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Mechanism of Large Stokes Shift and Aggregation-Enhanced Emission of Osmapentalyne Cation in Solution: Combined MD Simulations and QM/MM Calculations

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Table S1: The major weighted atom orbits contribution for LUMO and LUMO+1 orbits of isolated OC in solvent(- meaning that the value is smaller than 0.1)

	Water				Ethanol			
	Abs		Emi		Abs		Emi	
	LUMO	LUMO+1	LUMO	LUMO+1	LUMO	LUMO+1	LUMO	LUMO+1
1Os d_{xz}	-	0.5094	0.3823	0.4433	-	0.505	0.3660	0.4519
1Os d_{yz}	0.3302	-	0.2507	0.2425	0.3299	-	0.2619	0.2329
2C p_x	-	0.2627	0.2123	0.2453	-	0.2585	0.2087	0.2615
2C p_y	0.2385	-	0.2319	0.1956	0.2320	-	0.2345	0.1903
2C p_z	-	0.4374	0.2736	0.3546	-	0.4309	0.2613	0.3511
3C p_y	0.2058	-	0.1186	0.1003	0.2043	-	0.1235	0.1038
4C p_y	0.4772	-	0.3522	0.2854	0.4769	-	0.3553	0.2780
7C p_y	0.4401	-	0.3352	0.2731	0.4406	-	0.3389	0.2666
8C p_y	0.3162	-	0.2556	0.1988	0.3214	-	0.2603	0.1976

