Supporting Information: Effect of microsolvation on the non-radiative decay of eumelanin monomer

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S1 Optimized ground state of gas phase DHI and the mono-hydrated species of DHI

S1.1 Optimized ground state geometry at (12o,10e) SA-CASSCF/6-311++g(d,p) level of theory

C	0.5398418239	1.4590480814	0.0000000000
C	-0.6920240928	0.7894290274	0.0000000000
C	-0.7807795430	-0.6085472932	0.0000000000
C	0.4014282579	-1.3725481500	0.0000000000
C	1.6158778061	-0.7157485491	0.0000000000
C	1.6902638125	0.6929326031	0.0000000000
C	-2.1866842352	-0.9394361834	0.0000000000
C	-2.8654114749	0.2386513882	0.0000000000
N	-1.9711322823	1.2927062712	0.0000000000
O	2.8245860334	-1.3536267515	0.0000000000
O	2.8929696395	1.3084981618	0.0000000000
H	-2.6221156100	-1.9175963240	0.0000000000
H	-3.9203729094	0.4183904932	0.0000000000
H	0.6180610767	2.5306661922	0.0000000000
H	0.3669807643	-2.4489287539	0.0000000000
H	-2.2154709936	2.2518594524	0.0000000000
H	3.5815943911	0.6651962961	0.0000000000
H	2.7205125357	-2.2878289617	0.0000000000

S1.2 Optimized ground state geometry of conformer D-O1 at (14o,14e)/6-311++g(d,p) level of theory

C	-0.9781395630	-1.6398767354	0.0000000000
C	-1.6670637706	-0.4185733624	0.0000000000
C	-0.9865756396	0.8302439573	0.0000000000
C	0.4223009877	0.8408494541	0.0000000000
C	1.0966642943	-0.3625520943	0.0000000000
C	0.4022969705	-1.5954719030	0.0000000000

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C        -2.0048185254        1.8495947661        0.0000000000
C        -3.2078163246        1.2096970954        0.0000000000
N        -3.0120839920       -0.1564993767        0.0000000000
O         2.4548494772       -0.4775136667        0.0000000000
O         1.0997515195       -2.7528304634        0.0000000000
H        -1.8592068228        2.9105087048        0.0000000000
H        -4.1980158183        1.6162473873        0.0000000000
H        -1.4776862898       -2.5915704360        0.0000000000
H         0.9755710237        1.7640361838        0.0000000000
H        -3.7324968035       -0.8362641991        0.0000000000
H         2.0233179902       -2.5604676521        0.0000000000
H         2.8845783499        0.3651414162        0.0000000000
O         3.8590951886        2.1044544944        0.0000000000
H         4.3322055590        2.4118014048        0.7562603146
H         4.3322055590        2.4118014048       -0.7562603146
```

S1.3 Optimized ground state geometry of conformer D-O2 at (14o,14e)/6-311++g(d,p) level of theory

```
C        -0.3976557173       -1.3568904273        0.0000000000
C        -1.5970472704       -0.6400326289        0.0000000000
C        -1.6291569226        0.7654211985        0.0000000000
C        -0.4092692711        1.4697220079        0.0000000000
C         0.7770913117        0.7664192785        0.0000000000
C         0.7939552371       -0.6465511616        0.0000000000
C        -3.0134619827        1.1546149420        0.0000000000
C        -3.7459793969        0.0005924727        0.0000000000
N        -2.8963831131       -1.0861027505        0.0000000000
O         2.0025063725        1.3860750958        0.0000000000
O         1.9465596369       -1.3513407391        0.0000000000
H        -3.4095572955        2.1494298888        0.0000000000
H        -4.8072110238       -0.1359246541        0.0000000000
H        -0.3643699353       -2.4309423546        0.0000000000
H        -0.3958016175        2.5471412031        0.0000000000
H        -3.1806934997       -2.0347910641        0.0000000000
H         2.7272833511       -0.7824347591        0.0000000000
H         1.8925841601        2.3196413641        0.0000000000
O         4.7544756885       -0.1318983810        0.0000000000
H         4.7277199740        0.4365121244        0.7508744192
H         4.7277199740        0.4365121244       -0.7508744192
```

S1.4 Optimized ground state geometry of conformer D-N1 at (14o,14e)/6-311++g(d,p) level of theory

