Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Do inverse dithienylethene behave as normal one ? A joint spectroscopic and theoretical investigation

Stéphane Aloïse[*], *Michel Sliwa*, *Guy Buntinx*, *Stéphanie Delbaere*, *Aurélie Perrier*, *François Maurel*, *Denis Jacquemin*, *Michinori Takeshita*.

I. Energetic and structural parameters in vacuum and in acetonitrile (ACN).

TABLE S1. Energetic and geometrical parameters for both the ground state S_0 and the excited state S_1(opt) of the different OF conformers and CF isomer computed at the ωB97x/6-31+G(d) level of theory (**vacuum**). ΔE is the relative electronic energy difference taking the most stable system as reference, ΔG the relative Gibbs free energy and μ the dipole moment. The dihedral angles (ξ_1, ξ_2) and (ϕ_1, ϕ_2) are defined in Scheme 1 and Rcc is the distance between the reactive carbon atoms (3 and 3' in Scheme 1).

			ΔE (eV)	ΔE (kcal/mol)	ΔG (kcal/mol)	μ (D)	(ξ_1, ξ_2)	(ϕ_1, ϕ_2)	Rcc (A)
Ground State S_0	OF	AP1	0.000	0.0	0.0	7.4	(45.9,46.0)	(164.4,-174.3)	3.576
		P2	0.069	1.6	1.5	7.0	(48.3,-143.4)	(157.0,-171.5)	4.386
		AP3	0.120	2.8	1.8	6.5	(152.0,106.2)	(-160.0,167.1)	5.384
	CF		0.723	16.7	19.4	9.1	(5.0,3.7)	(-172.7,-151.8)	1.550
	TS		*2.583*	*59.5*	*58.0*	8.2	(18.1,17.4)	(-174.4,159.1)	2.084
Excited State S_1(opt)	OF	AP1	3.411	78.6	78.8	10.5	(23.6,22.7)	(177.9,150.7)	2.816
		P2	3.424	78.9	77.7	9.7	(24.1,-160.1)	(176.8,143.8)	4.351
		AP3	3.465	79.9	77.9	8.9	(161.4,171.5)	(-140.5,-161.5)	5.805
	CF		3.438	79.2	79.6	8.9	(14.3,13.6)	(-172.7,161.5)	1.737

TABLE S2. Energetic and geometrical parameters for both the ground state S_0 and the excited state S_1(opt) of the different OF conformers and CF isomer computed at the PCM(**ACN**)-ωB97x/6-31+G(d) level of theory. See Table S1 for more details.

			ΔE (eV)	ΔE (kcal/mol)	ΔG (kcal/mol)	μ (D)	(ξ_1, ξ_2)	(ϕ_1, ϕ_2)	Rcc (A)
Ground-State S_0	OF	AP1	0.000	0.0	0.0	8.7	(45.7,45.7)	(165.5, -175.8)	3.583
		P2	0.072	1.7	1.5	8.1	(-143.2, 48.2)	(157.2, -172.2)	4.382
		AP3	0.129	3.0	2.7	7.5	(151.7,106.1)	(167.9,-160.3)	5.380
	CF		0.684	15.8	23.0	10.9	(5.0,3.9)	(152.2,-172.8)	1.551
	TS		*2.556*	*58.9*	*57.6*	10.8	(17.9,17.3)	(-175.6,159.5)	2.092
Excited-State S_1(opt)	OF	AP1	3.208	73.9	75.3	12.8	(22.4,23.3)	(149.4,173.0)	3.045
		P2	3.162	72.9	70.3	11.8	(23.0,-161.8)	(141.7,174.2)	4.455
		AP3	3.176	73.2	70.9	10.7	(162.1,172.1)	(-139.7,-160.5)	5.863
	CF		3.276	75.5	Denis	11.7	(13.2,12.9)	(-173.5,163.1)	1.672

