# Supporting Information (32 pages)

# for

# A Theoretical Study on the Nature of On- and Off-States of Reversibly Photoswitching Fluorescent Protein Dronpa: Absorption, Emission, Protonation and Raman

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**Complete citation of Reference 21:** Case, D. A.; Darden, T. A.; Cheatham, III, T. E.; Simmerling, C. L.; Wang, J.; Duke, R. E.; Luo, R.; Merz, K. M.; Wang, B.; Pearlman, D. A.; Crowley, M.; Brozell, S.; Tsui, V.; Gohlke, H.; Mongan, J.; Hornak, V.; Cui, G.; Beroza, P.; Schafmeister, C.; Caldwell, J. W.; Ross, W. S.; Kollman, P. A.; 2006, AMBER 9, University of California, San Francisco.

**Complete citation of Reference 23:** Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman; J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A., Gaussian03 Development Version, G.01 and G.03, Gaussian, Inc.: Wallingford, CT, 2007.

**Complete citation of Reference 33:** MOLPRO 2006.1 is a package of ab initio programs written by H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, P. Celani, T. Korona, G. Rauhut, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, A. W. Lloyd, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklaß, P. Palmieri, R. Pitzer, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni, and T. Thorsteinsson.

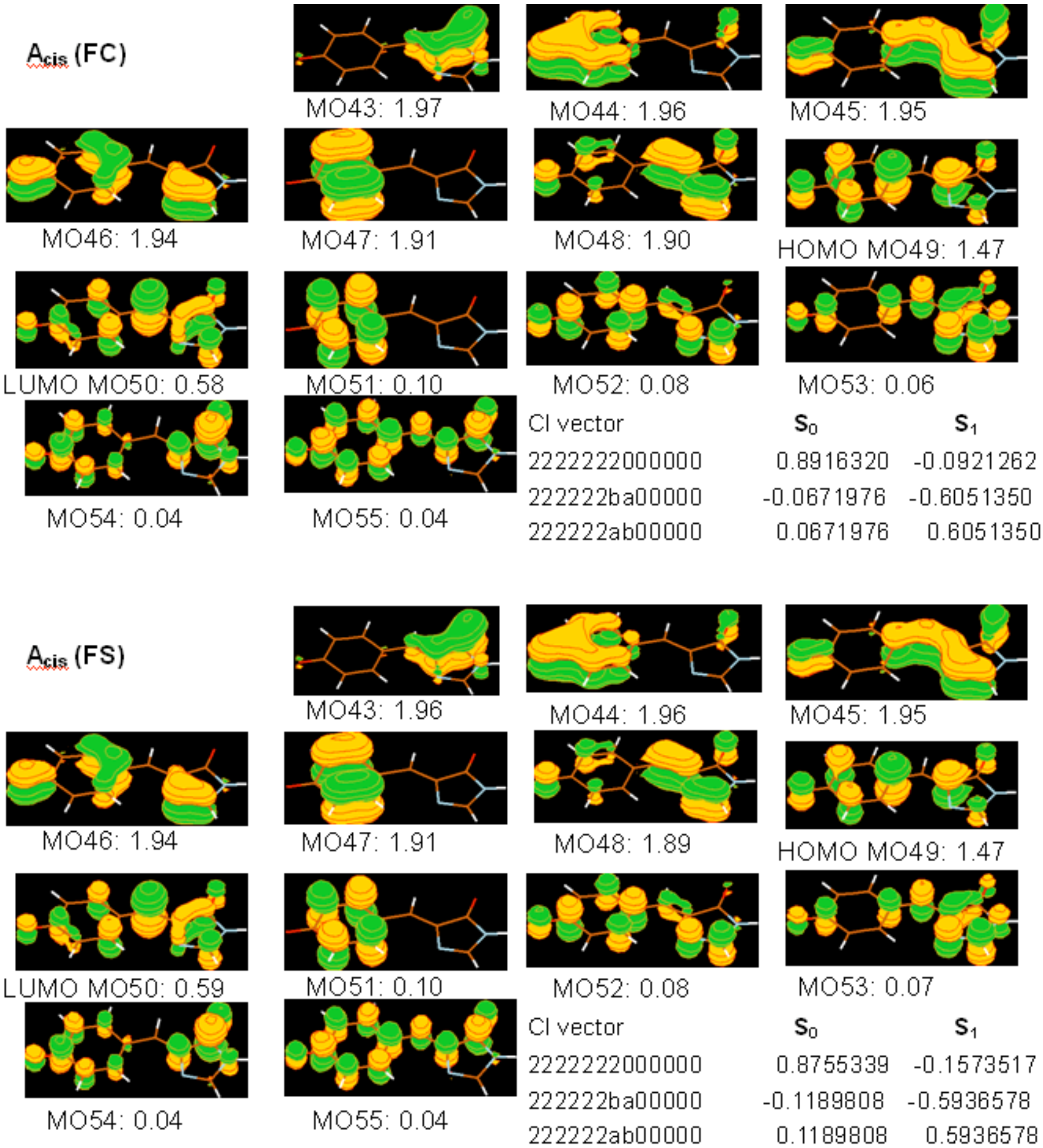



**Figure S1.** The active space of the ground state (FC) and excited state (FS) $\mathbf{A}_{\mathbf{cis}}$ for the SA2-CASSCF(14e,13o)/6-31G(d) calculation. The occupation numbers and major electronic configurations are also included. In this Supporting Information, **FC** (Frank-Condon) and **FS** (fluorescence state) were designated as the nearly planar ground-state and excited-state minimum, respectively.

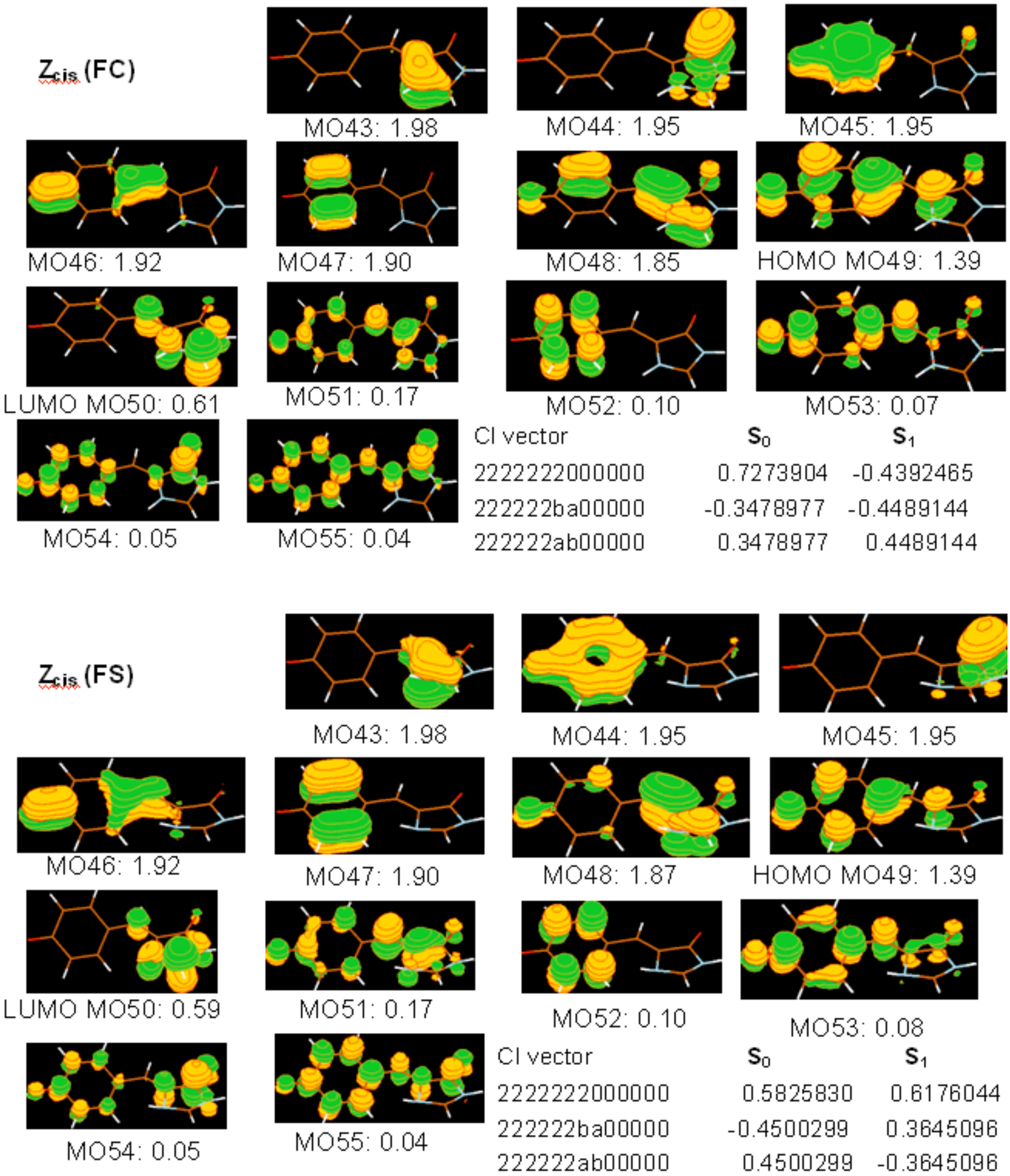



**Figure S2.** The active space of the ground state (FC) and excited state (FS) $\mathbf{Z_{cis}}$ for the SA2-CASSCF(14e,13o)/6-31G(d) calculation. The occupation numbers and major electronic configurations are also included.

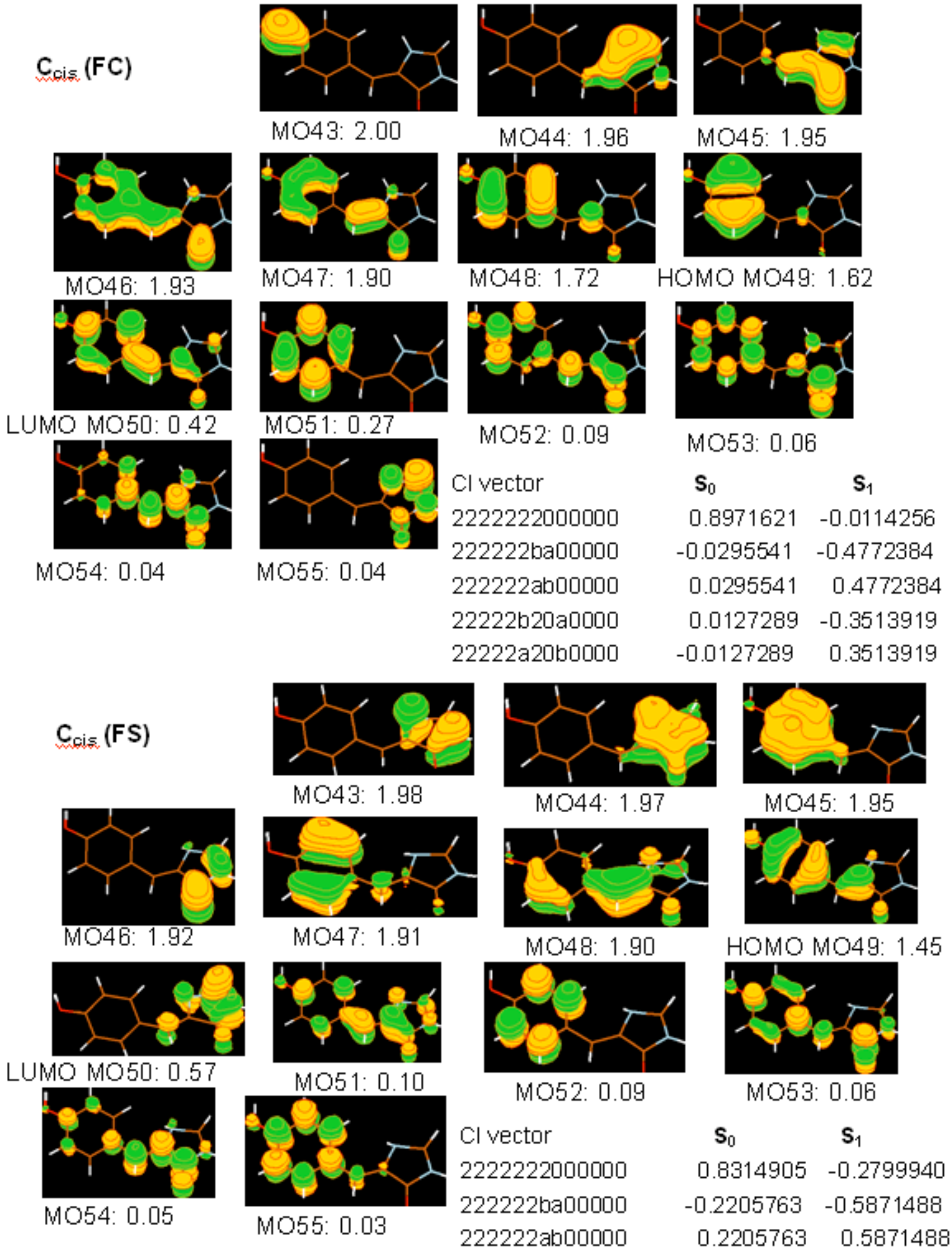
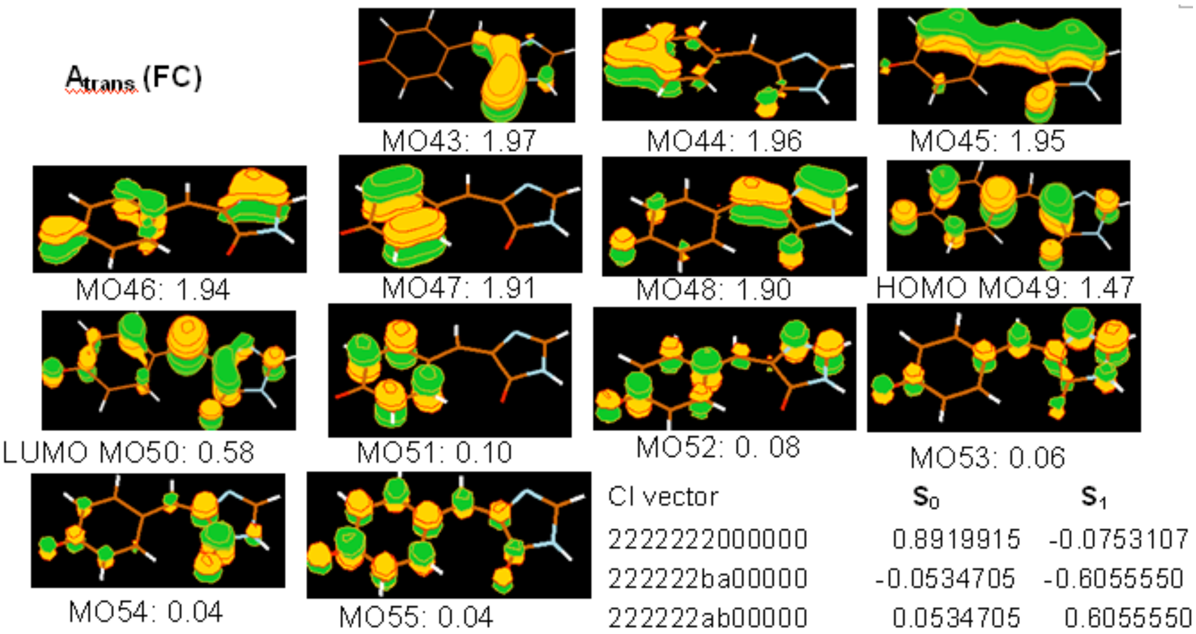



**Figure S3.** The active space of the ground state (FC) and excited state (FS) $\mathbf{C_{cis}}$ for the SA2-CASSCF(14e,13o)/6-31G(d) calculation. The occupation numbers and major electronic configurations are also included.



