885	-1.676073	0.737152
19	1	0	-6.315241	-1.275470	-0.998916
20	6	0	-2.800559	3.189465	-0.442115
21	1	0	-3.695763	3.400016	0.145263
22	1	0	-2.873445	3.647610	-1.425896
23	1	0	-1.921473	3.561119	0.087161
24	6	0	5.128594	-0.978700	-0.396460
25	1	0	5.992973	-0.436970	-0.791370
26	1	0	4.740246	-1.568170	-1.231035
27	6	0	4.665574	1.304560	0.422582
28	1	0	5.652185	1.120749	0.857757
29	1	0	4.049785	1.695335	1.236824
30	6	0	5.564601	-1.883172	0.748961
31	1	0	6.323335	-2.591246	0.403749
32	1	0	4.721607	-2.452681	1.148598
33	1	0	5.995261	-1.296659	1.565523
34	6	0	4.779905	2.321089	-0.705954
35	1	0	5.206925	3.255591	-0.331039
36	1	0	3.802349	2.542534	-1.142222
37	1	0	5.429767	1.946794	-1.502073
38	7	0	4.141065	0.016607	-0.006867
39	8	0	-2.684063	1.781152	-0.680498
40	8	0	-2.568434	1.439250	1.530154
41	8	0	-4.847609	-0.306494	0.110424
42	8	0	-3.960655	-2.314440	-0.362983

Optimized geometry of the CAM-B3LYP/6-311++G** excited singlet state (S_1) of compound **1** in dichloromethane

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.786784	-0.226256	-0.081518
2	6	0	1.778377	0.733701	-0.379251
3	1	0	2.056129	1.717990	-0.726467
4	6	0	0.450262	0.441665	-0.255006
5	1	0	-0.273010	1.198469	-0.518396
6	6	0	-0.003713	-0.850505	0.175403
7	6	0	1.020196	-1.815803	0.443021
8	1	0	0.720883	-2.807310	0.762654
9	6	0	2.343752	-1.526498	0.330086
10	1	0	3.064436	-2.292020	0.575647
11	6	0	-1.352068	-1.230165	0.274862
12	1	0	-1.542727	-2.294523	0.366917
13	6	0	-2.504066	-0.398093	0.141917
14	6	0	-3.687411	-1.050279	-0.410174
15	6	0	-2.488815	0.950985	0.689820
16	6	0	-6.011928	-1.021886	-0.781956
17	1	0	-6.832608	-0.337651	-0.582496
18	1	0	-6.182782	-1.974031	-0.279320
19	1	0	-5.916206	-1.194143	-1.854229
20	6	0	-3.402789	3.122789	0.697751
21	1	0	-3.630401	3.088880	1.763577
22	1	0	-4.188598	3.648925	0.161651
23	1	0	-2.445985	3.624540	0.551529
24	6	0	5.148763	-0.930926	0.036997
25	1	0	6.002082	-0.627454	-0.571142
26	1	0	4.818830	-1.890466	-0.359175
27	6	0	4.574371	1.417111	-0.489602
28	1	0	5.550577	1.531472	-0.016211
29	1	0	3.917628	2.148822	-0.019823
30	6	0	5.571099	-1.057758	1.497656
31	1	0	6.373542	-1.792741	1.586599
32	1	0	4.738518	-1.380270	2.124653
33	1	0	5.939357	-0.104638	1.881738
34	6	0	4.692241	1.671795	-1.989410
35	1	0	5.076655	2.678846	-2.162723
36	1	0	3.723896	1.583955	-2.484145
37	1	0	5.379225	0.961363	-2.453023
38	7	0	4.102574	0.069944	-0.172375
39	8	0	-3.375866	1.805623	0.144957
40	8	0	-1.695150	1.317665	1.548414
41	8	0	-4.843610	-0.379761	-0.267185
42	8	0	-3.655098	-2.163138	-0.919283