

Supporting Information

Orientation and Order of Xanthene Dyes in the One-Dimensional Channels of Zeolite L: Bridging the gap between experimental data and molecular behavior.

by

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Four movies are available via the internet at the ACS web page <http://pubs.acs.org> :

Movie1 refers to simulation D4

Movie2 refers to simulation W2.

Movie3 refers to optimization Opt5

Movie4 refers to optimization Opt6.

Calculations with Gaussian basis sets.

Calculations with Gaussian basis sets were performed on a series of molecular models containing Ox⁺ or Py⁺, described in the following. The adopted levels of theory/basis sets are specified accordingly for each system. In all the geometry optimizations no atomic positions were kept fixed; in some cases, explicitly stated below, symmetry constraints were imposed (e.g. C_{2v} for isolated oxonine).

All calculations reported below were performed with the Gaussian g09 package.(1)

Optimized Oxonine Structure in the vacuum

Oxonine geometry was optimized at the MP2/cc-pvtz level of theory, a C_{2v} symmetry was considered. Excitation energies were calculated for the two lowest states at different level of theory and basis set adopting the MP2/cc-pvtz optimized geometry. Data reported in Table S1 refer to the first (homo-lumo) excitation. Wavelength in nm, excitation transition dipole in AU.

Table S1. Basis set and level of theory dependence of the first electronic excitation wavelength λ (in nm), oscillator strength f , and excitation dipole μ components (in AU) calculated for Oxonine cation. In the case of CIS(D) and CASMP2 approaches, only excitation energies are available.

| aug-cc-pvdz | f | μ_x | μ_y | μ_z | λ |
|-------------|-------|---------|---------|---------|-----------|
| EOM-CCSD | 1.005 | 0.0 | 0.0 | 3.667 | 449.6 |
| CIS | 1.359 | 0.0 | 0.0 | 4.018 | 360.9 |
| CIS(D) | - | - | - | - | 479.5 |

| 6-311++G(d,p) | f | μ_x | μ_y | μ_z | λ |
|---------------|-------|---------|---------|---------|-----------|
| EOM-CCSD | 1.015 | 0.0 | 0.0 | 3.689 | 450.6 |
| CASMP2(6,8) | - | - | - | - | 458.2 |
| CIS | 1.370 | 0.0 | 0.0 | 4.022 | 358.7 |
| CIS(D) | - | - | - | - | 479.3 |

| 3-21++G(d,p) ^{a)} | f | μ_x | μ_y | μ_z | λ |
|----------------------------|-------|---------|---------|---------|-----------|
| EOM-CCSD | 1.031 | 0.0 | 0.0 | 3.706 | 446.0 |
| CIS | 1.392 | 0.0 | 0.0 | 4.035 | 355.2 |
| CIS(D) | - | - | - | - | 470.8 |

a) The 3-21++G(d,p) basis set has been built from the split-valence 3-21G basis set augmented with diffuse and polarization functions taken from the 6-31++g(d,p) basis set.

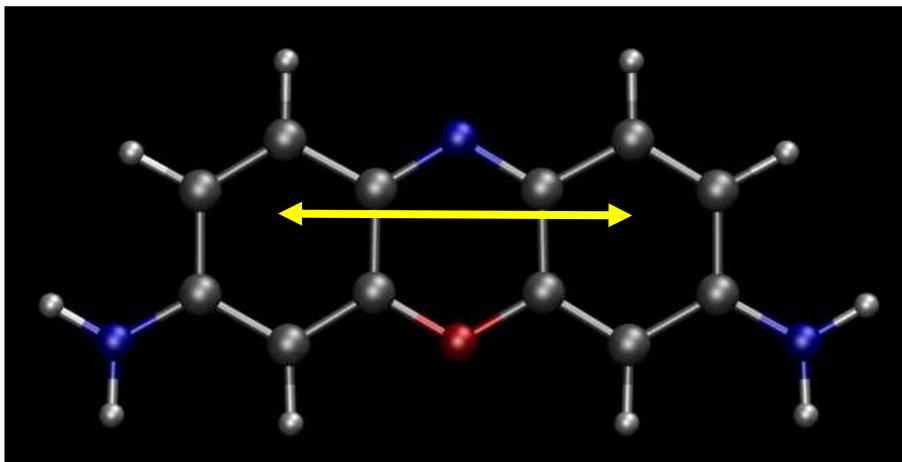


Figure S1. Optimized structure of oxonine. Atom color code: H, white; C, gray; N, blue; O, red. The yellow arrow indicates the orientation of the Electronic Transition Dipole Moment corresponding to the first electronic excitation (homo-lumo).

