Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Electronic Structure and Absorption Spectra of Fluorescent Nucleoside Analogues

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## Supplemental Informations

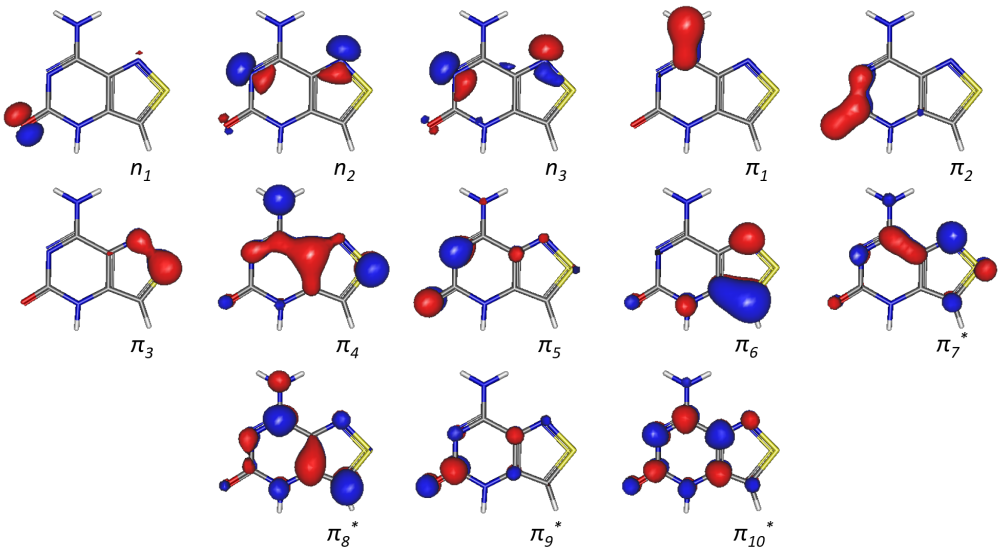


Figure S1: Active space for $^{tz}$**C** molecule with 3 orbitals $n$ and 10 orbitals $\pi$ containing 18 electrons calculated at SA(8)-CASSCF/cc-pVDZ level.

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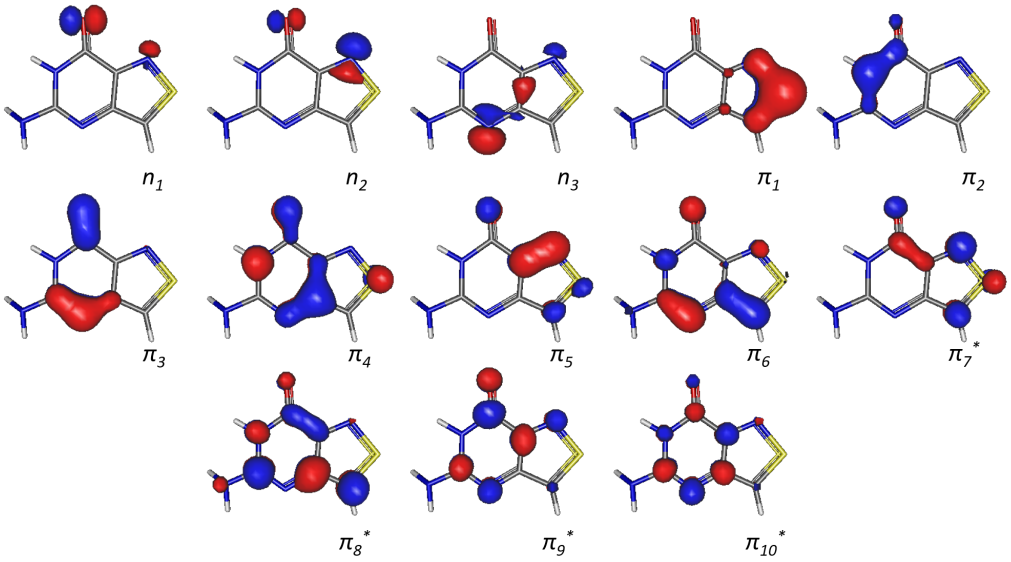


Figure S2: Active space for $^{tz}$**G** molecule with 3 orbitals *n* and 10 orbitals π containing 18 electrons calculated at SA(6)-CASSCF/cc-pVDZ level.

