Tuning ESIPT Fluorophores into Dual Emitters :
Electronic supporting Information

Cloé Azarias[a], Simon Budzák[a], Adèle D. Laurent[a], Gilles Ulrich[b] and Denis Jacquemin[*a,c]

[a] *CEISAM, UMR CNRS 6230, BP 92208, Université de Nantes, 2, Rue de la Houssinière, 44322 Nantes, Cedex 3, France. Tel: +33-2-51-12-55-64; E-mail: Denis.Jacquemin@univ-nantes.fr*
[b] *Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES) UMR7515 CNRS Université de Strasbourg, 25 rue Becquerel, 67087 Strasbourg Cedex 02 (France)*
[c] *Institut Universitaire de France, 1, rue Descartes, F-75005 Paris Cedex 05, France.*

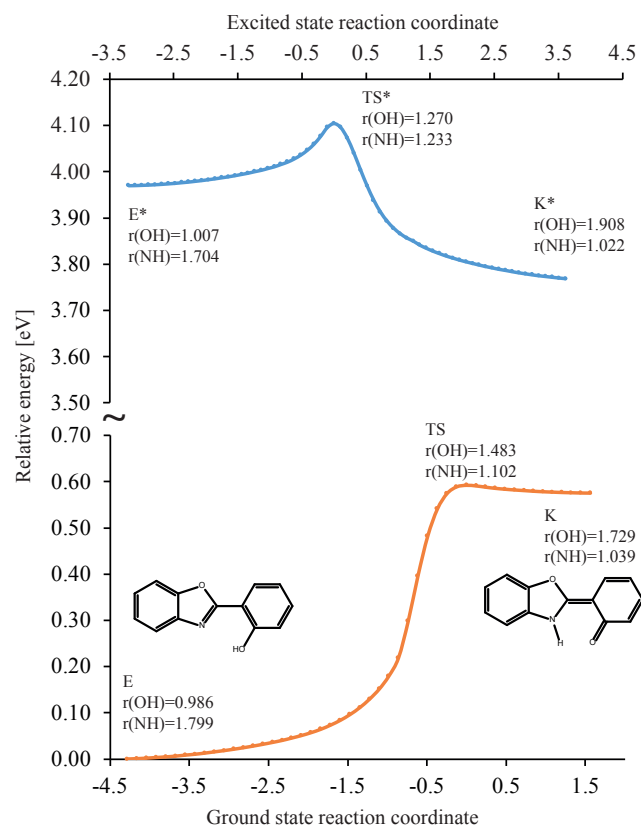# S1 Extra examples of potential energy surface/IRC

