## Supporting Information

1. Computational details
2. Vertical energies
3. 2TU: Min $\pi \pi^{*}(\mathbf{S} 2), \operatorname{Min} n \pi^{*}(\mathbf{S} 2)$ and $\operatorname{Min}{ }^{3} n \pi^{*}(\mathbf{S} 2)$ structures
4. Details on 2TU decay paths and PA/SE signals
5. 24TU: Min $\pi \pi^{*}\left(S_{2}\right)$, $\operatorname{Min} n \pi *\left(S_{2}\right)$, $\operatorname{Min}{ }^{3} \pi \pi^{*}\left(S_{2}\right)$ and $\operatorname{Min}{ }^{3} n \pi *\left(S_{2}\right)$ structures.
6. Details on 24TU decay paths and PA/SE signals
7. Details on PL mesurements
8. Sample preparation
9. Experimental setup
10. Cartesian coordinates of QM part

## 1. Computational details

## a. Classical molecular dynamics

The 2-thiouracil (2TU) and 2,4-dithioracil (24TU) starting geometry were obtained running a classical molecular dynamics simulation, using the AMBER 12 suite ${ }^{[1]}$ with the ff10 force field. Periodic boundary conditions were applied to a $35 \times 34 \times 31 \AA$ and $36 \times 34 \times 31 \AA$ periodic box containing 1229 and 1255 water molecules, described by the TIP3P force field ${ }^{[2]}$. The hydrogencontaining bonds were restrained by the SHAKE algorithm ${ }^{[3]}$ while the water geometry was rigidized by the SETTLE scheme ${ }^{[4]}$. Non-bonding and electrostatic interactions were evaluated with a cutoff of $9 \AA$, making use of the method for quantification of the long-range electrostatics. The time step was set to 0.5 fs and integration of the equations of motion was done with the leap-frog algorithm. Thermalization of the systems was reached by heating of the pre-optimized system to 300 K in 15 ps steps of 100 K . A production run at 300 K and 1 atm was carried out for 500 ps . The lowest energy structure along the dynamics was selected as a starting point for subsequent $\mathrm{QM} / \mathrm{MM}$ refinement.

## b. QM/MM layers partitioning.



Figure S1. High/Medium/Low layer paritioning of 2 TU and 24 TU in the $\mathrm{QM} / \mathrm{MM}$ protocol. The High layer comprises the thiouracil, the Medium layer comprises all waters in $3 \AA$ distance of the QM region (encircled with a dashed line). The rest of waters are included in the Low layer.

QM/MM calculations were executed with the COBRAMM program, developed in our group interfacing various QM codes with $\mathrm{AMBER}^{[5]}$. The High/Medium/Low layers partitioning was applied to a spherical droplet centred at 2 TU and 24 TU with a radius of $12 \AA$ (containing 261 and 265 waters), obtained from the cubic box The QM region comprises the thionucleobase. The water molecules in $3 \AA$ distance were included in the movable (MM) Medium layer (Figure S1). The remaining water molecules were kept fixed in the (MM) Low layer.

## 2. Vertical energies



Figure S2. Calculated spectra of 2TU, 24TU and 4TU, taken from Chemical Physics 515 (2018) 643-653 publication (MS-RASPT2/SA-6-RASSCF(12,9|2,4)/ANO-L level for 2TU and 4TU, MS-RASPT2/SA-9$\operatorname{RASSCF}(2,2|14,10| 2,2) / \mathrm{ANO}-\mathrm{L}_{\mathrm{S}}$ for 24 TU . In the present work the decay path of 2 TU and 24 TU have been mapped at MS-CASPT2/SA-11-CASSCF(16,12)/ANO-RCC and (MS-CASPT2/SA-11-CASSCF $(16,12) /$ ANO-RCC) level, respectively, resembling the order of the states of the present spectra, which employs a larger active space, to better resemble the experimental spectra. Each orbitals square represents the Franck-Condon electronic transition involved in the band with the same line colour. The $\pi$ bonding orbitals of 24 TU , in the FC region are still delocalized on both the sulphur atoms; along the relaxation path they localize on S 2 or S 4 , so the respective states $\pi \pi^{*}$ or $\pi \pi^{*}$ ' are labelled with '(S4)' or '(S2)', italics character ${ }^{[6]}$.

