Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information for

The Doorstop Proton: Acid-controlled Photoisomerization in Pyridine-Based Azo Dyes

Shea M. Martin, Zachary J. Knepp, Ing Angsara Thongchai, Kiera Englehart, Keyri Sorto, Athina Jaffer, Lisa A. Fredin*, Elizabeth R. Young*

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Additional Experimental Data

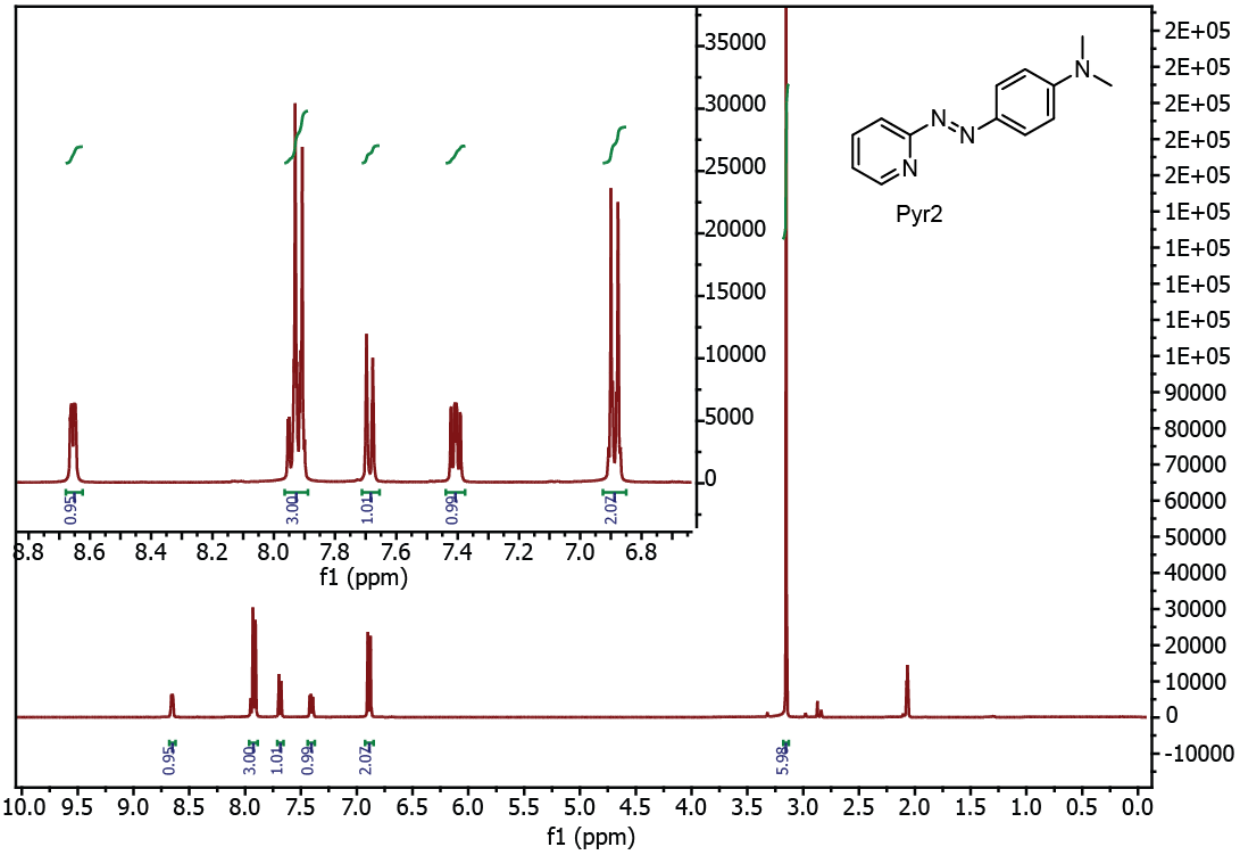


Figure S1. ^{1}H NMR spectrum of **Pyr2** collected on a 400 MHz NMR.

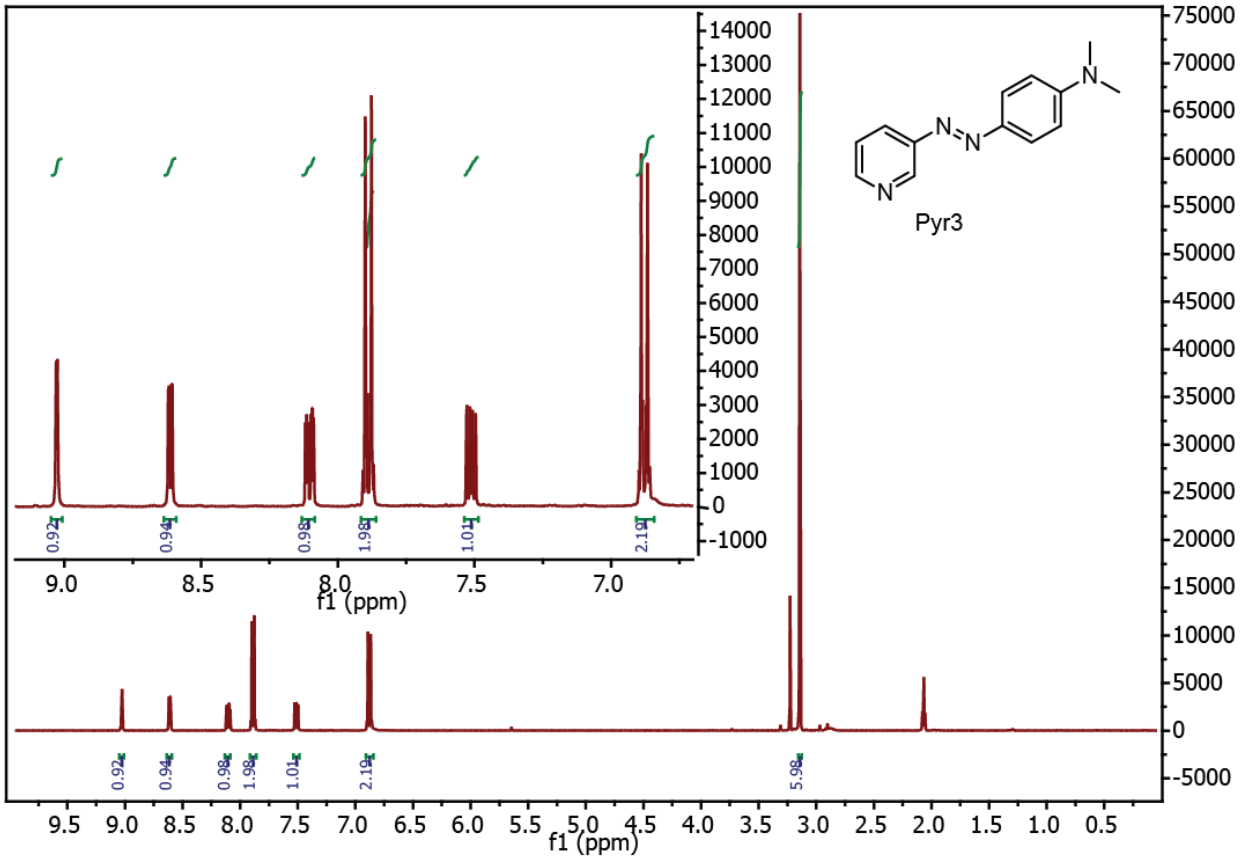


Figure S2. NMR spectrum of **Pyr3**.