Fig. S1 Energy profile for PT along the ground and excited state IRC for the dye number **1**. Energy scale is relative to the ground state enol form calculated at the M062X/6-31G(d) level. Bond lengths are in Å, reaction coordinate is defined in mass weighted coordinates $(\text{Bohr}\sqrt{AMU}^{-1})$
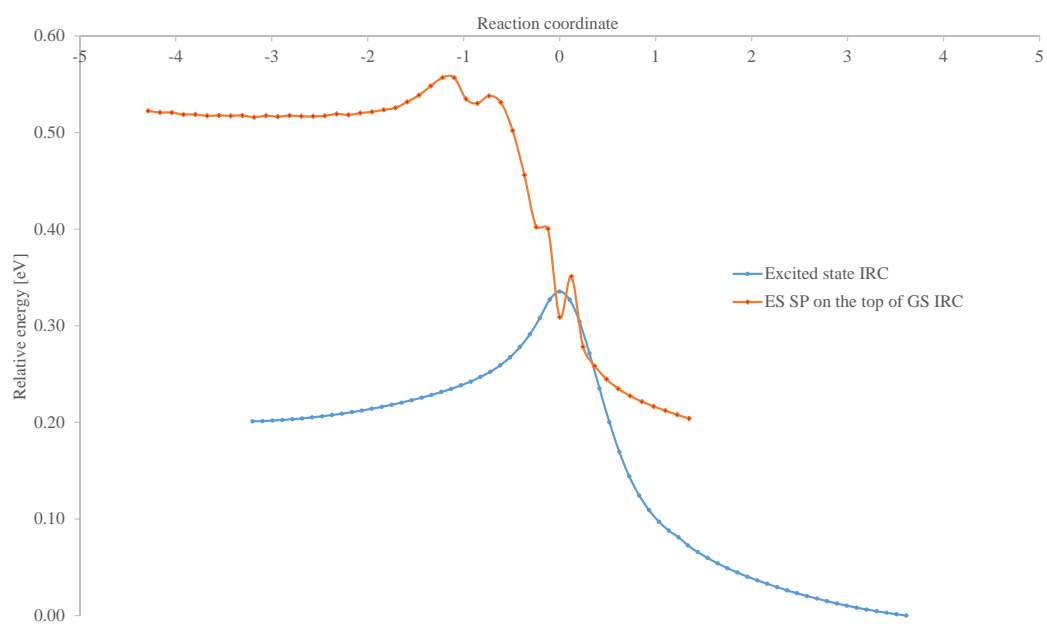
Fig. S2 Energy profile for PT along the excited state IRC and the reaction profile in ES calculated as single point on the top of ground state IRC. Energy scale is relative to the K* form calculated at the M062X/6-31G(d) level. Reaction coordinate is defined in mass weighted coordinates (Bohr$\sqrt{AMU}^{-1}$)