Table S1. Vertical excitation energies and oscillator strength $(f)$ of 2 TU ground state minimum at the MS-RASPT2/SA-6-RASSCF $(12,9 \mid 2,4) /$ ANO-L ${ }_{S} \quad$ (Chemical Physics 515 (2018) 643-653) and at the MS-CASPT2/SA-11-CASSCF $(16,12) /$ ANO-RCC level, both in water.

| 2TU |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | MS-RASPT2/SA-6RASSCF(12,9\|2,4) /ANO-Ls |  | $\begin{aligned} & \text { MS-CASPT2/SA- } \\ & \text { 11- } \\ & \text { CASSCF(16,12)/ } \\ & \text { ANO-RCC } \end{aligned}$ |  | Exp. |
| State | Energy (eV) | $f$ | Energy (eV) | $f$ |  |
| $n \pi^{*}\left(\mathrm{~S}_{2}\right)$ | 4.04 | 0.01 | 3.75 | 0.00 |  |
| $\pi \pi^{*}\left(\mathrm{~S}_{2}\right)$ | 4.14 | 0.36 | 3.84 | 0.23 | 4.28 |
| $\pi \pi^{* \prime}\left(\mathrm{~S}_{2}\right)$ | 4.54 | 0.15 | 4.17 | 0.20 | 4.59 |
| $n \pi^{* \prime}\left(\mathrm{~S}_{2}\right)$ | 4.94 | 0.00 | 4.35 | 0.07 |  |
| Active space orbitals $(16,12)$ |  |  |  |  |  |
|  |  | bond |  |  | 2) |
|  |  |  |  |  |  |

Table S2. Vertical excitation energies and oscillator strength $(f)$ of 24 TU ground state minimum at the MS-RASPT2/SA-9RASSCF $(2,2|14,10| 2,2) /$ ANO-L $_{S}$ (Chemical Physics 515 (2018) 643653 ) and at the MS-CASPT2/SA-11-CASSCF $(18,14) /$ ANO-RCC level, both in water. The '(S2)' or '(S4)', italics character, indicates that along the relaxation path the n or the $\pi$ orbitals are localizing on the corresponding sulphur, instead, in the FC region they are still delocalized on both.

| 24TU |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | MS-RASPT2/SA-9-RASSCF(2,2\|14,10|2,2)/ANO-L |  | MS-CASPT2/SA-11CASSCF(18,14)/ANO -RCC |  | Exp. |
| State | Energy (eV) | $f$ | Energy (eV) | $f$ |  |
| $\pi \pi^{*}\left(S_{4}\right)$ | 3.76 | 0.18 | 3.33 | 0.17 | 3.44 |
| $\pi \pi^{*}\left(S_{2}\right)$ | 4.22 | 0.36 | 3.74 | 0.30 |  |
| $\pi \pi^{* \prime}\left(S_{4}\right)$ | 4.56 | 0.36 | 4.18 | 0.37 | 4.51 |
| $\pi \pi^{* \prime}\left(S_{2}\right)$ | 4.85 | 0.23 | 4.38 | 0.14 | 4.77 |
| $\pi \pi^{*}\left(S_{4}\right)$ | 3.51 | 0.02 | 3.18 | 0.00 |  |
| $\pi \pi^{* \prime}\left(S_{2}\right)$ | 3.90 | 0.00 | 3.56 | 0.00 |  |
| $\pi \pi^{* \prime}\left(S_{2}\right)$ | 4.32 | 0.00 | 3.94 | 0.00 |  |
| $\pi \pi^{* \prime}\left(S_{4}\right)$ | 5.08 | 0.01 | 4.66 | 0.02 |  |
| Active space orbitals (18,14) |  |  |  |  |  |
|  |  |  |  |  |  |
| Antibonding |  |  |  |  |  |

3. 2TU: Min $\pi \pi^{*}(\mathbf{S} 2)$, $\operatorname{Min} \mathbf{n} \pi *(\mathbf{S} 2)$ and $\operatorname{Min}^{3} n{ }^{\mathbf{n}}{ }^{*}(\mathbf{S} 2)$ structures

$\mathrm{C} 2-\mathrm{N} 3-\mathrm{C} 4-\mathrm{C} 5=9^{\circ}$

$\mathrm{C} 2-\mathrm{N} 3-\mathrm{C} 4-\mathrm{C} 5=9^{\circ}$

$\mathrm{C} 2-\mathrm{N} 3-\mathrm{C} 4-\mathrm{C} 5=18^{\circ}$

Figure S3. Comparison of $\operatorname{Min} \pi \pi^{*}(\mathrm{~S} 2)$, $\operatorname{Min}^{3} \mathrm{n} \pi^{*}(\mathrm{~S} 2)$ and $\operatorname{Min} n \pi^{*}(\mathrm{~S} 2) 2 T U$ structures. They are similar, and they do not show a large geometrical distortion: the dihedral angle values documented are small, they lead just to a tiny boat distortion of the ring, along the dashed axes.

