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Supporting Information

Theoretical Study on the thermal *cis* - *trans* Isomerization of Azoheteroarene Photoswitches

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Table S1 Optimized geometry parameters for the *cis* forms of compounds **8** and **11**.

		Method							
		B3LYP	CAM-B3LYP	M06-2X	M06	PBE0	MP2	B3LYP [a]	Expt.
8-*cis*	$D_1(N_1N_2C_3C_4)$	180.0	180.0	180.0	180.0	180.0	173.8	180.0	169.2
	$D_2(C_6C_5N_1N_2)$	93.8	93.1	91.9	92.7	93.3	114.0	93.5	93.5
11-*cis*	$D_1(N_1N_2C_3C_4)$	151.2	147.7	148.7	151.0	151.5	143.6	152.9	154.3
	$D_2(C_6C_5N_1N_2)$	141.1	137.7	136.6	138.8	140.0	140.0	140.7	133.2

Note: Selected bond lengths in Å, bond angles and dihedral angles in ° of the stationary-point geometry that is involved in various functionals as calculated in comparison to the experimental data[1].

[a] taken from work of Fuchter.

Table S2 The absorption band energies of the *trans* and *cis* forms of compounds **8** and **11**.

	$n \rightarrow \pi^*$ / λ_{max} (nm)				$\pi \rightarrow \pi^*$ / λ_{max} (nm)			
	8-*cis*	**8**-*trans*	**11**-*cis*	**11**-*trans*	**8**-*cis*	**8**-*trans*	**11**-*cis*	**11**-*trans*
B3LYP	413.78	446.81	473.67	446.29	299.47	345.73	310.00	348.23
CAM-B3LYP	397.39	426.14	455.76	426.95	262.71	327.76	284.32	332.19
PBE0	407.50	444.43	467.24	446.22	288.68	341.73	300.44	345.17
M06-2X	431.62	465.16	494.89	464.82	262.88	321.83	284.75	327.69
M06	432.13	469.22	495.69	469.59	298.78	352.33	307.31	355.75
MP2	329.20	352.73	374.21	351.76	220.60	289.14	237.49	290.87
ωB97XD	395.90	430.98	454.62	431.76	261.80	325.81	284.34	330.65
LC-ωPBE	393.85	423.20	450.20	423.62	242.08	305.99	268.32	312.75
Expt.	403	417	441	425	275	328	296	335

Note: Calculated the absorption spectra in nanometers of the stationary-point geometries that are involved in various functionals as calculated in comparison to the experimental data[1].

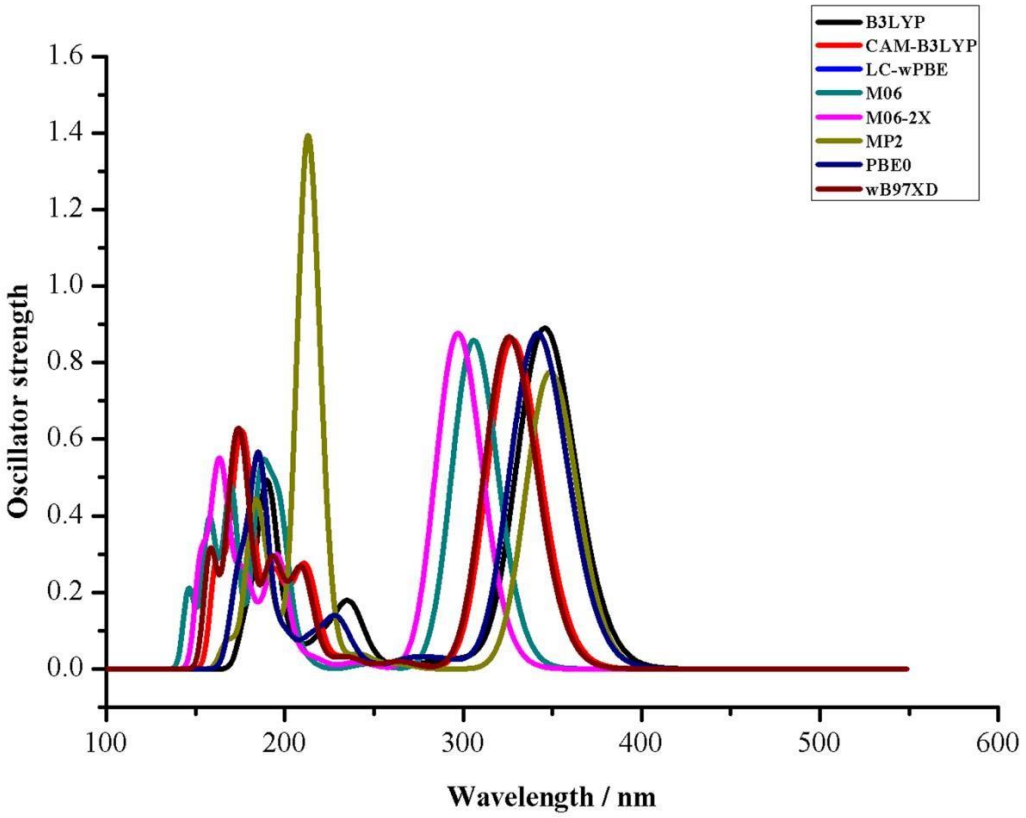
Table S3 The absorption band energies of the *trans* and *cis* forms of compounds **8** and **11**.

		CAM-B3LYP						
		6-31+G(d)	6-31+G(d,p)	6-311+G(d)	6-311+G(d,p)	6-311++G(d,p)[a]	6-311++G(2d,p)	Expt.
8-*cis*	**n → π* / λ_{max} (nm)**	394.7	394.7	397.2	397.1	397.4	395.5	403.0
	π → π* / λ_{max} (nm)	262.5	262.6	262.5	262.0	262.7	262.6	275.0
8-*trans*	**n → π* / λ_{max} (nm)**	423.1	423.6	425.2	426.2	426.1	424.4	417.0
	π → π* / λ_{max} (nm)	326.3	326.7	327.4	327.7	327.8	328.5	328.0
11-*cis*	**n → π* / λ_{max} (nm)**	452.4	452.6	455.5	455.8	455.8	453.8	441.0
	π → π* / λ_{max} (nm)	283.0	283.4	284.0	284.0	284.3	284.8	296.0
11-*trans*	**n → π* / λ_{max} (nm)**	419.2	419.5	422.3	422.0	422.8	421.1	425.0
	π → π* / λ_{max} (nm)	325.4	325.9	326.7	326.1	327.1	327.9	335.0

Note: Calculated the absorption spectra in nanometers of the stationary-point geometries that are involved in various basis sets as calculated in comparison to the experimental data[1].

[a] taken from this work.

Fig. S1 Simulated absorption spectra of the *trans* isomer of compound **2** based on the various functionals.



References:

1 C. E. Weston, R. D. Richardson, P. R. Haycock, A. J. P. White and M. J. Fuchter, *J. Am. Chem. Soc.*, 2014, **136**, 11878-11881.