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

Supplementary Information

Azaindolizine proton cranes attached to 7-hydroxyquinoline and 3-hydroxypyridine: a comparative theoretical study

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Table S1. Relative energies and other electronic and structural parameters of **7HQ-A** in ground (M06-2X/TZVP) and first singlet excited (CAM-B3LYP/TZVP) state in toluene and acetonitrile (in brackets).

Structure	ΔE	ΔE+ZPE	ΔG	μ	α	axle length	atomic charge		HOMO-LUMO gap
							O	N	
	[kcal/mol]			[D]	[°]	[Å]			eV
Ground state									
E	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	4.2 (5.1)	0 (0)	1.467 (1.468)	-0.680 (-0.694)	-0.538 (-0.550)	6.0 (6.0)
TS (E-KE)	– (7.03)	(5.17)	(5.63)	(8.9)	(0)	(1.450)			
KE	(6.99)	(6.20)	(6.21)	(9.6)	(0)	(1.449)	(-0.772)	(-0.503)	(5.5)
TS (KE-KK)	26.99 (18.60)	27.48 (19.27)	27.96 (19.87)	12.0 (13.4)	90 (86)	1.459 (1.464)			
KK	11.63 (7.85)	11.14 (7.53)	11.14 (7.50)	9.4 (11.5)	180 (180)	1.435 (1.444)	-0.702 (-0.747)	-0.504 (-0.501)	5.0 (5.3)
TS (KK-K)	13.94 (11.0)	10.88 (7.97)	11.06 (7.98)	8.2 (10.2)	180 (180)	1.441 (1.447)			
K	7.99 (5.51)	8.24 (5.83)	8.26 (5.86)	6.7 (8.8)	180 (180)	1.458 (1.460)	-0.664 (-0.713)	-0.552 (-0.558)	5.1 (5.2)
Excited state									
E*	12.61 (11.32)	11.72 (10.97)	12.16 (11.00)	4.1 (4.9)	0 (0)	1.410 (1.406)	-0.625 (-0.643)	-0.542 (-0.552)	5.6 (5.6)
TS (E*-KE*)	16.08 (13.99)	12.43 (11.14)	13.15 (11.59)	5.6 (6.4)	0 (0)	1.409 (1.406)			
KE*	11.18 (9.30)	10.05 (8.85)	10.21 (8.52)	8.3 (9.5)	0 (0)	1.423 (1.409)	-0.625 (-0.667)	-0.514 (-0.503)	5.1 (5.4)
TS (KE*-KK*)	20.95 (27.98)	20.07 (27.63)	20.24 (27.19)	12.3 (13.3)	92 (91)	1.460 (1.451)			
KK*	10.05 (7.94)	8.94 (7.52)	9.26 (7.40)	9.0 (10.8)	180 (180)	1.422 (1.411)	-0.597 (-0.642)	-0.521 (-0.515)	5.0 (5.3)
TS (KK*-K*)	13.28 (10.68)	9.94 (8.03)	10.85 (8.52)	8.2 (10.0)	180 (180)	1.422 (1.423)			
K*	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	7.3 (9.2)	180 (180)	1.431 (1.435)	-0.622 (-0.642)	-0.517 (-0.525)	4.8 (5.1)

Table S2. Bond lengths of the bonds of the tautomeric forms of the studied compounds in ground and excited state in toluene and in acetonitrile (in brackets).

Bond	Bond length, Å			
7HQ-A				
	E	**E***	**KE**	**KE***
O-C	1.338 (1.342)	1.322 (1.326)	-	1.251 (1.259)
C-C (quinoline)	1.394 (1.393)	1.464 (1.468)	-	1.472 (1.490)
C-C (axle)	1.467 (1.468)	1.410 (1.406)	-	1.423 (1.409)
C-N	1.377 (1.379)	1.384 (1.386)	-	1.398 (1.398)
7HQ-B				
	E	**E***	**KE**	**KE***
O-C	1.341 (1.344)	1.325 (1.328)	-	1.256 (1.261)
C-C	1.393 (1.393)	1.470 (1.472)	-	1.468 (1.487)
C-C (axle)	1.472 (1.473)	1.418 (1.413)	-	1.430 (1.413)
C-N	1.349 (1.350)	1.364 (1.366)	-	1.419 (1.412)
7HQ-C				
	E	**E***	**KE**	**KE***
O-C	1.330 (1.335)	1.324 (1.329)	1.254 (1.260)	1.254 (1.257)
C-C	1.394 (1.394)	1.462 (1.465)	1.438 (1.435)	1.494 (1.495)
C-C (axle)	1.458 (1.459)	1.397 (1.391)	1.420 (1.424)	1.410 (1.408)
C-N	1.323 (1.325)	1.359 (1.366)	1.348 (1.348)	1.361 (1.365)
3HP-A				
	E	**E***	**KE**	**KE***
O-C	1.345 (1.347)	1.326 (1.326)	-	1.255 (1.256)
C-C	1.407 (1.407)	1.436 (1.446)	-	1.469 (1.477)
C-C (axle)	1.465 (1.465)	1.406 (1.394)	-	1.428 (1.403)
C-N	1.369 (1.370)	1.359 (1.368)	-	1.393 (1.395)
3HP-B				
	E	**E***	**KE**	**KE***
O-C	1.346 (1.348)	1.342 (1.330)	-	1.261 (1.258)
C-C	1.407 (1.407)	1.408 (1.450)	-	1.472 (1.480)
C-C (axle)	1.468 (1.469)	1.448 (1.396)	-	1.429 (1.409)
C-N	1.342 (1.342)	1.313 (1.357)	-	1.409 (1.406)
3HP-C				
	E	**E***	**KE**	**KE***
O-C	1.339 (1.342)	1.320 (1.323)	1.262 (1.267)	1.259 (1.256)
C-C	1.404 (1.404)	1.453 (1.457)	1.437 (1.434)	1.472 (1.479)
C-C (axle)	1.459 (1.460)	1.385 (1.380)	1.424 (1.431)	1.414 (1.405)
C-N	1.314 (1.316)	1.364 (1.370)	1.345 (1.338)	1.363 (1.368)

Table S3. Spectra characteristics (B3LYP/TZVP//M06-2X/TZVP) (λ_{max} of S_0-S_1 and S_0-S_2 transitions corresponding oscillator strengths of all tautomeric forms) of the studied compounds in toluene and in acetonitrile (in brackets).

