Electronic supplementary information

Visible-Light-Driven Two-Way Photoisomerization of 1-(1-Pyrenyl)-2-(2-quinolyl)ethylene in Neutral and Protonated Forms

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Synthetic details

^{1}H NMR spectra were recorded on Bruker Avance III spectrometer (500 MHz) with $CDCl_3$ as a solvent and tetramethylsilane as an internal standard. IR spectra were performed using Spectrum BX-2 Fourier spectrometer. The elemental analysis was measured with Elementar vario MICRO cube analyzer. Melting point was determined on a Koffler hot stage apparatus with a heating rate of 4°C/min. Microwave-assisted reaction was carried out in a DAEWOO-KOR-4115SA microwave oven (600 W, 2450 MHz).

(*E*)-2-(2-Pyren-1-yl-vinyl)quinoline (1P2QE)

A mixture of 198 mg (1.38 mmol) of quinaldine, 350 mg (1.52 mmol) of 1-pyrenecarboxaldexyde and 94 mg (0.69 mmol) of zinc chloride in the glass test tube was placed into a 100-ml beaker containing 15–20 ml of water and subjected to MW irradiation at a power of 600 W in 5 periods of 4-min with 30-s intervals (overall irradiation time 20 min). The mixture was cooled and treated with a 5% solution of potassium hydroxide. The solid residue was collected by filtration and dissolved in 50 ml of toluene – hexane (4:1) boiling mixture, than, 0.5 ml of concentrated hydrochloric acid was added. After cooling, the precipitate was filtered off, treated with the solution of sodium hydrocarbonate in water – acetone, dried and, finally, recrystallized from the mixture of hexane and toluene (2:1) to afford 285 mg (yield 58 %) of **1P2QE** as yellow crystalline powder with mp 132-134 ^{o}C (mp 136 ^{o}C according to [S1]). ^{1}H NMR (500 MHz, $CDCl_3$, RT): δ 7.53 (ddd, *J* = 1.1, 6.9, 8.0 Hz, 1H, Het), 7.67 (d, *J* = 16.0 Hz, 1H, =CH-Het), 7.75 (ddd, *J* = 1.4, 6.9, 8.4 Hz, 1H, Het), 7.81-7.85 (m, 2H, Het), 8.02 (t, *J* = 7.6 Hz, 1H, Ar), 8.06-8.11 (m, 2H, Ar), 8.15-8.23 (m, 6H, Ar, Het), 8.47 (d, *J* = 8.1 Hz, 1H, Ar), 8.63 (d, *J* = 9.3 Hz, 1H, Ar), 8.85 (d, *J* = 16.0 Hz, 1H, =CH-Ar); ^{13}C NMR (125 MHz, $CDCl_3$, RT): δ 119.3, 122.6, 123.5, 124.5, 124.7, 124.8, 124.9, 125.1, 125.7, 125.8, 127.0, 127.1, 127.3, 127.5, 128.6, 128.9, 129.4, 130.4 (2C), 130.7, 131.0, 131.1 (2C), 135.9, 147.8, 155.5; IR (neat): 3050, 3042 (ν_{CH}), 1628 ($\nu_{C=C}$), 1611, 1588, 1550, 1502, 1462, 1437, 1424, 1372, 1317, 1305, 1279, 1240, 1211, 1195, 1187, 1174, 1140, 1121, 1108, 965 ($\delta_{CH=CH}$), 958, 866, 840, 811, 818, 784, 768, 751, 715, 682. Elemental analysis calcd (%) for $C_{27}H_{17}N$: C 91.24, H 4.82, N 3.94; found: C 90.95, H 4.98, N 3.76.

[S1]. G. Drefahl, K. Ponsold, E. Gerlach, *Chem. Ber.*, 1960, **93**, 481-485.