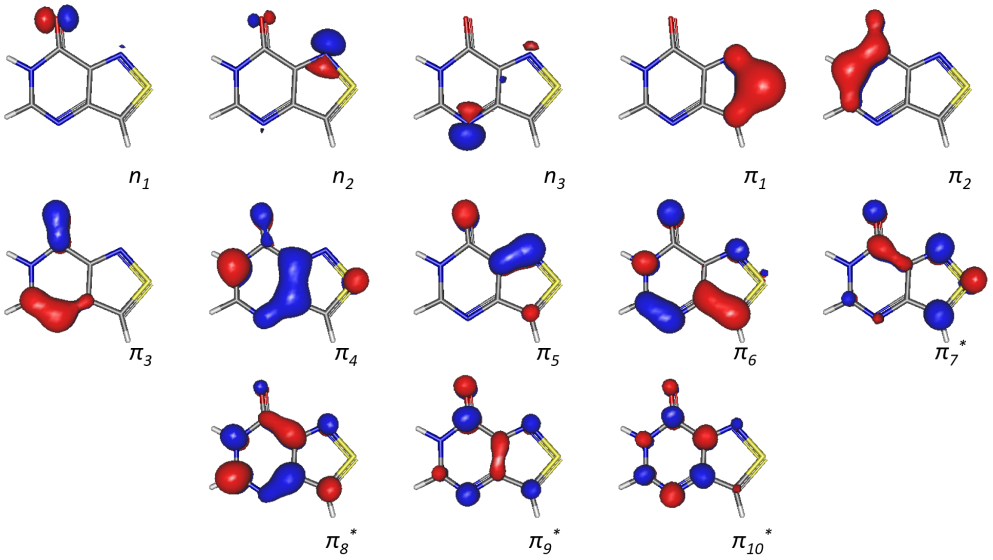


Figure S3: Active space for $^{tz}$**I** molecule with 3 orbitals *n* and 10 orbitals π containing 18 electrons calculated at SA(6)-CASSCF/cc-pVDZ level.

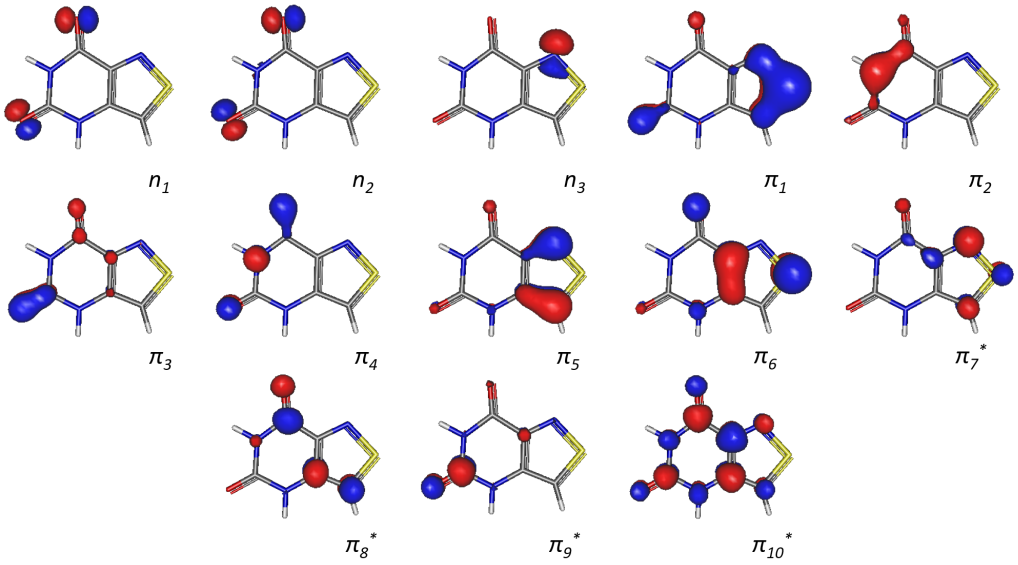


Figure S4: Active space for $^{tz}$**U** molecule with 3 orbitals *n* and 10 orbitals π containing 18 electrons calculated at SA(10)-CASSCF/cc-pVDZ level.

Table S1: Optimized geometric parameter of the new emissive RNA alphabet in gas phase, dioxane and water at MP2/cc-pVDZ level. The bond distance in Å and bond angle in degree.

| | Coordinates | Gas | Dioxane | | Water | |
|---|---|---|---|---|---|---|
| | | | PCM | ASEC-FEG | PCM | ASEC-FEG |
| $^{tz}$**A** | N1−C2 | 1.371 | 1.370 | 1.369 | 1.369 | 1.370 |
| | C2−N3 | 1.329 | 1.329 | 1.330 | 1.330 | 1.333 |
| | C4−C5 | 1.430 | 1.430 | 1.431 | 1.430 | 1.431 |
| | C5−N7 | 1.360 | 1.360 | 1.360 | 1.360 | 1.360 |
| | C4−C9 | 1.412 | 1.412 | 1.411 | 1.412 | 1.409 |
| | S8−C9 | 1.702 | 1.701 | 1.700 | 1.700 | 1.700 |
| | N7−S8 | 1.674 | 1.674 | 1.677 | 1.673 | 1.675 |
| | S8−C9−C4 | 108.4 | 108.3 | 108.3 | 108.3 | 108.3 |
| | S8−N7−C5 | 106.1 | 106.2 | 106.2 | 106.3 | 106.6 |
| | C2−N1−C6 | 117.1 | 117.2 | 117.4 | 117.3 | 117.7 |
| | C2−N3−C4 | 112.6 | 112.6 | 112.4 | 112.7 | 112.2 |
| $^{tz}$**C** | N1−C2 | 1.402 | 1.400 | 1.400 | 1.396 | 1.398 |
| | C4−C5 | 1.418 | 1.417 | 1.420 | 1.416 | 1.420 |
| | C5−C6 | 1.462 | 1.461 | 1.464 | 1.459 | 1.462 |
| | C5−N7 | 1.351 | 1.316 | 1.352 | 1.353 | 1.356 |
| | C4−C9 | 1.399 | 1.399 | 1.399 | 1.399 | 1.401 |
| | S8−C9 | 1.719 | 1.717 | 1.716 | 1.715 | 1.712 |
| | N7−S8 | 1.673 | 1.672 | 1.674 | 1.671 | 1.671 |
| | S8−C9−C4 | 108.1 | 108.0 | 108.1 | 107.9 | 108.2 |
| | S8−N7−C5 | 107.0 | 107.0 | 106.9 | 106.9 | 107.0 |
| | C2−N1−C6 | 120.5 | 120.5 | 121.0 | 120.5 | 120.9 |
| | C2−N3−C4 | 123.1 | 122.9 | 122.1 | 122.6 | 120.8 |
| $^{tz}$**I** | N1−C2 | 1.379 | 1.379 | 1.378 | 1.379 | 1.381 |
| | C2−N3 | 1.304 | 1.304 | 1.305 | 1.304 | 1.308 |
| | N3−C4 | 1.393 | 1.393 | 1.392 | 1.393 | 1.392 |
| | C4−C5 | 1.431 | 1.431 | 1.431 | 1.431 | 1.432 |
| | C5−N7 | 1.351 | 1.351 | 1.352 | 1.351 | 1.355 |
| | N1−H | 1.019 | 1.019 | 1.020 | 1.019 | 1.021 |
| | N7−S8 | 1.674 | 1.674 | 1.676 | 1.674 | 1.675 |