```
C         0.1618260872       -1.0931787173        0.0000000000
C        -0.5879324269        0.0916553167        0.0000000000
```

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C       0.0319327461      1.3754563561      0.0000000000
C       1.4380519658      1.4513895828      0.0000000000
C       2.1674183999      0.2814190604      0.0000000000
C       1.5388141790     -0.9843923116      0.0000000000
C      -1.0339962540      2.3396953916      0.0000000000
C      -2.2024086453      1.6333586015      0.0000000000
N      -1.9407805998      0.2830175582      0.0000000000
O       3.5370243487      0.2385816016      0.0000000000
O       2.2910310225     -2.1095475450      0.0000000000
H      -0.9446049778      3.4067690408      0.0000000000
H      -3.2117945931      1.9894799137      0.0000000000
H      -0.2934596410     -2.0663882444      0.0000000000
H       1.9434583099      2.4030106172      0.0000000000
H      -2.6266222125     -0.4373493311      0.0000000000
H       3.2048780317     -1.8783999145      0.0000000000
H       3.9057443741      1.1030670532      0.0000000000
O      -3.9593039730     -2.0771423761      0.0000000000
H      -4.2189825907     -2.5759194919      0.7561497498
H      -4.2189825907     -2.5759194919     -0.7561497498
```

S2 Orbitals used in active space based mathods in case of D-O1 microsolvated species

S2.1 CASSCF natural orbitals used in (14o,14e) active space for the calculation of VEEs

(a)

(b)
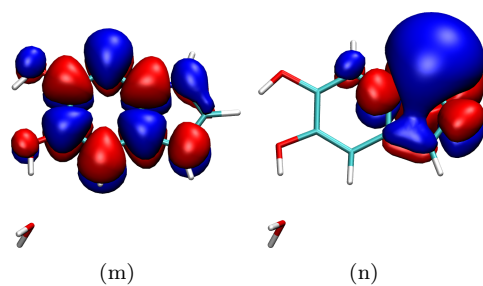
(c)

(d)

(e)

(f)

(g)

(h)

(i)

(j)

(k)

(l)

(m) (n)
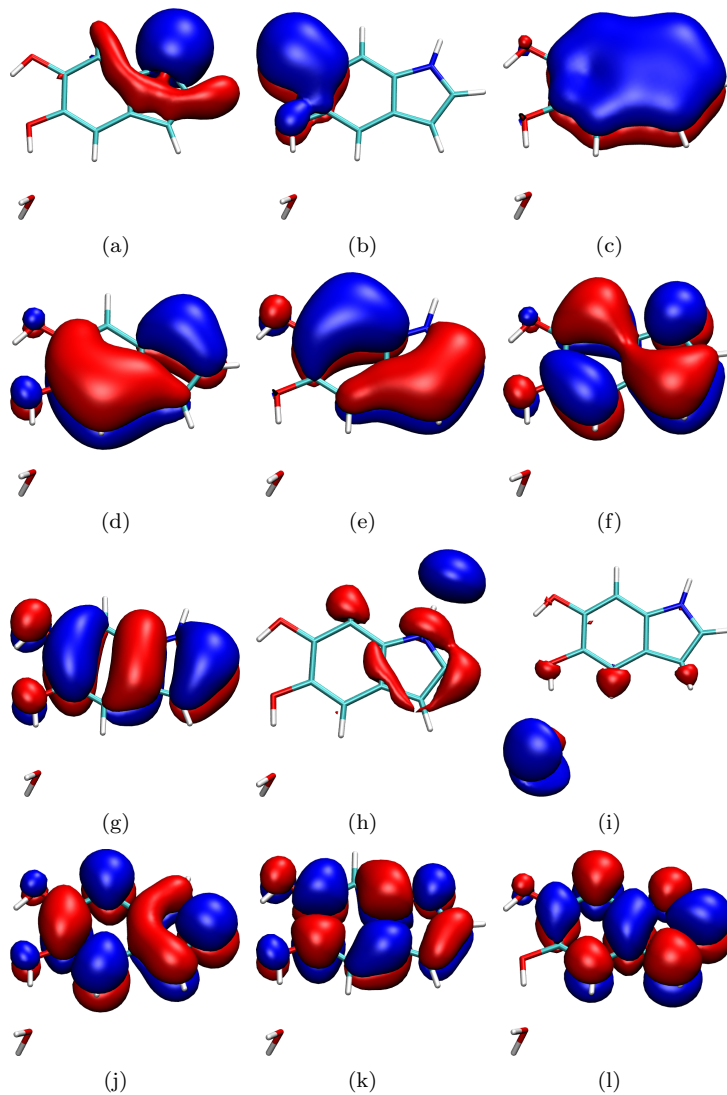
Figure S1: CASSCF natural orbitals involved in (14o,14e)/6-311++g(d,p) active space for the calculation of VEEs of all conformations of mono-hydrated DHI