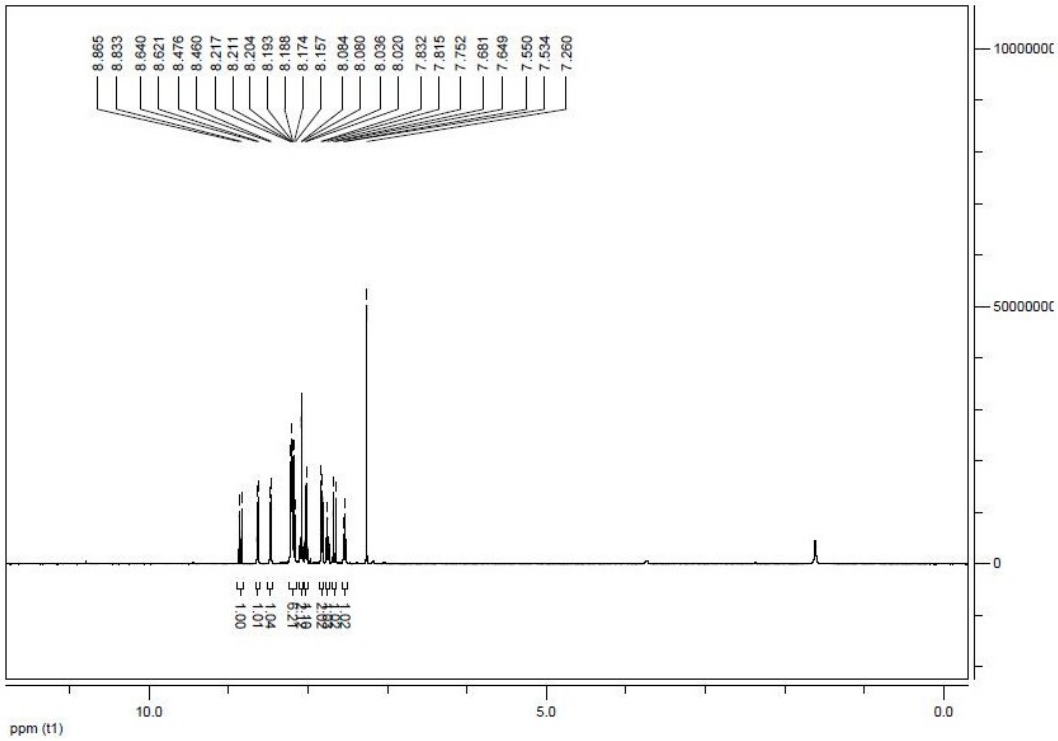


Figure S1. ^{1}H NMR spectrum of 1P2QE in chloroform-d.

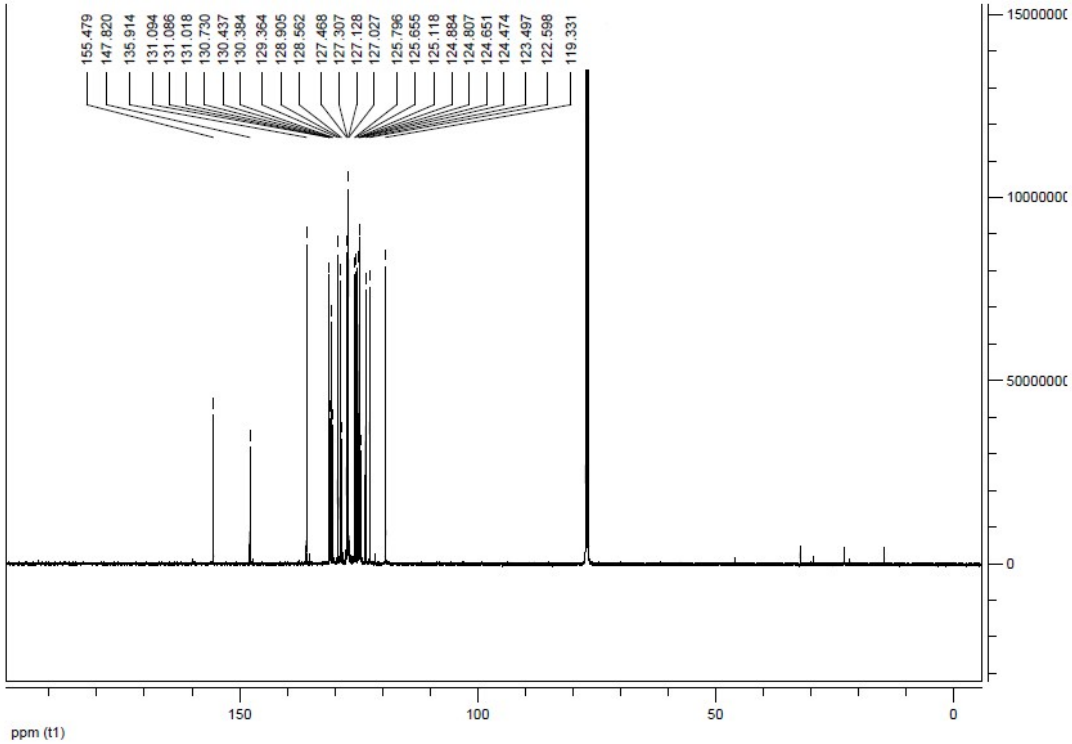


Figure S2. ^{13}C NMR spectrum of 1P2QE in chloroform-d.

