ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Experimental and computational studies of protolytic and tautomeric equilibria of Erythrosin B and Eosin Y in water/DMSO

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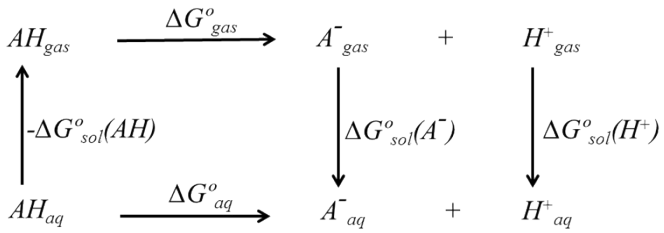
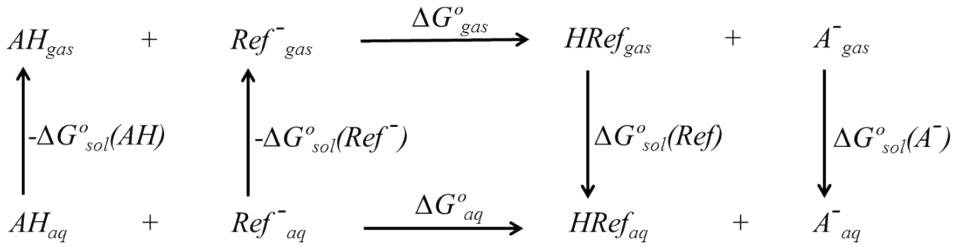
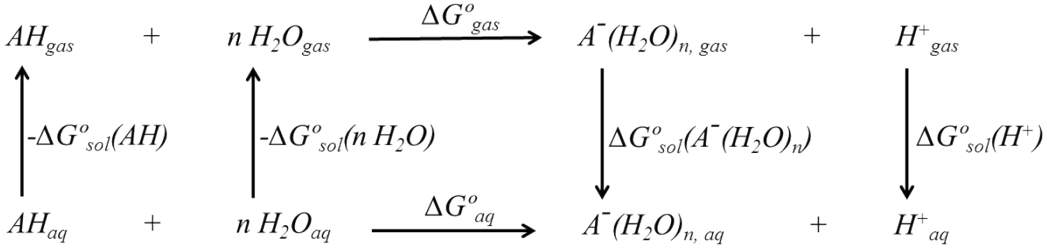


Scheme SI-1 Thermodynamic cycle utilized to obtain the Standard Gibbs Free Energy for the deprotonation of HA in water or DMSO (aq=dmso) media.[44]



Scheme SI-2 Proton exchange method including a referential acid (HRef) in the thermodynamic cycle to obtain the Gibbs Free Energy of dissociation ($^{\Delta G}{}_{aq}$) of HA in water (or DMSO, with aq = dmso) with the continuum solvation model.[44]



Scheme SI-3 Thermodynamic cycle of Gibbs Free Energy of dissociation ($^{\Delta G^o}{}_{aq}$) of HA in water with the *implicit-explicit* solvation model.[46-50]

$$pK_a = \frac{\Delta G^o{}_{aq}}{RT\ ln10} - log[H_2O] \qquad \text{(Eq. SI-1)}$$

Using the referential values of $G_{gas}(H^+)$= -6.28 kcal/mol, $\Delta G_{sol}(H^+)$= -265.9 kcal/mol and $\Delta G_{sol}(H_2O)$= -6.32 kcal/mol,[46-50]at 298.15 K, we have:

$$\Delta G^{o}{}_{aq} = G_{gas}\left(A^{-}(H_2O)_n\right) - G_{gas}(HA) - G_{gas}(nH_2O) + \Delta G_{sol}\left(A^{-}(H_2O)_n\right) - \Delta G_{sol}(HA) - 265.9$$

(Eq. SI-2)

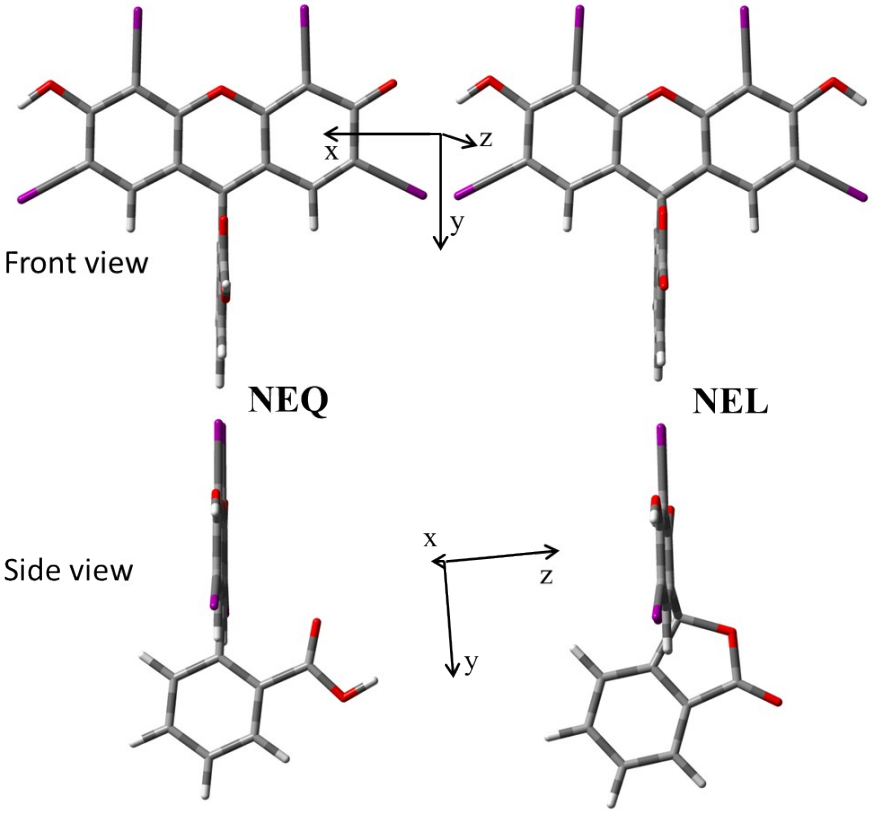


Fig.SI-1 Frontal and lateral view of the tautomers NEQ and NEL of ERY optimized with B3LYP/DGDZVP and IEF-PCM/UFF in water.

Table SI-1 Dihedral angles among atoms C^{13}-C^{9}-$C^{1'}$-$C^{2'}$ and $C^{1'}$-$C^{2'}$-$C^{7'}$-$O^{8'}$ for tautomers of the ERY and EOS obtained by B3LYP/DGDZVP and B3LYP/6-311++G(d,p) in water with the solvent model IEF-PCM/UFF.

