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


# Electronic Supplementary Information

# for

# On the chemiluminescence emission of luminol: Protic and aprotic solvents and encapsulation to improve the properties in aqueous solution

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**ADDITIONAL FIGURES**

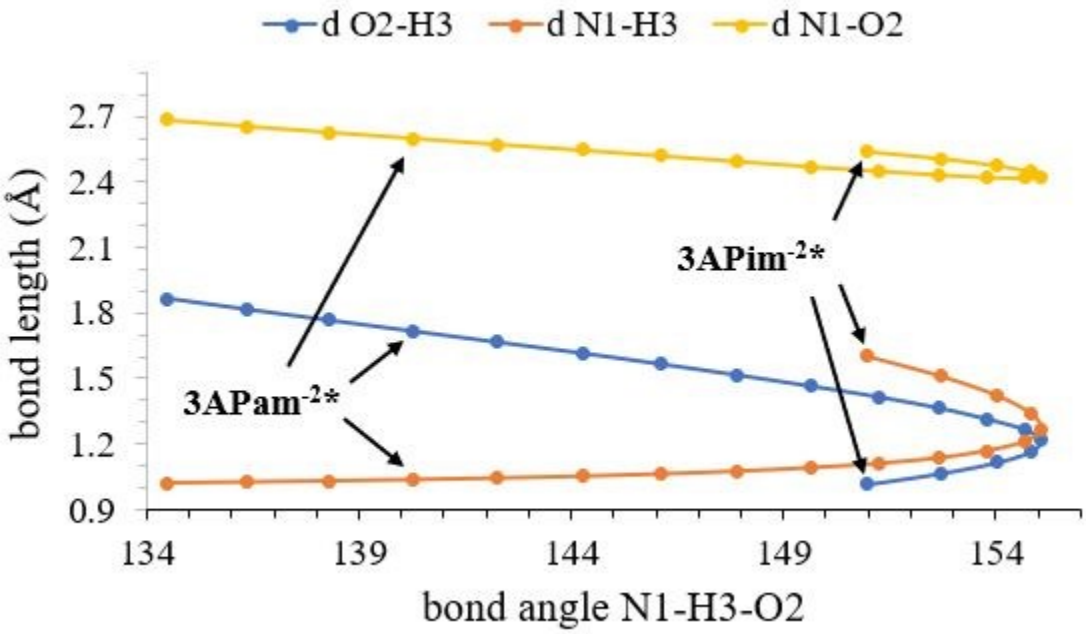


**Figure S1.** Evolution of relevant bond angle and lengths along the excited-state proton transfer conversion from **$^1$(3APim$^{-2}$)*** to **$^1$(3APam$^{-2}$)*** in water computed at the TDDFT/B3LYP/6-31G** level using 5 explicit water molecules and PCM. Maximum values of the geometrical variables correspond to the energy maxima of Figure 3.

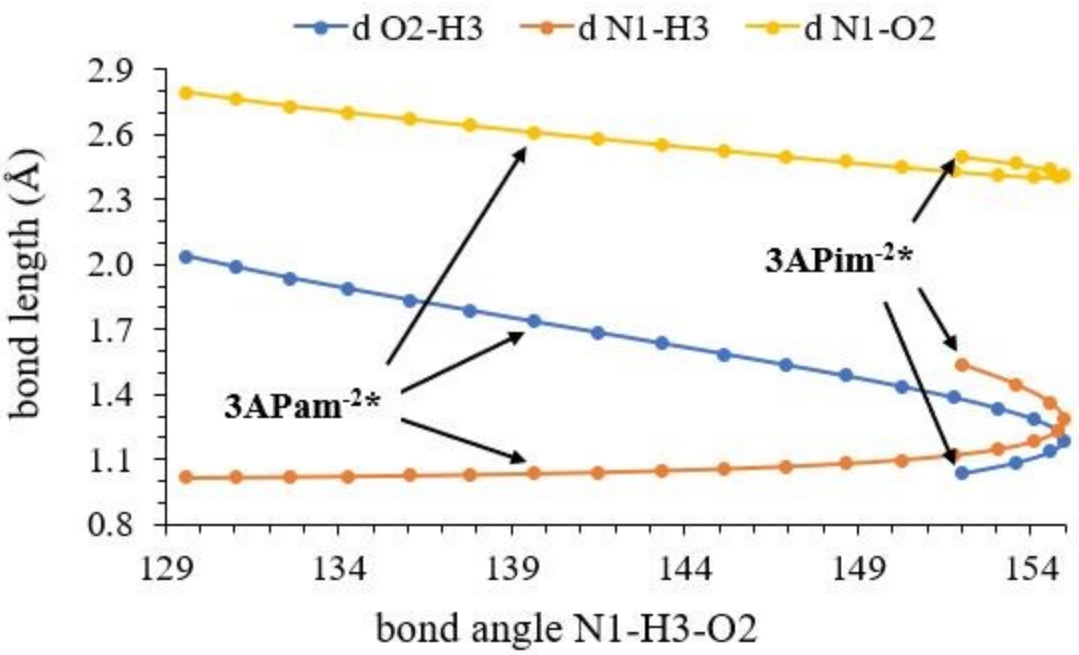


**Figure S2.** Evolution of the bond angle and lengths along the excited-state proton transfer conversion from **$^1$(3APim$^{-2}$)*** to **$^1$(3APam$^{-2}$)*** in DMSO computed at the TDDFT/B3LYP/6-31G** level using 5 explicit water molecules and PCM. Maximum values of the geometrical variables correspond to the energy maxima of Figure 3.