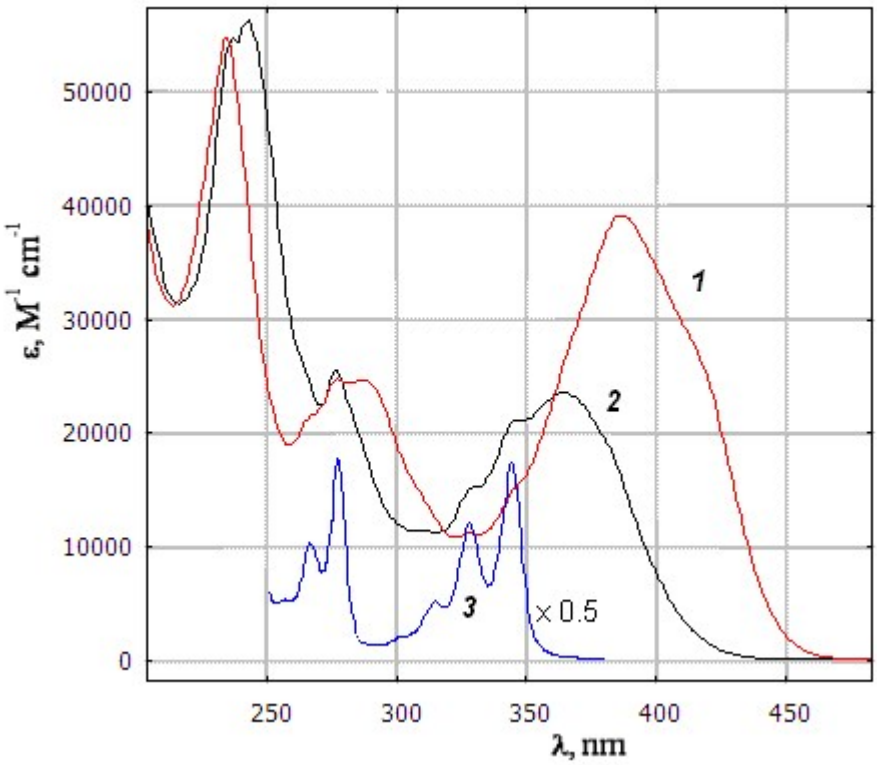


Fig. S3. Absorption spectra of *E*-1P2QE (*1*), *Z*-1P2QE (*2*) and 1-carboxyethylpyrene (*3*) [T. Mizushima, A. Yoshida, A. Harada, Y. Yoneda, T. Minatani, S. Murata, *Org. Biomol. Chem.*, 2006, **4**, 4336].

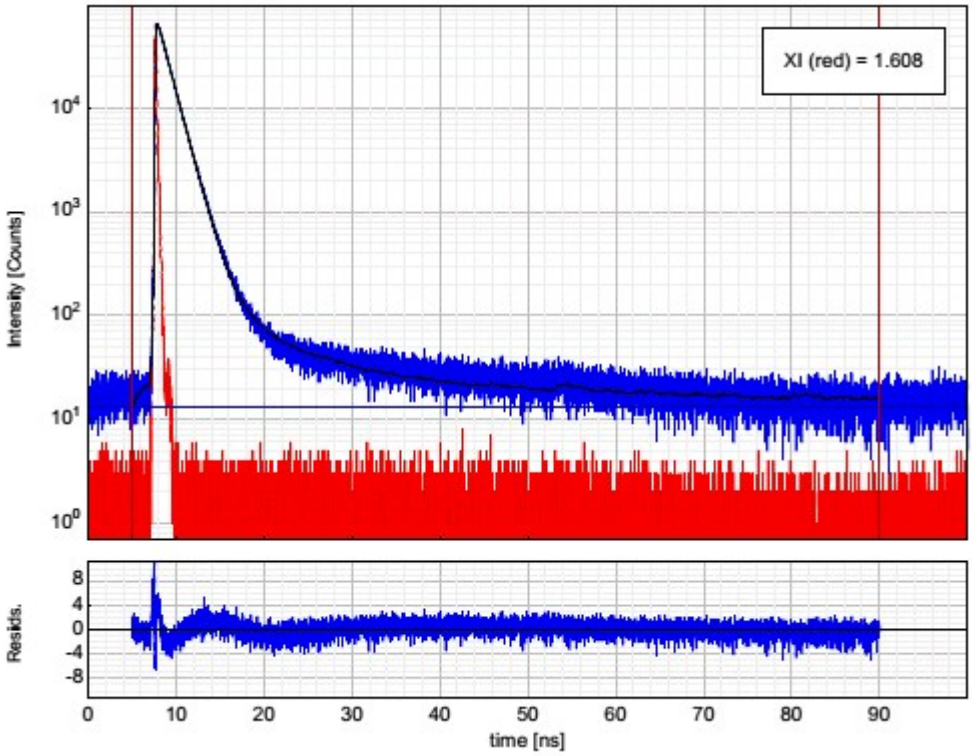


Fig. S4. Fluorescence decay profile of *E*-1P2QE in ethanol at room temperature: λ_{ex} = 400 nm, λ_{em} = 475 nm, the excitation function is also shown. The distribution of weighted residuals is shown in the bottom panel. The black solid line is calculated with the double-exponential function.