		ERY Dihedral angle (º)		**EOS Dihedral angle (º)**	
		C^{13}-C^{9}-$C^{1'}$-$C^{2'}$	$C^{1'}$-$C^{2'}$-$C^{7'}$-$O^{8'}$	C^{13}-C^{9}-$C^{1'}$-$C^{2'}$	$C^{1'}$-$C^{2'}$-$C^{7'}$-$O^{8'}$
B3LYP/ DGDZVP	NEQ	-88.45	2.09	-88.47	1.90
	NEL	-115.37	0.00	-115.60	0.00
	MAC	-91.17	1.38	-91.26	1.49
	MAF	-92.38	0.00	-92.43	0.00
	DA	-94.49	0.00	-94.49	0.00
	MET-NE	-89.33	2.56	-89.39	2.64
	MET-MA	-92.59	-0.02	-92.83	0.32
B3LYP/ 6-311++G(d.p)	NEQ	-87.62	1.48	-87.56	0.97
	NEL	-115.13	0.04	-115.38	0.00
	MAC	-90.20	1.38	-90.43	1.58
	MAF	-90.82	-1.92	-90.71	-2.24
	DA	-94.20	0.00	-94.27	-0.01
	MET-NE	-88.50	1.64	-88.81	2.02
	MET-MA	-91.17	-2.27	-91.28	-2.05

Table SI-2 Symbolic Z-matrix cartesian plane (x, y, z) of optimized species of ERY, ERYMET, EOS and EOSMET with B3LYP/DGDZVP and IEF-PCM/UFF in water.

ERI-NEZ	ERI-NEL
Charge = 0 Multiplicity = 1 C 3.66747 0.57995 -0.03186 C 2.50575 1.33268 0.07444 C 1.24653 0.72614 0.16093 C 1.18303 -0.67160 0.12706 C 2.34823 -1.44829 0.02534 C 3.60939 -0.83137 -0.05294 C 0.00004 1.55545 0.37096 C -1.18904 -0.66502 0.12669 C -1.24890 0.73062 0.16090 C -2.50883 1.34170 0.07504 H -2.58092 2.42672 0.09868 C -3.66895 0.59197 -0.03109 C -3.61599 -0.82043 -0.05432 C -2.35810 -1.44104 0.02335 H 2.57981 2.41751 0.09728 C 0.00208 2.87755 -0.37669 C 0.00204 3.11996 -1.74925 C 0.00337 3.93146 0.53323 C 0.00365 4.45532 -2.17496 H 0.00074 2.30456 -2.47307 C 0.00501 5.26819 0.12215 C 0.00519 5.51941 -1.25260 H 0.00359 4.67518 -3.24277 H 0.00599 6.07992 0.84968 H 0.00638 6.54611 -1.61794 O -0.00517 -1.35270 0.19089 O -4.78992 -1.48087 -0.15774 O 4.68803 -1.63981 -0.15084 H 5.53601 -1.14034 -0.19548 C 0.00213 3.37233 1.89877 O 0.00049 2.00920 1.80651 O 0.00208 3.93982 2.97868 I 2.23294 -3.56664 -0.01434 I -2.22225 -3.55984 -0.01851 I -5.54935 1.57856 -0.15758 I 5.53863 1.58935 -0.15959 H -4.67907 -2.46009 -0.15622	Charge = 0 Multiplicity = 1 C 3.66388 0.59042 -0.05040 C 2.50279 1.34110 0.05990 C 1.24730 0.72832 0.15787 C 1.18627 -0.66976 0.12866 C 2.35337 -1.44491 0.02369 C 3.60794 -0.82069 -0.06442 C -0.00000 1.55305 0.38258 C -1.18626 -0.66977 0.12866 C -1.24730 0.72832 0.15786 C -2.50279 1.34110 0.05989 H -2.56613 2.42342 0.07700 C -3.66387 0.59041 -0.05041 C -3.60793 -0.82070 -0.06442 C -2.35336 -1.44491 0.02369 H 2.56612 2.42343 0.07701 C -0.00000 2.88800 -0.34314 C -0.00000 3.15885 -1.71066 C -0.00001 3.92398 0.58660 C -0.00001 4.50159 -2.11004 H 0.00000 2.36235 -2.44959 C -0.00002 5.26762 0.20128 C -0.00002 5.54677 -1.16747 H -0.00001 4.74153 -3.16987 H -0.00002 6.06132 0.94288 H -0.00002 6.57719 -1.51136 O 0.00000 -1.35287 0.20197 O 4.70431 -1.60891 -0.16568 H 5.50808 -1.05386 -0.21797 C -0.00001 3.34034 1.94352 O -0.00001 1.97760 1.82304 O -0.00002 3.88858 3.03083 I 2.25231 -3.56266 -0.00474 I -2.25230 -3.56267 -0.00471 I -5.54908 1.57568 -0.19420 I 5.54908 1.57569 -0.19419 O -4.70430 -1.60892 -0.16568 H -5.50808 -1.05387 -0.21796
ERI-NEQ	**ERI-MAC**
Charge =0 Multiplicity = 1 C 3.62552 0.55840 -0.20419 C 2.45917 1.29651 -0.24255 C 1.19903 0.66427 -0.18328 C 1.16439 -0.74531 -0.09056 C 2.33835 -1.50534 -0.04776 C 3.58509 -0.85734 -0.10142 C -0.04305 1.38807 -0.20962 C -1.21640 -0.75672 -0.09073 C -1.23675 0.68432 -0.18413 C -2.52441 1.32605 -0.22604 H -2.55286 2.40762 -0.29107 C -3.67298 0.60427 -0.18466 C -3.69187 -0.87209 -0.09155 C -2.37222 -1.49786 -0.04882 H 2.50265 2.37637 -0.32003 C -0.02619 2.87611 -0.37294 C -0.09325 3.38066 -1.67894 C 0.06408 3.78258 0.70910 C -0.07080 4.75846 -1.91854 H -0.16237 2.68912 -2.51388 C 0.08242 5.16503 0.45631 C 0.01766 5.65365 -0.84887 H -0.12368 5.12620 -2.93950 H 0.14770 5.85449 1.29050	Charge =-1 Multiplicity = 1 C 3.62541 0.56892 -0.17052 C 2.45967 1.30991 -0.17815 C 1.19981 0.68082 -0.11870 C 1.16235 -0.72791 -0.05604 C 2.33717 -1.49125 -0.04378 C 3.58468 -0.84747 -0.09967 C -0.04034 1.41829 -0.11125 C -1.21658 -0.73445 -0.05645 C -1.23570 0.70083 -0.13380 C -2.51970 1.33919 -0.18242 H -2.54601 2.42172 -0.23217 C -3.67097 0.61579 -0.16007 C -3.69552 -0.85636 -0.07926 C -2.37664 -1.47689 -0.03114 H 2.50100 2.39150 -0.22687 C -0.02155 2.89786 -0.33117 C -0.08770 3.36835 -1.65349 C 0.07347 3.81289 0.73403 C -0.05616 4.74069 -1.91944 H -0.16200 2.66028 -2.47520 C 0.10124 5.18616 0.45278 C 0.03965 5.65405 -0.86242 H -0.10738 5.09147 -2.94698 H 0.17046 5.87623 1.28849

