Supplementary Information for

Photoisomerization of phytochrome chromophore models: An XMS-CASPT2 study

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1. Vertical excitation energies of the models

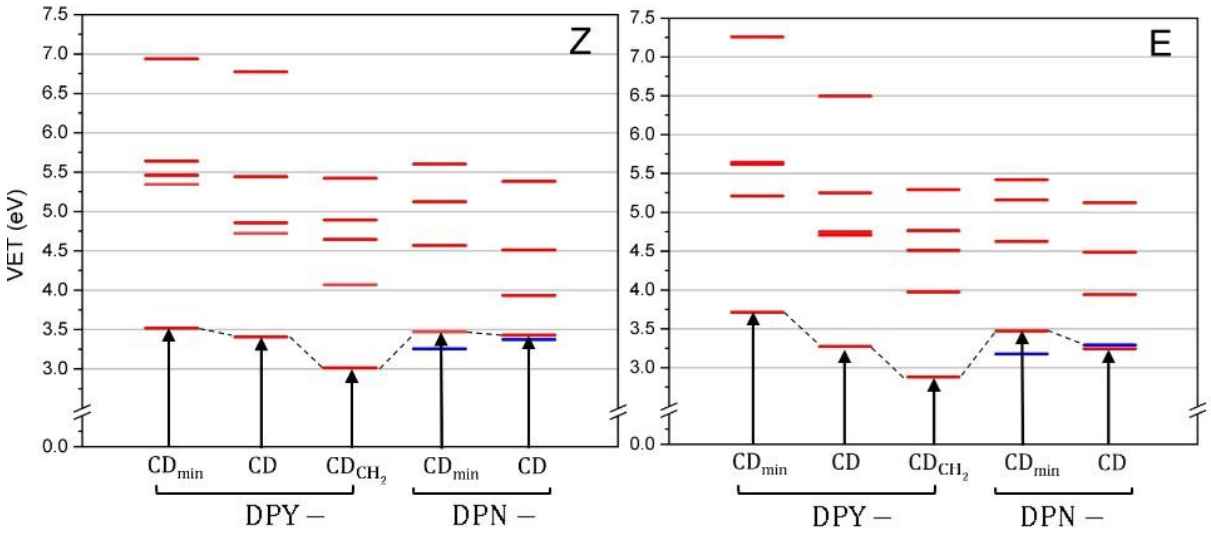

Fig. S1. Vertical excitation energies for all the models at the ADC(2) level of theory in the *Z* (left) and *E* (right) isomers.

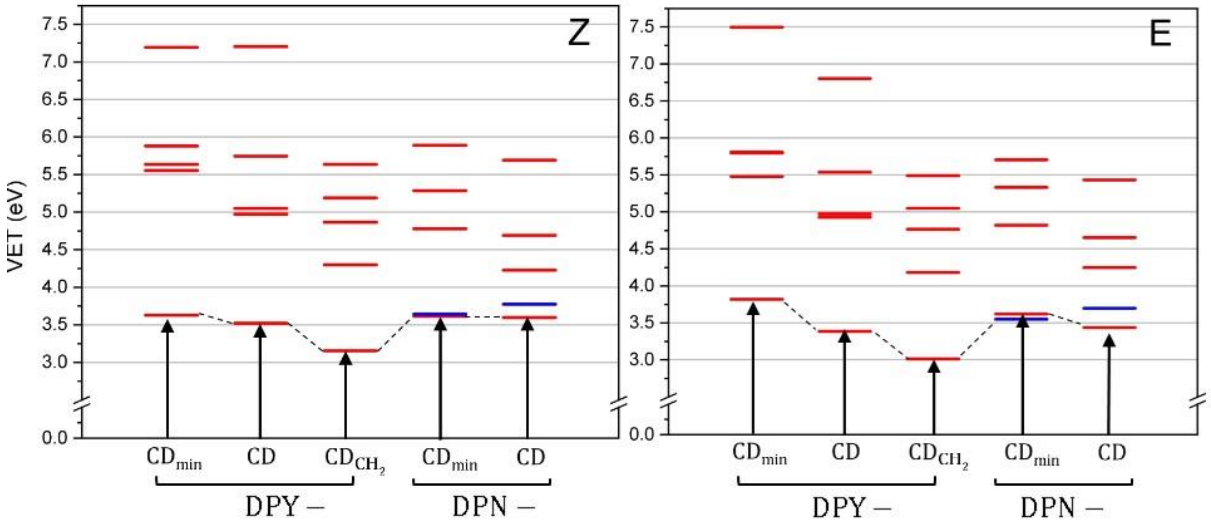

Fig. S2. Vertical excitation energies for all the models at the SCS-ADC(2) level of theory in the *Z* (left) and *E* (right) isomers.