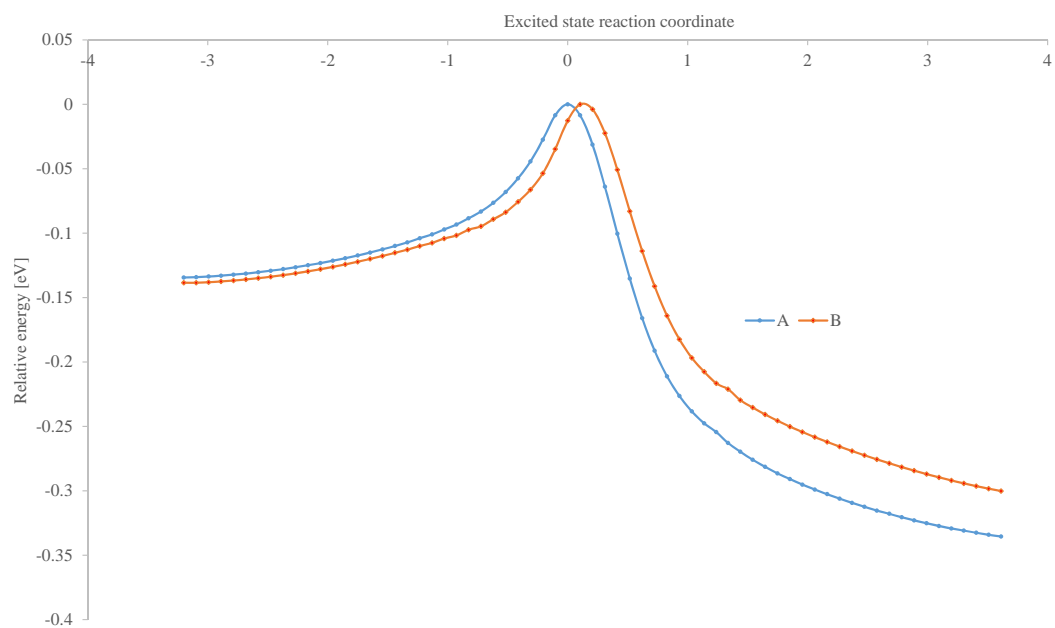
Fig. S3 Energy profile for PT along the excited state IRC (6-31G(d) basis set) A and the reaction profile in ES calculated as 6-311+G(2d,p) single points on the top of ES IRC - B. Energy scale is relative to the TS* form. Reaction coordinate is defined in mass weighted coordinates $(\text{Bohr}\sqrt{AMU}^{-1})$

S2 Comparison between TD-DFT and experimantal values for the compounds of Table 1 and 4

Table S1 Available experimental values compared to theoretical (TD)DFT simulations for HBO-ESIPT dyes. All theoretical values have been obtained from TD-DFT calculations and have not been corrected with ADC(2). See Table **1** for more details.

