Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information for: TD-DFT and CC2 insights into the dual-emissive behavior of 2-(2'-hydroxyphenyl)oxazoles core and their derivatives

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Table S1: Fluorescence wavelengths (in nm) of the E* and K* tautomers computed in gas phase and toluene for compounds **1** and **2** obtained with TD-DFT (using four different functionals), and with addition of ADC(2) and CC2 corrections using three solvent models : LR, cLR, and LR+cLR. The experimental values[1] are 434 nm (E*) and 532 nm (K*) for **1**, and 424 nm (E*) and 535 nm (K*) for **2**.

			Compound 1				**Compound 2**			
			Gas	**LR**	**cLR**	**LR+cLR**	**Gas**	**LR**	**cLR**	**LR+cLR**
PBE0	**TD-DFT**	**E***	479	476	534	538	465	478	473	488
		K*	646	597	667	679	662	609	681	693
	ADC(2)	**E***	402	400	440	443	416	427	422	434
		K*	552	516	567	576	556	518	569	577
	CC2	**E***	400	399	438	441	413	423	419	430
		K*	533	499	547	555	541	505	553	561
M06-2X	**TD-DFT**	**E***	390	403	389	404	413	428	416	431
		K*	476	474	468	482	478	475	469	482
	ADC(2)	**E***	394	407	393	407	424	440	428	443
		K*	544	541	533	551	541	538	530	547
	CC2	**E***	390	403	389	403	422	437	425	440
		K*	516	514	506	522	517	514	507	522
CAM-B3LYP	**TD-DFT**	**E***	392	406	391	407	413	428	415	430
		K*	466	466	458	472	467	467	459	472
	ADC(2)	**E***	391	405	390	406	424	439	426	442
		K*	543	543	532	550	538	538	528	545
	CC2	**E***	387	401	386	401	420	435	422	438
		K*	513	514	504	520	512	512	503	519
MN15	**TD-DFT**	**E***	412	423	411	425	435	451	439	455
		K*	512	505	503	518	515	507	506	519
	ADC(2)	**E***	396	408	396	409	424	439	427	442
		K*	551	543	541	557	546	537	535	550
	CC2	**E***	393	403	393	405	420	435	423	438
		K*	522	515	513	528	522	513	512	526

Table S2: Difference between experimental and vertical theoretical TD-DFT fluorescence wavelengths calculated in nm (eV) in gas and toluene using three solvent models (LR, cLR, and LR+cLR). The experimental values have been taken from Ref. 1.

		Exp - Theo nm (eV)							
		Compound 1				**Compound 2**			
	State	**Gas**	**LR**	**cLR**	**LR+cLR**	**Gas**	**LR**	**cLR**	**LR+cLR**
PBE0	**E***	–45 (0.27)	–42 (0.25)	–100 (0.53)	-105 (0.55)	–41 (0.26)	–54 (0.33)	–49 (0.30)	–64 (0.38)
	K*	–114 (0.41)	–65 (0.25)	–135 (0.47)	–147 (0.51)	–127 (0.45)	–74 (0.28)	–146 (0.50)	–158 (0.53)
M06-2X	**E***	44 (–0.32)	31 (–0.22)	45 (–0.33)	30 (–0.21)	11 (–0.08)	-4 (0.03)	8 (–0.05)	–7 (0.04)
	K*	56 (–0.27)	57 (–0.28)	64 (–0.32)	50 (–0.24)	57 (–0.28)	60 (–0.29)	66 (–0.33)	53 (–0.26)
CAM-B3LYP	**E***	42 (–0.30)	28 (–0.19)	43 (–0.31)	27 (–0.19)	11 (–0.07)	–4 (0.03)	9 (–0.06)	–6 (0.04)
	K*	66 (–0.33)	66 (–0.33)	74 (–0.38)	60 (–0.30)	68 (–0.34)	68 (–0.34)	76 (–0.38)	63 (–0.31)
MN15	**E***	22 (–0.15)	11 (–0.07)	23 (–0.16)	9 (–0.06)	–11 (0.08)	–28 (0.18)	–15 (0.10)	–31 (0.20)
	K*	20 (–0.09)	27 (–0.12)	29 (–0.13)	14 (–0.06)	20 (–0.09)	28 (–0.13)	29 (–0.13)	16 (–0.07)

Table S3: Difference between K* and E* fluorescence wavelengths computed in toluene for compounds **1** and **2** using three solvent models (LR, cLR, and LR+cLR). The experimental values are taken from Ref. 1. All values are given in nm (eV).