MP2/cc-pvtz optimized atomic coordinates for cationic Oxonine (Å)

| | | | |
|---|-------------|------------|-------------|
| o | 0.00000000 | 0.00000000 | 1.15526326 |
| n | 0.00000000 | 0.00000000 | -1.63480461 |
| n | -4.71167255 | 0.00000000 | 1.15262007 |
| n | 4.71167255 | 0.00000000 | 1.15262007 |
| c | -3.54293016 | 0.00000000 | 0.50241183 |
| c | -2.33154213 | 0.00000000 | 1.19292986 |
| c | -1.16229394 | 0.00000000 | 0.47634880 |
| c | -1.13588893 | 0.00000000 | -0.94359976 |
| c | -2.37799761 | 0.00000000 | -1.62210213 |
| c | -3.54055621 | 0.00000000 | -0.92226592 |
| c | 1.13588893 | 0.00000000 | -0.94359976 |
| c | 1.16229394 | 0.00000000 | 0.47634880 |
| c | 2.33154213 | 0.00000000 | 1.19292986 |
| c | 3.54293016 | 0.00000000 | 0.50241183 |
| c | 3.54055621 | 0.00000000 | -0.92226592 |
| c | 2.37799761 | 0.00000000 | -1.62210213 |
| h | 2.29756064 | 0.00000000 | 2.26916094 |
| h | -2.29756064 | 0.00000000 | 2.26916094 |
| h | -2.36094136 | 0.00000000 | -2.69846762 |
| h | -4.48416710 | 0.00000000 | -1.44136296 |
| h | 4.48416710 | 0.00000000 | -1.44136296 |
| h | 2.36094136 | 0.00000000 | -2.69846762 |
| h | -5.57990485 | 0.00000000 | 0.65127245 |
| h | -4.75168719 | 0.00000000 | 2.15460877 |
| h | 4.75168719 | 0.00000000 | 2.15460877 |
| h | 5.57990485 | 0.00000000 | 0.65127245 |

Hexa-hydrated Oxonine

The structure of hexa-hydrated oxonine was optimized at the MP2/D95** level of theory adopting a C_s symmetry.

Optimized coordinates of $Ox^+(H_2O)_6$.

| | | | |
|---|-----------|-----------|-----------|
| O | -0.775179 | -0.015684 | 0.000000 |
| N | 2.033710 | -0.041215 | 0.000000 |
| N | -0.776248 | 0.018334 | 4.747230 |
| N | -0.776248 | 0.018334 | -4.747230 |
| C | -0.124662 | -0.007022 | 3.573224 |
| C | -0.822868 | 0.021129 | 2.346341 |
| C | -0.094979 | -0.025094 | 1.171281 |
| C | 1.338383 | -0.008758 | 1.148866 |
| C | 2.024329 | -0.028408 | 2.401751 |
| C | 1.316710 | 0.010701 | 3.573789 |
| C | 1.338383 | -0.008758 | -1.148866 |
| C | -0.094979 | -0.025094 | -1.171281 |
| C | -0.822868 | 0.021129 | -2.346341 |
| C | -0.124662 | -0.007022 | -3.573224 |
| C | 1.316710 | 0.010701 | -3.573789 |
| C | 2.024329 | -0.028408 | -2.401751 |
| H | -1.909028 | 0.020141 | -2.307629 |
| H | -1.909028 | 0.020141 | 2.307629 |
| H | 3.110843 | -0.005945 | 2.387000 |
| H | 1.827114 | 0.009315 | 4.532964 |
| H | 1.827114 | 0.009315 | -4.532964 |
| H | 3.110843 | -0.005945 | -2.387000 |
| H | -0.247783 | -0.031507 | 5.613503 |
| H | -1.790975 | -0.037919 | 4.769615 |
| H | -1.790975 | -0.037919 | -4.769615 |
| H | -0.247783 | -0.031507 | -5.613503 |
| O | 4.970423 | 0.227119 | 0.000000 |
| H | 4.022003 | 0.030142 | 0.000000 |
| H | 5.392460 | -0.634677 | 0.000000 |
| O | -3.711495 | -0.128061 | 4.556455 |
| H | -4.288846 | 0.599277 | 4.806841 |
| H | -4.224136 | -0.915260 | 4.762663 |
| O | -3.711495 | -0.128061 | -4.556455 |
| H | -4.288846 | 0.599277 | -4.806841 |
| H | -4.224136 | -0.915260 | -4.762663 |
| O | -3.781622 | 0.315761 | 0.000000 |
| H | -4.503340 | -0.319334 | 0.000000 |
| H | -4.235892 | 1.163095 | 0.000000 |
| O | 1.128998 | -0.059858 | 7.014098 |
| H | 1.351243 | -0.819417 | 7.561031 |
| H | 1.333710 | 0.696897 | 7.571802 |
| O | 1.128998 | -0.059858 | -7.014098 |
| H | 1.351243 | -0.819417 | -7.561031 |
| H | 1.333710 | 0.696897 | -7.571802 |

