

Supporting Information

Table S1. Relative energies, natural charges and structural parameters, related to the switching, in toluene. The corresponding values for acetonitrile are given in brackets.

Comp.	Form	ΔE	ΔG	μ	α	axle	Natural charge*		
		[kcal/mol]		[D]	[°]	[Å]	O _{PTP}	N _{PCU}	N _{PTP}
7OHQ	E	0.0 (0.0)	0.0 (0.0)	1.4 (1.8)	-	-	-0.65	-	-0.42
	K	11 (6.7)	11 (6.9)	10.0 (12.8)	-	-	-0.64	-	-0.47
HQBT	E	0.0 (0.0)	0.0 (0.0)	2.9 (3.4)	0 (0)	1.460	-0.66	-0.50	-0.44
	TS (PT O-N)	6.0 (5.4)	4.0 (3.3)	2.6 (3.1)	0 (0)				
	KE	5.5 (4.5)	5.1 (4.3)	2.9 (3.6)	0 (0)	1.410	-0.68	-0.51	-0.46
	TS (KE-KK)	30 (24)	32 (26)	8.3 (9.5)	90 (90)				
	KK	6.2 (4.3)	6.4 (4.6)	5.9 (7.6)	180 (180)	1.403	-0.64	-0.52	-0.50
	TS (PT N-N)	10 (8.1)	8.3 (6.0)	7.3 (9.3)	180 (180)				
	K	6.4 (3.1)	5.9 (2.9)	8.8 (11.3)	180 (180)	1.445	-0.63	-0.53	-0.48
HQPy	E	0.0 (0.0)	0.0 (0.0)	2.6 (3.1)	24 (25)	1.483	-0.67	-0.49	-0.44
	TS (PT O-N)	- (-)	- (-)	- (-)	- (-)				
	KE	- (-)	- (-)	- (-)	- (-)	-			

	TS (KE-KK)	24 (17)	25 (18)	8.7 (10.0)	91 (90)				
	KK	7.8 (5.6)	6.1 (3.0)	6.8 (8.7)	180 (180)	1.440	-0.67	-0.52	-0.48
	TS (PT N-N)	9.9 (7.6)	5.1 (3.6)	7.3 (9.3)	180 (179)				
	K	7.9 (5.4)	6.8 (4.9)	7.7 (10.0)	173 (164)	1.476	-0.66	-0.51	-0.48
HQ1iQ	E	0.0 (0.0)	0.0 (0.0)	3.0 (3.6)	45 (47)	1.485	-0.67	-0.49	-0.43
	TS (PT O-N)	7.7 (7.1)	6.0 (5.2)	4.0 (4.7)	23 (24)				
	KE	7.6 (6.5)	6.9 (6.3)	4.3 (5.6)	24 (27)	1.441	-0.70	-0.48	-0.45
	TS (KE-KK)	18 (12)	18 (12)	7.9 (9.2)	92 (91)				
	KK	11 (8.4)	10 (8.2)	5.6 (7.4)	148 (145)	1.434	-0.65	-0.49	-0.52
	TS (PT N-N)	14 (12)	11 (9.2)	6.4 (8.4)	150 (150)				
	K	9.5 (5.9)	9.5 (5.8)	7.8 (10.7)	135 (129)	1.479	-0.64	-0.50	-0.48
HQ3iQ	E	0.0 (0.0)	0.0 (0.0)	2.9 (3.4)	25 (27)	1.484	-0.68	-0.48	-0.44
	TS (PT O-N)	- (-)	- (-)	- (-)	- (-)				
	KE	- (-)	- (-)	- (-)	- (-)	-			
	TS	25	26	10.5	91				