State	S_0-S_1		S_0-S_2	
	λ_{max}, nm	***f***	λ_{max}, nm	***f***
7HQ-A				
E	363 (359)	0.29 (0.24)	327 (319)	0.13 (0.11)
KK	474 (429)	0.35 (0.35)	392 (380)	0.07 (0.05)
K	472 (456)	0.09 (0.08)	373 (360)	0.00 (0.33)
7HQ-B				
E	352 (350)	0.22 (0.18)	316 (315)	0.03 (0.06)
KK	441 (403)	0.01 (0.18)	411 (393)	0.38 (0.15)
K	461 (444)	0.09 (0.09)	379 (359)	0.00 (0.02)
7HQ-C				
E	366 (357)	0.32 (0.34)	312 (305)	0.01 (0.01)
KE	382 (377)	0.37 (0.35)	334 (326)	0.31 (0.27)
KK	382 (377)	0.40 (0.40)	334 (326)	0.30 (0.30)
K	463 (440)	0.07 (0.08)	349 (334)	0.00 (0.17)
ZW	548 (483)	0.06 (0.06)	496 (436)	0.01 (0.01)
3HP-A				
E	331 (325)	0.45 (0.41)	290 (288)	0.06 (0.08)
KK	530 (446)	0.28 (0.29)	435 (372)	0.00 (0.00)
K	408 (392)	0.51 (0.51)	365 (345)	0.00 (0.00)
3HP-B				
E	319 (317)	0.24 (0.24)	295 (292)	0.01 (0.00)
KK	496 (418)	0.00 (0.10)	439 (401)	0.51 (0.38)
K	405 (390)	0.50 (0.49)	375 (353)	0.00 (0.00)
3HP-C				
E	320 (317)	0.75 (0.71)	286 (286)	0.04 (0.03)
KE	389 (379)	0.57 (0.54)	359 (348)	0.00 (0.00)
KK	389 (379)	0.57 (0.54)	359 (348)	0.00 (0.00)
K	414 (401)	0.59 (0.57)	352 (338)	0.00 (0.00)
ZW	455 (413)	0.05 (0.10)	422 (392)	0.61 (0.52)

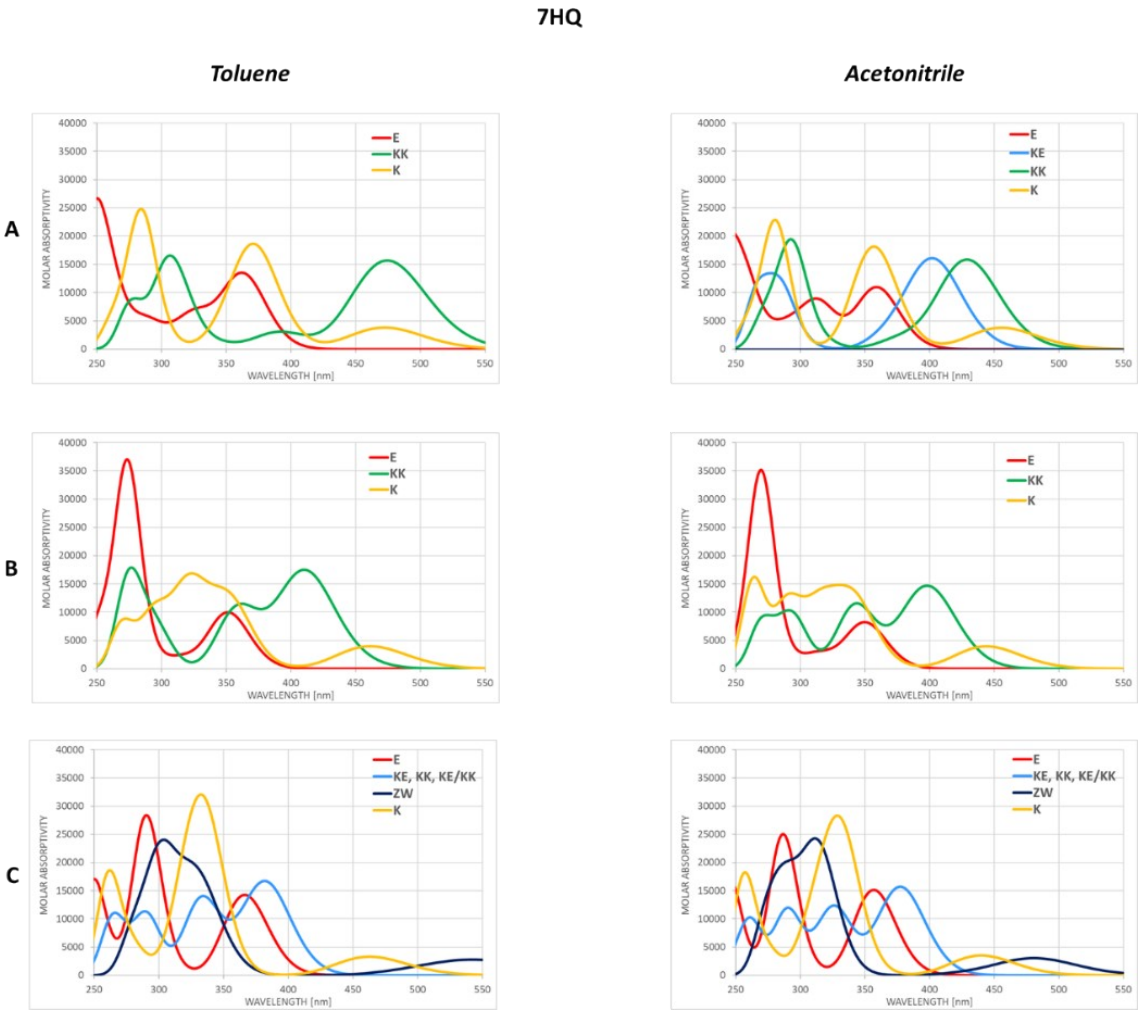

Figure S1. Predicted (B3LYP/TZVP//M06-2X/TZVP) absorption spectra of **7HQ** derivatives in toluene and acetonitrile.