The excitation wavelength λ at the CIS(D)/3-21++g(d,p) level corresponds to 499.0 nm.

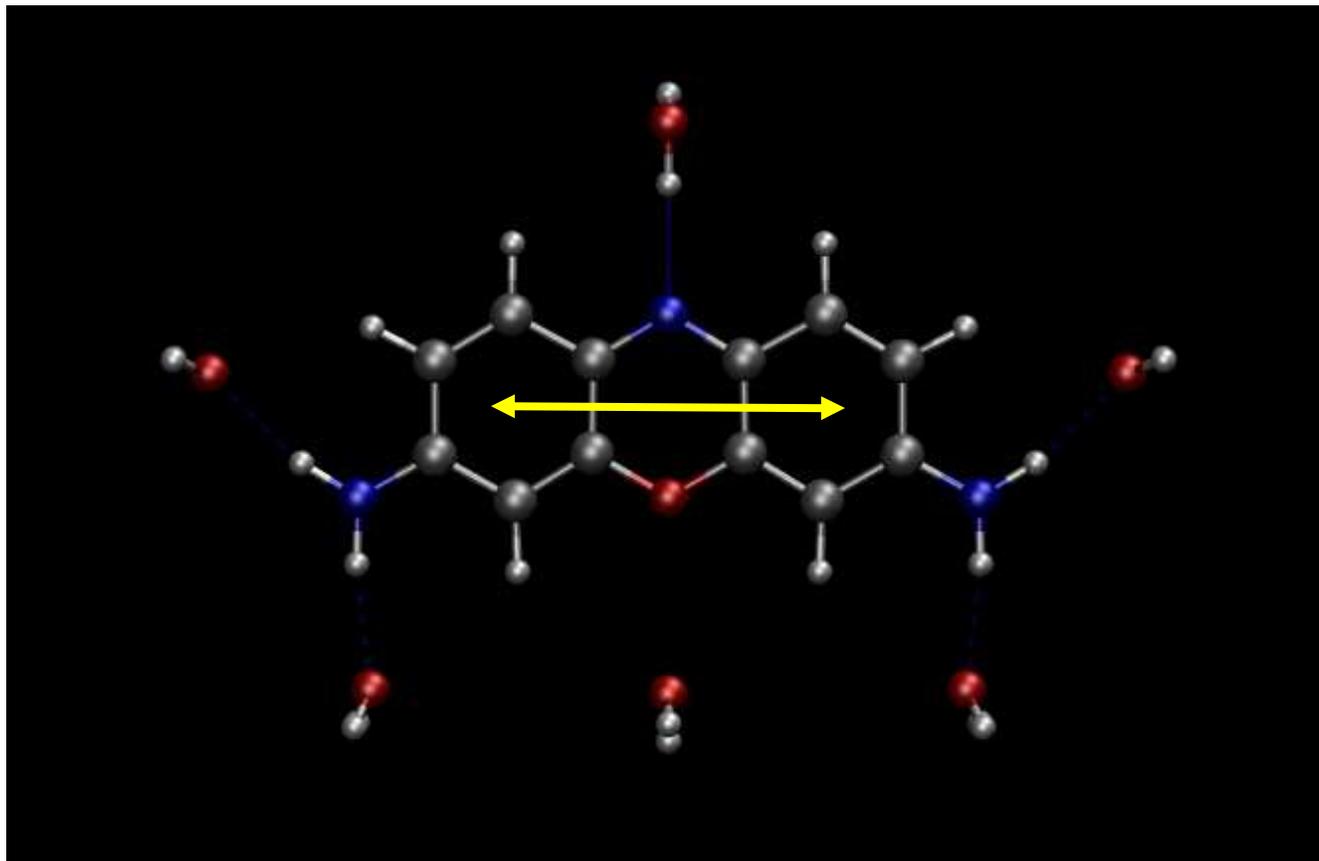


Figure S2. Optimized structure of Ox(H₂O)₆. Atom color code: H, white; C, gray; N, blue; O, red. The yellow arrow indicates the orientation of the Electronic Transition Dipole Moment corresponding to the first electronic excitation (homo-lumo).

Ox(H₂O)₅Cl

The structure of cationic oxonine in contact with one Cl⁻ anion and 5 water molecules has been optimized at the PBE0/D95** level of theory (the basis set for chlorine was 6-31+g(d)).

Optimized atomic coordinates

| | | | |
|----|-----------|-----------|-----------|
| O | -0.392591 | -0.158627 | -0.099652 |
| N | 0.271627 | 2.560830 | -0.030862 |
| N | -4.965114 | 0.854892 | -0.064067 |
| N | 4.154206 | -1.356515 | -0.016254 |
| C | -3.705273 | 1.295520 | -0.067512 |
| C | -2.659568 | 0.340958 | -0.089613 |
| C | -1.366474 | 0.777371 | -0.081421 |
| C | -1.004688 | 2.167448 | -0.051468 |
| C | -2.075537 | 3.113122 | -0.039937 |
| C | -3.380302 | 2.700564 | -0.048397 |
| C | 1.224778 | 1.619671 | -0.040263 |
| C | 0.900002 | 0.221943 | -0.071421 |
| C | 1.846355 | -0.768321 | -0.072935 |
| C | 3.214101 | -0.405358 | -0.035842 |