A1 = 11556.6 + 65.8 - 65.8 Cnts
t1 = 1.33331 + 0.00560 - 0.00560 ns
A2 = 35.44 + 3.66 - 3.66 Cnts
t2 = 7.202 + 0.392 - 0.392 ns
Bkgr. Dec = 12.89 + 1.03 - 1.03 Cnts
Bkgr. IRF = 0.318 + 0.116 - 0.116 Cnts
Shift IRF = -0.00385 + 0.00196 - 0.00196 ns
A Scat = 18000 + 15600 - 15600 Cnts
Period Rep = 0.00883 + 0.00326 - 0.00326 ns
Average Lifetime: tAv.1=1.42896 ns (intensity weighted) tAv.2=1.35125 ns (amplitude weighted)
Fractional Intensities of the Positive Decay Components: t1 (1.33331 ns): 98.37% t2 (7.202 ns): 1.63%
Fractional Amplitudes of the Positive Decay Components: τ_1 (1.33331 ns): 99.69% τ_2 (7.202 ns): 0.31%

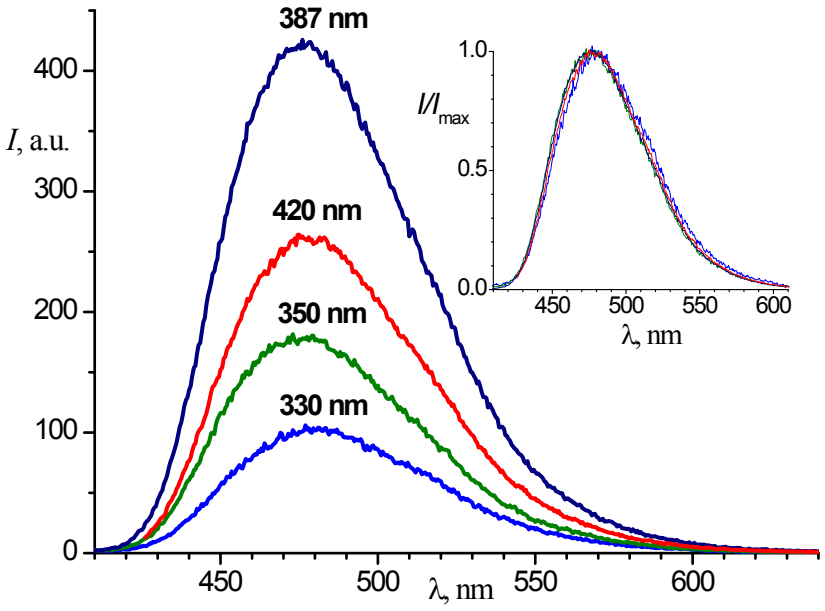


Fig. S5. Fluorescence spectrum of *E*-1P2QE in dependence on excitation wavelength. Insert: normalized fluorescence spectra.

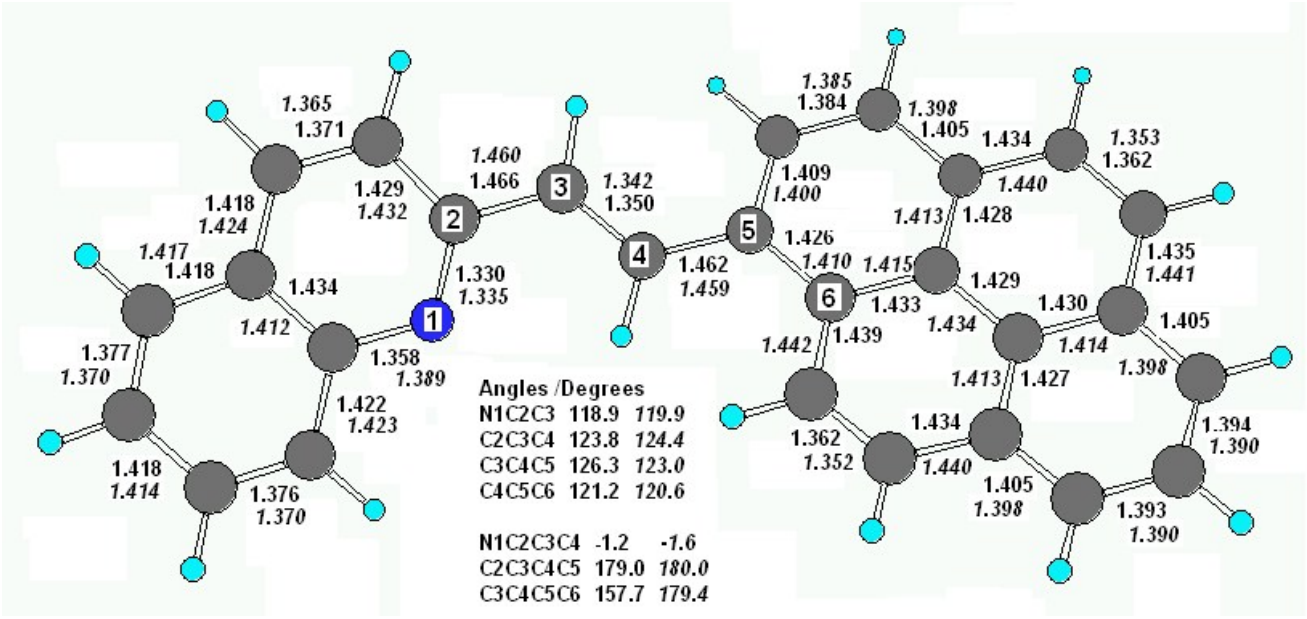


Fig. S6. Calculated optimized parameters for the *E*-1P2QE *s-cis* conformer in the S_0 state, bond length (Å), valence and dihedral angles, B3LYP/6-31G* and *PM3* (italics) data.

