Tuning of dye optical properties by environmental effects: a QM/MM and experimental study

Supporting Information

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1. Force field parameters for the *a* and *b* fluorophores

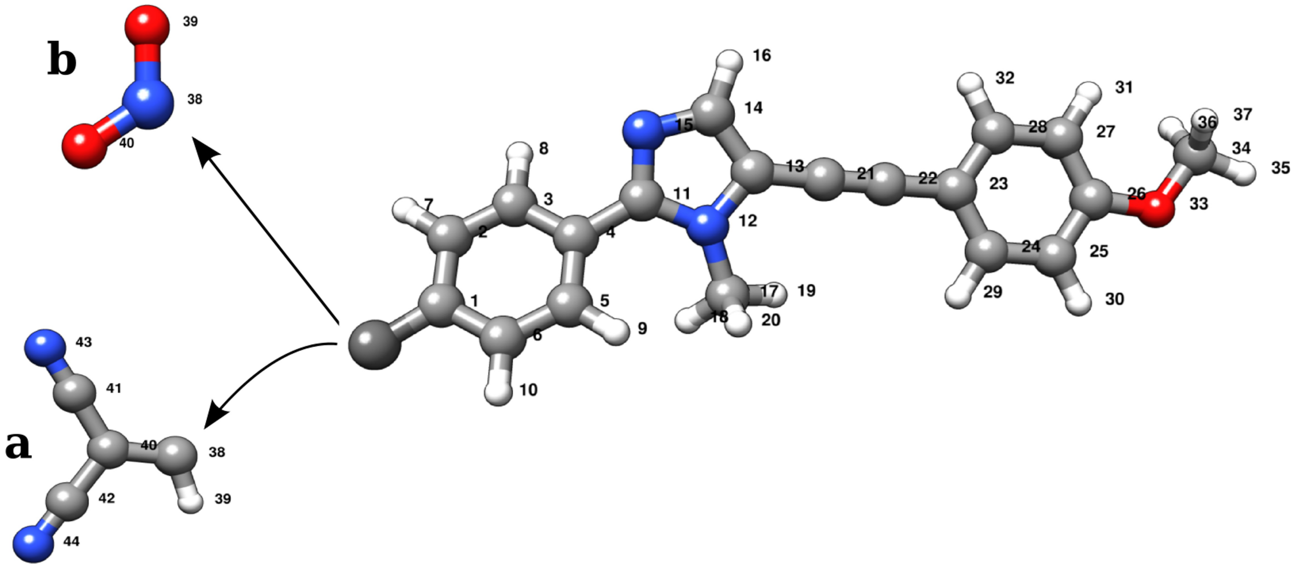

Figure 1 Main scaffold, structures and atom numbers used in the topology files of the two investigated dyes.

Index	Atom type	CM5 charge	epsilon	sigma	Index	Atom type	CM5 charge	epsilon	sigma
1	CZ	-0.014692	0.355	0.29288	26	CE	0.097115	0.355	0.29288
2	CA	-0.077903	0.355	0.29288	27	CA	-0.115905	0.355	0.29288
3	CA	-0.080194	0.355	0.29288	28	CA	-0.085843	0.355	0.29288
4	C!	0.016234	0.355	0.29288	29	HA	0.111585	0.242	0.12552
5	CA	-0.092009	0.355	0.29288	30	HA	0.114977	0.242	0.12552
6	CA	-0.074794	0.355	0.29288	31	HA	0.112094	0.242	0.12552
7	HA	0.111753	0.242	0.12552	32	HA	0.112284	0.242	0.12552
8	HA	0.115161	0.242	0.12552	33	OS	-0.231589	0.029	0.58576
9	HA	0.114037	0.242	0.12552	34	CT	-0.12639	0.355	0.276144
10	HA	0.117279	0.242	0.12552	35	HV	0.117978	0.25	0.12552
11	CR	0.236292	0.355	0.29288	36	HV	0.106994	0.25	0.12552