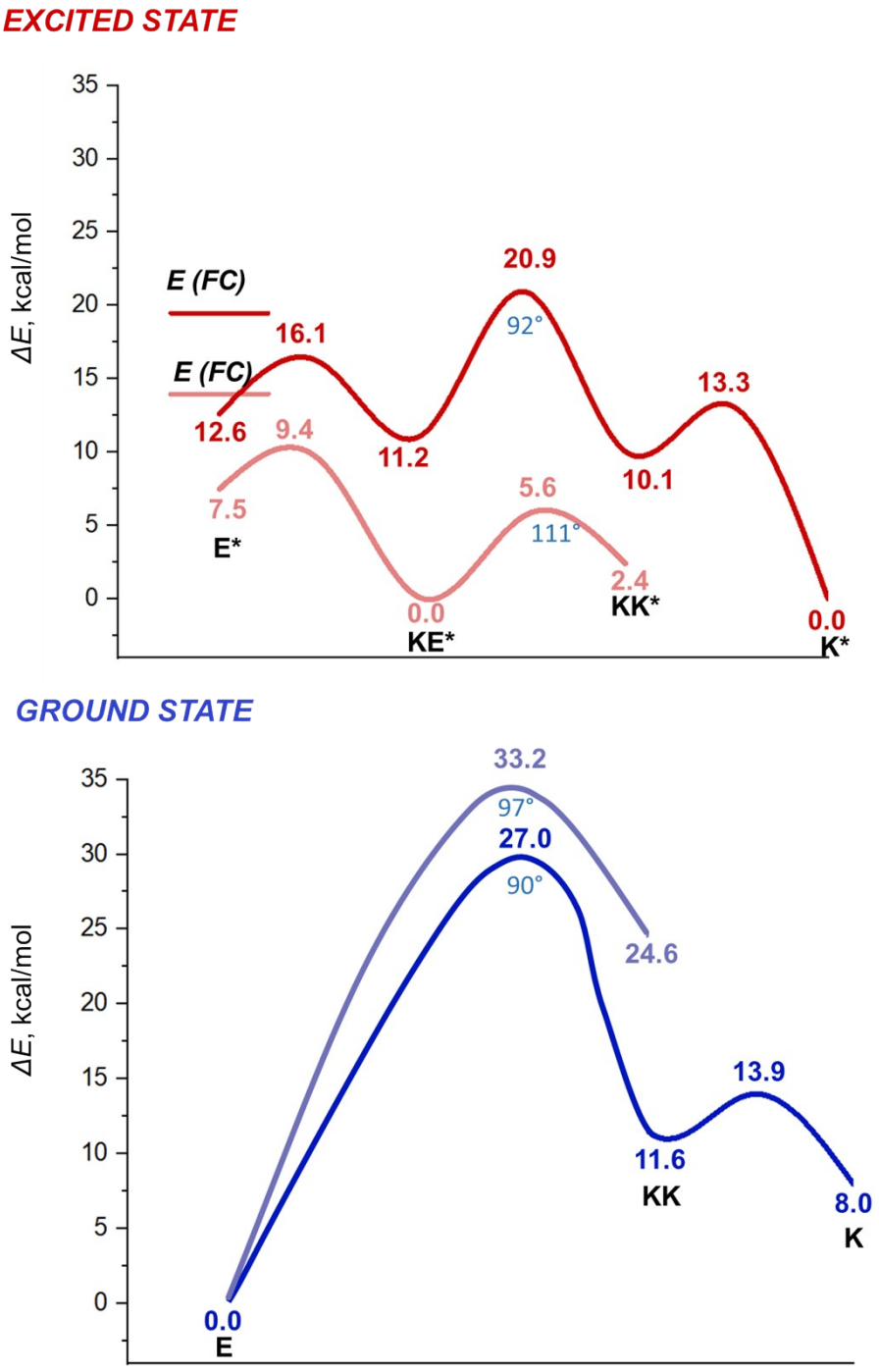

Figure S2. Ground (M06-2X/TZVP) and excited (CAM-B3LYP/TZVP) state PES of **7HQ-A** (saturated) and **P-A** (pale) in toluene. Relative energies are given in kcal/mol units.

Table S4. Relative energies and other electronic and structural parameters of **P-A** in ground (M06-2X/TZVP) and first singlet excited (CAM-B3LYP/TZVP) state in toluene and acetonitrile (in brackets).

Structure	ΔE	ΔE+ZPE	ΔG	μ	α	axle length
	[kcal/mol]			[D]	[°]	[Å]
Ground state						
E	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	6.6 (7.8)	4 (3)	1.465 (1.466)
TS (E-KE)	( )	( )	( )	( )	( )	( )
KE	( )	( )	( )	( )	( )	( )
TS (KE-KK)	33.22 (23.23)	33.19 (23.47)	33.83 (24.22)	15.4 (17.8)	97 (98)	1.461 (1.467)
KK	24.62 (17.15)	24.11 (17.14)	23.86 (17.04)	13.9 (16.7)	180 (180)	1.432 (1.445)
TS (KK-K)	( )	( )	( )	( )	( )	( )
K	( )	( )	( )	( )	( )	( )
Excited state						
E*	7.49 (6.47)	6.47 (5.46)	6.52 (5.71)	6.5 (7.5)	0 (0)	1.418 (1.409)
TS (E*-KE*)	9.38 (8.86)	6.16 (5.63)	6.67 (6.17)	8.1 (9.5)	0 (0)	1.409 (1.396)
KE*	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	12.6 (14.2)	4 (0)	1.439 (1.408)
TS (KE*-KK*)	5.63 (16.16)	5.97 (16.07)	6.63 (15.97)	16.2 (17.7)	111 (92)	1.464 (1.457)
KK*	2.40 (2.46)	2.44 (2.45)	2.02 (1.69)	14.2 (16.0)	179 (180)	1.441 (1.409)
TS (KK*-K*)	( )	( )	( )	( )	( )	( )
K*	( )	( )	( )	( )	( )	( )

Table S5. Relative energies and other electronic and structural parameters of **3HP-A** in ground (M06-2X/TZVP) and first singlet excited (CAM-B3LYP/TZVP) state in toluene and acetonitrile (in brackets).