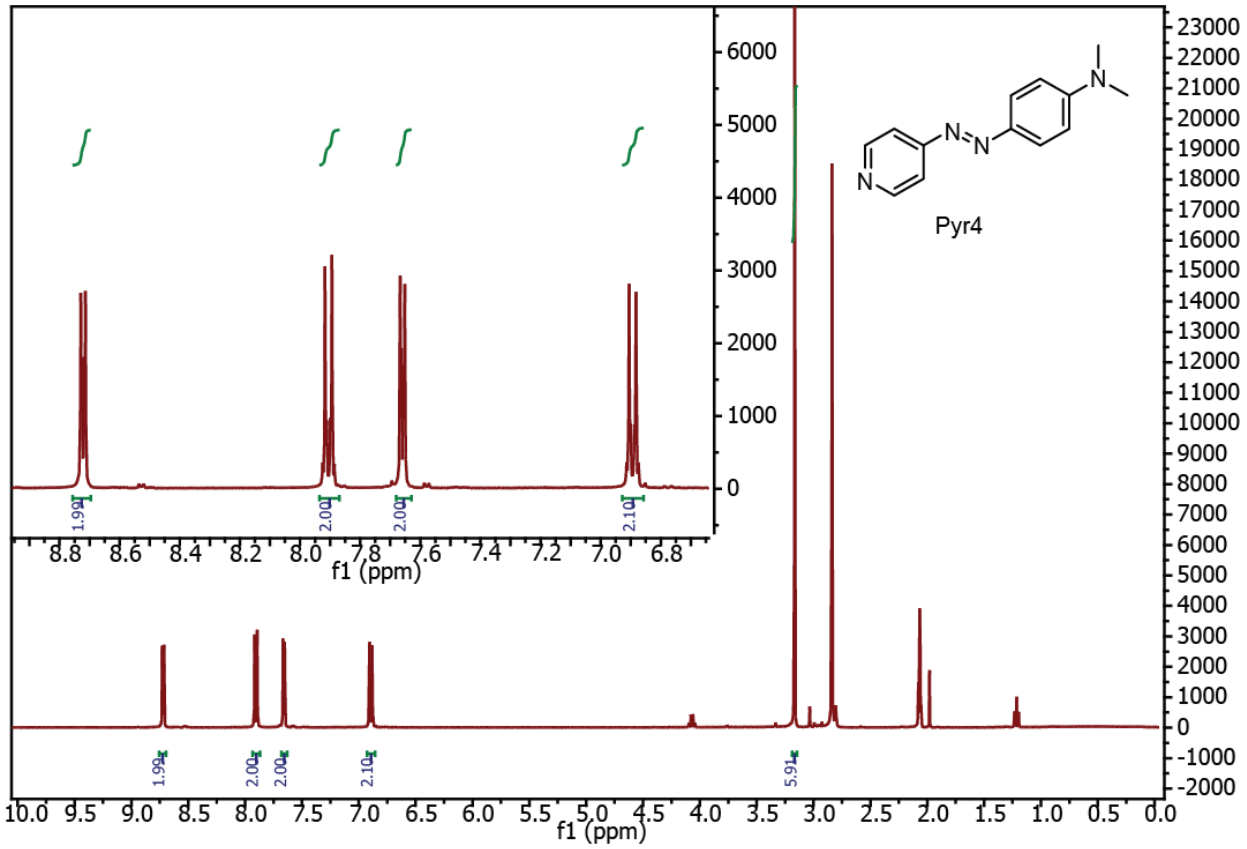


Figure S3. NMR spectrum of **Pyr4**.

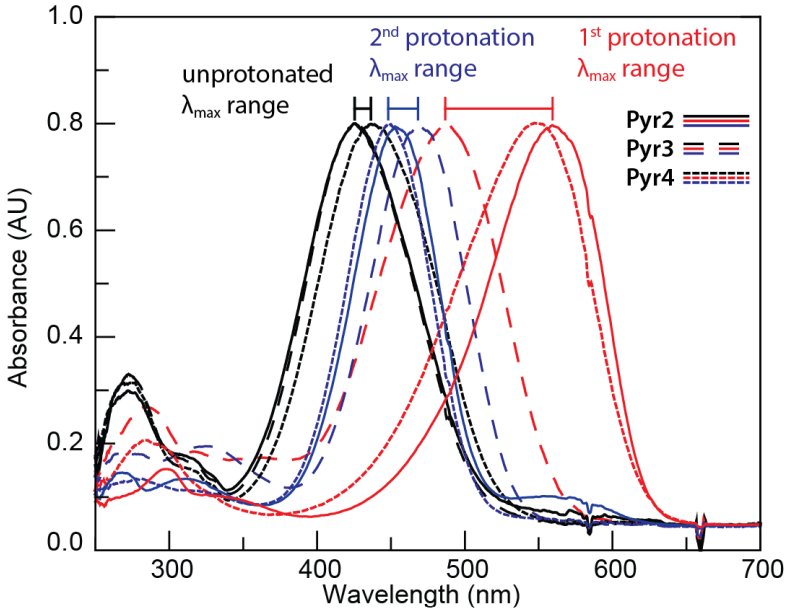


Figure S4. Overlaid absorption spectra of unprotonated (black), singly protonated (red) and doubly protonated (blue) **Pyr2** (solid lines), **Pyr3** (long dashed lines), and **Pyr4** (short dashed lines) highlighting the relative blueshifting of the λ_{max} of **Pyr3-H** compared to **Pyr2-H** and **Pyr4-H**.

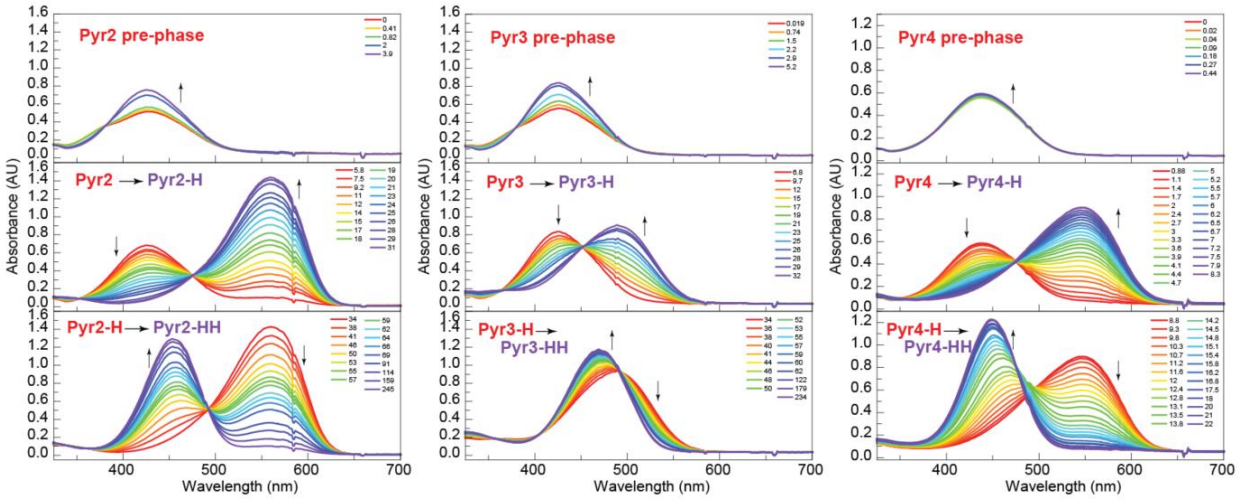


Figure S5. Titration data for **Pyr2**, **Pyr3**, and **Pyr4** separated out by pre-phase, first protonation phase, and second protonation phase.

For **Pyr2**, the pre-protonation phase occurs from 0 – 4 mol eq HBF_4, the first protonation phase occurs over 4 – 31 mol eq HBF_4, and the second protonation phase occurs over 35 – 245 mol eq HBF_4.

For **Pyr3**, the pre-protonation phase occurs from 0 – 5.5 mol eq HBF_4, the first protonation phase occurs over 6 – 32 mol eq HBF_4, and the second protonation phase occurs over 34 – 234 mol eq HBF_4.

For **Pyr4**, the pre-protonation phase occurs from 0 – 0.5 mol eq HBF_4, the first protonation phase occurs over 0.5 – 8.3 mol eq HBF_4, and the second protonation phase occurs over 8.8 – 22 mol eq HBF_4.