12	NA	-0.278203	0.325	0.71128	37	HV	0.106948	0.25	0.12552
13	CW	0.101919	0.355	0.29288					
14	CV	0.02153	0.355	0.29288			**a**		
15	NB	-0.408453	0.325	0.71128	38	CL	-0.022113	0.355	0.317984
16	HY	0.126081	0.242	0.12552	39	HL	0.13151	0.242	0.12552
17	CM	-0.105589	0.355	0.76144	40	CD	0.019259	0.355	0.317984
18	HC	0.121021	0.25	0.12552	41	CN	0.211037	0.33	0.276144
19	HC	0.120628	0.25	0.12552	42	CN	0.201518	0.33	0.276144
20	HC	0.11887	0.25	0.12552	43	NN	-0.356313	0.32	0.71128
21	CK	-0.065676	0.33	0.87864	44	NN	-0.369598	0.32	0.71128
22	CK	-0.044361	0.33	0.87864			**b**		
23	C!	-0.019544	0.355	0.29288	38	NO	0.062924	0.325	0.50208
24	CA	-0.087302	0.355	0.29288	39	ON	-0.188437	0.296	0.71128
25	CA	-0.107599	0.355	0.29288	40	ON	-0.186432	0.296	0.71128

Table 1 Indices, atom types, LJ terms and charges used for **a** and **b**. Indices refer to those reported in Figure 1. In the **a** and **b** sections, only parameters relative to the **a** or the **b** dye respectively are stored.

Bonds	b^0_μ/nm	K^s_μ/kJ mol^{-1} nm^{-2}	**Bonds**	b^0_μ/nm	K^s_μ/kJ mol^{-1} nm^{-2}
1 2	0.1414	315699.207	25 26	0.1404	347563.214
2 3	0.1383	355365.18	26 27	0.1401	347563.214
3 4	0.1412	322199.123	23 28	0.1405	333025.144
4 5	0.1407	322199.123	27 28	0.1393	348716.415
1 6	0.1412	315699.207	24 29	0.1086	336132.25
5 6	0.1386	355365.18	25 30	0.1086	336132.25
2 7	0.1083	338818.342	27 31	0.1083	336132.25
3 8	0.1084	338818.342	28 32	0.1086	336132.25
5 9	0.1083	338818.342	26 33	0.136	332011.511
6 10	0.1087	338818.342	33 34	0.1427	264301.282
4 11	0.146	320098.726	34 35	0.109	313438.804
11 12	0.1376	310883.584	34 36	0.1096	313438.804
12 13	0.1389	309257.087	34 37	0.1096	313438.804
13 14	0.1391	369872.098			
11 15	0.1337	370395.568		**a**	
14 15	0.1354	332448.31	1 38	0.1443	331364.784
14 16	0.1081	346296.187	38 39	0.1088	330151.178
12 17	0.1461	246654.559	38 40	0.137	324566.43
17 18	0.109	318908.58	40 41	0.1428	327488.968
17 19	0.1091	318908.58	40 42	0.1428	327488.968
17 20	0.1094	318908.58	41 43	0.1162	1119155.778
13 21	0.1405	406572.33	42 44	0.1162	1119155.778
21 22	0.1218	872113.995		**b**	
22 23	0.1421	408943.544	1 38	0.1464	154137.162
23 24	0.1412	333025.144	38 39	0.1231	470490.51
24 25	0.1385	348716.415	38 40	0.1231	470490.51

Table 2 Fitted stretching parameters.

Angles	θ^0_μ/nm	K^b_μ/kJ mol^{-1} rad^{-2}	**Angles**	θ^0_μ/nm	K^b_μ/kJ mol^{-1} rad^{-2}
1 2 3	120.73	253.9221	22 23 24	120.97	173.8313
2 1 6	117.63	193.1521	22 23 28	120.87	173.8313
1 2 7	120.67	317.778	23 24 25	120.85	157.5618
2 1 43	125.51	335.0622	24 23 28	118.16	126.5979
2 3 4	121.43	245.4664	23 24 29	119.46	313.9231
3 2 7	118.6	331.085	24 25 26	120.35	222.8489