Structure	ΔE	ΔE+ZPE	ΔG	μ	α	axle length	atomic charge		HOMO-LUMO gap
							O	N	
	[kcal/mol]			[D]	[°]	[Å]			eV
Ground state									
E	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	4.6 (5.4)	0 (0)	1.465 (1.465)	-0.679 (-0.691)	-0.529 (-0.541)	6.4 (6.5)
TS (E-KE)	( )	( )	( )	( )	( )	( )			
KE	( )	( )	( )	( )	( )	( )	( )	( )	( )
TS (KE-KK)	32.25 (45.45)	32.24 (45.07)	32.63 (45.51)	14.0 (15.5)	93 (93)	1.472 (1.479)			
KK	18.39 (12.42)	18.13 (12.37)	18.11 (12.33)	12.4 (14.7)	180 (180)	1.437 (1.448)	-0.738 (-0.783)	-0.479 (-0.475)	4.7 (5.3)
TS (KK-K)	31.26 (27.53)	28.28 (24.65)	28.41 (24.81)	10.0 (11.6)	180 (180)	1.449 (1.456)			
K	11.24 (8.56)	11.24 (8.74)	10.98 (8.51)	5.3 (6.4)	180 (180)	1.445 (1.448)	-0.704 (-0.750)	-0.509 (-0.518)	5.4 (5.6)
Excited state									
E*	8.96 (10.69)	8.09 (9.69)	8.51 (9.96)	4.6 (5.3)	0 (0)	1.406 (1.394)	-0.623 (-0.631)	-0.555 (-0.571)	6.2 (6.2)
TS (E*-KE*)	11.28 (13.01)	8.05 (9.57)	8.61 (10.04)	6.8 (7.8)	0 (0)	1.401 (1.392)			
KE*	1.82 (3.60)	1.71 (3.26)	1.94 (3.29)	11.2 (12.6)	0 (0)	1.428 (1.403)	-0.603 (-0.630)	-0.506 (-0.505)	5.0 (5.4)
TS (KE*-KK*)	12.46 (25.8)	12.15 (25.13)	12.50 (25.22)	14.9 (16.0)	92 (87)	1.467 (1.458)			
KK*	1.49 (4.25)	1.44 (3.87)	1.60 (3.68)	12.4 (14.0)	180 (180)	1.430 (1.404)	-0.564 (-0.603)	-0.508 (-0.509)	4.7 (5.3)
TS (KK*-K*)	19.80 (21.12)	16.94 (18.02)	17.40 (18.29)	9.4 (11.1)	180 (180)	1.409 (1.401)			
K*	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	5.5 (6.3)	180 (180)	1.405 (1.398)	-0.527 (-0.579)	-0.519 (-0.579)	5.4 (5.5)

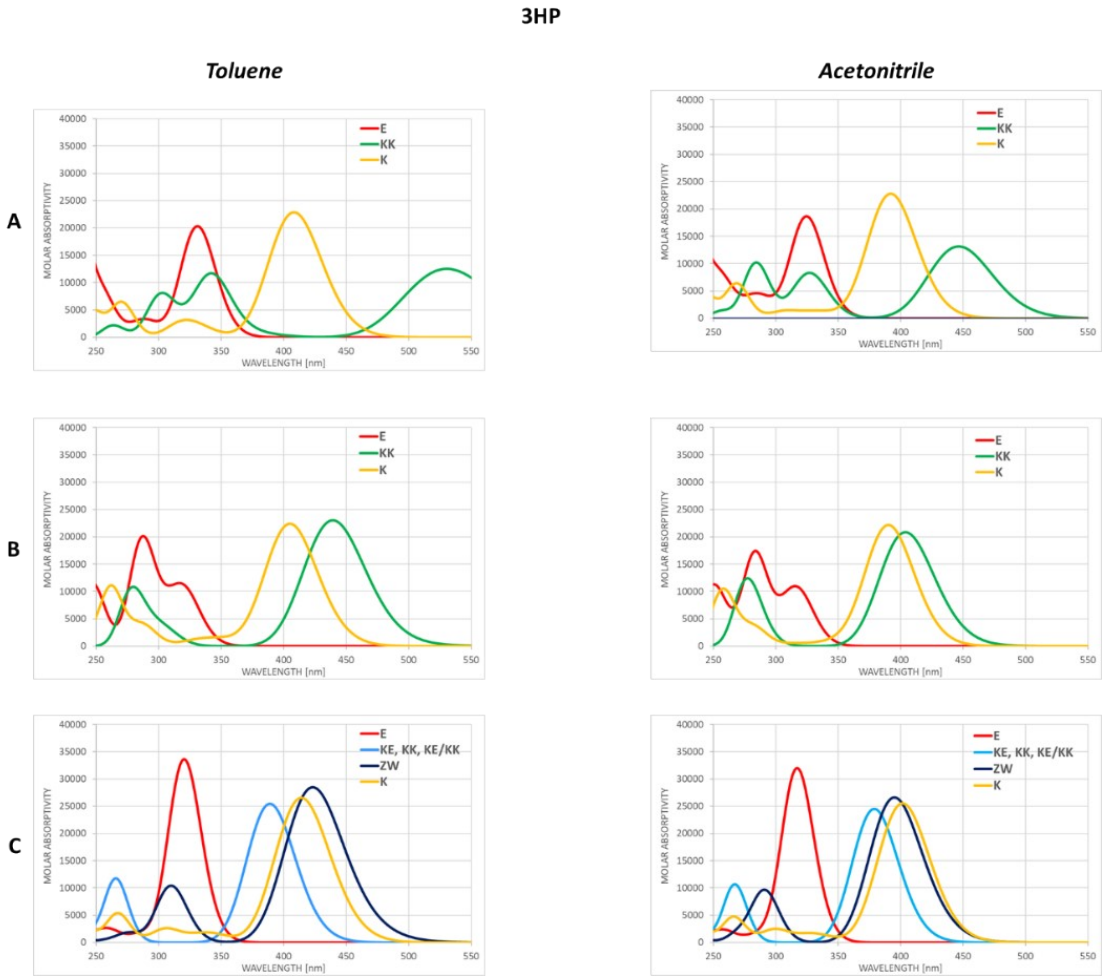

Figure S3. Predicted (B3LYP/TZVP//M06-2X/TZVP) absorption spectra of **3HP** derivatives in toluene and acetonitrile.