II. Structural parameters in vacuum and comparison with RX data

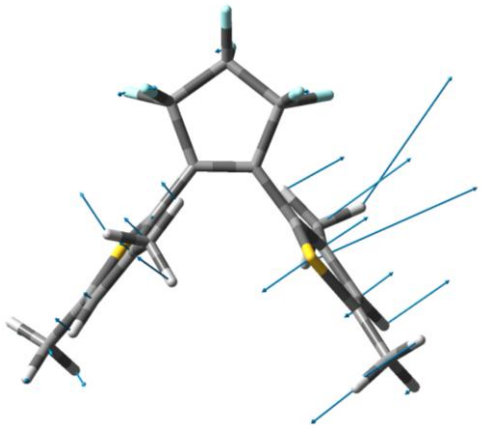
TABLE S3. Selected geometrical parameters obtained through X Ray diffraction experiments and calculated at the ωB97X/6-31+G(d) level in vacuum. The distances are in Å and the dihedral angles in degrees. The atom numbering is given in Scheme 1.

Distances	Exp.	Calc.	Calc/Exp. difference	Calc/Exp. Difference in %
C1-C2	1.741	1.740	-0.001	-0.054
C2-C3	1.373	1.374	0.001	0.046
C3-C4	1.420	1.432	0.012	0.815
C4-C5	1.356	1.364	0.008	0.572
C5-C1	1.726	1.724	-0.001	-0.078
C2-C6	1.454	1.461	0.007	0.511
C1'-C2'	1.742	1.740	-0.002	-0.106
C2'-C3'	1.380	1.375	-0.005	-0.362
C3'-C4'	1.423	1.431	0.008	0.564
C4'-C5'	1.357	1.364	0.007	0.528
C5'-C1'	1.721	1.724	0.003	0.170
C2'-C6'	1.455	1.463	0.008	0.544
C6-C6'	1.356	1.352	-0.004	-0.312
C3-C3'	3.569	3.576	0.008	0.215
Dihedral angle				
C6-C6'-C2'-C3'	39.86	46.125	6.265	15.718
C6'-C6-C2-C3	42.847	46.024	3.177	7.415

III. Characterization of the transition states in Hexane

III.1. Transition state connecting AP1 and P2

Representation of the imaginary vibrational mode (24i cm^{-1})



Cartesian coordinates

C	-2.96567000	-0.14703300	0.11883800
C	-1.97882400	-1.33568600	-0.01697200
C	-0.61038400	-0.69984000	0.03002100
C	-0.68537600	0.62986900	-0.12999800
C	-2.11585000	1.08415300	-0.29176900
F	-2.18416700	-1.97270200	-1.20457700
F	-2.16915300	-2.25199700	0.96223500
F	-3.33473200	-0.02149400	1.41412600
F	-4.07245600	-0.29434700	-0.62932200
F	-2.41463400	2.16678500	0.46563800
F	-2.38134800	1.41758400	-1.58624600
C	2.18942600	3.26386300	0.33110100
C	2.21692900	2.84360200	-0.96481800
S	0.91833800	2.47947300	1.20104100
C	1.21196700	1.87178400	-1.28915800
C	0.43614500	1.57949100	-0.20144800
C	2.63448700	-2.90740800	-0.15335700
C	2.33001600	-2.72075800	1.16166300
S	1.48939200	-2.10025200	-1.16623500
C	1.15865600	-1.92282100	1.38558200
C	0.60278800	-1.51449800	0.20513900
C	1.05730800	1.27666900	-2.65973400
H	0.22177400	0.57198900	-2.70789100
H	0.87730800	2.06123500	-3.40320200
H	1.96708100	0.74045600	-2.95286000
H	3.62202100	3.81247700	1.84760900
C	3.08664400	4.25973300	1.00319400
H	2.52203900	5.11893700	1.38086700
H	3.82745300	4.62804500	0.28754700
C	3.77642400	-3.68055600	-0.74228000
H	3.42192600	-4.50818300	-1.36607000
H	4.38952800	-4.09933100	0.06106400
H	4.41676300	-3.04350600	-1.36188400
C	0.63209000	-1.59413500	2.75346400
H	2.93905300	3.21302900	-1.68869100
H	2.92525300	-3.13991700	1.96904600
H	-0.17744100	-0.85914200	2.71220100
H	0.24390100	-2.49260600	3.24653900
H	1.42740800	-1.18403700	3.38535400