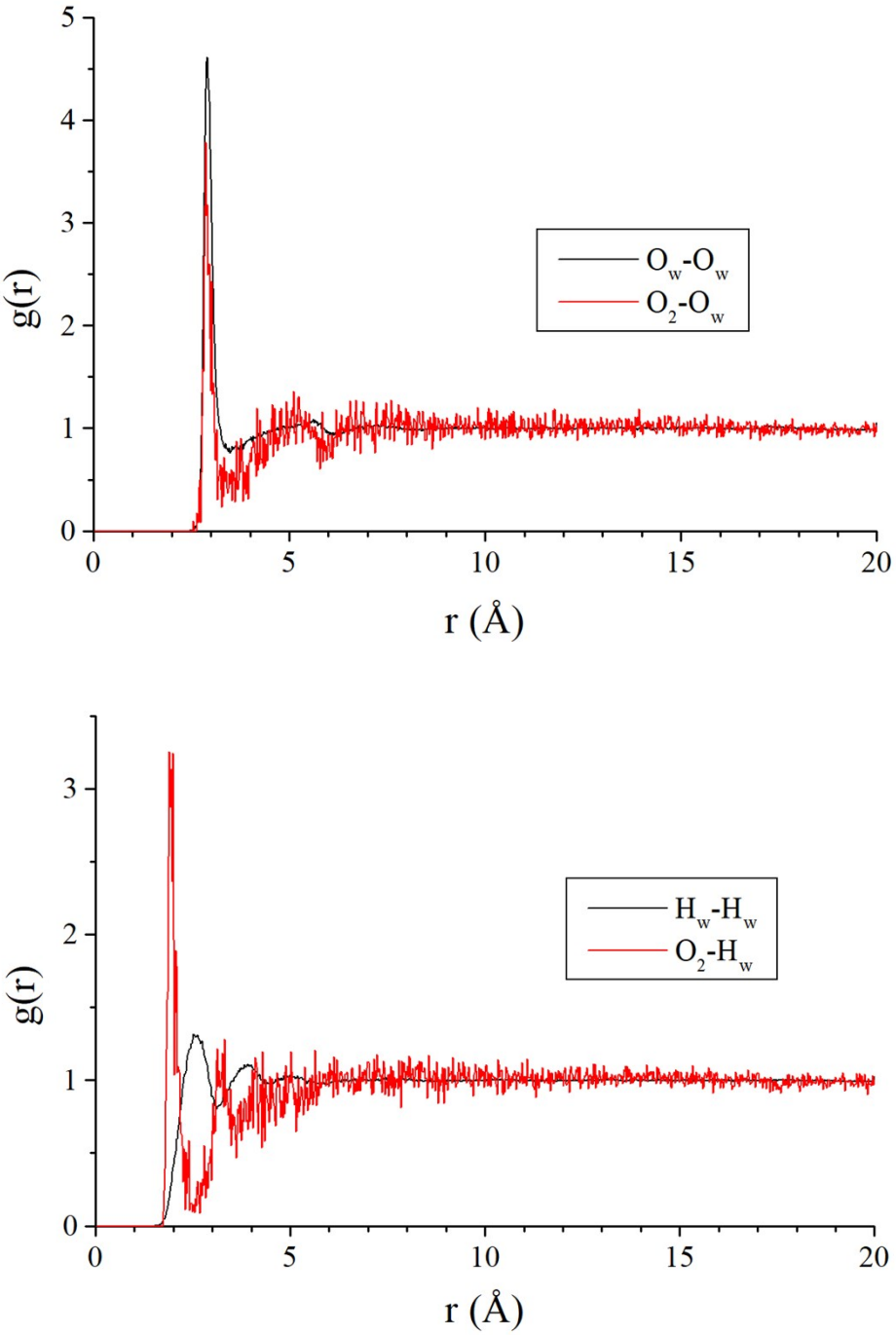


**Figure S3.** Radial distribution functions between the O(2) atom of **$^1$(3APam$^{-2}$)*** and the water oxygen ($O_w$, top) and hydrogen ($H_w$, bottom) atoms along the 1 ns MD simulation. The radial distribution function between the water oxygen ($O_w$, top) and hydrogen ($H_w$, bottom) atoms is also shown.

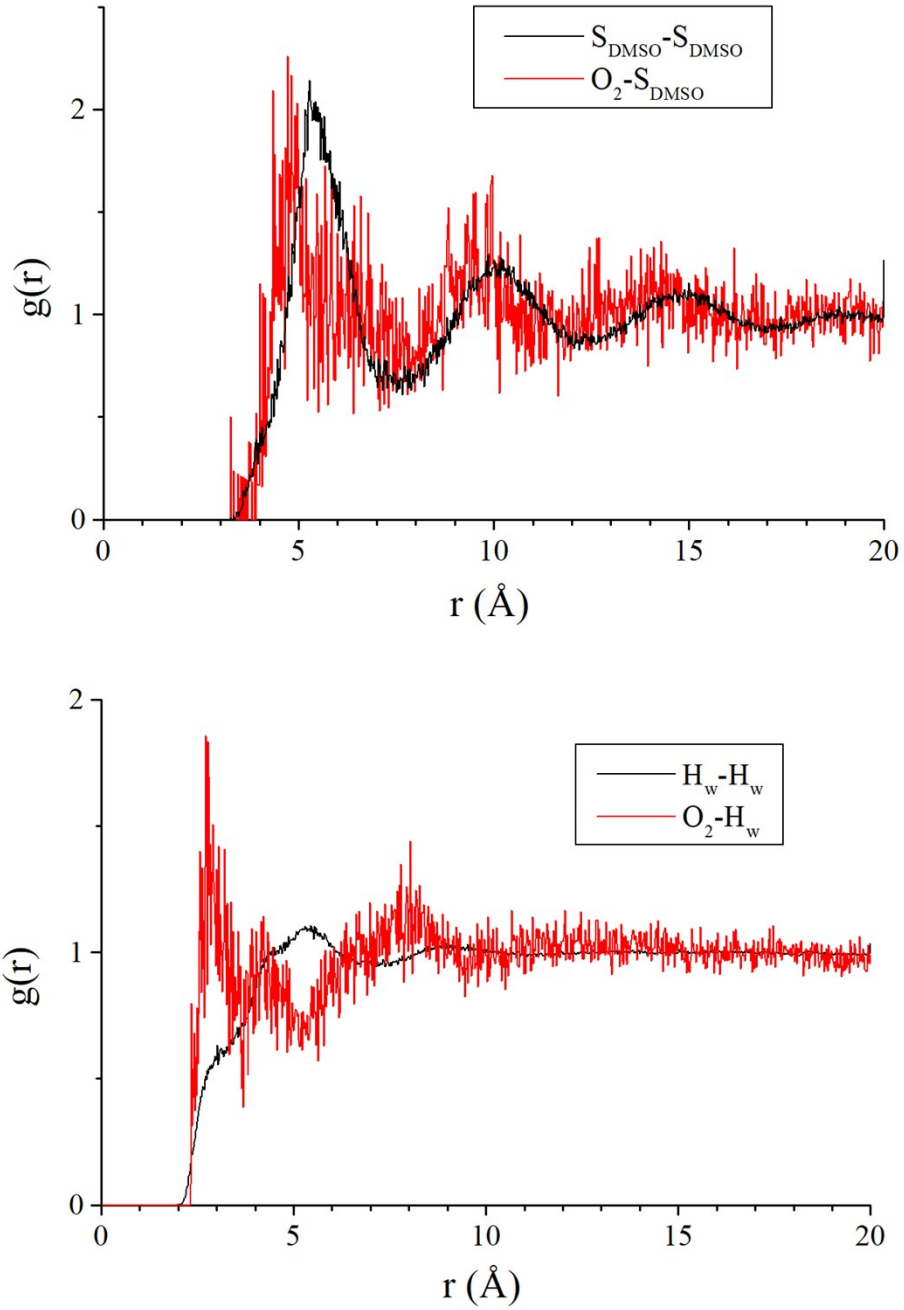


**Figure S4.** Radial distribution function between the O(2) atom of **$^1$(3APim$^{-2}$)*** and the sulfur ($S_{DMSO}$, top) and hydrogen (($H_{DMSO}$, bottom) atoms of DMSO along the 1 ns MD simulation. The radial distribution function between the intermolecular DMSO sulfur and hydrogen atoms are also shown.