		Structures				Experiment				Theory			
	R_1	R_2	R_3	R_4	Solvent	Observations	λ_{fl}^{E*}	λ_{fl}^{K*}	Ref.	λ_{fl}^{E*}	λ_{fl}^{K*}	ΔG^{ES}	$\Delta G^{ES\#}$
1	H	H	H	H	3MP	Keto	—	ca.480	1	328	410	-0.161	-0.005
2	H	H	H	H	CH	Keto	—	ca.490	2	328	409	-0.162	-0.003
3	H	H	H	H	CHL	Keto	—	ca.489	3	330	405	-0.173	0.020
4	H	H	H	NH$_2$	DCM	Keto	—	551	4	426	512	-0.070	0.031
						Keto (4/5) + Enol (1/5)	442	565	5				
5	H	H	H	CHO	CHL	Keto + vw Enol	ca. 405	474	6	330	388	-0.208	0.029
6	H	H	H	CHO	DIOX	Keto	—	483	6	328	392	-0.198	0.012
7	H	H	NEt$_2$	H	CHL	Enol	382	—	3	344	383	0.232	0.269
						Enol	451	—	7				
8	H	H	NEt$_2$	H	DIOX	Enol	471	—	7	341	395	0.201	0.251
9	H	H	NH$_2$	H	DCM	Keto (7/8) + Enol (1/8)	376	467	5	334	383	0.114	0.218
						Keto (3/5) + Enol (2/5)	390	460	8				
10	H	H	NH$_2$	H	CHL	Keto (3/4) + Enol (1/4)	390	460	8	333	387	0.096	0.201
11	H	H	NH$_2$	H	DIOX	Keto (3/4) + Enol (1/4)	415	487	9	331	394	0.060	0.167
12	H	H	OMe	H	CHL	Keto + vw Enol	ca. 375	ca. 467	3	329	398	-0.028	0.103
13	H	H	Me	H	3MP	Keto	—	ca.480	1	329	413	-0.108	0.030
14	H	C=C(CN)$_2$	H	H	CH	Keto + w Enol	ca. 425	ca. 550	10	387	506	0.174	0.227
15	H	C=C(CN)$_2$	H	H	CHL	Keto + Enol	ca. 450	ca. 625	10	401	542	0.069	0.315
16	H	CHO	H	H	CHL	Keto	—	ca. 517	3	345	423	-0.068	0.071
17	H	COOEt	H	H	CHL	Keto	—	ca. 495	3	340	418	-0.118	0.048
18	H	NH$_2$	H	H	n-HEP	Keto + vw Enol	390	500	11	357	405	0.075	0.163
19	H	NH$_2$	H	H	DCM	Keto (9/10) + Enol (1/10)	420	485	11	378	399	0.131	0.236
20	H	COOEt	NEt$_2$	H	CHL	Enol	421	—	3	363	396	0.340	0.338
21	H	COOEt	OMe	H	CHL	Keto + vw Enol	ca. 375	ca. 482	3	341	412	0.022	0.173
22	H	NH$_2$	NEt$_2$	H	DIOX	Enol	460	—	7	359	383	0.285	0.292
23	H	NO$_2$	NEt$_2$	H	DIOX	Keto + Enol	476	656	7	396	465	0.434	0.419
24	NH$_2$	H	NEt$_2$	H	DIOX	Enol	440	—	7	352	389	0.240	0.270
25	NO$_2$	H	NEt$_2$	H	DIOX	Enol	440	—	7	425	521	0.363	0.346
26	NH$_2$	H	H	H	n-HEP	Keto (9/10) + Enol (1/10)	400	500	12	364	409	0.034	0.171
27	NH$_2$	H	H	H	DCM	Enol + vw Keto	450	ca. 480	12	384	402	0.015	0.187
28	H	H	H	H	CH	Keto	—	470	2	327	404	-0.273	-0.029
						Keto	—	ca. 470	13				
29	H	H	H	H	DIOX	Keto + vwEnol	350	468	14	327	400	-0.272	-0.027
30	H	H	H	NH$_2$	DCM	Keto	—	539	4	408	490	-0.192	-0.072
						Keto + vwEnol	414	544	5				
31	H	H	H	NH$_2$	DIOX	Keto + Enol	414	568	14	397	482	-0.121	-0.050
32	H	H	H	OMe	DIOX	Keto + wEnol	368	530	14	359	456	-0.275	-0.059
33	H	H	H	OH	DIOX	Keto + vwEnol	358	525	14	357	448	-0.250	-0.101
34	H	H	H	Me	DIOX	Keto + vwEnol	352	489	14	334	422	-0.224	-0.018
35	H	H	H	Cl	DIOX	Keto	—	474	14	337	414	-0.303	-0.057
36	H	H	H	F	DIOX	Keto + vwEnol	350	486	14	337	418	-0.273	-0.081
37	H	H	NH$_2$	H	DCM	Enol	445	—	5	333	374	-0.035	0.102
38	H	H	NEt$_2$	H	CH	Keto + vwEnol	ca. 370	ca. 453	15	340	384	0.050	0.130
39	H	H	NEt$_2$	H	DIOX	Enol	386	—	16	340	382	0.039	0.131
40	H	NH$_2$	NEt$_2$	H	DIOX	Enol	431	—	16	355	377	0.139	0.175
41	H	NO$_2$	NEt$_2$	H	DIOX	Keto + vwEnol	—	531	16	400	479	0.247	0.235