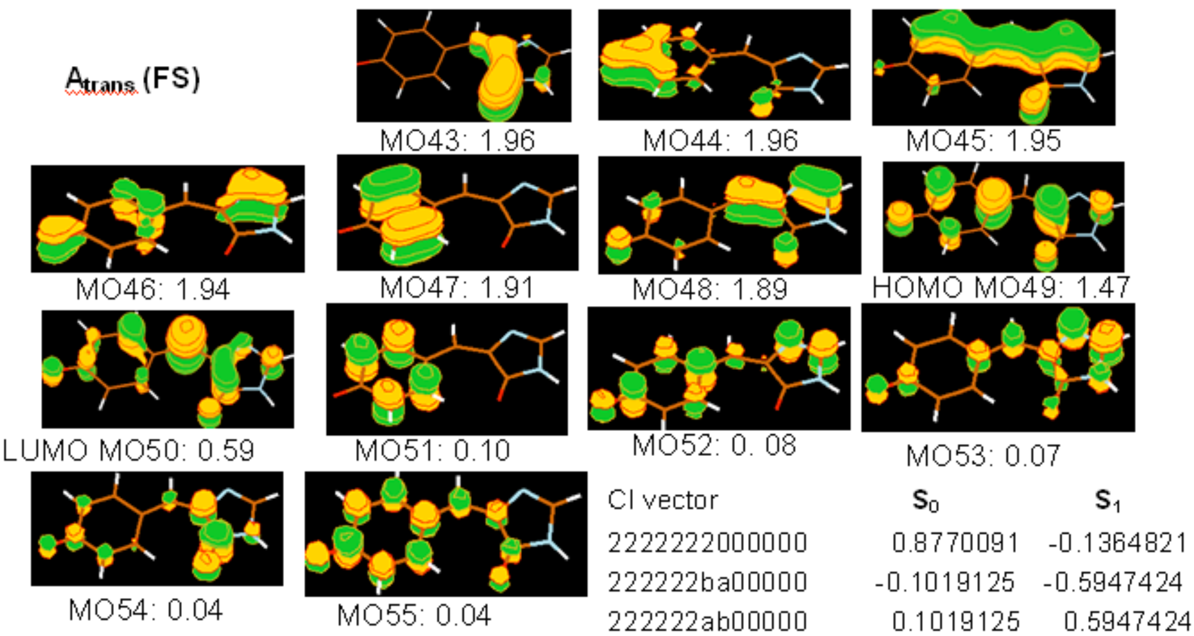




**Figure S4.** The active space of the ground state (FC) and excited state (FS) $\mathbf{A_{trans}}$ for the SA2-CASSCF(14e,13o)/6-31G(d) calculation. The occupation numbers and major electronic configurations are also included.

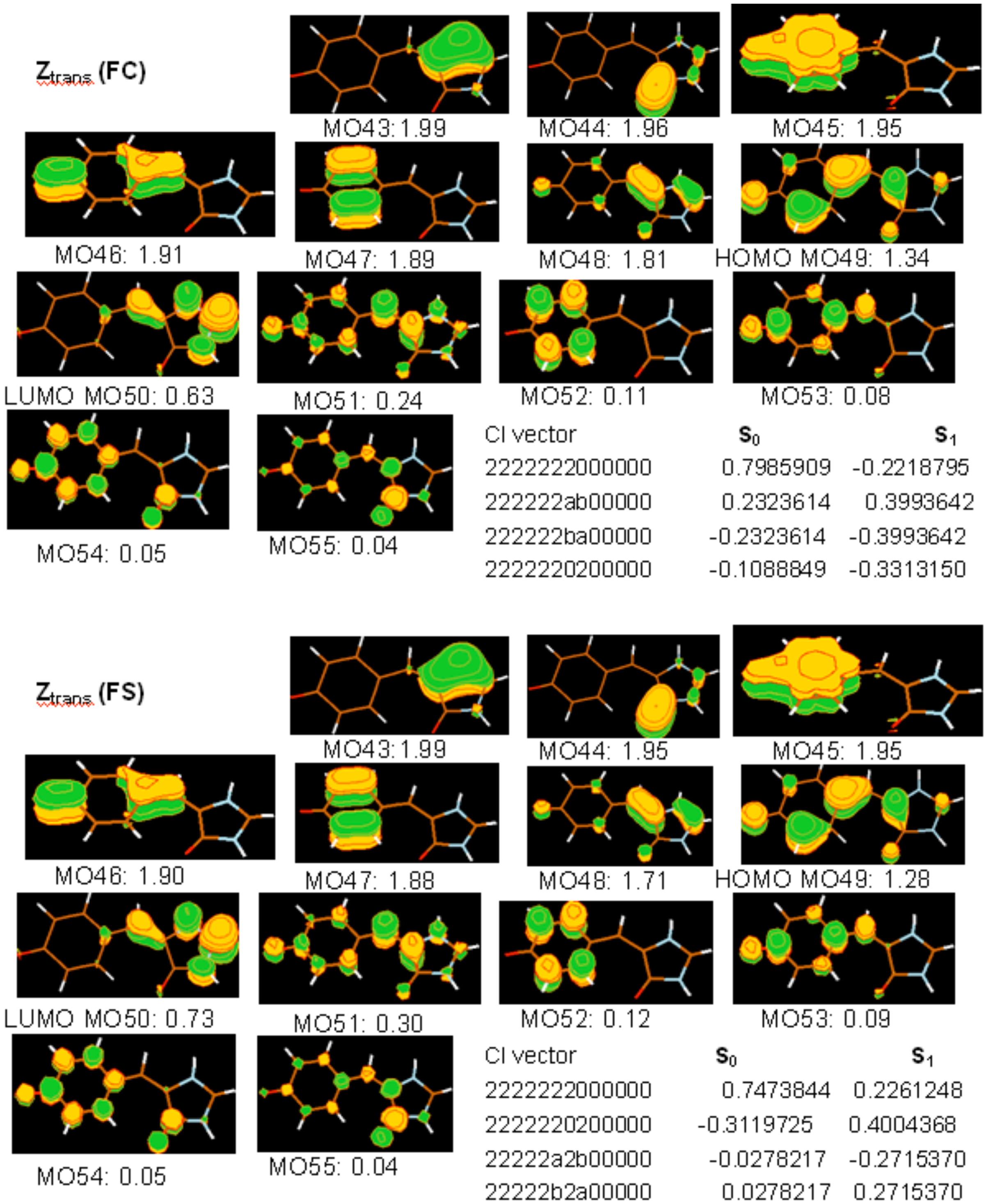



**Figure S5.** The active space of the ground state (FC) and excited state (FS) $\mathbf{Z_{trans}}$ for the SA2-CASSCF(14e,13o)/6-31G(d) calculation. The occupation numbers and major electronic configurations are also included.

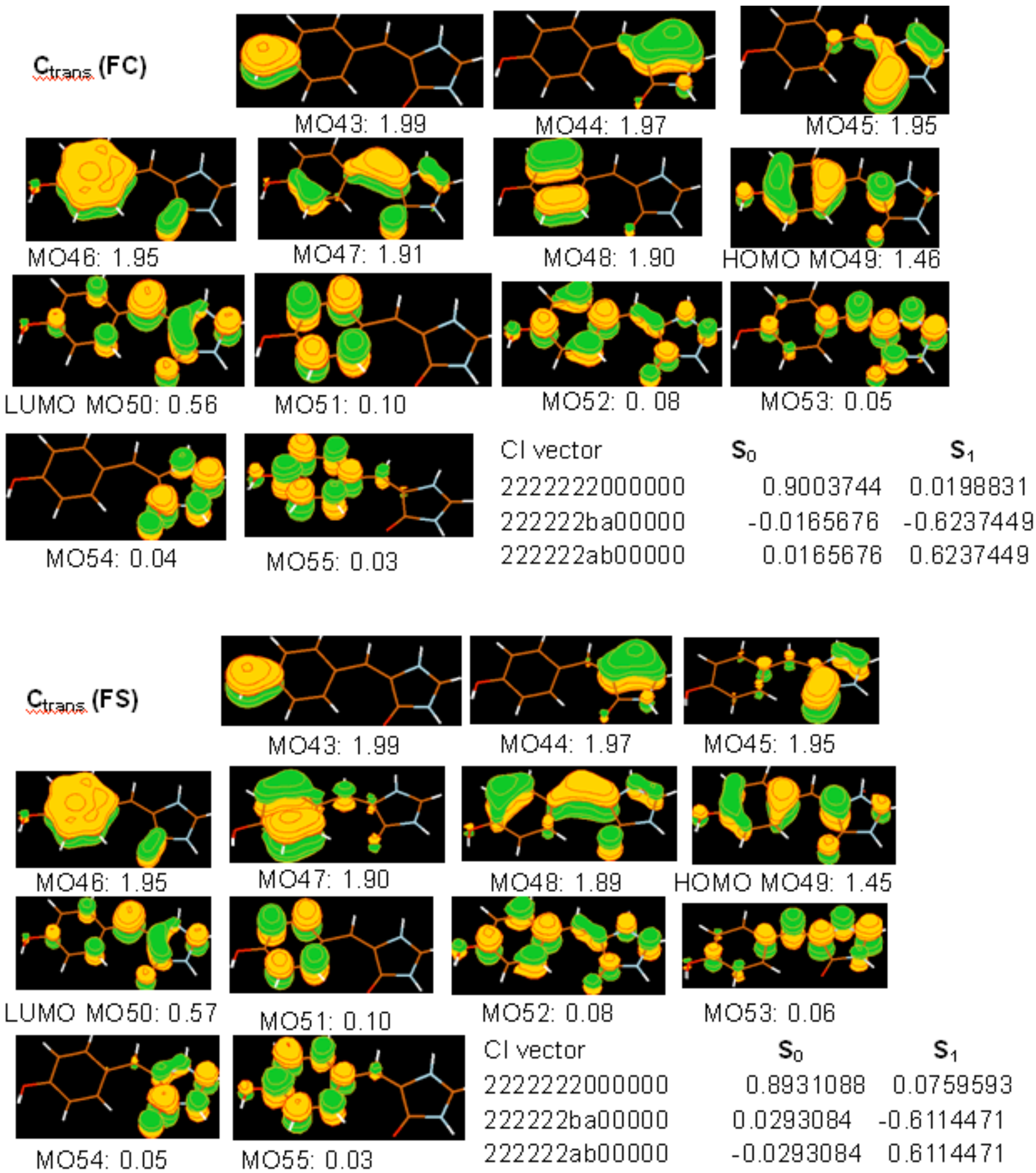
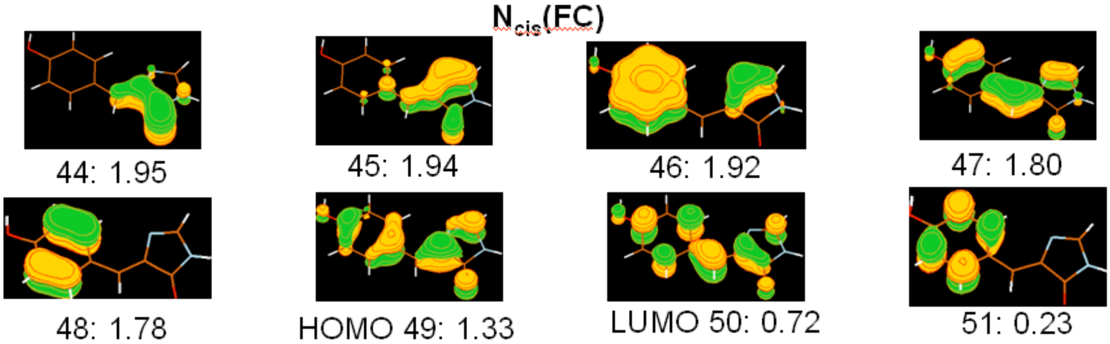
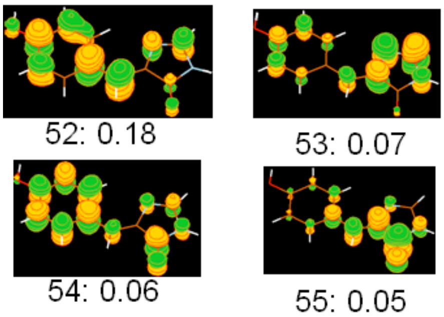



**Figure S6.** The active space of the ground state (FC) and excited state (FS) $\mathbf{C_{trans}}$ for the SA2-CASSCF(14e,13o)/6-31G(d) calculation. The occupation numbers and major electronic configurations are also included.

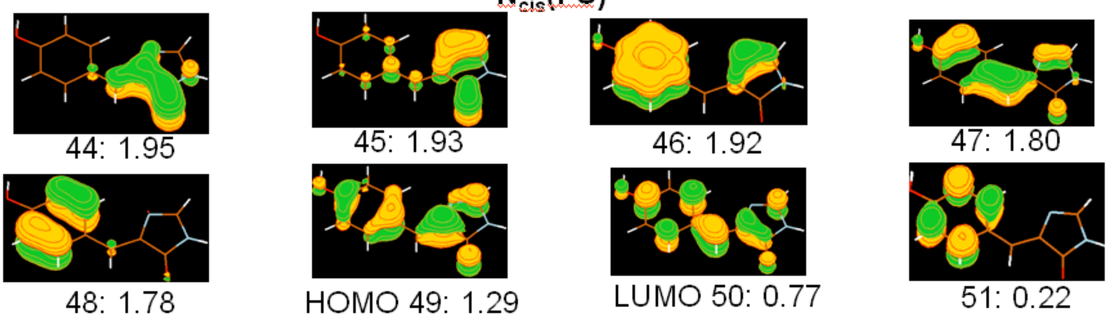
### $N_{cis}$(FC)

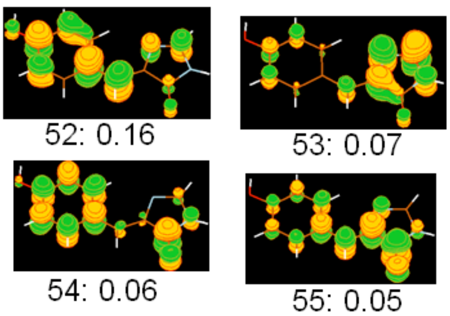



| CI vector | 1.1 | 2.1 | 3.1 | 4.1 |
|---|---|---|---|---|
| 222222000000 | 0.8723893 | 0.0075977 | -0.0239981 | 0.1838104 |
| 22222ba00000 | 0.0917225 | -0.0271680 | 0.1393445 | -0.5928590 |
| 22222ab00000 | -0.0917225 | 0.0271680 | -0.1393445 | 0.5928590 |
| 222220200000 | -0.1197194 | 0.0218366 | 0.5201259 | 0.1203731 |
| 22222a0b0000 | -0.0043699 | 0.3875213 | -0.0181414 | -0.0084862 |
| 22222b0a0000 | 0.0043699 | -0.3875213 | 0.0181414 | 0.0084862 |
| 2222b2a00000 | -0.0064279 | -0.3674091 | -0.0833663 | 0.0035008 |
| 2222a2b00000 | 0.0064279 | 0.3674091 | 0.0833663 | -0.0035008 |

### $N_{cis}$(FS)

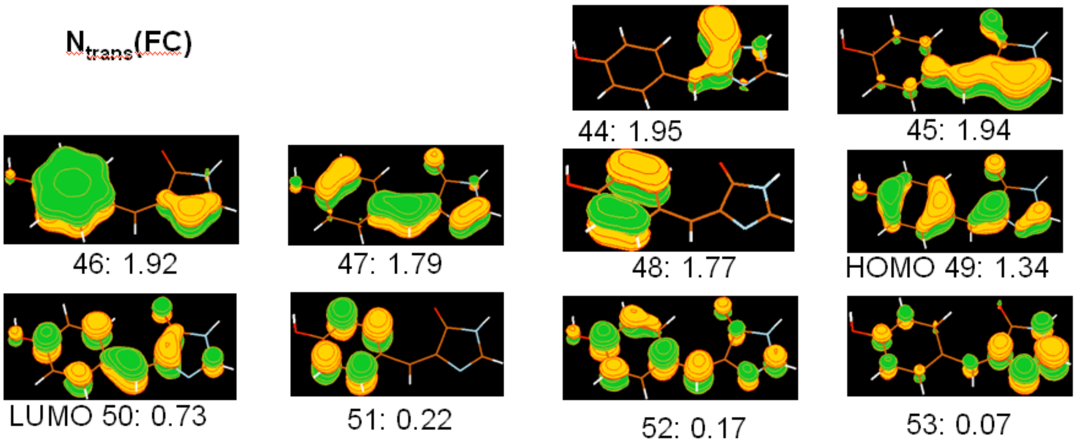


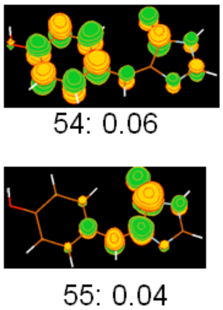




| CI vector | 1.1 | 2.1 | 3.1 | 4.1 |
|---|---|---|---|---|
| 222222000000 | 0.8395509 | 0.0616543 | -0.1058673 | -0.2777844 |
| 22222ba00000 | 0.1608106 | -0.0821053 | 0.1286930 | 0.5576942 |
| 22222ab00000 | -0.1608106 | 0.0821053 | -0.1286930 | -0.5576942 |
| 222220200000 | -0.1569534 | 0.2220322 | -0.4841561 | 0.1240707 |
| 22222b0a0000 | 0.0071985 | -0.3551159 | -0.1558990 | -0.0022525 |
| 22222a0b0000 | -0.0071985 | 0.3551159 | 0.1558990 | 0.0022525 |
| 2222b2a00000 | -0.0028297 | -0.3438470 | -0.0293788 | -0.0508882 |
| 2222a2b00000 | 0.0028297 | 0.3438470 | 0.0293788 | 0.0508882 |
| 222a22b00000 | 0.0104034 | 0.0013992 | -0.3139789 | 0.0518790 |
| 222b22a00000 | -0.0104034 | -0.0013992 | 0.3139789 | -0.0518790 |

**Figure S7.** The active space of the ground state (FC) and excited state (FS) $\mathbf{N_{cis}}$ for the SA4-CASSCF(12e,12o)/6-31G(d) calculation. The ground and excited-state chromophore are optimized by SA2-CASSCF(12e,12o)/6-31G(d) and SA4-CASSCF(12e,12o)/6-31G(d) levels, respectively. The occupation numbers and major electronic configurations are also included.