H 0.03440 6.72460 -1.02893 O -0.01949 -1.41361 -0.03855 O -4.75167 -1.52084 -0.05245 O 4.69215 -1.62317 -0.05349 H 5.49320 -1.06136 -0.09326 C 0.13356 3.27758 2.11038 O 0.15583 2.09589 2.42557 O 0.17180 4.26667 3.03222 H 0.21873 3.84057 3.91120 I 2.26794 -3.61695 0.09875 I -2.32736 -3.61235 0.08179 I -5.55987 1.57732 -0.25292 I 5.50844 1.54849 -0.30174	H 0.06307 6.72196 -1.06503 O -0.02140 -1.39867 -0.00397 O -4.75834 -1.50862 -0.05480 O 4.69303 -1.61721 -0.08575 H 5.49243 -1.05379 -0.12934 C 0.13726 3.30881 2.17529 O 0.12563 2.04365 2.30533 O 0.19523 4.16542 3.09883 I 2.26396 -3.60660 0.05681 I -2.33122 -3.59508 0.07878 I -5.55754 1.59708 -0.23787 I 5.51000 1.55940 -0.26255
ERI-MAF Charge =-1 Multiplicity = 1 C 3.65085 0.57481 -0.18679 C 2.49587 1.30134 -0.23392 C 1.21759 0.66601 -0.18832 C 1.19592 -0.76169 -0.09343 C 2.36077 -1.50374 -0.04705 C 3.67992 -0.88958 -0.08565 C 0.00000 1.37170 -0.21796 C -1.19590 -0.76169 -0.09342 C -1.21758 0.66600 -0.18835 C -2.49586 1.30133 -0.23400 H -2.53113 2.38254 -0.30744 C -3.65084 0.57478 -0.18685 C -3.67990 -0.88960 -0.08562 C -2.36075 -1.50375 -0.04698 H 2.53113 2.38257 -0.30731 C -0.00000 2.86073 -0.38804 C 0.00004 3.35204 -1.70137 C -0.00005 3.78255 0.68496 C 0.00003 4.72627 -1.95908 H 0.00007 2.64856 -2.52930 C -0.00005 5.16313 0.41426 C -0.00001 5.63612 -0.89772 H 0.00007 5.08039 -2.98638 H -0.00009 5.86411 1.24124 H -0.00002 6.70525 -1.08975 O 0.00001 -1.42559 -0.04545 O -4.74587 -1.54538 -0.03830 O 4.74589 -1.54536 -0.03837 C -0.00009 3.30657 2.09884 O -0.00011 2.13523 2.44905 O -0.00010 4.31940 2.99950 H -0.00014 3.91094 3.88784 I 2.31034 -3.62291 0.08565 I -2.31031 -3.62291 0.08591 I -5.53698 1.56326 -0.26228 I 5.53699 1.56330 -0.26214	ERI-DA Charge =-2 Multiplicity = 1 C 3.64921 0.58361 -0.15714 C 2.49340 1.31184 -0.18689 C 1.21614 0.67873 -0.14428 C 1.19472 -0.74700 -0.06892 C 2.36195 -1.49072 -0.03850 C 3.68079 -0.87997 -0.07618 C -0.00000 1.39527 -0.14825 C -1.19471 -0.74701 -0.06892 C -1.21613 0.67872 -0.14427 C -2.49340 1.31183 -0.18688 H -2.52536 2.39426 -0.24050 C -3.64921 0.58359 -0.15713 C -3.68079 -0.87998 -0.07621 C -2.36193 -1.49073 -0.03853 H 2.52535 2.39427 -0.24052 C -0.00000 2.87895 -0.35622 C 0.00000 3.33101 -1.68805 C -0.00003 3.81533 0.69786 C -0.00000 4.69702 -1.98303 H 0.00001 2.60556 -2.49819 C -0.00003 5.18409 0.38352 C -0.00002 5.63052 -0.93981 H 0.00000 5.02612 -3.01918 H -0.00004 5.88951 1.20877 H -0.00002 6.69572 -1.15856 O 0.00001 -1.41464 -0.02440 O -4.74850 -1.53825 -0.04433 O 4.74851 -1.53823 -0.04431 C -0.00003 3.38126 2.16994 O -0.00000 2.13219 2.38469 O -0.00006 4.30087 3.03842 I 2.31062 -3.61302 0.06535 I -2.31061 -3.61304 0.06526 I -5.53587 1.57624 -0.22835 I 5.53587 1.57625 -0.22839
ERYMET-NE Charge = 0 Multiplicity = 1 C 3.63781 0.51266 -0.16558 C 2.468721.25118 -0.21347 C 1.213950.6135 -0.20537 C 1.18382-0.79776 -0.14638 C 2.36058-1.55606 -0.09724 C 3.60579-0.90205 -0.10579 C -0.037451.33219 -0.24632 C -1.20088-0.82213 -0.20233 C -1.222930.62695 -0.26563 C -2.51511.26788 -0.3263 H -2.544992.3508 -0.36939 C -3.66180.54679 -0.33065 C -3.67666-0.94095 -0.27115 C -2.34623-1.56929 -0.20569	ERYMET-MA Charge = -1 Multiplicity = 1 C 3.63696 0.52572 -0.16759 C 2.481711.2494 -0.20181 C 1.204270.60871 -0.20347 C 1.18519-0.82566 -0.16309 C 2.34885-1.56483 -0.12778 C 3.67658-0.94719 -0.12652 C -0.015591.3061 -0.23165 C -1.2123-0.82899 -0.21681 C -1.233540.60532 -0.25807 C -2.511561.24246 -0.31362 H -2.548762.32609 -0.34363 C -3.665160.51557 -0.33114 C -3.70248-0.95745 -0.29184 C -2.37431-1.5714 -0.2336