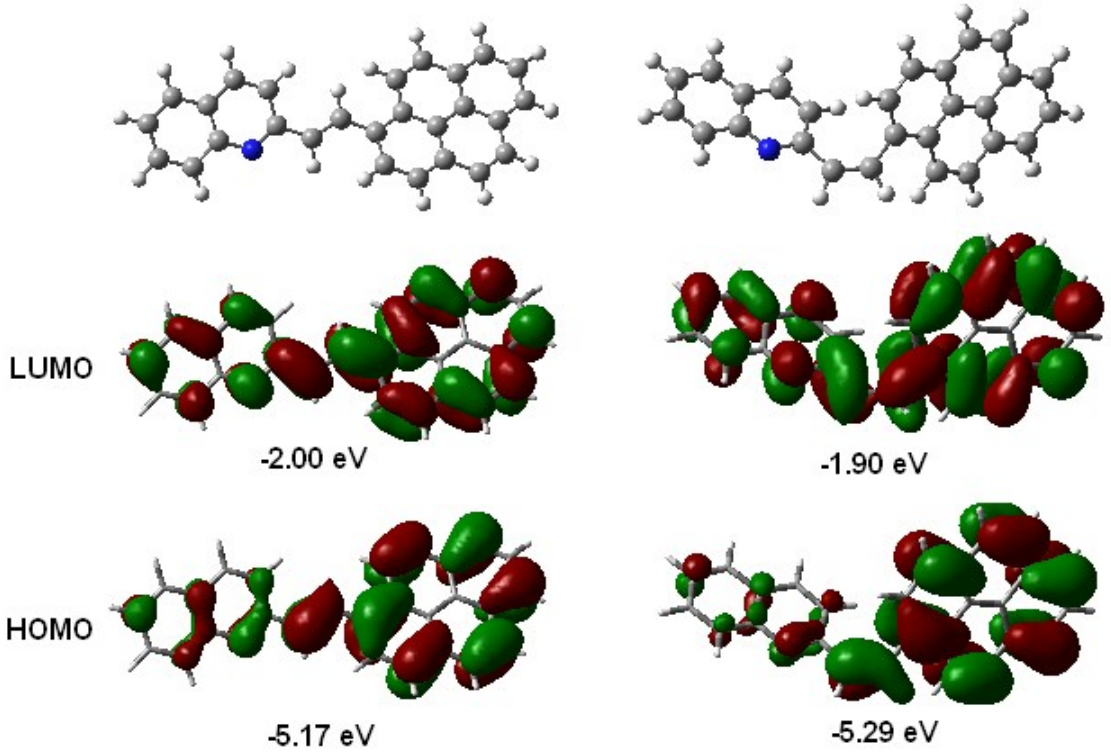


Fig. S7. Structure and energy of the frontier molecular orbitals for the *s-trans* conformer of *E*-1P2QE (left) and *Z*-1P2QE (right) calculated at B3LYP/6-31G* level.

Table S1. Absorption spectra of the *E*-1P2QE conformers, calculated by TD B3LYP/6-31G* (20 states, Solvent=Ethanol): transitions, energies, wavelengths and oscillator strengths.

Conformer	Excitation	$E_{calc.}$(eV)	$\lambda_{calc.}$ (nm)	*f*
s-cis	S_1 HOMO→ LUMO (98 %)	2.78	446.3	1.0832
	S_2 HOMO-1→ LUMO (44 %) HOMO→ LUMO+1 (41 %)	3.37	367.5	0.1242
	S_4 HOMO-2→ LUMO (38 %) HOMO-1→ LUMO (36 %)	3.73	332.2	0.1362
	S_5 HOMO-3→ LUMO (60 %)	3.85	322.4	0.1192
	S_7 HOMO→ LUMO+2 (52%)	4.02	308.3	0.1856
s-trans	S_1 HOMO→ LUMO (98 %)	2.87	432.3	1.2966
	S_2 HOMO-1→ LUMO (43 %) HOMO→ LUMO+1 (35 %)	3.43	361.7	0.1007
	S_6 HOMO→ LUMO+2 (54%)	4.01	309.2	0.3146