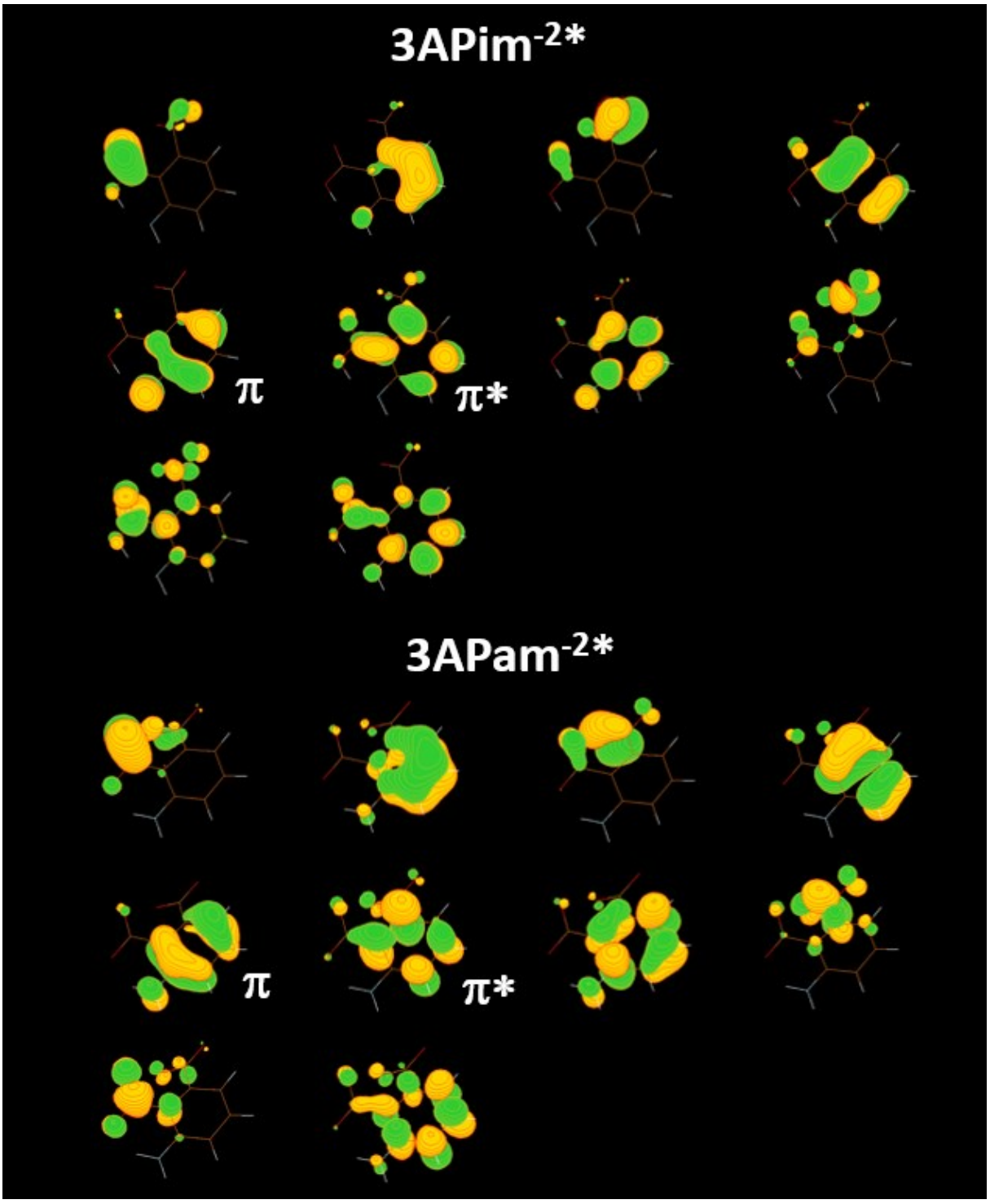


**Figure S5.** Orbitals used in the CAS(10,10) computations. Orbitals mainly contributing to the chemiluminescence emission are labelled.

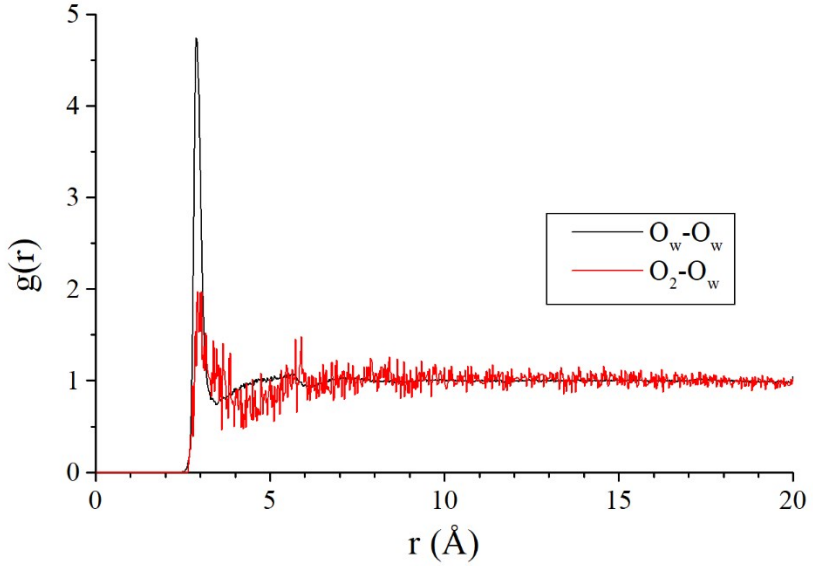


**Figure S6.** Radial distribution function between the O(2) atom of **L** and the water oxygen atoms ($O_w$) along the 1 ns MD simulation. The radial distribution function between the water oxygen atoms ($O_w$) is also shown.

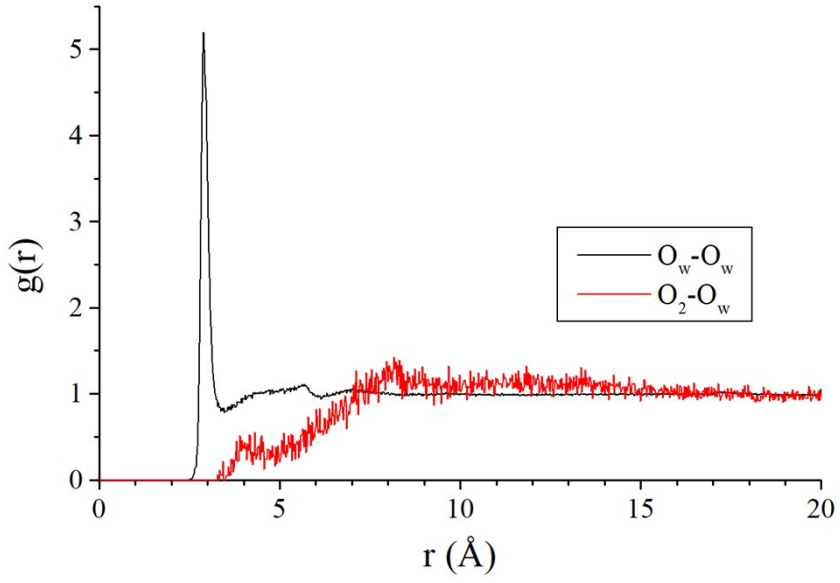


**Figure S7.** Radial distribution function between the O(2) atom of **LCAP** and the water oxygen atoms ($O_w$) along the 1 ns MD simulation. The radial distribution function between the water oxygen atoms ($O_w$) is also shown.

