

## Supporting Information for manuscript: *Fluorescence Spectra of Organic Dyes in Solution: A Time Dependent Multilevel Approach*

The TRITC intramolecular FF was parameterized by means of the JOYCE program, through a least square minimization of the functional  $I^{intra}$

$$I^{intra} = \sum_{g=0}^{N_{geom}} W_g [U_g - E_g^{intra}]^2 + \sum_{K \leq L}^{3N-6} \frac{2W''_{KL}}{(3N-6)(3N-5)} \left[ H_{KL} - \left( \frac{\partial^2 E^{intra}}{\partial Q_K \partial Q_L} \right) \right]_{g=0}^2 \quad (1)$$

where  $N_{geom}$  is the number of the sampled conformations,  $Q_K$  is the  $K^{th}$  normal coordinate and  $U_g$  is the QM computed energy in the  $g^{th}$  geometry, with respect to the absolute minimum ( $g = 0$ ). The QM Hessian matrix  $H_{KL}$  and the FF Hessian are evaluated at  $g = 0$ . The employed intramolecular FF,  $E^{intra}$ , is:

$$E^{intra} = E^{stretch} + E^{bend} + E^{Rtors} + E^{Ftors} + E^{nb} \quad (2)$$

The first three terms have a harmonic expression

$$E^{stretch} = \frac{1}{2} \sum_{\mu=1}^{N_s} k_{\mu}^s (r_{\mu} - r_{\mu}^0)^2; \quad E^{bend} = \frac{1}{2} \sum_{\mu=1}^{N_b} k_{\mu}^b (\theta_{\mu} - \theta_{\mu}^0)^2; \quad E^{Rtors} = \frac{1}{2} \sum_{\mu=1}^{N_{Rt}} k_{\mu}^t (\phi_{\mu} - \phi_{\mu}^0)^2 \quad (3)$$

where  $k_{\mu}^s, k_{\mu}^b, k_{\mu}^t$  and  $r_{\mu}^0, \theta_{\mu}^0, \phi_{\mu}^0$  are the force constants and equilibrium values for stretching, bending and rigid torsional internal coordinates, respectively. For flexible dihedrals a sum of cosines is used, namely

$$E^{Ftors} = \sum_{\mu=1}^{N_{Fdihedrals}} \sum_{j=1}^{N_{\mu}} k_{j\mu}^d [1 + \cos(n_{\mu}^j \delta_{\mu} - \gamma_{\mu}^j)] \quad (4)$$

where  $k_{j\mu}^d$  is the force constant,  $\delta_{\mu}$  the flexible dihedral,  $n_{\mu}^j$  and  $\gamma_{\mu}^j$  the multiplicity and phase factor for the  $j$ -th cosine.  $N_{\mu}$  is the number of cosine functions employed for dihedral  $\mu$ . The last term of equation (2) is computed as

$$E^{nb} = \sum_{i=1}^{N_{sites}} \sum_{j=1}^{N_{sites}} [E_{ij}^{LJ \text{ intra}}] \quad (5)$$

where the interaction between the  $i$ -th and  $j$ -th atoms is described through a 12-6 Lennard Jones potential ( $E_{ij}^{LJ \text{ intra}}$ ). It should be noticed that  $E^{nb}$  is an off-diagonal term, and couples all internal coordinates which involve atoms  $i$  and  $j$ . In order to obtain a more accurate description of the lowest energy geometries, three different weights  $W_g$  were imposed in equation (1): 0.03, 0.012 and 0.005 for the conformations with an internal energy lower than 10 kJ/mol, between 10 and 20 kJ/mol, and higher than 20 kJ/mol, respectively. The diagonal and off diagonal elements of the weight matrix  $W''$  were set to  $0.017 \text{ \AA}^4 \cdot \text{amu}^2$  and  $0.008 \text{ \AA}^4 \cdot \text{amu}^2$ , respectively.