S3   Density variation plots for selected compounds

Figure S4 depicts the density variation plots for the singly-substituted HBO series. For all compounds, one notices an increase (decrease) of density figures on the nitrogen atom (hydroxyl group) though the amplitude of this effect is strongly system-dependent. This means that after photon absorption, the nitrogen (OH group) becomes more basic (acidic). For both R_1 and R_2 positions, compared with the non-substituted dye, adding OMe, NH_2 and NMe_2 groups, induces a loss (gain) of the electronic density on the hydroxyl group (nitrogen atom), indicating less acidic (basic) functions. The ESIPT process is therefore expected to be less efficient, or not effective at all for those cases.
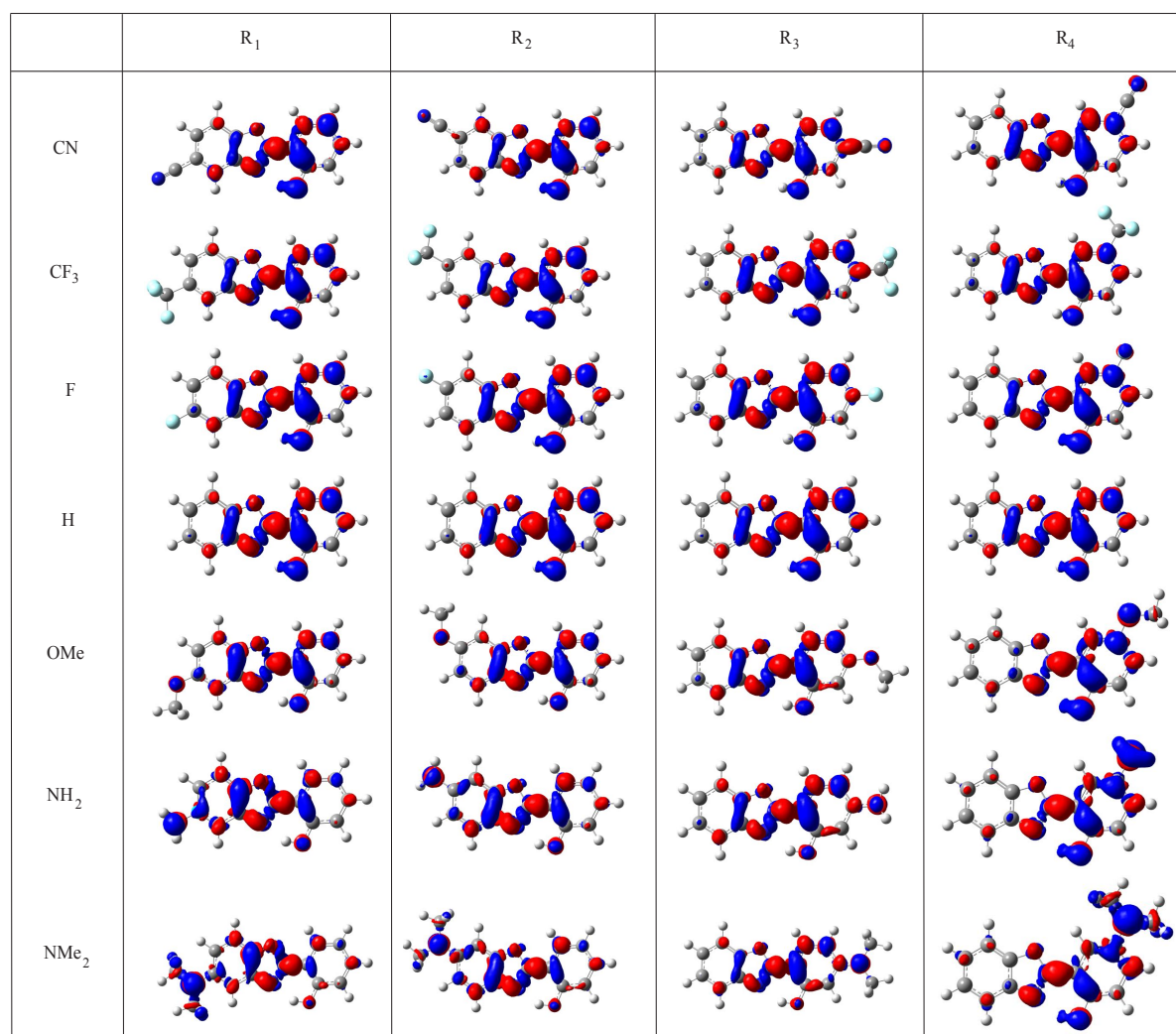

Fig. S4 Density difference plots (isovalue=0.0018 a.u.). The red/blue zones indicate an increase/decrease of the electronic density upon absorption of light.

S4 Relative E*/K* free energies for the substituted compounds and barrier for proton transfer when dual emission is possible

S4.1 Singly-substituted HBX, X=O, X=NH and X=CH$_2$

Table S2 ΔG^{ES} and $\Delta G^{ES\#}$ values for the singly-substituted HBX, X=O, X=NH and X=CH$_2$ series in cyclohexane. The $\Delta G^{ES\#}$ values are only reported for intermediate HBO and HBI cases that present a ΔG^{ES} between 0.00 and -0.20 eV. Data are given in eV.