Table S6. Relative energies and other electronic and structural parameters of **7HQ-B** in ground (M06-2X/TZVP) and first singlet excited (CAM-B3LYP/TZVP) state in toluene and acetonitrile (in brackets).

Structure	ΔE	ΔE+ZPE	ΔG	μ	α	axle length	atomic charge		HOMO-LUMO gap
							O	N	
	[kcal/mol]			[D]	[°]	[Å]			eV
Ground state									
E	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	2.4 (2.8)	8 (13)	1.472 (1.473)	-0.676 (-0.686)	-0.361 (-0.367)	6.1 (6.1)
TS (E-KE)	( )	( )	( )	( )	( )	( )			
KE	( )	( )	( )	( )	( )	( )	( )	( )	( )
TS (KE-KK)	34.07 (25.21)	34.00 (25.14)	34.66 (25.78)	11.9 (13.3)	92 (87)	1.460 (1.465)			
KK	17.43 (13.37)	16.14 (12.08)	16.15 (11.83)	9.6 (12.1)	180 (180)	1.432 (1.441)	-0.683 (-0.732)	-0.351 (-0.342)	5.4 (5.5)
TS (KK-K)	18.01 (14.41)	14.83 (11.07)	15.22 (11.28)	9.3 (11.7)	180 (180)	1.438 (1.445)			
K	8.13 (5.01)	8.16 (4.88)	8.28 (4.36)	8.4 (11.0)	180 (179)	1.463 (1.464)	-0.650 (-0.703)	-0.380 (-0.378)	5.2 (5.3)
Excited state									
E*	14.20 (13.51)	13.02 (12.37)	12.68 (12.08)	2.2 (2.6)	3 (6)	1.418 (1.413)	-0.623 (-0.639)	-0.369 (-0.377)	5.8 (5.8)
TS (E*-KE*)	20.23 (18.33)	16.82 (14.69)	17.12 (14.67)	4.4 (4.8)	10 (9)	1.414 (1.412)			
KE*	16.98 (14.49)	16.38 (13.90)	16.76 (13.78)	7.8 (7.9)	29 (19)	1.431 (1.413)	-0.615 (-0.662)	-0.390 (-0.382)	5.3 (5.5)
TS (KE*-KK*)	24.31 (30.71)	23.09 (29.61)	23.75 (30.00)	10.9 (13.0)	132 (93)	1.447 (1.466)			
KK*	17.40 (13.54)	14.94 (11.50)	15.81 (11.63)	9.3 (11.6)	180 (180)	1.426 (1.422)	-0.598 (-0.636)	-0.349 (-0.349)	5.5 (5.5)
TS (KK*-K*)	17.43 (14.38)	14.19 (10.58)	14.28 (10.26)	9.2 (11.4)	180 (180)	1.427 (1.429)			
K*	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	9.1 (11.4)	173 (168)	1.440 (1.444)	-0.603 (-0.626)	-0.334 (-0.335)	4.9 (5.2)