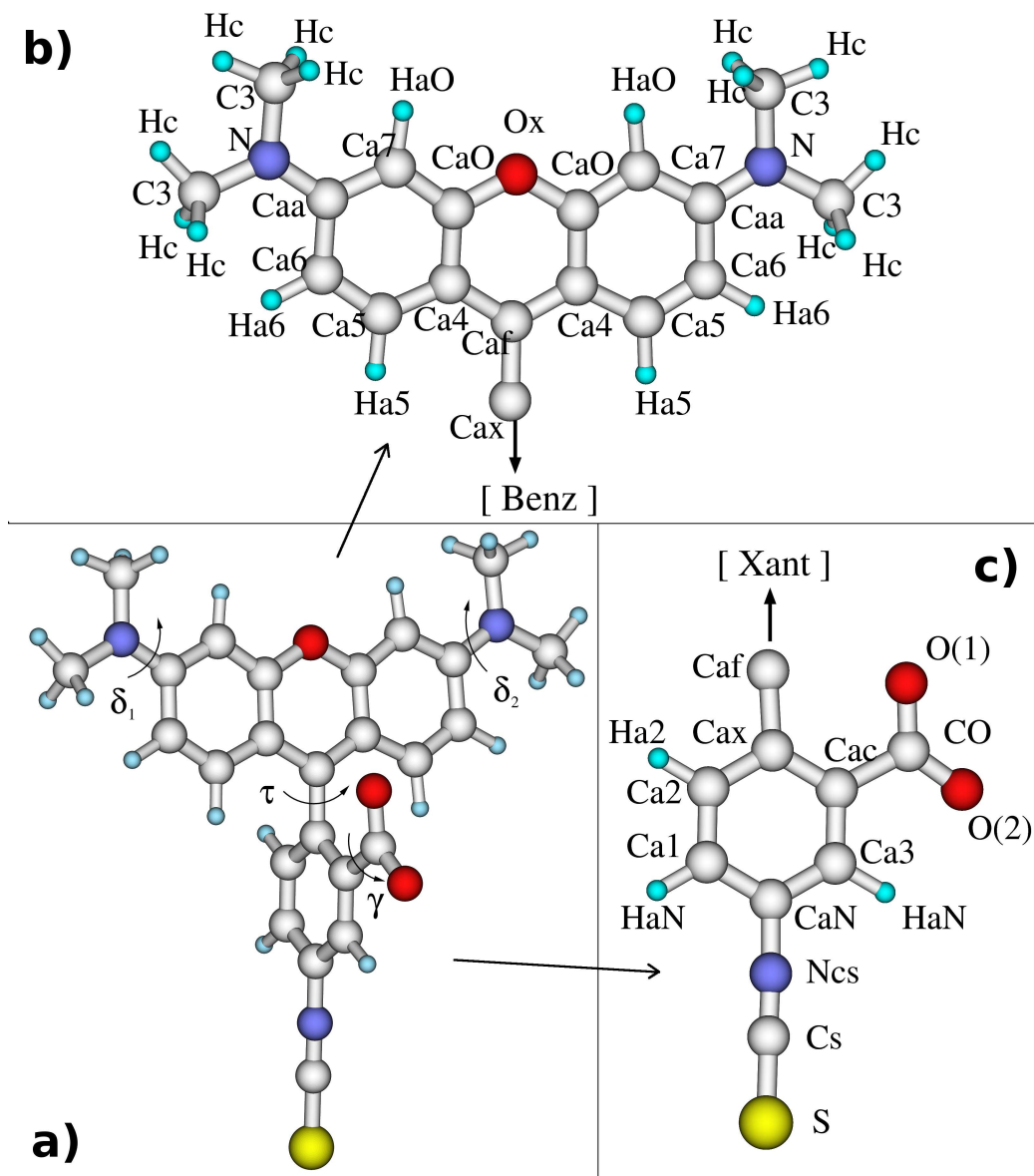


Figure 1: Tetramethyl-rhodamine iso-thiocyanate (TRITC) zwitterionic structure. a) minimum energy conformation and dihedral definition; b) Interaction sites definitions adopted for the xantheno moiety in the FF parameterization; c) Interaction sites definition adopted for the benzenoid moiety in the FF parameterization. O(1) and O(2) refer to the same atom type, O, in Tables 1 to 7