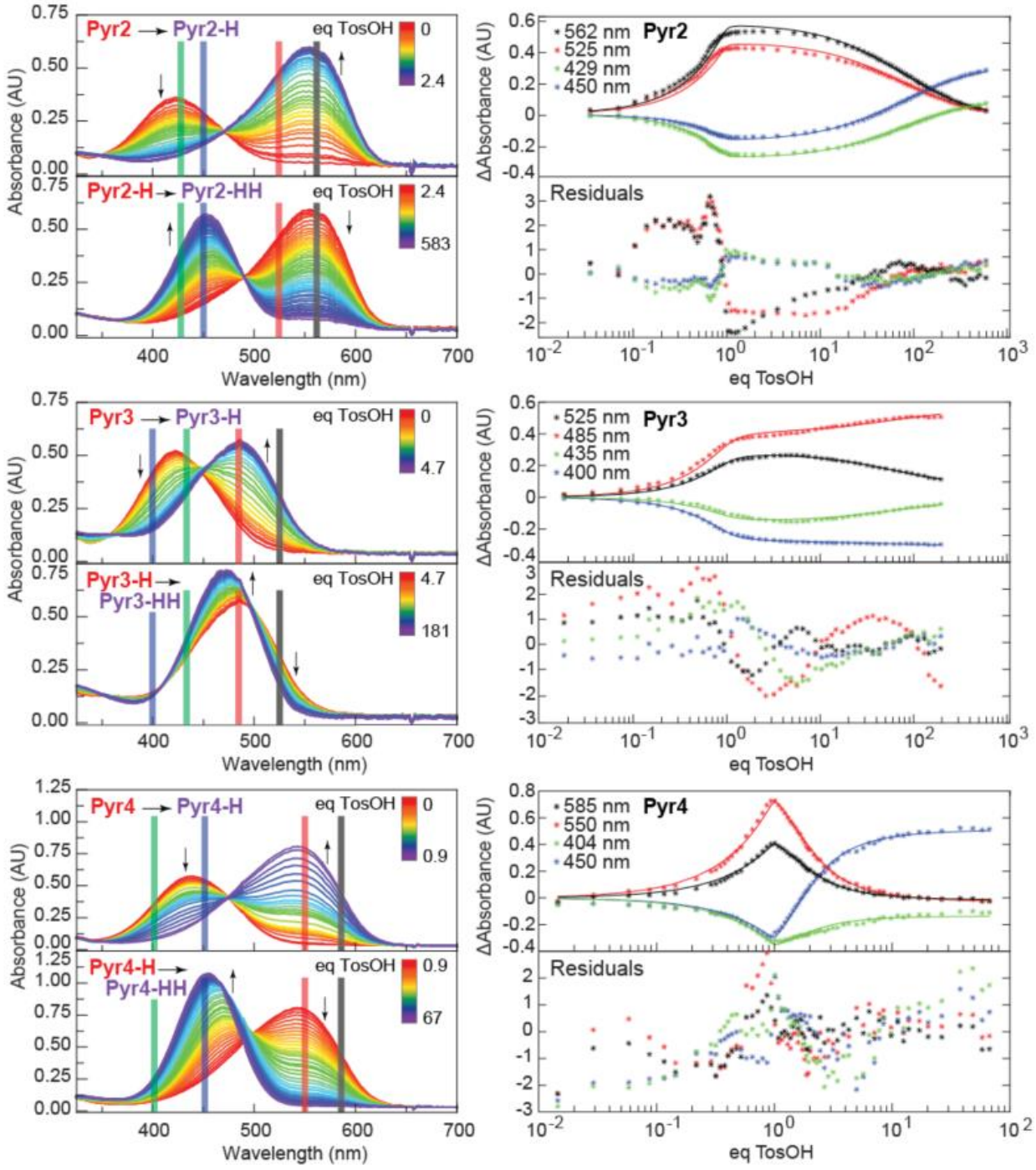


Figure S6. 3 Non-linear fitting to entire titration curve of **Pyr2**, **Pyr3** and **Pyr4**. Simultaneous fitting was performed at four wavelengths which are shown overlaid on titration spectra in left panels.

Table S1. Experimentally- vs Computationally-Determined 1st and 2nd pK_as for Each Dye.

Dye	Experimental Fitting pK_{a1}	Experimental Fitting pK_{a2}	DFT pK_{a1}	DFT pK_{a2}
Pyr2	14.9 (0.8)	11.3 (0.2)	14.16	6.86
Pyr3	14.6 (0.4)	11.4 (0.9)	12.81	8.02
Pyr4	15.3 (1.2)	13.8 (0.3)	14.70	9.80

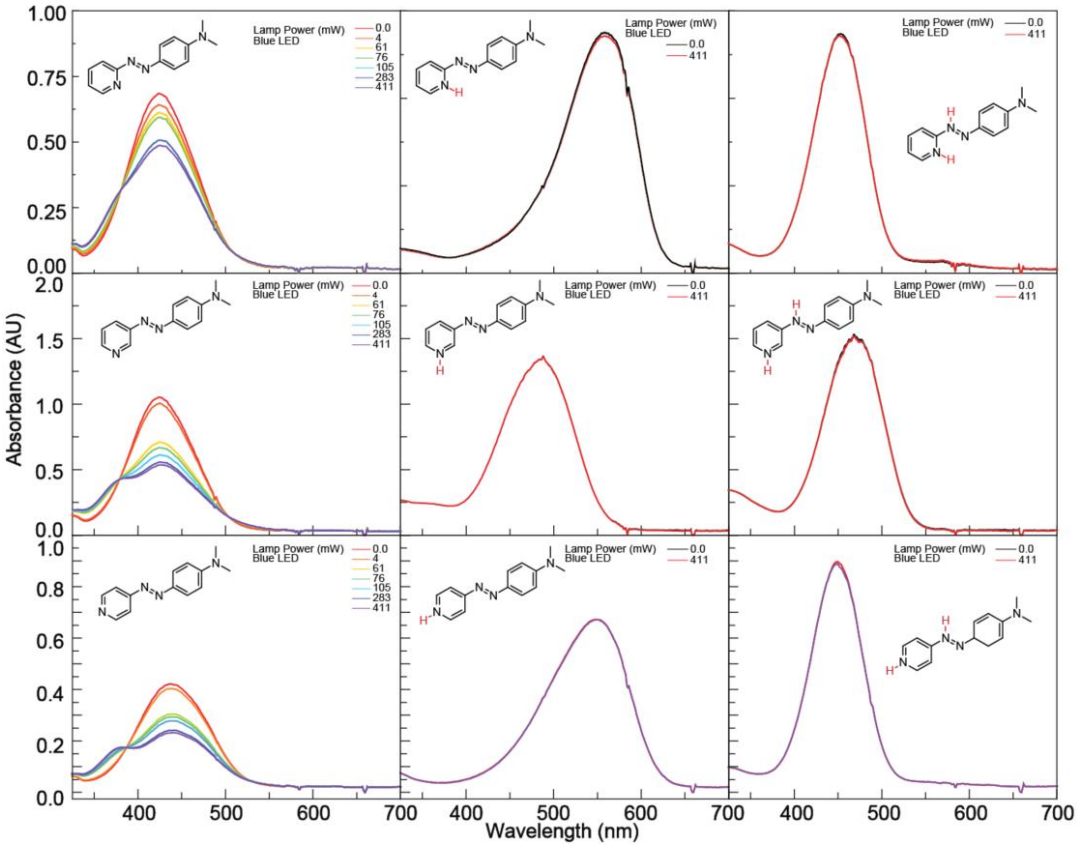


Figure S7. Photolysis of **Pyr2**, **Pyr3** and **Pyr4** (top to bottom) for each protonation state (non-protonated, singly protonated and doubly protonated) (left to right).

Photolysis of the non-protonated species are shown at various irradiation intensities that promote further extent of isomerization with increasing power. Photolysis of the singly and doubly protonates species was carried out with the highest lamp power and the spectra show no change up irradiation.

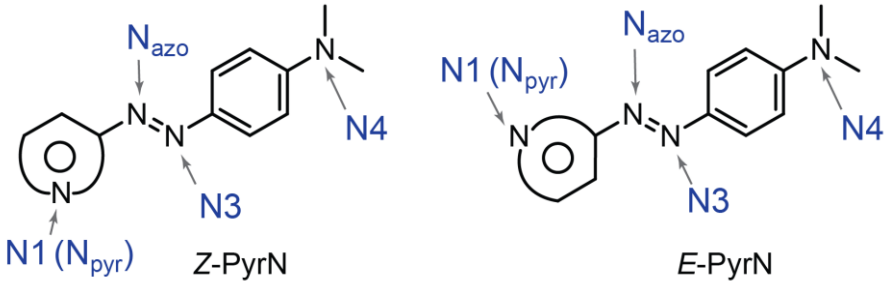
Table S2. Maximum peak height ratios of the *trans* illuminated and un-illuminated. Values are reported as (*trans*-peak height after illumination) / (*trans*-peak height before illumination) of the primary absorption feature (abs @ 425 nm for **Pyr2** and **Pyr3**, 435 nm for **Pyr4**) with standard deviations.

Dye	*Trans-illuminated / trans-dark* peak height ratio (standard deviation)
Pyr2	0.62 (0.10)
Pyr3	0.56 (0.07)
Pyr4	0.59 (0.06)

The smaller the value of the ratio indicated less trans-isomer remains and a larger conversion to the cis-isomer

Computational Data

Table S3. Energies of protonation of each basic nitrogen (NX) site of *trans*-PyrN, PyrN-H, and PyrN-HH, including pyridine ring rotational isomers (*E* and *Z*) for **Pyr2** and **Pyr3.** Energies are relative to the lowest energy structural isomer of each protonated state and are shaded. CAM-B3LYP/6-311g(d,p)/PCM(MeCN) level of theory.



protonation	site	Energy (eV)				
		Pyr2		**Pyr3**		**Pyr4**
		E-trans	*Z-trans*	*E-trans*	*Z-trans*	*trans*
PyrN	-	0.000	0.052	0.000	0.026	0.000
PyrN-H	N1	0.042	0.000	0.000	0.013	0.000
	N2	0.121	0.253	0.145	0.161	0.239
	N3	0.640	0.240	0.463	0.486	0.643
	N4	0.459	0.497	0.283	0.310	0.457
PyrN-HH	N1N2	0.143	0.000	0.013	0.000	0.000
	N1N3	0.448	0.680	0.434	0.482	0.533
	N1N4	0.162	0.127	0.079	0.098	0.279
	N2N3	1.135	0.809	1.276	1.274	1.472
	N2N4	0.775	0.892	0.895	0.916	1.192
	N3N4	0.959	0.535	0.821	0.869	1.230

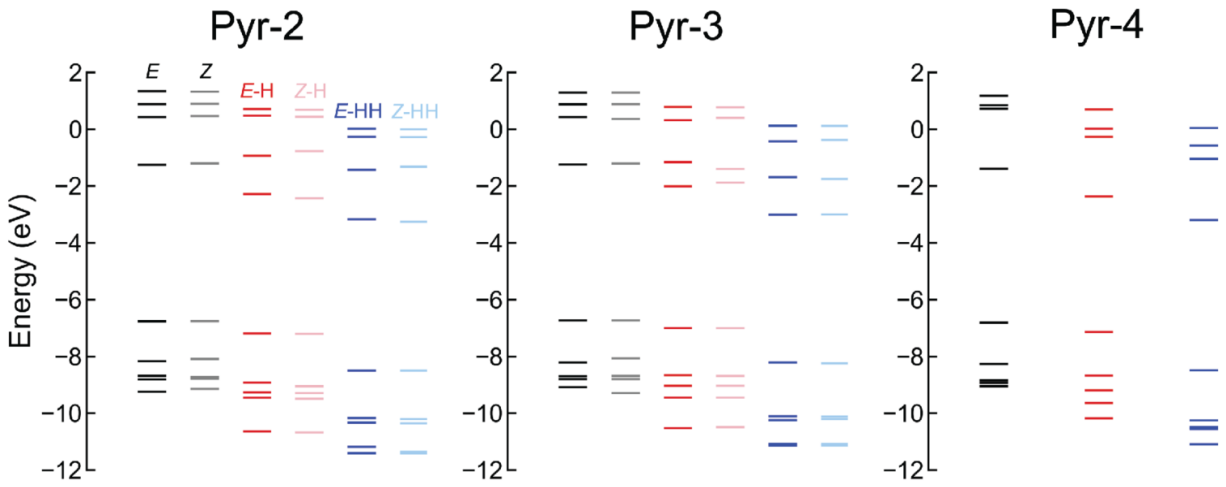


Figure S8. Comparison of molecular orbital energies for the *E*- and *Z*- configuration of **Pyr2**, **Pyr3** and **Pyr4** and their singly and doubly protonated states.