III.2. Transition state connecting AP1 and AP3

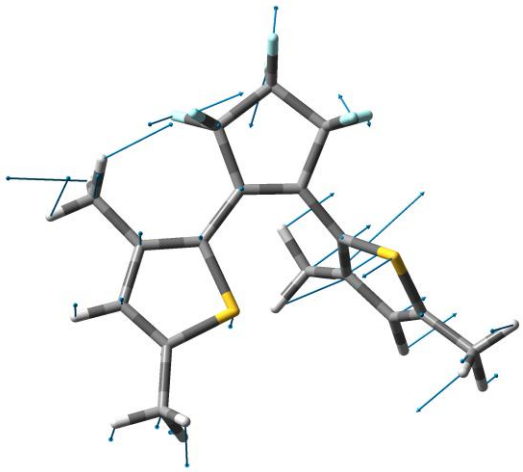
Representation of the imaginary vibrational mode (20i cm^{-1})

Cartesian coordinates

C	-2.96794700	-0.11072500	0.12685400
C	-1.99645600	-1.31207000	-0.00852500
C	-0.62009200	-0.69335400	0.03347500
C	-0.67873100	0.63698000	-0.12757100
C	-2.10361500	1.10927800	-0.28717100
F	-2.21273400	-1.94930100	-1.19403900
F	-2.19579400	-2.22351200	0.97342000
F	-3.33319600	0.02165200	1.42255400
F	-4.07778400	-0.24546900	-0.61917200
F	-2.38720900	2.19661300	0.46915700
F	-2.36745200	1.44422100	-1.58165300
C	2.23644300	3.22616900	0.33387000
C	2.23815900	2.82900300	-0.96959100
S	0.97021600	2.44091900	1.21027600
C	1.21632400	1.87519500	-1.29496600
C	0.45453100	1.57265600	-0.20033300
C	2.59830100	-2.93696000	-0.16913300
C	2.30582200	-2.74498800	1.14783000
S	1.45415300	-2.11932500	-1.17472900
C	1.14483600	-1.93405800	1.37934000
C	0.58412700	-1.52234800	0.20248800
C	1.03217700	1.30648800	-2.67303500
H	0.80236800	2.10126400	-3.39164300
H	1.94697200	0.80621200	-3.01015300
H	0.21697800	0.57775600	-2.70923200
H	2.60888900	5.06035900	1.40672300
C	3.15632200	4.19919100	1.00878400
H	3.89283100	4.56797000	0.28895200
H	3.69644100	3.73196700	1.83927500
C	3.72735300	-3.72329100	-0.76540600
H	3.35930500	-4.54665200	-1.38697700
H	4.34071500	-4.14922300	0.03396400
H	4.37095000	-3.09348400	-1.38902300
C	0.63439400	-1.59455300	2.75065700
H	2.95368300	3.20218400	-1.69808300
H	2.90257900	-3.16942900	1.95133800
H	1.43442300	-1.16828000	3.36581600
H	-0.18341500	-0.86863500	2.71237200
H	0.26319100	-2.49101500	3.26010100

III.3. Transition state connecting AP3 and P2

Representation of the imaginary vibrational mode (30i cm^{-1})