2 3 8	119.92	331.085	25 24 29	119.69	333.5413
3 4 5	118.05	173.1986	24 25 30	120.86	333.5413
4 3 8	118.65	334.2055	25 26 27	119.59	211.48
3 4 11	118.12	352.7555	26 25 30	118.79	306.2763
4 5 6	120.53	245.4664	25 26 33	115.89	309.6693
4 5 9	120.81	334.2055	26 27 28	119.75	222.8489
5 4 11	123.8	352.7555	26 27 31	121.13	306.2763
1 6 5	121.62	253.9221	27 26 33	124.52	309.6693
1 6 10	119.19	317.778	23 28 27	121.3	157.5618
6 1 43	116.85	335.0622	23 28 32	119.38	313.9231
6 5 9	118.63	331.085	28 27 31	119.13	333.5413
5 6 10	119.19	331.085	27 28 32	119.32	333.5413
4 11 12	126.64	281.2499	26 33 34	118.63	92.5806
4 11 15	122.48	236.5187	33 34 35	105.78	508.21
11 12 13	106.84	233.2102	33 34 36	111.15	508.21
12 11 15	110.88	263.8464	33 34 37	111.14	508.21
11 12 17	129.13	223.0908	35 34 36	109.5	321.1039
12 13 14	105.33	181.1476	35 34 37	109.5	321.1039
13 12 17	123.78	190.9795	36 34 37	109.68	321.1039
12 13 21	123.8	228.1906			
13 14 15	110.55	208.6338		**a**	
13 14 16	127.02	236.8634	1 38 39	114.32	489.3336
14 13 21	130.87	229.9816	1 38 40	131.6	107.8855
11 15 14	106.41	210.1101	39 38 40	114.08	248.6584
15 14 16	122.43	340.9489	38 40 41	119.06	167.314
12 17 18	109.83	477.4827	38 40 42	125.76	167.314
12 17 19	108.37	477.4827	41 40 42	115.18	206.1414
12 17 20	111.24	477.4827	40 41 43	178.44	684.4887
18 17 19	108.99	328.7599	40 42 44	179.95	684.4887
18 17 20	109.66	328.7599		**b**	
19 17 20	108.7	328.7599	1 38 39	118.2	443.4879
13 21 22	178.62	141.9975	1 38 40	118.2	443.4879
21 22 23	179.78	57.2501	39 38 40	123.65	1110.8395

Table 3 Fitted bending parameters.

Harmonic dihedrals	Φ^0_μ/°	K^t_μ/kJ mol^{-1} rad^{-2}	Harmonic dihedrals	Φ^0_μ/°	K^t_μ/kJ mol^{-1} rad^{-2}
1 2 3 4	0	41.625	17 12 13 21	0	147.627
2 3 4 5	0	112.976	21 13 14 16	0	91.483
3 4 5 6	0	112.976	23 24 25 26	0	100.257
4 5 6 1	0	41.625	24 25 26 27	0	81.101
2 1 6 5	0	102.567	25 26 27 28	0	81.101
6 1 2 3	0	102.567	26 27 28 23	0	100.257
7 2 3 8	0	45.925	24 23 28 27	0	92.593
8 3 4 11	0	124.124	28 23 24 25	0	92.593
11 4 5 9	0	124.124	22 23 24 29	0	113.375
9 5 6 10	0	45.925	29 24 25 30	0	41.63
11 12 13 14	0	98.884	30 25 26 33	0	118.527
12 13 14 15	0	189.666	33 26 27 31	0	118.527
13 14 15 11	0	289.976	31 27 28 32	0	41.63
12 11 15 14	0	269.018	22 23 28 32	0	113.375
15 11 12 13	0	160.815		**a**	
4 11 12 17	0	8.72	39 38 40 42	0	137.51

Table 4 Fitted rigid torsion parameters.

Periodic dihedrals	γ^{j}_{μ}	K^{t}_{μ}/kJ mol^{-1} rad^{-2}	Periodic dihedrals	γ^{j}_{μ}	K^{t}_{μ}/kJ mol^{-1} rad^{-2}
5 4 11 12	1	0.365		4	1.016
	2	-7.023	26 33 34 35	3	2.088
	3	0.195			
	4	3.293		**a**	
	5	-0.126	2 1 38 39	2	-7.292
	6	0.203		4	1.096
11 12 17 18	3	-0.405		**b**	
	6	0.067	2 1 38 39	2	-6.413
27 26 33 34	2	6.799		4	0.652

Table 5 Fitted flexible torsion parameters.