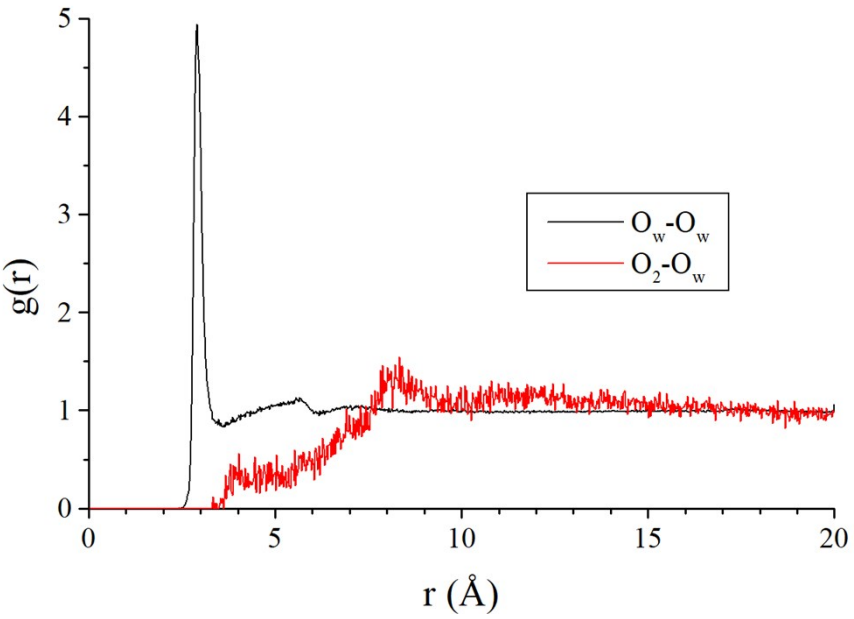


**Figure S8.** Radial distribution function between the O(2) atom of **3APCAP$^{-2}$*** and the water oxygen atoms ($O_w$) along the 1 ns MD simulation. The radial distribution function between the water oxygen atoms ($O_w$) is also shown.

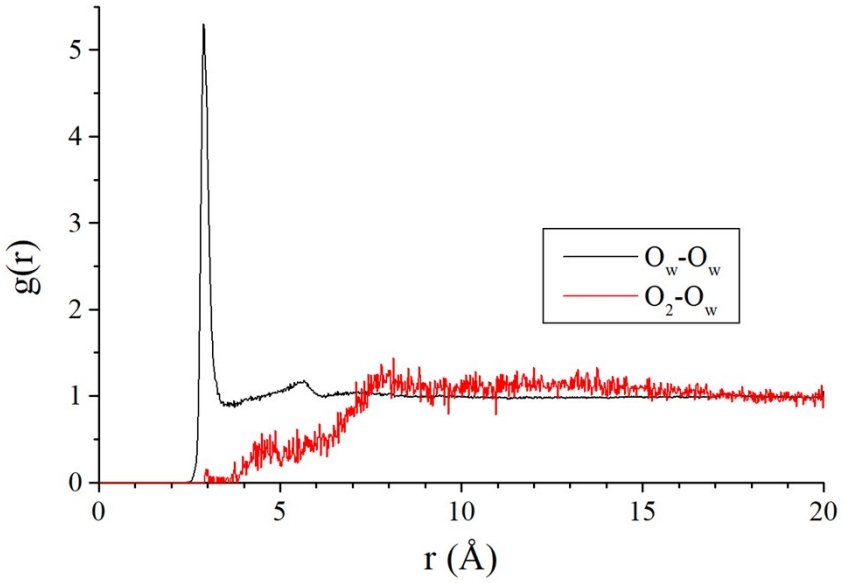


**Figure S9.** Radial distribution function between the O(2) atom of **LCAP-PPh$_3$** and the water oxygen atoms ($O_w$) along the 1 ns MD simulation. The radial distribution function between the water oxygen atoms ($O_w$) is also shown.

**ADDITIONAL TABLES**

**Table S1.** Vertical excitation energies (VEE) computed at the CASSCF/CASPT2/ANO-S-VDZP level with PCM and associated oscillator strengths (*f*) with the CAS(18,14) (CAS(10,10) within square brackets) at the TDDFT/B3LYP/6-31G** equilibrium structures.

| | | VEE | $f^b$ |
|---|---|---|---|
| **3APim$^{-2}$*** | **DMSO** | 2.22 (558) | 0.0903 |
| | | [ 2.15 (577) ] | |
| | **Water** | 2.07 (599) | 0.1166 |
| | | [ 2.10 (590) ] | |
| **3APam$^{-2}$*** | **DMSO** | 2.93 (423) | 0.0551 |
| | | [ 2.98 (416) ] | |
| | **Water** | 2.93 (423) | 0.0583 |
| | | [ 3.14 (395) ] | |
| **3APCAPim$^{-2}$*** | **Water** | -[a] | 0.0702 |

[a] Value not obtained due to technical problems related to the large size of this system. Note that considering the 3APim$^{-2}$* moiety as QM part and the CAP moiety as MM part, the CASPT2/MM produces a value of VEE of 2.36 eV.
[b] All values computed with the CASSCF method to allow comparisons between 3AP and 3APCAP systems.

**Table S2.** Cartesian coordinates (in Å) of the main structures computed in this work with the TDDFT method, the B3LYP functional and the 6-31G** basis set.