| | Coordinates | Gas | Dioxane | | Water | |
|---|---|---|---|---|---|---|
| | | | PCM | ASEC-FEG | PCM | ASEC-FEG |
| $^{tz}$**U** | N3−C4 | 1.386 | 1.385 | 1.385 | 1.385 | 1.392 |
| | C4−C5 | 1.422 | 1.421 | 1.421 | 1.420 | 1.422 |
| | C5−C6 | 1.483 | 1.481 | 1.483 | 1.477 | 1.475 |
| | C4−C9 | 1.396 | 1.396 | 1.400 | 1.397 | 1.399 |
| | C5−N7 | 1.348 | 1.349 | 1.350 | 1.351 | 1.355 |
| | N7−S8 | 1.668 | 1.669 | 1.672 | 1.669 | 1.671 |
| | S8−C9 | 1.716 | 1.715 | 1.715 | 1.713 | 1.711 |
| | S8−C9−C3 | 107.9 | 107.3 | 108.0 | 107.9 | 108.3 |
| | C5−N7−S8 | 107.3 | 107.9 | 107.2 | 107.2 | 107.1 |
| | C2−N1−C6 | 130.4 | 130.2 | 129.5 | 129.9 | 128.4 |
| | C2−N3−C4 | 123.1 | 123.0 | 122.5 | 122.8 | 121.2 |
| $^{tz}$**G** | N3−C4 | 1.389 | 1.388 | 1.387 | 1.385 | 1.386 |
| | C4−C5 | 1.430 | 1.430 | 1.429 | 1.429 | 1.427 |
| | C5−C6 | 1.474 | 1.472 | 1.473 | 1.469 | 1.471 |
| | C4−C9 | 1.403 | 1.404 | 1.405 | 1.405 | 1.408 |
| | C5−N7 | 1.352 | 1.353 | 1.354 | 1.354 | 1.359 |
| | N7−S8 | 1.673 | 1.673 | 1.676 | 1.673 | 1.678 |
| | S8−C9 | 1.708 | 1.707 | 1.707 | 1.706 | 1.704 |
| | S8−C9−C4 | 108.6 | 108.6 | 108.7 | 108.7 | 108.8 |
| | S8−N7−C5 | 106.6 | 106.6 | 106.6 | 106.7 | 106.7 |
| | C2−N1−C6 | 126.1 | 126.1 | 125.5 | 126.0 | 124.6 |
| | C2−N3−C4 | 113.7 | 113.8 | 114.0 | 114.0 | 114.3 |
| $^{tz}$**I** | S8−C9 | 1.705 | 1.705 | 1.705 | 1.705 | 1.701 |
| | C4−C9 | 1.403 | 1.403 | 1.404 | 1.403 | 1.405 |
| | C2−N3−C4 | 113.1 | 113.1 | 113.1 | 113.1 | 113.2 |
| | C6−N1−C2 | 126.0 | 126.1 | 126.0 | 126.1 | 125.7 |
| | S8−C9−C4 | 108.4 | 108.4 | 108.2 | 108.4 | 108.1 |
| | S8−N7−C5 | 106.7 | 106.7 | 106.6 | 106.7 | 106.6 |

Table S2: Cartesian coordinates for $^{tz}$**A** with 5 water molecules optimized at MP2/cc-pVDZ level (in Angstroms).

| | | | |
|---|---|---|---|
| N | 0.4314 | -0.6851 | -1.8233 |
| N | 0.6591 | 1.4459 | -0.6563 |
| C | 0.0826 | 1.3570 | 1.7595 |
| N | -0.4655 | -1.1118 | 1.7221 |
| N | -0.2629 | -2.6421 | -0.7969 |
| C | 0.7262 | 0.6416 | -1.7159 |
| C | 0.2411 | 0.7910 | 0.4793 |
| C | -0.0826 | -0.6018 | 0.5207 |
| C | 0.0340 | -1.3350 | -0.7171 |
| S | -0.4202 | 0.1395 | 2.8328 |
| H | 0.2475 | 2.3814 | 2.0930 |
| H | -0.5059 | -3.1997 | 0.0320 |
| H | -0.1064 | -3.0915 | -1.6930 |
| H | 1.0273 | 1.1051 | -2.6619 |
| O | 3.0722 | -0.5629 | 0.0403 |
| H | 2.9367 | 0.3812 | -0.1185 |
| H | 2.9487 | -0.9207 | -0.8490 |
| O | -1.6158 | 2.4791 | -2.4407 |
| H | -2.2411 | 1.9775 | -1.9006 |
| H | -0.8605 | 2.5631 | -1.8358 |
| O | -0.0579 | 2.5863 | 4.5094 |
| H | 0.6891 | 2.5014 | 5.1164 |
| H | -0.7634 | 2.9023 | 5.0886 |
| O | -0.5614 | 0.6127 | -4.5092 |
| H | -0.9911 | 1.2615 | -3.9270 |
| H | -0.4201 | -0.1282 | -3.9033 |
| O | -0.9936 | -3.9134 | 1.6645 |
| H | -0.7874 | -3.0130 | 1.9886 |
| H | -1.9601 | -3.9219 | 1.7016 |