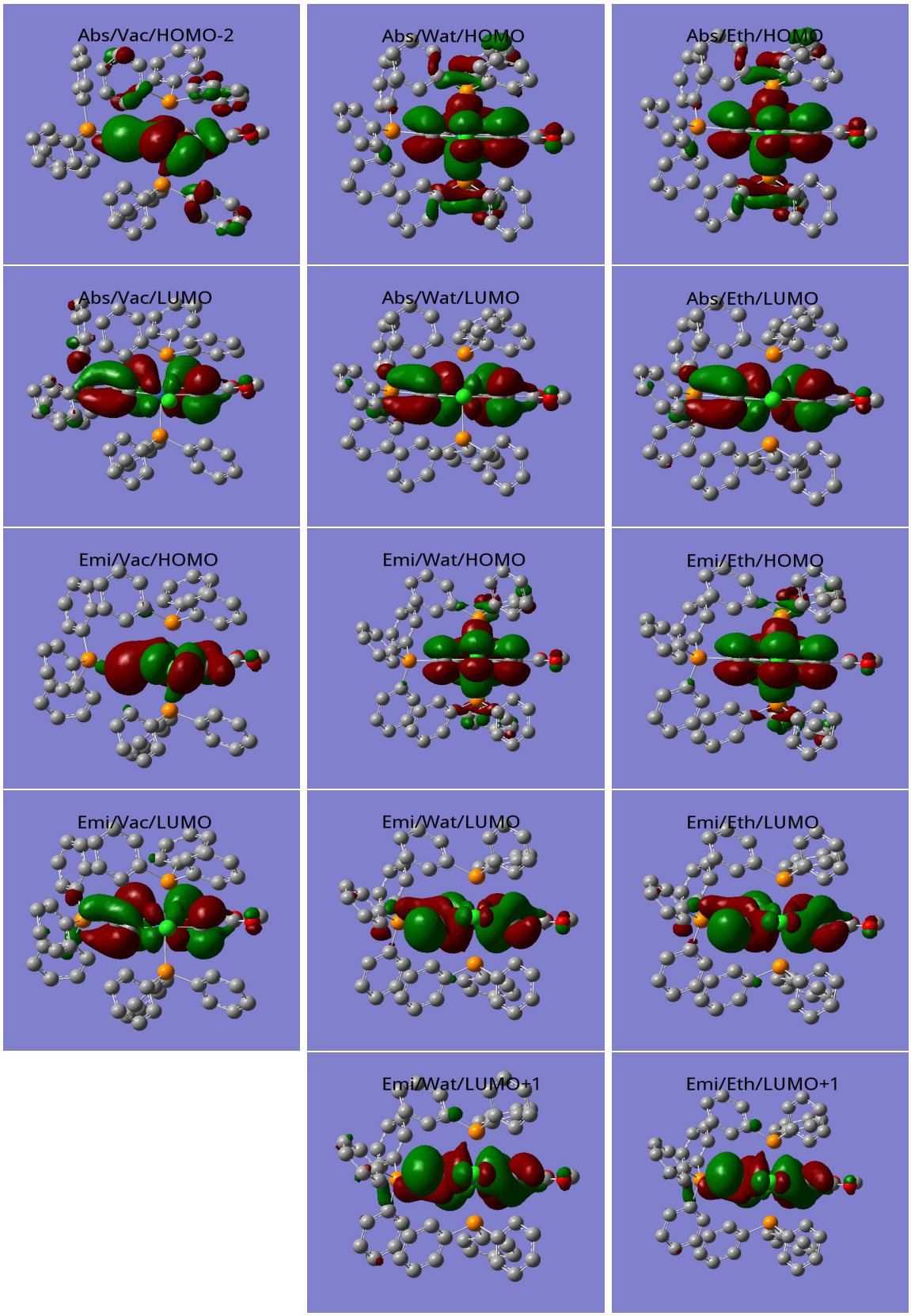

Fig. S1: The detailed orbits of isolated OC.

Table S2: The structure parameters of ground (S_0) and excited (S_1) sates of isolated OC at the CAM-B3LYP level (the units of bond lengths and angles are Å and degree, respectively)

	Vacuum		Water		Ethanol	
	S_0	S_1	S_0	S_1	S_0	S_1
1Os-2C	1.8312	1.8895	1.8243	1.9668	1.8261	1.9637
1Os-5C	2.0923	2.2053	2.0921	1.9978	2.0925	1.9996
1Os-8C	2.0236	2.0328	2.0394	2.0724	2.0382	2.0747
1Os-16Cl	2.4642	2.4063	2.5119	2.4833	2.5102	2.4785
1Os-13P	2.4615	2.4635	2.4590	2.4793	2.4650	2.4810
1Os-14P	2.4464	2.4436	2.4481	2.4747	2.4511	2.4785
∠2C-1Os-5C	73.313	68.301	72.928	78.758	72.920	78.880
∠2C-1Os-16Cl	116.47	110.96	113.62	100.69	114.04	99.747
∠8C-1Os-5C	74.526	73.123	74.688	78.000	74.644	77.966
∠8C-1Os-16Cl	95.690	108.98	98.769	102.56	98.390	103.41
∠2C-8C-1Os-5C	-0.918	-17.60	-1.244	-2.914	-0.875	-2.556
∠2C-8C-1Os-16Cl	-178.7	171.25	-179.0	177.73	-179.0	177.75
∠2C-8C-1Os-13P	-95.73	-104.4	-93.94	-91.11	-94.13	-91.02
∠2C-8C-1Os-14P	95.548	84.476	91.848	86.740	92.083	86.944

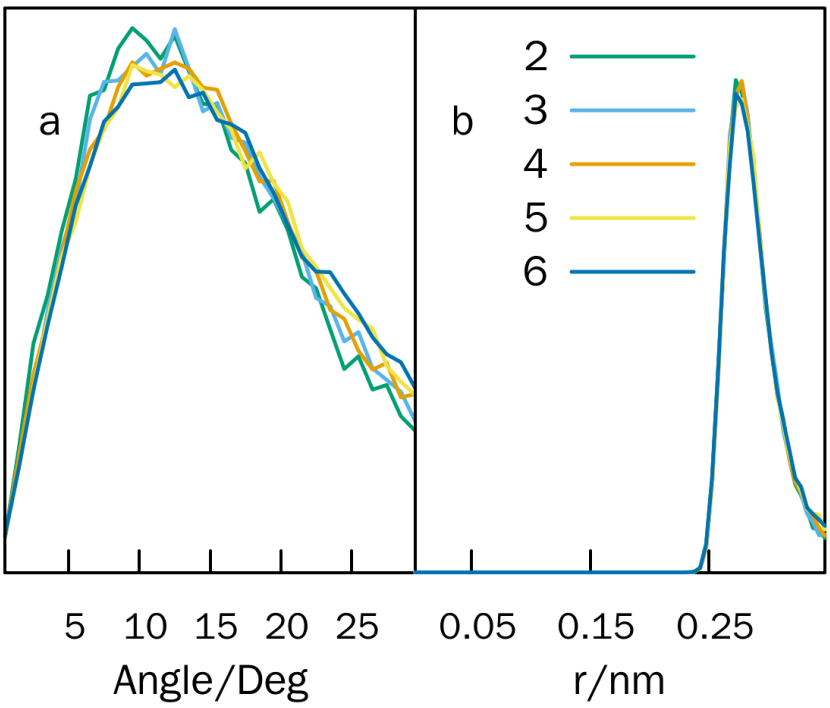

Fig. S2: The average distribution of (a)angle and (b)length of H-bonds between water molecules and OCs in solutions