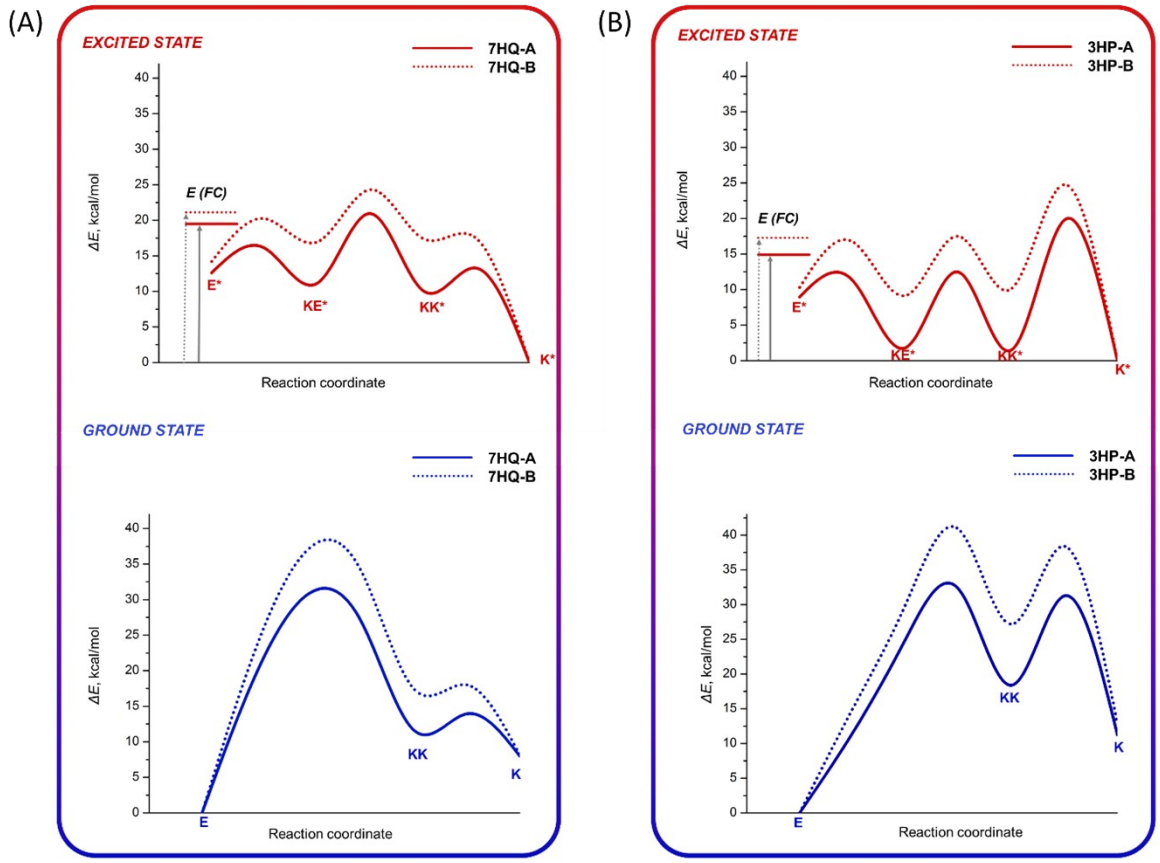

Figure S4. Comparison between the PES in toluene of **7HQ-A** and **7HQ-B** (A); **3HP-A** and **3HP-B** (B).

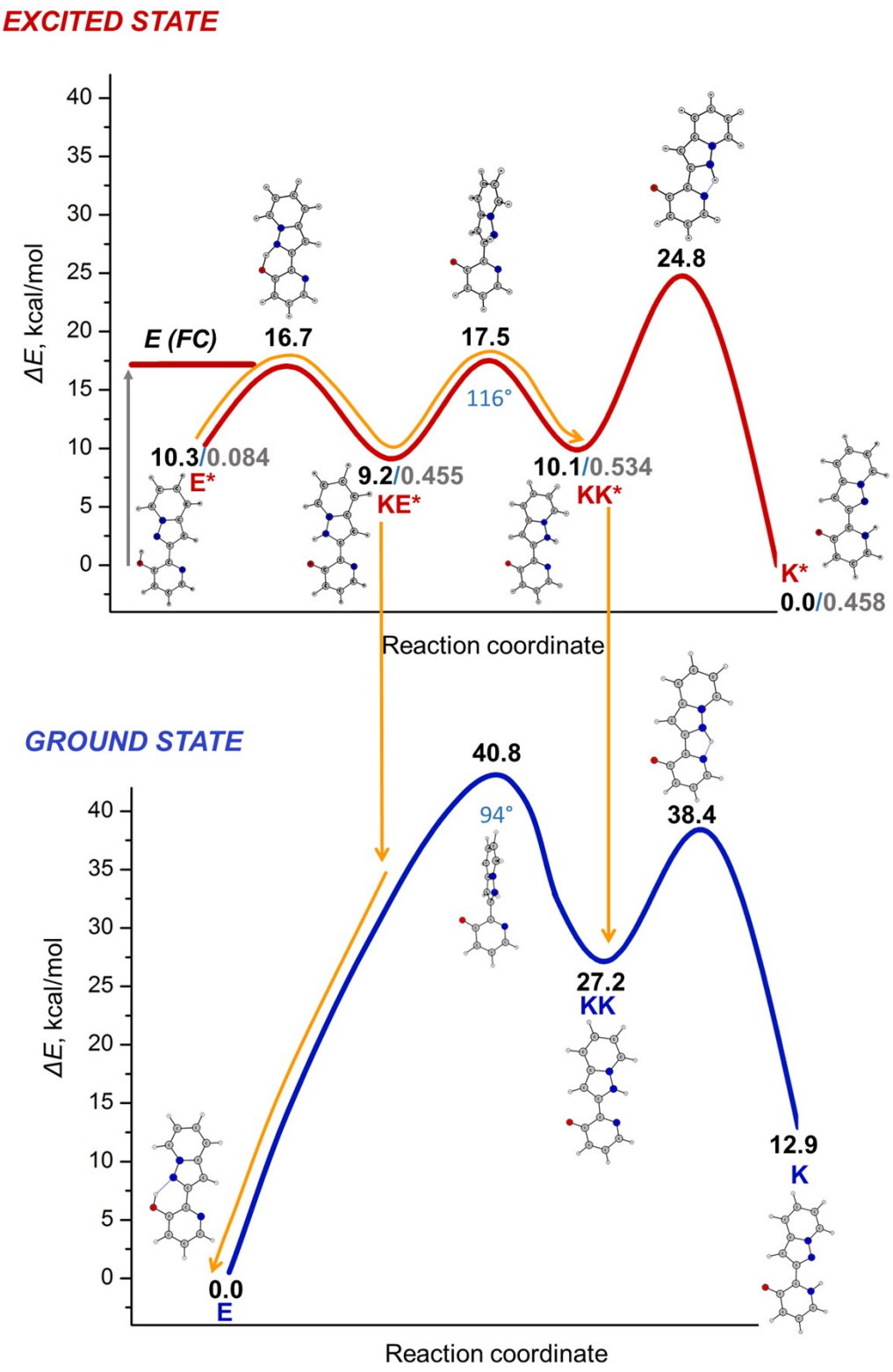

Figure S5. Ground (M06-2X/TZVP) and excited (CAM-B3LYP/TZVP) state PES of **3HP-B** in toluene. The orange arrows indicate the supposed PT pathways. Relative energies are given in kcal/mol units (black), followed by the dipole moment in D (grey).

Table S7. Relative energies and other electronic and structural parameters of **3HP-B** in ground (M06-2X/TZVP) and first singlet excited (CAM-B3LYP/TZVP) state in toluene and acetonitrile (in brackets).