## 4. Details on 2TU decay paths and PA/SE signals



Figure S4. This is the more detailed version of Figure 3 in the main text: a larger number of calculated critical points and SE/PA values are documented.
$\pi \pi^{*}(\mathrm{~S} 2)$ (on the right) and $\pi \pi^{* \prime}(\mathrm{~S} 2)$ (on the left) decay paths, starting from the Franck-Condon region. The two bright states are excited with the same pumping pulse at $\lambda=270$, see Figure 1. The inset EADS panel shows the time constants: the red and blue curves are at 167 fs and long living lifetimes, respectively. Stimulated emission (SE, negative signals) and photoinduced absorption (PA, positive signals) are associated to the calculated SE or PA values evaluated on different minima: they are indicated with red and blue squares if they match with 167 or long living lifetimes signals, respectively.

## 5. 24TU: Min $\pi \pi^{*}\left(S_{2}\right), \operatorname{Min} \mathrm{n} \pi *\left(S_{2}\right)$, $\operatorname{Min}^{3} \boldsymbol{\pi} \pi *\left(S_{2}\right)$ and $\operatorname{Min}^{3} \mathbf{n} \pi *\left(S_{2}\right)$ structures.



Figure S5. Comparison of $\operatorname{Min} \pi \pi^{*}(S 2)$, $\operatorname{Min}{ }^{3} \mathrm{n} \pi^{*}(S 2)$, Min $n \pi^{*}(S 2)$ and $\operatorname{Min}{ }^{3} \pi \pi^{*}(S 2) 24 \mathrm{TU}$ structures. They are similar, and they do not show a large geometrical distortion: the dihedral angle values documented are small, they lead just to a tiny boat distortion of the ring, along the dashed axes.

## 6. Details on 24TU decay paths and PA/SE signals



Figure S6. This is the more detailed version of Figure 4a in the main text: a larger number of calculated critical point and $\mathrm{SE} / \mathrm{PA}$ values are documented. Calculated 24TU decay paths pumping with a wavelength of 330 nm . $\pi \pi^{*}(S 2)$ (on the right) and $\pi \pi^{*}(S 4)$ (on the left). The inset EADS panel shows the time constants: the black, red and blue curves are at $109 \mathrm{fs}, 435$ and long living lifetimes, respectively. Stimulated emission (SE, negative signals) and photoinduced absorption (PA, positive signals) are associated to the calculated SE or PA values evaluated on the
different minima: they are indicated with black, red and blue squares if they match with the three different lifetimes signals, $109 \mathrm{fs}, 435 \mathrm{fs}$ and long living, respectively.

24TU
pump at 270 nm


Figure S7. This is the more detailed version of Figure 4 b in the main text: a larger number of calculated critical point and SE/PA values are documented. Calculated 24 TU decay paths pumping with a $270 \mathrm{~nm} . \pi \pi^{* \prime}(S 2)$ (on the right) and $\pi \pi^{* \prime}(S 4)$ (on the left). The inset EADS panel shows the time constants: the black, red and blue curves are at $136 \mathrm{fs}, 217$ and long living lifetimes, respectively.

## 7. PL measurements



Figura S8. Photoluminescence: 2,4-dithiouracil (a) illuminated at 330 nm and (b) illuminated at 270 nm . (c) 4thiouracil illuminated at 330 nm .

We acquired the steady state emission spectra at room temperature using a Cary Eclipse spectrophotometer, with a white lamp excitation. The spectra were measured at 1000 V PMT voltage with excitation and emission slit-widths of 5 nm and averaging times of 0.9 s . To clear the lamp scattering peaks we performed a background subtraction using the PBS solution. The sample concentrations used were about 0.02 mM .

## a) 2,4-dithiouracil result:

In the 2,4-dithiouracil photoluminescence (PL) excited at 275 nm (Figure S8b) we observe a band from 300 nm to 360 nm (peaking at 320 nm ) and another broad band that extends from 360 nm until 700 nm (peaking at 515 nm ). The calculations predicted emissions at 370 nm (from $\pi \pi^{* \prime}(S 4)$, Figure S7 on the left), which agrees with the first PL band, and at 538 nm and 385 nm (Figure S7), which agree with the broad PL band around $380-700 \mathrm{~nm}$ (Figure S8b). In the pump-probe experiments, we observed a stimulated emission in the short time scale peaking around 400 nm (black line in the EADS, Figure S7 inset) and a stimulated emission peaking around 500 nm (red line in EADS); these results match with the broad PL band. The band from 300 nm to 360 nm was covered by GSB in the pump-probe experiments (Figure 2, in the main text).