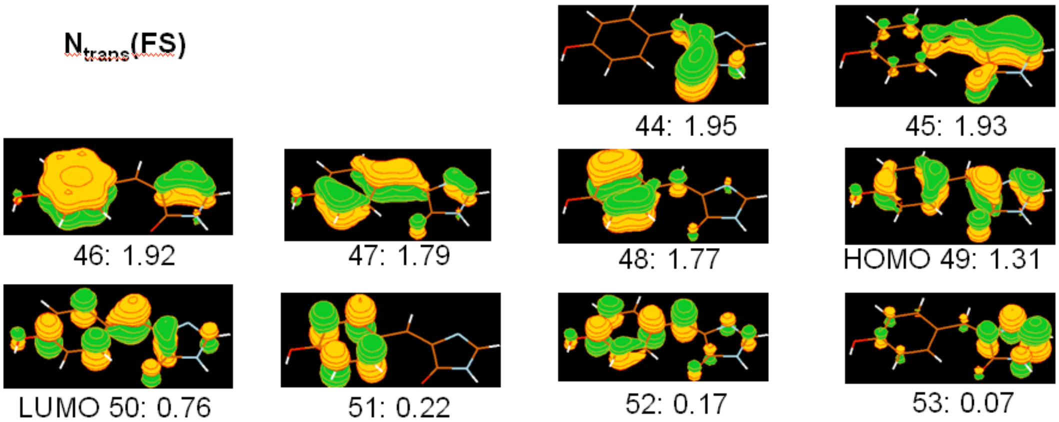
$N_{trans}$(FC)

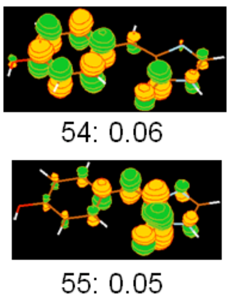



| CI vector | 1.1 | 2.1 | 3.1 | 4.1 |
|---|---|---|---|---|
| 222222000000 | 0.8707121 | -0.0086856 | -0.0121985 | 0.2022340 |
| 22222ba00000 | -0.0990330 | -0.0206498 | -0.0836766 | 0.5972057 |
| 22222ab00000 | 0.0990330 | 0.0206498 | 0.0836766 | -0.5972057 |
| 222220200000 | -0.1175999 | -0.0203705 | 0.5217071 | 0.0736095 |
| 22222a0b0000 | 0.0062430 | 0.3850644 | 0.0184169 | 0.0002205 |
| 22222b0a0000 | -0.0062430 | -0.3850644 | -0.0184169 | -0.0002205 |
| 2222b2a00000 | -0.0039588 | 0.3713631 | -0.0870511 | 0.0105394 |
| 2222a2b00000 | 0.0039588 | -0.3713631 | 0.0870511 | -0.0105394 |
| 222b22a00000 | 0.0191989 | 0.0887665 | 0.3177717 | 0.0718853 |
| 222a22b00000 | -0.0191989 | -0.0887665 | -0.3177717 | -0.0718853 |

$N_{trans}$(FS)




| CI vector | 1.1 | 2.1 | 3.1 | 4.1 |
|---|---|---|---|---|
| 222222000000 | 0.8378546 | -0.0731263 | -0.1448728 | -0.2711431 |
| 22222ba00000 | -0.1669060 | -0.1027379 | -0.2186164 | -0.5140417 |
| 22222ab00000 | 0.1669060 | 0.1027379 | 0.2186164 | 0.5140417 |
| 222220200000 | -0.1501627 | -0.2140584 | -0.4471823 | 0.1941220 |
| 22222b0a0000 | -0.0089176 | -0.3495418 | 0.1563148 | -0.0124956 |
| 22222a0b0000 | 0.0089176 | 0.3495418 | -0.1563148 | 0.0124956 |
| 2222b2a00000 | 0.0008810 | 0.3461176 | -0.0045140 | -0.0733380 |
| 2222a2b00000 | -0.0008810 | -0.3461176 | 0.0045140 | 0.0733380 |
| 222b22a00000 | 0.0030878 | 0.0385152 | -0.3117530 | 0.0969959 |
| 222a22b00000 | -0.0030878 | -0.0385152 | 0.3117530 | -0.0969959 |

**Figure S8.** The active space of the ground state (FC) and excited state (FS) $\mathbf{N_{trans}}$ for the SA4-CASSCF(12e,12o)/6-31G(d) calculation. The ground and excited-state chromophore are optimized by SA2-CASSCF(12e,12o)/6-31G(d) and SA4-CASSCF(12e,12o)/6-31G(d) levels, respectively. The occupation numbers and major electronic configurations are also included.

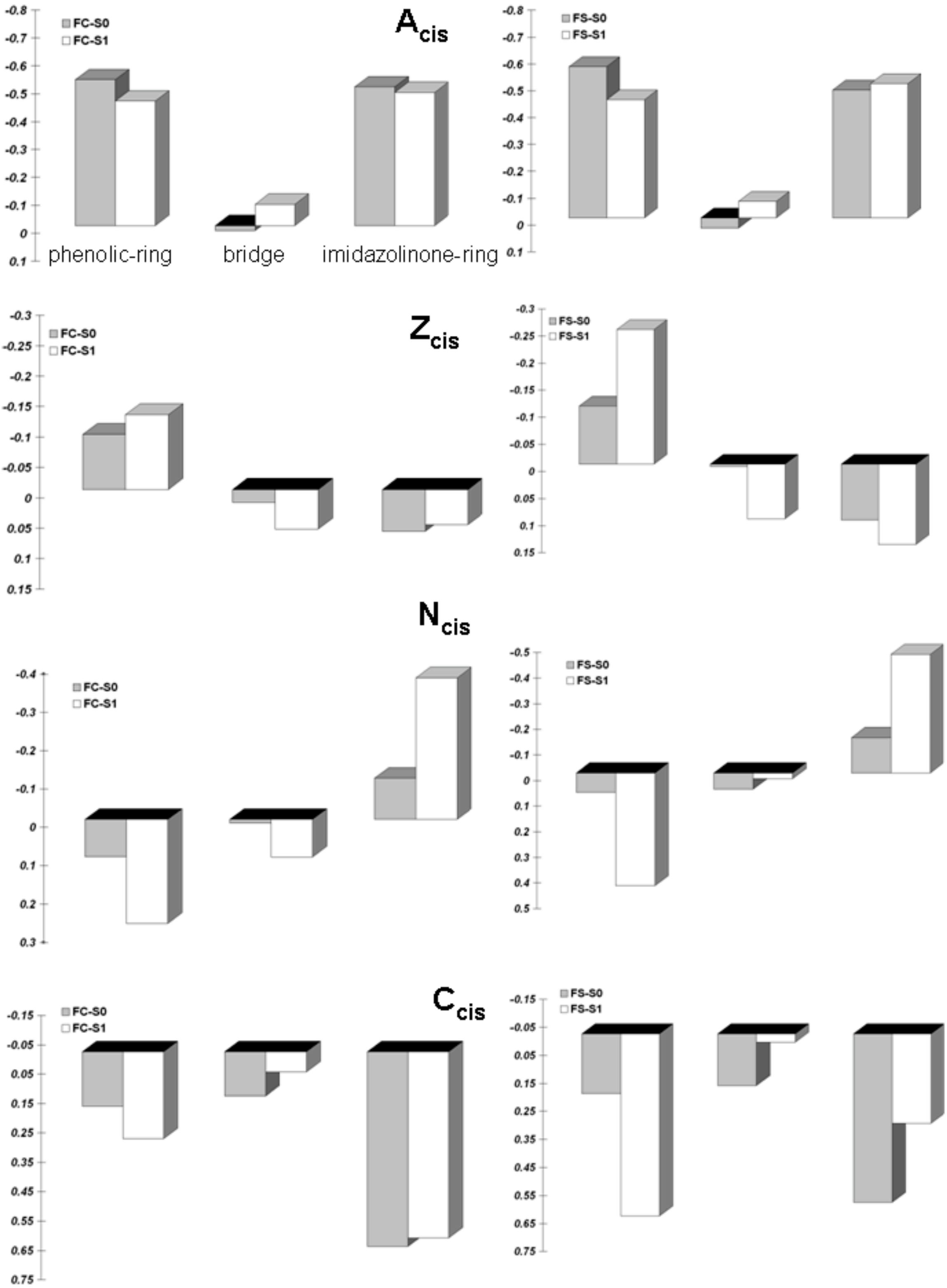



**Figure S9.** The $S_0$ and $S_1$ Mulliken charge analysis at **FS** and **FC** of the *cis* chromophores in four protonation states calculated by the SA2-CASSCF(14e,13o)/6-31G(d) method, except for $\mathbf{N_{cis}}$ by SA4-CASSCF(12e,12o)/6-31G(d).

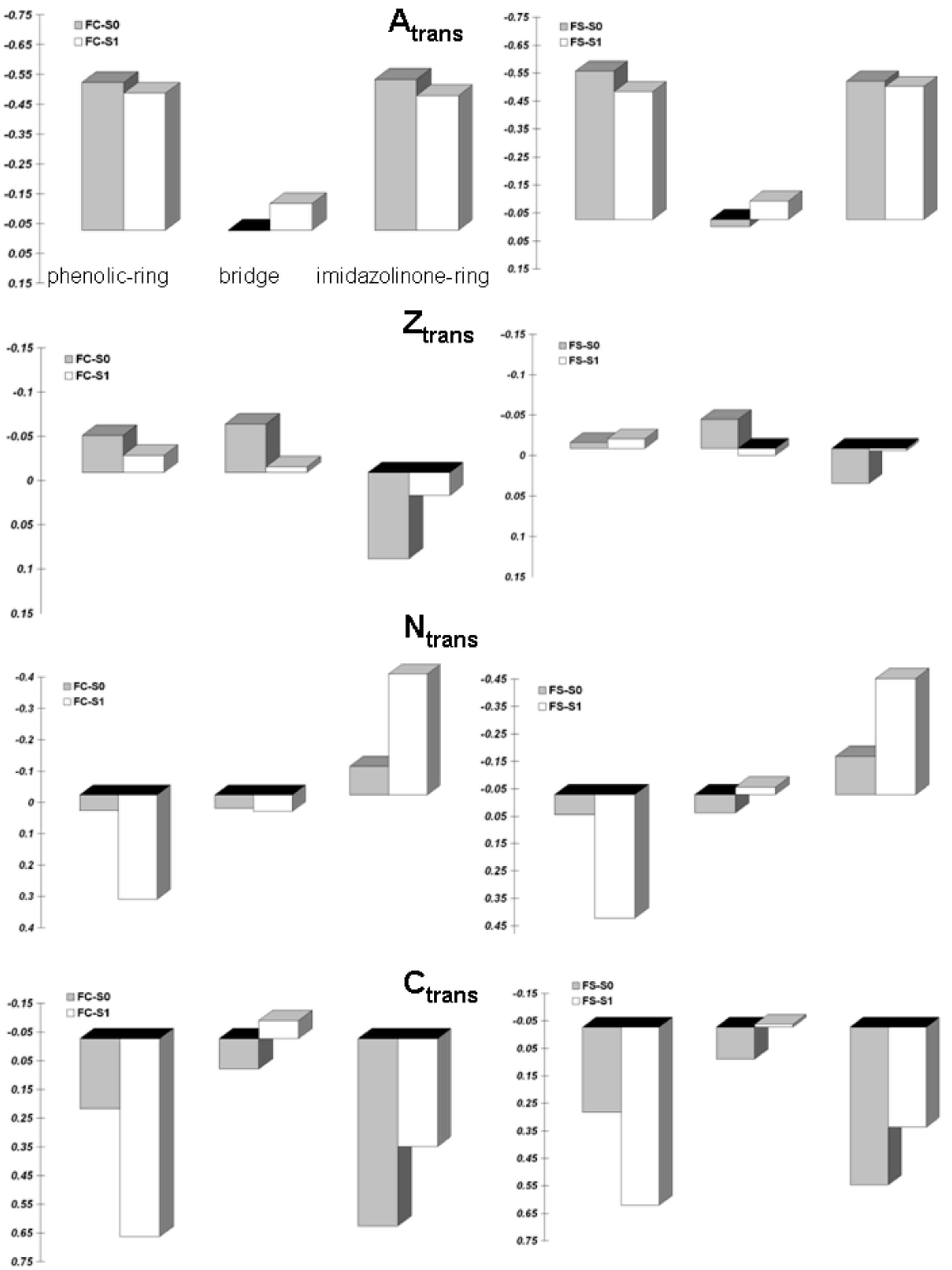



**Figure S10.** The $S_0$ and $S_1$ Mulliken charge analysis at **FS** and **FC** of the *trans* chromophores in four protonation states calculated by the SA2-CASSCF(14e,13o)/6-31G(d) method, except for $\mathbf{N_{trans}}$ by SA4-CASSCF(12e,12o)/6-31G(d).