2. MD Simulation Analysis of the b fluorophore

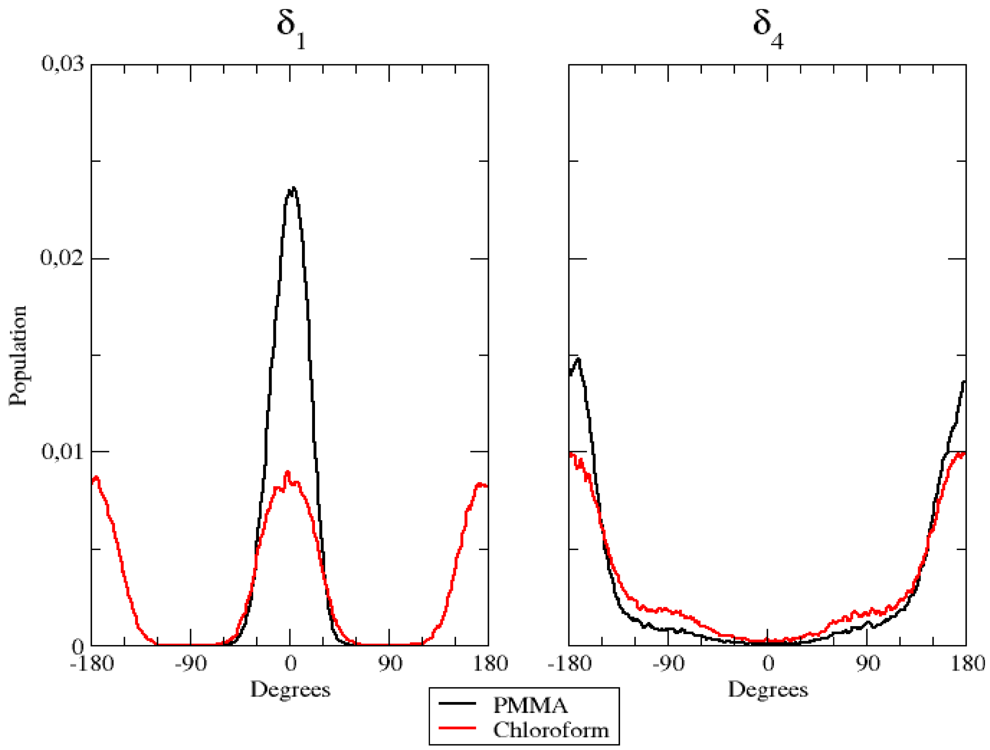

Figure 2 Population distribution of the δ_1 (left panel) and δ_4 (right panel) flexible dihedrals in the two considered environments.

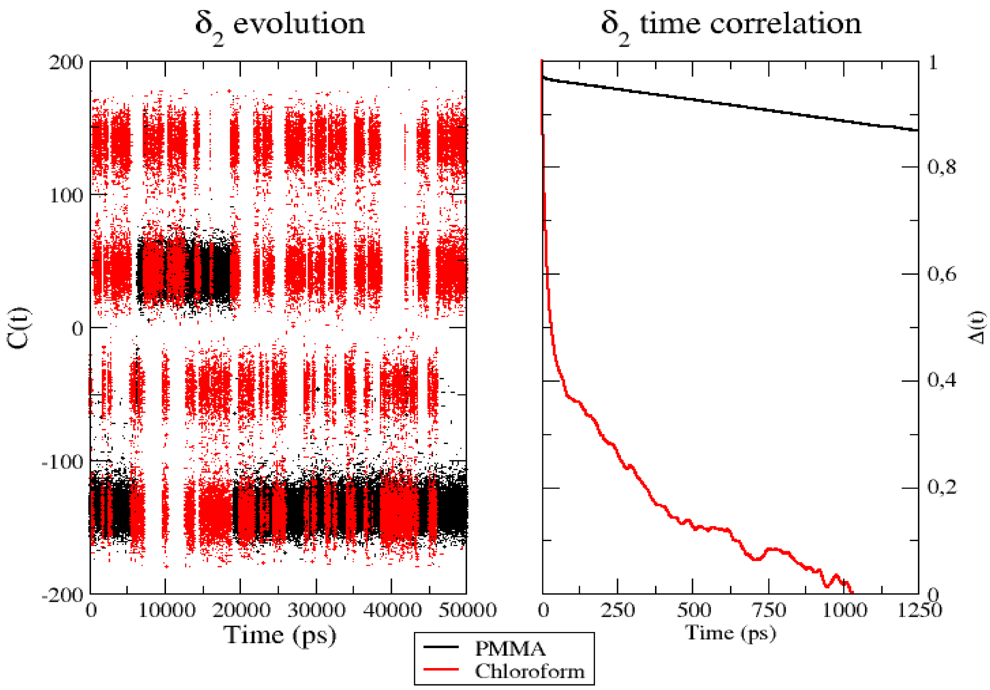

Figure 3 Population distribution of the δ_2 dihedral in PMMA matrix (black) and in chloroform solution (red). Right: time correlation of the δ_2 dihedral in the two considered environments.