IC	QM	MM	IC	QM	MM
Ox-CaO	1.367	1.370	O-CO-O	125.4	124.6
Ca4-CaO	1.423	1.421	O-CO-Cac	117.3	117.6
Ca7-CaO	1.383	1.382	CO-Cac-Cax	123.0	123.3
Ca7-Caa	1.421	1.423	CaO-Ox-CaO	120.4	120.5
Caa-N	1.364	1.362	C3-N-C3	118.8	118.6
C3-N	1.460	1.463	CaN-Ncs-Cs	175.9	176.3
Cax-Caf	1.475	1.475	Ca4-Caf-Ca4	116.9	117.0
Cax-Cac	1.420	1.423			
Cac-CO	1.522	1.527	O-CO-Cac-Cax ( $\gamma$ )	43.0	48.7
CaN-Ncs	1.374	1.372	Ca4-Caf-Cax-Cac ( $\tau$ )	60.0	66.9
Ncs-Cs	1.182	1.183	Ca7-Caa-N-C3 ( $\delta$ )	0.1	-1.3
Cs-S	1.609	1.612	CO-Cac-Cax-Caf	6.4	3.8
CO-O	1.263	1.259			

Table 1: Optimized values of some of the relevant internal coordinates (IC) as obtained at TD-DFT level (QM) and with the parameterized  $S_1$ -FF (MM) in the first excited state. All bond lengths are reported in Å, all angles in degrees.

Atom Type	$S_0$	$S_1$
S	-0.206949	-0.198325
Cs	-0.099418	-0.084037
Ncs	0.238107	0.201101
CaN	-0.019164	0.006855
Ca1	-0.118165	-0.065824
Ca2	-0.172342	-0.178247
Ha2	0.111673	0.125722
Ha1	0.156129	0.159051
Ca3	-0.223782	-0.266728
Ha3	0.144573	0.161674
Cac	0.150197	0.187379
CO	0.624849	0.459815
O	-0.751860	-0.368361
Cax	0.051943	-0.012987
Caf	0.054553	-0.078347
Ca4	0.097412	0.096292
Ca5	-0.180561	-0.275770
Ca6	-0.175371	-0.163168
Caa	0.127827	0.086714
N	-0.013534	-0.070737
C3	-0.156280	-0.176725
Hc	0.096078	0.095876
Ca7	-0.259313	-0.251421
HaO	0.157369	0.147437
Ha6	0.157140	0.144379
Ha5	0.140427	0.164214
CaO	0.209892	0.211876
Ox	-0.238872	-0.303619

Table 2: RESP atomic charges for the  $S_0$  and  $S_1$  states of the zwitterionic form of TRITC

Bond ( $\mu$ )	$k_{\mu}^s$ (kJ · mol <sup>-1</sup> · Å <sup>-2</sup> )	$r_{\mu}^0$ (Å)	Bond ( $\mu$ )	$k_{\mu}^s$ (kJ · mol <sup>-1</sup> · Å <sup>-2</sup> )	$r_{\mu}^0$ (Å)
S–Cs	3638	1.609	Caf–Ca4	2088	1.438
Cs–Ncs	9269	1.182	Ca4–Ca5	2944	1.426
Ncs–CaN	3281	1.374	Ca5–Ca6	3435	1.378
CaN–Ca1	3174	1.406	Ca6–Caa	2803	1.432
Ca1–Ca2	3321	1.389	Caa–Ca7	2958	1.421
Ca2–Cax	2847	1.412	Ca7–CaO	3304	1.383
Cac–Cax	2434	1.420	CaO–Ca4	2532	1.423
Ca3–Cac	3146	1.397	CaO–Ox	2979	1.367
CaN–Ca3	3099	1.402	CaX–HaX	3419	1.083
Ca*–Ha*	3391	1.085	Caa–N	3047	1.364
Cac–CO	3004	1.522	N–C3	2401	1.460
CO–O	4059	1.263	C3–HC	3120	1.095
Cax–Caf	2498	1.475			

Table 3: Fitted stretching parameters,  $k_{\mu}^s$  and  $r_{\mu}^0$ , reported in equation (3). Labels refer to those reported in Figure 1, Ca\* and Ha\* stand for any carbon and hydrogen atoms in the benzoic moiety, whereas CaX and HaX indicate the same atoms in the xanthene block.