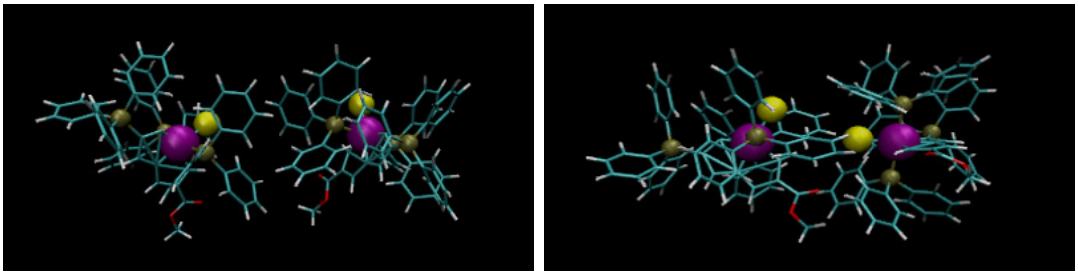

Fig. S3: (left)The H-type aggregate dimer 1 and (right)J-type aggregate dimer 1′ in OCs aggregate

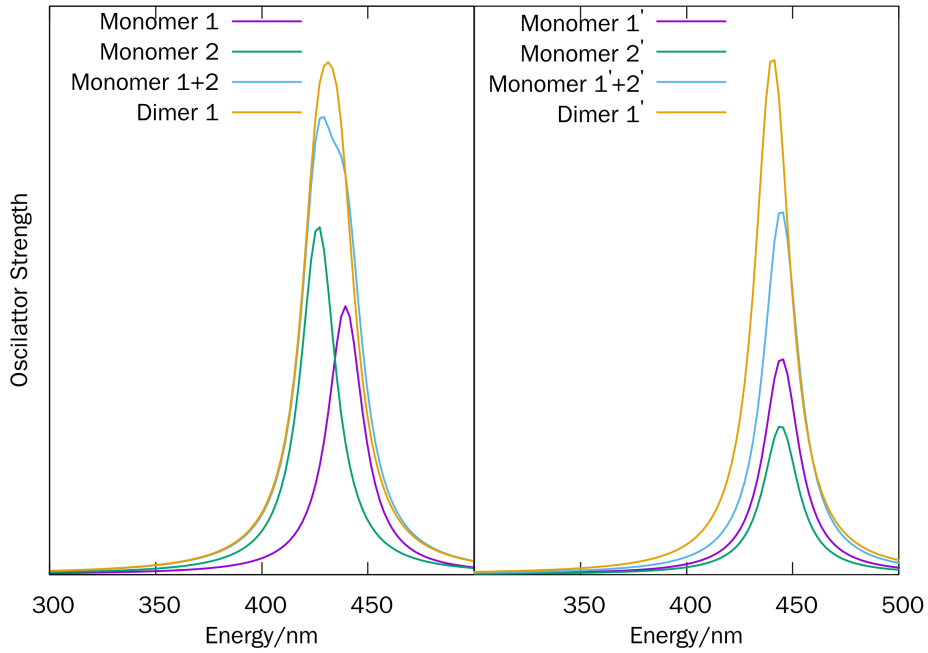

Fig. S4: The spectra of (left)H-type aggregate dimer 1 and (right)J-type aggregate dimer 1′ in OCs aggregate

Table S3: The orbital transitions for the absorption and emission of isolated OC at the CAP-B3LYP level (H and L are abbreviated notations of HOMO and LUMO, respectively)

	Vacuum		Water		Ethanol	
	Abs.	Emi.	Abs.	Emi.	Abs.	Emi.
Orb. Trans.	H-2→L -0.42999 H-1→L 0.44052	H←L 0.67930	H→L 0.64374	H←L -0.47229 H←L+1 -0.45249	H→L 0.64080	H←L -0.45351 H←L+1 -0.47672