	(KE-KK)	(18)	(18)	(11.9)	(89)				
	KK	10.0 (7.7)	8.4 (5.4)	7.8 (10.0)	180 (180)	1.450	-0.68	-0.46	-0.52
	TS (PT N-N)	11 (8.8)	6.3 (4.6)	7.6 (9.9)	180 (180)				
	K	8.2 (5.6)	6.7 (5.1)	7.6 (10.1)	173 (164)	1.477	-0.66	-0.50	-0.48
HQ2Q	E	0.0 (0.0)	0.0 (0.0)	2.5 (3.0)	25 (27)	1.481	-0.67	-0.48	-0.44
	TS (PT O-N)	- (3.7)	- (0.44)	- (4.1)	- (5)				
	KE	- (3.6)	- (2.2)	- (4.6)	- (9)				
	TS (KE-KK)	24 (17)	24 (18)	9.7 (11.1)	91 (91)				
	KK	5.9 (4.4)	3.7 (3.1)	6.5 (8.3)	180 (175)	1.432	-0.65	-0.49	-0.51
	TS (PT N-N)	9.2 (7.2)	4.7 (3.2)	7.1 (9.1)	180 (179)				
	K	7.7 (5.0)	7.0 (5.0)	7.6 (10.0)	167 (161)	1.472	-0.65	-0.51	-0.48
HQPm	E	0.0 (0.0)	0.0 (0.0)	1.5 (1.5)	33 (34)	1.478	-0.67	-0.51	-0.41
	TS (PT O-N)	- (-)	- (-)	- (-)	- (-)				
	KE	- (-)	- (-)	- (-)	- (-)	-			
	TS (KE-KK)	28 (20)	28 (20)	10.2 (11.8)	92 (90)				

	KK	13 (9.4)	12 (8.4)	8.4 (10.9)	172 (173)	1.421	-0.60	-0.51	-0.52
	TS (PT N-N)	14 (10)	11 (6.9)	8.9 (11.5)	172 (174)				
	K	9.3 (5.5)	9.3 (5.7)	9.1 (12.0)	155 (153)	1.466	-0.60	-0.53	-0.49
HQPy'	E	0.0 (0.0)	0.0 (0.0)	3.7 (4.0)	23 (24)	1.478	-0.67	-0.47	-0.45
	TS (PT O-N)	- (-)	- (-)	- (-)	- (-)				
	KE	- (-)	- (-)	- (-)	- (-)	-			
	TS (KE-KK)	31 (23)	31 (24)	8.1 (9.8)	91 (91)				
	KK	9.7 (7.4)	6.3 (5.3)	10.2 (12.3)	180 (179)	1.426	-0.64	-0.48	-0.51
	TS (PT N-N)	11 (8.1)	7.5 (4.2)	11.2 (13.5)	180 (180)				
	K	7.4 (4.1)	6.2 (3.6)	12.7 (15.5)	171 (168)	1.467	-0.64	-0.49	-0.48
HQPy''	E	0.0 (0.0)	0.0 (1.71)	5.5 (6.6)	20 (24)	1.488	-0.68	-0.54	-0.45
	TS (PT O-N)	- (2.05)	- (0.0)	- (8.3)	- (0)	-			
	KE	- (1.75)	- (1.77)	- (9.3)	- (2)				
	TS (KE-KK)	18 (11)	20 (14)	11.2 (12.6)	90 (90)				
	KK	5.0	4.1	7.1	180	1.445	-0.69	-0.51	-0.52

		(2.7)	(3.1)	(8.8)	(180)				
	TS (PT N-N)	8.5 (6.6)	5.3 (5.1)	5.9 (7.7)	179 (179)				
	K	7.7 (5.7)	5.8 (5.9)	5.4 (7.3)	180 (177)	1.480	-0.67	-0.56	-0.49
BPOH	E	0.0 (0.0)	0.0 (0.0)	2.4 (2.7)	0 (0)	1.483	-0.67	-0.49	-0.40
	TS (PT O-N)								
	KE								
	TS (KE-KK)	34 (25)	34 (26)	10.4 (11.8)	91 (91)				
	KK	17 (13)	17 (13)	8.1 (10.3)	180 (180)	1.436	-0.70	-0.45	-0.45
	TS (PT N-N)	26 (23)	23 (20)	7.4 (9.0)	180 (180)				
	K	13 (10)	13 (10)	5.7 (7.1)	180 (180)	1.470	-0.69	-0.47	-0.39
DMAPP	E	0.0 (0.0)	0.0 (0.0)	4.9 (6.0)	33 (32)	1.486	-0.68	-0.49	-0.44
	TS (PT O-N)	- (-)	- (-)	- (-)	- (-)				
	KE	- (-)	- (-)	- (-)	- (-)	-			
	TS (KE-KK)	31 (23)	31 (23)	11.3 (13.1)	82 (80)				
	KK	17 (13)	17 (13)	9.8 (12.6)	163 (160)	1.439	-0.70	-0.48	-0.49
	TS	19	16	10.8	179				

	(PT N-N)	(14)	(11)	(13.2)	(179)				
	K	19 (13)	17 (13)	11.5 (14.4)	175 (159)	1.473	-0.72	-0.52	-0.42

* no tautomeric proton added.