| C | 3.573397 | 0.991271 | -0.019598 |
| C | 2.611928 | 1.964578 | -0.019936 |
| H | 1.526793 | -1.805883 | -0.111536 |
| H | -2.910124 | -0.718860 | -0.105236 |
| H | -1.818711 | 4.169461 | -0.027855 |
| H | -4.187981 | 3.428983 | -0.039321 |
| H | 4.629351 | 1.249853 | -0.001514 |
| H | 2.868007 | 3.022513 | -0.005525 |
| H | -5.741313 | 1.497762 | -0.042332 |
| H | -5.127045 | -0.174924 | -0.062043 |
| H | 3.855935 | -2.341074 | 0.016167 |
| H | 5.138762 | -1.097861 | -0.004390 |
| O | 1.604149 | 5.123915 | 0.250657 |
| H | 1.021486 | 4.356335 | 0.107080 |
| H | 1.532510 | 5.320124 | 1.189542 |
| O | 2.967797 | -3.946106 | 0.166901 |
| H | 2.003612 | -3.957291 | -0.043445 |
| H | 3.060159 | -4.463521 | 0.972062 |
| O | 0.348689 | -3.787814 | -0.469372 |
| H | -0.521632 | -3.663468 | -0.006260 |
| H | 0.117977 | -4.048722 | -1.365911 |
| O | 6.884499 | -0.306629 | -0.065112 |
| H | 7.521425 | -0.360777 | 0.654697 |
| H | 7.399211 | -0.346839 | -0.877816 |
| O | -2.045775 | -3.525224 | 0.655895 |
| H | -2.334577 | -4.085697 | 1.382047 |
| H | -2.881442 | -3.113299 | 0.322485 |
| Cl | -4.787288 | -2.269999 | -0.050417 |

The calculated excitation wavelength λ is 510.1 nm at CIS(D)/3-21++g(d,p) level (6-31+g(d) for Cl).