Angle ( $\mu$ )	$k_{\mu}^b$ (kJ · mol <sup>-1</sup> · rad <sup>-2</sup> )	$\theta_{\mu}^0$ (°)	Angle ( $\mu$ )	$k_{\mu}^b$ (kJ · mol <sup>-1</sup> · rad <sup>-2</sup> )	$\theta_{\mu}^0$ (°)
S–Cs–NCs	137.4	180.0	Caf–Ca4–CaO	434.8	120.0
Cs–Ncs–CaN	137.4	176.0	Ca4–Caf–Ca4	253.7	116.9
Ncs–CaN–Ca*	438.8	120.0	Ca4–Ca5–Ca6	437.9	122.6
Ca1–CaN–Ca3	198.0	120.0	Ca5–Ca6–Caa	799.9	120.8
CaN–Ca1–Ca2	754.1	119.1	Ca6–Caa–Ca7	391.7	117.7
Ca1–Ca2–Cax	518.9	122.1	CaO–Ca4–Ca5	623.1	115.4
Ca2–Cax–Cac	666.8	118.0	Caa–Ca7–CaO	697.8	120.0
Ca3–Cac–Cax	367.4	120.0	Ca4–CaO–Ca7	82.2	123.4
CaN–Ca3–Cac	757.7	120.8	Ca7–CaO–Ox	804.8	115.3
Ca3–Cac–CaO	486.8	117.0	Ca4–CaO–Ox	717.0	121.3
CO–CaC–Cax	289.5	123.0	CaO–Ox–CaO	375.8	120.4
Cac–CO–O	384.2	117.3	Caa–Ca7–HaO	341.3	122.0
O–CO–O	384.2	125.4	CaO–Ca7–HaO	310.9	117.9
Ca2–Cax–Caf	650.9	119.0	CaX–CaX–HaX	327.0	120.0
Cac–Cax–Caf	506.4	123.0	Ca7–Caa–N	520.2	121.0
Ca1–Ca2–Ha2	335.2	118.8	Caa–N–C3	387.1	120.6
Cax–Ca2–Ha2	335.2	119.1	C3–N–C3	661.2	118.8
Ca*–Ca*–HaN	320.6	120.0	N–C3–HC	463.9	109.0
Cax–Caf–Ca4	425.3	121.5	HC–C3–HC	311.1	108.5
Caf–Ca4–Ca5	721.8	124.6			

Table 4: Fitted bending parameters,  $k_{\mu}^b$  and  $\theta_{\mu}^0$ , reported in equation (3). Labels refer to those reported in Figure 1. If not specified, Ca\* and Ha\* stand for any carbon and hydrogen atoms in the benzoic moiety, whereas CaX and HaX indicate the same atoms in the xanthene block.

Dihedral ( $\mu$ )	$k_{\mu}^t$ (kJ · mol <sup>-1</sup> · rad <sup>-2</sup> )	$\phi_{\mu}^0$ (°)	Dihedral ( $\mu$ )	$k_{\mu}^t$ (kJ · mol <sup>-1</sup> · rad <sup>-2</sup> )	$\phi_{\mu}^0$ (°)
Ncs–CaN–Ca*–Ca*	157.73	180	Ca4–Caf–Ca4–CaO	69.88	0
Ca*–Ca*–Ca*–Ca*	84.95	0	Caa–Ca7–CaO–Ox	173.12	180
Ncs–CaN–Ca*–HaN	40.91	0	Ca5–Ca4–CaO–Ox	16.13	180
Ca*–Ca*–Ca*–Ha*	61.57	180	Caf–Ca4–CaO–Ox	39.28	0
Caf–Cax–Ca2–Ha2	61.57	0	Ca4–CaO–Ox –CaO	25.95	0
CO –Cac–Ca3–HaN	61.57	0	Ca7–CaO–Ox –CaO	25.95	180
HaN–Ca1–Ca2–Ha2	42.61	0	CaX–CaX–CaX–N	51.00	180
CO–Cac–Cax–Ca2	171.60	180	CaX–CaX–Ca6–Ha6	59.84	180
CO–Cac–Ca3–CaN	102.86	180	CaX–CaX–Ca5–Ha5	57.66	180
CO–Cac–Cax–Caf	40.48	0	Caf–Ca4–Ca5–Ha5	57.66	0
Ca*–Ca*–Cax–Caf	40.48	180	CaX–CaX–CaX–HaO	48.79	180
Cax–Caf–Ca4–Ca5	40.48	0	Ox–CaO–Ca7–HaO	51.92	0
Cax–Caf–Ca4–CaO	40.48	180	N–Caa–Ca7–HaO	26.32	0
Caf–Ca4–CaX–CaX	69.88	180	N–Caa–Ca6–Ha6	34.17	0
Ca4–Ca5–Ca6–Caa	69.88	0	Ha5–Ca5–Ca6–Ha6	41.03	0
Ca4–Caf–Ca4–Ca5	69.88	180			
Ca5–Ca6–Cac–Ca7	69.88	0	CO–O –O –Cac	1006.78	0
CaO–Ca4–Ca5–Ca6	69.88	0	CaN–Ncs–Ca1–Ca3	75.07	0
Ca4–CaO–Ca7–Caa	69.88	0	Caf–Ca2–Cac–Cax	40.48	0
CaO–Ca7–Caa–Ca6	69.88	0	Cax–Ca4–Ca4–Caf	40.48	0
Ca7–CaO–Ca4–Ca5	69.88	0			