		λ_{fluo} (K*-E*)			
Compound		**LR**	**cLR**	**LR+cLR**	**Exp**
1	**M06-2X**	71 (–0.46)	78 (–0.53)	78(–0.50)	98 (–0.53)
	CAM-B3LYP	60 (–0.39)	67 (–0.46)	65 (–0.42)	
	MN15	82 (–0.48)	92 (–0.55)	92 (–0.52)	
2	**M06-2X**	47 (–0.29)	52 (-0.33)	51 (–0.31)	111 (–0.61)
	CAM-B3LYP	39 (–0.24)	44 (–0.28)	42 (–0.26)	
	MN15	55 (–0.30)	67 (–0.37)	64 (–0.34)	

Table S4: Statistical data obtained from the comparison of experimental and theoretical emission wavelengths for compounds **1** and **2** in toluene: mean signed error (MSE) and mean absolute error (MAE). All values are given in nm (eV).

	MSE		**MAE**	
	E*	**K***	**E***	**K***
CAM-B3LYP	11 (–0.08)	62 (–0.31)	17 (0.12)	62 (0.31)
MN15	–11 (0.07)	15 (–0.08)	20 (0.13)	15 (0.08)

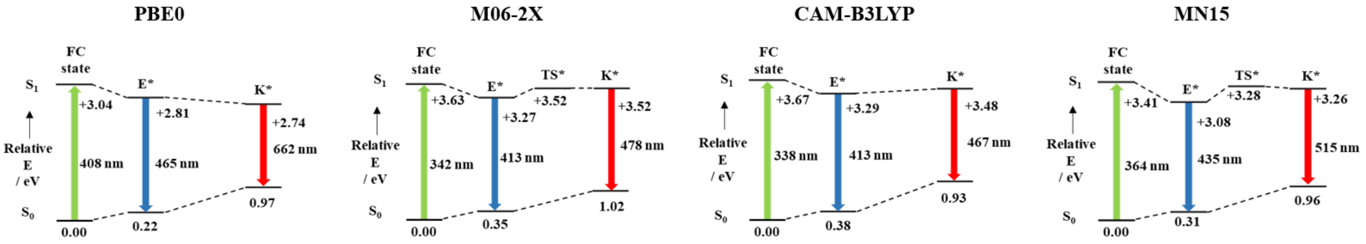
Table S5: Energy difference, ΔE^{ES} (E+ZPVE), between E* and K* tautomers computed in toluene for compounds **1** and **2**, applying post-HF corrections [ADC(2) and CC2)] using the geometries obtained of TD-DFT level. cLR and LR+cLR solvent corrections are used. All values are given in eV.

		1		**2**	
		cLR	LR+cLR	cLR	LR+cLR
PBE0	**ADC(2)**	0.18	0.16	0.09	0.14
	CC2	0.12	0.10	0.00	0.04
M06-2X	**ADC(2)**	–0.11	–0.07	0.13	0.16
	CC2	–0.16	–0.12	0.06	0.09

Table S6: Difference between experimental and theoretical vertical fluorescence wavelengths for **1** and **2** calculated with ADC(2) and CC2 methods and cLR and LR+cLR solvent models. All values are given in nm (eV).

			Exp - Theo nm (eV)			
			1		**2**	
	Functional	**State**	**cLR**	**LR+cLR**	**cLR**	**LR+cLR**
ADC(2)	**CAM-B3LYP**	**E***	44 (–0.32)	28 (–0.20)	–2 (0.01)	–17 (0.12)
		K*	0 (0.00)	–19 (0.08)	7 (–0.03)	–10 (0.04)
	MN15	**E***	39 (–0.28)	25 (–0.18)	–3 (0.02)	–18 (0.12)
		K*	–9 (0.04)	–25 (0.10)	–1 (0.00)	–15 (0.06)
CC2	**CAM-B3LYP**	**E***	48 (–0.36)	33 (–0.24)	2 (–0.01)	–14 (0.09)
		K*	29 (–0.13)	12 (–0.05)	32 (-0.15)	16 (–0.07)
	MN15	**E***	41 (–0.30)	29 (–0.20)	1 (–0.01)	–14 (0.09)
		K*	19 (–0.09)	4 (–0.02)	23 (–0.10)	9 (–0.04)

