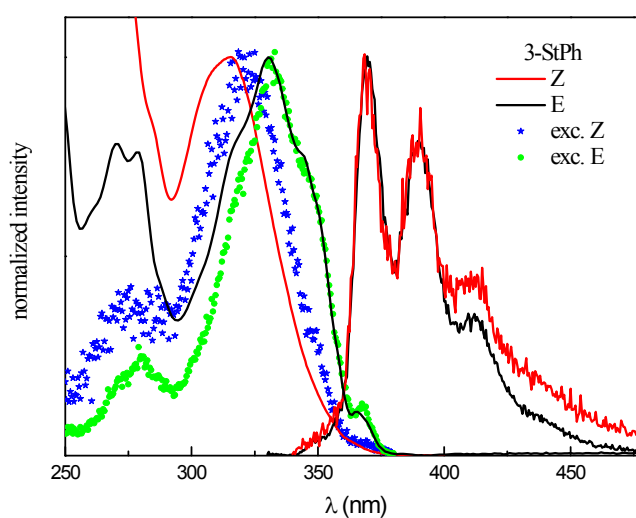
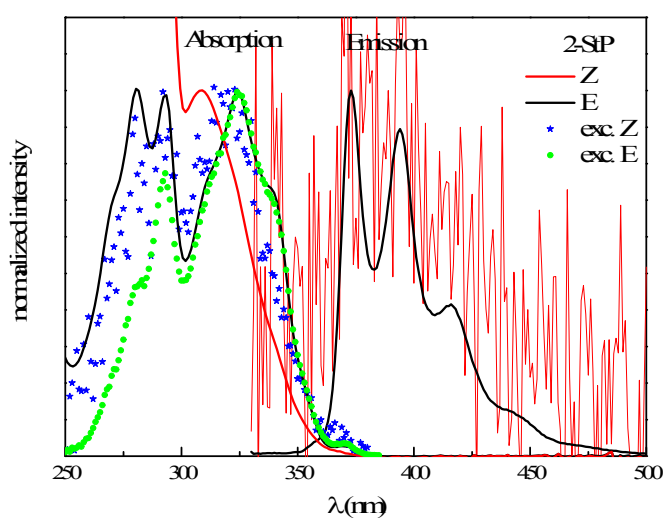


SUPPORTING INFORMATION

Effect of the size of polycyclic aryl groups on the competition between adiabatic/diabatic photoisomerization mechanisms of *cis*-styrylarenes

A. Cesaretti, B. Carlotti,* F. Elisei and A. Spalletti

Department of Chemistry, Biology and Biotechnology and Centro di Eccellenza sui Materiali Innovativi Nanostrutturati (CEMIN), University of Perugia, via Elce di Sotto 8, 06123 Perugia, Italy.



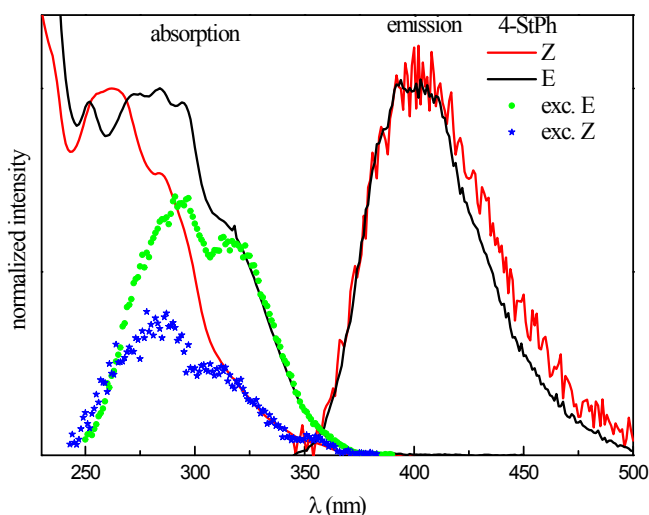


Figure 1S. Normalized absorption, fluorescence excitation and emission spectra obtained by exciting Z and E isomers of *n*-StP (with *n* = 2, 3 and 4) in MCH/3MP at room temperature.