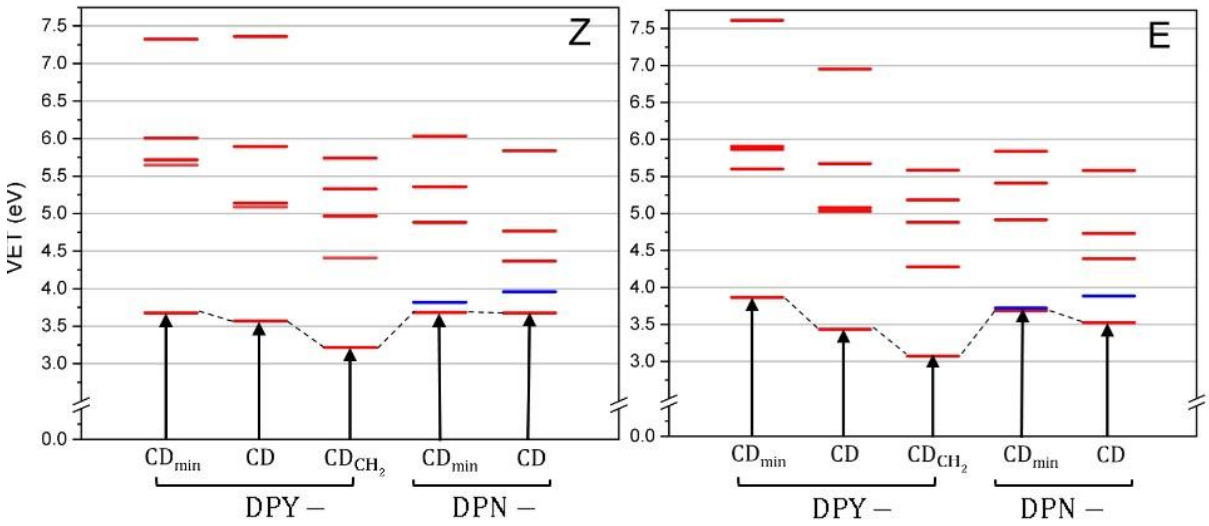

Fig. S3. Vertical excitation energies for all the models at the SOS-ADC(2) level of theory in the *Z* (left) and *E* (right) isomers.

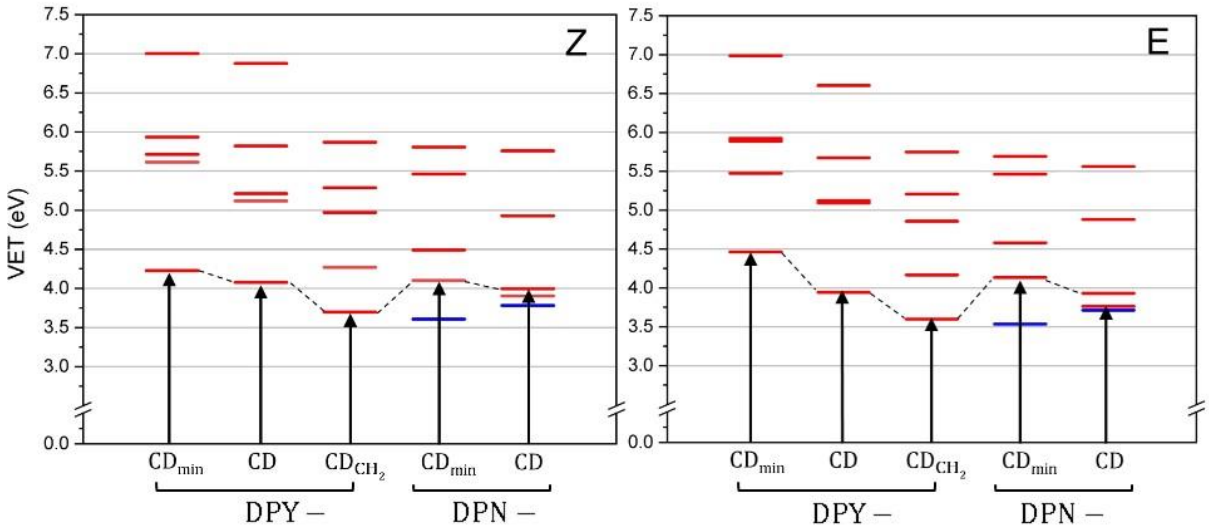

Fig. S4. Vertical excitation energies for all the models at the TD-CAM-B3LYP (TDA) level of theory in the *Z* (left) and *E* (right) isomers.

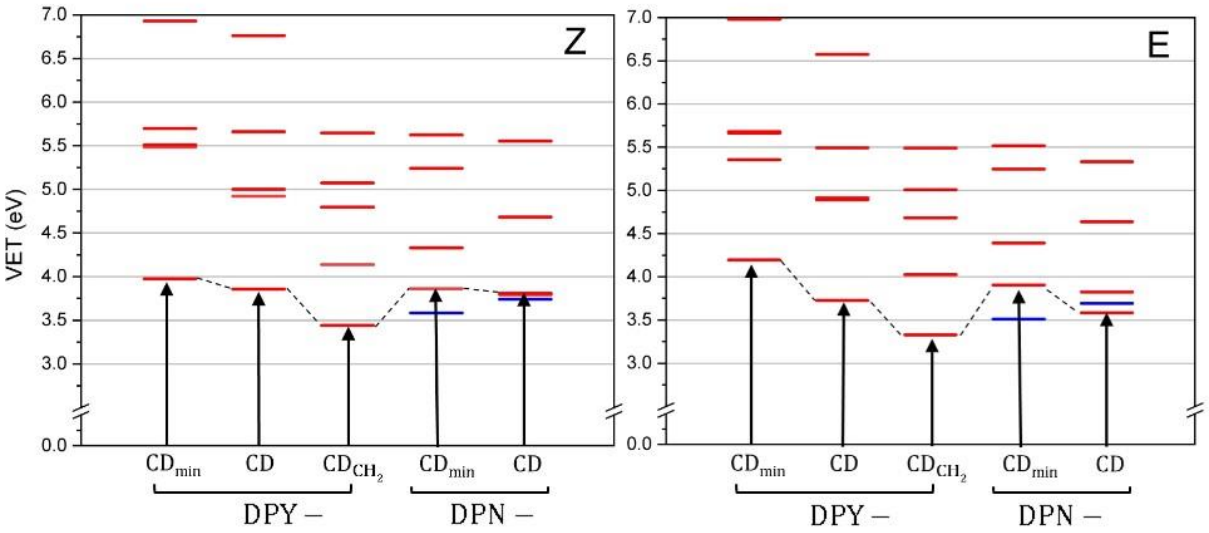

Fig. S5. Vertical excitation energies for all the models at the TD-CAM-B3LYP level of theory in the *Z* (left) and *E* (right) isomers.