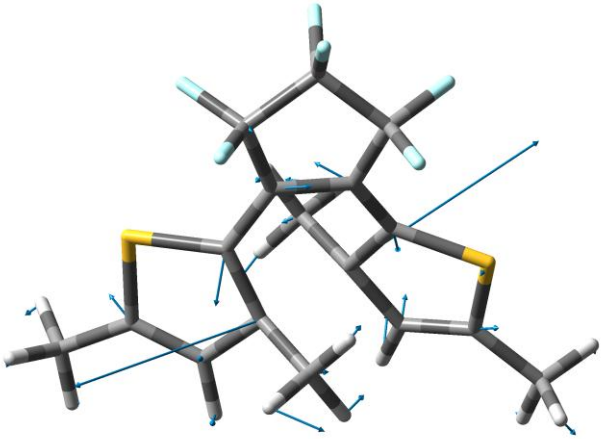


Cartesian coordinates

C	-2.32363600	-1.86020800	0.00989100
C	-2.39709300	-0.31010800	-0.08683300
C	-0.96826800	0.18564500	0.00352000
C	-0.12107600	-0.87383800	0.02215500
C	-0.83010700	-2.17811900	-0.20150900
F	-3.18420700	0.15766500	0.91836200
F	-2.98681800	0.04901400	-1.26017500
F	-3.12402800	-2.46222100	-0.88878900
F	-2.70032100	-2.25815800	1.24505900
F	-0.62918100	-2.63648000	-1.47505300
F	-0.41264300	-3.16371600	0.63092500
C	3.79150500	-1.17035200	-0.10698900
C	3.44539900	-0.74476000	1.14205200
S	2.38875200	-1.39840800	-1.08781000
C	2.03551700	-0.58626900	1.33571100
C	1.33568300	-0.89371900	0.19845000
C	0.64649100	3.75295500	-0.29323000
C	-0.69443700	3.93869300	-0.13324600
S	1.03602300	2.08335600	-0.25135500
C	-1.45044100	2.73560600	0.01659000
C	-0.63633000	1.61242700	-0.02051800
C	1.43265700	-0.10194100	2.62158600
H	0.35180400	-0.26833800	2.65230300
H	1.88144800	-0.61518900	3.47856000
H	1.60986000	0.97385900	2.74656900
H	5.37148600	-0.86360700	-1.54451800
C	5.16380100	-1.44959200	-0.64291200
H	5.28632300	-2.50838900	-0.89556300
H	5.91303900	-1.19146200	0.11111500
C	1.70852800	4.79380800	-0.47952500
H	1.25836600	5.79008700	-0.44899000
H	2.21625900	4.67714800	-1.44296100
H	2.46779500	4.73696000	0.30779300
C	-2.94444700	2.83727500	0.18711100
H	4.17777000	-0.54887200	1.92128600
H	-1.15726900	4.92185500	-0.12415600
H	-3.25855500	2.53115600	1.18869700
H	-3.24967500	3.87769900	0.04392500
H	-3.49275000	2.22795900	-0.53418800

III.4. Transition state connecting AP1 and CF

Representation of the imaginary vibrational mode (936i cm^{-1})



Cartesian coordinates

6	-0.02594	-0.05081	-0.00676
6	-0.02096	-0.05862	1.40537
16	1.41291	0.02464	2.39167
6	0.46561	0.42151	3.82001
6	1.16438	0.62424	5.12794
1	1.72303	-0.27182	5.42034
1	0.43485	0.84652	5.91198
1	1.87582	1.45597	5.07346
6	-0.85757	0.47788	3.55614
1	-1.59833	0.6679	4.33002
6	-1.23607	0.19216	2.17627
6	-2.43772	-0.71555	1.98116
1	-2.25544	-1.66895	2.49054
1	-3.33809	-0.26477	2.41245
1	-2.62934	-0.93273	0.92775
6	-1.05917	0.54448	-0.74521
6	-2.04866	1.34885	-0.14392
16	-3.69876	1.45972	-0.68968
6	-4.20085	2.20292	0.82455
6	-5.6338	2.59389	1.00751
1	-5.94844	3.31029	0.24048
1	-6.29551	1.72302	0.93974
1	-5.77361	3.05627	1.98884
6	-3.16803	2.36686	1.67888
1	-3.28372	2.85386	2.64492
6	-1.86809	1.91919	1.18956
6	-0.6964	2.85139	1.44372
1	0.22897	2.48934	0.98992
1	-0.91765	3.83438	1.01178
1	-0.52903	2.98043	2.51849
6	0.98881	-0.66953	-0.91296
9	0.9905	-2.03257	-0.83321
9	2.26657	-0.27278	-0.64973
6	0.54913	-0.23519	-2.34094
9	0.74431	-1.19601	-3.26114
9	1.2528	0.85991	-2.71312
6	-0.94586	0.16094	-2.18472
9	-1.72951	-0.91832	-2.50094
9	-1.28817	1.14966	-3.04816