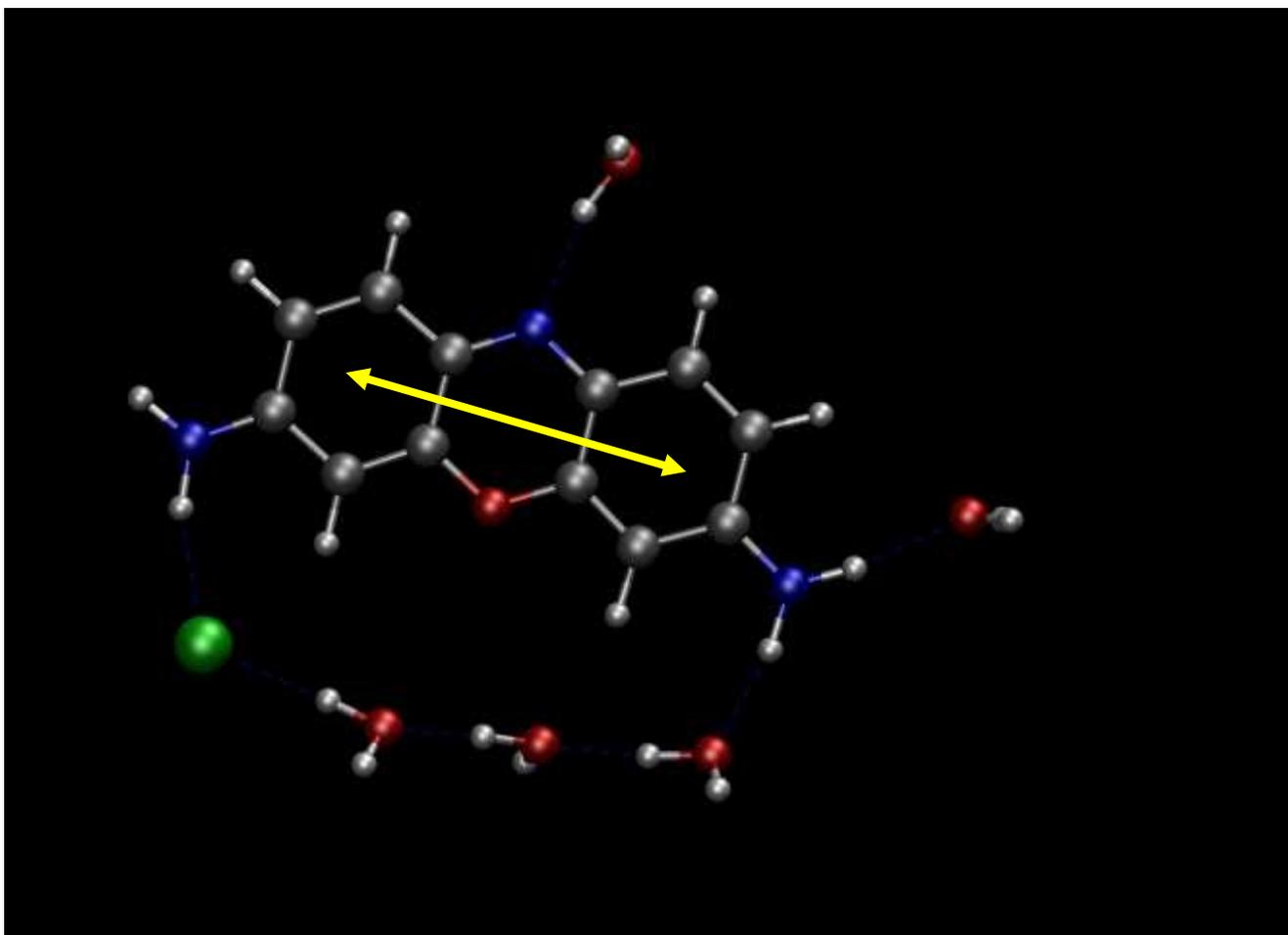


Figure S3. Optimized structure of Ox(H₂O)₅ Cl. Atom color code: H, white; C, gray; N, blue; O, red; Cl, green. The yellow arrow indicates the orientation of the Electronic Transition Dipole Moment corresponding to the first electronic excitation (homo-lumo).

Electronic transition dipole moment orientation calculated on a hydrated oxonine structure extracted from an optimized structure of a ZL/Ox⁺ adduct. Excitation wavelength calculated at the Cis(D)/3-21++G(d,p) level, transition dipole calculated at the Cis/3-21++G(d,p) level of theory.