2. Table of vertical excitation energies of models

Table S1. Vertical excitation energies (VET) in eV and oscillator strengths (f) for the models in the *Z* isomer. The nπ* and ππ* transitions are shown in blue and black, respectively.

Model	XMS-CASPT2	CAM-B3LYP	CAM-B3LYP (TDA)	ADC(2)	SCS-ADC(2)	SOS-ADC(2)
	VET (f)	VET (f)	VET (f)	VET (f)	VET (f)	VET (f)
DPY-CD_{min}	3.40 (0.74)	3.98 (0.71)	4.23 (0.98)	3.52 (0.64)	3.63 (0.66)	3.67 (0.67)
	4.93 (0.02)	5.48 (0.09)	5.61 (0.04)	5.34 (0.03)	5.55 (0.06)	5.65 (0.09)
		5.51 (0.06)	5.71 (0.16)	5.46 (0.26)	5.64 (0.23)	5.72 (0.22)
		5.70 (0.08)	5.93 (0.11)	5.64 (0.08)	5.88 (0.08)	6.01 (0.08)
		6.93 (0.04)	7.00 (0.07)	6.94 (0.06)	7.20 (0.04)	7.33 (0.03)
DPY-CD	3.25 (0.76)	3.86 (0.79)	4.08 (1.07)	3.41 (0.64)	3.52 (0.67)	3.57 (0.68)
	4.55 (0.11)	4.92 (0.10)	5.12 (0.08)	4.72 (0.18)	4.97 (0.23)	5.09 (0.26)
		5.00 (0.05)	5.21 (0.07)	4.85 (0.12)	5.05 (0.10)	5.14 (0.07)
		5.66 (0.06)	5.82 (0.09)	5.44 (0.06)	5.75 (0.07)	5.89 (0.07)
		6.76 (0.10)	6.87 (0.12)	6.77 (0.17)	7.21(0.02)	7.36 (0.02)
DPY-CD_{CH2}	3.03 (0.61)	3.44 (0.86)	3.70 (1.23)	3.01 (0.73)	3.15 (0.77)	3.21 (0.78)
	4.01 (0.00)	4.14 (0.03)	4.27 (0.03)	4.07 (0.11)	4.30 (0.12)	4.41 (0.12)
		4.80 (0.06)	4.97 (0.05)	4.64 (0.08)	4.87 (0.09)	4.97 (0.10)
		5.07 (0.16)	5.29 (0.22)	4.89 (0.13)	5.19 (0.16)	5.33 (0.18)
		5.65 (0.10)	5.87 (0.12)	5.42 (0.14)	5.64 (0.14)	5.74 0.14)
DPN-CD_{min}	3.27 (0.03)	3.58 (0.00)	3.61 (0.00)	3.26 (0.00)	3.61 (0.59)	3.68 (0.68)
	3.30 (0.68)	3.86 (0.65)	4.09 (0.76)	3.47 (0.62)	3.64 (0.07)	3.82 (0.00)
		4.32 (0.19)	4.49 (0.41)	4.56 (0.23)	4.78 (0.22)	4.88 (0.21)
		5.25 (0.05)	5.47 (0.06)	5.14 (0.08)	5.30 (0.09)	5.38 (0.10)
		5.61(0.06)	5.79 (0.13)	5.59 (0.08)	5.88 (0.10)	6.02 (0.10)
DPN-CD	3.25 (0.61)	3.74 (0.09)	3.78 (0.01)	3.37 (0.00)	3.60 (0.59)	3.67 (0.62)
	3.39 (0.00)	3.79 (0.70)	3.90 (0.04)	3.43 (0.53)	3.77 (0.00)	3.96 (0.00)
		3.81 (0.00)	4.00 (1.00)	3.94 (0.22)	4.23 (0.21)	4.37 (0.20)
		4.68(0.07)	4.93 (0.09)	4.51 (0.11)	4.69 (0.12)	4.77 (0.13)
		5.55 (0.11)	5.76 (0.16)	5.38 (0.11)	5.69 (0.14)	5.84 (0.15)

Table S2. Vertical excitation energies (VET) in eV and oscillator strengths (f) for the models in the *E* isomer. The nπ* and ππ* transitions are shown in blue and black, respectively.