In the 2,4-dithiouracil PL excited at 330 nm (Figure S8a) we observe only a broad band that extends from 360 nm until 700 nm (peaking at 500 nm ). That is also in agreement with the calculations and the pump-probe experiments. The calculations was predicted emissions at 449 nm and at 538 nm (Figure S6), in agreement with the broad PL band. In the pump-probe experiments, we observed a broad stimulated emission in the short time scale peaking around 420 nm (black line in the EADS, Figure S6 inset) and another broad stimulated emission peaking around 500 nm (red line in EADS); these results also match with the broad PL band results.

## b) 2-thiouracil:

For measurements performed under the same conditions as above, we could not detect PL from the 2-thiouracil.

## c) 4-thiouracil:

Exciting 4-thiouracil at 330 nm , we observed two bands: one band peaking at 400 nm and another band peaking at 520 nm (Figure S8b). These results are in agreement with the literature results,
reported by Taras-Goslinska et al ${ }^{[7]}$. which assigned the first peak as due to a PL from the bright singlet state and the second one as a phosphorescence coming from the triplet state. The result is also in good agreement with the pump-probe experiments, as we observed a stimulated emission at 400 nm and a PA signal about 550 nm due to the triplet state in our previous work ${ }^{[8]}$. And it is also in agreement with the calculations.

## 8. Sample preparation

The PBS solution, 16 mM concentration and 7.4 pH , was prepared by dissolving 0.15 g of sodium dihydrogen phosphate and 0.27 g of sodium hydrogen phosphate in 200 mL of ultrapure water. 4Thiouracil ( $97 \%$ purity), 2-Thiouracil ( $\geq 99 \%$ purity), 2,4-dithiouracil ( $98 \%$ purity) were purchased from Sigma-Aldrich and used as received. 2TU, 4TU and 24 TU in PBS solution were prepared to obtain an optical density about 0.5 at the pump wavelength.

## 9. Experimental setup

The experimental TA setup starts with a Ti:Sapphire laser at 800 nm wavelength and 100 fs pulse duration which pumps a non-collinear optical parametric amplifier (NOPA) generating sub-20-fs visible pulses. Our setup allows us to obtain broadband sub-20-fs pump pulses at 330 nm or at 270 nm . Pump pulses at 330 nm are generated by a sum frequency mixing of the NOPA land the fundamental beam. Pump pulses centered at 270 nm come from second harmonic of visible NOPA. Probe pulses ( $350-600 \mathrm{~nm}$ spectral range) are obtained by focusing the fundamental beam on a $\mathrm{CaF}_{2}$ plate.

## 10. Cartesian coordinates of QM part

| $\underline{2 T U}$ |  |  |
| :---: | :---: | :---: |
| x | y | Z |
| Min GS |  |  |
| N 18.403175 | 17.249011 | 14.500341 |
| C 18.611756 | 16.345333 | 15.513430 |
| N 17.621684 | 16.327185 | 16.452338 |
| C 16.493385 | 17.076732 | 16.358130 |
| C 16.283906 | 17.914676 | 15.312981 |
| C 17.267464 | 18.000455 | 14.275574 |
| S 19.948326 | 15.379312 | 15.565656 |
| O 17.157657 | 18.685952 | 13.241638 |
| H 15.362777 | 18.467249 | 15.229867 |
| H 15.781902 | 16.954063 | 17.161790 |
| H 19.119941 | 17.240759 | 13.771186 |
| H 17.701288 | 15.659531 | 17.224328 |
| Min $\pi \pi^{*}$ (S2) |  |  |
| N 18.399442 | 17.291251 | 14.478945 |
| C 18.520594 | 16.404917 | 15.470795 |
| N 17.591813 | 16.324433 | 16.412669 |
| C 16.445834 | 17.151397 | 16.411042 |
| C 16.253372 | 17.958375 | 15.273062 |
| C 17.188417 | 18.072163 | 14.247801 |
| S 19.906392 | 15.364873 | 15.498879 |
| O 17.152399 | 18.731435 | 13.163961 |
| H 15.323748 | 18.497068 | 15.172575 |


| H | 15.746695 | 16.987966 | 17.208413 |
| :--- | :--- | :--- | :--- |
| H | 19.114320 | 17.276916 | 13.749464 |
| H | 17.688009 | 15.622142 | 17.149593 |


| Min $n \pi *(\mathrm{~S} 2)$ |  |  |  |
| :--- | :--- | :--- | :--- |
| N | 18.441484 | 17.347948 | 14.503976 |
| C | 18.529952 | 16.372662 | 15.465688 |
| N | 17.593472 | 16.328611 | 16.423238 |
| C | 16.493003 | 17.137212 | 16.407977 |
| C | 16.254416 | 17.942194 | 15.280530 |
| C | 17.206451 | 18.037083 | 14.254410 |
| S | 19.830849 | 15.215948 | 15.382005 |
| O | 17.130233 | 18.661129 | 13.171119 |
| H | 15.317225 | 18.459797 | 15.165860 |
| H | 15.818548 | 16.998253 | 17.233303 |
| H | 19.130675 | 17.355867 | 13.751192 |
| H | 17.642869 | 15.628925 | 17.164533 |

