Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information for

Intersystem Crossing in a Dibenzofuran-Based Room Temperature Phosphorescent Luminophore Investigated by Non-Adiabatic Dynamics

Pelin Ulukan,[1] Elise Lognon,[2] Saron Catak,[1] and Antonio Monari[2,]*

1) Bogazici University 34342 Bebek/Istanbul Turkey.
2) Université Paris Cité and CNRS, ITODYS, F-75006 Paris, France.

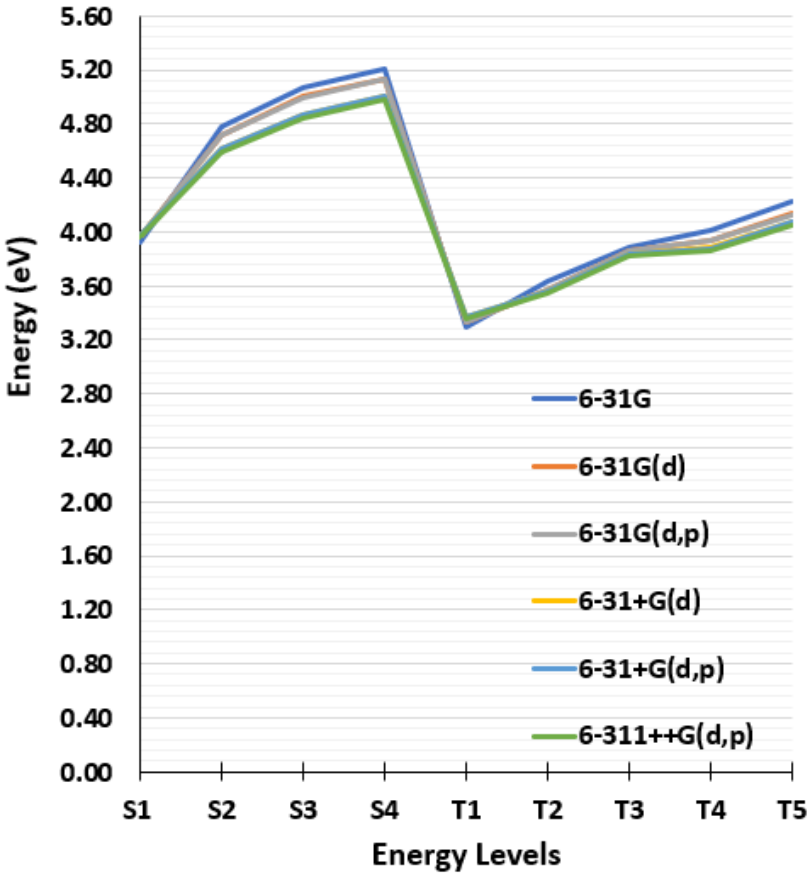


Figure S1. Vertical transitions energies calculated from the Franck-Condon geometry with different d exchange correlation functionals.

Table S1 3D representations of the S_0, S_1, T_1, T_2 and T_3 equilibrium geometries of the RTP luminophore, as optimized at M06-2X/6-31+G(d,p) level of theory in toluene.

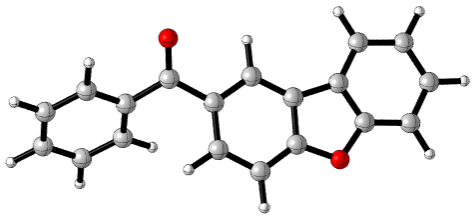
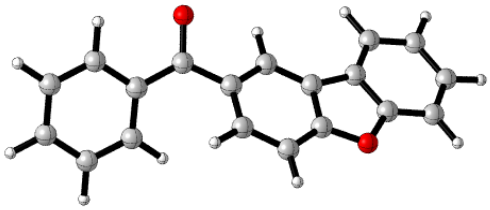
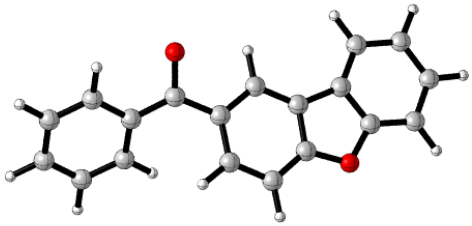
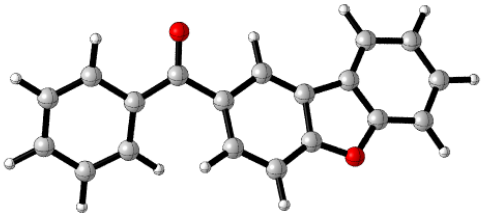
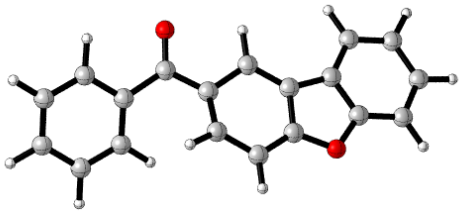
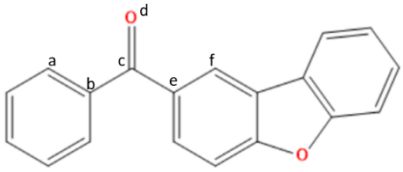
 S_0 Equilibrium Geometry	 S_1 Equilibrium Geometry
 T_1 Equilibrium Geometry	 T_2 Equilibrium Geometry
 T_3 Equilibrium Geometry	