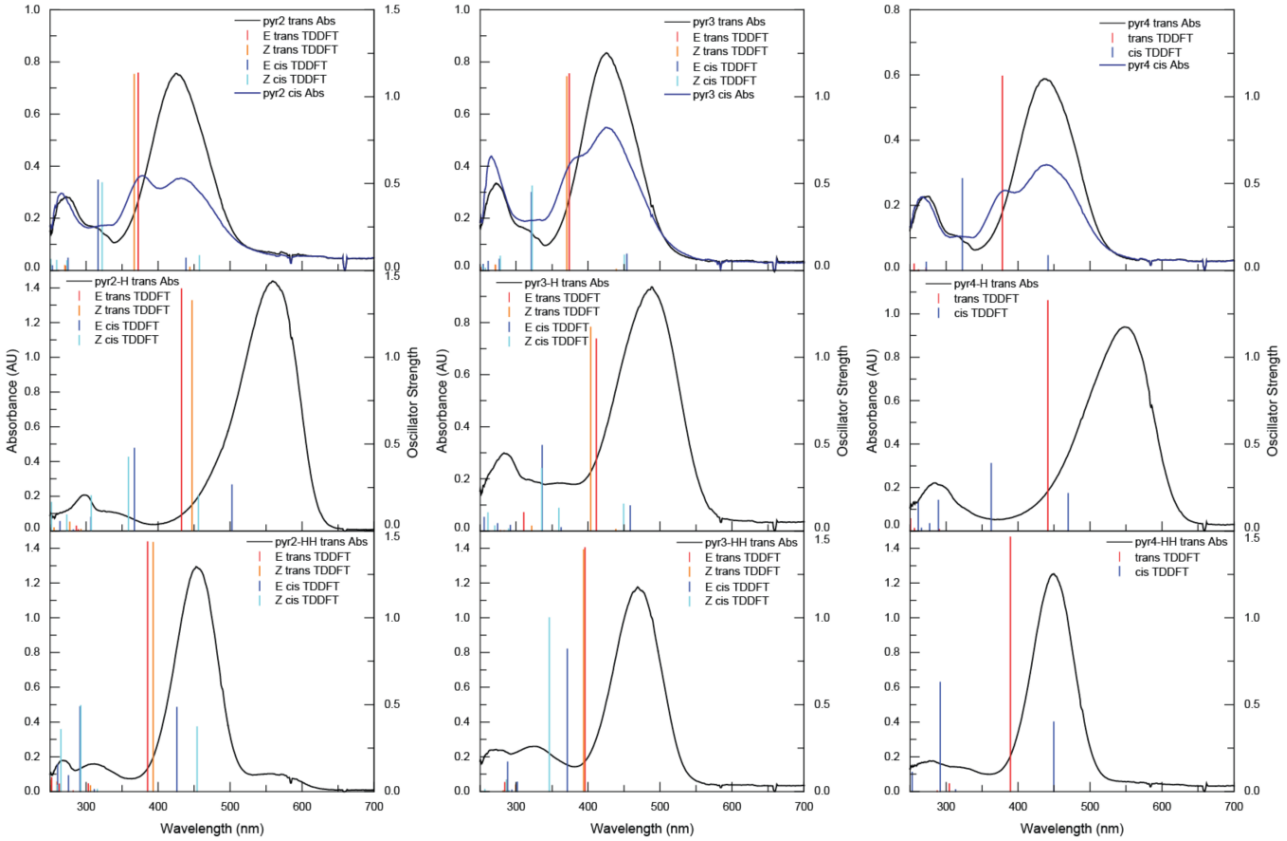


Figure S9. TDDFT predicted transitions for the *E*- and *Z*- configuration of both *trans*- and *cis*-isomers of **Pyr2**, **Pyr3**, and **Pyr4** for each protonation state (overlaid with experimental data, where available).

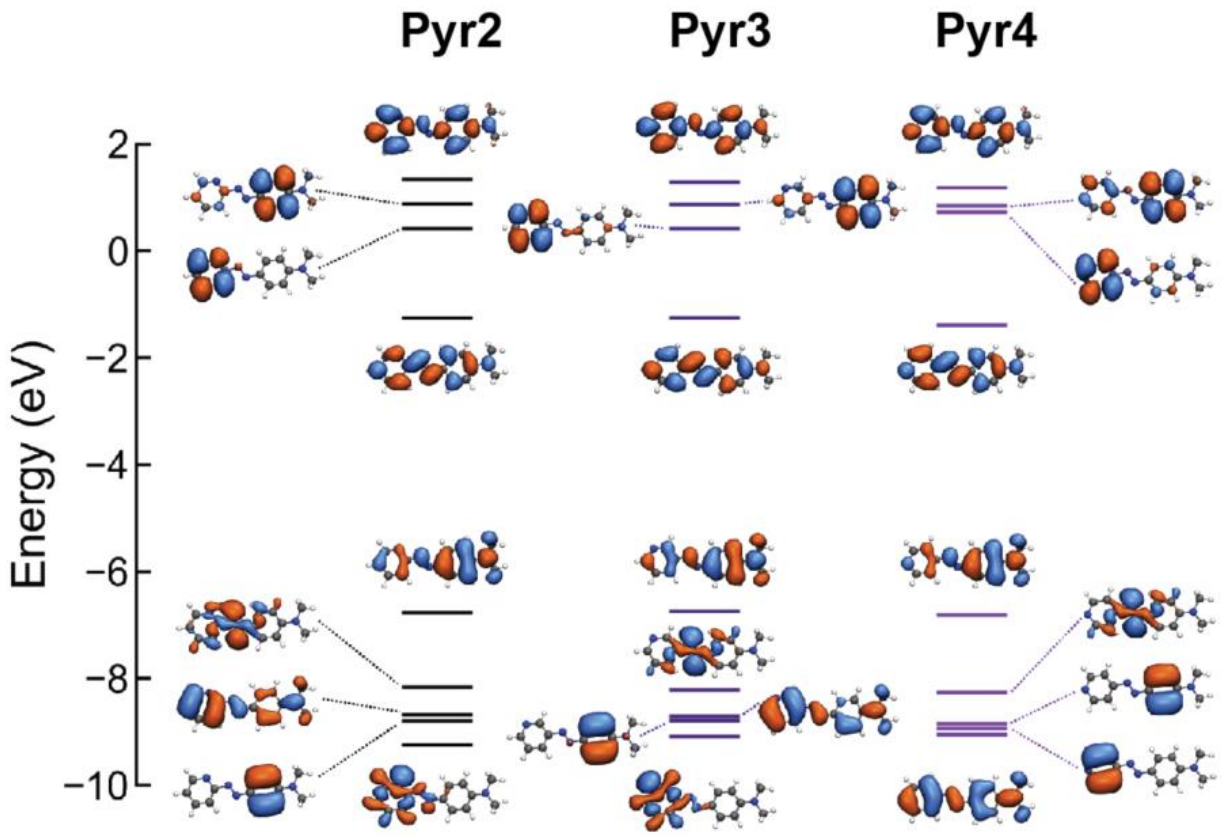


Figure S10. MO diagram comparing **Pyr2**, **Pyr3** and **Pyr4** shows that the shapes of the orbitals are relatively consistent across the series.