Structure	ΔE	ΔE+ZPE	ΔG	μ	α	axle length	atomic charge		HOMO-LUMO gap
							O	N	
	[kcal/mol]			[D]	[°]	[Å]			eV
Ground state									
E	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	3.5 (4.0)	0 (0)	1.468 (1.469)	-0.673 (-0.683)	-0.349 (-0.355)	6.6 (6.6)
TS (E-KE)	( )	( )	( )	( )	( )	( )			
KE	( )	( )	( )	( )	( )	( )	( )	( )	( )
TS (KE-KK)	40.85 (30.61)	40.38 (30.38)	40.80 (30.92)	13.8 (15.5)	94 (93)	1.475 (1.479)			
KK	27.17 (20.78)	26.33 (20.15)	25.90 (19.92)	12.3 (14.8)	180 (180)	1.433 (1.445)	-0.720 (-0.771)	-0.323 (-0.314)	5.1 (5.5)
TS (KK-K)	38.40 (33.94)	35.11 (30.81)	34.78 (30.64)	10.7 (12.7)	180 (180)	1.451 (1.460)			
K	12.91 (9.66)	12.89 (9.86)	12.29 (9.43)	6.9 (8.4)	180 (180)	1.452 (1.454)	-0.694 (-0.744)	-0.334 (-0.334)	5.5 (5.6)
Excited state									
E*	10.29 (13.33)	9.51 (12.21)	9.81 (12.55)	3.5 (3.9)	0 (0)	1.448 (1.396)	-0.650 (-0.629)	-0.291 (-0.398)	6.3 (6.3)
TS (E*-KE*)	16.73 (17.38)	14.11 (14.59)	14.82 (15.30)	5.9 (6.7)	7 (5)	1.402 (1.395)			
KE*	9.15 (8.84)	9.36 (9.06)	9.66 (9.37)	10.1 (11.2)	21 (12)	1.429 (1.409)	-0.601 (-0.631)	-0.378 (-0.373)	5.3 (5.5)
TS (KE*-KK*)	17.50 (26.14)	17.23 (25.99)	17.65 (26.38)	14.1 (15.5)	116 (91)	1.463 (1.448)			
KK*	10.13 (9.33)	9.97 (9.42)	10.07 (9.43)	12.1 (13.7)	174 (177)	1.431 (1.410)	-0.572 (-0.605)	-0.371 (-0.373)	5.0 (5.3)
TS (KK*-K*)	24.78 (25.12)	22.15 (22.41)	22.67 (22.91)	9.9 (11.6)	180 (180)	1.414 (1.405)			
K*	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	7.0 (8.2)	180 (180)	1.411 (1.404)	-0.505 (-0.559)	-0.347 (-0.352)	5.4 (5.5)

Table S8. Relative energies of different IPT mechanisms for the conversion **E** to **K** in **7HQ-C** in ground (M06-2X/TZVP) and first singlet excited (CAM-B3LYP/TZVP) state in toluene.

Structure	ΔE	ΔE+ZPE	ΔG
	[kcal/mol]		
Path I			
Ground state			
E	0.00	0.00	0.00
TS (E-KE/KK)	5.63	3.22	3.46
KE/KK	3.91	3.86	3.86
TS (KE/KK -K)	10.17	7.44	7.68
K	6.23	6.06	5.56
Excited state			
E*	10.38	9.63	9.73
TS (E*-KE*/KK*)	14.30	10.78	10.90
KE*/KK*	8.98	8.16	7.94
TS (KE*/KK* -K*)	12.34	9.15	9.49
K*	0.00	0.00	0.00
Path II			
Ground state			
E	0.00	0.00	0.00
TS (E-ZW)	13.06	10.51	11.04
ZW	12.91	12.04	12.25
TS (ZW-K)	14.14	11.66	12.11
K	6.23	6.06	5.56
Excited state			
E*	10.38	9.63	9.73
TS (E*-ZW*)	13.81	10.68	11.16
ZW*	1.64	2.31	2.68
TS (ZW*-K*)	4.93	2.31	2.68
K*	0.00	0.00	0.00
Path III			
Ground state			
E	0.00	0.00	0.00
TS (E-KE)	5.63	3.22	3.46
KE	3.91	3.86	3.86
TS (KE-KK)	10.17	7.44	7.68
KK*	5.63	3.22	3.46
TS (KK*-K*)	3.91	3.86	3.86
K*	6.23	6.06	5.56
Excited state			
E*	10.38	9.63	9.73
TS (E*-KE*)	14.30	10.78	10.90
KE*	8.98	8.16	7.94
TS (KE*-KK*)	22.59	22.48	22.60
TS (KE*-KK*)	20.94	21.11	20.50
TS (KE*-KK*)	22.59	22.48	22.57
KK*	8.98	8.16	7.94
TS (KK*-K*)	12.34	9.15	9.49
K*	0.00	0.00	0.00