Table S3: Comparison between ASEC-DIP and ASEC-FEG approaches to statistic of the hydrogen bonds occurring in 1,4-dioxane and water for the modified RNA nucleobases.

| | | $^{tz}$**A** | | $^{tz}$**C** | | $^{tz}$**G** | | $^{tz}$**U** | | $^{tz}$**I** | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | N° of HB | DIP | FEG | DIP | FEG | DIP | FEG | DIP | FEG | DIP | FEG |
| Dio | 0 | 3.7 | 3.5 | – | – | – | – | 0.1 | 0.1 | 96.8 | 97.1 |
| | 1 | 32.7 | 31.4 | 4.0 | 4.6 | 11.7 | 9.0 | 6.4 | 5.9 | 3.2 | 2.9 |
| | 2 | 63.0 | 64.1 | 37.8 | 38.4 | 42.7 | 37.5 | 89.8 | 90.8 | — | — |
| | 3 | 0.6 | 1.0 | 56.6 | 55.2 | 44.4 | 52.8 | 3.7 | 3.1 | — | — |
| | 4 | — | — | 1.5 | 1.7 | 1.1 | 0.7 | 0.1 | — | — | — |
| | ⟨HB⟩ | 1.61 | 1.63 | 2.55 | 2.54 | 2.35 | 2.45 | 1.97 | 1.97 | 0.03 | 0.03 |
| Wat | 2 | — | — | — | — | — | — | — | — | 3.3 | 2.3 |
| | 3 | 1.4 | 0.3 | – | – | – | – | 0.1 | – | 19.7 | 15.6 |
| | 4 | 9.6 | 3.8 | 0.4 | – | 0.1 | – | 1.2 | 0.5 | 41.3 | 40.4 |
| | 5 | 29.4 | 21.8 | 3.2 | 0.5 | 1.6 | 0.4 | 9.0 | 5.0 | 27.3 | 29.9 |
| | 6 | 34.7 | 39.5 | 16.3 | 4.7 | 8.4 | 4.0 | 31.7 | 24.3 | 7.2 | 9.8 |
| | 7 | 19.5 | 26.1 | 35.6 | 27.9 | 23.7 | 18.0 | 37.1 | 39.7 | 1.1 | 1.8 |
| | 8 | 4.5 | 7.5 | 30.1 | 41.3 | 32.2 | 36.0 | 17.0 | 23.5 | 0.1 | 0.2 |
| | 9 | 0.8 | 0.9 | 11.9 | 21.2 | 23.9 | 29.5 | 3.6 | 6.2 | — | — |
| | 10 | 0.1 | 0.1 | 2.2 | 3.9 | 8.5 | 10.2 | 0.4 | 0.7 | — | — |
| | 11 | — | — | 0.2 | 0.4 | 1.5 | 1.7 | — | — | — | — |
| | 12 | — | — | — | — | 0.1 | 0.2 | – | – | — | — |
| | ⟨HB⟩ | 5.78 | 6.14 | 7.37 | 7.91 | 7.98 | 8.26 | 6.72 | 7.02 | 4.19 | 4.35 |

Table S4: Average number of hydrogen bonds in each site that makes HB for the new emissive RNA alphabet.

| Molecule | | Dioxane | | Water | |
|---|---|---|---|---|---|
| | | ASEC-DIP | ASEC-FEG | ASEC-DIP | ASEC-FEG |
| | N10−H11···O | 0.69 | 0.71 | 0.86 | 0.98 |
| | N10−H12···O | 0.92 | 0.91 | 1.00 | 1.00 |
| | N10···H−O | — | — | 0.10 | 0.02 |
| $^{tz}$**A** | N1···H−O | — | — | 1.48 | 1.69 |
| | N3···H−O | — | — | 1.77 | 1.88 |
| | N7···H−O | — | — | 0.56 | 0.54 |
| | S8···H−O | — | — | 0.02 | 0.02 |
| | N10−H11···O | 0.66 | 0.63 | 0.83 | 0.91 |
| | N10−H12···O | 0.92 | 0.94 | 0.91 | 0.97 |
| | N3−H···O | 0.98 | 0.97 | 1.02 | 1.01 |
| | N10···H−O | — | — | 0.06 | 0.02 |
| $^{tz}$**C** | N1···H−O | — | — | 1.74 | 1.98 |
| | N3···H−O | — | — | 0.08 | 0.11 |
| | N7···H−O | — | — | 0.48 | 0.46 |
| | S8···H−O | — | — | 0.02 | 0.03 |
| | O11···H−O | — | — | 2.25 | 2.43 |
| | N11−H12···O | 0.61 | 0.67 | 0.97 | 0.97 |
| | N11−H13···O | 0.77 | 0.81 | 0.86 | 0.95 |
| | N1−H···O | 0.97 | 0.97 | 1.01 | 1.01 |
| | N11···H−O | — | — | 0.24 | 0.12 |
| $^{tz}$**G** | N1···H−O | — | — | 0.02 | 0.01 |
| | N3···H−O | — | — | 1.61 | 1.72 |
| | N7···H−O | — | — | 0.72 | 0.80 |
| | S8···H−O | — | — | 0.28 | 0.33 |
| | O11···H−O | — | — | 2.28 | 2.27 |
| | N1−H···O | 0.98 | 0.98 | 0.97 | 1.01 |
| | N3−H···O | 0.99 | 1.02 | 1.04 | 1.02 |
| | N1···H−O | — | — | 0.03 | 0.04 |
| | N3···H−O | — | — | 0.04 | 0.04 |
| $^{tz}$**U** | N7···H−O | — | — | 0.65 | 0.56 |
| | S8···H−O | — | — | 0.14 | 0.16 |
| | O10···H−O | — | — | 1.93 | 2.07 |
| | O11···H−O | — | — | 1.94 | 2.12 |
| | N1−H···O | 0.03 | 0.03 | 0.12 | 0.13 |
| | N1···H−O | — | — | 0.00 | 0.00 |
| | N3···H−O | — | — | 1.15 | 1.10 |
| $^{tz}$**I** | N7···H−O | — | — | 0.65 | 0.67 |
| | S8···H−O | — | — | 0.17 | 0.20 |
| | O10···H−O | — | — | 2.10 | 2.25 |