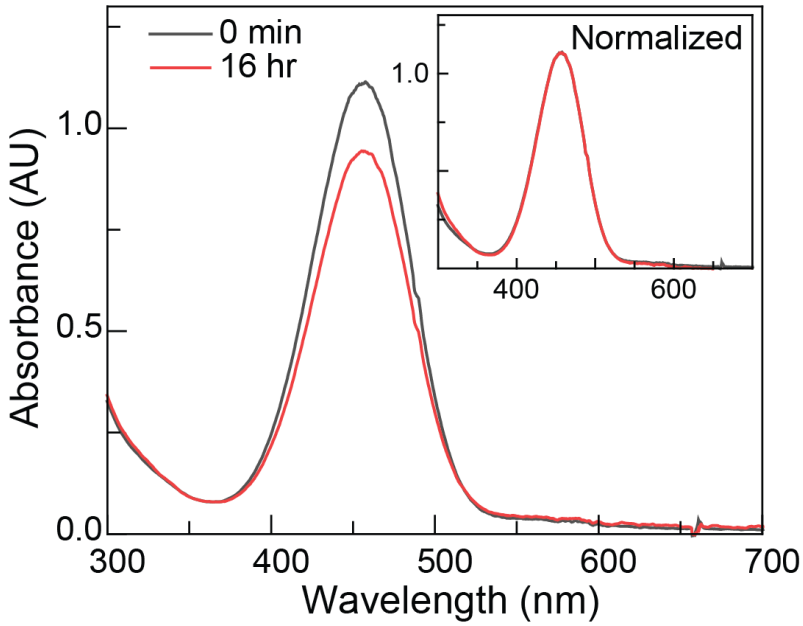


Figure S11. Longer (16-hr) timespan illumination of **Pyr2-HH** over the course of 16 hours in deoxygenated solution of acetonitrile.

The dye undergoes a small amount photodegradation without undergoing photoisomerization. The inset shows the two spectra normalized at the peak maximum to accentuate the lack of change of absorption spectrum that would correspond to isomerization.

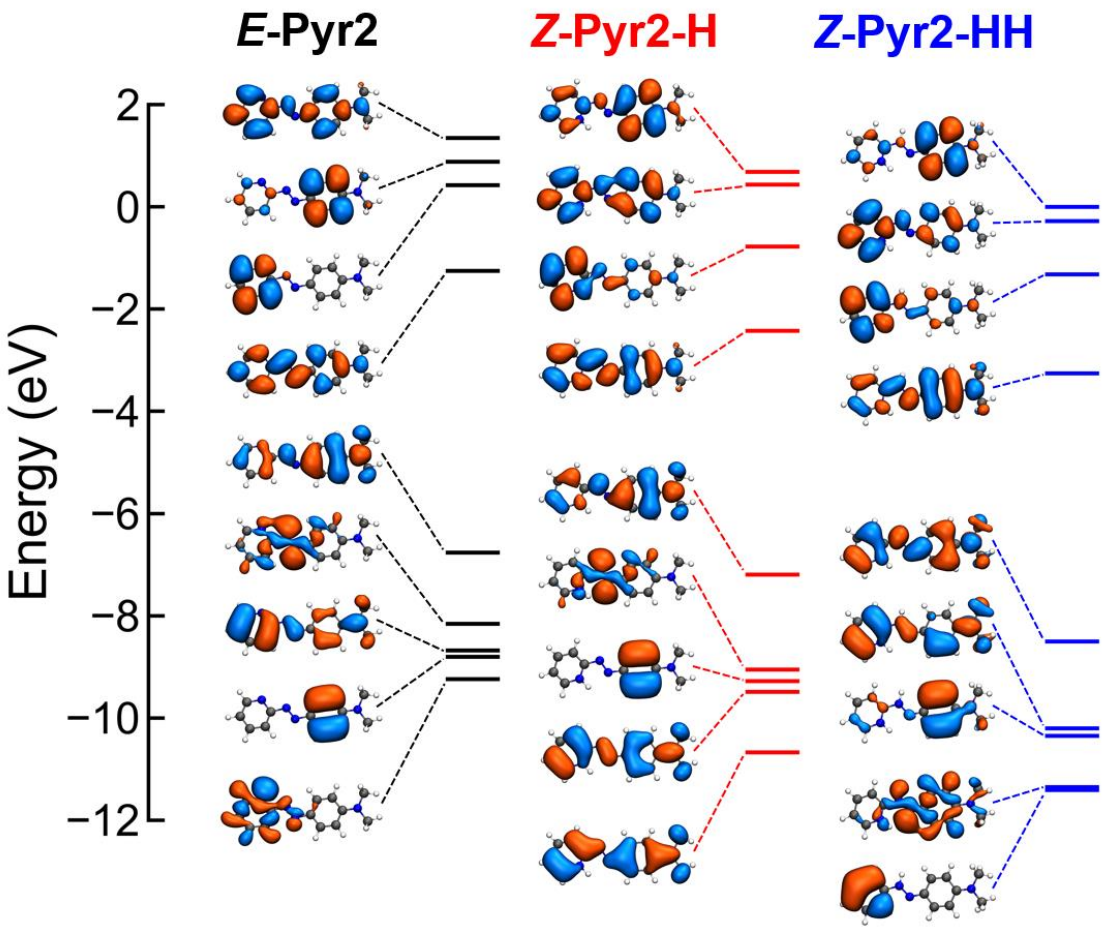


Figure S12. MO diagram comparing ***E*-Pyr2**, ***Z*-Pyr2-H** and ***Z*-Pyr3-HH**.

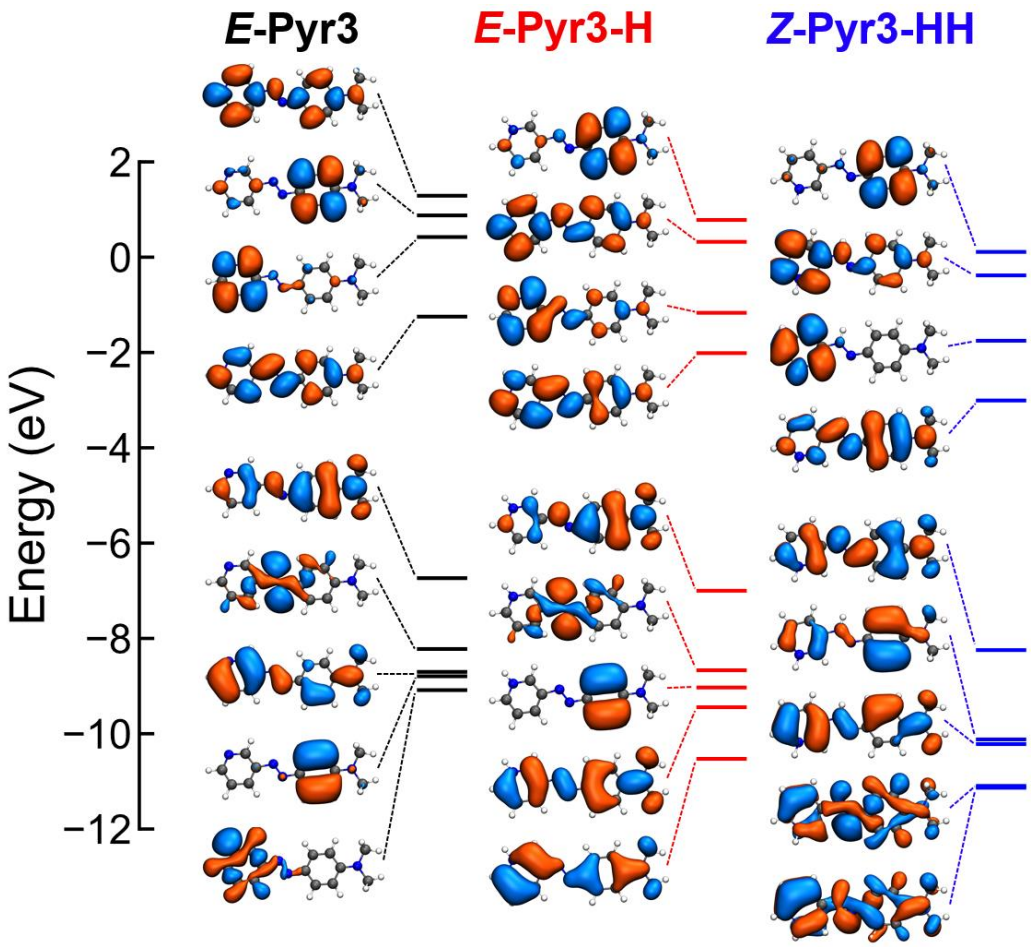


Figure S13. MO diagram comparing *E*-**Pyr3**, *E*-**Pyr3-H** and *Z*-**Pyr3-HH**.