$\lambda = 496.0$ nm

$\mu_x = -0.056$ au

$\mu_y = -0.095$ au

$\mu_z = 4.087$ au

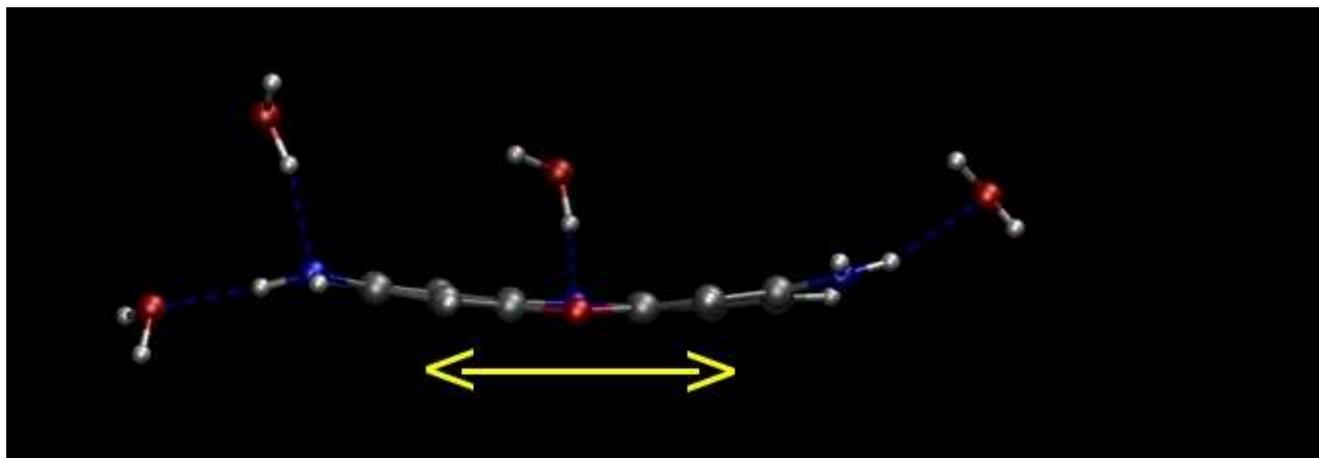


Figure S4. Structure of Ox(H₂O)₄ extracted from a Zeolite L/Ox⁺ hydrated adduct. Atom color codes: H, white; C, gray; N, blue; O, red. The yellow arrow indicates the orientation of the Electronic Transition Dipole Moment corresponding to the first electronic excitation (homo-lumo).

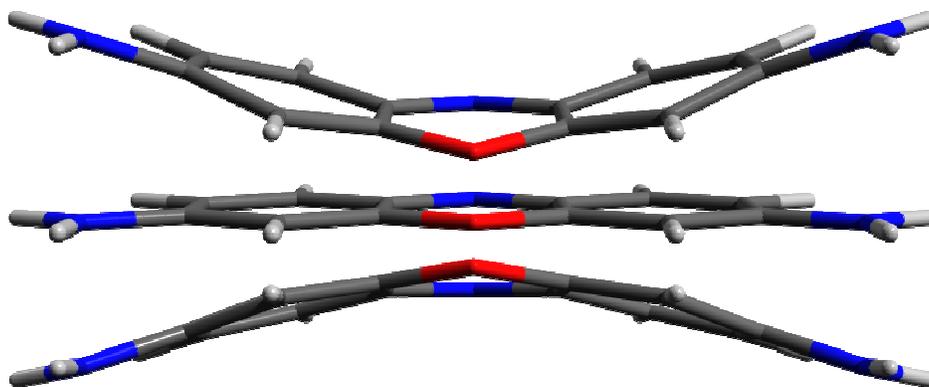


Figure S5. Oxonine deformation as described by the lowest energy (70 cm^{-1}) vibrational eigenvector. The harmonic vibrational modes of gas phase oxonine were calculated at the HF/cc-pvtz level from the optimized geometry at MP2/cc-pvtz level (C_{2v} symmetry) . Atom color code: H, white; C, gray; N, blue; O, red.

Oxonine-H₂O and Pyronine-H₂O complexes.