Min ${ }^{3} \pi \pi *$ (S2)

| N | 18.393952 | 17.287761 | 14.465225 |
| :--- | :---: | :---: | :---: |
| C | 18.558311 | 16.363975 | 15.490939 |
| N | 17.602025 | 16.322567 | 16.444652 |
| C | 16.485121 | 17.079056 | 16.418888 |
| C | 16.266734 | 17.937356 | 15.280328 |
| C | 17.220109 | 18.038178 | 14.240001 |
| S | 19.918671 | 15.357179 | 15.500151 |
| O | 17.165409 | 18.710845 | 13.193139 |
| H | 15.352111 | 18.481151 | 15.197399 |
| H | 15.775153 | 16.946233 | 17.215035 |
| H | 19.115371 | 17.270049 | 13.746921 |
| H | 17.722451 | 15.623619 | 17.197455 |

Min ${ }^{3} \mathrm{n} \pi^{*}(\mathrm{~S} 2)$
$\begin{array}{llll}\mathrm{N} & 18.406546 & 17.273796 & 14.481253\end{array}$
C $\quad 18.53573416 .383846 \quad 15.486230$
$\begin{array}{llll}\mathrm{N} & 17.617505 & 16.306830 & 16.438203\end{array}$
$\begin{array}{lllll}\text { C } & 16.461706 & 17.097311 & 16.406501\end{array}$
$\begin{array}{llll}\text { C } & 16.271251 & 17.936569 & 15.289898\end{array}$
$\begin{array}{llll}\text { C } & 17.199757 & 18.047842 & 14.260655\end{array}$
$\begin{array}{llll}\mathrm{S} & 19.906555 & 15.318374 & 15.469870\end{array}$
$\begin{array}{llll}\text { O } & 17.165017 & 18.718144 & 13.206254\end{array}$
$\begin{array}{llll}\mathrm{H} & 15.347016 & 18.481441 & 15.203298\end{array}$
$\begin{array}{llll}\mathrm{H} & 15.771955 & 16.953754 & 17.213735\end{array}$
$\begin{array}{llll}\mathrm{H} & 19.102670 & 17.269206 & 13.737474\end{array}$
H $\quad 17.708022 \quad 15.615286 \quad 17.190820$
Min $\pi \pi^{*}(\mathrm{~S} 2)$

| N | 18.504996 | 17.400355 | 14.587852 |
| :--- | :--- | :--- | :--- |
| C | 18.779888 | 16.635304 | 15.710033 |
| N | 17.685370 | 16.370014 | 16.495007 |
| C | 16.485968 | 16.982005 | 16.327182 |


| C | 16.271825 | 17.828697 | 15.277517 |
| :--- | :---: | :---: | :---: |
| C | 17.305451 | 18.017155 | 14.288141 |
| S | 19.746916 | 15.102228 | 15.287700 |
| O | 17.166878 | 18.664187 | 13.240856 |
| H | 15.310515 | 18.290064 | 15.126065 |
| H | 15.731481 | 16.746276 | 17.061049 |
| H | 19.254759 | 17.445290 | 13.892049 |
| H | 17.779278 | 15.687680 | 17.250691 |

Min $n \pi^{* '(S 2)}$
$\begin{array}{llll}\mathrm{N} & 18.476569 & 17.367935 & 14.521832\end{array}$
C $\quad 18.682461 \quad 16.463077 \quad 15.584582$
$\begin{array}{lllll}\mathrm{N} & 17.584935 & 16.265964 & 16.409332\end{array}$
$\begin{array}{llll}\text { C } & 16.468638 & 17.019127 & 16.318710\end{array}$
$\begin{array}{llll}\text { C } & 16.290267 & 17.926552 & 15.301727\end{array}$
$\begin{array}{llll}\text { C } & 17.303117 & 18.055191 & 14.288465\end{array}$
$\begin{array}{llll}\mathrm{S} & 19.731123 & 15.063527 & 15.216351\end{array}$
$\begin{array}{llll}\text { O } & 17.191588 & 18.758225 & 13.261847\end{array}$
$\begin{array}{llll}\mathrm{H} & 15.369271 & 18.473192 & 15.198204\end{array}$
$\begin{array}{llll}\text { H } & 15.740586 & 16.854368 & 17.097676\end{array}$
$\begin{array}{llll}\mathrm{H} & 19.186515 & 17.396683 & 13.791425\end{array}$
$\begin{array}{llll}\mathrm{H} & 17.625369 & 15.564447 & 17.147150\end{array}$
Min ${ }^{3} \pi \pi^{*}$ (S2)