H 2.510162.33334 -0.25587 C -0.022942.8254 -0.36491 C -0.023923.37303 -1.65633 C -0.01663.69971 0.74626 C -0.017514.75654 -1.85449 H -0.035592.70436 -2.51316 C -0.017335.0895 0.53637 C -0.014045.6185 -0.75421 H -0.020225.15578 -2.86551 H -0.020745.74929 1.39684 H -0.012626.69535 -0.90011 O 0.00542-1.47254 -0.13728 O -4.72479-1.58528 -0.27759 O 4.71914-1.66423 -0.05858 C -0.003783.14672 2.13796 O 0.139471.96717 2.41053 O -0.164464.10653 3.07619 C -0.161733.6414 4.44553 I 2.2901-3.66722 -0.01083 I -2.30493-3.67928 -0.11585 I -5.548611.50371 -0.42426 I 5.521181.51552 -0.1786 H -0.30584.5346 5.05293 H 0.790933.16203 4.68168 H -0.974692.92989 4.60517 H 5.50989-1.08983 -0.07075	H 2.517212.33313 -0.23023 C -0.015212.80164 -0.34111 C 0.013023.34609 -1.63469 C -0.041093.68552 0.7622 C 0.015894.72649 -1.84455 H 0.032942.66809 -2.48367 C -0.037975.07541 0.54136 C -0.009745.5972 -0.75069 H 0.038085.11789 -2.85893 H -0.058015.74093 1.39689 H -0.007766.67369 -0.90313 O -0.01325-1.48964 -0.16221 O -4.76168-1.60506 -0.30944 O 4.73731-1.59185 -0.09666 C -0.07183.15616 2.16261 O -0.077551.98124 2.47315 O -0.093484.15539 3.08951 C -0.123083.70732 4.45909 I 2.30386-3.68386 -0.07377 I -2.32588-3.69029 -0.17751 I -5.552251.50255 -0.42337 I 5.523531.51796 -0.17535 H -0.132494.61662 5.0616 H 0.760423.10498 4.68433 H -1.019293.1111 4.64767
EOS-NEZ 1 1 C 3.66504 0.32816 0.02173 C 2.51302 1.09058 0.11182 C 1.25005 0.48312 0.15515 C 1.18243 -0.91272 0.09700 C 2.34945 -1.68906 0.00280 C 3.61056 -1.08042 -0.03467 C -0.00001 1.31962 0.32572 C -1.18231 -0.91280 0.09700 C -1.25002 0.48305 0.15516 H -2.59263 2.17126 0.15377 C -3.66500 0.32793 0.02170 C -3.61043 -1.08065 -0.03467 C -2.34929 -1.68921 0.00284 H 2.59254 2.17142 0.15386 C -0.00006 2.59389 -0.50294 C -0.00001 2.75366 -1.88725 C -0.00027 3.69949 0.34243 C -0.00016 4.06034 -2.39230 H 0.00014 1.89962 -2.55885 C -0.00043 5.00840 -0.14874 C -0.00037 5.17720 -1.53543 H -0.00012 4.21556 -3.46775 H -0.00058 5.85890 0.52698 H -0.00048 6.17695 -1.96018 O 0.00008 -1.60020 0.12373 O -4.70775 -1.86610 -0.12849 O 4.70793 -1.86580 -0.12851 H 5.50761 -1.30426 -0.14865 C -0.00026 3.22221 1.74023 O -0.00007 1.85252 1.72465 O -0.00039 3.85076 2.78260 Br 2.23580 -3.58977 -0.07958 Br -2.23552 -3.58991 -0.07944 Br -5.38278 1.18262 -0.02680 Br 5.38277 1.18295 -0.02671 H -5.50748 -1.30461 -0.14861 C -2.51303 1.09042 0.11178	**EOS-NEL** 0 1 C 3.66500 0.32804 0.02140 C 2.51302 1.09051 0.11151 C 1.25004 0.48309 0.15502 C 1.18237 -0.91277 0.09700 C 2.34936 -1.68915 0.00282 C 3.61048 -1.08054 -0.03485 C 0.00000 1.31957 0.32573 C -1.18237 -0.91277 0.09700 C -1.25004 0.48309 0.15502 C -2.51302 1.09051 0.11151 H -2.59258 2.17136 0.15341 C -3.66500 0.32804 0.02140 C -3.61048 -1.08054 -0.03485 C -2.34936 -1.68915 0.00282 H 2.59258 2.17136 0.15341 C 0.00000 2.59404 -0.50263 C -0.00000 2.75414 -1.88692 C 0.00000 3.69945 0.34297 C -0.00000 4.06094 -2.39166 H -0.00000 1.90027 -2.55873 C 0.00000 5.00848 -0.14789 C -0.00000 5.17760 -1.53453 H -0.00000 4.21640 -3.46708 H 0.00000 5.85882 0.52804 H -0.00000 6.17745 -1.95908 O 0.00000 -1.60019 0.12387 O 4.70782 -1.86597 -0.12871 H 5.50753 -1.30446 -0.14889 C 0.00000 3.22187 1.74068 O 0.00000 1.85215 1.72480 O 0.00000 3.85018 2.78318 Br 2.23566 -3.58986 -0.07930 Br -2.23566 -3.58986 -0.07930 Br -5.38276 1.18278 -0.02722 Br 5.38276 1.18278 -0.02723 O -4.70782 -1.86597 -0.12871 H -5.50753 -1.30446 -0.14889
EOS-NEQ 0 1	**EOS-MAC** -1 1

C 3.60689 0.30498 -0.22464 C 2.44597 1.04720 -0.27380 C 1.18698 0.41115 -0.20700 C 1.15689 -0.99655 -0.09327 C 2.33425 -1.74990 -0.04563 C 3.58059 -1.10835 -0.10938 C -0.06098 1.12610 -0.24828 C -1.21534 -1.02460 -0.08725 C -1.24954 0.41393 -0.20752 C -2.54406 1.04125 -0.25761 H -2.59307 2.12081 -0.34062 C -3.68018 0.30288 -0.19962 C -3.69267 -1.17183 -0.08280 C -2.36443 -1.77330 -0.02911 H 2.49703 2.12579 -0.36435 C -0.05571 2.60937 -0.44960 C -0.13109 3.07752 -1.76868 C 0.03041 3.54525 0.60717 C -0.12070 4.44844 -2.04545 H -0.19760 2.36307 -2.58431 C 0.03670 4.92052 0.31713 C -0.03623 5.37291 -1.00062 H -0.17998 4.78791 -3.07583 H 0.09867 5.63294 1.13204 H -0.02915 6.43871 -1.20972 O -0.01787 -1.67456 -0.02719 O -4.74439 -1.83123 -0.03502 O 4.69304 -1.86363 -0.06000 H 5.48363 -1.29045 -0.11982 C 0.10776 3.07806 2.02102 O 0.13680 1.90511 2.36703 O 0.14517 4.09138 2.91594 H 0.19784 3.68928 3.80582 Br 2.26190 -3.64522 0.10323 Br -2.27375 -3.67226 0.12659 Br -5.38460 1.16563 -0.26599 Br 5.31095 1.17658 -0.31296	C 3.60677 0.32005 -0.19955 C 2.44651 1.06574 -0.21593 C 1.18778 0.43345 -0.14316 C 1.15489 -0.97381 -0.05836 C 2.33278 -1.73070 -0.03919 C 3.57997 -1.09372 -0.10790 C -0.05835 1.16278 -0.14566 C -1.21546 -0.99750 -0.05705 C -1.24843 0.43583 -0.15652 C -2.53964 1.05908 -0.21450 H -2.58686 2.14016 -0.27814 C -3.67819 0.31799 -0.18344 C -3.69581 -1.15311 -0.08586 C -2.36839 -1.74871 -0.02350 H 2.49529 2.14622 -0.28157 C -0.05109 2.63844 -0.38997 C -0.12339 3.08654 -1.71974 C 0.03720 3.57142 0.66008 C -0.10450 4.45466 -2.00782 H -0.19291 2.36466 -2.52980 C 0.05206 4.94015 0.35668 C -0.01556 5.38589 -0.96590 H -0.16044 4.78833 -3.04080 H 0.11565 5.64419 1.18111 H -0.00236 6.45052 -1.18593 O -0.01965 -1.65426 0.00818 O -4.75034 -1.81718 -0.06065 O 4.69340 -1.85352 -0.08758 H 5.48271 -1.27882 -0.14484 C 0.10678 3.09139 2.10917 O 0.10809 1.82835 2.25964 O 0.15610 3.96326 3.01864 Br 2.25703 -3.63012 0.07574 Br -2.27444 -3.65301 0.10610 Br -5.38334 1.18917 -0.26197 Br 5.31253 1.19157 -0.29978
EOS-MAF -1 1 C 3.64640 0.29378 -0.21391 C 2.49886 1.02967 -0.26925 C 1.21773 0.40051 -0.21234 C 1.19203 -1.02476 -0.09341 C 2.35523 -1.76716 -0.03835 C 3.67860 -1.16880 -0.09495 C 0.00000 1.10632 -0.25303 C -1.19208 -1.02473 -0.09340 C -1.21774 0.40054 -0.21233 C -2.49886 1.02973 -0.26923 H -2.54724 2.10931 -0.35790 C -3.64641 0.29387 -0.21389 C -3.67866 -1.16871 -0.09493 C -2.35530 -1.76710 -0.03834 H 2.54727 2.10924 -0.35792 C 0.00002 2.59211 -0.44832 C -0.00002 3.06067 -1.76994 C 0.00009 3.53215 0.60874 C 0.00001 4.43029 -2.05117 H -0.00007 2.34308 -2.58567 C 0.00013 4.90793 0.31438 C 0.00008 5.35821 -1.00555 H -0.00002 4.76677 -3.08440 H 0.00018 5.62308 1.12912 H 0.00011 6.42389 -1.21595 O -0.00003 -1.68953 -0.03022 O -4.74131 -1.82916 -0.04870 O 4.74124 -1.82927 -0.04872 C 0.00013 3.08058 2.03062	**EOS-DA** -2 1 C 3.64471 0.30559 -0.18802 C 2.49653 1.04384 -0.22062 C 1.21628 0.41716 -0.16426 C 1.19090 -1.00669 -0.06765 C 2.35612 -1.75150 -0.03291 C 3.67910 -1.15664 -0.09144 C -0.00000 1.13410 -0.17631 C -1.19086 -1.00672 -0.06765 C -1.21627 0.41713 -0.16427 C -2.49653 1.04377 -0.22063 H -2.54178 2.12499 -0.28797 C -3.64470 0.30550 -0.18803 C -3.67905 -1.15673 -0.09145 C -2.35606 -1.75156 -0.03291 H 2.54175 2.12506 -0.28794 C -0.00003 2.61518 -0.40057 C 0.00002 3.05280 -1.73727 C -0.00011 3.56291 0.64341 C -0.00003 4.41552 -2.04705 H 0.00009 2.31866 -2.53953 C -0.00017 4.92818 0.31405 C -0.00013 5.36026 -1.01400 H 0.00000 4.73348 -3.08669 H -0.00024 5.64232 1.13172 H -0.00018 6.42304 -1.24429 O 0.00003 -1.67495 -0.00571 O -4.74327 -1.82021 -0.06462 O 4.74334 -1.82009 -0.06461 C -0.00013 3.14677 2.12084