A) Gas phase



B) Toluene

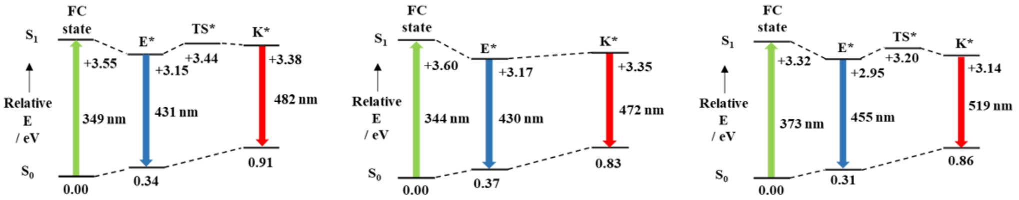


Figure S1: Potential energy diagrams in eV (E+ZPVE) for compound **2** in gas phase and toluene for four exchange-correlation functionals with the 6-311+G(2d,p) atomic basis set, using the LR+cLR approach for modelling solvent effects. The ESIPT TS has been determined with M06-2X and MN15 only.

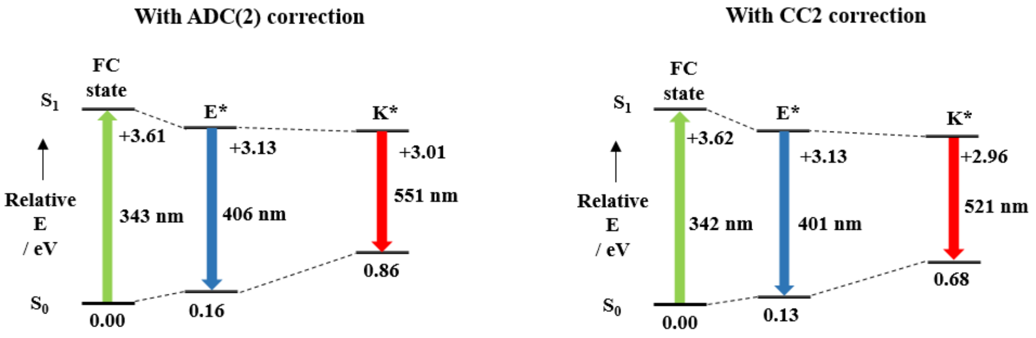


Figure S2: Potential energy diagrams in eV (E+ZPVE) for compound **1** in toluene (using the LR+cLR solvent model). The CAM-B3LYP functional and the 6-311+G(2d,p) atomic basis set are selected for the TD-DFT structure calculations. The ADC(2) and CC2 energy calculations use the *aug*-cc-pVDZ basis set.

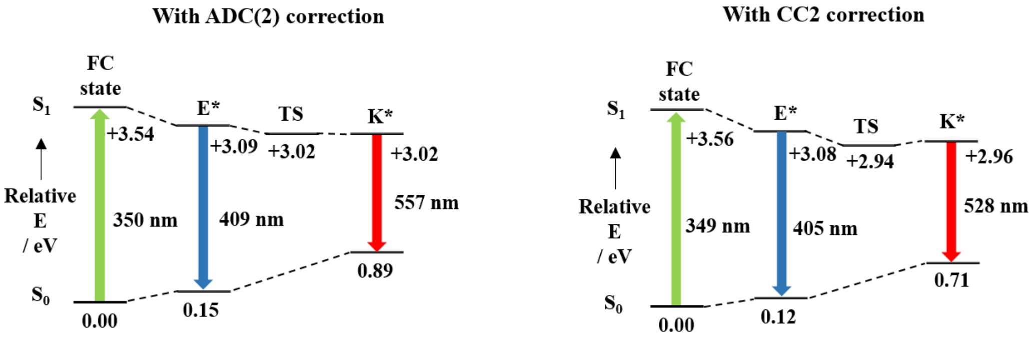


Figure S3: Potential energy diagrams in eV (E+ZPVE) for compound **1** in toluene (using the LR+cLR solvent model). The MN15 functional and the 6-311+G(2d,p) atomic basis set are selected for the TD-DFT structure calculations. The ADC(2) and CC2 energy calculations use the *aug*-cc-pVDZ basis set.