Model	XMS-CASPT2	CAM-B3LYP	CAM-B3LYP (TDA)	ADC(2)	SCS-ADC(2)	SOS-ADC(2)
	VET (f)	VET (f)	VET (f)	VET (f)	VET (f)	VET (f)
DPY-CD_{min}	3.62 (0.97)	4.20 (0.87)	4.46 (1.21)	3.71 (0.80)	3.82 (0.83)	3.86 (0.84)
	4.78 (0.00)	5.36 (0.00)	5.47 (0.00)	5.21 (0.00)	5.48 (0.01)	5.60 (0.02)
		5.66 (0.05)	5.89 (0.03)	5.62 (0.12)	5.80 (0.16)	5.87 (0.16)
		5.68 (0.10)	5.92 (0.14)	5.64 (0.15)	5.81 (0.13)	5.91 (0.12)
		6.98 (0.00)	6.99 (0.00)	7.26 (0.00)	7.50 (0.00)	7.61 (0.00)
DPY-CD	3.11 (0.78)	3.73 (0.73)	3.94 (1.01)	3.27 (0.63)	3.39 (0.65)	3.44 (0.66)
	4.51 (0.07)	4.89 (0.07)	5.09 (0.09)	4.70 (0.11)	4.93 (0.13)	5.03 (0.14)
		4.91 (0.07)	5.12 (0.06)	4.75 (0.12)	4.97 (0.13)	5.08 (0.14)
		5.49 (0.02)	5.67 (0.05)	5.25 (0.04)	5.54 (0.04)	5.68 (0.04)
		6.57 (0.00)	6.60 (0.02)	6.50 (0.05)	6.80 (0.02)	6.95 (0.01)
DPY-CD_{CH2}	2.89 (0.97)	3.33 (0.96)	3.60 (1.40)	2.88 (0.82)	3.01 (0.85)	3.07 (0.86)
	3.87 (0.04)	4.03 (0.04)	4.17 (0.04)	3.98 (0.11)	4.18 (0.11)	4.28 (0.11)
		4.68 (0.04)	4.86 (0.04)	4.51 (0.09)	4.76 (0.11)	4.88 (0.12)
		5.01 (0.01)	5.21 (0.03)	4.76 (0.02)	5.05 (0.02)	5.18 (0.02)
		5.49 (0.06)	5.75 (0.07)	5.29 (0.05)	5.49 (0.05)	5.59 (0.06)
DPN-CD_{min}	3.22 (0.00)	3.51 (0.00)	3.53 (0.00)	3.17 (0.00)	3.54 (0.00)	3.68 (0.79)
	3.35 (0.88)	3.89 (0.66)	4.12 (0.71)	3.46 (0.72)	3.61 (0.77)	3.71 (0.00)
		4.38 (0.33)	4.58 (0.69)	4.62 (0.28)	4.82 (0.26)	4.91 (0.25)
		5.25 (0.04)	5.47 (0.06)	5.17 (0.10)	5.35 (0.11)	5.43 (0.12)
		5.51 (0.02)	5.68 (0.04)	5.41 (0.03)	5.69 (0.04)	5.83 (0.04)
DPN-CD	3.07 (0.55)	3.58 (0.54)	3.71 (0.15)	3.24 (0.44)	3.44 (0.52)	3.53 (0.54)
	3.31 (0.01)	3.69 (0.00)	3.76 (0.46)	3.29 (0.03)	3.70 (0.00)	3.89 (0.00)
		3.82 (0.12)	3.93 (0.25)	3.94 (0.15)	4.25 (0.14)	4.39 (0.14)
		4.64 (0.07)	4.88 (0.10)	4.49 (0.12)	4.66 (0.13)	4.73 (0.13)
		5.33 (0.14)	5.56 (0.18)	5.12 (0.13)	5.43 (0.17)	5.58 (0.18)