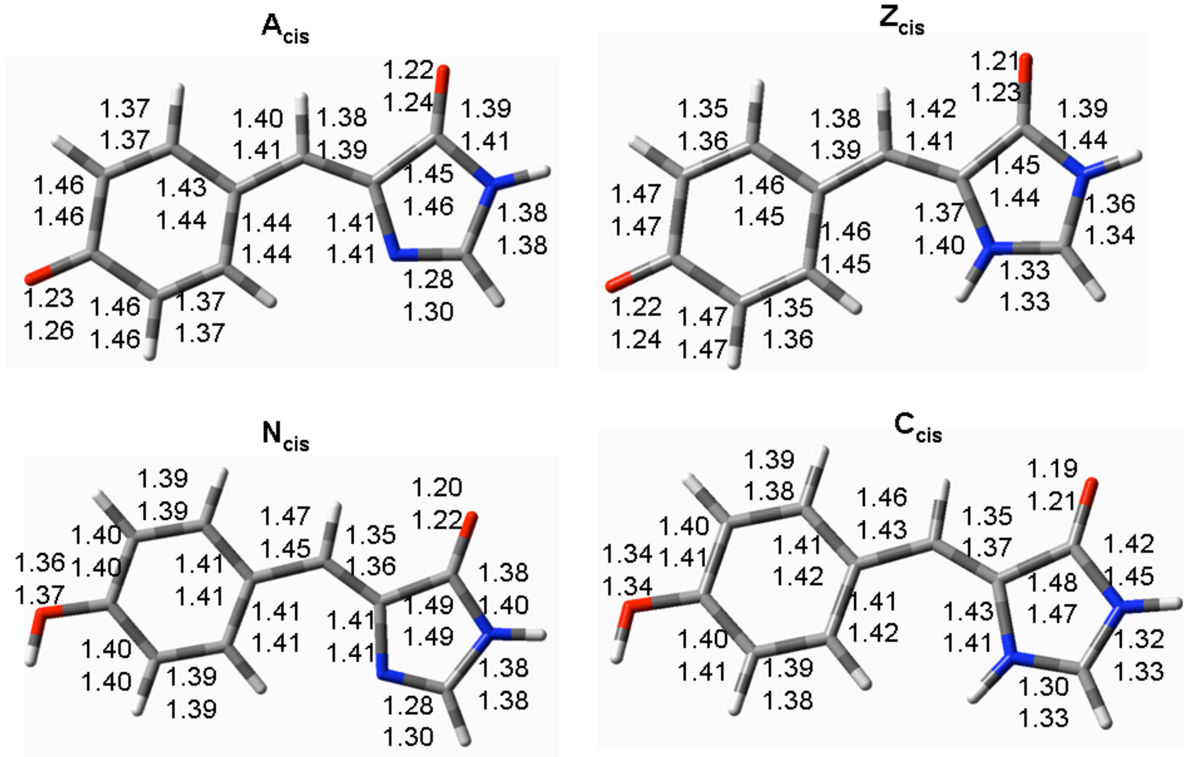



**Figure S11.** The bond lengths of the *cis* conformers at **FC** optimized by the SA2-CASSCF(14e,13o)/6-31G(d) (upper) and B3LYP/6-31+G(d,p) methods (lower).

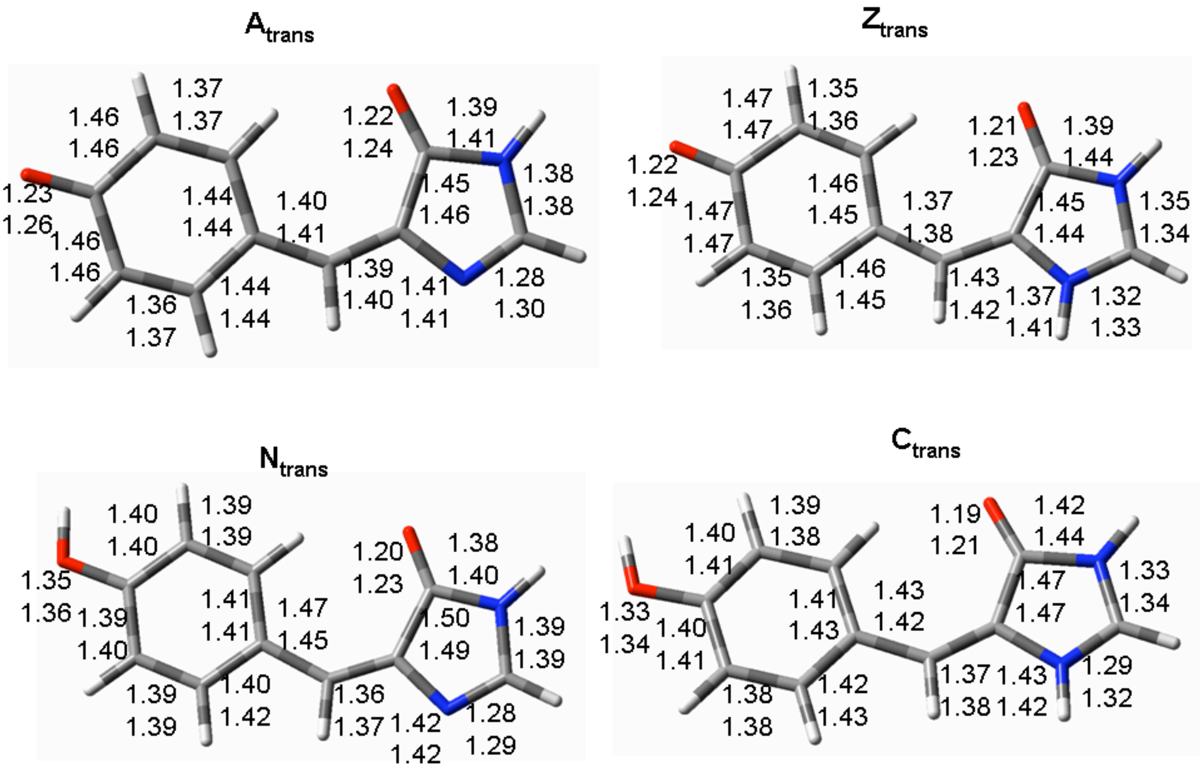



**Figure S12.** The bond lengths of the *trans* conformers at **FC** optimized by the SA2-CASSCF(14e,13o)/6-31G(d) (upper) and B3LYP/6-31+G(d,p) methods (lower).

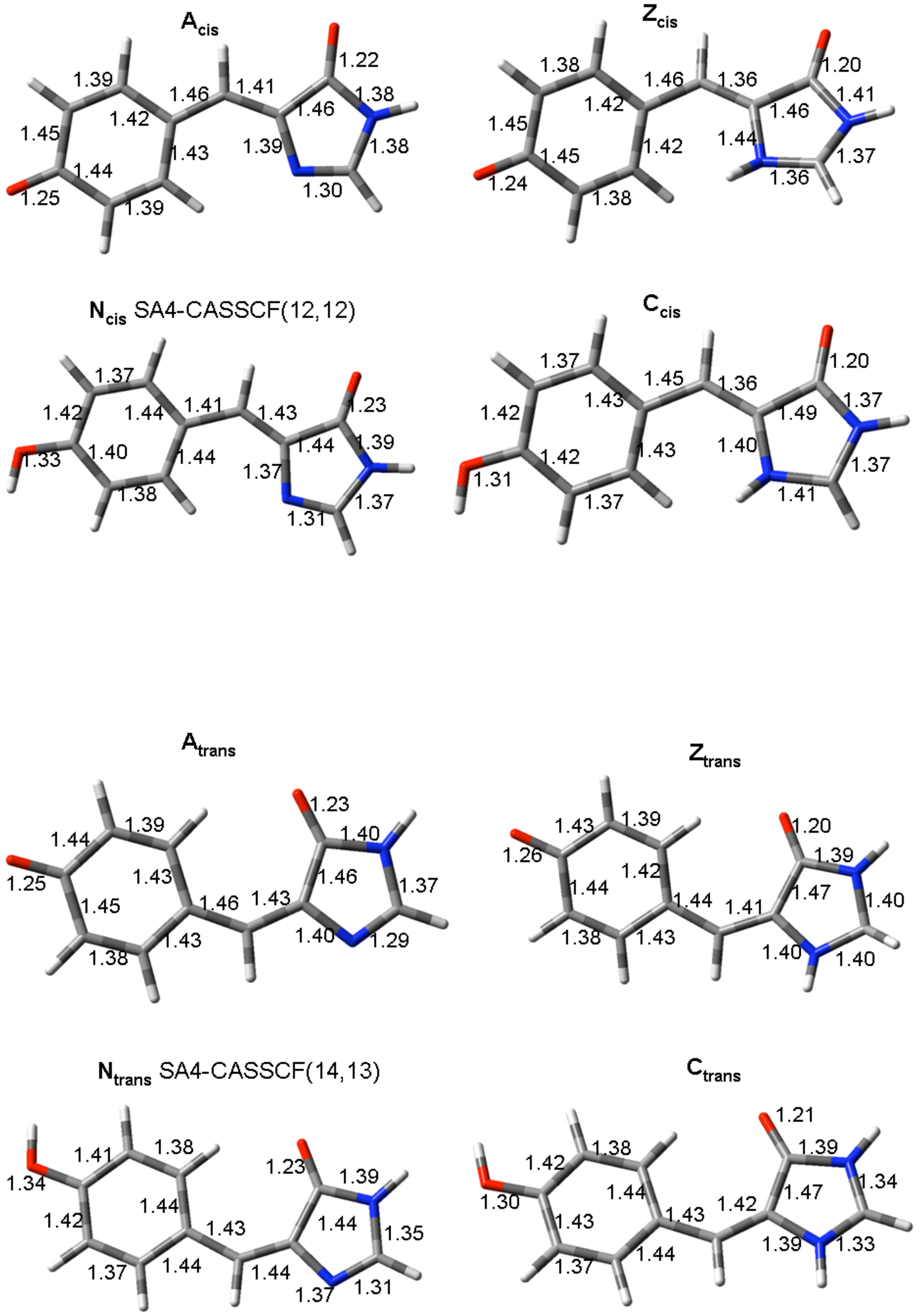



**Figure S13.** The bond lengths of the *cis* and *trans* conformers at **FS** optimized by the SA2-CASSCF(14e,13o)/6-31G(d) method. The $\mathbf{N_{cis}}$ and $\mathbf{N_{trans}}$ were optimized by the SA4-CASSCF(12e,12o)/6-31G(d) and SA4-CASSCF(14e,13o)/6-31G(d) methods, respectively.

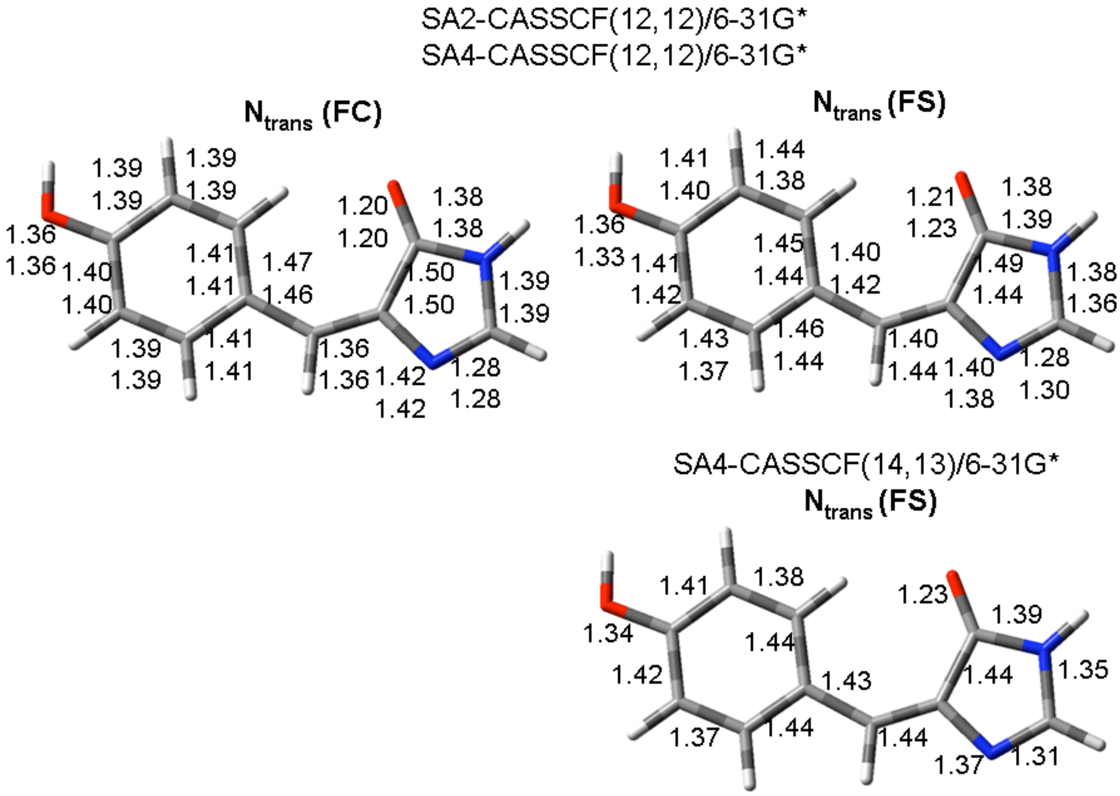



**Figure S14.** The bond lengths of $\mathbf{N_{trans}}$ at **FC** and **FS** optimized by the SA2-CASSCF(12e,12o)/6-31G(d), SA4-CASSCF(12e,12o)/6-31G(d) and SA4-CASSCF(14e, 13o)/6-31G(d) methods, respectively.

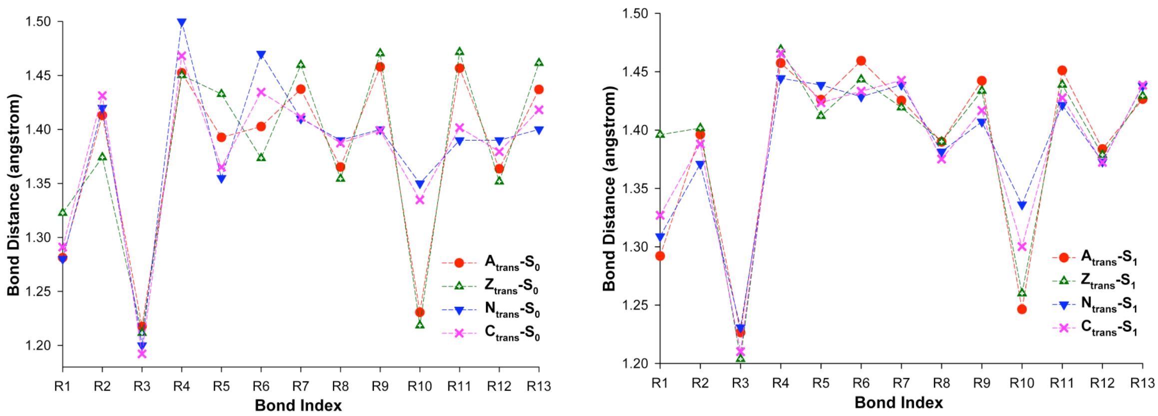



**Figure S15**. The key bond lengths of the ground-state (left) and excited-state (right) *trans* chromophore at the different protonation states in the gas phase calculated by the SA2-CASSCF(14e,13o)/6-31G(d) method, except for the excited-state $\mathbf{N_{trans}}$ by SA4-CASSCF(14e,13o)/6-31G(d) method.