Table S2 Evolution of the torsion angles around the carbonyl moiety for the FC, S_1, T_1, T_2 and T_3 equilibrium geometries, respectively.



a-b-c-d=α
d-c-e-f=β

Torsion Angle	FC / S_1 / T_1 / T_2 / T_3
α	-30.50 / -15.35 / -19.29 / -9.40 /-17.34
β	-26.60 / -34.85 / -26.60 / -23.12 / -15.26

Table S3 Excited states energies calculated with different basis sets using the CAM-B3LYP and with different functionals using the 6-31G basis set in toluene at the S_0 equilibrium geometry.

	S_1	S_2	S_3	S_4	T_1	T_2	T_3	T_4	T_5
6-31G	3.92	4.78	5.07	5.21	3.30	3.63	3.88	4.01	4.22
6-31G(d)	3.96	4.72	5.00	5.13	3.33	3.58	3.86	3.94	4.13

6-31G(d,p)	3.96	4.71	4.99	5.13	3.33	3.57	3.85	3.94	4.13
6-31+G(d)	3.98	4.62	4.87	5.01	3.37	3.56	3.84	3.88	4.08
6-31+G(d,p)	3.98	4.61	4.87	5.00	3.37	3.56	3.84	3.88	4.07
6-311++G(d,p)	3.97	4.59	4.84	4.98	3.35	3.54	3.82	3.86	4.05
	S_1	**S_2**	**S_3**	**S_4**	**T_1**	**T_2**	**T_3**	**T_4**	**T_5**
M06-2X	3.81	4.66	4.92	5.04	3.35	3.85	3.99	4.17	4.24
PBE0	3.79	4.14	4.34	4.70	3.19	3.45	3.64	3.75	3.79
ωB97XD	3.97	4.66	4.93	5.05	3.40	3.64	3.91	3.96	4.13
CAM-B3LYP	3.98	4.61	4.87	5.00	3.37	3.56	3.84	3.88	4.07

Table S4 Excited states energies calculated with different basis sets using the CAM-B3LYP functional and with different functionals using the 6-31G basis set in toluene at the S_1 equilibrium geometry.

	S_1	**S_2**	**S_3**	**S_4**	**T_1**	**T_2**	**T_3**	**T_4**	**T_5**
6-31G	3.37	4.63	4.77	5.01	2.74	3.32	3.62	3.91	4.15
6-31G(d)	3.38	4.56	4.74	4.97	2.76	3.33	3.56	3.83	4.07
6-31G(d,p)	3.38	4.56	4.74	4.97	2.76	3.33	3.55	3.83	4.06
6-31+G(d)	3.42	4.44	4.62	4.85	2.83	3.34	3.52	3.77	4.00
6-31+G(d,p)	3.42	4.44	4.61	4.85	2.83	3.33	3.52	3.76	4.00
6-311++G(d,p)	3.41	4.41	4.60	4.83	2.82	3.33	3.51	3.74	3.98
	S_1	**S_2**	**S_3**	**S_4**	**T_1**	**T_2**	**T_3**	**T_4**	**T_5**
M06-2X	3.22	4.65	4.79	5.07	2.71	3.48	3.97	4.13	4.32
PBE0	3.20	3.98	4.13	4.67	2.57	3.22	3.51	3.65	3.77
ωB97XD	3.37	4.69	4.84	5.01	2.77	3.41	3.72	3.99	4.21
CAM-B3LYP	3.37	4.63	4.77	5.01	2.74	3.32	3.62	3.91	4.15

Table S5 Excited states energies calculated with different basis sets using the CAM-B3LYP functional and with different functionals using the 6-31G basis set in toluene at the T_1 equilibrium geometry.