| N | 18.505112 | 17.376105 | 14.548519 |
| :--- | :--- | :--- | :--- |
| C | 18.756717 | 16.510170 | 15.636668 |
| N | 17.648341 | 16.275909 | 16.434745 |
| C | 16.500546 | 16.963990 | 16.330449 |
| C | 16.311799 | 17.881948 | 15.316020 |
| C | 17.330435 | 18.043943 | 14.308173 |
| S | 19.753312 | 15.099340 | 15.270175 |
| O | 17.188913 | 18.726115 | 13.275650 |
| H | 15.373107 | 18.394644 | 15.194283 |
| H | 15.756410 | 16.745322 | 17.081696 |
| H | 19.230763 | 17.412772 | 13.830669 |
| H | 17.720788 | 15.576256 | 17.176447 |

Min ${ }^{3} \mathrm{n} \pi^{* \prime}(\mathrm{~S} 2)$
$\begin{array}{llll}\mathrm{N} & 18.529342 & 17.395975 & 14.529347\end{array}$
C $\quad 18.804614 \quad 16.518913 \quad 15.596947$
$\begin{array}{llll}\mathrm{N} & 17.717794 & 16.307324 & 16.440396\end{array}$
$\begin{array}{llll}\text { C } & 16.537349 & 16.959871 & 16.301670\end{array}$
$\begin{array}{llll}\text { C } & 16.318256 & 17.838253 & 15.279468\end{array}$
$\begin{array}{llll}\text { C } & 17.350422 & 18.041911 & 14.286123\end{array}$
$\begin{array}{llll}\mathrm{S} & 19.620503 & 14.984888 & 15.197112\end{array}$
$\begin{array}{llll}\text { O } & 17.206811 & 18.747983 & 13.270679\end{array}$
$\begin{array}{llll}\mathrm{H} & 15.367280 & 18.327727 & 15.160018\end{array}$
$\begin{array}{llll}\mathrm{H} & 15.795782 & 16.740907 & 17.054020\end{array}$
$\begin{array}{llll}\mathrm{H} & 19.256111 & 17.467520 & 13.818768\end{array}$
$\begin{array}{llll}\text { H } & 17.807062 & 15.652314 & 17.216238\end{array}$

Min $G S$

| C | 17.758259 | 16.301956 | 14.599256 |
| :--- | :---: | :---: | :---: |
| N | 18.131411 | 17.579559 | 14.275706 |
| C | 18.362328 | 18.552341 | 15.193150 |
| C | 18.263603 | 18.303587 | 16.524494 |
| C | 17.939247 | 16.986065 | 16.971378 |
| N | 17.663614 | 16.092123 | 15.958480 |
| H | 18.477682 | 19.068405 | 17.253531 |
| S | 17.895147 | 16.522793 | 18.563305 |
| S | 17.459146 | 15.141303 | 13.472569 |
| H | 18.646601 | 19.512947 | 14.789116 |
| H | 17.358847 | 15.157816 | 16.223301 |
| H | 18.249556 | 17.797768 | 13.287046 |

$\operatorname{Min} \pi \pi^{*}(S 2)$

| C | 17.737444 | 16.395065 | 14.677117 |
| :--- | :---: | :---: | :---: |
| N | 18.148996 | 17.600023 | 14.266823 |
| C | 18.378202 | 18.650339 | 15.170108 |
| C | 18.287811 | 18.357527 | 16.529253 |
| C | 17.934614 | 17.094496 | 17.023293 |
| N | 17.594048 | 16.154520 | 15.978759 |
| H | 18.523867 | 19.127565 | 17.246267 |
| S | 17.883480 | 16.551371 | 18.633141 |
| S | 17.408489 | 15.181007 | 13.506756 |
| H | 18.664385 | 19.592064 | 14.740294 |
| H | 17.234797 | 15.247050 | 16.257530 |
| H | 18.284239 | 17.759205 | 13.268286 |

$\operatorname{Min} n \pi^{*}(S 2)$

| C | 17.773886 | 16.476948 | 14.660338 |
| :--- | :--- | :--- | :--- |
| N | 18.220205 | 17.663933 | 14.255209 |
| C | 18.429384 | 18.713373 | 15.178601 |
| C | 18.360901 | 18.401293 | 16.532915 |
| C | 17.983831 | 17.143311 | 17.019398 |
| N | 17.597582 | 16.232431 | 15.954591 |
| H | 18.610075 | 19.161192 | 17.256605 |
| S | 17.847700 | 16.562511 | 18.621565 |
| S | 17.428566 | 15.244455 | 13.488943 |
| H | 18.721664 | 19.655771 | 14.754605 |
| H | 17.181494 | 15.349798 | 16.239023 |
| H | 18.360147 | 17.833122 | 13.255933 |