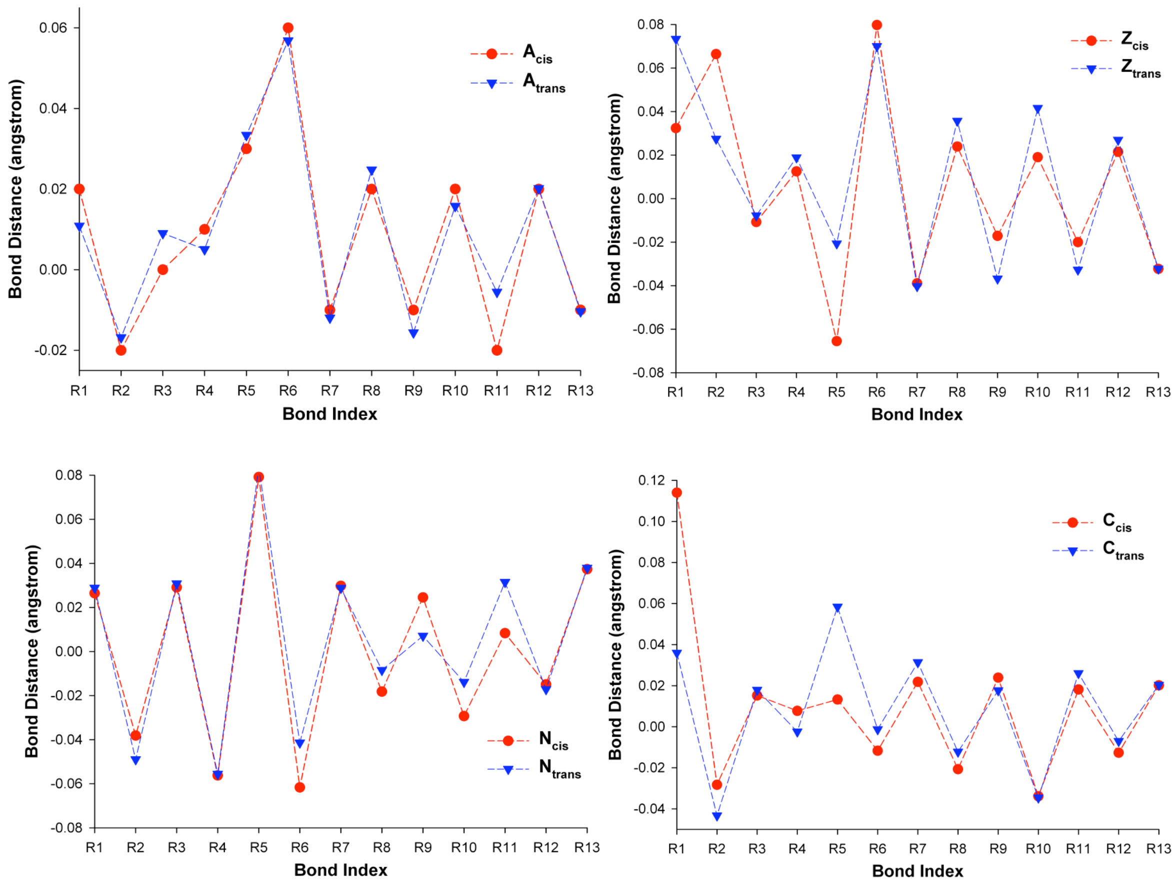



**Figure S16.** The bond length differences between the excited state and ground state chromophores in the gas phase calculated by the SA2-CASSCF(14e,13o)/6-31G(d) method, except for the excited-state $\mathbf{N_{cis}}$ and $\mathbf{N_{trans}}$ by SA4-CASSCF(12e,12o)/6-31G(d) and SA4-CASSCF(14e,13o)/6-31G(d) methods, respectively.

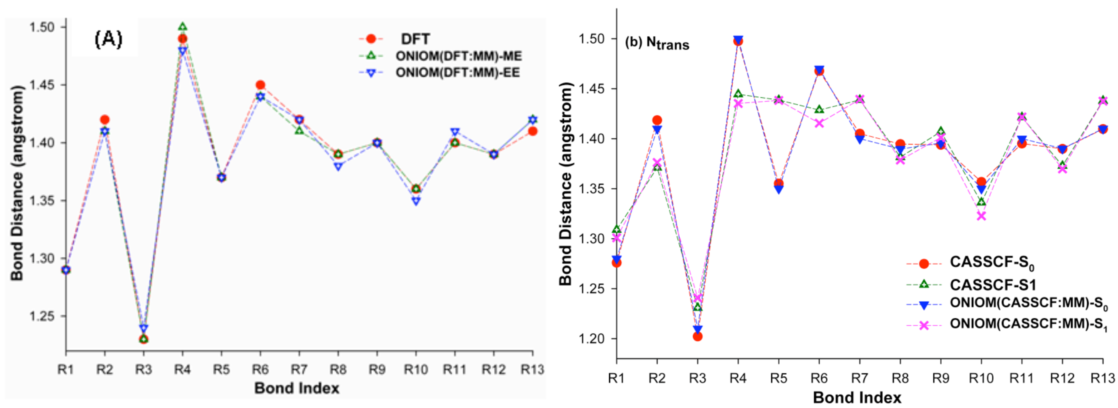



**Figure S17.** Calculated key bond lengths of $\mathbf{N_{trans}}$: (A) the ground state chromophore in the gas phase by the B3LYP/6-31+G(d,p) method and in the protein by the ONIOM(B3LYP/ 6-31+G(d,p):AMBER)-ME and -EE methods. (B) the ground state ($S_0$) and excited state ($S_1$) chromophore in the gas phase by the state-average (SA) CASSCF(12e,12o)/6-31G(d) method and in the protein by the ONIOM(SA-CASSCF(12e,12o)/6-31G(d):AMBER)-ME method. Two-state-average (SA2) for the ground state and four-state-average (SA4) for the excited state.

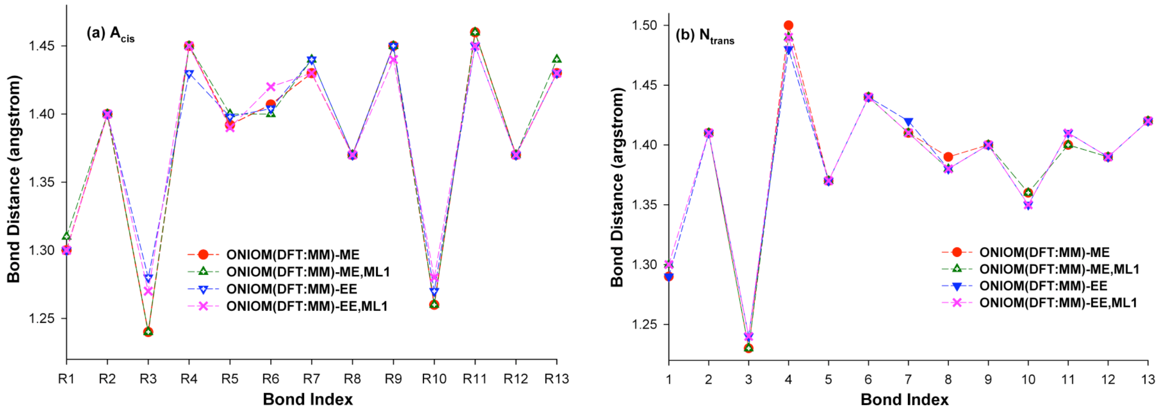



**Figure S18.** The key bond lengths of the ground state chromophores in the proteins calculated by the ONIOM(B3LYP/6-31+G(d,p):AMBER)-EE and -ME methods for both small QM model and larger QM model.

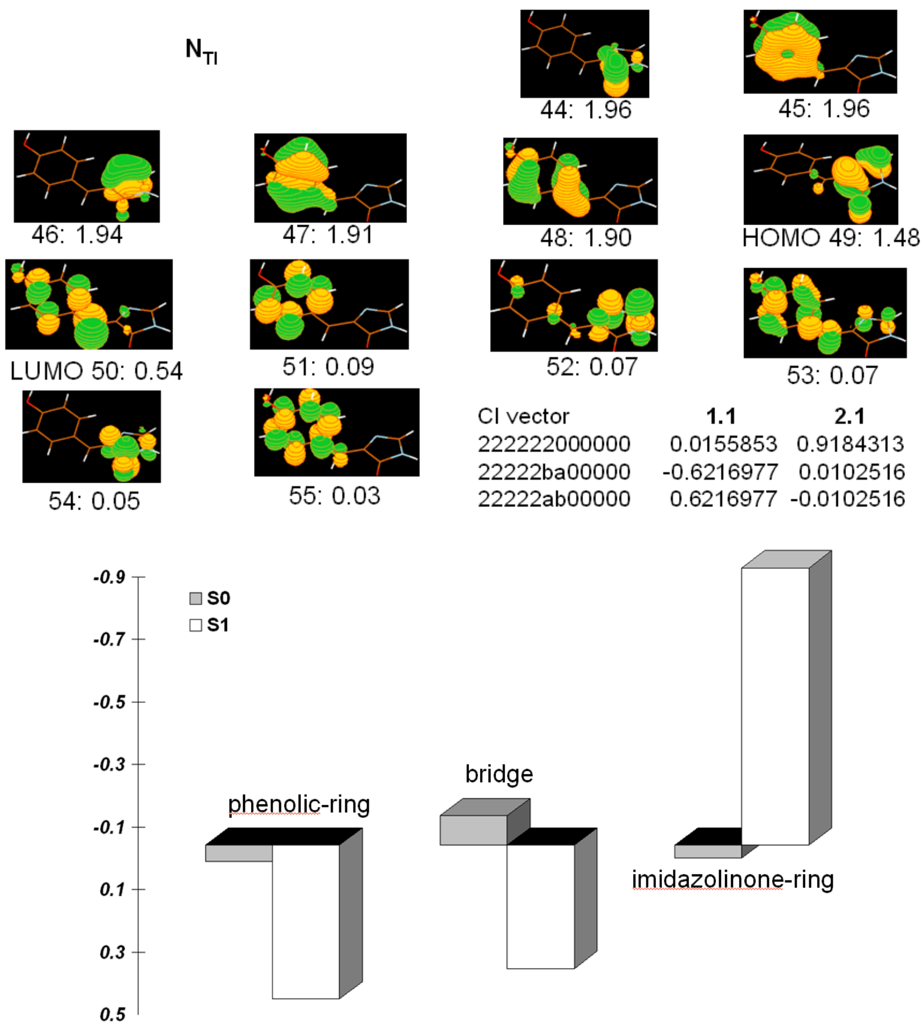



**Figure S19.** The active space of $\mathbf{N_{TI}}$ in the SA2-CASSCF(12e,12o)/6-31G(d) calculation (top). The occupation numbers and major electronic configurations are also included. The Mulliken charge analysis at $\mathbf{N_{TI}}$ by the SA2-CASSCF(12e,12o)/6-31G(d) method (bottom).

**Raman Spectra:** As shown in Figures S11-S12, the chromophore skeleton is partly altered by the protonation state of the chromophore. Such structural changes should be reflected by IR and Raman spectrum. For the simple illustration, the calculated Raman spectra for $\mathbf{A_{cis}}$, $\mathbf{Z_{cis}}$ and $\mathbf{N_{trans}}$ in the gas-phase are showed in Figure S20. The experimental Raman spectra of the anionic and neutral GFP analogues in solution[1,2] show different Raman markers for the different protonated states, which provide a clear signature in the double bond stretching region between 1500 and 1700 $cm^{-1}$. The Raman spectra calculated in the gas-phase show different dominant bands for $\mathbf{A_{cis}}$ (1592.8 $cm^{-1}$), $\mathbf{N_{trans}}$ (1593.3 $cm^{-1}$) and $\mathbf{Z_{cis}}$ (1616.9 $cm^{-1}$). $\mathbf{Z_{cis}}$ has a higher wave number for the marker band of the C=O, C=C and C=N stretching mode than $\mathbf{A_{cis}}$. Therefore, the Raman spectra can also help assign the protonation state of Dronpa and other fluorescence proteins, such as asFP595.[3]

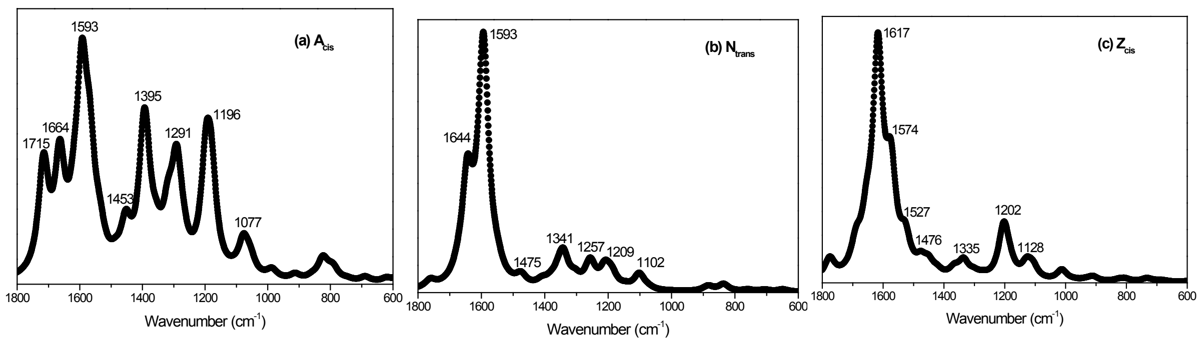



**Figure S20.** Raman spectra for (a) $\mathbf{A_{cis}}$, (b) $\mathbf{N_{trans}}$ and (c) $\mathbf{Z_{cis}}$ in the gas phase calculated by the B3LYP/6-31+G(d,p) method.

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[1] (b) Altoe, P.; Bernardi, F.; Garavelli, M.; Orlandi, G.; Negri, F. *J. Am. Chem. Soc.* **2005**, *127*, 3952.

[2] Bell, A. F.; He, X.; Wachter, R. M.; Tonge, P. J. *Biochemistry* **2000**, *39*, 4423.

[3] During our manuscript preparation, the preresonant spectroscopy and model calculations on the GFP and its variants have also recently been employed to study photochromic fluorescent proteins. The Raman spectra shows *cis-trans* isomerization and a change of protonation state of the chromophore in the studied fluorescent proteins: Luin, S.; Voliani, V.; Lanza, G.; Bizzarri, R.; Nifosì, R.; Amat, P.; Tozzini, V.; Serresi, M.; Beltram, F. *J. Am. Chem. Soc.* **2009**, *131*, 96.

**Table S1.** Absorption and emission energies (in eV) of the chromophore evaluated by the CASPT2/6-31G(d)//CASSCF/6-31G(d) method with the smaller active space [(12e,11o) or (12e,12o)]. Two- and three-state average approaches (SA2 and SA3, respectively) were used.

| **Method** | ***Cis*** | | ***Trans*** | |
|---|---|---|---|---|
| | CASPT2// SA2-CASSCF | CASPT2// SA3-CASSCF | CASPT2// SA2-CASSCF | CASPT2// SA3-CASSCF |
| **Absorption** | | | | |
| Anionic | 2.72 | 2.72 | 2.73 | 2.72 |
| Zwitterionic | 3.12 | 3.05 | 3.50 | 3.44 |
| Neutral | 4.28 | 4.24 | 4.16 | 4.24 |
| Cationic | 3.14 | -[a] | 2.91 | 2.95 |
| **Emission** | | | | |
| Anionic | 2.48 | 2.46 | 2.50 | 2.48 |
| Zwitterionic | - | - | 2.17 | 2.14 |
| Neutral | 3.77 | 3.74 | 3.75 | 3.73 |
| Cationic | 2.11 | 2.14 | 2.59 | 2.66 |

[a]The CASPT2 calculation failed to converge.