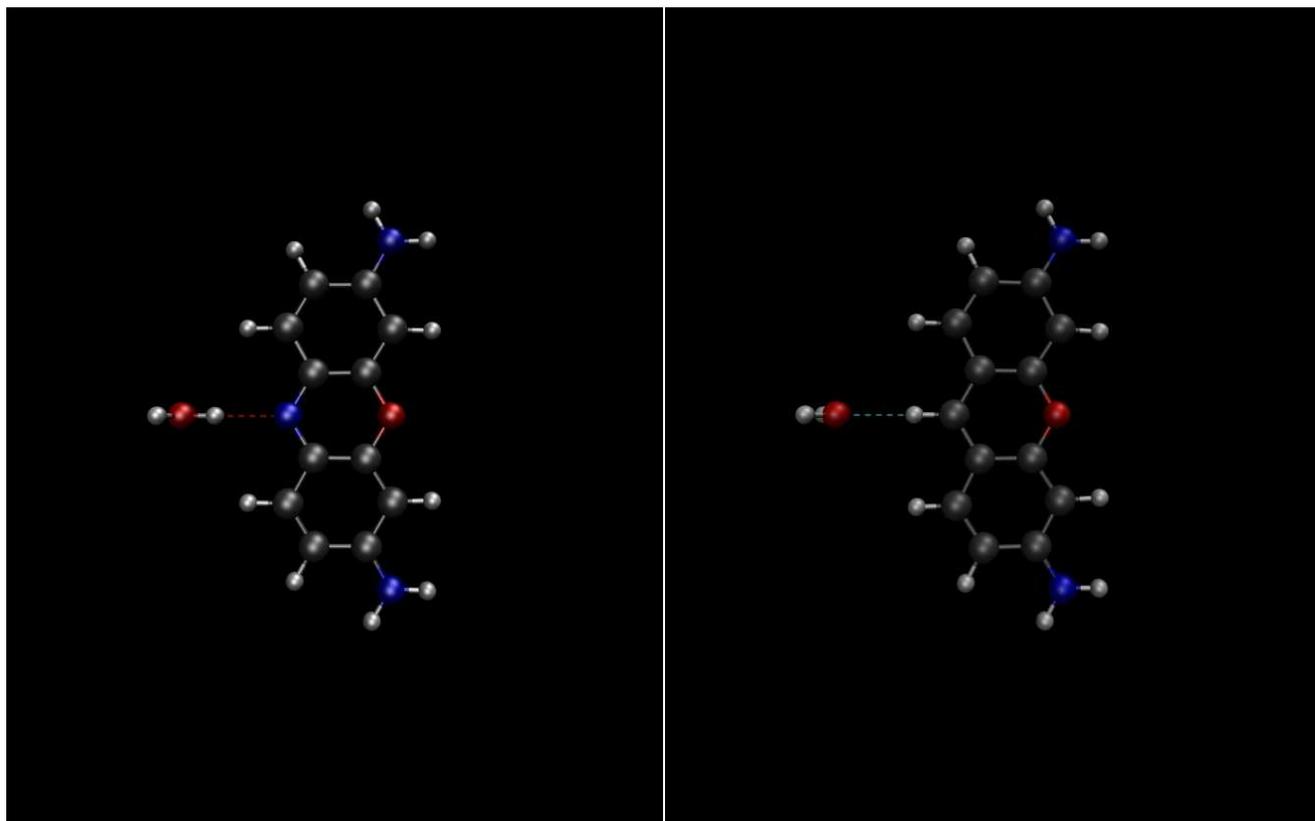


Figure S6. **Left panel:** ball-and-stick representation of the Oxonine cation complex with one water molecule hydrogen bonded to the nitrogen of the central ring (C_s symmetry). **Right panel:** ball-and-stick representation of the Pyronine cation complex with one water molecule hydrogen bonded to the CH of the central ring (C_{2v} symmetry). Atom color code: H, white; C, gray; N, blue; O, red.

Optimized (MP2/cc-pvtz) coordinates for the Ox⁺·H₂O complex (in Å).

| | | | |
|---|-----------|-----------|-----------|
| 8 | 1.537974 | 0.009790 | 0.000000 |
| 7 | -1.258447 | 0.049267 | 0.000000 |
| 7 | 1.523321 | -0.026393 | 4.732995 |
| 7 | 1.523321 | -0.026393 | -4.732995 |
| 6 | 0.873755 | -0.009074 | 3.558985 |
| 6 | 1.574139 | -0.005491 | 2.344313 |
| 6 | 0.856572 | 0.010651 | 1.168789 |
| 6 | -0.569467 | 0.030505 | 1.144739 |
| 6 | -1.260054 | 0.024514 | 2.387629 |
| 6 | -0.558139 | 0.003791 | 3.555579 |
| 6 | -0.569467 | 0.030505 | -1.144739 |
| 6 | 0.856572 | 0.010651 | -1.168789 |
| 6 | 1.574139 | -0.005491 | -2.344313 |
| 6 | 0.873755 | -0.009074 | -3.558985 |
| 6 | -0.558139 | 0.003791 | -3.555579 |
| 6 | -1.260054 | 0.024514 | -2.387629 |
| 1 | 2.654982 | -0.018389 | -2.314518 |
| 1 | 2.654982 | -0.018389 | 2.314518 |