	S_1	**S_2**	**S_3**	**S_4**	**T_1**	**T_2**	**T_3**	**T_4**	**T_5**
6-31G	3.17	4.51	4.61	4.92	2.52	3.06	3.54	3.82	4.03
6-31G(d)	3.17	4.44	4.59	4.89	2.54	3.07	3.49	3.73	3.97
6-31G(d,p)	3.17	4.44	4.59	4.89	2.53	3.07	3.49	3.72	3.97
6-31+G(d)	3.22	4.32	4.46	4.76	2.62	3.11	3.44	3.67	3.89
6-31+G(d,p)	3.21	4.31	4.46	4.76	2.62	3.11	3.44	3.66	3.89
6-311++G(d,p)	3.20	4.29	4.44	4.74	2.61	3.10	3.42	3.64	3.88
	S_1	**S_2**	**S_3**	**S_4**	**T_1**	**T_2**	**T_3**	**T_4**	**T_5**
M06-2X	3.04	4.52	4.63	4.97	2.51	3.16	3.83	4.06	4.20
PBE0	3.00	3.89	4.04	4.54	2.36	2.95	3.41	3.51	3.73
ωB97XD	3.16	4.57	4.68	4.92	2.55	3.13	3.63	3.91	4.11
CAM-B3LYP	3.17	4.51	4.61	4.92	2.52	3.06	3.54	3.82	4.03

Table S6 Excited states energies calculated with different basis sets using the CAM-B3LYP functional and with different functionals using the 6-31G basis set in toluene at the T_2 equilibrium geometry.

	S_1	S_2	S_3	S_4	T_1	T_2	T_3	T_4	T_5
6-31G	3.71	4.48	4.66	5.00	3.02	3.29	3.45	3.86	4.14
6-31G(d)	3.72	4.42	4.62	4.96	3.02	3.25	3.45	3.76	4.06
6-31G(d,p)	3.72	4.42	4.61	4.96	3.02	3.25	3.45	3.76	4.06
6-31+G(d)	3.72	4.30	4.52	4.85	3.03	3.21	3.47	3.72	4.00
6-31+G(d,p)	3.72	4.29	4.52	4.84	3.02	3.21	3.47	3.71	4.00
6-311++G(d,p)	3.71	4.27	4.50	4.82	3.01	3.19	3.45	3.69	3.98
	S_1	S_2	S_3	S_4	T_1	T_2	T_3	T_4	T_5
M06-2X	3.58	4.50	4.69	5.06	3.07	3.50	3.62	4.15	4.30
PBE0	3.49	3.96	4.09	4.72	2.86	3.21	3.29	3.67	3.78
ωB97XD	3.71	4.55	4.71	5.00	3.08	3.37	3.51	3.95	4.19
CAM-B3LYP	3.71	4.48	4.66	5.00	3.02	3.29	3.45	3.86	4.14

Table S7 Excited states energies calculated with different basis sets using the CAM-B3LYP functional and with different functionals using the 6-31G basis set in toluene at the T_3 equilibrium geometry.

	S_1	S_2	S_3	S_4	T_1	T_2	T_3	T_4	T_5
6-31G	2.84	4.26	4.32	4.70	2.22	2.52	3.32	3.70	3.85
6-31G(d)	2.83	4.20	4.29	4.67	2.22	2.52	3.27	3.61	3.79
6-31G(d,p)	2.83	4.20	4.29	4.67	2.22	2.52	3.27	3.61	3.79
6-31+G(d)	2.89	4.06	4.15	4.50	2.33	2.60	3.20	3.51	3.75
6-31+G(d,p)	2.89	4.06	4.15	4.49	2.33	2.60	3.20	3.51	3.75
6-311++G(d,p)	2.88	4.04	4.14	4.47	2.31	2.59	3.18	3.49	3.73
	S_1	S_2	S_3	S_4	T_1	T_2	T_3	T_4	T_5
M06-2X	2.75	4.26	4.32	4.72	2.24	2.55	3.53	3.83	4.11
PBE0	2.67	3.69	3.81	4.29	2.06	2.40	3.17	3.26	3.69
ωB97XD	2.83	4.33	4.39	4.72	2.26	2.58	3.39	3.79	3.94
CAM-B3LYP	2.84	4.26	4.32	4.70	2.22	2.52	3.32	3.70	3.85

Table S8 Topological Φ_s index of the S_1, T_1, T_2, and T_3 states obtained from the S_0 equilibrium geometries with different functionals using the 6-31G basis set.