Table 5: Fitted rigid torsion parameters,  $k_{\mu}^t$  and  $\phi_{\mu}^0$ , reported in equation (3). Labels refer to those reported in Figure 1. If not specified, Ca\* and Ha\* stand for any carbon and hydrogen atoms in the benzoic moiety, whereas CaX and HaX indicate the same atoms in the xanthene block.

Dihedral ( $\mu$ )	$n_{\mu}^j$	$k_{j\mu}^d$ (kJ/mol)	$\gamma_{\mu}^j$
Cac-Cax-Caf-Ca4 ( $\tau$ )	-5.169	0	0
	8.187	2	0
	9.155	4	0
	0.950	6	0
	0.453	8	0
	-0.682	10	0
O-CO-Cac-Cax ( $\gamma$ )	-0.978	0	0
	2.573	2	0
	-0.811	4	0
	-0.450	6	0
	0.146	8	0
	-0.051	10	0
CaX-Caa-N-C3 ( $\delta$ )	0	11.2450	0
	2	-12.6715	0
	4	1.3720	0
	6	0.0560	0
Caa-N-C3-HC	3	4.495	0

Table 6: Fitted flexible torsion parameters,  $k_{j\mu}^d$ , reported in equation (4). Labels refer to those reported in Figure 1, CaX stands for any carbon atom in the in the xanthene moiety.



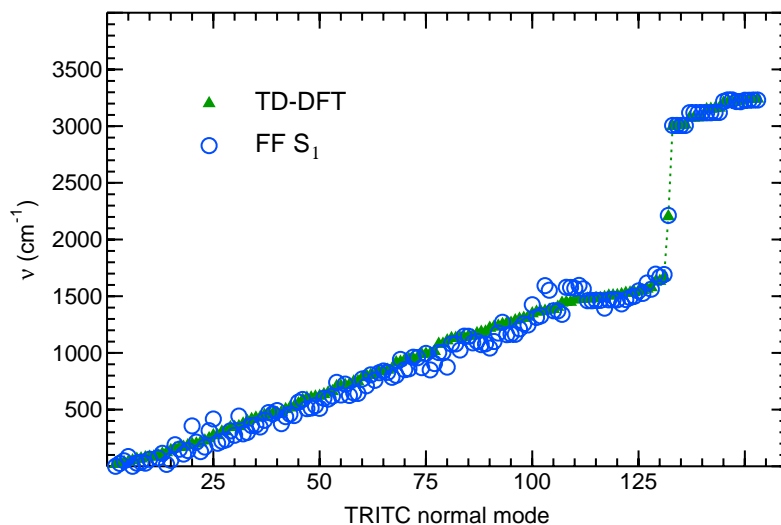


Figure 2: Comparison between computed TD-DFT and JOYCE fitted TRITC frequencies.

Pair ( $i, j$ )	$\epsilon_{ij}$ (kJ/mol)	$\sigma_{ij}$ (Å)
O–Ca5	1.30	3.60
O–Ha5	0.50	3.20

Table 7: Non-bonded coupling parameters reported in equation (5). Labels refer to those reported in Figure 1. No other intramolecular non-bonded interaction was adopted in the FF.