O 0.00003 1.91551 2.40119 O 0.00028 4.10894 2.91356 H 0.00029 3.71595 3.80884 Br 2.26903 -3.67307 0.11783 Br -2.26914 -3.67301 0.11785 Br -5.34541 1.18634 -0.29384 Br 5.34541 1.18620 -0.29387	O -0.00005 1.90064 2.35198 O -0.00017 4.07775 2.97716 Br 2.26740 -3.66168 0.09456 Br -2.26729 -3.66175 0.09454 Br -5.34481 1.20185 -0.26997 Br 5.34480 1.20198 -0.26995
EOSMET-NE 0 1 C 3.60503 0.17634 -0.35110 C 2.44617 0.91677 -0.45092 C 1.18531 0.29056 -0.34195 C 1.15111 -1.10610 -0.13305 C 2.32636 -1.85796 -0.03465 C 3.57465 -1.22587 -0.14006 C -0.06029 1.00583 -0.43031 C -1.22084 -1.12585 -0.12176 C -1.25081 0.30101 -0.34001 C -2.54338 0.92747 -0.43090 H -2.58832 1.99882 -0.58901 C -3.68177 0.19877 -0.31836 C -3.69863 -1.26407 -0.09917 C -2.37230 -1.86498 -0.01031 H 2.49978 1.98669 -0.61374 C -0.04989 2.47092 -0.73786 C -0.10902 2.84027 -2.08946 C 0.02493 3.48036 0.24899 C -0.09360 4.18662 -2.46632 H -0.16681 2.06769 -2.85113 C 0.03633 4.83013 -0.14218 C -0.02021 5.18470 -1.49035 H -0.13970 4.44982 -3.51946 H 0.09052 5.59968 0.61945 H -0.00860 6.23250 -1.77664 O -0.02551 -1.77472 -0.02087 O -4.75216 -1.91513 -0.00053 O 4.68484 -1.97955 -0.03799 C 0.09016 3.11254 1.69679 O 0.13038 1.96129 2.11185 O 0.10254 4.18721 2.50521 C 0.17360 3.91654 3.92721 Br 2.24843 -3.73909 0.23968 Br -2.28776 -3.74980 0.27002 Br -5.38428 1.06030 -0.43894 Br 5.31121 1.03653 -0.49590 H 0.17243 4.89491 4.40531 H 1.09204 3.37508 4.16221 H -0.69318 3.33316 4.24362 H 5.47736 -1.41298 -0.12761	EOSMET-MA -1 1 C 3.64758 0.18031 -0.32522 C 2.49878 0.90812 -0.43615 C 1.21853 0.28189 -0.34122 C 1.19501 -1.13198 -0.12585 C 2.35949 -1.86677 -0.01861 C 3.68189 -1.27074 -0.10721 C -0.00015 0.98191 -0.43303 C -1.18870 -1.13595 -0.12680 C -1.21662 0.27788 -0.34206 C -2.49881 0.89990 -0.43822 H -2.54825 1.97089 -0.60003 C -3.64532 0.16836 -0.32826 C -3.67514 -1.28281 -0.11046 C -2.35089 -1.87458 -0.02079 H 2.54482 1.97930 -0.59773 C -0.00247 2.44824 -0.74432 C 0.00046 2.80657 -2.10084 C -0.00822 3.47045 0.23279 C -0.00208 4.14786 -2.49391 H 0.00466 2.02441 -2.85503 C -0.01088 4.81690 -0.17468 C -0.00777 5.15779 -1.52704 H 0.00029 4.39861 -3.55125 H -0.01526 5.59564 0.57931 H -0.00976 6.20291 -1.82358 O 0.00421 -1.79367 -0.02140 O -4.73641 -1.94019 -0.01374 O 4.74515 -1.92473 -0.00938 C -0.01112 3.13216 1.69022 O -0.00322 1.99442 2.13998 O -0.02366 4.22883 2.47410 C -0.02770 3.99077 3.90246 Br 2.27709 -3.75921 0.25657 Br -2.26275 -3.76694 0.25376 Br -5.34604 1.05185 -0.46076 Br 5.34560 1.06928 -0.45637 H -0.03724 4.97990 4.35819 H 0.86873 3.44139 4.19696 H -0.91803 3.42765 4.18949

Table SI-3 Total Dipole moment (μ) resulted from B3LYP/6-311++G(d.p) with SMD-Coulomb in water, DMSO and vacuum for protolytic and tautomeric forms of ERY, ERIMET, EOS and EOSMET.