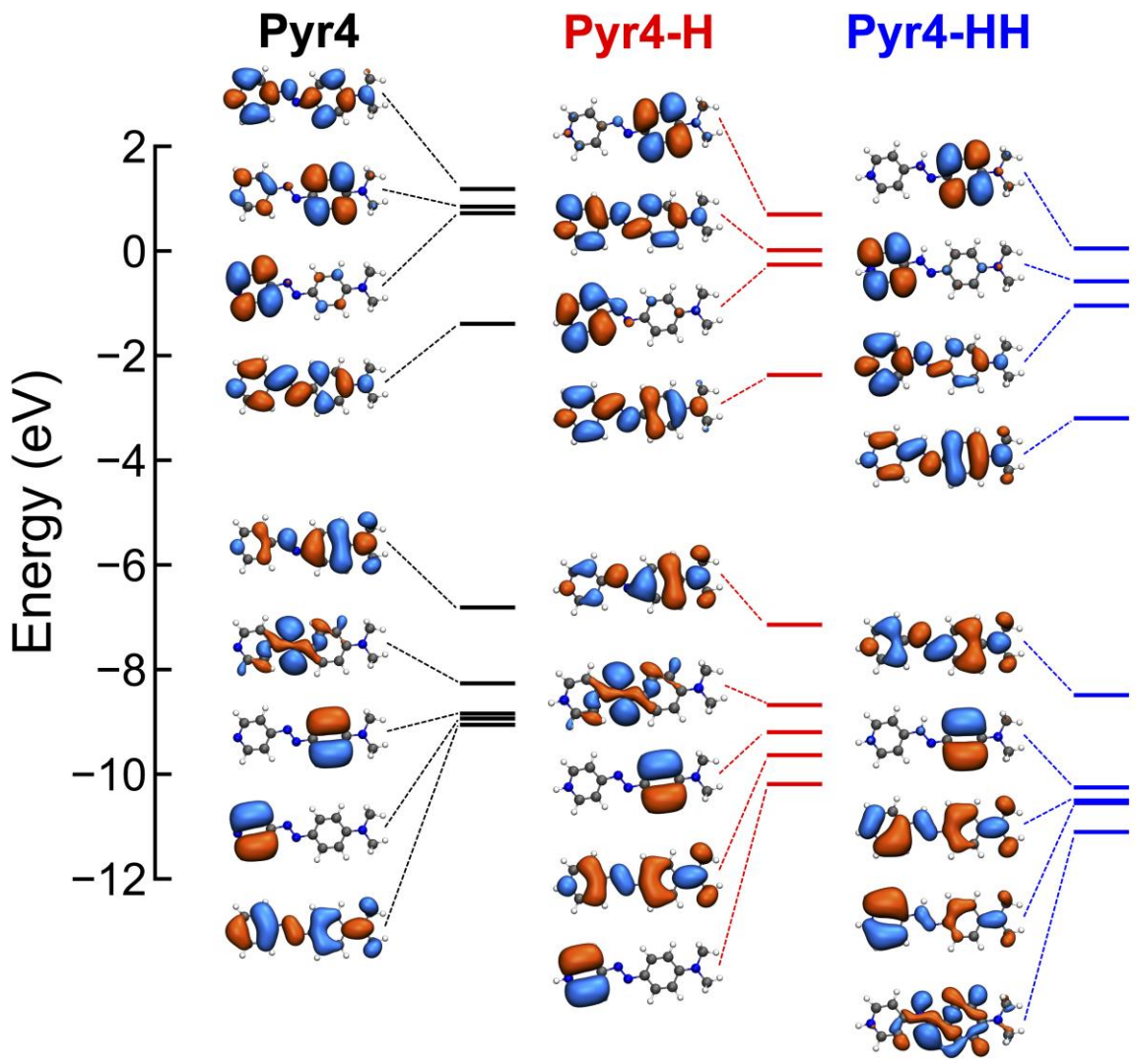


Figure S14. MO diagram comparing **Pyr4**, **Pyr4-H** and **Pyr4-HH**.

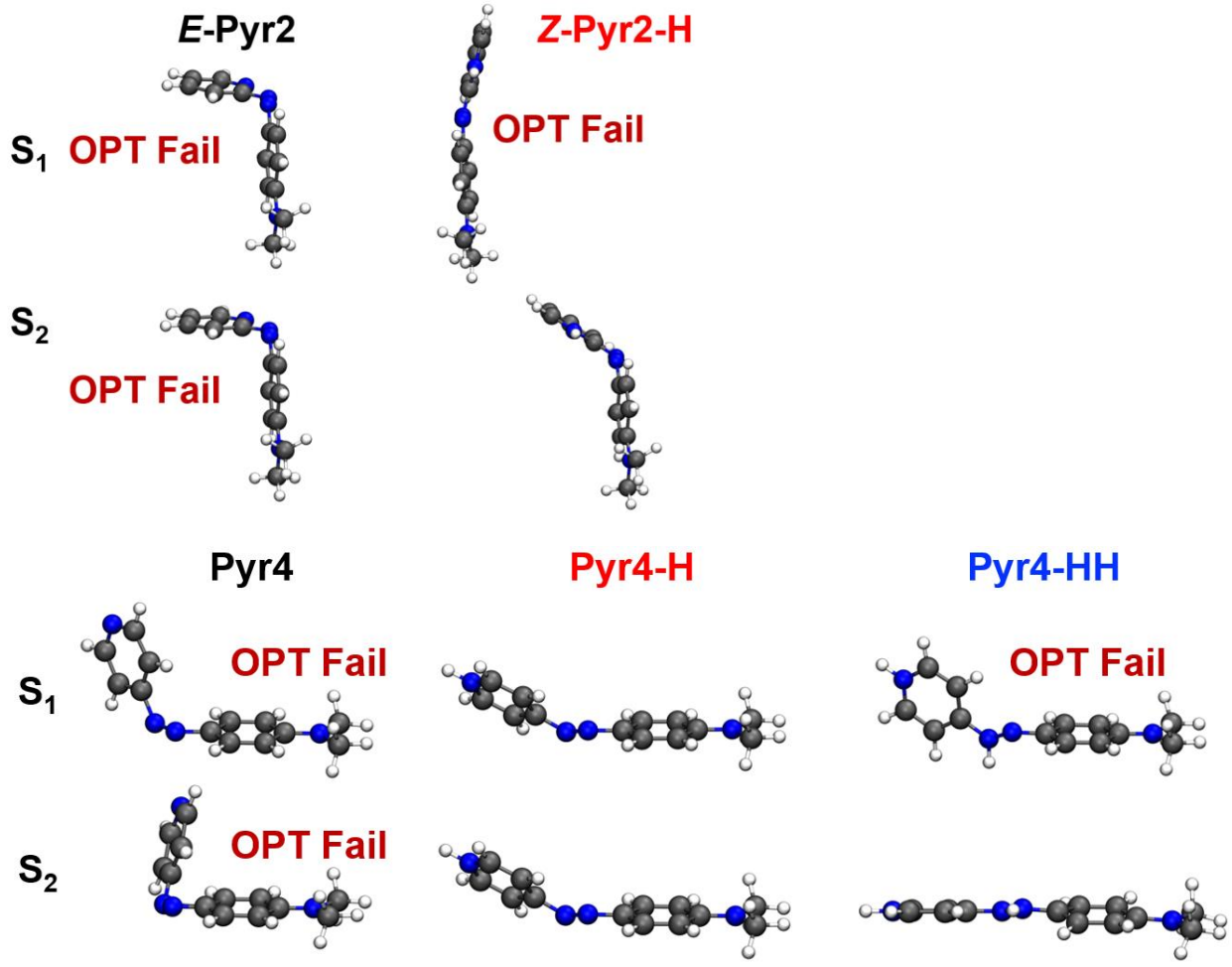


Figure S15: Pseudo-optimized structures of S_1 and S_2 excited states of **Pyr2(H/HH)** and **Pyr4(H/HH)**. S_1 excited state optimizations failed to converge with the geometries oscillating in energy around structures that resemble a rotational transition state. The observed oscillations are likely the result of the S_1/S_0 conical intersections and the multireference nature of these regions and are therefore indescribable with standard DFT methods.