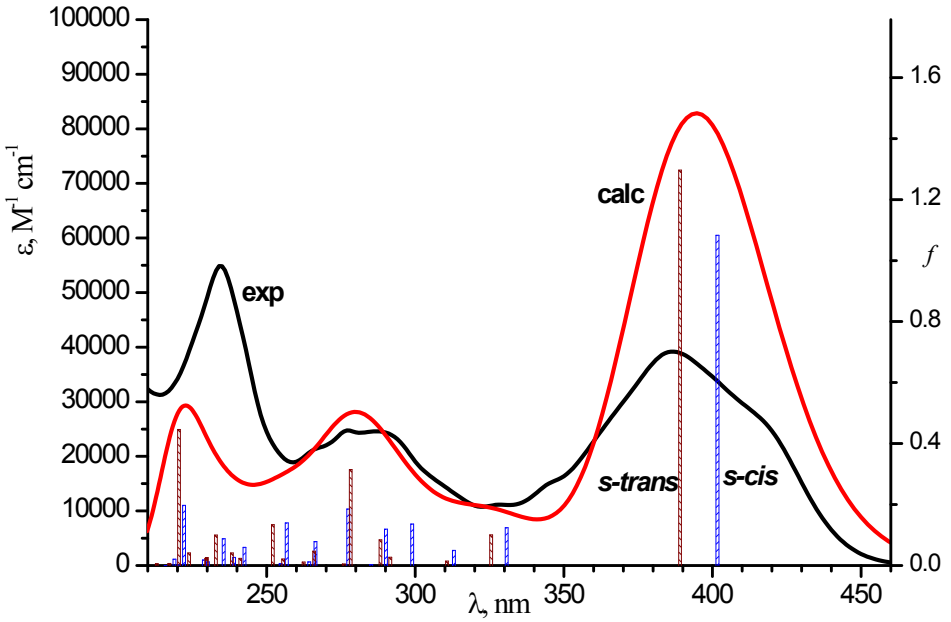


Fig. S8. Absorption spectra of the *E*-1P2QE in ethanol, experimental (black line) and calculated by TD DFT (sticks and red line) at B3LYP/6-31G* level as a 1:1 mixture of two conformers, a scaling factor of 0.9 was used.

Theoretical spectra were obtained by convoluting the calculated transition energies and oscillator strengths of the different electronic transitions with Gaussian functions with full width at half maximum of 3000 cm^{-1}.

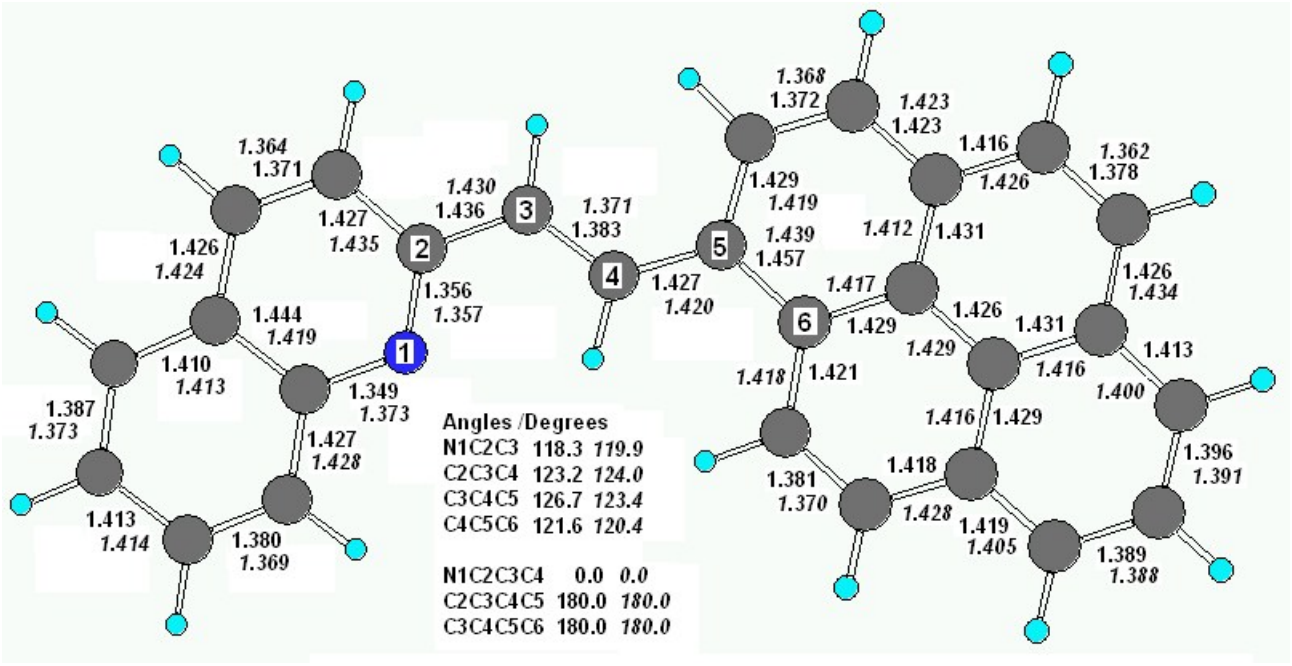


Fig. S9. Calculated optimized parameters for the *E*-1P2QE *s-cis* conformer in the S_1 state, bond length (Å), valence and dihedral angles, TD B3LYP/6-31G* and *PM3-CI(2×2)* (italics) data.