R$_1$	R$_2$	R$_3$	R$_4$	X=O ΔG^{ES}	$\Delta G^{ES\#}$	X=NH ΔG^{ES}	$\Delta G^{ES\#}$	X=CH$_2$ ΔG^{ES}
CN	H	H	H	-0.276		-0.353		-0.439
CF$_3$	H	H	H	-0.253		-0.374		-0.421
F	H	H	H	-0.275		-0.344		-0.429
H	H	H	H	-0.314		-0.388		-0.463
OMe	H	H	H	-0.164	0.014	-0.238		-0.319
NH$_2$	H	H	H	0.056		-0.010	0.161	-0.182
NMe$_2$	H	H	H	0.226		0.140		-0.026
H	CN	H	H	-0.246		-0.350		-0.402
H	CF$_3$	H	H	-0.285		-0.399		-0.449
H	F	H	H	-0.285		-0.374		-0.434
H	H	H	H	-0.314		-0.388		-0.463
H	OMe	H	H	-0.184	-0.069	-0.268		-0.298
H	NH$_2$	H	H	-0.057	0.018	-0.152	0.018	-0.183
H	NMe$_2$	H	H	0.091		0.029		-0.008
H	H	CN	H	-0.262		-0.356		-0.425
H	H	CF$_3$	H	-0.349		-0.417		-0.484
H	H	F	H	-0.336		-0.361		-0.454
H	H	H	H	-0.314		-0.388		-0.463
H	H	OMe	H	-0.188	-0.035	-0.260		-0.312
H	H	NH$_2$	H	-0.161	0.013	-0.219		-0.336
H	H	NMe$_2$	H	0.004	0.129	-0.010	a	-0.225
H	H	H	CN	-0.323		-0.397		-0.472
H	H	H	CF$_3$	-0.350		-0.452		-0.485
H	H	H	F	-0.254		-0.362		-0.427
H	H	H	H	-0.314		-0.388		-0.463
H	H	H	OMe	-0.204	-0.134	-0.346		-0.348
H	H	H	NH$_2$	-0.001	-0.090	-0.157	-0.124	-0.143
H	H	H	NMe$_2$	0.050		-0.126	-0.114	-0.170

aThe TS calculation failed to properly converge.

S4.2 Doubly-substituted HBO

The additivity equation reads

$$\Delta(\Delta G^{ES}_{R_1,R_3})_{add} = \Delta(\Delta G^{ES}_{R_1}) + \Delta(\Delta G^{ES}_{R_3}) \tag{S1}$$

Table S3 Theoretical results for a series of HBO dyes in cyclohexane. The data reported in this Table corresponds to the additive contribution of the substituents $[\Delta(\Delta G^{ES}_{R_1,R_3})_{add}]$ calculated as the sum of the contribution of each substituent $[\Delta(\Delta G^{ES}_{R_x})]$ found in Table 2 in the main text. For more details, see the caption of Table 2.

$R_1 \backslash R_3$	$\Delta(\Delta G^{ES}_{R_1,R_3})_{add}$						
	CN	CF$_3$	F	H	OMe	NH$_2$	NMe$_2$
CN	0.091	0.003	0.016	0.038	0.167	0.191	0.356
CF$_3$	0.114	0.026	0.039	0.061	0.188	0.214	0.379
F	0.092	0.004	0.017	0.039	0.166	0.192	0.357
H	0.053	-0.035	-0.022	0.000	0.127	0.153	0.318
OMe	0.203	0.115	0.128	0.150	0.277	0.303	0.468
NH$_2$	0.407	0.335	0.348	0.370	0.497	0.523	0.688
NMe$_2$	0.593	0.505	0.518	0.540	0.667	0.693	0.858

Table S4 ΔG^{ES} and $\Delta G^{ES\#}$ values for the doubly-substituted HBO series in cyclohexane. The $\Delta G^{ES\#}$ values are only reported for intermediate cases, *i.e.*, when a ΔG^{ES} between 0.00 and -0.20 eV is computed. Data are given in eV.