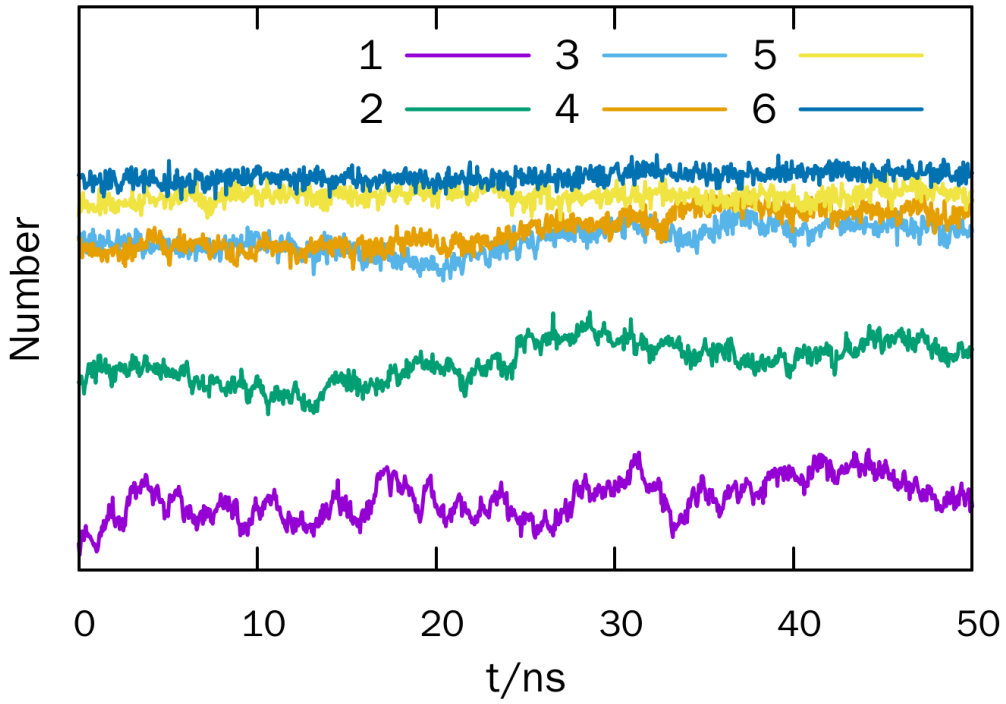

Fig. S5: The numbers of minimum distance between the OCs in aggregate with 0.6 nm threshold