3. Excited state relaxed scans

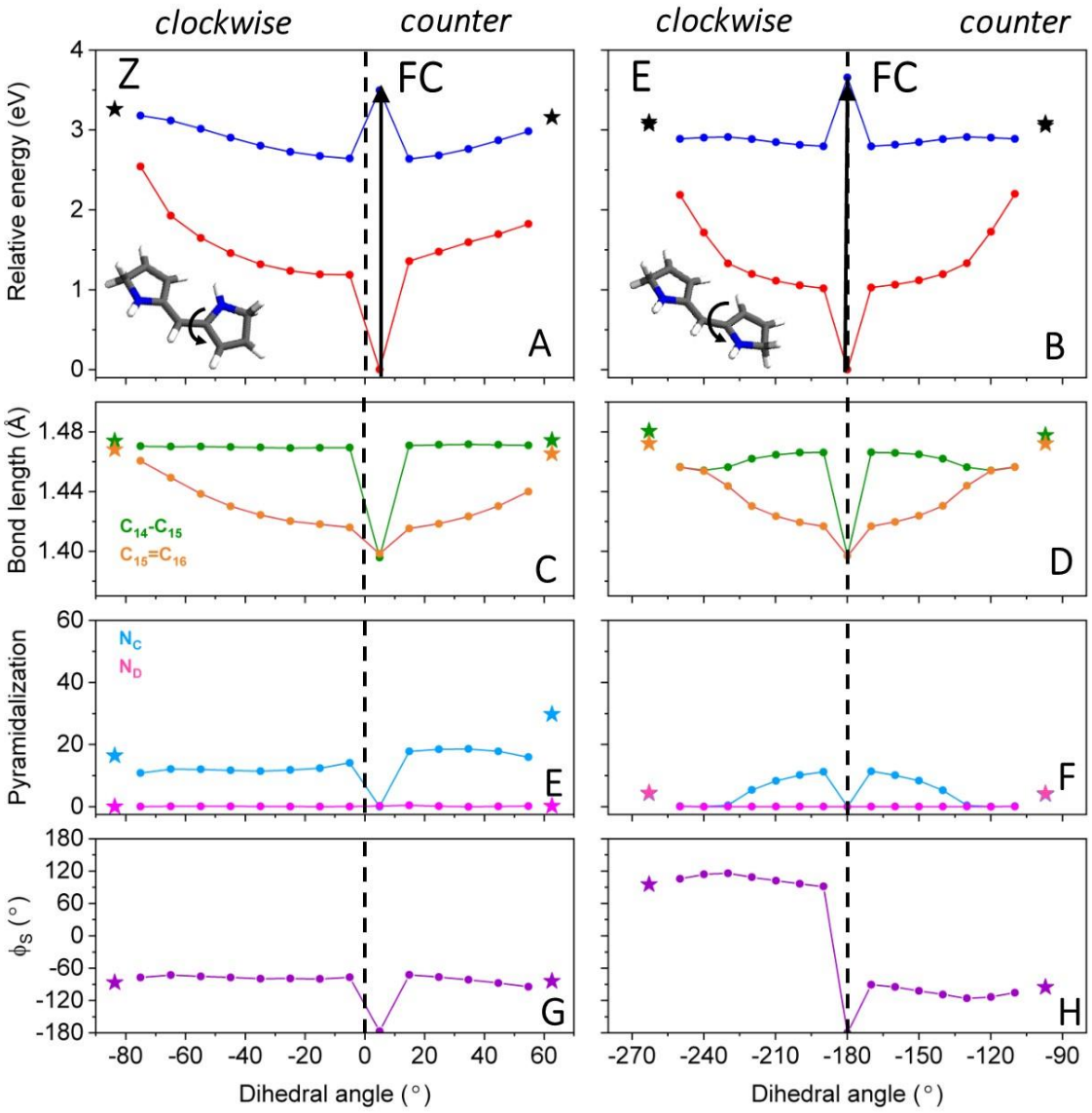

Fig. S6. Excited state relaxed scans of the DPY − CD_{min} model. **A, B** Excited state and ground state energies of the *Z* and *E* isomer. **C, D** Changes of the $C_{14} - C_{15}$ single bond and $C_{15} = C_{16}$ double bond. **E, F** Pyramidalization angle at the N_C and N_D atoms. G, H Changes of the ϕ_S dihedral angle. The star indicates the corresponding values at the MECI.