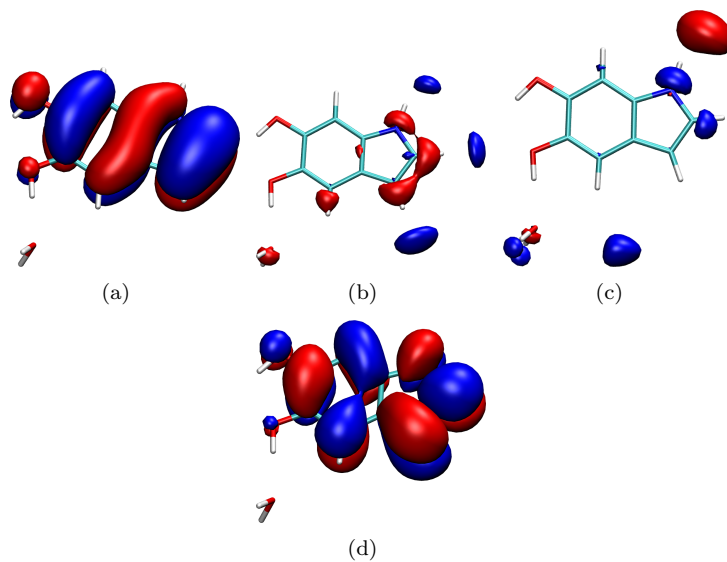## S2.2 CASSCF natural orbitals used in (4o,2e) active space for MECP search

(a) (b) (c)

(d)

Figure S2: CASSCF natural orbitals used in (4o,2e) active space for MECP search of D-O1 microsolvated species

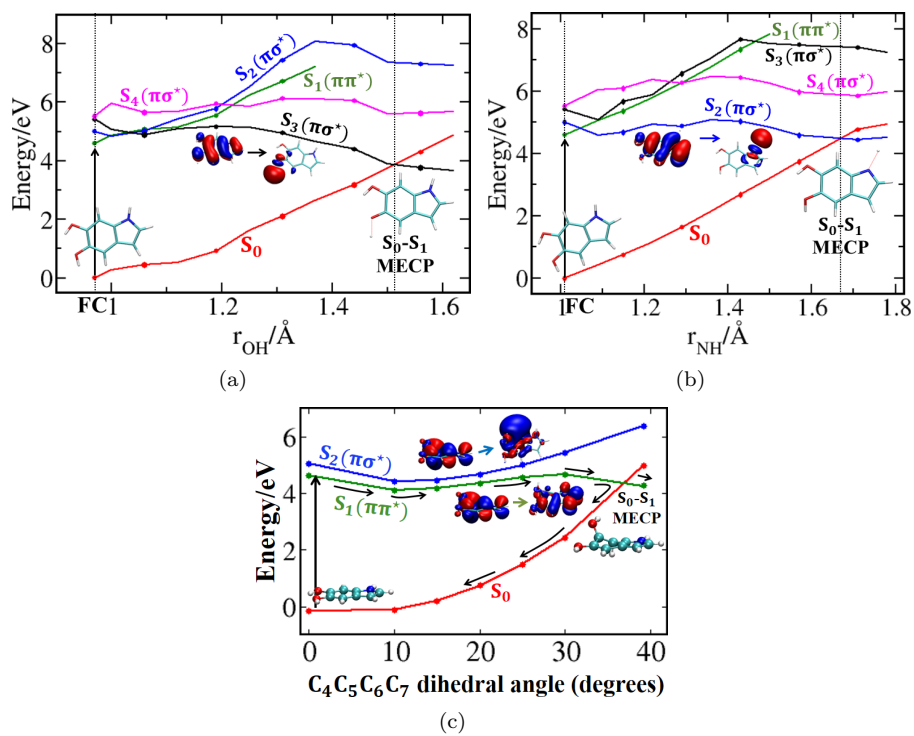## S3 SA-CASPT2 potential energy surfaces (PESs) of DHI in gas phase