IV. Frontier orbitals

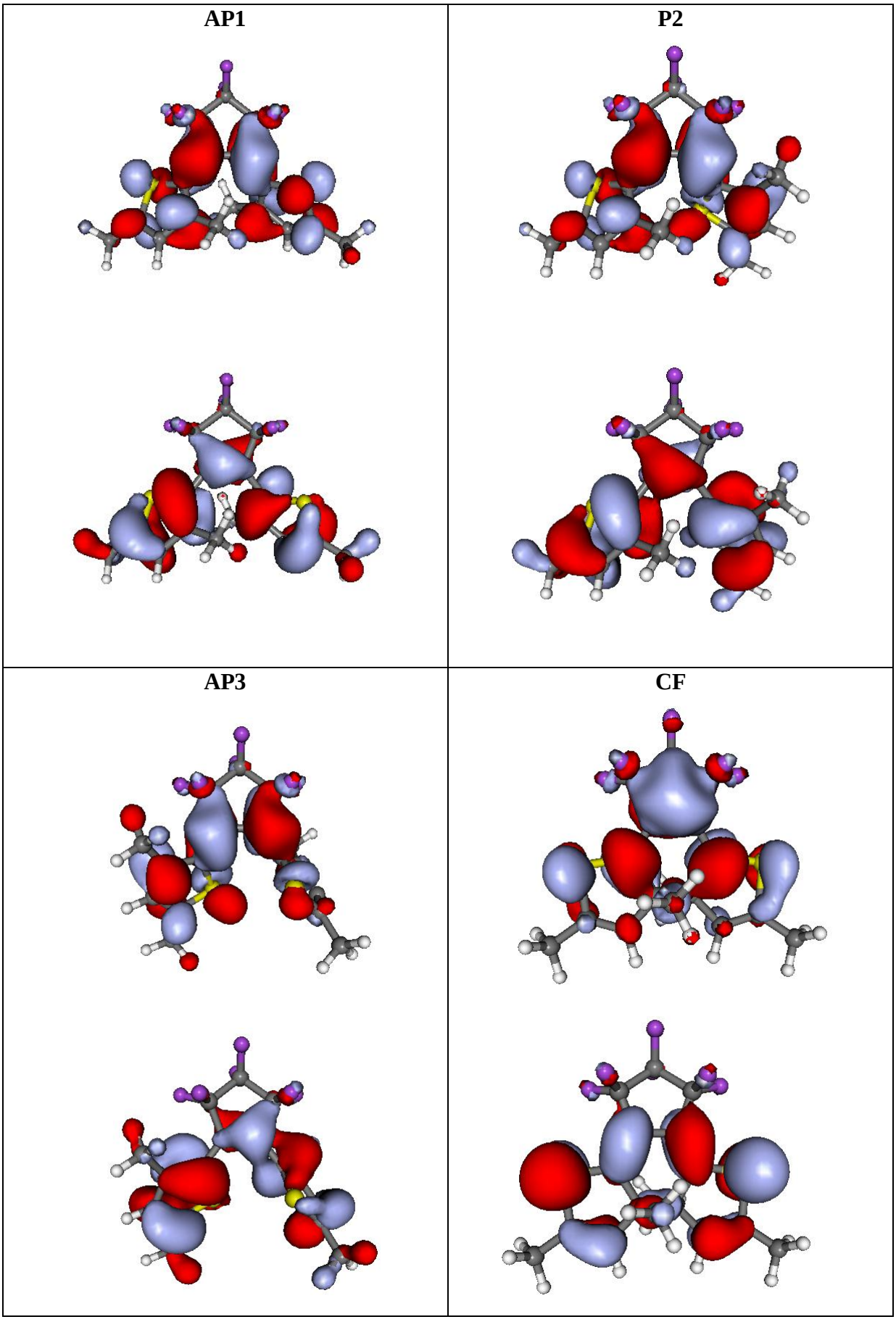
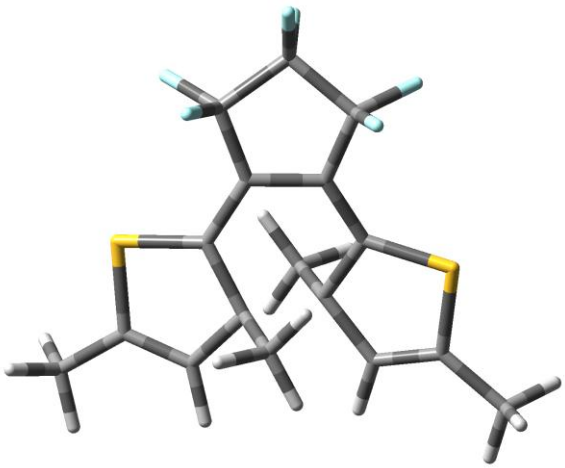