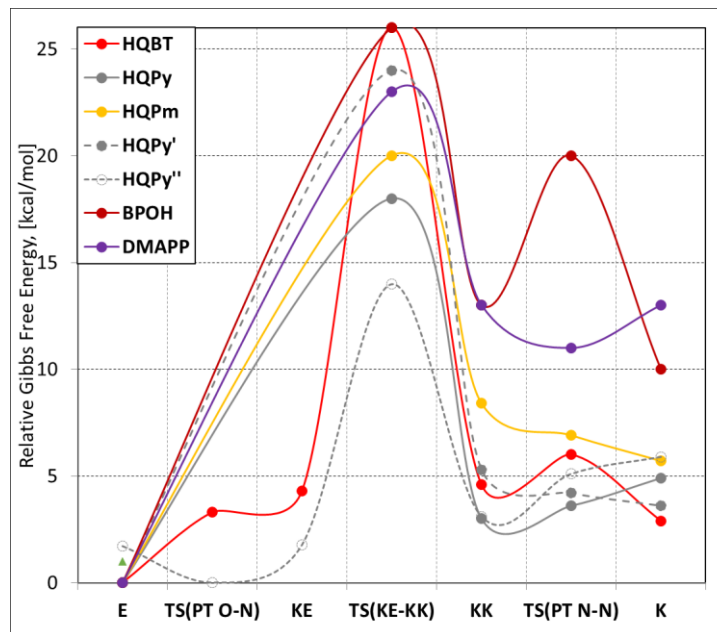
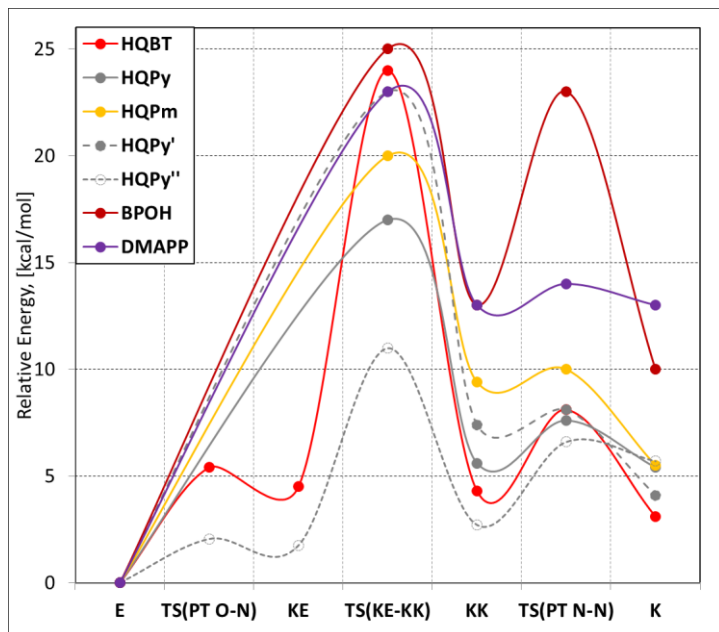