**Table S2.** Absorption and emission energies of the different forms of the chromophore calculated by the SAC-CI(Level2)/D95(d)//SA2-CASSCF/6-31G(d) method with the small active space [(12e,11o) or (12e,12o)].

| **Method** | ***Cis*** | ***Trans*** |
|---|---|---|
| | SAC-CI// SA2-CASSCF | SAC-CI// SA2-CASSCF |
| **Absorption** | | |
| Anionic | 2.55 | 2.56 |
| Zwitterionic | 2.49 | 2.78 |
| Neutral | 3.67 | 3.63 |
| Cationic | 3.00 | 2.75 |
| **Emission** | | |
| Anionic | 2.31 | 2.29 |
| Zwitterionic | - | 2.25 |
| Neutral | 3.27 | 3.18 |
| Cationic | 1.27 | 2.31 |

**Table S3(a).** Absorption and emission energies of the chromophore in the gas phase calculated by SA4-CASSCF, SS-CASPT2 and MS-CASPT2 with ANO-S basis sets and IPEA zero-order Hamiltonian.

| Method | SA4-CASSCF | SS-CASPT2 | MS-CASPT2 |
|---|---|---|---|
| | $\mathbf{N_{cis}}$ (absorption)[a] | | |
| $\mathbf{S_1}$ | 4.56[e]/4.56[f] | 4.53[e]/4.52[f] | 4.07[e]/3.90[f] |
| $\mathbf{S_2}$ | 5.42[e]/5.28[f] | 5.08[e]/4.94[f] | 4.60[e]/4.55[f] |
| $\mathbf{S_3}$ | 5.78[e]/5.56[f] | 4.18[e]/3.90[f] | 5.33[e]/4.99[f] |
| | $\mathbf{N_{cis}}$ (emission)[b,e] | | |
| $\mathbf{S_1}$ | 4.18 | 4.15 | 3.32 |
| $\mathbf{S_2}$ | 4.30 | 4.25 | 4.31 |
| $\mathbf{S_3}$ | 4.87 | 3.42 | 4.46 |
| | $\mathbf{N_{trans}}$ (absorption)[a] | | |
| $\mathbf{S_1}$ | 4.55[e]/4.56[f]/4.54[b,e] | 4.53[e]/4.52[f]/4.51[b,e] | 4.10[e]/3.77[f]/4.09[b,e] |
| $\mathbf{S_2}$ | 5.43[e]/5.26[f]/5.39[b,e] | 5.16[e]/4.82[f]/5.16[b,e] | 4.59[e]/4.54[f]/4.58[b,e] |
| $\mathbf{S_3}$ | 5.69[e]/5.51[f]/5.66[b,e] | 4.06[e]/3.99[f]/4.02[b,e] | 5.29[e]/5.09[f]/5.25[b,e] |
| | $\mathbf{N_{trans}}$ (emission) | | |
| $\mathbf{S_1}$ | 4.20[b,e]/4.07[d,f] | 4.15[b,e]/3.72[d,f] | 3.15[b,e]/2.97[d,f] |
| $\mathbf{S_2}$ | 4.30[b,e]/4.23[d,f] | 4.13[b,e]/4.22[d,f] | 4.35[b,e]/4.28[d,f] |
| $\mathbf{S_3}$ | 4.76[b,e]/4.69[d,f] | 3.50[b,e]/3.57[d,f] | 4.60[b,e]/4.45[d,f] |
| | $\mathbf{Z_{cis}}$ (absorption)[c,f] | | |
| $\mathbf{S_1}$ | 3.33 | 3.17 | 2.88 |
| $\mathbf{S_2}$ | 3.86 | 3.29 | 4.16 |
| $\mathbf{S_3}$ | 4.48 | 4.49 | 4.71 |

[a]Geometry optimized by SA2-CASSCF(12e,12o)/6-31G(d). [b]Geometry optimized by SA4-CASSCF(12e,12o)/6-31G(d). [c]Geometry optimized by SA2-CASSCF(14e,13o)/6-31G(d). [d]Geometry optimized by SA4-CASSCF(14e,13o)/6-31G(d). [e](12e,12o) was used in these calculations. [f](14e,13o) was used in these calculations.

**Table S3(b).** Absorption and emission energies of the chromophore in the gas phase calculated by SS-CASPT2 and MS-CASPT2 with ANO-S basis sets and the original zero-order Hamiltonian.

| Method | SS-CASPT2 | MS-CASPT2 |
|---|---|---|
| | **$N_{cis}$** (absorption)[a] | |
| **$S_1$** | 4.14[e]/4.13[f] | 3.62[e]/3.49[f] |
| **$S_2$** | 4.65[e]/4.47[f] | 4.22[e]/4.18[f] |
| **$S_3$** | 3.77[e]/3.49[f] | 4.97[e]/4.52[f] |
| | **$N_{cis}$** (emission)[b,e] | |
| **$S_1$** | 3.72 | 2.98 |
| **$S_2$** | 3.85 | 3.94 |
| **$S_3$** | 3.05 | 4.11 |
| | **$N_{trans}$** (absorption)[a] | |
| **$S_1$** | 4.13[e]/4.13[f]/4.12[b,e] | 3.69[e]/3.31[f]/3.70[b,e] |
| **$S_2$** | 4.72[e]/4.33[f]/4.72[b,e] | 4.21[e]/4.17[f]/4.20[b,e] |
| **$S_3$** | 3.66[e]/3.57[f]/3.62[b,e] | 4.89[e]/4.68[f]/4.84[b,e] |
| | **$N_{trans}$** (emission) | |
| **$S_1$** | 3.72[b,e]/3.34[d,f] | 2.78[b,e]/2.54[d,f] |
| **$S_2$** | 3.73[b,e]/3.81[d,f] | 3.99[b,e]/3.91[d,f] |
| **$S_3$** | 3.11[b,e]/3.16[d,f] | 4.31[b,e]/4.17[d,f] |

[a]Geometry optimized by SA2-CASSCF(12e,12o)/6-31G(d). [b]Geometry optimized by SA4-CASSCF(12e,12o)/6-31G(d). [c]Geometry optimized by SA2-CASSCF(14e,13o)/6-31G(d). [d]Geometry optimized by SA4-CASSCF(14e,13o)/6-31G(d). [e](12e,12o) was used in these calculations. [f](14e,13o) was used in these calculations.

**Table S4.** The calculated absorption energies (in eV) and oscillator strengths (in the parentheses) of the chromophore in the proteins by ONIOM(TD-B3LYP/6-31++G(d,p): AMBER)-EE at ONIOM(B3LYP/6-31+G(d,p):AMBER)-EE optimized structures.

| Conformation in proteins | ***Cis*** (On-state) | | ***Trans*** (Off-state) | |
|---|---|---|---|---|
| QM model | MS | ML1 | MS | ML1 |
| Anionic, **A** | 3.11(0.84) | 3.04(0.98) | 3.05(0.68) | 2.98(0.81) |
| Zwitterionic, **Z** | 3.09(0.79) | 2.96(0.95) | 3.20(0.85) | 3.03(1.03) |
| Neutral, **N** | 3.39(0.71) | 3.30(0.37)[a] | 3.33(0.53) | 3.17(0.27)[b] |
| Cationic, **C** | 3.18(0.73) | 3.26(0.54) | 3.17(0.69) | 3.11(0.81) |

[a]The vertical absorption energy and oscillator strength for another excitation (HOMO-2 → LUMO) is 3.55 eV and 0.33, respectively. [b]The vertical absorption energy and oscillator strength for another excitation (HOMO-1 → LUMO) is 3.40 eV and 0.36, respectively.

**Table S5(a).** Absorption and emission energies of the chromophore in the proteins calculated by ONIOM-EE, SA4-CASSCF, SS-CASPT2 and MS-CASPT2 with ANO-S basis sets and the IPEA zero-order Hamiltonian.

| Method | SA4-CASSCF | SS-CASPT2 | MS-CASPT2 |
|---|---|---|---|
| | | $N_{trans}$ (absorption)[a] | |
| $S_1$ | 4.61[c]/4.61[d] | 4.54[c]/4.53[d] | 3.68[c]/3.62[d] |
| $S_2$ | 5.26[c]/5.17[d] | 4.03[c]/3.89[d] | 4.60[c]/4.57[d] |
| $S_3$ | 5.71[c]/5.49[d] | 5.06[c]/4.79[d] | 5.53[c]/5.14[d] |
| | | $N_{trans}$ (emission)[b] | |
| $S_1$ | 3.92[c]/3.81[d] | 3.00[c]/2.94[d] | 3.22[c]/3.12[d] |
| $S_2$ | 4.22[c]/4.21[d] | 4.14[c]/4.12[d] | 4.31[c]/4.28[d] |
| $S_3$ | 4.44[c]/4.35[d] | 4.32[c]/4.14[d] | 4.52[c]/4.37[d] |

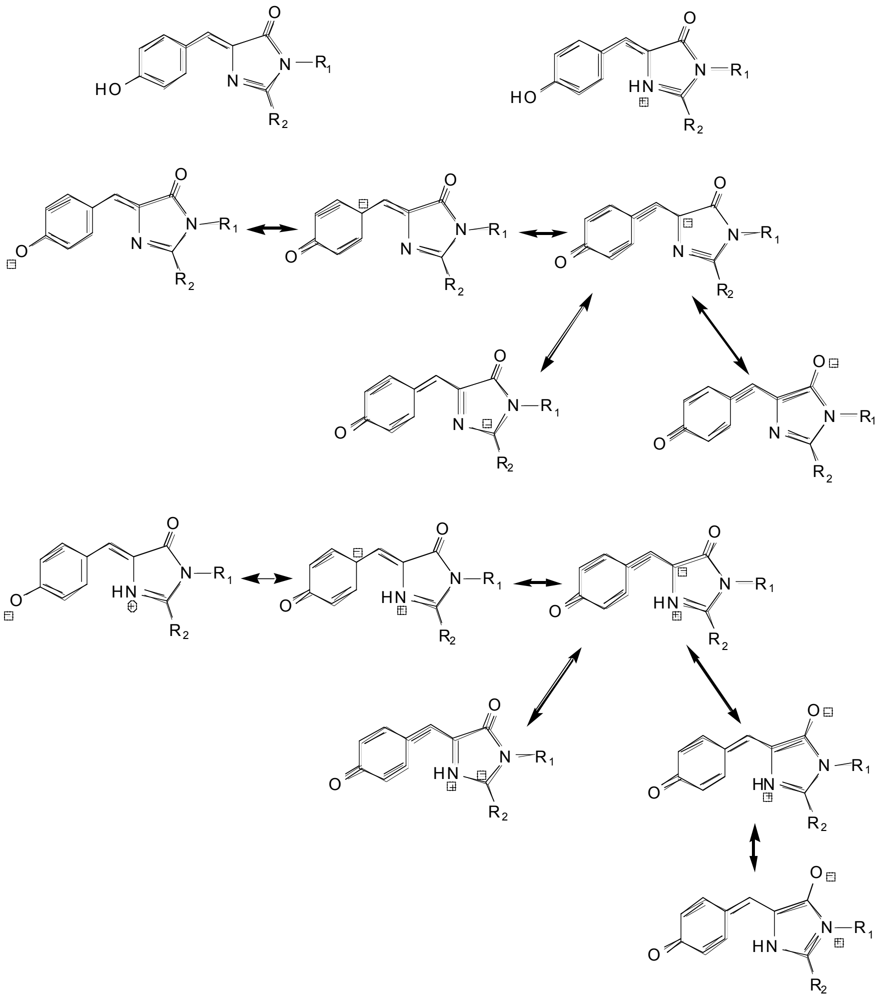
[a]Geometry optimized by SA2-CASSCF(12e,12o)/6-31G(d). [b]Geometry optimized by SA4-CASSCF(12e,12o)/6-31G(d). [c](12e,12o) was used in these calculations. [d](14e,13o) was used in these calculations.

**Table S5(b).** Absorption and emission energies of the chromophore in the proteins calculated by ONIOM-EE, SS-CASPT2 and MS-CASPT2 with ANO-S basis sets and the original zero-order Hamiltonian.

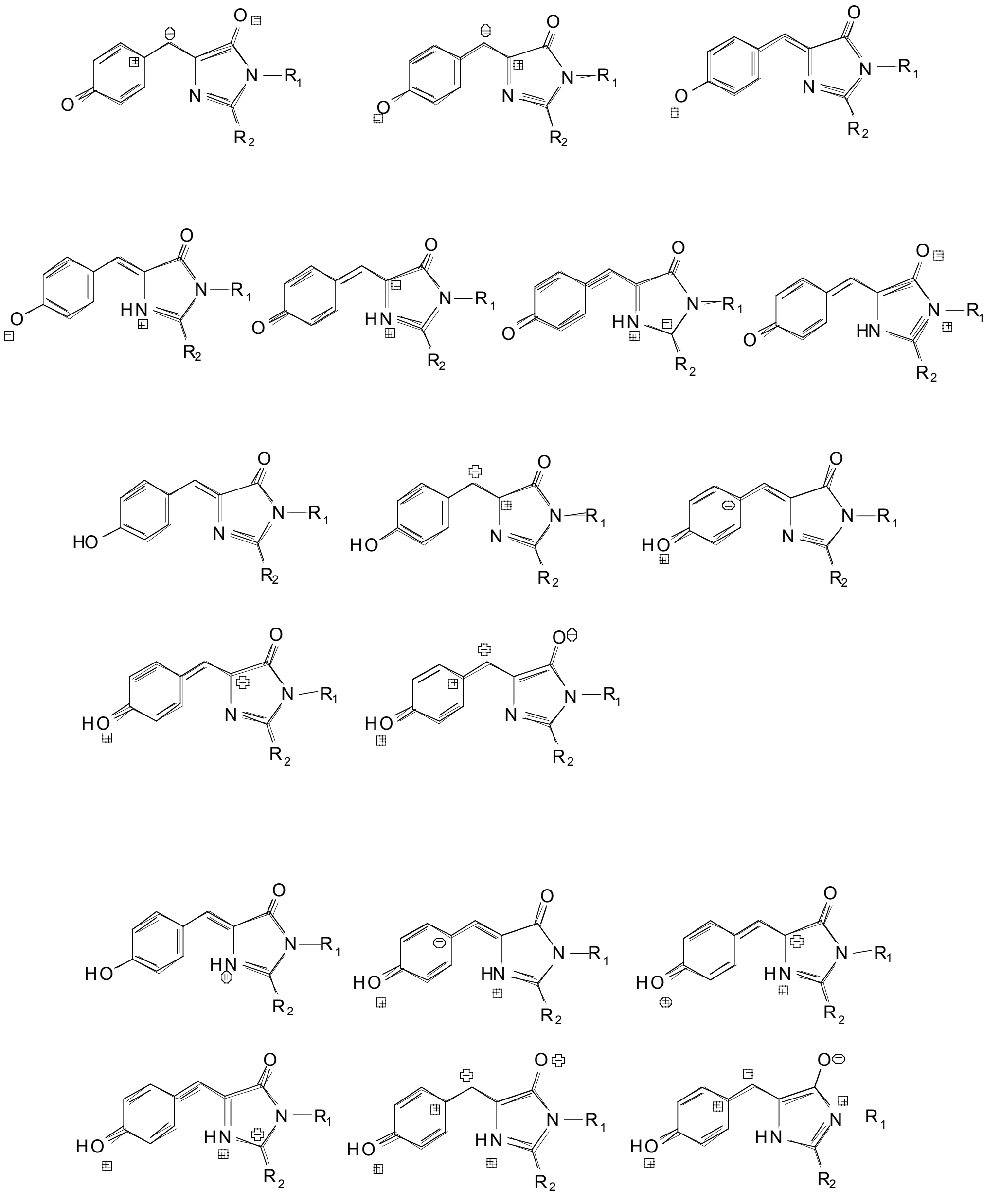
| Method | SS-CASPT2 | MS-CASPT2 |
|---|---|---|
| | $N_{trans}$ (absorption)[a] | |
| $S_1$ | 4.07[c]/4.05[d] | 3.24[c]/3.16[d] |
| $S_2$ | 3.50[c]/3.36[d] | 4.11[c]/4.11[d] |
| $S_3$ | 4.29[c]/4.28[d] | 4.60[c]/4.55[d] |
| | $N_{trans}$ (emission)[b] | |
| $S_1$ | 2.69[c]/2.58[d] | 2.84[c]/2.92[d] |
| $S_2$ | 3.66[c]/3.72[d] | 3.76[c]/3.95[d] |
| $S_3$ | 3.71[c]/3.86[d] | 3.83[c]/4.10[d] |

[a]Geometry optimized by SA2-CASSCF(12e,12o)/6-31G(d). [b]Geometry optimized by SA4-CASSCF(12e,12o)/6-31G(d). [c](12e,12o) was used in these calculations. [d](14e,13o) was used in these calculations.