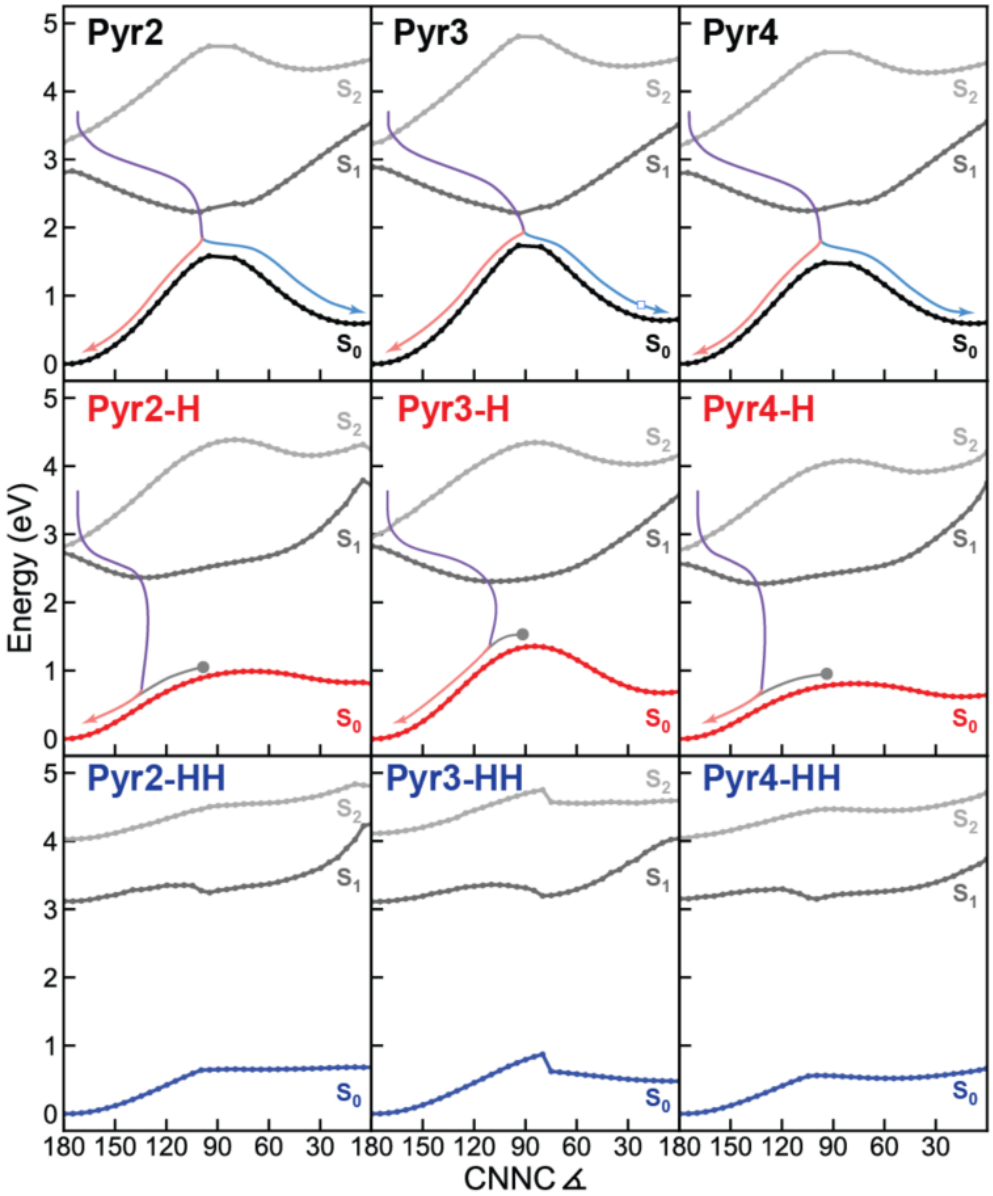


Figure S16. Potential energy curves for the ground and excited states of **Pyr2**, **Pyr3**, and **Pyr4**.

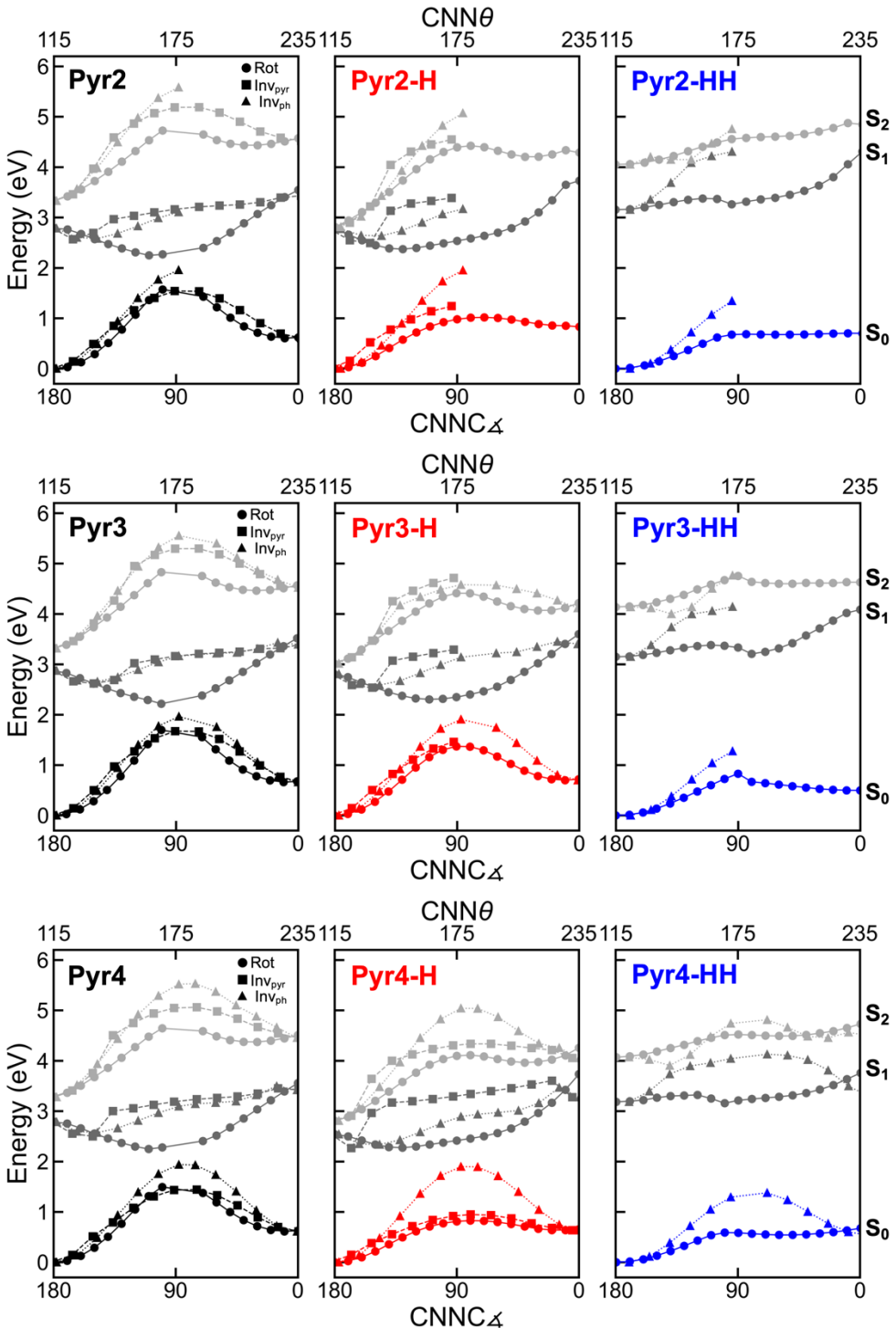


Figure S20. Dihedral rotation and pyridine (pyr) and phenyl (ph) inversion potential energy surfaces for the ground (S_0) and excited states (S_1/S_2) of **Pyr2**, **Pyr3**, and **Pyr4** (and their singly and doubly pronated versions) at CAM-B3LYP/6-311G(d,p)/PCM(MeCN) level of theory. The top axis represents CNN inversion coordinate(s) and the bottom axis represents the CNNC dihedral angle.

Table C1: *E-trans*-**Pyr2** CAM-B3LYP/6-311g(d,p)/pcm(acetonitrile)

Excited State	Energy (eV)	Wavelength (nm)	Oscillator Strength	Orbital Transitions
1	2.7856	445.1	0	59→61 (0.68662) 59→67 (-0.14983)
2	3.3294	372.39	1.1354	58→61 (0.10118) 60→61 (0.68892)
3	4.5709	271.25	0.0236	57→61 (-0.40571) 57→64 (-0.12373) 60→63 (0.54545)
4	4.7493	261.06	0.0006	56→61 (0.66046) 56→62 (0.13298) 56→64 (-0.16278)
5	4.9751	249.21	0.0491	55→61 (-0.23955) 55→64 (0.10055) 58→61 (0.55659) 58→62 (0.18045) 60→62 (0.24768)

Table C2: *Z-trans*-**Pyr2** CAM-B3LYP/6-311g(d,p)/pcm(acetonitrile)

Excited State	Energy (eV)	Wavelength (nm)	Oscillator Strength	Orbital Transitions
1	2.7908	444.26	0.0168	58→61 (-0.11231) 59→61 (0.67023) 59→67 (-0.15042)
2	3.3799	366.83	1.1279	58→61 (0.11090) 60→61 (0.68205)
3	4.5602	271.88	0.0015	56→61 (0.66075) 56→62 (-0.16215) 56→64 (-0.13042)
4	4.5829	270.53	0.0272	57→61 (-0.38216) 57→64 (-0.11402) 60→63 (0.55502) 60→64 (-0.10581)
5	4.997	248.12	0.0356	55→61 (-0.20257) 55→64 (0.11038) 58→61 (0.50932) 58→62 (-0.20493) 59→61 (0.10287) 60→62 (-0.31275)

Table C3: *E-trans*-**Pyr2-H** CAM-B3LYP/6-311g(d,p)/pcm(acetonitrile)

Excited State	Energy (eV)	Wavelength (nm)	Oscillator Strength	Orbital Transitions
1	2.7655	448.33	0.0001	59→61 (0.68772) 59→66 (-0.13137)
2	2.8661	432.6	1.3929	60→61 (0.69394)
3	4.2889	289.08	0.007	58→61 (0.64666) 60→62 (-0.12046) 60→63 (0.12561) 60→64 (-0.16927)
4	4.3266	286.57	0.027	57→62 (-0.18251) 58→61 (0.13437) 60→62 (0.65795)
5	4.9438	250.79	0.0165	57→61 (0.67576)

Table C4: *Z-trans*-**Pyr2-H** CAM-B3LYP/6-311g(d,p)/pcm(acetonitrile)

Excited State	Energy (eV)	Wavelength (nm)	Oscillator Strength	Orbital Transitions
1	2.7728	447.14	1.3247	57→61 (-0.10337) 60→61 (0.69367)
2	2.812	440.91	0.0001	59→61 (0.68796) 59→66 (-0.12976)
3	4.2338	292.84	0.0086	58→61 (0.66455) 58→62 (0.11081) 60→64 (-0.15307)
4	4.4734	277.16	0.0507	57→61 (0.14708) 57→62 (-0.16229) 60→62 (0.65444)
5	4.8561	255.32	0.0175	57→61 (0.66000) 60→61 (0.10813) 60→62 (-0.15954)