Figure S3: (a) SA-CASPT2 PES of isolated DHI along r_{O_5H} elongation (b) SA-CASPT2 PES of DHI along r_{N_1H} elongation. (c) SA-CASPT2 PES of isolated DHI along six membered ring puckering

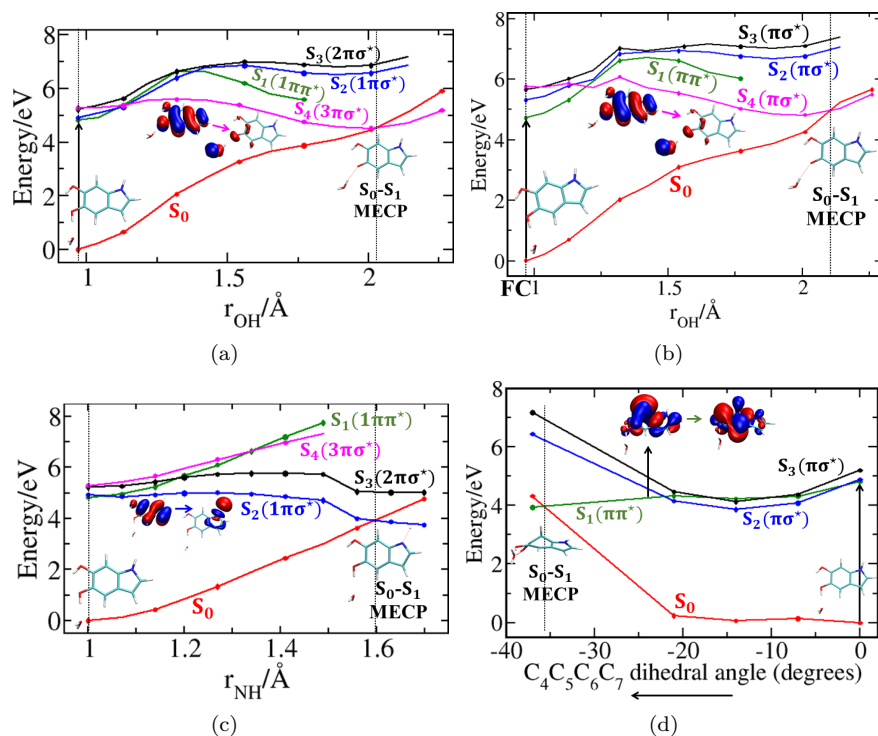# S4 SA-CASSCF PESs of D-O1 microsolvated species

Figure S4: (a) SA-CASSCF PES of D-O1 along r_{O_5H} elongation. (b) MS-CASPT2 PES of D-O1 along r_{O_5H} elongation. (c) SA-CASSCF PES of D-O1 along r_{N_1H} elongation. (d) SA-CASSCF PES of D-O1 along six member ring puckering.
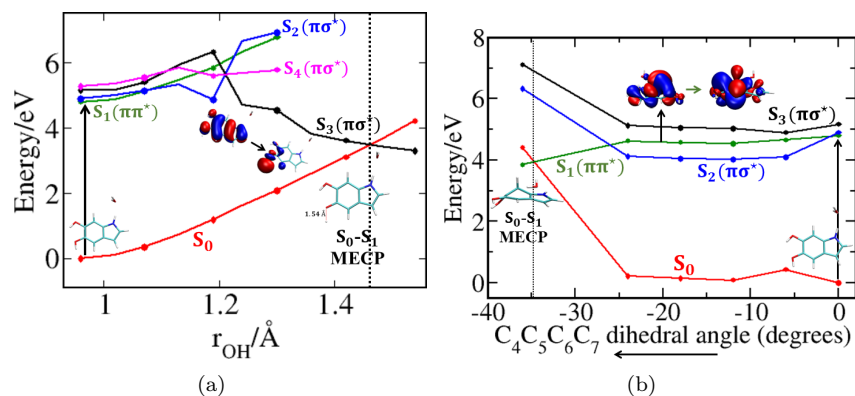
S5 SA-CASSCF PESs of D-N1 microsolvated species