Figure S1: Frontier orbitals computed at the PCM(hexane)ωB97X/6-31+G(d) (Threshold: 0.02 a.u.). For each conformer top: LUMO, down: HOMO

V. Characterization of the CF excited state minimum in Hexane



Cartesian coordinates

6	-3.064234	-0.040069	-0.224873
6	-2.161870	-1.252446	0.138155
6	-0.778585	-0.705737	0.111239
6	-0.793382	0.692483	-0.037413
6	-2.185221	1.207075	0.066586
9	-2.358276	-2.289713	-0.732769
9	-2.518723	-1.737704	1.368285
9	-4.225395	-0.034208	0.457567
9	-3.358000	-0.073045	-1.547629
9	-2.484830	1.686033	1.320097
9	-2.465400	2.223441	-0.793893
6	2.390120	2.899323	0.092454
6	2.757844	1.659672	-0.285530
16	0.650681	3.061799	0.241572
6	1.656659	0.694507	-0.532285
6	0.395066	1.413315	-0.209338
6	2.450772	-2.841100	-0.142187
6	2.802533	-1.596456	0.234675
16	0.712245	-3.038358	-0.250509
6	1.688304	-0.657049	0.516945
6	0.432734	-1.402789	0.233772
6	1.700995	0.147310	-1.970383
1	1.632671	0.976948	-2.680815
1	2.642925	-0.385012	-2.143757
1	0.870639	-0.538952	-2.161323
1	3.008978	4.916585	-0.322037
6	3.263526	4.088858	0.348623
1	4.312245	3.824698	0.186096
1	3.153357	4.447390	1.377830
6	3.342470	-4.009198	-0.432275
1	3.209393	-4.364167	-1.460014
1	3.127027	-4.846375	0.240348
1	4.389473	-3.722332	-0.299810
6	1.765999	-0.106106	1.952078
1	3.797866	1.395318	-0.467475
1	3.841139	-1.310164	0.389487
1	0.928082	0.563958	2.166761
1	1.736508	-0.934815	2.666149
1	2.701799	0.445855	2.094633

VI. Spectroscopic parameters in Vacuum

TABLE S3: Theoretical 0-0 energies, Stokes shift, λ_{abs}^{max} and λ_{fluo}^{max} in **vacuum**. All calculated values were obtained at the PBE0/6-31+G(d) //ωB97x/6-31+G(d) level of theory.

	λ_{abs}^{max} (nm)	λ_{fluo}^{max} (nm)	[0-0]]Energy (nm)	Stokes shift (eV)
AP1	342	590	415	1.53
P2	354	507	432	1.06
AP3	350	523	433	1.17
CF	430			