| | | | |
|---|-----------|-----------|-----------|
| 1 | -2.341765 | 0.023087 | 2.365922 |
| 1 | -1.080863 | -0.006196 | 4.502825 |
| 1 | -1.080863 | -0.006196 | -4.502825 |
| 1 | -2.341765 | 0.023087 | -2.365922 |
| 1 | 1.018505 | -0.035847 | 5.601758 |
| 1 | 2.527294 | -0.041969 | 4.775208 |
| 1 | 2.527294 | -0.041969 | -4.775208 |
| 1 | 1.018505 | -0.035847 | -5.601758 |
| 8 | -4.192273 | -0.159874 | 0.000000 |
| 1 | -3.241916 | 0.015615 | 0.000000 |
| 1 | -4.599044 | 0.709581 | 0.000000 |

Optimized (MP2/cc-pvtz) coordinates for the $\text{Py}^+\cdot\text{H}_2\text{O}$ complex (in Å).

| | | | |
|---|-----------|-----------|-----------|
| 8 | 0.000000 | 0.000000 | -1.516145 |
| 7 | 0.000000 | 4.722715 | -1.659138 |
| 7 | 0.000000 | -4.722715 | -1.659138 |
| 6 | 0.000000 | 0.000000 | 1.267843 |
| 6 | 0.000000 | 3.571756 | -0.957725 |
| 6 | 0.000000 | 2.331491 | -1.605144 |
| 6 | 0.000000 | 1.177275 | -0.845770 |
| 6 | 0.000000 | 1.204869 | 0.571605 |
| 6 | 0.000000 | 2.474180 | 1.208848 |
| 6 | 0.000000 | 3.620984 | 0.468099 |
| 6 | 0.000000 | -1.204869 | 0.571605 |
| 6 | 0.000000 | -1.177275 | -0.845770 |
| 6 | 0.000000 | -2.331491 | -1.605144 |
| 6 | 0.000000 | -3.571756 | -0.957725 |
| 6 | 0.000000 | -3.620984 | 0.468099 |
| 6 | 0.000000 | -2.474180 | 1.208848 |
| 1 | 0.000000 | -2.259668 | -2.683930 |
| 1 | 0.000000 | 2.259668 | -2.683930 |
| 1 | 0.000000 | 2.508836 | 2.290226 |
| 1 | 0.000000 | 4.585546 | 0.957895 |
| 1 | 0.000000 | -4.585546 | 0.957895 |
| 1 | 0.000000 | -2.508836 | 2.290226 |
| 1 | 0.000000 | 5.610765 | -1.191768 |
| 1 | 0.000000 | 4.720921 | -2.662928 |
| 1 | 0.000000 | -4.720921 | -2.662928 |
| 1 | 0.000000 | -5.610765 | -1.191768 |
| 1 | 0.000000 | 0.000000 | 2.353769 |
| 8 | 0.000000 | 0.000000 | 4.471326 |
| 1 | -0.756760 | 0.000000 | 5.063852 |
| 1 | 0.756760 | 0.000000 | 5.063852 |

The MP2/cc-pvtz binding energies for the two complexes are $8.45 \text{ kcal mol}^{-1}$ and $5.67 \text{ kcal mol}^{-1}$ for $\text{Py}^+\cdot\text{H}_2\text{O}$ and $\text{Ox}^+\cdot\text{H}_2\text{O}$ respectively. Binding energies amount to $6.65 \text{ kcal mol}^{-1}$ and $3.39 \text{ kcal mol}^{-1}$ for $\text{Py}^+\cdot\text{H}_2\text{O}$ and $\text{Ox}^+\cdot\text{H}_2\text{O}$ respectively when considering the basis set superposition error correction.(2)

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(2) S.F. Boys, F. Bernardi; Mol.Phys. 19, 553, **1970**.