Figure S5: (a) SA-CASSCF PES of D-N1 along r_{O_5H} elongation. (b) SA-CASSCF PES of D-N1 along six member ring puckering.

S6 Topological parameters around the MECPs of isolated DHI and microsolvated species of DHI

Molecule	mode	σ_x	σ_y	d_{gh}	Δ_{gh}
DHI	OH MECP	0.02045	-1.40292	0.19324	-0.64809
	NH MECP	-0.87175	-0.12929	0.24844	0.89056
	six member ring puckered	0.0562	0.44572	0.16662	0.61658
D-O1	OH MECP	1.42065	-0.02887	0.20173	0.99563
	NH MECP	-0.96429	0.40707	0.20508	0.77298
	six member ring puckered	-0.43724	-0.02419	0.16782	0.68522
D-O2	OH MECP	-1.28578	-0.71556	0.18712	0.49274
D-N1	OH MECP	-0.74631	0.00167	0.37003	0.97398
	six member ring puckered	-0.36624	-0.28054	0.16288	0.60084

S7 g and h vectors around CIs of gas phase DHI and micro-solvated DHI species
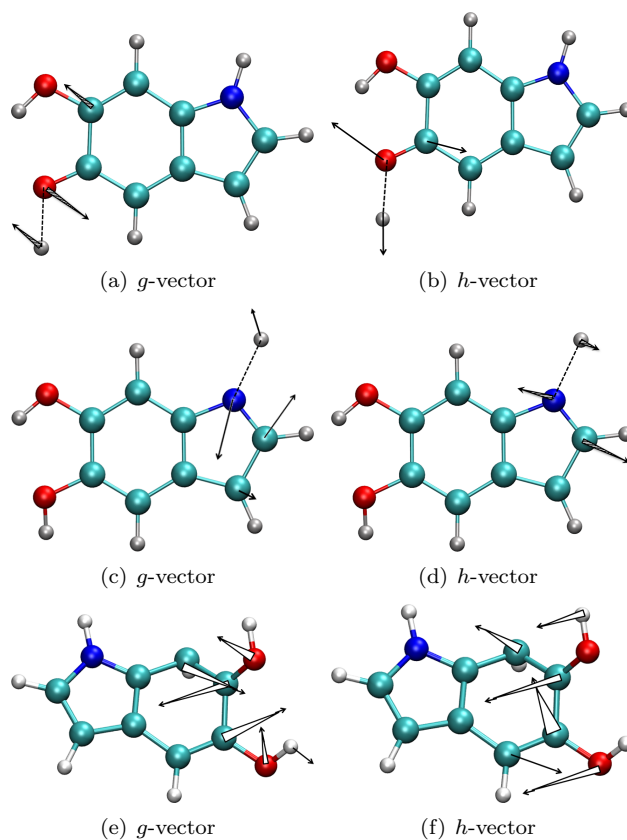
S7.1 g and h vectors around CIs of gas phase DHI

(a) g-vector

(b) h-vector

(c) g-vector

(d) h-vector

(e) g-vector

(f) h-vector

Figure S6: (a) g-vector around S_0-S_3 r_{O_5H} elongated CI of DHI. (b) h-vector around S_0-S_3 r_{O_5H} elongated CI of DHI. (c) g-vector around S_0-S_2 r_{N_1H} elongated CI of DHI. (d) h-vector around S_0-S_2 r_{N_1H} elongated CI of DHI. (e) g-vector around S_0-S_1 nonplanar CI of DHI. (f) h-vector around S_0-S_1 nonplanar CI of DHI.