**$^1$(3APim$^{-2}$)* - 5 water - PCM**

| | | | |
|---|---|---|---|
| C | 5.066557 | 2.494815 | 1.107128 |
| C | 4.089745 | 1.499071 | 1.510635 |
| C | 2.821950 | 1.486694 | 0.842556 |
| C | 2.465637 | 2.634892 | 0.055810 |
| C | 3.380646 | 3.620255 | -0.257990 |
| C | 4.718653 | 3.522177 | 0.214105 |
| C | 4.349995 | 0.656069 | 2.686431 |
| O | 3.442238 | 0.171035 | 3.394847 |
| C | 1.925449 | 0.292960 | 0.806420 |
| O | 2.442841 | -0.859883 | 0.910221 |
| N | 6.314999 | 2.372488 | 1.645469 |

| | | | |
|---|---|---|---|
| O | 0.664890 | 0.491705 | 0.598180 |
| O | 5.644165 | 0.394405 | 3.016820 |
| O | -0.828769 | 2.709513 | 0.758273 |
| O | 0.069737 | -2.225800 | 0.652208 |
| O | 8.340731 | 4.362432 | 0.344464 |
| O | 3.811858 | -1.558382 | 5.426910 |
| O | 6.186023 | -0.084090 | 5.832455 |
| H | 5.470075 | 4.260351 | -0.050191 |
| H | 1.443326 | 2.703199 | -0.300665 |
| H | 3.083579 | 4.466218 | -0.872800 |
| H | 6.981738 | 3.018372 | 1.210395 |
| H | 6.198286 | 1.107787 | 2.510558 |
| H | 6.129568 | 0.179521 | 4.896644 |
| H | 5.389890 | -0.647508 | 5.905204 |
| H | 1.030894 | -2.064000 | 0.783441 |
| H | -0.152021 | -1.277117 | 0.565347 |
| H | 4.190564 | -2.348912 | 5.019929 |
| H | 3.687606 | -0.935765 | 4.660848 |
| H | 8.907988 | 3.733672 | -0.122663 |
| H | 8.857206 | 4.598077 | 1.127509 |
| H | -0.244223 | 1.903972 | 0.742211 |
| H | -0.319446 | 3.335132 | 1.288485 |

**$^{1}$(3APim$^{-2}$)* - 1 water - PCM**

| | | | |
|---|---|---|---|
| C | 5.054448 | 2.512782 | 1.104851 |
| C | 4.093265 | 1.501168 | 1.515171 |
| C | 2.823111 | 1.475192 | 0.842177 |
| C | 2.455000 | 2.615581 | 0.058531 |
| C | 3.347662 | 3.621974 | -0.264224 |
| C | 4.689336 | 3.536498 | 0.212614 |
| C | 4.346955 | 0.660932 | 2.699907 |
| O | 3.457561 | 0.167457 | 3.412544 |
| C | 1.899416 | 0.276542 | 0.794447 |
| O | 2.423129 | -0.876945 | 0.831790 |
| N | 6.316037 | 2.413874 | 1.625901 |
| O | 0.655248 | 0.518022 | 0.649575 |
| O | 5.650400 | 0.397822 | 3.039763 |
| O | 8.463392 | 4.415324 | 0.321690 |
| H | 5.433248 | 4.282587 | -0.055389 |
| H | 1.431415 | 2.640683 | -0.306888 |
| H | 3.038078 | 4.463524 | -0.879657 |
| H | 6.949212 | 3.078383 | 1.170355 |
| H | 6.200367 | 1.073567 | 2.531089 |
| H | 8.963190 | 3.696786 | -0.089578 |
| H | 8.920224 | 4.555040 | 1.162570 |

**$^{1}$(3APim$^{-2}$)* - 5 DMSO - PCM**

| | | | |
|---|---|---|---|
| C | 3.8486120E+00 | 3.0593770E+00 | 1.2232300E-01 |
| C | 3.2137780E+00 | 1.7540990E+00 | 1.9223200E-01 |
| C | 2.1568430E+00 | 1.4716950E+00 | -7.3403700E-01 |
| C | 1.5788670E+00 | 2.5659660E+00 | -1.4557960E+00 |
| C | 2.1382280E+00 | 3.8297040E+00 | -1.4581310E+00 |
| C | 3.3295450E+00 | 4.0670050E+00 | -7.1111700E-01 |
| C | 3.5306990E+00 | 8.2654701E-01 | 1.2888960E+00 |
| O | 2.7487390E+00 | -5.3604000E-02 | 1.7018450E+00 |
| C | 1.7057520E+00 | 8.1085999E-02 | -1.0973940E+00 |
| O | 2.5810360E+00 | -8.3370701E-01 | -1.1305440E+00 |
| N | 4.9592710E+00 | 3.2439750E+00 | 8.9727501E-01 |
| O | 4.7600000E-01 | -6.4806999E-02 | -1.4220310E+00 |
| O | 4.7553630E+00 | 9.1540000E-01 | 1.8878520E+00 |
| H | 3.8141310E+00 | 5.0391120E+00 | -7.1243700E-01 |
| H | 6.8877600E-01 | 2.3558050E+00 | -2.0417460E+00 |
| H | 1.6868840E+00 | 4.6335700E+00 | -2.0341690E+00 |
| H | 5.4317940E+00 | 4.1257020E+00 | 6.6811100E-01 |
| H | 5.1310360E+00 | 1.8139820E+00 | 1.5983730E+00 |
| S | 7.6630740E+00 | 5.1796000E+00 | -1.1420730E+00 |
| C | 6.6199740E+00 | 4.7945580E+00 | -2.5892360E+00 |
| H | 7.2290480E+00 | 4.2987940E+00 | -3.3485630E+00 |
| H | 5.7815030E+00 | 4.1664740E+00 | -2.2751720E+00 |
| H | 6.2477170E+00 | 5.7446570E+00 | -2.9764660E+00 |
| C | 8.1572980E+00 | 3.4677110E+00 | -7.4221600E-01 |
| H | 8.7246530E+00 | 3.0554100E+00 | -1.5795860E+00 |
| H | 8.7908090E+00 | 3.5175800E+00 | 1.4498100E-01 |
| H | 7.2664120E+00 | 2.8706090E+00 | -5.3292600E-01 |
| O | 6.7268900E+00 | 5.6525790E+00 | -2.3236002E-02 |
| S | 6.0466130E+00 | -2.7485070E+00 | 2.7932240E+00 |
| C | 4.2299740E+00 | -2.8752210E+00 | 2.7037650E+00 |
| H | 3.8007280E+00 | -1.8839740E+00 | 2.5140130E+00 |
| H | 3.9605790E+00 | -3.5700460E+00 | 1.9036610E+00 |
| H | 3.8888880E+00 | -3.2652730E+00 | 3.6652860E+00 |
| C | 6.3145290E+00 | -2.0429230E+00 | 1.1327770E+00 |
| H | 5.8726850E+00 | -1.0423020E+00 | 1.1236990E+00 |
| H | 7.3961540E+00 | -1.9733900E+00 | 9.9513001E-01 |
| H | 5.8756170E+00 | -2.6878000E+00 | 3.6393000E-01 |
| O | 6.6100000E+00 | -4.1726250E+00 | 2.7968130E+00 |
| S | -2.6616470E+00 | -1.3614340E+00 | -8.8850002E-02 |
| C | -1.8449590E+00 | -2.2474970E+00 | -1.4565630E+00 |
| H | -1.7313580E+00 | -3.2900410E+00 | -1.1526830E+00 |
| H | -2.4723260E+00 | -2.1837980E+00 | -2.3502390E+00 |