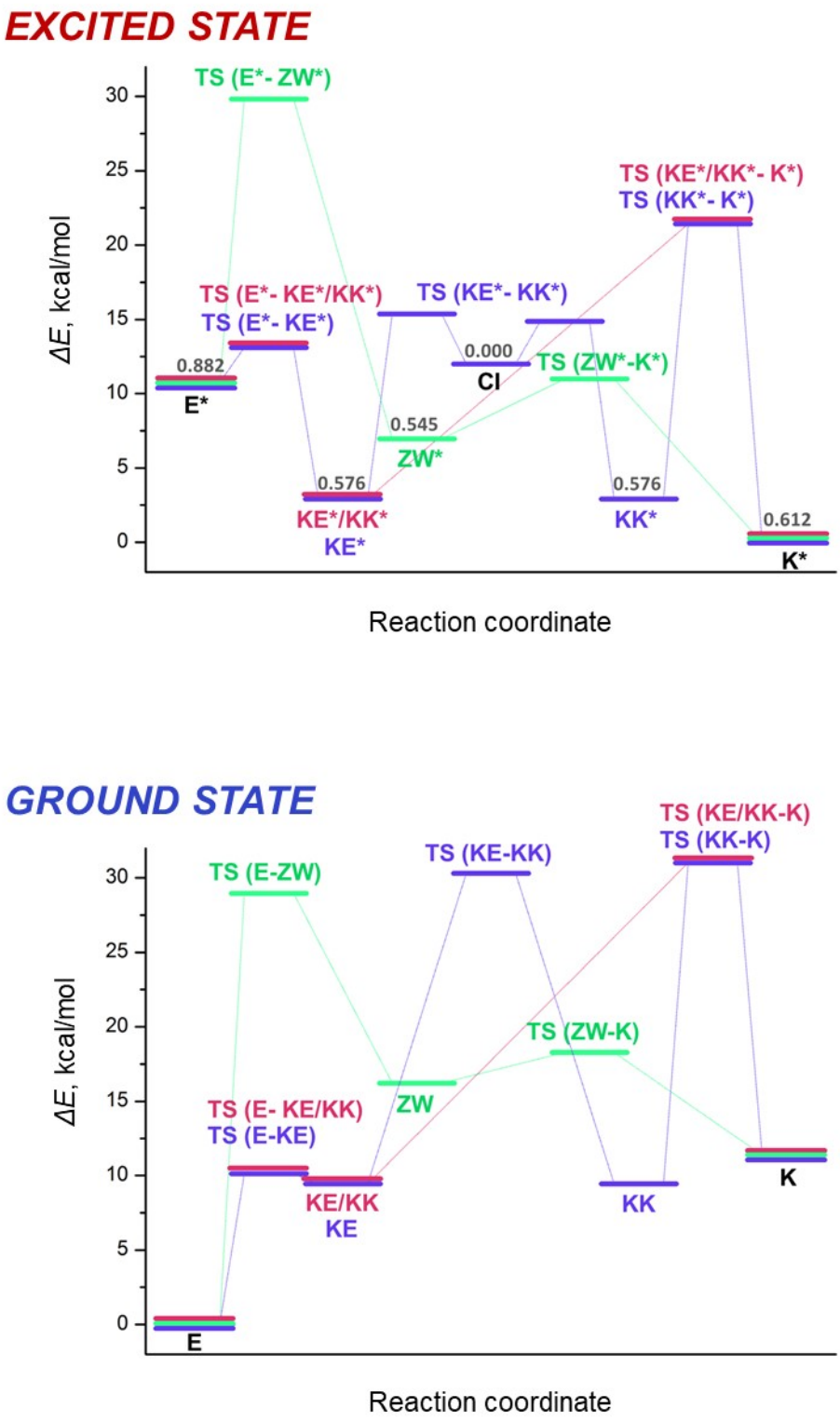

Figure S6. Alternative PESs of LRIPT of **3HP-C** in ground (M06-2X/TZVP) and first singlet excited (CAM-B3LYP) state in toluene. For the tautomeric forms in the excited state the oscillator strength is presented with gray color. The colors correspond to the colors from Scheme 5.

Table S9. Relative energies and other electronic and structural parameters of different IPT mechanisms for the conversion **E** to **K** in **3HP-C** in ground (M06-2X/TZVP) and first singlet excited (CAM-B3LYP/TZVP) state in toluene.

Structure	ΔE	ΔE+ZPE	ΔG
	[kcal/mol]		
Path I			
Ground state			
E	*0.00*	*0.00*	*0.00*
TS (E-KE/KK)	*10.12*	*7.76*	*8.13*
KE/KK	*9.44*	*9.07*	*9.09*
TS (KE/KK -K)	*31.01*	*27.98*	*27.97*
K	*11.38*	*11.47*	*11.28*
Excited state			
E*	*10.75*	*10.20*	*10.17*
TS (E*-KE*/KK*)	*13.11*	*9.79*	*9.32*
KE*/KK*	*2.91*	*2.61*	*2.28*
TS (KE*/KK* -K*)	*21.42*	*18.47*	*18.60*
K*	*0.00*	*0.00*	*0.00*
Path II			
Ground state			
E	*0.00*	*0.00*	*0.00*
TS (E-ZW)	*28.97*	*26.00*	*26.08*
ZW	*16.21*	*15.75*	*15.64*
TS (ZW-K)	*18.29*	*15.40*	*15.56*
K	*11.38*	*11.47*	*11.28*
Excited state			
E*	*10.75*	*10.20*	*10.17*
TS (E*-ZW*)	*29.82*	*26.73*	*26.60*
ZW*	*6.95*	*6.36*	*6.37*
TS (ZW*-K*)	*10.99*	*7.81*	*7.94*
K*	*0.00*	*0.00*	*0.00*
Path III			
Ground state			
E	*0.00*	*0.00*	*0.00*
TS (E-KE)	*10.12*	*7.76*	*8.13*
KE	*9.44*	*9.07*	*9.10*
TS (KE-KK)	*30.31*	*30.46*	*30.78*
KK*	*9.44*	*9.07*	*9.10*
TS (KK*-K*)	*31.01*	*27.98*	*27.97*
K*	*11.38*	*11.47*	*11.28*
Excited state			
E*	*10.75*	*10.20*	*10.17*
TS (E*-KE*)	*13.11*	*9.79*	*9.32*
KE*	*2.91*	*2.61*	*2.28*
TS (KE*-KK*)	*15.38*	*15.10*	*15.48*
TS (KE*-KK*)	*14.14*	*14.53*	*14.14*
TS (KE*-KK*)	*14.88*	*15.02*	*15.40*
KK*	*2.91*	*2.61*	*2.28*
TS (KK*-K*)	*21.42*	*18.47*	*18.60*
K*	*0.00*	*0.00*	*0.00*

Table S10. Relative energies and other electronic and structural parameters of **7HQ-A** in ground (M06-2X/TZVP) and first singlet excited (CAM-B3LYP/TZVP) state in toluene by using GD3 empirical dispersion correction.

Structure	ΔE	ΔE+ZPE	ΔG	μ	α	axle length
	[kcal/mol]			[D]	[°]	[Å]
Ground state						
E	0.00	0.00	0.00	4.2	0	1.467
TS (E-KE)						
KE						
TS (KE-KK)	26.96	27.46	27.93	12.0	90	1.459
KK	11.60	11.11	11.12	9.4	180	1.434
TS (KK-K)	13.92	10.86	11.03	8.2	180	1.441
K	7.98	8.23	8.24	6.7	180	1.458
Excited state						
E*	12.77	11.91	12.46	4.1	0	1.410
TS (E*-KE*)	16.38	12.71	13.55	5.5	0	1.408
KE*	11.17	10.05	10.27	8.3	0	1.423
TS (KE*-KK*)	21.13	20.28	20.59	12.3	92	1.458
KK*	9.87	8.79	9.24	9.1	180	1.422
TS (KK*-K*)	13.25	9.91	10.95	8.2	180	1.422
K*	0.00	0.00	0.00	7.3	180	1.430