Functional	S_1	T_1	T_2	T_3
M062X	0.45	0.48	0.95	0.88
PBE0	0.47	0.61	0.92	0.76
ωB97XD	0.45	0.57	0.93	0.90
CAMB3LYP	0.45	0.65	0.91	0.89

Table S9 Difference transition matrix obtained from the SH trajectories.

	S_0	S_1	T_1	T_2	T_3	T_4
S_0	0	0	0	0	0	0
S_1	0	0	0	-18	-10	-2

$\mathbf{T_1}$	0	0	0	46	-25	-5
$\mathbf{T_2}$	0	18	-46	0	38	-4
$\mathbf{T_3}$	0	10	25	-38	0	6
$\mathbf{T_4}$	0	2	5	4	-6	0

S_0 Equilibrium Geometry

H	4.378600	1.763800	-1.285100
C	4.477300	0.935700	-0.590200
C	4.682100	-1.161500	1.237800
C	3.322600	0.411300	0.001300
C	5.723900	0.397900	-0.288100
C	5.827000	-0.650900	0.627700
C	3.429900	-0.639100	0.919400
H	6.615500	0.797800	-0.760100
H	6.800500	-1.066200	0.869200
H	2.540300	-1.032300	1.402400
H	4.763000	-1.965800	1.961800
C	2.009200	1.056100	-0.322500
O	1.963800	2.248800	-0.579800
C	0.757400	0.237100	-0.324600
C	-1.582700	-1.201900	-0.417900
C	-0.446100	0.894800	-0.055300
C	0.768700	-1.133300	-0.652100
C	-0.406200	-1.875500	-0.712700
C	-1.629300	0.163900	-0.090000
H	-0.433600	1.955700	0.174000
H	1.710400	-1.618000	-0.887800
H	-0.409800	-2.925900	-0.979300
O	-2.826300	-1.763400	-0.412100
C	-3.035600	0.455200	0.136400
C	-3.701700	-0.759000	-0.076800
C	-3.774300	1.587900	0.486900
H	-3.283200	2.540800	0.656500
C	-5.154300	1.463200	0.611400
H	-5.748600	2.329300	0.882300
C	-5.793800	0.232400	0.391400
H	-6.871800	0.166900	0.495900
C	-5.075100	-0.908400	0.040800
H	-5.555100	-1.864700	-0.132600

S_1 Equilibrium Geometry

H	4.409100	1.959600	−1.044200
C	4.500500	1.072500	−0.425800
C	4.734300	−1.222500	1.140400
C	3.337400	0.384900	−0.019700
C	5.755900	0.606800	−0.052900
C	5.883800	−0.544500	0.724600
C	3.472200	−0.766700	0.783600
H	6.641400	1.145300	−0.376500
H	6.865600	−0.907000	1.010300
H	2.589000	−1.282200	1.145800
H	4.821600	−2.109000	1.761200
C	2.030700	0.893800	−0.398700
O	1.927100	2.110500	−0.837400
C	0.751200	0.157500	−0.381500
C	−1.632300	−1.223100	−0.416000
C	−0.434700	0.848600	−0.087800
C	0.714900	−1.214500	−0.729100
C	−0.475800	−1.926700	−0.732400
C	−1.637000	0.143900	−0.104900
H	−0.403400	1.902100	0.169400
H	1.636300	−1.714100	−1.008400
H	−0.509100	−2.979700	−0.987600
O	−2.889400	−1.756200	−0.374700
C	−3.030000	0.473100	0.148100
C	−3.731000	−0.727300	−0.034600
C	−3.732700	1.628600	0.499400
H	−3.215100	2.571200	0.645800
C	−5.112200	1.540600	0.655400
H	−5.678400	2.424900	0.927700
C	−5.787100	0.323500	0.465800
H	−6.863800	0.286700	0.594700
C	−5.105200	−0.839400	0.115000
H	−5.613000	−1.785300	−0.035100