Table S5: The six low-lying transitions energies (eV) with their respective oscillator strength (f) obtained at SA(6)-CASPT2(18,13) level for $^{tz}$**A** molecule (between parenthesis is reported the nature of the state).

| | | | 1,4-dioxane | | | | | | Water | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Gas-Phase | | ASEC-DIP | | ASEC-FEG | | C-PCM | | ASEC-DIP | | ASEC-FEG | | C-PCM | |
| | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ |
| $2^1(n\pi^*)$ | 3.62 | 0.002 | 3.70 | 0.003 | 3.71 | 0.003 | 3.71 | 0.002 | 3.97 | 0.108 | 3.77 | 0.142 | 3.83 | 0.054 |
| $3^1(\pi\pi^*)$ | 4.00 | 0.115 | 4.00 | 0.081 | 3.96 | 0.084 | 4.01 | 0.079 | 4.10 | 0.025 | 4.22 | 0.086 | 3.86 | 0.034 |
| $4^1(n\pi^*)$ | 4.05 | 0.074 | 4.02 | 0.124 | 4.04 | 0.121 | 4.03 | 0.121 | 4.14 | 0.142 | 4.28 | 0.048 | 4.07 | 0.129 |
| $5^1(\pi\pi^*)$ | 5.11 | 0.011 | 5.19 | 0.012 | 5.16 | 0.012 | 5.18 | 0.012 | 5.14 | 0.027 | 5.15 | 0.039 | 5.26 | 0.012 |
| $6^1(\pi\pi^*)$ | 5.32 | 0.088 | 5.28 | 0.080 | 5.27 | 0.082 | 5.30 | 0.083 | 5.21 | 0.015 | 5.18 | 0.013 | 5.28 | 0.074 |

Table S6: The eight low-lying transitions energies (eV) with their respective oscillator strength (f) obtained at SA(8)-CASPT2(18,13) level for $^{tz}$**C** molecule (between parenthesis is reported the nature of the state).

| | | | 1,4-dioxane | | | | | | Water | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Gas-Phase | | ASEC-DIP | | ASEC-FEG | | C-PCM | | ASEC-DIP | | ASEC-FEG | | C-PCM | |
| | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ |
| $2^1(\pi\pi^*)$ | 3.63 | 0.231 | 3.66 | 0.243 | 3.64 | 0.231 | 3.49 | 0.199 | 3.75 | 0.239 | 3.80 | 0.236 | 3.70 | 0.233 |
| $3^1(n\pi^*)$ | 4.25 | 0.000 | 4.38 | 0.001 | 4.37 | 0.001 | 4.45 | 0.000 | 4.87 | 0.118 | 4.54 | 0.245 | 4.43 | 0.159 |
| $4^1(n\pi^*)$ | 4.45 | 0.001 | 4.45 | 0.127 | 4.40 | 0.126 | 4.57 | 0.001 | 4.87 | 0.157 | 5.09 | 0.198 | 4.66 | 0.000 |
| $5^1(\pi\pi^*)$ | 4.47 | 0.100 | 4.65 | 0.001 | 4.53 | 0.001 | 4.71 | 0.098 | 5.05 | 0.007 | 5.11 | 0.021 | 4.80 | 0.000 |
| $6^1(\pi\pi^*)$ | 5.15 | 0.243 | 5.15 | 0.269 | 5.16 | 0.258 | 5.13 | 0.137 | 5.05 | 0.204 | 5.24 | 0.010 | 5.16 | 0.262 |
| $7^1(\pi\pi^*)$ | 5.36 | 0.045 | 5.46 | 0.009 | 5.39 | 0.020 | 5.54 | 0.003 | 5.56 | 0.004 | 5.33 | 0.004 | 5.60 | 0.005 |
| $8^1(n\pi^*)$ | 5.65 | 0.012 | 5.62 | 0.013 | 5.64 | 0.012 | 5.61 | 0.012 | 5.73 | 0.090 | 5.56 | 0.004 | 5.60 | 0.013 |

Table S7: The six low-lying transitions energies (eV) with their respective oscillator strength (f) obtained at SA(6)-CASPT2(18,13) level for $^{tz}$**G** molecule (between parenthesis is reported the nature of the state).