		μ (debye)						
		NEQ	**NEL**	**MAC**	**MAF**	**DA**	**MET-NE**	**MET-MA**
ERY	Water	19.59	9.46	20.82	15.85	14.68	19.80	17.09
	DMSO	17.85	9.00	18.69	14.99	13.16	18.08	15.67
	Vacuum	11.08	5.65	11.80	9.34	9.36	11.24	9.99
EOS	Water	18.47	9.02	19.46	17.40	14.52	18.66	18.13
	DMSO	11.81	6.03	12.92	11.23	9.23	12.06	11.98
	Vacuum	11.22	5.72	11.48	10.84	8.71	11.37	11.36

Table SI-4 Tautorization equilibrium constant (K_T) of ERY and EOS in water and DMSO obtained with the solvent model IEF-PCM and SMD combined with the van der Waals radii set UFF, Pauling and SMD-Coulomb, using B3LYP/DGDZVP, B3LYP/6-311++G(d,p), M06-2X/DGDZVP and M06-2X/LANL2DZ(d,p) levels of theory, at 298.15 K.

			ERYTROSIN				**EOSIN**			
			NEQ $\rightleftharpoons$ NEL, $K_{Q\text{-}L}$		**MAC $\rightleftharpoons$ MAF, K_M (10^4)**		**NEQ $\rightleftharpoons$ NEL, $K_{Q\text{-}L}$**		**MAC $\rightleftharpoons$ MAF, K_M (10^4)**	
		vdW radii	IEF-PCM	SMD	IEF-PCM	SMD	IEF-PCM	SMD	IEF-PCM	SMD
B3LYP / DGDZVP	WATER	UFF	0.217	0.217	2198.028	2198.028	1.717	1.721	1415.077	1412.682
		Paul.	0.0031	0.0031	15.005	15.005	*	0.033	*	8.975
		Coul.	*	0.046	*	0.420	*	0.0590	*	5.086
	DMSO	UFF	0.300	0.301	8734.296	8718.584	1.417	2.234	3893.333	12036.630
		Paul.	0.0049	0.0049	64.584	64.584	*	0.046	*	80.722
		Coul.	*	1.169	*	28973.357	*	4.353	*	119745.234
B3LYP / 6-311++G(d,p)	WATER	UFF	0.0263	0.0263	121.683	162.290	0.199	0.199	62.970	63.076
		Paul.	0.0003	0.0003	1.428	0.2528	*	0.0031	*	0.6397
		Coul.	*	0.0047	*	0.0054	*	0.0056	*	0.4501
	DMSO	UFF	0.0458	0.046	121.207	215.124	0.291	0.292	121.065	121.258
		Paul.	0.0006	0.0006	2.687	2.687	*	0.005	*	1.337
		Coul.	*	0.199	*	564.866	*	0.615	*	1216.845
M06-2X / DGDZVP	WATER	UFF	1.137	1.137	1656.093	1656.093	*	*	*	*
		Paul.	0.0262	0.0262	4.682	4.682	*	*	*	*
		Coul.	*	0.394	*	0.146	*	*	*	*
M06-2X / LANL2DZ(d,p)	WATER	UFF	8.589	11.164	18.993	25.167	*	*	*	*
		Paul.	0.141	0.171	0.135	0.044	*	*	*	*
		Coul.	*	1.672	-	0.0038	*	*	*	*
[a]Exp. (water)			0.27		0.41		1.24		0.77	
[a]Exp.(70 % DMSO)			5.51		12.89		1.16		0.63	

*Not Calculated. [a]Experimental values at 303.15 K

Table SI-5 Values of pK_a for the predicted protolytic equilibrium among different tautomers of ERY in water obtained from solvent model IEF-PCM and SMD combined with the model UFF, Pauling and SMD-Coulomb, at 298.15 K, in M06-2X/DGDZVP and M06-2X/LANL2DZ(d,p).

M06-2X		EQUILIBRIUM	acid-basic group	IEF-PCM		SMD		
				UFF	Paul.	UFF	Paul.	Coul.
DGDZVP	pK_{a1}	**NEQ⇌MAC**	**COOH**	**-5.26**	**-6.58**	**-5.18**	**-6.50**	**-6.61**
		NEQ⇌MAF	OH	-3.56	-2.42	-3.49	-2.26	-0.86
		NEL⇌MAC	OH	-0.62	-3.71	-0.72	-3.68	-2.61
		NEL⇌MAF	OH	1.07	0.44	0.97	0.56	3.14
	pK_{a2}	**MAC⇌DA**	**OH**	**6.01**	**6.42**	**6.05**	**6.40**	**7.91**
		MAF⇌DA	COOH	4.31	2.26	4.36	2.17	2.17
LANL2DZ(d.p)	pK_{a1}	**NEQ⇌MAC**	**COOH**	**3.82**	**2.59**	**3.23**	**1.13**	**2.60**
		NEQ⇌MAF	OH	-0.48	0.16	-0.69	-0.02	1.84
		NEL⇌MAC	OH	9.26	6.20	8.04	4.13	7.19
		NEL⇌MAF	OH	4.97	3.77	4.12	2.97	6.42
	pK_{a2}	**MAC⇌DA**	**OH**	**1.44**	**1.25**	**-0.38**	**-0.32**	**2.97**
		MAF⇌DA	COOH	5.73	3.67	3.54	0.83	3.74
[a]Exp.		ERI		$pK_{a1\text{-}COOH}$ = 2.35 ± 0.09		$pK_{a2\text{-}OH}$ = 3.79 ± 0.08		

[a]Experimental values at 303.15 K from Batistela *et al.*(2011)[15]

Table SI-6 Values of pK_a involving the tautomers of ERY and ERIMET in water, DMSO and vacuum obtained with IEF-PCM and SMD solvent models combined with the UFF, Pauling and SMD-Coulomb atomic radii set using B3LYP/DGDZVP and B3LYP/6-311++G(d,p) levels of theory at 298.15 K.