Min ${ }^{3} \pi \pi^{*}(S 2)$

| C | 17.684340 | 16.439951 | 14.702590 |
| :--- | :--- | :--- | :--- |
| N | 18.141703 | 17.610462 | 14.280084 |
| C | 18.397894 | 18.668219 | 15.186935 |
| C | 18.321251 | 18.384939 | 16.539448 |
| C | 17.928623 | 17.144623 | 17.040173 |
| N | 17.518919 | 16.214836 | 16.000357 |


| H | 18.604784 | 19.144665 | 17.251299 |
| :--- | :---: | :---: | :---: |
| S | 17.878241 | 16.577906 | 18.642086 |
| S | 17.300562 | 15.199031 | 13.549227 |
| H | 18.731140 | 19.587975 | 14.745338 |
| H | 17.106300 | 15.338639 | 16.302065 |
| H | 18.315517 | 17.770645 | 13.288887 |

Min ${ }^{3} n \pi^{*}(S 2)$

| C | 17.711149 | 16.404608 | 14.690280 |
| :--- | :--- | :--- | :--- |
| N | 18.148968 | 17.596910 | 14.291242 |
| C | 18.414450 | 18.652956 | 15.193802 |
| C | 18.312160 | 18.378008 | 16.546486 |
| C | 17.918060 | 17.137650 | 17.022001 |
| N | 17.563747 | 16.177629 | 15.999388 |
| H | 18.571785 | 19.144520 | 17.261412 |
| S | 17.848192 | 16.575315 | 18.647791 |
| S | 17.348783 | 15.184152 | 13.547432 |
| H | 18.727041 | 19.581533 | 14.756976 |
| H | 17.196825 | 15.283829 | 16.301773 |
| H | 18.275585 | 17.778994 | 13.294261 |

$\operatorname{Min} \pi \pi^{*}(S 4)$

| C | 17.783594 | 16.342831 | 14.637950 |
| :--- | :--- | :--- | :--- |
| N | 18.146021 | 17.616531 | 14.307740 |
| C | 18.343447 | 18.653143 | 15.158265 |
| C | 18.238285 | 18.378195 | 16.564533 |
| C | 17.899361 | 17.126265 | 16.947721 |
| N | 17.657263 | 16.146070 | 15.991503 |
| H | 18.477783 | 19.135937 | 17.288795 |
| S | 17.861996 | 16.469725 | 18.639170 |
| S | 17.526588 | 15.161732 | 13.499923 |
| H | 18.592878 | 19.605619 | 14.727089 |
| H | 17.315865 | 15.238995 | 16.284761 |
| H | 18.270391 | 17.791567 | 13.309563 |

Min $n \pi^{*}(S 4)$

| C | 17.618736 | 16.278793 | 14.589147 |
| :--- | :--- | :--- | :--- |
| N | 18.113771 | 17.509396 | 14.281196 |
| C | 18.372177 | 18.516499 | 15.204261 |
| C | 18.201616 | 18.240231 | 16.544836 |
| C | 17.703217 | 16.997461 | 16.921392 |
| N | 17.389351 | 16.056097 | 15.925782 |
| H | 18.457745 | 18.979609 | 17.289030 |
| S | 17.660776 | 16.459812 | 18.590361 |
| S | 17.331617 | 15.135631 | 13.416982 |
| H | 18.713480 | 19.455620 | 14.806464 |
| H | 16.885773 | 15.201906 | 16.149252 |
| H | 18.269983 | 17.712898 | 13.300072 |

Min ${ }^{3} \pi \pi^{*}(S 4)$
$\begin{array}{llll}\text { C } & 17.598900 & 16.265930 & 14.556241\end{array}$

| N | 18.112040 | 17.510967 | 14.290597 |
| :---: | :---: | :---: | :---: |
| C | 18.350340 | 18.484674 | 15.236048 |
| C | 18.103756 | 18.175058 | 16.571661 |
| C | 17.595327 | 16.927156 | 16.908131 |
| N | 17.348804 | 16.006716 | 15.870038 |
| H | 18.319799 | 18.891367 | 17.348989 |
| S | 17.842262 | 16.331394 | 18.521654 |
| S | 17.342062 | 15.176579 | 13.327897 |
| H | 18.674236 | 19.443518 | 14.872592 |
| H | 16.863104 | 15.130569 | 16.074253 |
| H | 18.289804 | 17.735119 | 13.314352 |
|  |  |  |  |
| Min | ${ }^{3} n \pi^{*}(S 4)$ |  |  |
| C | 17.609142 | 16.267729 | 14.585656 |
| N | 18.127211 | 17.493641 | 14.290688 |
| C | 18.359919 | 18.500132 | 15.218739 |
| C | 18.130081 | 18.228256 | 16.547295 |
| C | 17.593554 | 16.995544 | 16.918331 |
| N | 17.329517 | 16.046349 | 15.911159 |
| H | 18.374367 | 18.954590 | 17.308334 |
| S | 17.654154 | 16.431200 | 18.568607 |
| S | 17.342627 | 15.140422 | 13.390947 |
| H | 18.711485 | 19.439611 | 14.828950 |
| H | 16.804390 | 15.195272 | 16.120712 |
| H | 18.314299 | 17.691313 | 13.311736 |