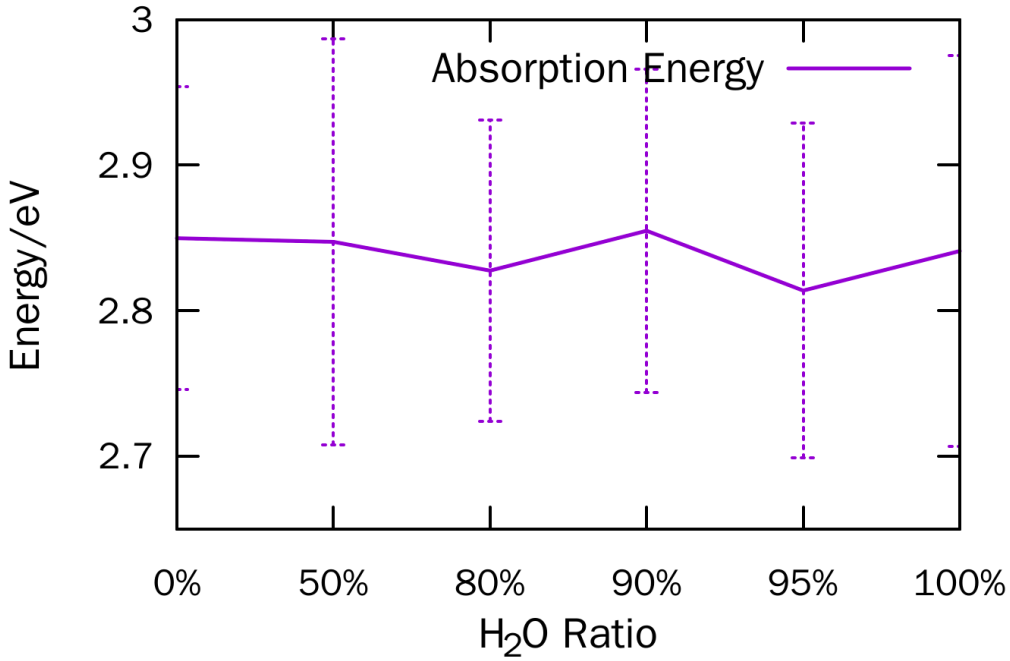

Fig. S6: The average absorption energy of OCs in aggregate with standard deviation.

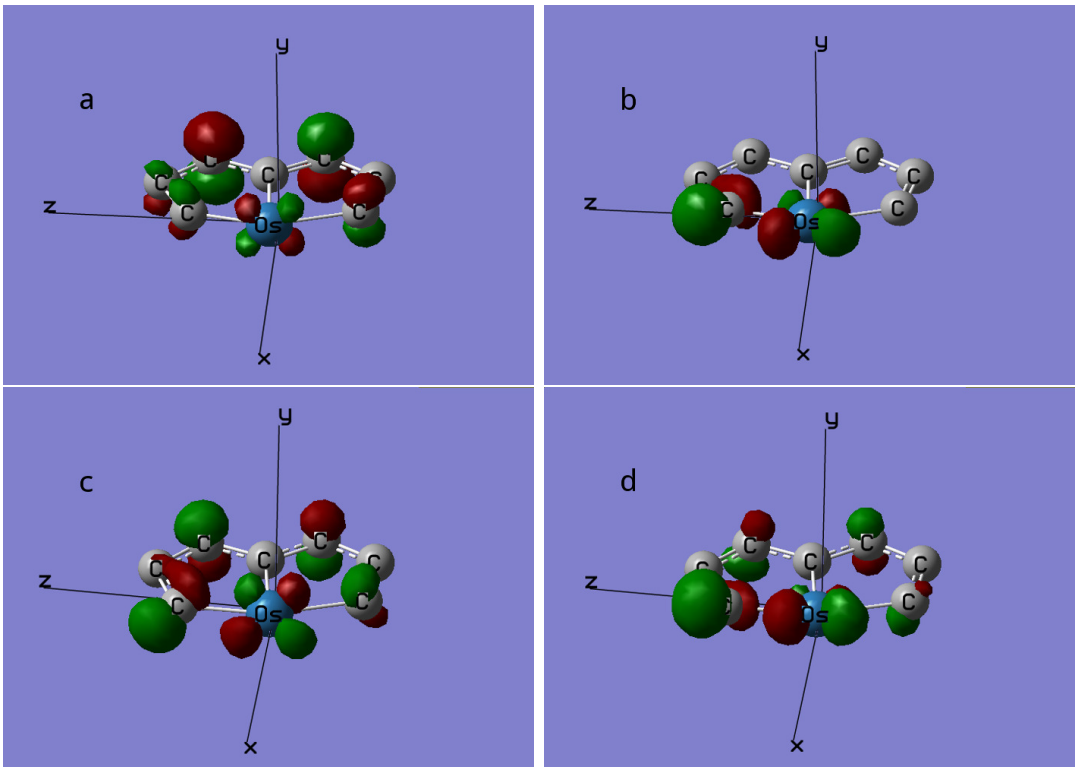

Fig. S7: The major atom orbits of osmium ring for (a) LUMO and (b) LUMO+1 orbits at S_0 geometry, (c) LUMO and (d) LUMO+1 orbits at S_1 geometry of isolated OC in solvent (isovalue is 0.07).