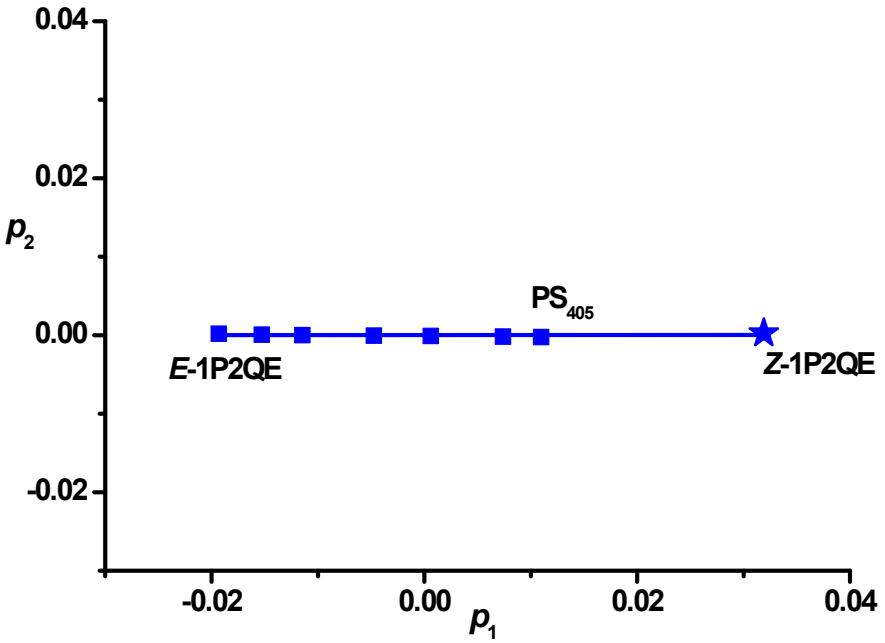


Fig. S10. Principal component analysis (score plot) of the spectral changes during photolysis of the *E*-1P2QE, data from Fig. 3; experimental spectra are given in the basis of two first singular vectors. Asterisk shows the spectrum of the *Z*-MSBQ (calculated by Fischer's method), which was added to the total spectral matrix.

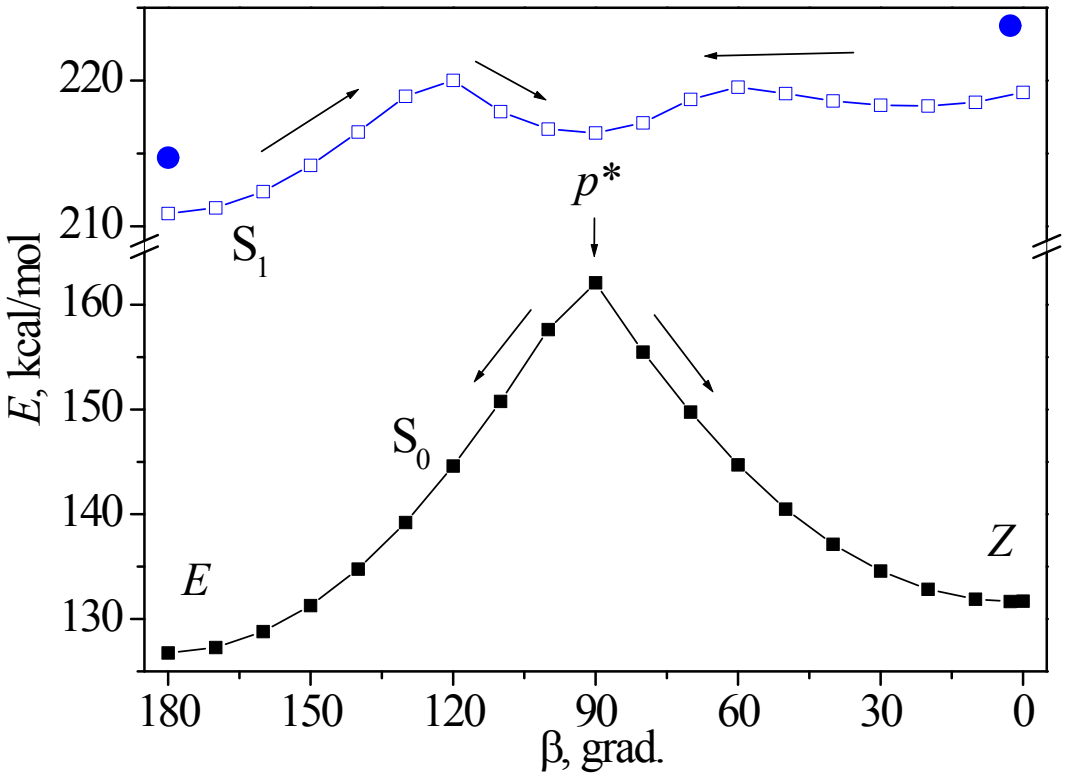
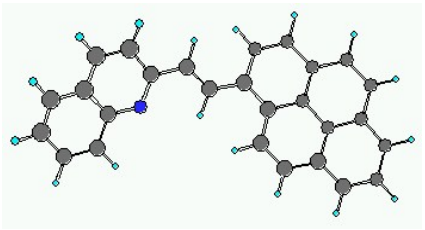


Fig. S11. Minimal energy paths of the isomerization reaction of the 1P2QE *s-trans*-conformer in the S_0 state (calculated by the PM3 method) and in the S_1 state (calculated by the PM3-CI(2×2) method); the arrows show the diabatic reaction path. The filled circles mark the location of the terms of the vertically excited isomers.