| | | | |
|---|---|---|---|
| H | -8.7216900E-01 | -1.7641480E+00 | -1.6104480E+00 |
| C | -2.6449480E+00 | 2.8399600E-01 | -8.7426501E-01 |
| H | -3.2166360E+00 | 2.4657900E-01 | -1.8058460E+00 |
| H | -3.1099170E+00 | 9.8513700E-01 | -1.7844800E-01 |
| H | -1.5947470E+00 | 5.3768000E-01 | -1.0569770E+00 |
| O | -4.1136460E+00 | -1.8384980E+00 | -3.3529991E-03 |
| S | 3.6513110E+00 | -4.5808330E+00 | -9.4925600E-01 |
| C | 3.5778220E+00 | -6.3057920E+00 | -1.5453390E+00 |
| H | 2.5991110E+00 | -6.7271760E+00 | -1.3043680E+00 |
| H | 3.7542730E+00 | -6.3263920E+00 | -2.6234620E+00 |
| H | 4.3588830E+00 | -6.8629960E+00 | -1.0251480E+00 |
| C | 2.3455670E+00 | -3.8922130E+00 | -2.0134310E+00 |
| H | 1.4009130E+00 | -4.3835910E+00 | -1.7643750E+00 |
| H | 2.2930060E+00 | -2.8167360E+00 | -1.7889030E+00 |
| H | 2.6046880E+00 | -4.0692320E+00 | -3.0611300E+00 |
| O | 4.9868250E+00 | -4.0053790E+00 | -1.4295380E+00 |
| S | 2.9685800E-01 | 3.3670400E-01 | 4.2510200E+00 |
| C | -1.3261690E+00 | 4.4425900E-01 | 5.0859160E+00 |
| H | -1.9588840E+00 | -3.8142700E-01 | 4.7516880E+00 |
| H | -1.1459650E+00 | 3.6100800E-01 | 6.1591810E+00 |
| H | -1.7918090E+00 | 1.4061000E+00 | 4.8573790E+00 |
| C | -3.0461500E-01 | 5.9446100E-01 | 2.5501890E+00 |
| H | 5.7513100E-01 | 5.3328500E-01 | 1.9037580E+00 |
| H | -1.0136190E+00 | -1.9833000E-01 | 2.2969620E+00 |
| H | -7.8329500E-01 | 1.5753100E+00 | 2.4839730E+00 |
| O | 1.0851270E+00 | 1.5808940E+00 | 4.6574730E+00 |

**$^{1}$(3APim$^{-2}$)* - 1 DMSO - PCM**

| | | | |
|---|---|---|---|
| C | 3.84861 | 3.05938 | 0.12232 |
| C | 3.21378 | 1.7541 | 0.19223 |
| C | 2.15684 | 1.4717 | -0.73404 |
| C | 1.57887 | 2.56597 | -1.4558 |
| C | 2.13823 | 3.8297 | -1.45813 |
| C | 3.32954 | 4.067 | -0.71112 |
| C | 3.5307 | 0.82655 | 1.2889 |
| O | 2.74874 | -0.0536 | 1.70185 |
| C | 1.70575 | 0.08109 | -1.09739 |
| O | 2.58104 | -0.83371 | -1.13054 |
| N | 4.95927 | 3.24398 | 0.89728 |
| O | 0.476 | -0.06481 | -1.42203 |
| O | 4.75536 | 0.9154 | 1.88785 |
| H | 3.81413 | 5.03911 | -0.71244 |
| H | 0.68878 | 2.35581 | -2.04175 |
| H | 1.68688 | 4.63357 | -2.03417 |
| H | 5.43179 | 4.1257 | 0.66811 |

| | | | |
|---|---|---|---|
| H | 5.13104 | 1.81398 | 1.59837 |
| S | 7.66307 | 5.1796 | -1.14207 |
| C | 6.61997 | 4.79456 | -2.58924 |
| H | 7.22905 | 4.29879 | -3.34856 |
| H | 5.7815 | 4.16647 | -2.27517 |
| H | 6.24772 | 5.74466 | -2.97647 |
| C | 8.1573 | 3.46771 | -0.74222 |
| H | 8.72465 | 3.05541 | -1.57959 |
| H | 8.79081 | 3.51758 | 0.14498 |
| H | 7.26641 | 2.87061 | -0.53293 |
| O | 6.72689 | 5.65258 | -0.02324 |

**$^{1}$(3APam$^{-2}$)* - 5 water - PCM**

| | | | |
|---|---|---|---|
| C | 5.0961850E+00 | 2.3980940E+00 | 1.0014820E+00 |
| C | 4.1261580E+00 | 1.4455260E+00 | 1.4907690E+00 |
| C | 2.8235770E+00 | 1.4576240E+00 | 8.5992201E-01 |
| C | 2.4602570E+00 | 2.6536170E+00 | 1.6326600E-01 |
| C | 3.3935810E+00 | 3.6225420E+00 | -2.0332000E-01 |
| C | 4.7479490E+00 | 3.4729350E+00 | 1.4738200E-01 |
| C | 4.4235200E+00 | 6.7139300E-01 | 2.7322370E+00 |
| O | 3.4716460E+00 | 4.5902400E-01 | 3.5437590E+00 |
| C | 1.9335690E+00 | 2.7927700E-01 | 8.3361400E-01 |
| O | 2.4247390E+00 | -8.6367801E-01 | 1.1089240E+00 |
| N | 6.3855240E+00 | 2.2555360E+00 | 1.3978300E+00 |
| O | 6.9707800E-01 | 4.5042700E-01 | 4.7117800E-01 |
| O | 5.6400990E+00 | 2.8415600E-01 | 2.9333230E+00 |
| O | -9.0122700E-01 | 2.5741470E+00 | 6.7869300E-01 |
| O | 1.0127200E-01 | -2.2492670E+00 | 6.5802900E-01 |
| O | 8.2924590E+00 | 4.2520090E+00 | 5.2311000E-01 |
| O | 3.6341980E+00 | -1.1907730E+00 | 5.6092900E+00 |
| O | 6.3490760E+00 | -3.7473600E-01 | 5.5479360E+00 |
| H | 5.5186270E+00 | 4.1587730E+00 | -1.8782300E-01 |
| H | 1.4123640E+00 | 2.7979950E+00 | -8.3245999E-02 |
| H | 3.0718220E+00 | 4.4932210E+00 | -7.6898000E-01 |
| H | 7.1052810E+00 | 2.9300580E+00 | 1.1161890E+00 |
| H | 6.5427440E+00 | 1.4485350E+00 | 2.0258970E+00 |
| H | 6.1714220E+00 | -1.1229800E-01 | 4.6165780E+00 |
| H | 5.4662130E+00 | -7.0587600E-01 | 5.8021980E+00 |
| H | 1.0404970E+00 | -2.0737720E+00 | 8.9400200E-01 |
| H | -9.9970000E-02 | -1.3076310E+00 | 4.8082400E-01 |
| H | 3.7686790E+00 | -2.0594700E+00 | 5.2079210E+00 |
| H | 3.5952730E+00 | -5.7225900E-01 | 4.8184220E+00 |
| H | 9.0677450E+00 | 3.8245190E+00 | 1.3337500E-01 |
| H | 8.6420270E+00 | 4.7165860E+00 | 1.2961990E+00 |
| H | -2.8342300E-01 | 1.7918750E+00 | 6.3839800E-01 |