**Scheme S1.** Resonance structures for the ground-state chromophores



**Scheme S2.** Resonance structures for the excited state chromophores



**Cartesian coordinates (in Å) and absolute energies (a.u.) of the CASSCF(14e,13o)-optimized structures**

**$A_{cis}$ (FC):**

**CASSCF/6-31G*:**

**FC(S0):** -641.543786001379 hartree

**FC(S1):** -641.421781551197 hartree

**CASPT2/6-31G*:**

**FC(S0):** -643.300066895141 hartree

**FC(S1):** -643.200683429753 hartree

| | | | |
|---|---|---|---|
| C | -1.4360465408 | -0.4452400853 | -0.1744435878 |
| N | -0.3359541545 | 0.1802773366 | 0.0356563030 |
| N | -1.2539358789 | -1.6796300574 | -0.7735617078 |
| C | 0.1099727274 | -1.8734843912 | -0.9712534098 |
| O | 0.5950433033 | -2.8668134345 | -1.4788257727 |
| C | 0.6915088192 | -0.6535695678 | -0.4393923714 |
| C | 2.0537530210 | -0.4041498897 | -0.4277686841 |
| C | 2.8254049495 | 0.6781199183 | 0.0238087855 |
| C | 2.3012106814 | 1.8699757447 | 0.6278755216 |
| C | 4.2513446542 | 0.6248561593 | -0.1122556756 |
| C | 3.1083967970 | 2.8883635679 | 1.0464555635 |
| C | 5.0790073316 | 1.6296778752 | 0.2983745025 |
| C | 4.5598644638 | 2.8431528370 | 0.9124209403 |
| O | 5.2880100042 | 3.7614580213 | 1.2897235549 |
| H | 1.2379473277 | 1.9525250653 | 0.7494824082 |
| H | 4.6843922074 | -0.2554213398 | -0.5619840126 |
| H | 2.6913359242 | 3.7732726580 | 1.4970294088 |
| H | 6.1468180669 | 1.5559446501 | 0.1804832037 |
| H | -1.9516290339 | -2.3367392211 | -1.0276809596 |
| H | -2.4125298733 | -0.0793007823 | 0.0750983780 |
| H | 2.6167920428 | -1.2184554246 | -0.8568326587 |

**$A_{cis}$ (FS):**

**CASSCF/6-31G*:**

**FS(S0):** -641.537469826444 hartree

**FS(S1):** -641.427393494410n hartree

**CASPT2/6-31G*:**

**FS(S0)**: -643.298038044879 hartree

**FS(S1)**: -643.207459526269 hartree

| | | | |
|---|---|---|---|
| C | -1.4133479548 | -0.3985835707 | -0.1539123392 |
| N | -0.2660097020 | 0.1795460362 | 0.0299705307 |
| N | -1.2831350687 | -1.6377377589 | -0.7512232194 |
| C | 0.0613288956 | -1.8846975335 | -0.9728354804 |
| O | 0.5195193458 | -2.8959596332 | -1.4870201339 |
| C | 0.7036510453 | -0.6837259193 | -0.4546255685 |
| C | 2.1048027026 | -0.4948568371 | -0.4747584615 |
| C | 2.8683832738 | 0.6528724714 | 0.0085166266 |
| C | 2.2921272853 | 1.8162742594 | 0.6030703549 |
| C | 4.2864708601 | 0.6280715979 | -0.1132959525 |
| C | 3.0825231817 | 2.8718517404 | 1.0405755392 |
| C | 5.0822199363 | 1.6759035901 | 0.3200986871 |
| C | 4.5205263940 | 2.8688170954 | 0.9275900369 |
| O | 5.2407470977 | 3.8090618279 | 1.3158809690 |
| H | 1.2282767354 | 1.8667074897 | 0.7095188429 |
| H | 4.7516912996 | -0.2364533343 | -0.5579786937 |
| H | 2.6274693103 | 3.7398123312 | 1.4861043545 |
| H | 6.1527893015 | 1.6327037651 | 0.2165279568 |
| H | -2.0085577980 | -2.2695870013 | -0.9916528808 |
| H | -2.3649387281 | 0.0112615856 | 0.1143418992 |
| H | 2.6641694266 | -1.3064625622 | -0.9024833379 |

**$Z_{cis}$ (FC):**

**CASSCF/6-31G*:**

**FC(S0):** -642.055344910342 hartree

**FC(S1):** -641.929258892667 hartree

**CASPT2/6-31G*:**

**FC(S0):** -643.802381741722 hartree

**FC(S1):** -643.689397172129 hartree

| | | | |
|---|---|---|---|
| C | -1.5485747904 | -0.5039053769 | -0.1886540709 |
| N | -0.3896187718 | 0.1069188330 | 0.0106108775 |
| N | -1.2624235327 | -1.6911164324 | -0.7777628354 |
| C | 0.1090341631 | -1.8553501645 | -0.9651273098 |
| O | 0.6304389529 | -2.8224751331 | -1.4678736301 |
| C | 0.6763820176 | -0.6352143286 | -0.4284089593 |
| C | 2.0710533696 | -0.3599052609 | -0.4077699624 |
| C | 2.8277128356 | 0.7007728855 | 0.0340569473 |
| C | 2.3206374242 | 1.9202931093 | 0.6473430505 |
| C | 4.2771278893 | 0.6223610313 | -0.1140380163 |
| C | 3.1359065219 | 2.9205751157 | 1.0570763322 |
| C | 5.1129234512 | 1.6078514403 | 0.2873973034 |
| C | 4.5980497041 | 2.8357291767 | 0.9062711464 |
| O | 5.3292366311 | 3.7372867181 | 1.2763794949 |
| H | 1.2643429381 | 2.0514552539 | 0.7876674729 |
| H | 4.6816447861 | -0.2666441474 | -0.5645278763 |
| H | 2.7470988302 | 3.8151347328 | 1.5076612695 |
| H | 6.1776611643 | 1.5293083568 | 0.1690381972 |
| H | -1.9287344894 | -2.3762485628 | -1.0519230719 |
| H | -2.5102565950 | -0.1279543048 | 0.0687914976 |

H 2.6150394276 -1.1815984181 -0.8387844196
H -0.3259583676 1.0024883160 0.4344787726

**$Z_{cis}$ (FS):**
**CASSCF/6-31G*:**
**FS(S0):** -642.026557991865 hartree
**FS(S1):** -641.959875944131 hartree
**CASPT2/6-31G*:**
**FS(S0):** -643.783756910114 hartree
**FS(S1):** -643.727666413347 hartree

C -1.3088012873 -0.5838975617 0.2652186989
C -0.0185978585 -1.7104399036 -1.2019104460
C 0.7522531175 -0.6237700308 -0.6010771917
C 2.0805710853 -0.3775716378 -0.7240988953
C 2.8398808142 0.7220211756 -0.1464491986
C 2.2839718496 2.0043145712 0.1249611565
C 4.2164124526 0.5247163604 0.1414977887
C 3.0381599936 3.0152103852 0.6738849346
C 4.9930767984 1.5151132590 0.6999771153
C 4.4381882396 2.8203252943 1.0059800074
N -0.1668056073 0.1461965206 0.1918287743
N -1.3345982502 -1.5305530417 -0.7255172689
O 0.3195028190 -2.5901934053 -1.9402502435
O 5.1192374296 3.7185678523 1.5154920268
H 1.2653829870 2.2085358849 -0.1512631843
H 4.6613366172 -0.4305155531 -0.0792270652
H 2.6150592656 3.9844799991 0.8631537473
H 6.0328511365 1.3537708844 0.9158794333
H -1.9842424274 -2.2853929369 -0.7272152475
H -2.1767152213 -0.2712147975 0.8058878675
H 2.6290608408 -1.1191113300 -1.2788612335
H 0.1815481755 0.5790707444 1.0262116007

**$N_{cis}$ (FC):**
**SA2-CASSCF/6-31G*:**
**FC(S0):** -642.110276142151 hartree
**FC(S1):** -641.94022971076 hartree
**CASPT2/6-31G*:**
**FC(S0):** -643.843450351084 hartree
**FC(S1):** -643.686889492736 hartree

C -1.3981046793 -0.4293370736 -0.1699081544
C 0.0840348189 -1.9021512486 -0.9824141448
C 0.7203710527 -0.6632918806 -0.4461749614
C 2.0539605416 -0.4570891724 -0.4529053387
C 2.8400533438 0.6853005109 0.0259784222
C 2.2840247910 1.8351758775 0.6127050710
C 4.2386669118 0.6264223616 -0.1105873783
C 3.1009450988 2.8790663483 1.0426171881
C 5.0579279598 1.6661895646 0.3172099360
C 4.4865125230 2.7989476553 0.8970530781
N -0.2970846581 0.1881942960 0.0361595030
N -1.2618258871 -1.6702862017 -0.7677072412
O 0.5773673843 -2.8755416967 -1.4812701313
O 5.3209213647 3.7879713114 1.2996758280
H 1.2228016704 1.9128664521 0.7319176395
H 4.6899071105 -0.2422154649 -0.5562537866
H 2.6564265288 3.7523324062 1.4899242061
H 6.1250518191 1.6140587860 0.2096179502
H -1.9904281987 -2.3007970828 -1.0084959549
H -2.3645681254 -0.0450804701 0.0874296022
H 2.6238615372 -1.2643680033 -0.8792655022
H 4.8302116324 4.5051861748 1.6768246894

**$N_{cis}$ (FS):**
**SA4-CASSCF(12e,12o)/6-31G*:**
**FC(S0):** -642.24963812 hartree
**FC(S1):** -642.09612443 hartree
**FC(S2):** -642.09144947 hartree
**FC(S3):** -642.07072206 hartree
SS-**CASPT2/6-31G*:**
**FS(S0):** -644.1802100797 hartree
**FS(S1):** -644.0275844091 hartree
**FC(S2):** -644.0238563567 hartree
**FC(S3):** -644.0545383565 hartree
MS-**CASPT2/6-31G*:**
**FS(S0):** -644.18261424 hartree
**FS(S1):** -644.0606074 hartree
**FC(S2):** -644.02433089 hartree
**FC(S3):** -644.01863667 hartree

C -1.3838143164-0.3544061954-0.1359326732
C 0.0831991149-1.8362981776-0.9510266157
C 0.7198753907-0.6543935888-0.4419252870
C 2.1386050811-0.4942784572-0.4768884954
C 2.88358079300.6044214963-0.0155464721
C 2.26744353421.76525011550.5812507982
C 4.31553533790.6051029780-0.1268278304

C 3.03110734902.82527055441.0228617689
C 5.06885067801.66424043980.3151751975
C 4.42833521772.78950628150.8970674429
N -0.22418717920.21749061290.0439636413
N -1.2604538664-1.5840441460-0.7269572865
O 0.5492420668-2.8500174296-1.4666295201
O 5.21308506893.77777690531.3031211337
H 1.20198175881.78283024440.6725956988
H 4.7998255025-0.2457293292-0.5668015923
H 2.55927942143.68478660971.4659675909
H 6.13891886631.67347616810.2361487090
H -1.9923774518-2.2106061269-0.9658956494
H -2.32817093420.06580156840.1364077696
H 2.6755969219-1.3179821269-0.9081809559
H 4.71557618494.49335505341.6801831476

**$C_{cis}$ (FC):**

**CASSCF/6-31G*:**

**FC(S0):** -642.466861661966 hartree

**FC(S1):** -642.299746417262 hartree

**CASPT2/6-31G*:**

**FC(S0):** -644.202640041297 hartree

**FC(S1):** -644.054443751618 hartree

C -1.5059455479 -0.5372577638 -0.2106230682
C 0.1098117643 -1.8982674717 -0.9836417474
C 0.7181028322 -0.6595280129 -0.4444830656
C 2.0376438177 -0.3919365180 -0.4218047684
C 2.8320644242 0.7359639761 0.0499560803
C 2.3174640543 1.9084886118 0.6430108426
C 4.2267572122 0.6369755561 -0.1038103405
C 3.1553083355 2.9311620320 1.0617301546
C 5.0747897978 1.6580938466 0.3134921082
C 4.5403734140 2.8105868328 0.8987530847
N -0.4000340041 0.1062367953 0.0068922614
N -1.2858237372 -1.7097868997 -0.7840370034
O 0.6075328585 -2.8555617419 -1.4767754818
O 5.4038785357 3.7609266406 1.2813669520
H 1.2635985923 2.0518565851 0.7907459407
H 4.6513344814 -0.2425353692 -0.5518168289
H 2.7375939525 3.8146227633 1.5106872704
H 6.1380315873 1.5790716076 0.1946302151
H -1.9867574470 -2.3729912290 -1.0430496571
H -2.4760570123 -0.1613514308 0.0445459801
H 2.6090548307 -1.1978526294 -0.8485016123
H 4.9671567275 4.5087653725 1.6678705317
H -0.3639610998 1.0072521366 0.4320611720

**$C_{cis}$ (FS):**

**CASSCF/6-31G*:**

**FS(S0):** -642.423536519463 hartree

**FS(S1):** -642.335353742397 hartree

**CASPT2/6-31G*:**

**FS(S0):** -644.18496941396 hartree

**FS(S1):** -644.102679581711 hartree

C -1.4756898608 -0.5986270103 0.1171901050
C 0.0474792226 -1.7485214852 -1.1180099762
C 0.7314299717 -0.6053311370 -0.4520833460
C 2.0707964572 -0.3962555141 -0.5595359535
C 2.8483573805 0.7015017795 -0.0283125580
C 2.2773207783 1.9473532803 0.3844765931
C 4.2680773999 0.5588772911 0.0396311534
C 3.0687672249 2.9758176648 0.8362081857
C 5.0663170392 1.5737291684 0.4998119818
C 4.4740300525 2.8008010258 0.9087772627
N -0.2658663476 0.1236332853 0.2069468574
N -1.2728046859 -1.6258630195 -0.7707749919
O 0.5452014280 -2.5915483998 -1.8145122149
O 5.2861675634 3.7276322629 1.3412272051
H 1.2218000627 2.1044564689 0.2955256669
H 4.7134298507 -0.3653520009 -0.2756112354
H 2.6334453040 3.9136646457 1.1294590008
H 6.1329102174 1.4780213100 0.5617332802
H -1.9774172747 -2.2624566310 -1.0745057716
H -2.4227277173 -0.0995490997 0.1853607163
H 2.6057138166 -1.1604399704 -1.0913977883
H 4.8511637323 4.5353628238 1.5958880652
H -0.0559876154 0.4960272615 1.1097067622

**$A_{trans}$ (FC):**

**CASSCF/6-31G*:**

**FC(S0):** -641.539158191781 hartree

**FC(S1):** -641.417074979664 hartree

**CASPT2/6-31G*:**

**FC(S0):** -643.2965982 hartree

**FC(S1):** -643.196832 hartree

C 0.4623103467 1.0316605525 -0.5041088026
C 2.1387282974 -0.3106827122 0.1845695602
C 2.4404554509 1.0970396978 0.3764755893

| | | | |
|---|---|---|---|
| C | 3.5425724017 | 1.7734529505 | 0.8934707717 |
| C | 4.7870732801 | 1.4135426462 | 1.4310748796 |
| C | 5.6643928117 | 2.4661172229 | 1.8638338383 |
| C | 5.2900434164 | 0.0777262475 | 1.5994204677 |
| C | 6.8969019286 | 2.2405522198 | 2.4017190486 |
| C | 6.5206238112 | -0.1710518505 | 2.1354997481 |
| C | 7.4164617015 | 0.8910241900 | 2.5769612600 |
| N | 1.3422597408 | 1.8604379503 | -0.0795030503 |
| N | 0.8667712965 | -0.2841847212 | -0.3784182034 |
| O | 2.7404703163 | -1.3451088058 | 0.4086889541 |
| O | 8.5257836558 | 0.6664424658 | 3.0601186771 |
| H | 5.3243549088 | 3.4844379343 | 1.7547730885 |
| H | 4.6729280482 | -0.7428730079 | 1.2916901508 |
| H | 7.5272090062 | 3.0555318723 | 2.7150348065 |
| H | 6.8745471452 | -1.1815439670 | 2.2510357136 |
| H | 3.3758540309 | 2.8390169824 | 0.8633172773 |
| H | -0.4921852415 | 1.2933937893 | -0.9168795149 |
| H | 0.3670363070 | -1.1013306569 | -0.6351709600 |