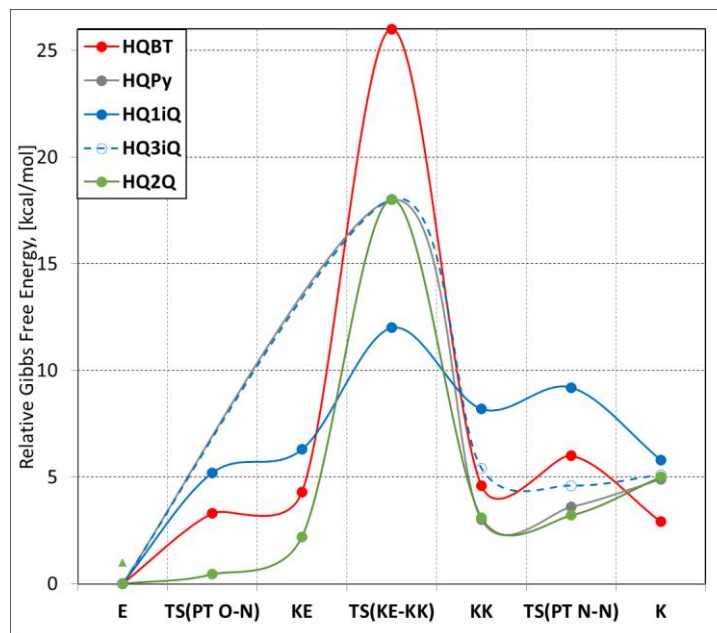
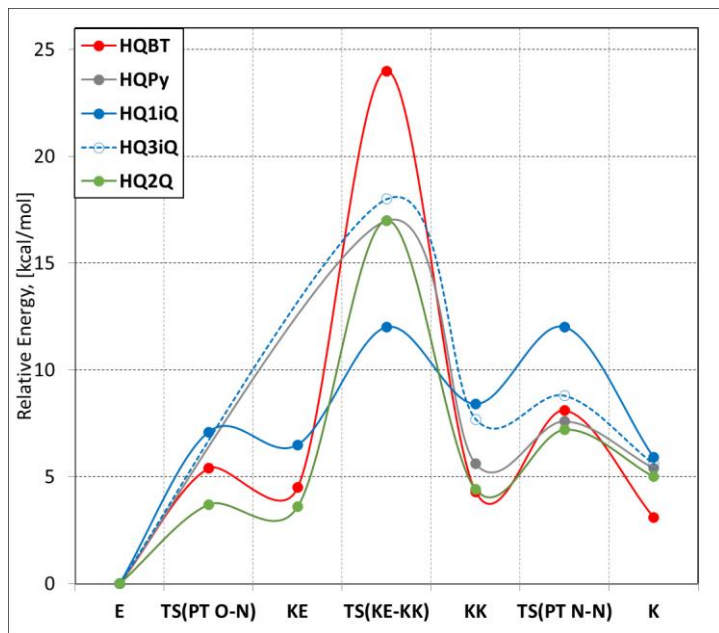