| | | | 1,4-dioxane | | | | | | Water | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Gas-Phase | | ASEC-DIP | | ASEC-FEG | | C-PCM | | ASEC-DIP | | ASEC-FEG | | C-PCM | |
| | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ |
| $2^1(\pi\pi^*)$ | 3.87 | 0.095 | 3.76 | 0.116 | 3.76 | 0.116 | 3.82 | 0.113 | 3.73 | 0.130 | 3.63 | 0.125 | 3.75 | 0.121 |
| $3^1(n\pi^*)$ | 4.45 | 0.017 | 4.61 | 0.001 | 4.60 | 0.000 | 4.64 | 0.001 | 4.69 | 0.048 | 4.61 | 0.054 | 4.70 | 0.001 |
| $4^1(\pi\pi^*)$ | 4.65 | 0.111 | 4.69 | 0.083 | 4.68 | 0.085 | 4.69 | 0.093 | 4.88 | 0.001 | 4.80 | 0.001 | 4.76 | 0.070 |
| $5^1(n\pi^*)$ | 5.06 | 0.007 | 5.05 | 0.006 | 5.04 | 0.006 | 5.08 | 0.007 | 5.25 | 0.006 | 5.19 | 0.006 | 5.11 | 0.006 |
| $6^1(\pi\pi^*)$ | 5.31 | 0.214 | 5.30 | 0.269 | 5.30 | 0.280 | 5.33 | 0.259 | 5.29 | 0.408 | 5.22 | 0.356 | 5.35 | 0.315 |

Table S8: The ten low-lying transitions energies (eV) with their respective oscillator strength (f) obtained at SA(10)-CASPT2(18,13) level for $^{tz}$**U** molecule (between parenthesis is reported the nature of the state).

| | | | 1,4-dioxane | | | | | | Water | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Gas-Phase | | ASEC-DIP | | ASEC-FEG | | C-PCM | | ASEC-DIP | | ASEC-FEG | | C-PCM | |
| | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ |
| $2^1(\pi\pi^*)$ | 4.09 | 0.165 | 4.00 | 0.163 | 3.99 | 0.162 | 4.10 | 0.152 | 3.92 | 0.174 | 3.92 | 0.170 | 3.98 | 0.169 |
| $3^1(n\pi^*)$ | 4.48 | 0.001 | 4.56 | 0.001 | 4.53 | 0.000 | 4.56 | 0.001 | 4.88 | 0.001 | 4.78 | 0.000 | 4.65 | 0.001 |
| $4^1(n\pi^*)$ | 5.46 | 0.011 | 5.28 | 0.147 | 5.35 | 0.131 | 5.43 | 0.121 | 5.13 | 0.206 | 5.10 | 0.202 | 5.38 | 0.159 |
| $5^1(\pi\pi^*)$ | 5.48 | 0.172 | 5.38 | 0.077 | 5.37 | 0.096 | 5.49 | 0.123 | 5.50 | 0.202 | 5.49 | 0.198 | 5.57 | 0.010 |
| $6^1(\pi\pi^*)$ | 5.58 | 0.064 | 5.54 | 0.010 | 5.53 | 0.010 | 5.52 | 0.011 | 5.61 | 0.066 | 5.55 | 0.060 | 5.62 | 0.113 |
| $7^1(n\pi^*)$ | 6.06 | 0.000 | 5.60 | 0.212 | 5.64 | 0.200 | 6.13 | 0.000 | 5.65 | 0.010 | 5.63 | 0.010 | 6.23 | 0.000 |
| $8^1(\pi\pi^*)$ | 6.30 | 0.228 | 6.06 | 0.001 | 6.03 | 0.000 | 6.26 | 0.256 | 6.30 | 0.259 | 6.17 | 0.001 | 6.32 | 0.213 |
| $9^1(n\pi^*)$ | 6.45 | 0.000 | 6.31 | 0.266 | 6.28 | 0.257 | 6.66 | 0.000 | 6.31 | 0.000 | 6.23 | 0.268 | 6.68 | 0.000 |
| $10^1(n\pi^*)$ | 6.63 | 0.000 | 6.63 | 0.000 | 6.60 | 0.000 | 7.70 | 0.015 | 7.11 | 0.000 | 7.01 | 0.000 | 6.94 | 0.000 |

Table S9: The six low-lying transitions energies (eV) with their respective oscillator strength (f) obtained at SA(6)-CASPT2(18,13) level for $^{tz}$**I** molecule (between parenthesis is reported the nature of the state).

| | | | 1,4-dioxane | | | | | | Water | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Gas-Phase | | ASEC-DIP | | ASEC-FEG | | C-PCM | | ASEC-DIP | | ASEC-FEG | | C-PCM | |
| | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ | $\Delta E$ | $f$ |
| $2^1(\pi\pi^*)$ | 4.03 | 0.104 | 4.01 | 0.109 | 3.99 | 0.108 | 4.01 | 0.109 | 3.73 | 0.130 | 3.63 | 0.125 | 4.01 | 0.109 |
| $3^1(n\pi^*)$ | 4.54 | 0.001 | 4.58 | 0.119 | 4.57 | 0.125 | 4.57 | 0.124 | 4.69 | 0.048 | 4.61 | 0.054 | 4.55 | 0.000 |
| $4^1(\pi\pi^*)$ | 4.55 | 0.136 | 4.62 | 0.001 | 4.58 | 0.001 | 4.58 | 0.000 | 4.88 | 0.001 | 4.80 | 0.001 | 4.57 | 0.127 |
| $5^1(n\pi^*)$ | 4.95 | 0.005 | 4.99 | 0.005 | 4.98 | 0.005 | 4.98 | 0.005 | 5.25 | 0.006 | 5.19 | 0.006 | 4.96 | 0.005 |
| $6^1(\pi\pi^*)$ | 5.44 | 0.050 | 5.44 | 0.067 | 5.45 | 0.056 | 5.44 | 0.059 | 5.29 | 0.408 | 5.22 | 0.356 | 5.42 | 0.055 |