Table C5: *E-trans*-**Pyr2-HH** CAM-B3LYP/6-311g(d,p)/pcm(acetonitrile)

Excited State	Energy (eV)	Wavelength (nm)	Oscillator Strength	Orbital Transitions
1	3.2165	385.46	1.4359	60→61 (0.69581)
2	4.0915	303.03	0.0432	58→61 (0.66480) 59→61 (0.21867)
3	4.3957	282.06	0.0029	57→61 (0.68850) 57→65 (-0.11550)
4	4.7224	262.55	0.042	56→63 (0.10141) 59→61 (0.11774) 59→62 (0.22833) 60→62 (0.63442)
5	4.9194	252.03	0.0793	58→61 (-0.20497) 59→61 (0.64359) 60→62 (-0.13508)

Table C6: *Z-trans*-**Pyr2-HH** CAM-B3LYP/6-311g(d,p)/pcm(acetonitrile)

Excited State	Energy (eV)	Wavelength (nm)	Oscillator Strength	Orbital Transitions
1	3.1545	393.04	1.433	60→61 (0.69650)
2	4.0524	305.95	0.0327	58→61 (0.65642) 59→61 (0.23923)
3	4.5118	274.8	0.0017	57→61 (0.68844) 57→65 (-0.11044)
4	4.7814	259.3	0.0544	58→61 (-0.17045) 59→61 (0.40323) 59→62 (0.17217) 60→62 (0.49842)
5	4.9519	250.38	0.0636	58→61 (-0.16301) 59→61 (0.50662) 59→62 (-0.11550) 60→62 (-0.42378)

Table C7: *E-trans*-**Pyr3** CAM-B3LYP/6-311g(d,p)/pcm(acetonitrile)

Excited State	Energy (eV)	Wavelength (nm)	Oscillator Strength	Orbital Transitions
1	2.8751	431.23	0	59→61 (0.68654) 59→66 (-0.15591)
2	3.3154	373.96	1.1305	58→61 (0.10513) 60→61 (0.68766)
3	4.5687	271.38	0.0277	57→61 (0.38304) 57→64 (0.11474) 60→63 (0.55827) 60→64 (0.11372)
4	4.8171	257.38	0.0015	56→61 (0.63795) 56→62 (0.14972) 56→64 (-0.23603)
5	4.944	250.78	0.0153	55→61 (-0.21431) 55→64 (0.11884) 58→61 (0.46997) 58→62 (0.23561) 60→62 (0.37731)

Table C8: *Z-trans*-**Pyr3** CAM-B3LYP/6-311g(d,p)/pcm(acetonitrile)

Excited State	Energy (eV)	Wavelength (nm)	Oscillator Strength	Orbital Transitions
1	2.8229	439.2	0.0057	56→61 (-0.13881) 59→61 (0.67072) 59→66 (-0.14130)
2	3.3468	370.46	1.1148	58→61 (0.10497) 60→61 (0.68610)
3	4.5725	271.15	0.0302	57→61 (-0.38277) 57→64 (-0.12031) 60→63 (0.55920) 60→64 (-0.10480)
4	4.9239	251.8	0.0003	56→61 (0.60897) 56→64 (-0.19575) 59→61 (0.13915) 59→64 (-0.19982)
5	4.9909	248.42	0.0097	56→62 (0.35212) 58→61 (0.16293) 59→62 (0.55088) 60→62 (0.13403)

Table C9: *E-trans*-**Pyr3-H** CAM-B3LYP/6-311g(d,p)/pcm(acetonitrile)

Excited State	Energy (eV)	Wavelength (nm)	Oscillator Strength	Orbital Transitions
1	2.8071	441.69	0	59→61 (0.65229) 59→62 (0.20537) 59→63 (0.10974) 59→66 (-0.13855)
2	3.0136	411.42	1.104	57→61 (-0.11643) 60→61 (0.68003) 60→62 (0.11724)
3	3.9893	310.79	0.105	57→62 (-0.14143) 60→61 (-0.11254) 60→62 (0.67463)
4	4.4431	279.05	0	59→61 (-0.21879) 59→62 (0.66677)
5	4.4538	278.38	0.0004	58→61 (0.54639) 58→62 (0.19771) 58→63 (0.13960) 60→63 (-0.12630) 60→64 (-0.34661)
6	4.9673	249.6	0.134	58→61 (0.36885) 60→63 (0.29970) 60→64 (0.50562)

Table C10: *Z-trans*-**Pyr3-H** CAM-B3LYP/6-311g(d,p)/pcm(acetonitrile)

Excited State	Energy (eV)	Wavelength (nm)	Oscillator Strength	Orbital Transitions
1	2.8271	438.55	0.0088	59→61 (0.66995) 59→62 (-0.13235) 59→66 (-0.13796)
2	3.0732	403.44	1.1717	57→61 (-0.10947) 60→61 (0.68313)
3	3.8526	321.82	0.0278	57→62 (-0.15866) 60→62 (0.67979)
4	4.3714	283.63	0.0005	59→61 (0.13265) 59→62 (0.68973)
5	4.4637	277.76	0.0004	58→61 (0.56890) 58→63 (-0.14261) 60→63 (0.13418) 60→64 (-0.35175)
6	4.9866	248.63	0.1198	58→61 (0.37709) 60→63 (-0.30065) 60→64 (0.50107)

Table C11: *E-trans*-**Pyr3-HH** CAM-B3LYP/6-311g(d,p)/pcm(acetonitrile)

Excited State	Energy (eV)	Wavelength (nm)	Oscillator Strength	Orbital Transitions
1	3.1328	395.76	1.403	60→61 (0.69898)
2	4.1377	299.65	0.0322	58→61 (0.18026) 59→61 (0.66883)
3	4.3608	284.31	0.0507	58→62 (0.17131) 60→62 (0.65953)
4	4.3884	282.53	0.0025	57→61 (0.67990) 57→65 (-0.11777)
5	5.0428	245.87	0.0135	56→61 (-0.11903) 58→61 (0.65173) 59→61 (-0.18809)

Table C12: *Z-trans*-**Pyr3-HH** CAM-B3LYP/6-311g(d,p)/pcm(acetonitrile)

Excited State	Energy (eV)	Wavelength (nm)	Oscillator Strength	Orbital Transitions
1	3.1483	393.81	1.39	60→61 (0.69928)
2	4.138	299.62	0.0376	58→61 (0.25375) 59→61 (0.65187)
3	4.311	287.6	0.0657	58→62 (0.18110) 60→62 (0.66635)
4	4.4002	281.77	0.0022	56→61 (0.34986) 57→61 (0.59109) 57→65 (-0.10162)
5	5.008	247.57	0.0263	58→61 (0.63653) 59→61 (-0.25297)

Table C13: Pyr4 CAM-B3LYP/6-311g(d,p)/pcm(acetonitrile)

Excited State	Energy (eV)	Wavelength (nm)	Oscillator Strength	Orbital Transitions
1	2.7854	445.12	0	59→61 (0.68840) 59→66 (-0.15217)
2	3.2779	378.24	1.1174	56→61 (-0.10726) 60→61 (0.68956)
3	4.5581	272.01	0.0132	58→61 (0.44214) 58→64 (0.12708) 60→62 (0.12726) 60→63 (0.49263) 60→64 (0.14087)
4	4.7374	261.71	0.0023	55→61 (0.63530) 55→63 (0.11247) 55→64 (-0.26998)
5	4.8508	255.6	0.0361	56→62 (-0.15845) 57→61 (0.64048) 57→64 (-0.14325) 60→62 (0.16154)

Table C14: Pyr4-H CAM-B3LYP/6-311g(d,p)/pcm(acetonitrile)

Excited State	Energy (eV)	Wavelength (nm)	Oscillator Strength	Orbital Transitions
1	2.5404	488.05	0.0001	59→61 (0.68570) 59→66 (-0.13255)
2	2.8092	441.34	1.3253	57→61 (-0.10437) 60→61 (0.69282)
3	4.2655	290.67	0.0086	58→61 (0.65536) 58→63 (-0.14963) 60→64 (-0.20031)
4	4.8424	256.04	0.0135	56→61 (0.25000) 57→62 (-0.15584) 58→61 (-0.10826) 60→62 (0.56059) 60→63 (0.10390) 60→64 (-0.24238)
5	4.9478	250.58	0.0691	56→61 (0.21938) 58→61 (0.16111) 60→62 (0.17354) 60→63 (-0.40497) 60→64 (0.44562)

Table C15: Pyr4-HH CAM-B3LYP/6-311g(d,p)/pcm(acetonitrile)

Excited State	Energy (eV)	Wavelength (nm)	Oscillator Strength	Orbital Transitions
1	3.1837	389.43	1.4636	60→61 (0.69778)
2	4.0694	304.67	0.0437	59→61 (0.69444)
3	4.3099	287.67	0.0031	56→61 (0.68701) 56→65 (-0.12074)
4	5.0554	245.25	0.0215	58→61(0.66909)
5	5.1253	241.91	0.0273	57→61 (0.55169) 57→62 (-0.15342) 58→62 (0.16284) 58→63 (0.12079) 60→62 (-0.15196) 60→63 (-0.29335)