S7.2   *g* and *h* vectors around CIs of D-O1

(a) *g*-vector

(b) *h*-vector

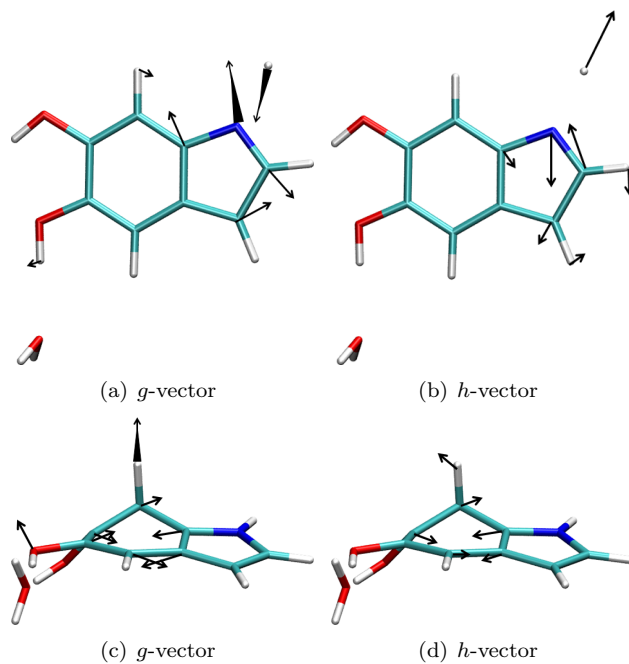(c) *g*-vector

(d) *h*-vector

Figure S7: (a) *g*-vector around S_0-S_2 r_{N_1H} elongated CI of D-O1. (b) *h*-vector around S_0-S_2 r_{N_1H} elongated CI of D-O1. (c) *g*-vector around S_0-S_1 nonplanar CI of D-O1. (d) *h*-vector around S_0-S_1 nonplanar CI of D-O1.

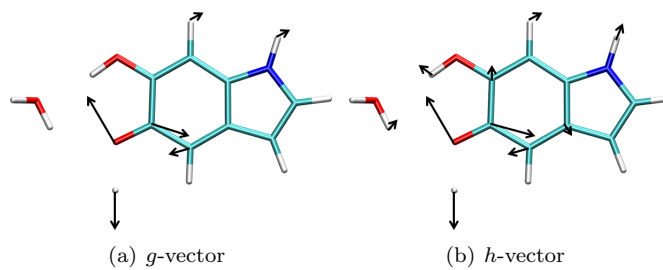## S7.3   *g* and *h* vectors around CIs of gas phase D-O2

(a) *g*-vector

(b) *h*-vector

Figure S8: (a) *g*-vector around S_0-S_2 r_{O_5H} elongated CI of D-O2. (b) *h*-vector around S_0-S_2 r_{O_5H} elongated CI of D-O2.

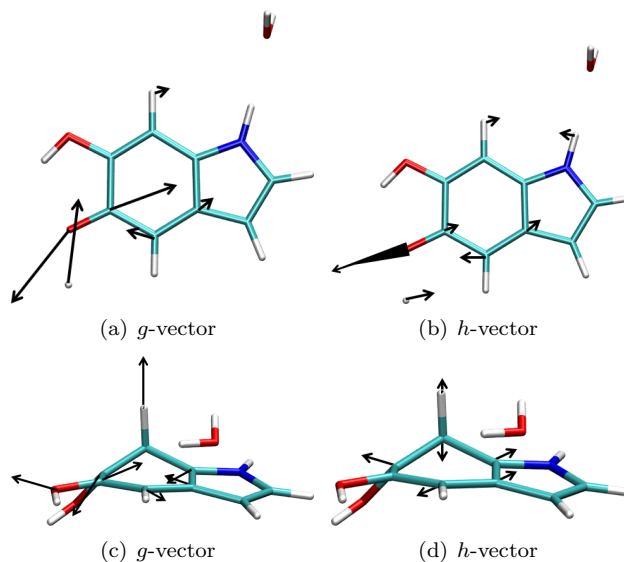## S7.4 g and h vectors around CIs of gas phase D-N1