Table S10: Charge distribution (e) for $^{tz}$**A** base in gas phase, dioxane and water obtained at MP2/cc-pVDZ level.

| Atom | Gas | Dioxane | | | Water | | |
|---|---|---|---|---|---|---|---|
| | | PCM | ASEC-DIP | ASEC-FEG | PCM | ASEC-DIP | ASEC-FEG |
| N1 | -0.67 | -0.69 | -0.70 | -0.70 | -0.72 | -0,84 | -0.88 |
| C2 | 0.57 | 0.58 | 0.58 | 0.57 | 0.59 | 0,69 | 0.69 |
| N3 | -0.67 | -0.69 | -0.70 | -0.69 | -0.71 | -0,86 | -0.87 |
| C4 | 0.45 | 0.46 | 0.45 | 0.44 | 0.46 | 0,53 | 0.54 |
| C5 | -0.02 | -0.03 | -0.01 | -0.02 | -0.03 | -0,06 | -0.08 |
| C6 | 0.58 | 0.60 | 0.60 | 0.61 | 0.62 | 0,71 | 0.77 |
| N7 | -0.35 | -0.36 | -0.37 | -0.37 | -0.38 | -0,38 | -0.39 |
| S8 | 0.21 | 0.23 | 0.23 | 0.22 | 0.26 | 0,28 | 0.28 |
| C9 | -0.29 | -0.29 | -0.28 | -0.28 | -0.29 | -0,31 | -0.33 |
| N10 | -0.67 | -0.69 | -0.71 | -0.72 | -0.72 | -0,77 | -0.80 |
| H11 | 0.30 | 0.31 | 0.33 | 0.34 | 0.34 | 0,37 | 0.41 |
| H12 | 0.34 | 0.36 | 0.38 | 0.38 | 0.38 | 0,42 | 0.45 |
| H13 | 0.20 | 0.21 | 0.21 | 0.21 | 0.22 | 0,22 | 0.22 |
| H14 | 0.01 | 0.01 | 0.00 | 0.00 | 0.01 | 0,00 | 0.00 |

Table S11: Charge distribution (e) for $^{tz}$**C** base in gas phase, dioxane and water obtained at MP2/cc-pVDZ level.

| Atom | Gas | Dioxane | | | Water | | |
|---|---|---|---|---|---|---|---|
| | | PCM | ASEC-DIP | ASEC-FEG | PCM | ASEC-DIP | ASEC-FEG |
| N1 | -0.70 | -0.74 | -0.75 | -0.75 | -0.79 | -0.86 | -0.92 |
| C2 | 0.92 | 0.94 | 0.94 | 0.93 | 0.95 | 1.03 | 1.06 |
| N3 | -0.73 | -0.74 | -0.75 | -0.74 | -0.74 | -0.78 | -0.79 |
| C4 | 0.36 | 0.36 | 0.36 | 0.36 | 0.36 | 0.38 | 0.40 |
| C5 | 0.05 | 0.04 | 0.04 | 0.03 | 0.03 | 0.02 | 0.00 |
| C6 | 0.57 | 0.59 | 0.60 | 0.62 | 0.63 | 0.68 | 0.72 |
| N7 | -0.35 | -0.36 | -0.37 | -0.37 | -0.38 | -0.39 | -0.39 |
| S8 | 0.20 | 0.22 | 0.20 | 0.19 | 0.24 | 0.24 | 0.26 |
| C9 | -0.34 | -0.33 | -0.32 | -0.32 | -0.32 | -0.31 | -0.31 |
| N10 | -0.69 | -0.70 | -0.73 | -0.74 | -0.72 | -0.76 | -0.77 |
| O11 | -0.56 | -0.59 | -0.60 | -0.61 | -0.63 | -0.71 | -0.75 |
| H12 | 0.31 | 0.32 | 0.34 | 0.35 | 0.34 | 0.36 | 0.37 |
| H13 | 0.36 | 0.37 | 0.40 | 0.41 | 0.39 | 0.42 | 0.42 |
| H14 | 0.38 | 0.39 | 0.41 | 0.41 | 0.40 | 0.44 | 0.46 |
| H15 | 0.21 | 0.22 | 0.22 | 0.22 | 0.23 | 0.23 | 0.23 |

Table S12: Charge distribution (e) for $^{tz}$**G** base in gas phase, dioxane and water obtained at MP2/cc-pVDZ level.