Table 1S. Calculated total energy (E) (ab-initio basis set 3-21G) and electronic spectra (transition energy, λ and oscillator strength, f , ZINDO/S) for the two rotamers of Z isomers of the investigated compounds.^aThe data in parentheses refers to the calculations performed with a larger basis set (6-31G*, present work).

compound	rotamer	R(C-C') (\AA)	E (kcal/mol)	% (293K)	λ (nm)	f (20x20)	
Stilbene		3.30	-335177.53		279	0.079	S ₁
					270	0.44	S ₃
1-StN	s-cis	3.42	-430430.34 (-432845.59)	83 (91)	312	0.025	S ₁
					291	0.39	S ₂
	s-trans	3.77	-430429.41 (-432844.25)	17 (9)	232	0.66	S ₆
					310	0.014	S ₁
2-StN	s-cis	3.31	-430431.25 (-432846.84)	42 (43)	280	0.32	S ₂
					223	1.02	S ₈
					317	0.008	S ₁
	s-trans	3.26	-430431.44 (-432847.00)	58 (57)	292	0.31	S ₂
					260	0.59	S ₄
					317	0.005	S ₁
1-StP	s-cis	3.41	-525685.94	86	283	0.63	S ₂
					262	0.41	S ₄
					329	0.011	S ₁
	s-trans	3.81	-525684.88	14	294	0.54	S ₂
					250	1.32	S ₆
					328	0.008	S ₁
2-StP	s-cis	3.31	-525687.25	48	288	0.32	S ₂
					248	0.68	S ₆
					332	0.002	S ₁
	s-trans	3.28	-525687.30	52	291	0.35	S ₂
					276	0.57	S ₃
					333	0.002	S ₁
3-StP	s-cis	3.31	-525687.38	56	290	0.41	S ₂
					276	0.56	S ₃
					331	0.005	S ₁

					301	0.46	S ₂
					243	0.95	S ₇
	s-trans	3.30	-525687.25	44	331	0.007	S ₁
					298	0.76	S ₂
					247	1.11	S ₆
4-StP	s-cis	3.39	-525681.56	100	333	0.01	S ₁
					293	0.23	S ₂
					279	0.42	S ₃
					254	0.80	S ₆
	s-trans		-525567.19	0	315	0.03	S ₁
					271	0.08	S ₂
					267	0.41	S ₃
9-StPh	s-cis	3.46	-525686.13	85	329	0.009	S ₁
					298	0.34	S ₂
					249	1.09	S ₆
	s-trans	3.80	-525685.13	15	327	0.008	S ₁
					288	0.31	S ₂
					247	1.34	S ₇
					264	0.83	S ₃
3-StCr	s-cis	3.35	-620940.88	66	343	0.003	S ₁
					313	0.44	S ₂
					276	0.78	S ₄
	s-trans	3.31	-620940.50	34	344	0.002	S ₁
					311	0.75	S ₂
					276	1.18	S ₄
3-StBPh	s-cis	3.30	-620933.69	35	353	0.01	S ₁
					314	0.29	S ₂
					286	1.35	S ₄
	s-trans	3.26	-620934.06	65	353	0.004	S ₁
					312	0.35	S ₂
					288	1.02	S ₄

^a from ref. 48.

Table 2S. Experimental parameters for the fluorescence decay obtained by exciting Z-2StN in MCH/3MP at different temperatures ($\lambda_{exc} = 316$ nm).

T (K)	τ_1 (ns)	% 1	τ_2 (ns)	% 2	χ^2
293	0.17	6	21.5	94	1.04
253	0.34	22	22.3	78	1.06
203	0.40	64	19.8	36	1.07
153	0.59	94	17.1	6	1.07
133	1.4	89	4.6	11	1.13
123	1.7	47	3.5	53	1.06
77	2.8	68	5.3	32	1.08