		EQUILIBRIUM	Group	WATERIEF-PCM		WATER SMD			DMSO SMD			VACUUM
				UFF	Paul.	UFF	Paul.	Coul.	UFF	Paul.	Coul.	
B3LYP / DGDZVP	pK_{a1}	MET-NE⇌MET-MA	OH	-2.29	-0.91	-0.89	0.48	1.86	-3.32	-1.59	1.18	294.27
		NEQ⇌MAC	COOH	**3.84**	**3.11**	**3.86**	**3.07**	**2.95**	2.25	1.50	7.31	307.16
		NEQ⇌MAF	OH	-1.63	-0.24	-1.59	-0.21	1.22	-3.32	-1.94	1.23	294.65
		NEL⇌MAC	OH	4.30	1.55	4.54	1.89	2.95	2.92	0.37	8.56	310.58
		NEL⇌MAF	OH	-1.17	-1.80	-0.92	-1.39	1.22	**-2.66**	**-3.07**	**2.48**	**298.08**
	pK_{a2}	MAC⇌DA	OH	**1.31**	**1.53**	**1.39**	**1.55**	**3.06**	-0.05	0.09	4.54	349.21
		MAF⇌DA	COOH	6.78	4.89	6.84	4.82	4.79	**5.52**	**3.53**	**10.62**	**361.71**
B3LYP / 6-311++G(d.p)	pK_{a1}	MET-NE⇌MET-MA	OH	0.20	1.51	0.21	1.50	2.88	-1.50	-0.21	3.10	297.83
		NEQ⇌MAC	COOH	**4.90**	**4.32**	**4.97**	**4.34**	**4.17**	3.36	2.75	8.36	309.14
		NEQ⇌MAF	OH	-0.19	1.09	0.60	2.27	3.78	-1.88	-0.59	2.70	296.75
		NEL⇌MAC	OH	4.26	1.60	4.50	1.93	2.95	2.89	0.41	8.54	311.18
		NEL⇌MAF	OH	-0.83	-1.64	0.14	-0.14	2.56	**-2.35**	**-2.94**	**2.88**	**298.80**
	pK_{a2}	MAC⇌DA	OH	**2.50**	**2.85**	**2.55**	**2.86**	**4.36**	1.11	1.42	5.73	350.48
		MAF⇌DA	COOH	7.59	6.09	6.92	4.93	4.76	**6.35**	**4.76**	**11.40**	**362.87**
Exp.		ERY		[a] $pK_{a1\text{-}COOH}$ = 2.35 ± 0.09		[a] $pK_{a2\text{-}OH}$ = 3.79 ± 0.08			[b] $pK_{a1\text{-}OH}$ = 4.58 ± 0.10		[b] $pK_{a2\text{-}COOH}$ = 5.93 ± 0.08	
		ERYMET		[a] $pK_{a1\text{-}OH}$ = 3.74 ± 0.07					[b] $pK_{a1\text{-}OH}$ = 4.64 ± 0.03			

[a]Experimental values in water at 303.15 K from Batistela *et al.* (2011)[15]. [b]Experimental values in 70% of DMSO at 303.15 K.

Table SI-7 Values of pK_a involving the tautomers of EOS and EOSMET in water, DMSO and vacuum obtained with IEF-PCM and SMD solvent models combined with the UFF, Pauling and SMD-Coulomb atomic radii set using B3LYP/DGDZVP and B3LYP/6-311++G(d,p) levels of theory at 298.15 K.

		EQUILIBRIUM	Group	WATER SMD			DMSO SMD			VACUUM
				UFF	Paul.	Coul.	UFF	Paul.	Coul.	
B3LYP / DGDZVP	pK_{a1}	MET-NE⇌MET-MA	OH	-2.31	-1.32	-1.06	-5.09	-3.72	-1.20	296.59
		NEQ⇌MAC	COOH	4.72	3.99	3.69	2.07	1.37	6.92	308.44
		NEQ⇌MAF	OH	**-1.25**	**0.23**	**0.16**	**-4.40**	**78.50**	**50.71**	**296.54**
		NEL⇌MAC	OH	5.25	2.80	2.76	2.12	-0.27	7.26	312.60
		NEL⇌MAF	OH	**-0.71**	**-0.96**	**-0.77**	**-4.36**	**76.86**	**51.05**	**300.69**
	pK_{a2}	MAC⇌DA	OH	0.96	1.42	1.42	-1.17	-1.25	-13.45	351.04
		MAF⇌DA	COOH	**6.92**	**4.92**	**4.95**	**5.30**	**-78.38**	**-57.25**	**362.95**
B3LYP / 6-311++G(d.p)	pK_{a1}	MET-NE⇌MET-MA	OH	0.69	2.02	1.85	-2.42	-1.07	1.41	299.68
		NEQ⇌MAC	COOH	5.49	4.93	4.52	3.34	2.81	8.11	309.77
		NEQ⇌MAF	OH	**0.13**	**1.57**	**1.31**	**-2.82**	**-1.39**	**0.96**	**298.34**
		NEL⇌MAC	OH	4.81	2.45	2.29	2.26	-0.03	7.37	312.46
		NEL⇌MAF	OH	**-0.54**	**-0.91**	**-0.92**	**-3.90**	**-4.22**	**0.21**	**301.03**
	pK_{a2}	MAC⇌DA	OH	2.47	2.87	2.90	-0.42	-0.02	3.76	352.32
		MAF⇌DA	COOH	**7.83**	**6.23**	**6.11**	**5.74**	**4.18**	**10.92**	**363.75**
Exp.	EOS	[a] $pK_{a1\text{-}OH}$ =2.02 ± 0.05 [a] $pK_{a2\text{-}COOH}$ = 3.80 ± 0.06					[b] $pK_{a1\text{-}OH}$ = 2.04 ± 0.05		[b] $pK_{a2\text{-}COOH}$ = 7.07 ± 0.09	
	EOSMET	[a] $pK_{a1\text{-}OH}$ = 2.11 ± 0.03					[b] $pK_{a1\text{-}OH}$ = 2.36 ± 0.07			

[a]Experimental values in water at 303.15 K from Batistela *et al.* (2011)[15]. [b] Experimental values in 70% (v/v) of DMSO at 303.15 K.

Table SI-8 Values of pK_a involving the tautomers of ERY and EOS, obtained by the **proton exchange method**, using B3LYP/DGDZVP and B3LYP/6-311++G(d,p) levels of theory with SMD-Coulomb continuum solvent model in water and DMSO, at 298.15 K.

				ERYTHROSIN B		EOSIN Y	
				Water	DMSO	Water	DMSO
B3LYP / DGDZVP	pK_{a1}	NEQ⇌MAC	COOH	**6.22**	4.64	8.24	11.87
		NEQ⇌MAF	OH	5.88	6.08	**4.72**	**55.66**
		NEL⇌MAC	OH	7.61	13.41	7.31	12.21
		NEL⇌MAF	OH	5.49	**7.32**	**3.79**	**56.00**
	pK_{a2}	MAC⇌DA	OH	**7.72**	9.38	5.97	-8.50
		MAF⇌DA	COOH	9.45	**15.46**	**9.50**	**-53.68**
B3LYP / 6-311++G(d.p)	pK_{a1}	NEQ⇌MAC	COOH	**6.42**	11.29	6.16	10.46
		NEQ⇌MAF	OH	6.02	5.63	**2.96**	**3.30**
		NEL⇌MAC	OH	5.19	11.47	3.94	9.71
		NEL⇌MAF	OH	4.80	**5.81**	**0.73**	**2.55**
	pK_{a2}	MAC⇌DA	OH	**6.62**	8.65	4.55	6.10
		MAF⇌DA	COOH	7.00	**14.32**	**7.76**	**13.26**
	EXPERIMENTAL			$pK_{a1\text{-}COOH}$=2.35± 0.09 $pK_{a2\text{-}OH}$=3.79± 0.09	*$pK_{a1\text{-}OH}$ = 4.58 ± 0.10 *$pK_{a2\text{-}COOH}$ = 5.93 ± 0.08	$pK_{a1\text{-}OH}$ =2.02 ± 0.05 $pK_{a2\text{-}COOH}$ = 3.80 ± 0.06	*$pK_{a1\text{-}OH}$ = 2.04 ± 0.05 *$pK_{a2\text{-}COOH}$ = 7.07 ± 0.09

*70 % DMSO

Table SI-9. Electronic stabilization energy (E_{stab}) of interaction between the orbitals σ bonding (σ, donor) and π antibonding (π*, acceptor) obtained for MAF of EOS (X=Br) and ERY (X=I) through NBO in B3LYP/DGDZVP with SMD-Coulomb in water.