| Atom | Gas | Dioxane | | | Water | | |
|---|---|---|---|---|---|---|---|
| | | PCM | ASEC-DIP | ASEC-FEG | PCM | ASEC-DIP | ASEC-FEG |
| N1 | -0.67 | -0.67 | -0.67 | -0.69 | -0.67 | -0.71 | -0.71 |
| C2 | 0.74 | 0.75 | 0.76 | 0.77 | 0.78 | 0.85 | 0.84 |
| N3 | -0.66 | -0.67 | -0.69 | -0.69 | -0.70 | -0.81 | -0.82 |
| C4 | 0.37 | 0.37 | 0.35 | 0.36 | 0.36 | 0.40 | 0.40 |
| C5 | 0.01 | 0.02 | 0.02 | 0.03 | 0.02 | 0.01 | 0.02 |
| C6 | 0.62 | 0.63 | 0.63 | 0.63 | 0.63 | 0.71 | 0.70 |
| N7 | -0.34 | -0.37 | -0.38 | -0.38 | -0.41 | -0.44 | -0.45 |
| S8 | 0.20 | 0.22 | 0.21 | 0.22 | 0.24 | 0.25 | 0.26 |
| C9 | -0.28 | -0.28 | -0.27 | -0.28 | -0.27 | -0.26 | -0.27 |
| O10 | -0.47 | -0.50 | -0.52 | -0.52 | -0.53 | -0.63 | -0.64 |
| N11 | -0.74 | -0.76 | -0.77 | -0.79 | -0.79 | -0.85 | -0.81 |
| H12 | 0.31 | 0.33 | 0.36 | 0.36 | 0.36 | 0.41 | 0.40 |
| H13 | 0.34 | 0.35 | 0.36 | 0.36 | 0.36 | 0.40 | 0.40 |
| H14 | 0.38 | 0.39 | 0.41 | 0.42 | 0.41 | 0.46 | 0.47 |
| H15 | 0.20 | 0.20 | 0.20 | 0.20 | 0.21 | 0.21 | 0.21 |

Table S13: Charge distribution (e) for $^{tz}$**U** base in gas phase, dioxane and water obtained at MP2/cc-pVDZ level.

| Atom | Gas | Dioxane | | | Water | | |
|---|---|---|---|---|---|---|---|
| | | PCM | ASEC-DIP | ASEC-FEG | PCM | ASEC-DIP | ASEC-FEG |
| N1 | -0.60 | -0.60 | -0.61 | -0.62 | -0.60 | -0.65 | -0.66 |
| C2 | 0.73 | 0.74 | 0.76 | 0.76 | 0.76 | 0.84 | 0.84 |
| N3 | -0.61 | -0.61 | -0.63 | -0.62 | -0.61 | -0.65 | -0.65 |
| C4 | 0.30 | 0.30 | 0.31 | 0.31 | 0.30 | 0.32 | 0.32 |
| C5 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 | 0.08 | 0.07 |
| C6 | 0.58 | 0.59 | 0.60 | 0.60 | 0.60 | 0.66 | 0.67 |
| N7 | -0.35 | -0.37 | -0.39 | -0.39 | -0.42 | -0.45 | -0.44 |
| S8 | 0.24 | 0.25 | 0.24 | 0.24 | 0.26 | 0.29 | 0.29 |
| C9 | -0.35 | -0.34 | -0.34 | -0.34 | -0.32 | -0.30 | -0.30 |
| O10 | -0.45 | -0.47 | -0.49 | -0.49 | -0.51 | -0.58 | -0.60 |
| O11 | -0.52 | -0.54 | -0.55 | -0.56 | -0.56 | -0.65 | -0.66 |
| H12 | 0.34 | 0.35 | 0.38 | 0.38 | 0.36 | 0.41 | 0.43 |
| H13 | 0.37 | 0.38 | 0.40 | 0.40 | 0.39 | 0.44 | 0.46 |
| H14 | 0.22 | 0.23 | 0.23 | 0.23 | 0.24 | 0.24 | 0.24 |

Table S14: Charge distribution (e) for $^{tz}$**I** base in gas phase, dioxane and water obtained at MP2/cc-pVDZ level.

| Atom | Gas | Dioxane | | | Water | | |
|---|---|---|---|---|---|---|---|
| | | PCM | ASEC-DIP | ASEC-FEG | PCM | ASEC-DIP | ASEC-FEG |
| N1 | -0.61 | -0.61 | -0.61 | -0.60 | -0.60 | -0.63 | -0.60 |
| C2 | 0.44 | 0.45 | 0.46 | 0.45 | 0.47 | 0.52 | 0.51 |
| N3 | -0.62 | -0.64 | -0.65 | -0.65 | -0.66 | -0.72 | -0.71 |
| C4 | 0.45 | 0.45 | 0.46 | 0.46 | 0.46 | 0.49 | 0.49 |
| C5 | -0.02 | -0.02 | -0.02 | -0.01 | -0.01 | -0.03 | 0.00 |
| C6 | 0.65 | 0.65 | 0.65 | 0.65 | 0.66 | 0.73 | 0.70 |
| N7 | -0.33 | -0.36 | -0.37 | -0.36 | -0.40 | -0.43 | -0.44 |
| S8 | 0.22 | 0.24 | 0.24 | 0.23 | 0.26 | 0.29 | 0.30 |
| C9 | -0.31 | -0.31 | -0.32 | -0.32 | -0.30 | -0.31 | -0.31 |
| O10 | -0.48 | -0.50 | -0.50 | -0.51 | -0.54 | -0.61 | -0.63 |
| H11 | 0.35 | 0.36 | 0.36 | 0.36 | 0.38 | 0.38 | 0.38 |
| H12 | 0.21 | 0.21 | 0.23 | 0.23 | 0.22 | 0.24 | 0.25 |
| H13 | 0.06 | 0.06 | 0.06 | 0.06 | 0.07 | 0.07 | 0.07 |