H -5.5658300E-01 3.0852470E+00 1.4218140E+00

**$^{1}$(3APam$^{-2}$)* - 5 DMSO - PCM**

| | | | |
|---|---|---|---|
| C | 3.875458 | 2.779302 | 0.056523 |
| C | 3.250556 | 1.486091 | 0.171037 |
| C | 2.036981 | 1.263476 | -0.603704 |
| C | 1.332220 | 2.422256 | -1.024226 |
| C | 1.900185 | 3.699549 | -1.002608 |
| C | 3.211643 | 3.891450 | -0.525910 |
| C | 3.701864 | 0.561179 | 1.249631 |
| O | 2.839324 | -0.128678 | 1.871744 |
| C | 1.621296 | -0.079247 | -1.071543 |
| O | 2.461811 | -1.034803 | -0.973321 |
| N | 5.136564 | 2.927641 | 0.540895 |
| O | 0.455000 | -0.203541 | -1.601295 |
| O | 4.961008 | 0.512962 | 1.533076 |
| H | 3.711136 | 4.853544 | -0.561985 |
| H | 0.322627 | 2.284263 | -1.404326 |
| H | 1.330086 | 4.549170 | -1.372022 |
| H | 5.585287 | 3.849626 | 0.588632 |
| H | 5.514455 | 2.067660 | 0.974205 |
| S | 7.406768 | 5.736655 | -0.755391 |
| C | 6.366712 | 5.741053 | -2.253721 |
| H | 7.012061 | 5.760512 | -3.134711 |
| H | 5.722270 | 4.858285 | -2.254554 |
| H | 5.759602 | 6.647075 | -2.219308 |
| C | 8.292344 | 4.174852 | -1.078800 |
| H | 8.902111 | 4.294754 | -1.976990 |
| H | 8.934773 | 3.987616 | -0.217021 |
| H | 7.574246 | 3.360692 | -1.198859 |
| O | 6.473449 | 5.487459 | 0.440309 |
| S | 5.974169 | -2.953407 | 2.865854 |
| C | 4.154340 | -2.967360 | 2.957352 |
| H | 3.778434 | -1.966925 | 2.704921 |
| H | 3.773016 | -3.713490 | 2.254416 |
| H | 3.891173 | -3.230678 | 3.984623 |
| C | 6.100676 | -2.591570 | 1.082692 |
| H | 5.738473 | -1.568283 | 0.936946 |
| H | 7.158160 | -2.663462 | 0.818266 |
| H | 5.506968 | -3.316195 | 0.518445 |
| O | 6.465202 | -4.387836 | 3.094200 |
| S | -2.800667 | -1.815432 | -1.071524 |
| C | -1.607100 | -2.522540 | -2.253603 |
| H | -1.486041 | -3.579515 | -2.007982 |

| | | | |
|---|---|---|---|
| H | -2.001353 | -2.416213 | -3.268496 |
| H | -0.669574 | -1.964994 | -2.125565 |
| C | -2.719544 | -0.106423 | -1.702693 |
| H | -3.056816 | -0.090043 | -2.743057 |
| H | -3.381745 | 0.504379 | -1.085863 |
| H | -1.675931 | 0.216965 | -1.615901 |
| O | -4.188705 | -2.378972 | -1.389257 |
| S | 2.422584 | -5.060887 | -0.772287 |
| C | 2.692029 | -6.651958 | -1.629054 |
| H | 1.872001 | -6.826552 | -2.329425 |
| H | 3.650604 | -6.624717 | -2.152859 |
| H | 2.701475 | -7.433743 | -0.867646 |
| C | 2.538407 | -3.976416 | -2.229361 |
| H | 1.723988 | -4.232693 | -2.912704 |
| H | 2.431643 | -2.941452 | -1.872981 |
| H | 3.506495 | -4.128727 | -2.714920 |
| O | 3.665255 | -4.815878 | 0.090844 |
| S | 1.048493 | 0.945193 | 4.697038 |
| C | -0.357494 | 1.256749 | 5.824049 |
| H | -1.011630 | 0.381640 | 5.835067 |
| H | 0.054926 | 1.422280 | 6.821012 |
| H | -0.902906 | 2.143645 | 5.492157 |
| C | 0.084517 | 0.811044 | 3.156786 |
| H | 0.816514 | 0.603787 | 2.370314 |
| H | -0.619594 | -0.019780 | 3.252297 |
| H | -0.447559 | 1.749740 | 2.980886 |
| O | 1.851794 | 2.243048 | 4.628022 |

**$^{1}$(3APCAPim$^{-2}$)* - PCM (water)**

H 0.182942 3.038329 -0.179631
H 2.108002 0.440662 -1.569584
H 0.066750 3.538579 -4.062926
H 0.768387 4.768535 -3.043318
C -2.608915 -0.695054 -0.815506
H -1.123146 2.535492 -2.122708
H -1.530794 4.224980 -2.398663
H 2.575440 3.340472 -3.258090
H 1.907576 2.768306 -1.755006
C 1.703575 2.828063 -2.830008
H 1.386629 -2.666029 2.561061
H -1.326912 -1.724896 1.504290
H 2.008256 2.289462 0.207178
H -5.868953 -1.730732 -0.758858
H -6.120896 0.373990 0.562492

H 0.121070 -0.766930 1.666471
C 0.196132 -0.803580 4.521744
H -1.494191 -1.967430 3.951565
C 0.350740 5.172341 -0.367118
C -0.957419 -1.100294 3.535578
H 3.789363 0.358279 3.311347
C -2.713928 0.397813 0.145906
H 3.010636 -0.651396 2.116020
C 3.811176 0.088817 2.248846
H 3.887881 2.234649 1.906239
H 1.578287 0.653147 0.635310
O -4.686190 -3.443654 -2.100053
C -3.738158 -1.586192 -0.961236
C -5.003583 -1.120227 -0.512524
C -5.142265 0.037710 0.228832
C -3.664445 -3.009030 -1.475747
O -2.635446 -3.700935 -1.199180
O -1.544884 -1.397840 -2.845440
C -1.520756 -0.732050 -1.795086
N -1.487161 0.947875 0.543765
O -0.440521 0.063518 -1.577087
C -3.972464 0.763460 0.622974
H -0.599837 0.536322 -0.696126
H -0.086787 -3.497021 2.996992
C -0.727500 3.554445 -2.060207
H 0.797054 0.038755 4.167659
H 2.554802 -3.527567 0.558021
H -4.082372 1.591623 1.307614
C -1.460001 1.797304 1.727475
C 1.630213 -3.542245 -0.034316
C 3.505894 1.340728 1.394318
C 2.024884 1.569025 1.035626
C -0.122882 2.227590 2.361029
H 1.323327 5.144320 -0.866765
C -0.455687 -1.562145 2.145785
C -2.113191 3.135654 1.274074
C -0.428241 3.854988 -0.562148
C -2.208234 1.175353 2.931993
C 0.455085 3.717427 -3.050612
C 0.365169 -2.871769 2.213482
C 1.199370 2.139485 2.154555
C 0.430894 -3.738048 0.924925
C -1.969941 0.042359 3.612955
C -1.688285 3.932220 0.279701
H -0.507208 -3.633964 0.364668
H 0.467034 -4.785916 1.252204