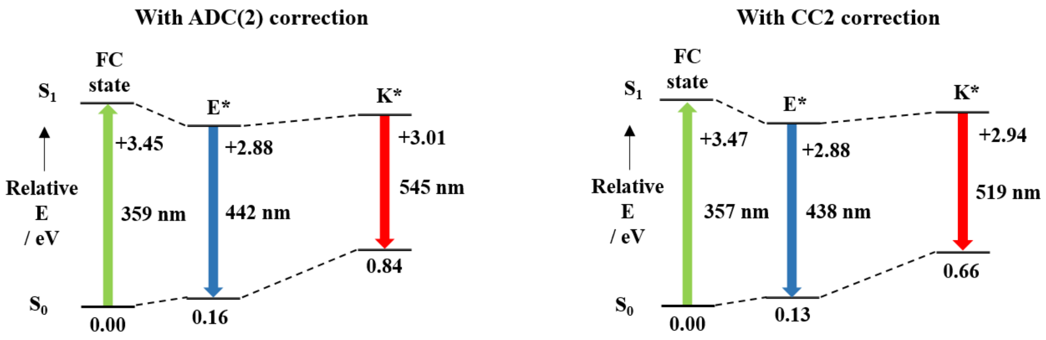


Figure S4: Potential energy diagrams in eV (E+ZPVE) for compound **2** in toluene (using the LR+cLR solvent model). The CAM-B3LYP functional and the 6-311+G(2d,p) atomic basis set are selected for the TD-DFT structure calculations. The ADC(2) and CC2 energy calculations use the *aug*-cc-pVDZ basis set.

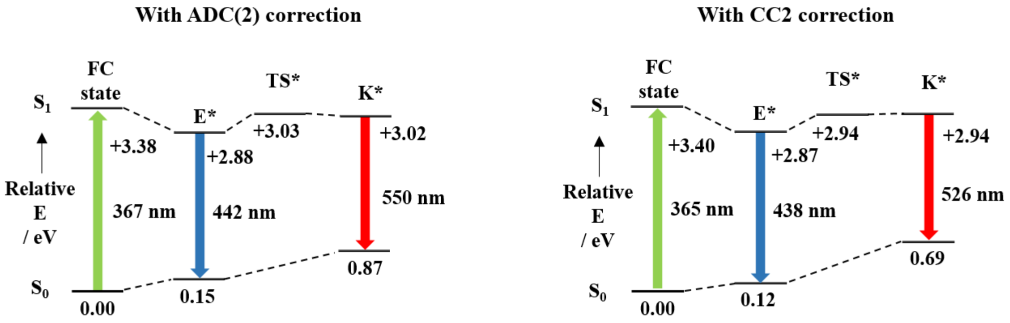
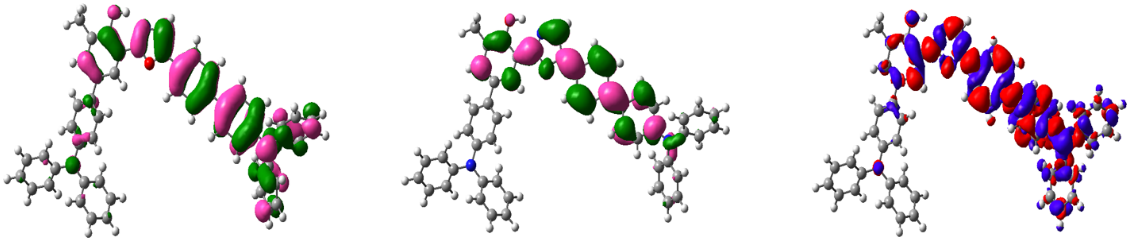