R_1	R_2	R_3	R_4	ΔG^{ES}	$\Delta G^{ES\#}$
CN	H	CN	H	-0.243	
CN	H	CF_3	H	-0.341	
CN	H	F	H	-0.238	
CN	H	H	H		
CN	H	OMe	H	-0.160	-0.048
CN	H	NH_2	H	-0.135	0.018
CN	H	NMe_2	H	0.036	
CF_3	H	CN	H	-0.243	
CF_3	H	CF_3	H	-0.312	
CF_3	H	F	H	-0.326	
CF_3	H	H	H		
CF_3	H	OMe	H	-0.150	-0.024
CF_3	H	NH_2	H	-0.108	0.057
CF_3	H	NMe_2	H	0.018	
F	H	CN	H	-0.224	
F	H	CF_3	H	-0.320	
F	H	F	H	-0.291	
F	H	H	H		
F	H	OMe	H	-0.138	-0.005
F	H	NH_2	H	-0.116	0.038
F	H	NMe_2	H	0.057	
OMe	H	CN	H	-0.042	0.104
OMe	H	CF_3	H	-0.125	0.076
OMe	H	F	H	-0.131	0.084
OMe	H	H	H		
OMe	H	OMe	H	-0.041	0.119
OMe	H	NH_2	H	-0.025	0.137
OMe	H	NMe_2	H	0.095	
NH_2	H	CN	H	0.208	
NH_2	H	CF_3	H	0.155	
NH_2	H	F	H	0.093	
NH_2	H	H	H		
NH_2	H	OMe	H	0.083	
NH_2	H	NH_2	H	0.031	
NH_2	H	NMe_2	H	0.126	
NMe_2	H	CN	H	0.428	
NMe_2	H	CF_3	H	0.358	
NMe_2	H	F	H	0.270	
NMe_2	H	H	H		
NMe_2	H	OMe	H	0.238	
NMe_2	H	NH_2	H	0.206	
NMe_2	H	NMe_2	H	0.253	

References

1   W. Al-Soufi, K. H. Grellmann and B. Nickel, *J. Phys. Chem.*, 1991, **95**, 10503–10509.

2   O. K. Abou-Zied, *RSC Adv.*, 2013, **3**, 8747–8755.

3   J. Seo, S. Kim, S. Park and S. Y. Park, *Bull. Korean. Chem. Soc.*, 2005, **26**, 1706–1710.

4   M. G. Holler, L. F. Campo, A. Brandelli and V. Stefani, *J. Photochem. Photobiol. A: Chem.*, 2002, **149**, 217–225.

5   F. S. Rodembusch, F. P. Leusin, L. F. Campo and V. Stefani, *J. Luminesc.*, 2007, **126**, 728–734.

6   R. F. Affeldt, A. C. de Amorim Borges, D. Russowsky and F. Severo Rodembusch, *New J. Chem.*, 2014, **38**, 4607–4614.

7   V. S. Padalkar, P. Ramasami and N. Sekar, *J. Luminesc.*, 2014, **146**, 527–538.

8   N. Jiang, C. Yang, X. Dong, X. Sun, D. Zhang and C. Liu, *Org. Biomol. Chem.*, 2014, **12**, 5250–5259.

9   M. Gutierrez, N. Alarcos, M. Liras, F. Sánchez and A. Douhal, *J. Phys. Chem. B*, 2015, **119**, 552–562.

10   J. Seo, S. Kim and S. Y. Park, *J. Am. Chem. Soc.*, 2004, **126**, 11154–11155.

11   N. Alarcos, M. Gutiérrez, M. Liras, F. ánchez and A. Douhal, *Phys. Chem. Chem. Phys.*, 2015, **17**, 16257–16269.

12   N. Alarcos, M. Gutiérrez, M. Liras, F. Sánchez, M. Moreno and A. Douhal, *Phys. Chem. Chem. Phys.*, 2015, **17**, 14569–14581.

13   F. A. S. Chipem and G. Krishnamoorthy, *J. Phys. Chem. B*, 2013, **117**, 14079–14088.

14   A. Douhal, F. Amat-Guerri, M. Lillo and A. Acuña, *J. Photochem. Photobiol. A: Chem.*, 1994, **78**, 127–138.

15   S. R. Vazquez, M. C. R. Rodriguez, M. Mosquera and F. Rodriguez-Prieto, *J. Phys. Chem. A*, 2008, **112**, 376–387.

16   V. S. Padalkar, P. Ramasami and N. Sekar, *J. Fluoresc.*, 2013, **23**, 839–851.