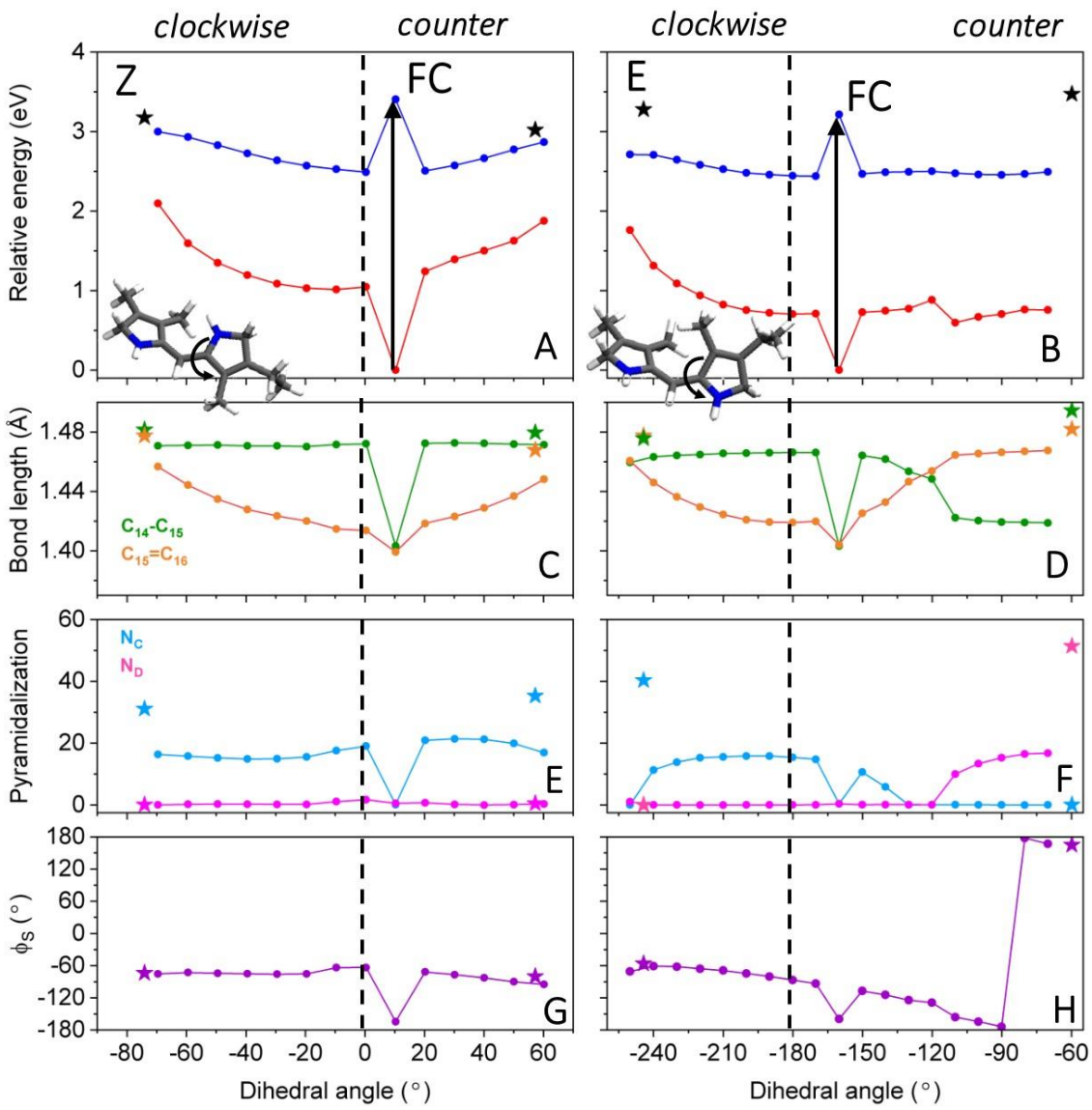

Fig. S7. Excited state relaxed scans of the DPY model. **A, B** Excited state and ground state energies of the *Z* and *E* isomer. **C, D** Changes of the $C_{14} - C_{15}$ single bond and $C_{15} = C_{16}$ double bond. **E, F** Pyramidalization angle at the N_C and N_D atoms. G, H Changes of the ϕ_S dihedral angle. The star indicates the corresponding values at the MECI.

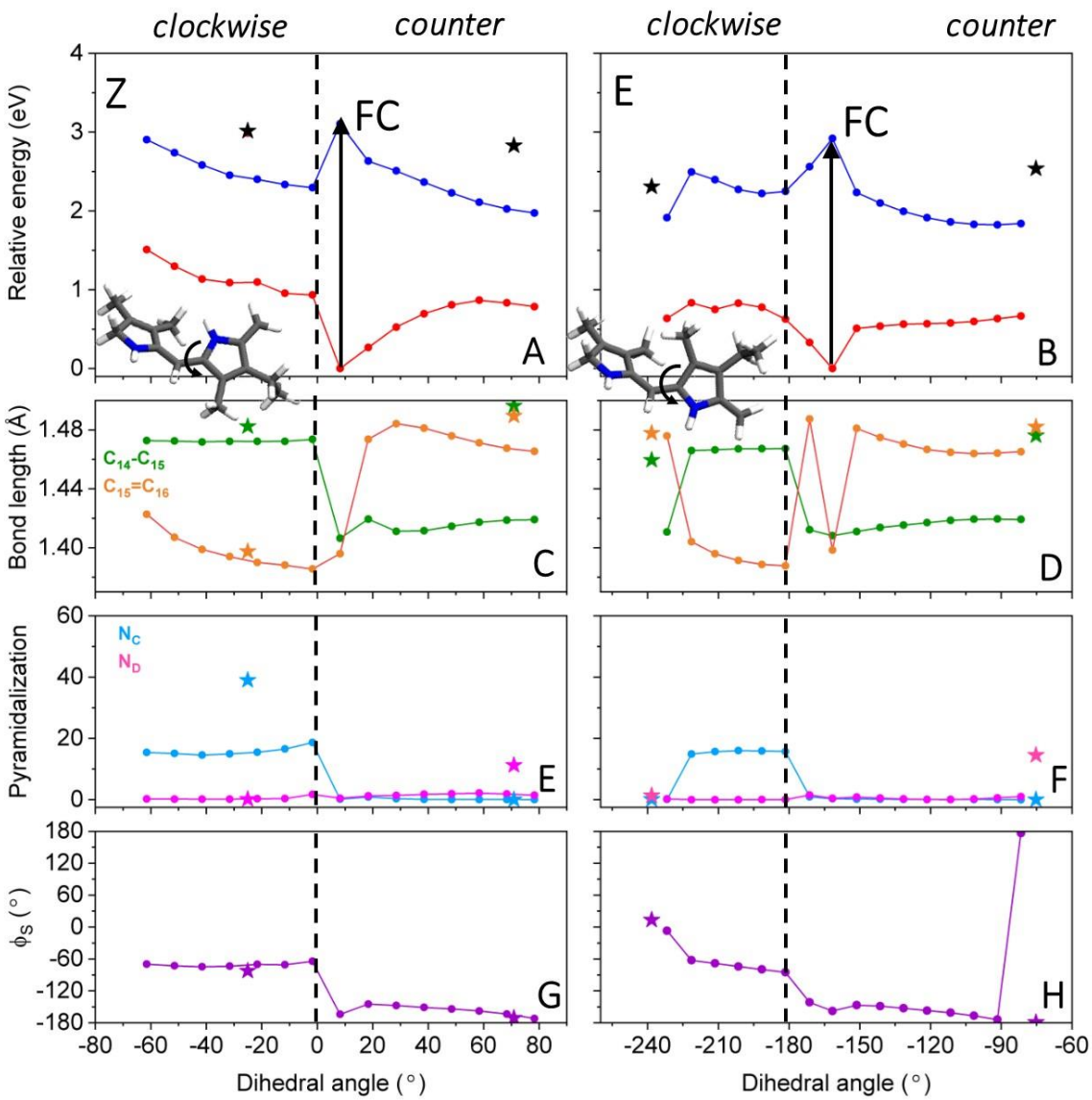

Fig. S8. Excited state relaxed scans of the DPY − CD_{CH2} model. **A, B** Excited state and ground state energies of the *Z* and *E* isomer. **C, D** Changes of the $C_{14} - C_{15}$ single bond and $C_{15} = C_{16}$ double bond. **E, F** Pyramidalization angle at the N_C and N_D atoms. G, H Changes of the ϕ_S dihedral angle. The star indicates the corresponding values at the MECI.