H 1.797342 2.656308 2.908320
H -0.193370 -0.547679 5.513267
H -2.301887 4.813463 0.076559
H -3.027441 3.416714 1.794906
H 4.461285 -2.482334 1.182775
H -2.628223 -0.086071 4.475023
H 1.698201 -4.441895 -0.664406
H -3.002580 1.804783 3.333314
H -0.379547 2.799424 3.252953
H 0.850326 -1.673367 4.637664
H 3.516205 0.678926 -2.590263
H 5.891513 0.190755 1.625674
H 1.287334 -1.231003 -3.406569
H 4.260683 -3.244147 -1.076251
H 4.068426 1.283145 0.458561
H 5.114337 -0.413709 -0.972526
H 6.067189 -2.069899 0.611140
H 5.571843 -1.062658 2.807828
C 1.627293 1.393593 -3.406315
H 1.941898 1.405287 -4.460219
C 5.163720 -0.582427 1.909683
H 0.580949 -2.322675 -1.457654
H 2.956283 -1.232852 -3.968259
H 1.554437 -1.404705 -0.351269
C 1.552341 -2.316502 -0.956475
H -0.208358 6.025221 -0.771473
C 2.459623 0.376143 -2.600110
C 4.447691 -1.155763 -0.514810
C 4.089705 -2.262262 -1.536602
H 0.527304 5.362796 0.696210
C 2.323864 -1.085460 -3.080359
H 3.533952 -0.617167 -0.271082
H 2.521740 -3.155981 -2.658310
C 2.631034 -2.231850 -2.067499
H 0.591297 1.049842 -3.382003
H 4.772121 -2.221762 -2.395484
C 5.069301 -1.650724 0.80083

**Table S3.** ESP charges (q) used in the QM/MM and MD computations of **$^1$(3APim$^{-2}$)*** and **$^1$(3APam$^{-2}$)*** in DMSO and water solutions, respectively.

| **$^1$(3APim$^{-2}$)* - DMSO** | | **$^1$(3APam$^{-2}$)* - water** | |
|---|---|---|---|
| Atom | q | Atom | q |
| C | 0.452138 | C | 0.394165 |
| C | -0.406498 | C | -0.322178 |
| C | -0.058538 | C | -0.101289 |
| C | -0.349763 | C | -0.197517 |
| C | -0.188368 | C | -0.180540 |
| C | -0.402058 | C | -0.376607 |
| C | 0.676136 | C | 0.719183 |
| O | -0.716091 | O | -0.724536 |
| C | 0.545140 | C | 0.591387 |
| O | -0.400512 | O | -0.672590 |
| N | -1.033376 | N | -0.779338 |
| O | -0.449901 | O | -0.710886 |
| O | -0.682885 | O | -0.775217 |
| H | 0.104576 | H | 0.137668 |
| H | 0.129109 | H | 0.106074 |
| H | 0.103184 | H | 0.112161 |
| H | 0.303160 | H | 0.385207 |
| H | 0.374547 | H | 0.394853 |

**Table S4.** ESP charges (q) used in the QM/MM and MD computations of **$^1$(3APCAPim$^{-2}$)*** in water solution. Charges are listed following the same order as the Cartesian coordinates of Table S2.

| Atom | q |
|---|---|
| H | 0.016457 |
| H | -0.337989 |
| H | 0.038174 |
| H | 0.029092 |
| C | -0.301827 |
| H | -0.020038 |
| H | -0.005571 |
| H | 0.008478 |
| H | -0.035220 |
| C | 0.050854 |
| H | 0.056788 |

| | |
|---|---|
| H | 0.070388 |
| H | 0.070364 |
| H | 0.121823 |
| H | 0.109264 |
| H | -0.065022 |
| C | -0.374349 |
| H | -0.028330 |
| C | -0.386139 |
| C | 0.367525 |
| H | 0.025991 |
| C | 0.548363 |
| H | -0.008164 |
| C | -0.034414 |
| H | 0.033002 |
| H | 0.372192 |
| O | -0.773029 |
| C | 0.023103 |
| C | -0.328733 |
| C | -0.051354 |
| C | 0.695703 |
| O | -0.750829 |
| O | -0.596472 |
| C | 0.480608 |
| N | -0.707599 |
| O | -0.219280 |
| C | -0.459761 |
| H | 0.192778 |
| H | 0.048887 |
| C | -0.001399 |
| H | 0.082318 |
| H | 0.010146 |
| H | 0.178231 |
| C | 0.183481 |
| C | -0.084829 |
| C | -0.055895 |
| C | -0.064588 |
| C | -0.106540 |
| H | 0.081537 |
| C | -0.106095 |
| C | -0.127036 |
| C | 0.393401 |
| C | -0.116623 |
| C | -0.148593 |
| C | -0.201494 |
| C | -0.281669 |
| C | 0.063147 |

| | |
|---|---|
| C | -0.311851 |
| C | -0.382771 |
| H | -0.011179 |
| H | -0.003738 |
| H | 0.110816 |
| H | 0.085913 |
| H | 0.128656 |
| H | 0.098313 |
| H | 0.017782 |
| H | 0.107743 |
| H | 0.018036 |
| H | 0.094814 |
| H | 0.098783 |
| H | 0.073308 |
| H | -0.017665 |
| H | 0.025261 |
| H | 0.013376 |
| H | 0.042158 |
| H | -0.058086 |
| H | -0.026194 |
| H | 0.021674 |
| H | 0.034534 |
| C | -0.101364 |
| H | 0.016293 |
| C | -0.109129 |
| H | 0.090909 |
| H | 0.039553 |
| H | 0.055936 |
| C | -0.152371 |
| H | 0.084207 |
| C | 0.160721 |
| C | 0.043331 |
| C | -0.287021 |
| H | 0.081167 |
| C | -0.206996 |
| H | 0.408130 |
| H | -0.002966 |
| C | 0.160289 |
| H | 0.018970 |
| H | 0.058013 |
| C | -0.090564 |

**Table S5.** SPC and Dreiding QEq charges (q) of the water solvent used in the QM/MM and MD computations.

| Atom | q | |
|---|---|---|
| | SPC | Dreiding QEq |
| O | -0.820 | -0.701 |
| H | 0.410 | 0.350 |

**Table S6.** Dreiding QEq charges (q) of the DMSO solvent used in the QM/MM and MD computations.

| Atom | q |
|---|---|
| S | -0.187 |
| O | -0.403 |
| C | -0.119 |
| C | -0.114 |
| H | 0.091 |
| H | 0.175 |
| H | 0.143 |
| H | 0.178 |
| H | 0.090 |
| H | 0.146 |