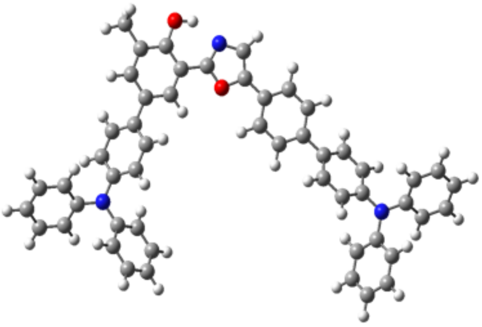
Figure S5: Potential energy diagrams in eV (E+ZPVE) for compound **2** in toluene (using the LR+cLR solvent model). The MN15 functional and the 6-311+G(2d,p) atomic basis set are selected for the TD-DFT structure calculations. The ADC(2) and CC2 energy calculations use the *aug*-cc-pVDZ basis set.



HOMO **LUMO** **EDD**

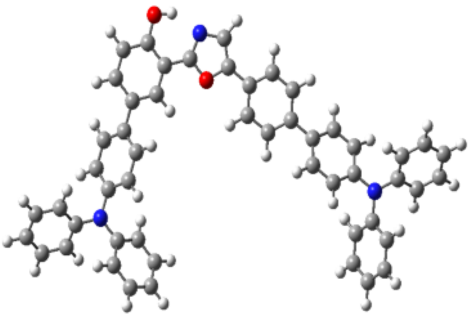
q^{CT}= 0.58 e / d^{CT} = 2.62Å

Figure S6: HOMO/LUMO and Electron density difference (EDD) plot of **2** obtained with TD-MN15. A contour threshold of 0.02 a.u. has been considered for MOs and 0.0004 a.u. for density. In the EDD plots the blue (red) zones indicate decrease (increase) of electronic density upon absorption. The CT parameters are displayed as well.[2]



2

$\Delta E^{ES} = 0.07$ eV / $\lambda_{E^*/K^*} = 438/526$ nm



3

$\Delta E^{ES} = 0.09$ eV / $\lambda_{E^*/K^*} = 439/525$ nm

Figure S7: Molecular structure of compounds **2** and **3** and their computed properties obtained with TD-MN15 using 6-311+G(2d,p) atomic basis set.

Table S7: Theoretical estimates of the transferred charge (q^{CT} in e), the CT distance (d^{CT} in Å), and the change in Merz-Kollman charge over the hydroxyl group upon excitation (Δq_{OH}) together with the energy difference between E* and K* tautomers (ΔE^{ES}) for the dyes (**1-16**). The obtained q^{CT}, d^{CT}, and Δq_{OH} are computed at the PCM TD-MN15/6-311+G(2d,p) level while the is determined with CC2 using *aug*-cc-pVDZ basis set.

compound	**q^{CT}**	**d^{CT}**	Δq_{OH}	ΔE^{ES}
1	0.59	2.92	+0.05	–0.12
2	0.58	2.62	+0.02	+0.07
3	0.59	2.76	+0.01	+0.09
4	0.44	0.77	+0.04	–0.12
5	0.55	2.48	+0.05	–0.12
6	0.67	3.39	+0.05	–0.02
7	0.59	3.46	+0.00	+0.23
8	0.49	2.02	+0.02	–0.01
9	0.56	3.28	+0.00	+0.11
10	0.51	0.92	+0.03	–0.11
11	0.57	1.55	+0.03	-0.07
12	0.43	0.29	+0.03	–0.12
13	0.50	2.84	+0.05	–0.07
14	0.47	2.14	+0.04	–0.07
15	0.59	3.84	+0.00	+0.16
16	0.77	4.73	+0.05	–0.02

Table S8: Raw TD-DFT results for the considered transition: CI weight, transition dipole moment (μ^{tr}) and oscillator strength (f) as obtained at the TD-MN15 level of theory for the lowest excited state on the **E*** and **K*** minimal geometry. H and L stands for HOMO and LUMO, respectively.