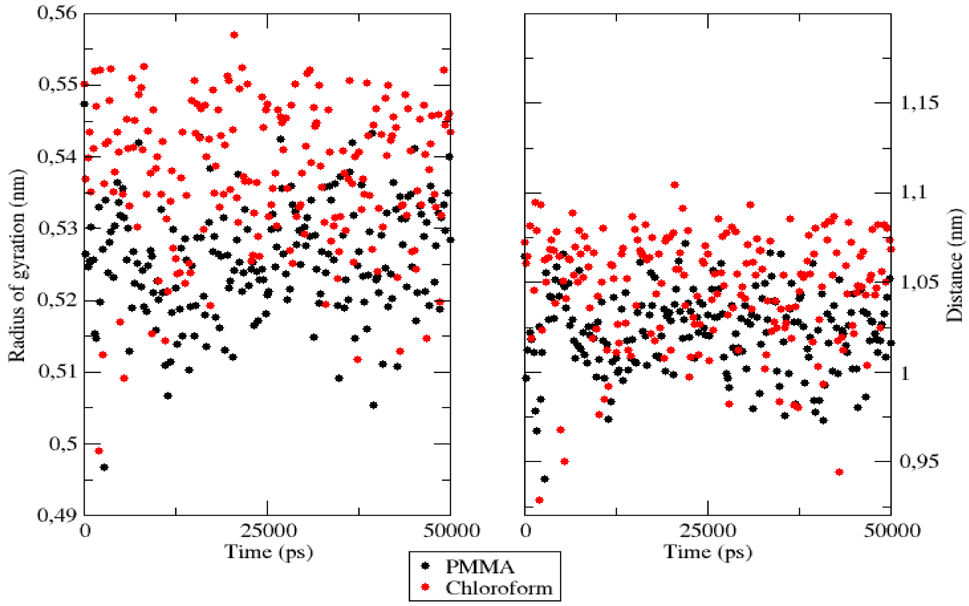

Figure 4 Left: gyration radius of the investigated dye among the sampled time in the two different simulations. Right: distance evolution between the two phenyl rings.

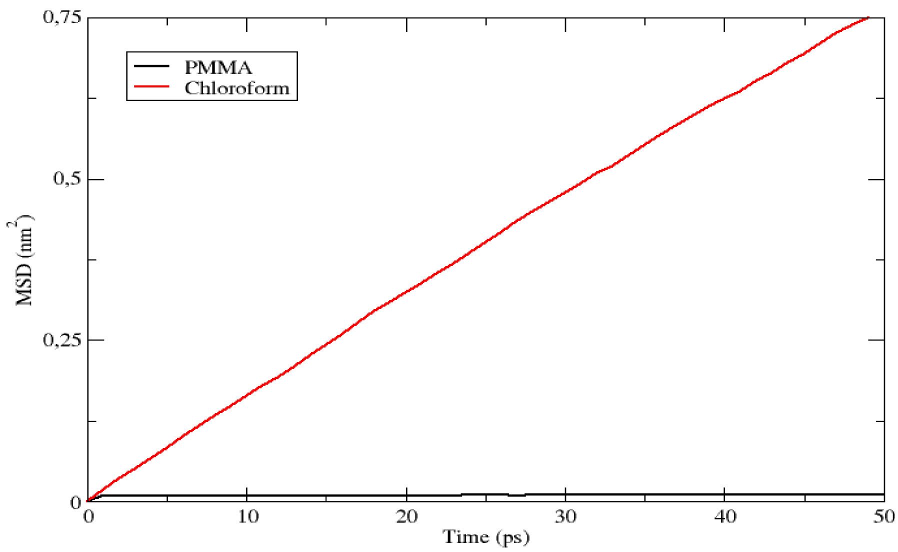

Figure 5 MSD(t) value computed in chloroform solution and in the PMMA matrix.