T_1 Equilibrium Geometry

H	4.311700	1.994500	−1.068600
C	4.462900	1.101900	−0.469700
C	4.849700	−1.217300	1.032400
C	3.339300	0.371300	−0.015400
C	5.748900	0.666300	−0.179700
C	5.954200	−0.497800	0.564100
C	3.558200	−0.789700	0.762200
H	6.599000	1.234600	−0.544100
H	6.960900	−0.837300	0.783800
H	2.712200	−1.331600	1.171900
H	4.999300	−2.111800	1.629100
C	2.011700	0.850400	−0.296800
O	1.902000	2.140000	−0.619800
C	0.752000	0.130800	−0.288800
C	−1.644200	−1.244600	−0.356100
C	−0.446600	0.830200	−0.043600
C	0.711100	−1.254900	−0.599500
C	−0.481400	−1.960000	−0.622000
C	−1.649400	0.129900	−0.079500
H	−0.421500	1.888800	0.193900
H	1.634400	−1.766700	−0.848200
H	−0.513200	−3.017900	−0.856400
O	−2.905800	−1.771000	−0.338200
C	−3.047700	0.471200	0.126800
C	−3.750100	−0.729800	−0.046400
C	−3.753200	1.638100	0.430800
H	−3.234200	2.581300	0.569300
C	−5.137100	1.561400	0.550400
H	−5.705400	2.454900	0.785800
C	−5.813400	0.343600	0.371300
H	−6.893500	0.315300	0.471100
C	−5.128700	−0.830900	0.067700
H	−5.637600	−1.777500	−0.073400

T_2 Equilibrium Geometry

H	4.303400	2.161500	−0.708400
C	4.469400	1.188200	−0.265300
C	4.735900	−1.335800	0.942700
C	3.284200	0.377500	−0.032400
C	5.721600	0.704500	0.020900
C	5.885500	−0.563900	0.615400
C	3.476900	−0.884600	0.651800
H	6.597100	1.306000	−0.204500
H	6.875700	−0.942700	0.843000
H	2.618100	−1.471900	0.959300
H	4.863000	−2.290900	1.443400
C	2.017300	0.984000	−0.374500
O	1.895500	2.169700	−0.678400
C	0.785300	0.148400	−0.339100
C	−1.615600	−1.235800	−0.363500
C	−0.451600	0.871300	−0.150500
C	0.731800	−1.260500	−0.690000
C	−0.439600	−1.963200	−0.675100
C	−1.626900	0.167300	−0.117800
H	−0.373700	1.941800	−0.010800
H	1.650700	−1.761100	−0.974200
H	−0.490900	−3.020000	−0.911000
O	−2.841900	−1.769000	−0.294900
C	−3.030300	0.484300	0.117700
C	−3.715300	−0.729600	−0.003200
C	−3.748100	1.642400	0.409600
H	−3.245200	2.598500	0.509300
C	−5.130500	1.537000	0.568900
H	−5.710700	2.424700	0.796100
C	−5.783900	0.305200	0.440900
H	−6.859700	0.256200	0.570500
C	−5.080500	−0.867000	0.148300
H	−5.570900	−1.827800	0.044300

T_3 Equilibrium Geometry

H	4.256200	2.102400	−0.764000
C	4.414300	1.115100	−0.342100
C	4.732100	−1.384600	0.851900
C	3.287300	0.417700	0.098200
C	5.685300	0.553000	−0.227100
C	5.849300	−0.698600	0.366600
C	3.463700	−0.822900	0.718500
H	6.553000	1.094800	−0.593000
H	6.840800	−1.129100	0.471300
H	2.603300	−1.347900	1.133700
H	4.855000	−2.343300	1.346900
C	1.944700	1.124400	−0.017200
O	1.821200	2.331000	−0.156700
C	0.793400	0.295500	−0.210000
C	−1.564800	−1.253300	−0.348100
C	−0.487800	0.973000	−0.292300
C	0.778000	−1.080700	−0.687600
C	−0.367100	−1.892600	−0.610400
C	−1.647900	0.166700	−0.228600
H	−0.486600	2.053900	−0.280700
H	1.685800	−1.496000	−1.113000
H	−0.321300	−2.957700	−0.812200
O	−2.802400	−1.839700	−0.211800
C	−3.013400	0.439700	0.013100
C	−3.671100	−0.826700	0.004000
C	−3.762500	1.619500	0.229400
H	−3.274200	2.587100	0.241700
C	−5.119700	1.490500	0.420100
H	−5.730100	2.370000	0.587500
C	−5.743500	0.214400	0.401200
H	−6.816200	0.158100	0.553400
C	−5.036800	−0.964700	0.193600
H	−5.517100	−1.935000	0.176700