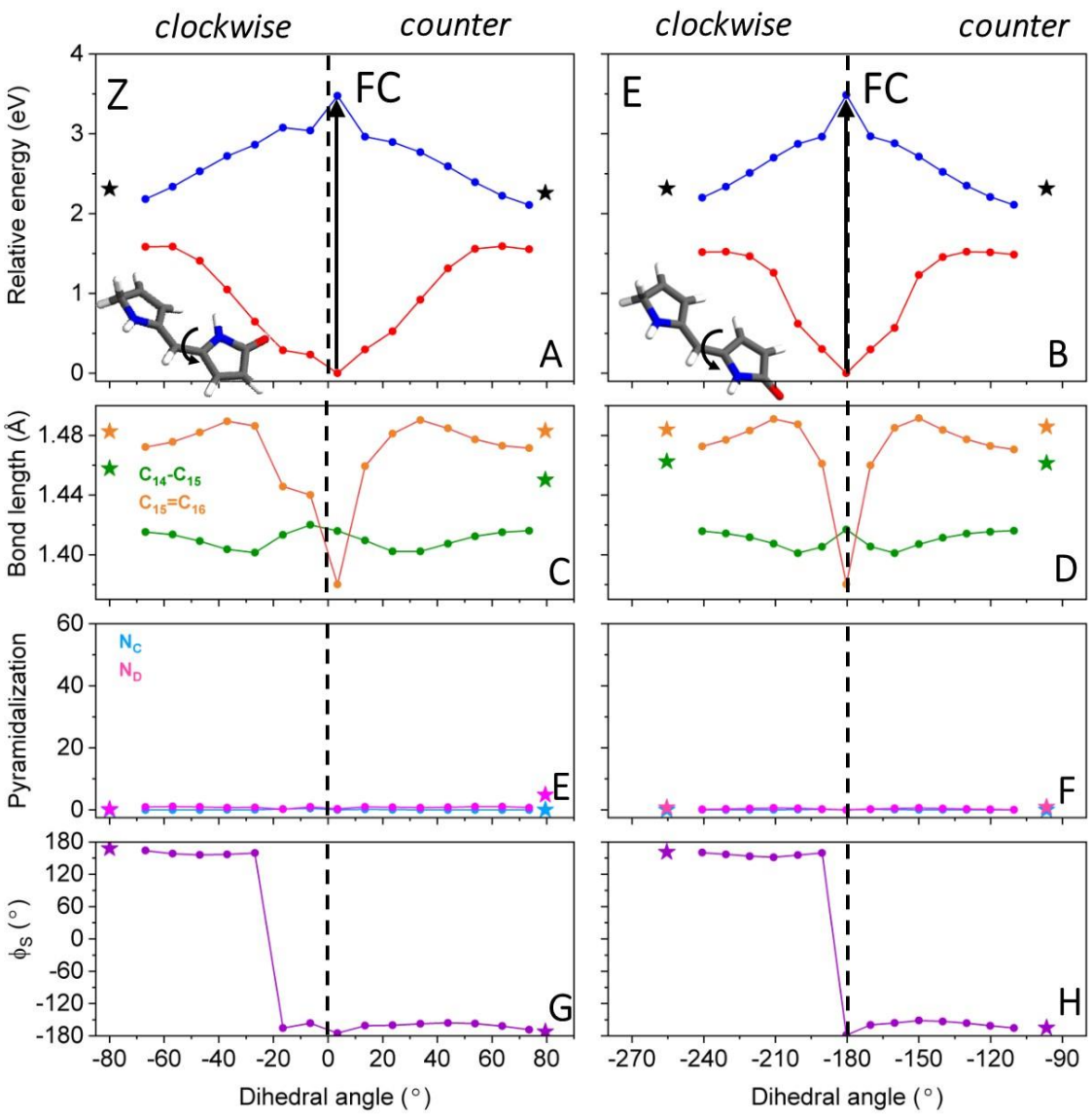

Fig. S9. Excited state relaxed scans of the DPN − CD_{min} model. **A, B** Excited state and ground state energies of the *Z* and *E* isomer. **C, D** Changes of the $C_{14} - C_{15}$ single bond and $C_{15} = C_{16}$ double bond. **E, F** Pyramidalization angle at the N_C and N_D atoms. G, H Changes of the ϕ_S dihedral angle. The star indicates the corresponding values at the MECI.