Min $\pi \pi^{* \prime}(S 2)$

| C | 17.513151 | 16.444924 | 14.654642 |
| :---: | :---: | :---: | :---: |
| N | 18.078227 | 17.632854 | 14.265633 |
| C | 18.399327 | 18.593810 | 15.171534 |
| C | 18.290343 | 18.345750 | 16.510933 |
| C | 17.928652 | 17.032499 | 16.988077 |
| N | 17.584823 | 16.138772 | 15.993982 |
| H | 18.562008 | 19.097091 | 17.236183 |
| S | 17.924273 | 16.603844 | 18.592004 |
| S | 17.438371 | 15.112269 | 13.404068 |
| H | 18.743391 | 19.531878 | 14.760475 |
| H | 17.215019 | 15.228979 | 16.266837 |
| H | 18.173578 | 17.824463 | 13.266738 |

Min $n \pi^{* \prime}(S 2)$

| C | 17.323312 | 16.371500 | 14.859825 |
| :--- | :--- | :--- | :--- |
| N | 18.011433 | 17.528394 | 14.494918 |
| C | 18.407943 | 18.435730 | 15.412497 |
| C | 18.297637 | 18.197253 | 16.755482 |
| C | 17.822914 | 16.921110 | 17.205342 |
| N | 17.408409 | 16.062492 | 16.228134 |
| H | 18.643829 | 18.910597 | 17.482489 |
| S | 17.777987 | 16.471968 | 18.815272 |
| S | 17.479866 | 14.988486 | 13.754514 |
| H | 18.827524 | 19.345612 | 15.013638 |


| H | 16.944689 | 15.214119 | 16.537695 |
| :--- | :--- | :--- | :--- |
| H | 18.089734 | 17.779642 | 13.514799 |


| Min | $\pi \pi^{* \prime}(S 4)$ |  |  |
| :---: | :--- | :--- | :--- |
| C | 17.633394 | 16.331984 | 14.556533 |
| N | 18.119053 | 17.653547 | 14.258453 |
| C | 18.398508 | 18.580982 | 15.133155 |
| C | 18.269419 | 18.348942 | 16.524233 |
| C | 17.891102 | 17.050892 | 16.881290 |
| N | 17.598587 | 16.134836 | 15.988890 |
| H | 18.514639 | 19.096144 | 17.259441 |
| S | 17.852577 | 16.562021 | 18.613358 |
| S | 17.417704 | 15.106429 | 13.435891 |
| H | 18.733065 | 19.530424 | 14.737045 |
| H | 17.300552 | 15.202348 | 16.265757 |
| H | 18.244387 | 17.863491 | 13.267159 |

## References:

[1] W. Z. D. A. Case, T. Darden, T. E. Cheatham, C. Simmerling, J. Wang, R. E. Duke, R. Luo, R. C. Walker, Univ. Calif. San Fr. 2012.
[2] W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, M. L. Klein, J. Chem. Phys. 1983, 79, 926-935.
[3] J. P. Ryckaert, G. Ciccotti, H. J. C. Berendsen, J. Comput. Phys. 1977, 23, 327-341.
[4] S. Miyamoto, P. A. Kollman, J. Am. Chem. Soc. 1992, 114, 3668-3674.
[5] P. Altoè, M. Stenta, A. Bottoni, M. Garavelli, AIP Conf. Proc. 2007, 963, 685-688.
[6] A. Nenov, I. Conti, R. Borrego-Varillas, G. Cerullo, M. Garavelli, Chem. Phys. 2018, 515, 643-653.
[7] K. Taras-Goślińska, G. Wenska, B. Skalski, A. Maciejewski, G. Burdziński, J. Karolczak, J. Photochem. Photobiol. A Chem. 2004, 168, 227-233.
[8] R. Borrego-varillas, D. C. Teles-ferreira, A. Nenov, I. Conti, L. Ganzer, C. Manzoni, M. Garavelli, A. M. De Paula, G. Cerullo, J. Am. Chem. Soc 2018, 140, 16087-16093.