Calculated optimized structures, B3LYP/6-31G* data.

s-cis E-1-(1-pyrenyl)-2-(2-quinolyl)ethylene (1P2QE), S_0, Total Energy HF=-1093.9178331 a.u. (1 a.u.= 627.5094709 kcal/mol = 27.2113834 eV)



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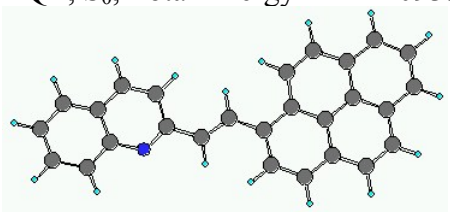
s-trans E-1P2QE, S_0, Total Energy HF= -1093.9162677 a.u.



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6	4.330104	-0.286074	0.072964
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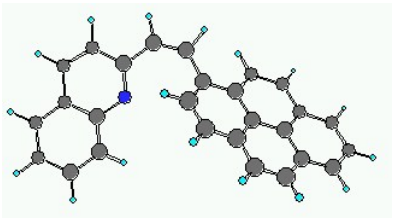
s-cis Z-1P2QE, S_0, Total Energy HF=-1093.9077973 a.u.



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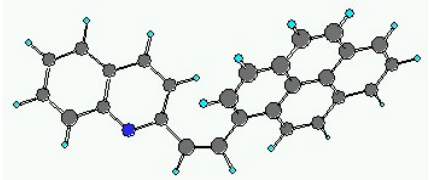
s-trans Z-1P2QE, S_0, Total Energy HF=-1093.9095896 a.u.



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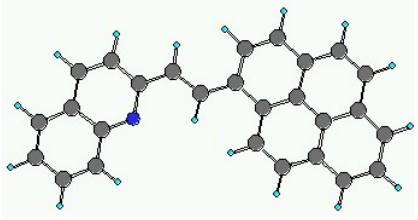
1	-0.067683	-2.785695	1.579216
1	-1.286741	0.122837	-0.840605
1	-2.964640	1.623758	-1.880962
1	0.622986	2.545211	1.982235
1	-0.925178	0.627226	2.046443
1	-6.591501	-1.384939	1.040693
1	1.420228	-2.971875	-0.145028
1	-8.374423	0.064387	0.070787
1	-7.773429	1.902463	-1.494760
1	-5.404878	2.302096	-2.098829
1	3.648410	-3.223412	-1.120511
1	2.823552	3.515990	1.368935
1	5.863877	-2.260396	-1.705675
1	5.059910	3.259749	0.368306
1	7.425722	-0.335196	-1.738036
1	6.747366	1.843496	-0.771645

s-cis E-1P2QE, S_i, Total Energy E(TD-HF/TD-KS) = -1093.81777933 a.u



Atomic Number	Coordinates (Angstroms) X	Y	Z
7	-3.458009	0.197172	-0.000068
6	-3.221776	-1.137829	0.000060
6	-1.857694	-1.587733	0.000026
6	-0.776168	-0.725472	-0.000124
6	0.604183	-1.088296	-0.000204
6	-4.281315	-2.093888	0.000246
6	-5.585861	-1.671496	0.000288
6	-5.868825	-0.273355	0.000150
6	-4.737632	0.623753	-0.000027
6	1.657321	-0.081093	-0.000165
6	3.029195	-0.481092	-0.000071
6	3.382664	-1.867853	-0.000079
6	2.334224	-2.830129	-0.000220
6	1.013627	-2.457088	-0.000288
6	-4.993031	2.028051	-0.000179
6	1.376429	1.311343	-0.000212
6	4.068372	0.495910	0.000022
6	-6.284628	2.512789	-0.000147
6	-7.386250	1.628130	0.000037
6	-7.175027	0.257446	0.000182
6	2.378708	2.261350	-0.000135
6	3.746831	1.888136	-0.000001
6	4.748311	-2.243036	0.000030
6	5.441600	0.092106	0.000135
6	4.793602	2.846324	0.000104
6	5.752043	-1.299260	0.000140
6	6.122269	2.443120	0.000223
6	6.447115	1.084970	0.000237
1	-1.712564	-2.665340	0.000143
1	-1.047569	0.323398	-0.000160
1	-4.039199	-3.153976	0.000348
1	-6.407390	-2.383961	0.000420
1	2.597934	-3.885260	-0.000282
1	0.254114	-3.230772	-0.000420
1	-4.133903	2.692225	-0.000319
1	0.348441	1.652869	-0.000330
1	-6.459712	3.585897	-0.000263
1	-8.398468	2.023359	0.000064
1	-8.019884	-0.428406	0.000321
1	2.120456	3.317213	-0.000180
1	4.996896	-3.301737	0.000021
1	4.538549	3.902956	0.000091
1	6.794831	-1.605282	0.000229
1	6.914553	3.186429	0.000305
1	7.489259	0.775341	0.000326