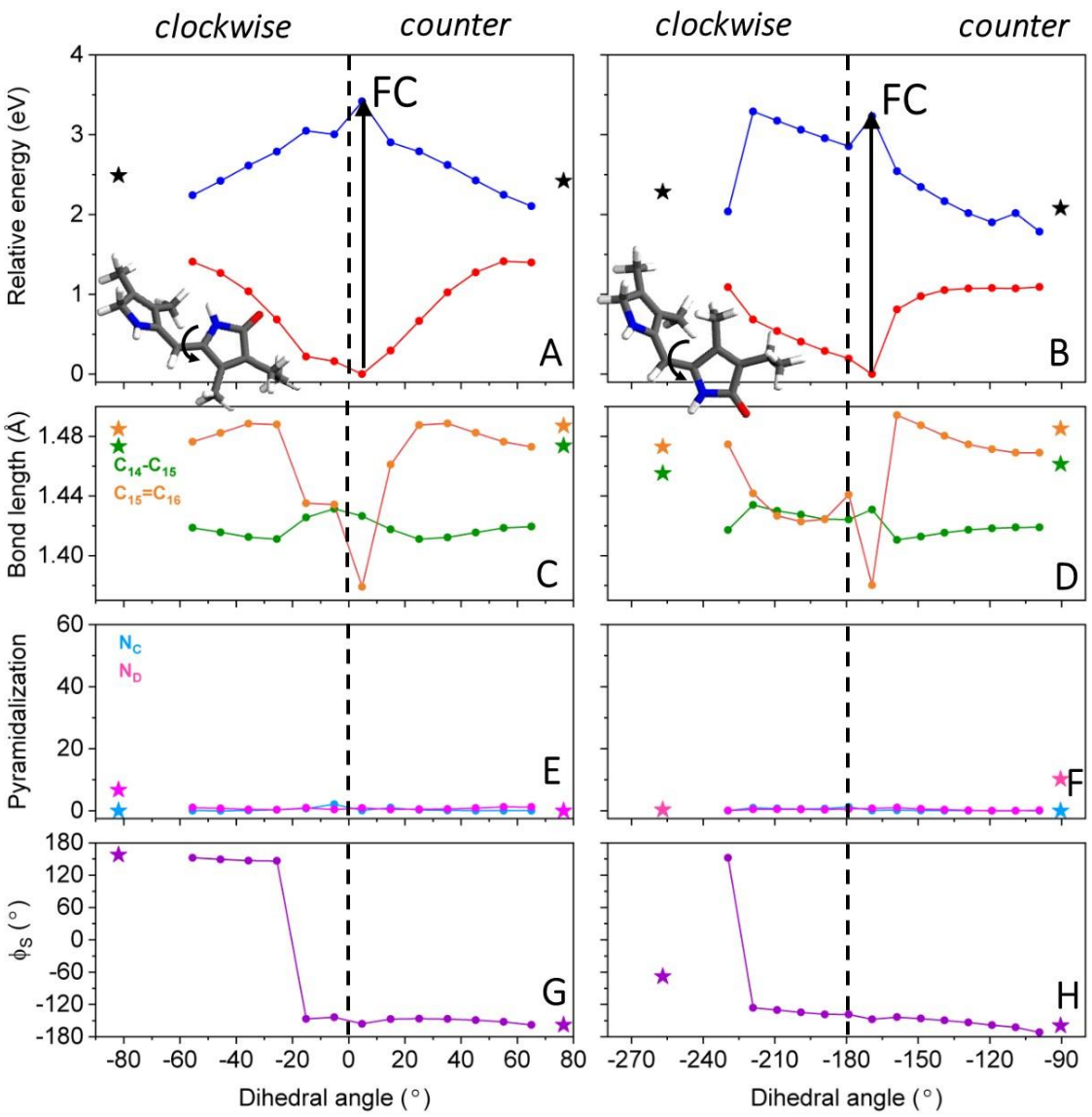

Fig. S10. Excited state relaxed scans of the DPN model. **A, B** Excited state and ground state energies of the Z and E isomer. **C, D** Changes of the $C_{14} - C_{15}$ single bond and $C_{15} = C_{16}$ double bond. **E, F** Pyramidalization angle at the N_C and N_D atoms. G, H Changes of the ϕ_S dihedral angle. The star indicates the corresponding values at the MECI.

4. Table of important parameters from LIICs

Table S3. Summary of important parameters computed at the MECIs for all the models in the *Z* conformation. "Cl" and "Co" stands for clockwise and counterclockwise directions respectively.

Parameter	DPY $-\mathrm{CD}_{\mathrm{min}}$		DPY $-\mathrm{CD}$		DPY $-\mathrm{CD}_{\mathrm{CH_2}}$		DPN $-\mathrm{CD}_{\mathrm{min}}$		DPN $-\mathrm{CD}$	
	Cl.	Co.	Cl.	Co.	Cl.	Co.	Cl.	Co.	Cl.	Co.
ϕ_S	-87°	-84°	-73°	-80°	-83°	-171°	172°	-176°	-157°	-158°
ϕ_D	-84°	63°	-74°	57°	-25°	71°	-74°	75°	-82°	77°
Barrier height from LIIC (eV)	0.47	0.07	0.23	0.06	0.00	0.00	0.17	0.00	1.53	0.00
Pyramidalization at C-ring	16°	30°	31°	35°	39°	0°	0°	0°	0	0°
Pyramidalization at D-ring	0°	0°	0°	0°	0°	11°	15°	16°	7°	0°

Table S4. Summary of important parameters computed at the MECIs and LIICs for all the models in the *E* conformation. "Cl" and "Co" stands for clockwise and counterclockwise directions respectively.

Parameter	DPY $-\mathrm{CD}_{\mathrm{min}}$		DPY $-\mathrm{CD}$		DPY $-\mathrm{CD}_{\mathrm{CH_2}}$		DPN $-\mathrm{CD}_{\mathrm{min}}$		DPN $-\mathrm{CD}$	
	Cl.	Co.	Cl.	Co.	Cl.	Co.	Cl.	Co.	Cl.	Co.
ϕ_S	95°	-95°	-56°	164°	13°	-179°	159°	-157°	-68°	-159°
ϕ_D	97	-97	116°	-60°	122°	-75°	107°	-89°	103°	-90°
Barrier height from LIIC (eV)	0.00	0.00	0.34	0.34	-	-	0.00	0.00	0.85	0.00
Pyramidalization at C-ring	4°	4°	40°	0°	0°	0°	0°	0°	0°	0°
Pyramidalization at D-ring	5°	4°	51°	0°	1°	15°	0°	18°	0°	10°