σ donor	π* acceptor	EOS E_{stab} (kcal/mol)	ERY E_{stab} (kcal/mol)
C4–X17	C2–C3	4.58	6.00
	C13–C14	5.97	7.19
C5–X18	C11–C12	5.97	7.19
	C6–C7	4.58	6.00
C7–X19	C8–C12	5.94	7.24
	C5–C6	4.42	5.77
C2 –X20	C1–C13	5.94	7.24
	C3–C4	4.42	5.77

Table SI-10 Polarization percentage of the chemical bonds C–X of the EOS (X=Br) and ERI (X=I) obtained for MAC and MAF forms through NBO in B3LYP/DGDZVP and SMD-Coulomb in water.

		Bond polarization (%)			
		C4 – X17	**C5 – X18**	**C7 – X19**	**C2 – X20**
EOS	**MAC**	48.94 – 51.06	47.74 – 52.26	47.12 – 52.88	47.27 – 52.73
	MAF	47.34 – 52.66	47.34 – 52.66	46.65 – 53.35	46.65 – 53.35
ERY	**MAC**	56.51 – 43.49	54.99 – 45.01	54.42 – 45.58	55.35 – 44.65
	MAF	54.55 – 45.45	54.55 – 45.45	53.92 – 46.08	53.92 – 46.08

Table SI-11 Wavelength of the maximum absorption peak (λ_{max}) of DA form and ester derivatives MET-MA and MET-NE of ERY and EOS obtained combining B3LYP, CAM-B3LYP or M06-2X functionals with DGDZVP or 6-311++G(d,p) basis set, using the SMD-Coulomb solvation model in water. In parenthesis are the absolute errors related to experimental values.

		Wavelenght (nm)					
		Experimental	**B3LYP / 6-311++G(d,p)#**	**B3LYP / DGDZVP**	**CAM-B3LYP/ 6-311++G(d,p)#**	**CAM-B3LYP / DGDZVP**	**M06-2X / DGDZVP**
ERY	DA	527	461 (66)	460 (67)	427 (100)	426 (101)	432 (95)
	MET-MA	527	468 (59)	467 (60)	435 (92)	435 (92)	440 (87)
	MET-NE	491	462 (29)	461 (30)	406 (85)	406 (85)	409 (82)
EOS	DA	515	453 (62)	452 (63)	424 (91)	422 (93)	427 (88)
	MET-MA	517	459 (58)	457 (60)	431 (86)	430 (87)	434 (83)
	MET-NE	470	446 (24)	447 (23)	399 (71)	399 (71)	401 (69)

#The iodine description for ERY was added *extrabasis* with 6-311G(d,p), without difuse (++) functions.

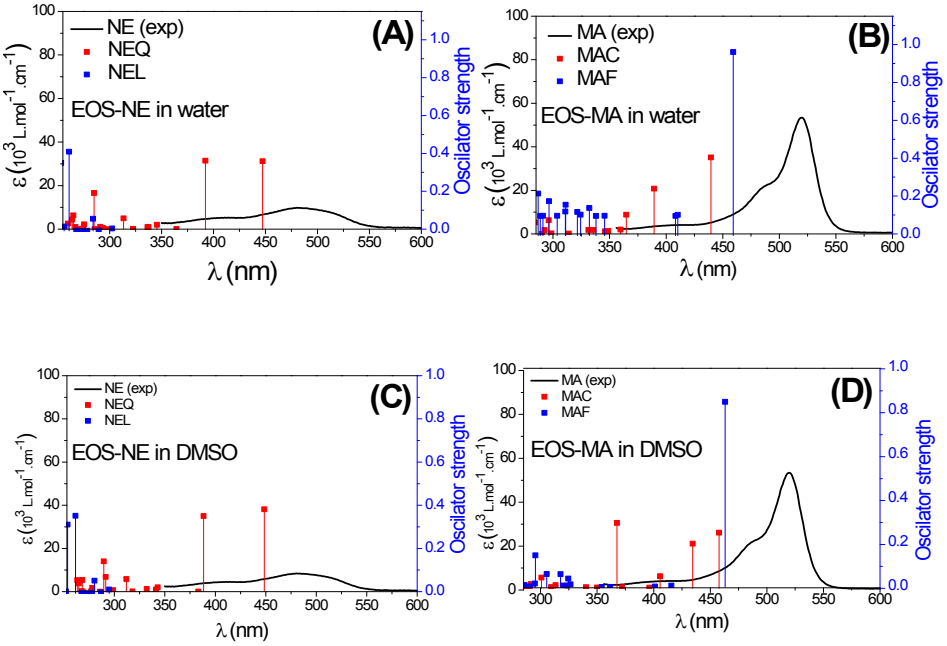


Fig. SI-2 Absorption spectra for the tautomer forms of neutral (NE) and monoanionic (MA) species determined experimentally using chemometry and estimated by TD-DFT using B3LYP/6-311++G(d,p) with SMD-Coulomb: (A) EOS-NE in water; (B) EOS-MA in water; (C) EOS-NE in DMSO; (D) EOS-MA in DMSO.

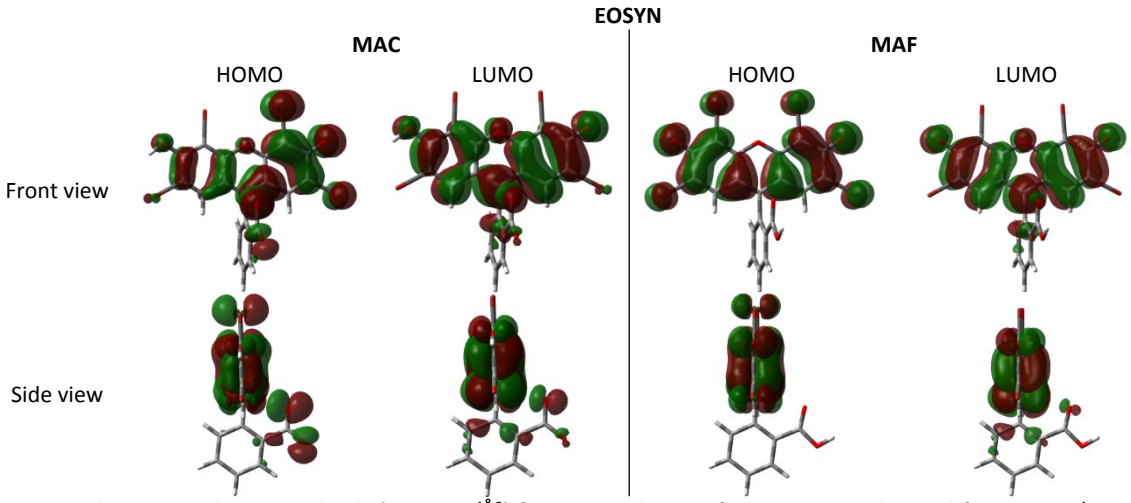


Fig. SI-3 Principal HOMO and LUMO orbitals (0.0004 e/Å^3) for MAC and MAF of EOS in water obtained from B3LYP/DGDZVP with IEF-PCM/UFF.