		ΔE (eV)	H-2 → L	H-1 → L	H-1 → L+1	H-1 → L+2	H → L	H → L+1	H → L+2	μ^{tr}	f
1	**E***	2.93		0.411			0.527		0.023	16.92	1.214
	K*	2.45		0.068			0.814	0.093		8.33	0.501
2	**E***	2.75	0.034				0.880			29.05	1.954
	K*	2.45	0.043	0.020			0.797	0.108		10.76	0.6445
3	**E***	2.74		0.039			0.880			28.59	1.920
	K*	2.46	0.053				0.797	0.098		10.56	0.635
4	**E***	2.93					0.963			20.61	1.480
	K*	2.62					0.866	0.103		9.23	0.593
5	**E***	2.93		0.133			0.797	0.029		14.71	1.055
	K*	2.40		0.028			0.847	0.111		7.61	0.448
6	**E***	2.88		0.092			0.809	0.056		8.18	0.578
	K*	2.37		0.036			0.842	0.108		7.40	0.429
7	**E***	2.74		0.031	0.022		0.898			29.03	1.952
	K*	2.62			0.028		0.856	0.086		13.84	0.887
8	**E***	2.82					0.938			24.31	1.678
	K*	2.64					0.899	0.065		10.94	0.707
9	**E***	2.77		0.028			0.923			26.21	1.783
	K*	2.64			0.029		0.898	0.046		12.97	0.838
10	**E***	2.83	0.022				0.938			23.64	1.639
	K*	2.44					0.874	0.081		8.32	0.496
11	**E***	2.78	0.033				0.919			25.48	1.738
	K*	2.41	0.027				0.867	0.075		8.69	0.513
12	**E***	2.92					0.960			20.71	1.484
	K*	2.66					0.901	0.054		10.56	0.689
13	**E***	2.83					0.930	0.024		24.35	1.688
	K*	2.61		0.021			0.765	0.201		10.63	0.659
14	**E***	2.84					0.942			24.47	1.705
	K*	2.61		0.020			0.761	0.198		11.75	0.753
15	**E***	2.75		0.040			0.910			25.96	1.750
	K*	2.66		0.080	0.026	0.021	0.840			15.76	1.026
16	**E***	2.73		0.097			0.774	0.100		8.87	0.594
	K*	2.17		0.023			0.854	0.111		7.33	0.389

Table S9: Total dipole moment of the studied systems (**1-16**) for the ground and excited state of various geometries. All values are in D and have been obtained at the TD-MN15 level.

Compound	Geometry	S_0	S_1
1	**E**	3.8	8.0
	E*	3.5	5.0
	K*	8.1	6.8
2	**E**	3.9	11.4
	E*	4.5	11.2
	K*	8.5	5.6
3	**E**	4.4	12.5
	E*	5.2	12.6
	K*	8.8	7.1
4	**E**	3.7	1.8
	E*	3.2	2.5
	K*	8.4	1.4
5	**E**	4.4	7.6
	E*	4.6	8.1
	K*	8.0	8.0
6	**E**	5.2	13.3
	E*	5.4	14.9
	K*	8.2	9.8
7	**E**	4.4	14.2
	E*	5.2	12.9
	K*	9.2	4.5
8	**E**	6.3	10.9
	E*	7.5	13.9
	K*	11.1	6.8
9	**E**	7.2	16.0
	E*	8.3	15.7
	K*	12.1	9.0
10	**E**	6.5	8.5
	E*	7.4	11.5
	K*	10.6	8.3
11	**E**	8.2	12.9
	E*	9.0	14.7
	K*	11.8	10.6
12	**E**	6.3	7.4
	E*	6.3	8.0
	K*	11.9	8.2
13	**E**	2.8	9.6
	E*	4.0	9.9
	K*	3.4	10.0
14	**E**	7.1	10.3
	E*	7.5	10.7
	K*	9.9	9.7
15	**E**	8.3	18.4
	E*	9.5	18.0
	K*	14.5	13.9
16	**E**	3.8	21.1
	E*	4.9	25.6
	K*	1.7	21.5

References

[1] B. Li, L. Zhou, H. Cheng, Q. Huang, J. Lan, L. Zhou and J. You, *Chem. Sci.*, 2018, **9**, 1213–1220.

[2] T. Le Bahers, C. Adamo and I. Ciofini, *J. Chem. Theory Comput.*, 2011, **7**, 2498–2506.