**A$_{trans}$ (FS):**

**CASSCF/6-31G*:**

**FS(S0):** -641.532843026794 hartree

**FS(S1):** -641.422575710067 hartree

**CASPT2/6-31G*:**

**FS(S0):** -643.2948968 hartree

**FS(S1):** -643.20371 hartree

| | | | |
|---|---|---|---|
| C | 0.4436467638 | 0.9817444151 | -0.5140849917 |
| C | 2.1502066018 | -0.3101982096 | 0.1893823669 |
| C | 2.4197454450 | 1.1109889823 | 0.3676790733 |
| C | 3.5160464561 | 1.8621876820 | 0.8848349276 |
| C | 4.8033401643 | 1.4562618278 | 1.4398389333 |
| C | 5.6885160159 | 2.4868001903 | 1.8753168654 |
| C | 5.2615254636 | 0.1147740028 | 1.5882032287 |
| C | 6.9324252997 | 2.2138674003 | 2.4165161546 |
| C | 6.5095543962 | -0.1678465949 | 2.1308452482 |
| C | 7.4208404352 | 0.8569113194 | 2.5775826624 |
| N | 1.3173975507 | 1.8345849414 | -0.0913747026 |
| N | 0.8747154044 | -0.3121174287 | -0.3760454816 |
| O | 2.7686600994 | -1.3438651229 | 0.4206500572 |
| O | 8.5417326121 | 0.6138221801 | 3.0654886063 |
| H | 5.3736917022 | 3.5131724766 | 1.7776814332 |
| H | 4.6286297404 | -0.6888198621 | 1.2740610680 |
| H | 7.5789599018 | 3.0131021047 | 2.7364949307 |
| H | 6.8324334812 | -1.1897471792 | 2.2322584645 |
| H | 3.3407735575 | 2.9221584275 | 0.8506676962 |
| H | -0.5130225303 | 1.2292780917 | -0.9281094377 |
| H | 0.3947740991 | -1.1434586446 | -0.6242838028 |

**Z$_{trans}$ (FC):**

**CASSCF/6-31G*:**

**FC(S0):** -642.055432085499 hartree

**FC(S1):** -641.920335059568 hartree

**CASPT2/6-31G*:**

**FC(S0):** -643.8029741 hartree

**FC(S1):** -643.6777492 hartree

| | | | |
|---|---|---|---|
| C | 0.4063389693 | 0.9840526205 | -0.5311035357 |
| C | 2.1454203655 | -0.3061167862 | 0.1874312599 |
| C | 2.4601864959 | 1.0956713013 | 0.3849102849 |
| C | 3.5735747125 | 1.8292496172 | 0.9092620538 |
| C | 4.7870021827 | 1.4551521844 | 1.4325976761 |
| C | 5.6906409296 | 2.5142368895 | 1.8772602397 |
| C | 5.2634768155 | 0.0841907028 | 1.5878968930 |
| C | 6.9076541606 | 2.2586325019 | 2.4071683826 |
| C | 6.4805801974 | -0.1850867379 | 2.1172881612 |
| C | 7.3920973336 | 0.8781076655 | 2.5657199853 |
| N | 1.3601454292 | 1.7788540175 | -0.0750913648 |
| N | 0.8734527974 | -0.2782268961 | -0.3758532019 |
| O | 2.7515069878 | -1.3303380664 | 0.4141304617 |
| O | 8.4869519804 | 0.6347155176 | 3.0418697551 |
| H | 5.3614105372 | 3.5338853667 | 1.7729003959 |
| H | 4.6263019947 | -0.7161478607 | 1.2721059131 |
| H | 7.5623658680 | 3.0469592583 | 2.7302011624 |
| H | 6.8272640620 | -1.1958930901 | 2.2297355514 |
| H | 3.4086244665 | 2.8958625432 | 0.8798371012 |
| H | -0.5318013751 | 1.2816564264 | -0.9351820542 |
| H | 0.3904990091 | -1.1111275766 | -0.6245165111 |
| H | 1.2863165603 | 2.7717471412 | -0.0669107595 |

**Z$_{trans}$ (FS):**

**CASSCF/6-31G*:**

**FS(S0):** -642.036664189999 hartree

**FS(S1):** -641.952478498332 hartree

**CASPT2/6-31G*:**

**FS(S0):** -643.7830184 hartree

**FS(S1):** -643.7058272 hartree

| | | | |
|---|---|---|---|
| C | 0.3575783154 | 0.9727246295 | -0.5819474740 |
| C | 2.2206352383 | -0.2619942024 | -0.0258197843 |
| C | 2.4722198542 | 1.1474554800 | 0.3034900690 |

C 3.5860302874 1.8647037887 0.7922597595
C 4.8299297518 1.4567787278 1.4004186038
C 5.7583239755 2.4916858554 1.7318899039
C 5.1876118012 0.1181432668 1.7083227543
C 6.9699600128 2.2185049053 2.3304387458
C 6.4047395280 -0.1724011371 2.3135788649
C 7.3382259486 0.8637576384 2.6459301017
N 1.3256129746 1.8506176555 -0.0909526008
N 0.8962012859 -0.3101767340 -0.4355262352
O 2.9527643712 -1.2168272803 0.0104058989
O 8.4408026017 0.6001349578 3.1960599427
H 5.5019041061 3.5116913798 1.5065444243
H 4.5221277012 -0.6804814024 1.4583428518
H 7.6626840038 3.0011122584 2.5771312181
H 6.6760587929 -1.1852032885 2.5452215668
H 3.4615108529 2.9311433965 0.7132941846
H -0.6767590895 1.1474741413 -0.3397488311
H 0.5845282380 -1.0833002076 -0.9788568021
H 1.0373199281 2.6544929116 0.4211806872

**$N_{trans}$ (FC):**

**CASSCF/6-31G*:**

**FC(S0):** -642.104913607878 hartree

**FC(S1):** -641.935023589486 hartree

**CASPT2/6-31G*:**

**FC(S0):** -643.84759696283 hartree

**FC(S1):** -643.692838715794 hartree

C 0.4727218124 1.0173326628 -0.5000650223
C 2.1438001477 -0.3195048796 0.1864907694
C 2.4445868940 1.1347072708 0.3795221916
C 3.5085119672 1.8087378759 0.8794043126
C 4.8058303703 1.4111236067 1.4391312940
C 5.6561834650 2.4535610294 1.8597655315
C 5.2672919094 0.0927301948 1.5897358966
C 6.9091392450 2.2026090594 2.4059274518
C 6.5239594284 -0.1631419426 2.1373401681
C 7.3471856113 0.8851176920 2.5461931898
N 1.3256814810 1.8715774655 -0.0868307667
N 0.8835100090 -0.2995596404 -0.3713533266
O 2.7792091243 -1.3112857283 0.4273482298
O 8.5746301074 0.6845738624 3.0831056044
H 5.3309754072 3.4734370794 1.7573633041
H 4.6569666474 -0.7300385904 1.2847273890
H 7.5484390311 3.0050242862 2.7229452237
H 6.8567361010 -1.1820719923 2.2431348902
H 8.7698712793 -0.2412169206 3.1316960878
H 3.3559579978 2.8734712294 0.8553278269
H -0.4846046804 1.2603897444 -0.9148417185
H 0.3787764372 -1.1150982239 -0.6296224561

**$N_{trans}$ (FS):**

**SA4-CASSCF(14,13)/6-31G*:**

**FS(S0):** -642.24789891 hartree

**FS(S1):** -642.09815708 hartree

**FS(S2):** -642.09241505 hartree

**FS(S3):** -642.07563622 hartree

**SS-CASPT2(14,13)/6-31G*:**

**FS(S0):** -644.1780749128 hartree

**FS(S1):** -644.0412683258 hartree

**FS(S2):** -644.0229212441 hartree

**FS(S3):** -644.0469612608 hartree

**MS-CASPT2(14,13)/6-31G*:**

**FS(S0):** -644.17982261 hartree

**FS(S1):** -644.07078919 hartree

**FS(S2):** -644.02240459 hartree

**FS(S3):** -644.01620936 hartree

C 0.47128316050.9389170970-0.5040600724
C 2.1981501295-0.29216777440.2115940558
C 2.43548772421.12320061960.3752394461
C 3.52782890561.90377436680.8921548894
C 4.78461047471.49323968991.4332860900
C 5.69469914222.51330464751.8792841984
C 5.22312586120.12993069291.5719689560
C 6.92316168962.21077842902.4122922140
C 6.4601597667-0.17027723372.1088799604
C 7.32631634700.85325497962.5355143988
N 1.34439053531.8171975813-0.0804019364
N 0.9243798658-0.3258416404-0.3550623695
O 2.8359564970-1.31695039260.4524016354
O 8.53238549070.62071281793.0614591858
H 5.39772265803.54118138591.7896632107
H 4.5765512685-0.65950310341.2524317596
H 7.59763679542.97736480652.7432588569
H 6.7647312828-1.19839619042.2018627255
H 8.7174025446-0.30885307843.1054106905
H 3.34689349662.96044514370.8552675007
H -0.48621742521.1715628631-0.9194156562

H 0.4587035828-1.1704005670-0.5965836687

**$C_{trans}$ (FC):**

**CASSCF/6-31G*:**

**FC(S0):** -642.461052586423 hartree

**FC(S1):** -642.321496000667 hartree

**CASPT2/6-31G*:**

**FC(S0):** -644.2103264 hartree

**FC(S1):** -644.1069738 hartree

| | | | |
|---|---|---|---|
| C | 0.4367788193 | 0.9850666508 | -0.5176747003 |
| C | 2.1513792072 | -0.3034233022 | 0.1904175211 |
| C | 2.4847375632 | 1.1114585800 | 0.3963448958 |
| C | 3.5458262136 | 1.8098351955 | 0.8960654313 |
| C | 4.8135784733 | 1.4203557580 | 1.4429685066 |
| C | 5.6694258199 | 2.4690060257 | 1.8661782092 |
| C | 5.2700340668 | 0.0932186851 | 1.5910755598 |
| C | 6.9120728179 | 2.2131692698 | 2.4075300780 |
| C | 6.5197517806 | -0.1647880617 | 2.1354708470 |
| C | 7.3457394253 | 0.8874530225 | 2.5455993352 |
| N | 1.3320992244 | 1.8092401635 | -0.0866207101 |
| N | 0.8502405468 | -0.2669870897 | -0.3854492292 |
| O | 2.7402774105 | -1.3163752357 | 0.4101821115 |
| O | 8.5558501084 | 0.6960418127 | 3.0751618886 |
| H | 5.3480054019 | 3.4899576514 | 1.7654288327 |
| H | 4.6622171129 | -0.7315202720 | 1.2871906899 |
| H | 7.5575727705 | 3.0083318259 | 2.7269119319 |
| H | 6.8524617504 | -1.1820156454 | 2.2413718088 |
| H | 8.7791867585 | -0.2240978834 | 3.1364952342 |
| H | 3.3999955629 | 2.8775386491 | 0.8751357035 |
| H | -0.5092565146 | 1.2770934124 | -0.9255421586 |
| H | 0.3378026957 | -1.0832154575 | -0.6463098694 |
| H | 1.2250005846 | 2.8035672849 | -0.0934311676 |

**$C_{trans}$ (FS):**

**CASSCF/6-31G*:**

**FS(S0):** -642.451309143477 hartree

**FS(S1):** -642.332084723135 hartree

**CASPT2/6-31G*:**

**FS(S0):** -644.2085234 hartree

**FS(S1):** -644.1152357 hartree

| | | | |
|---|---|---|---|
| C | 0.4073733259 | 0.9350986900 | -0.5329254807 |
| C | 2.1697879094 | -0.2832383311 | 0.1993888238 |
| C | 2.4571818412 | 1.1419352795 | 0.3855502631 |
| C | 3.5469353006 | 1.8992449561 | 0.9004447296 |
| C | 4.8071352224 | 1.4847299396 | 1.4429319674 |
| C | 5.7073939600 | 2.5160423119 | 1.8848891548 |
| C | 5.2434047231 | 0.1165798945 | 1.5805478533 |
| C | 6.9366878085 | 2.2203486330 | 2.4185312451 |
| C | 6.4743659822 | -0.1840029931 | 2.1147266847 |
| C | 7.3376714582 | 0.8555656668 | 2.5406121808 |
| N | 1.3241101465 | 1.7866937074 | -0.0909624863 |
| N | 0.8997637538 | -0.3015556435 | -0.3651551965 |
| O | 2.8143711729 | -1.2775462577 | 0.4446556063 |
| O | 8.5121386471 | 0.6356080936 | 3.0530179308 |
| H | 5.4111315634 | 3.5438722681 | 1.7954870215 |
| H | 4.6026360357 | -0.6778151292 | 1.2635015177 |
| H | 7.6145357720 | 2.9823723372 | 2.7507048383 |
| H | 6.7881291282 | -1.2077623744 | 2.2120655796 |
| H | 8.7371419254 | -0.2890473120 | 3.1150081647 |
| H | 3.3929158772 | 2.9630450103 | 0.8757274538 |
| H | -0.5415100642 | 1.1926319736 | -0.9435889001 |
| H | 0.4347981174 | -1.1496866711 | -0.6064366728 |
| H | 1.2026779931 | 2.7757969902 | -0.1042215289 |

**$N_{TI}$:**

**CASSCF(12e,12o)/6-31G*:**

**S0:** -642.008729038378 hartree

**S1:** -641.951904128644 hartree

C 1.2659810139 0.2630304999 -1.1373258093
C 1.3728632892 0.7278423734 1.0733713922
C 2.5108852675 1.1497358043 0.3498734208
C 3.5369355866 2.0249470050 0.8672138733
C 4.7571755953 1.6156052494 1.4022000317
C 5.6981227359 2.5714898600 1.8885831775
C 5.0770766302 0.2334630299 1.4873922007
C 6.8953257087 2.1689816031 2.4241089085
C 6.2784256695 -0.1728374760 2.0260391004
C 7.1858139068 0.7906051312 2.4943637759
N 2.3929154895 0.8806063661 -1.0176459078
N 0.6189613696 0.1149356486 0.0693250104
O 1.0506883072 0.8080247870 2.2540316602
O 8.3560609958 0.4596757401 3.0257380138
H 5.4575165903 3.6166359490 1.8308741044
H 4.3551497302 -0.4705642336 1.1264248634
H 7.6200942266 2.8662309859 2.7971033160
H 6.5234724224 -1.2175501549 2.0957815843
H 8.4847842611 -0.4807468168 3.0493418999
H 3.3904096679 3.1021264843 0.8748806253

H 0.8670127015 -0.1181981774 -2.0547475555

H -0.2829140555 -0.2700010437 0.2228623698

**CASSCF(14e,13o)/6-31G*:**

**S0:** -642.01343339166 hartree

**S1:** -641.955459240170 hartree

C 1.2718585332 0.2564521206 -1.1326777705

C 1.3753656775 0.7331657473 1.0741386109

C 2.5083325113 1.1626920440 0.3472195348

C 3.5370539890 2.0351420805 0.8657757173

C 4.7552863374 1.6214807446 1.4009596742

C 5.6985835969 2.5738617704 1.8899645430

C 5.0715611464 0.2381558419 1.4836255981

C 6.8943029553 2.1671430483 2.4254908243

C 6.2715334200 -0.1723333377 2.0219000999

C 7.1812677991 0.7878472149 2.4926734608

N 2.3969433923 0.8831130616 -1.0154486989

N 0.6246315876 0.1162005970 0.0709029882

O 1.0530745188 0.8094823822 2.2564374002

O 8.3504591117 0.4527503927 3.0233936075

H 5.4606862110 3.6197327345 1.8343654104

H 4.3485761109 -0.4637558358 1.1207497857

H 7.6206060405 2.8616558078 2.8005845096

H 6.5139830072 -1.2177854384 2.0894469927

H 8.4766993584 -0.4880588724 3.0453996409

H 3.3923687149 3.1121189389 0.8733426031

H 0.8763135216 -0.1336986173 -2.0477691346

H -0.2667295410 -0.2913234256 0.2293136022

H 5.4575165903 3.6166359490 1.8308741044

H 4.3551497302 -0.4705642336 1.1264248634

H 7.6200942266 2.8662309859 2.7971033160

H 6.5234724224 -1.2175501549 2.0957815843

H 8.4847842611 -0.4807468168 3.0493418999

H 3.3904096679 3.1021264843 0.8748806253

H 0.8670127015 -0.1181981774 -2.0547475555

H -0.2829140555 -0.2700010437 0.2228623698