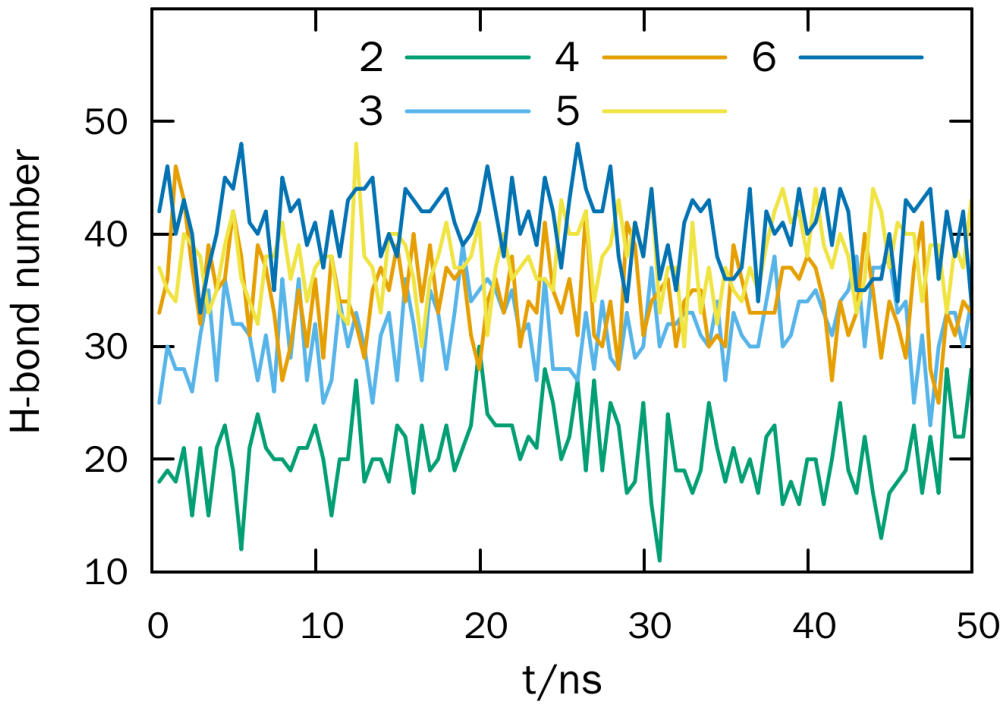

Fig. S8: The fluctuations of H-bond total number between water molecules and OCs in solutions.

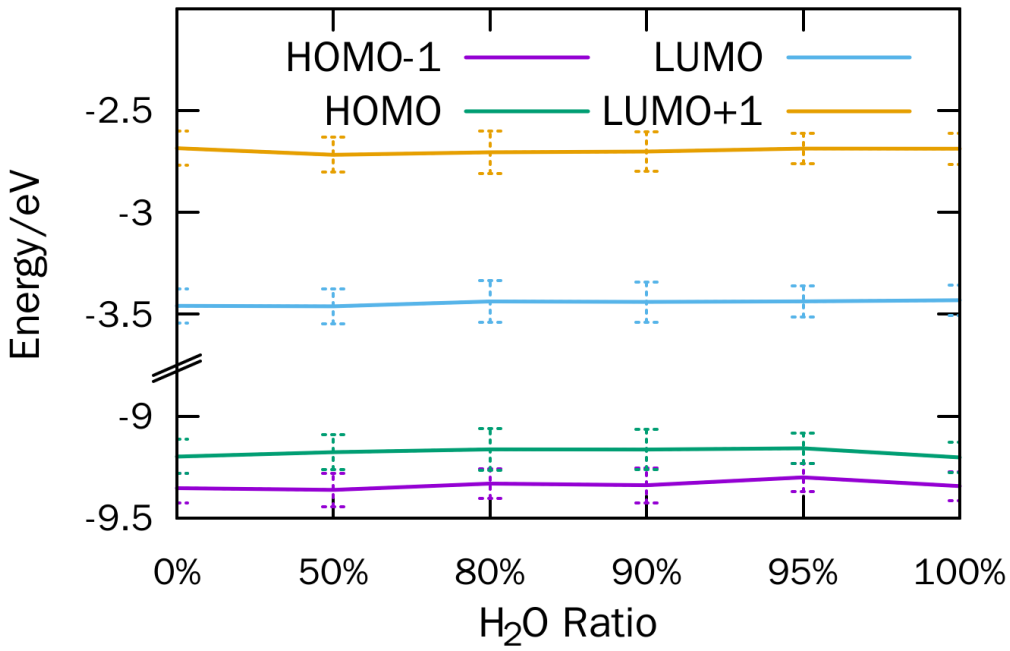

Fig. S9: The average and standard deviation values of orbits energies of HOMO-1, HOMO, LUMO and LUMO+1 orbits of OCs in aggregate.