(a) g-vector (b) h-vector

(c) g-vector (d) h-vector

Figure S9: (a) g-vector around S_0-S_3 r_{O_5H} elongated CI of D-N1. (b) h-vector around S_0-S_3 r_{O_5H} elongated CI of D-N1. (c) g-vector around S_0-S_1 nonplanar CI of D-N1. (d) h-vector around S_0-S_1 nonplanar CI of D-N1.
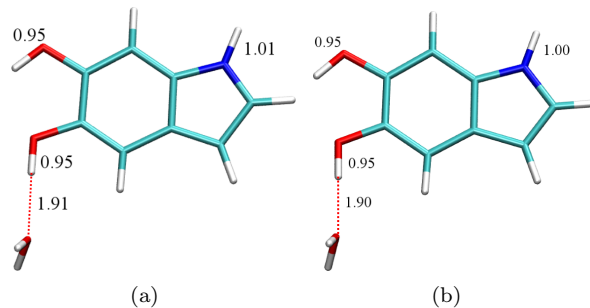
S8 Excited state optimized geometry of D-O1

(a) (b)

Figure S10: Optically active ($\pi\pi^\star$) excited state optimized geometry at $7°$ C_4-C_5-C_6-C_7 dihedral angle: (a) (14o,14e) CASSCF/6-311++g(d,p) (b) TDDFT/6-311++g(d,p)

S8.1 VEEs at excited state optimized geometries of D-O1

Table S1: VEEs in eV at $\pi\pi^\star$ excited state optimized geometries of D-O1 at CASPT2/6-311++g(d,p) level of theory

Geometry	S_1 ($\pi\sigma^\star$)	S_2 ($\pi\pi^\star$)
TDDFT optimized	3.62	4.38
CASSCF optimized	3.60	4.37

S9 Vertical ionization energies (VIEs) of DHI, the microsolvated species of DHI, 4-hydroxybenzothiazole (4-HBT) and 4-HBT+water

Table S2: The VIEs in eV of DHI and the microsolvated species of DHI with EOM-IP-CCSD/6-311++g(d,p) level of theory.

	Number	Orbital	EOM-IP-CCSD
DHI	1st IP	HOMO (39)	7.31
	2nd IP	HOMO-1 (38)	7.64
	3rd IP	HOMO-2 (37)	9.63
	4th IP	HOMO-3 (36)	10.56
	5th IP	HOMO-4 (35)	11.85
	Number	Orbital	EOM-IP-CCSD
D-O1	1st IP	HOMO (44)	6.97
	2nd IP	HOMO-1 (43)	7.29
	3rd IP	HOMO-2 (42)	9.36
	4th IP	HOMO-3 (41)	10.18
	5th IP	HOMO-4 (40)	11.43
	Number	Orbital	EOM-IP-CCSD
D-O2	1st IP	HOMO (44)	7.31
	2nd IP	HOMO-1 (43)	7.74
	3rd IP	HOMO-2 (42)	9.67
	4th IP	HOMO-3 (41)	10.61
	5th IP	HOMO-4 (40)	11.48
	Number	Orbital	EOM-IP-CCSD
D-N1	1st IP	HOMO (44)	7.01
	2nd IP	HOMO-1 (43)	7.32
	3rd IP	HOMO-2 (42)	9.35
	4th IP	HOMO-3 (41)	10.26
	5th IP	HOMO-4	(40)11.52

4-HBT	Number	Orbital	EOM-IP-CCSD
	1st IP	HOMO (39)	8.12
	2nd IP	HOMO-1 (38)	8.92
	3rd IP	HOMO-2 (37)	10.38
	4th IP	HOMO-3 (36)	10.53
	5th IP	HOMO-4 (35)	11.66

4-HBT+water	Number	Orbital	EOM-IP-CCSD
	1st IP	HOMO (44)	7.96
	2nd IP	HOMO-1 (43)	9.01
	3rd IP	HOMO-2 (42)	10.39
	4th IP	HOMO-3 (41)	10.61
	5th IP	HOMO-5 (39)	11.40