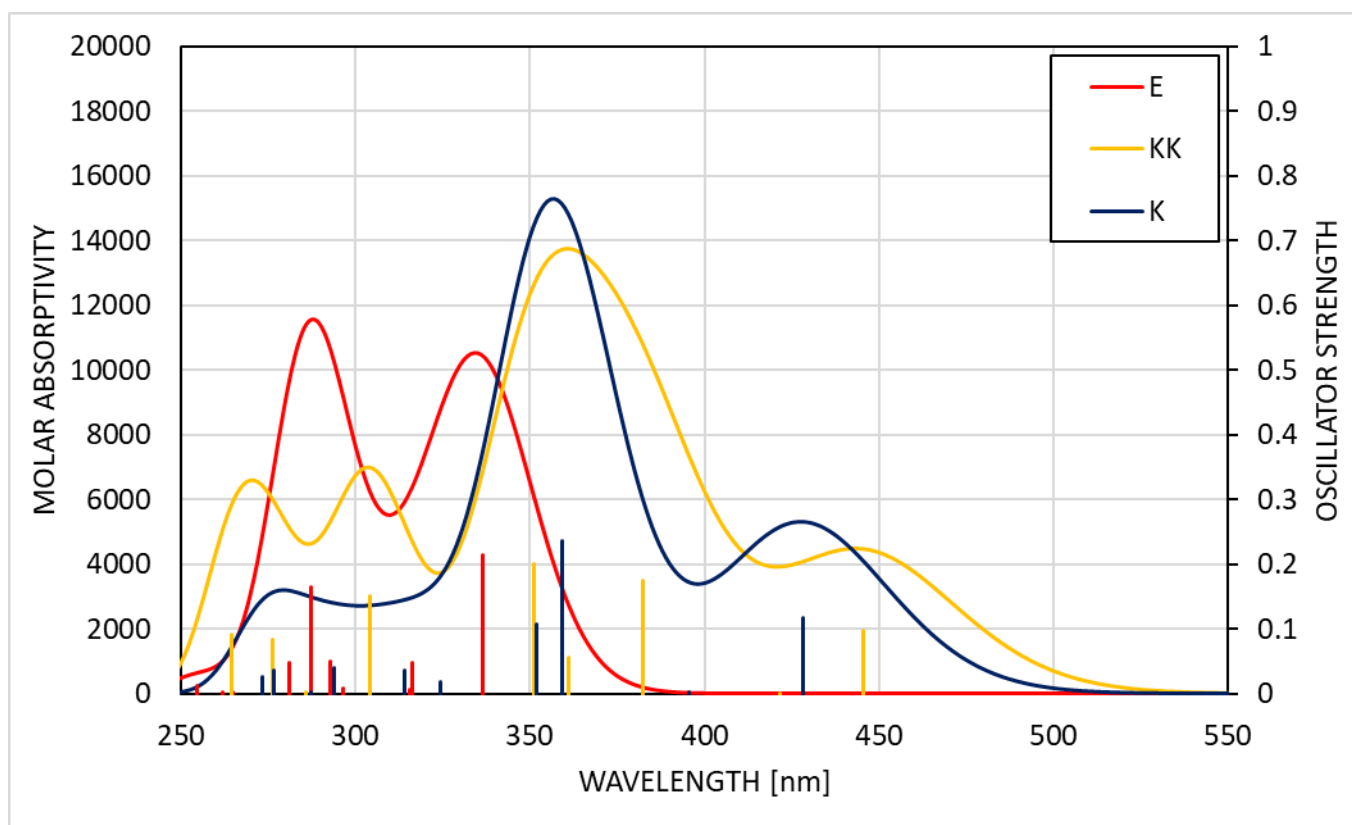
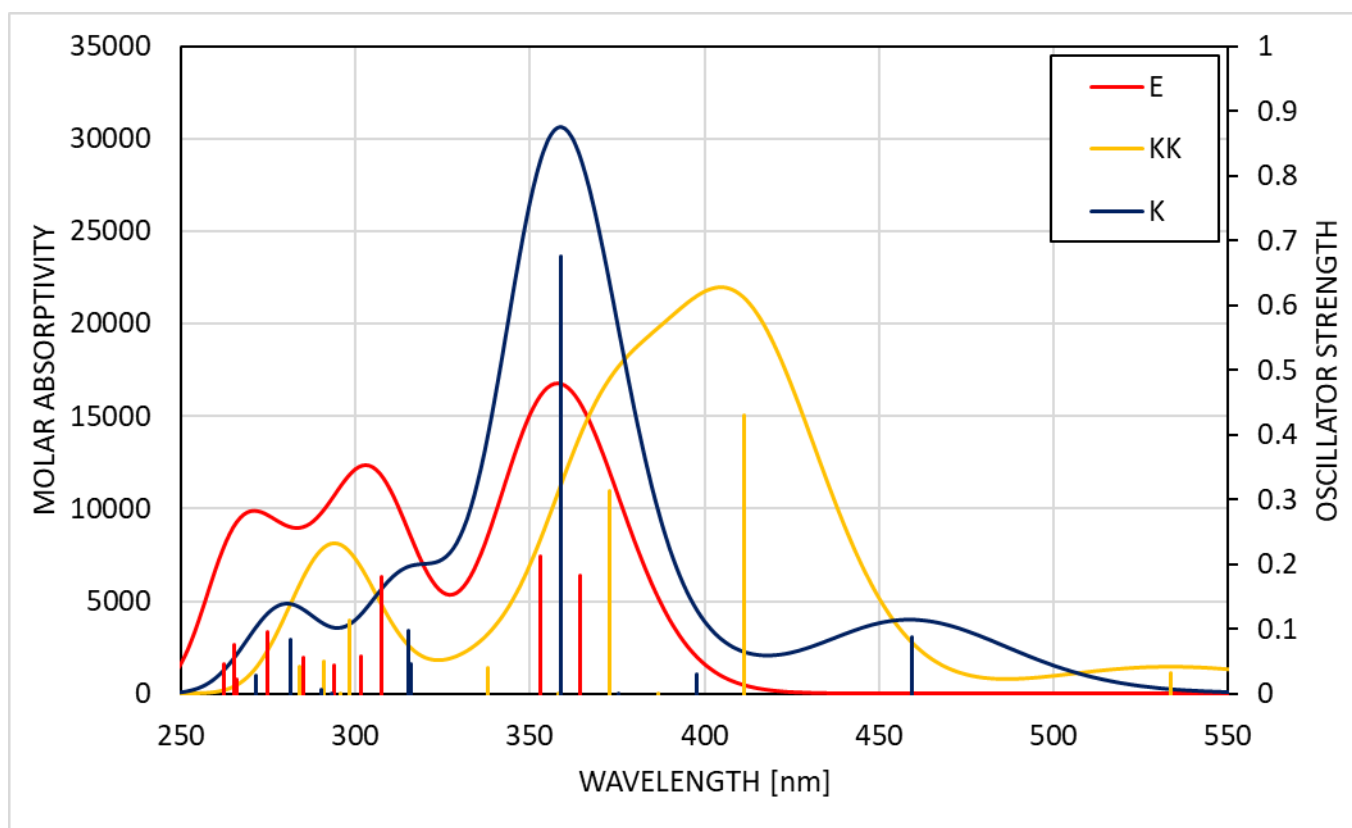


Figure S1. Ground state PESs of the studied compounds in acetonitrile presented as relative energies (left column) and as relative Gibbs free energies (right column). The values are given in Table S1.



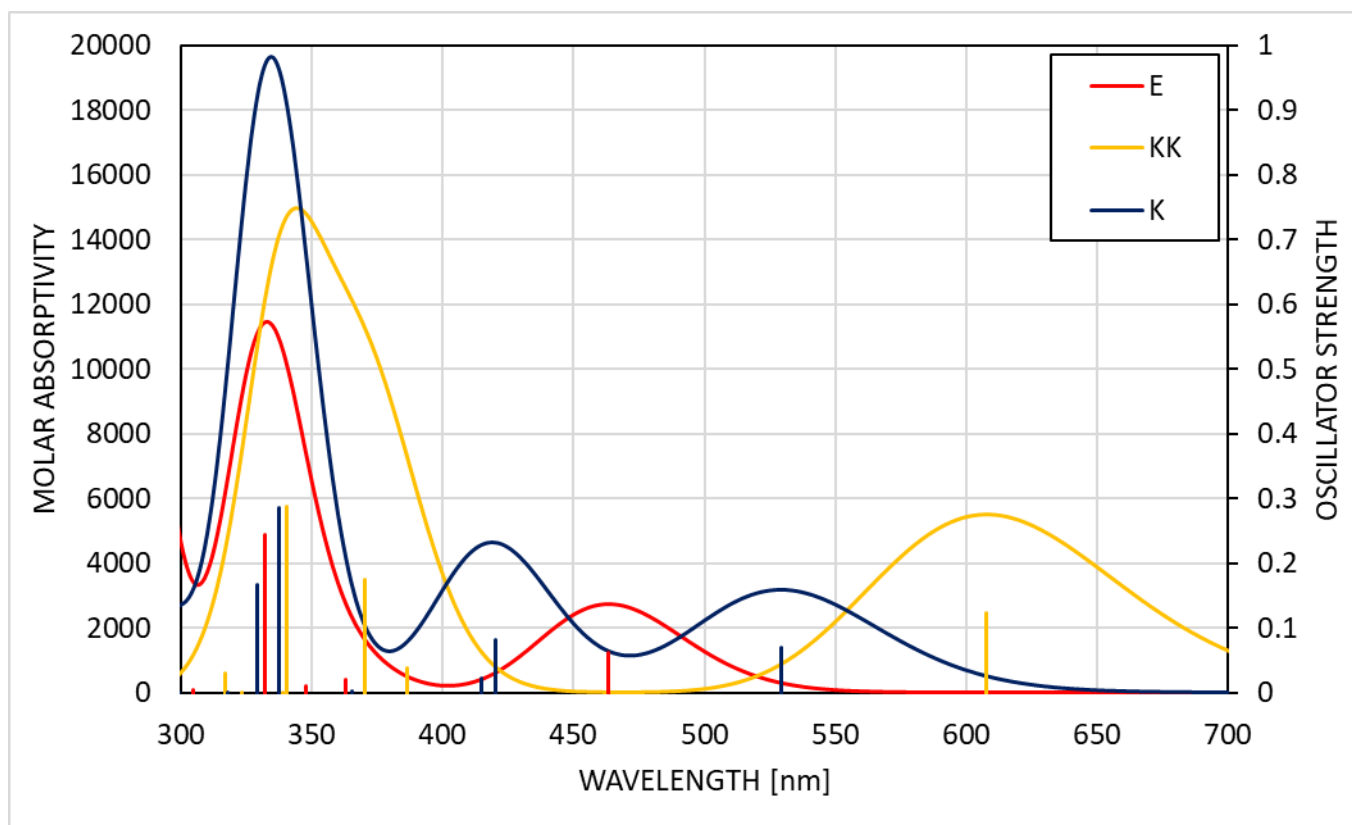


Figure S2. Simulated absorption spectra of (from top to down) **HQ3iQ**, **HQPm** and **HQPy'** in toluene.