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

Quantum Chemical and Molecular Dynamics Modelling of Hydroxylated Polybrominated Diphenyl Ethers

Supplementary Information

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Studied molecules and their partial charges

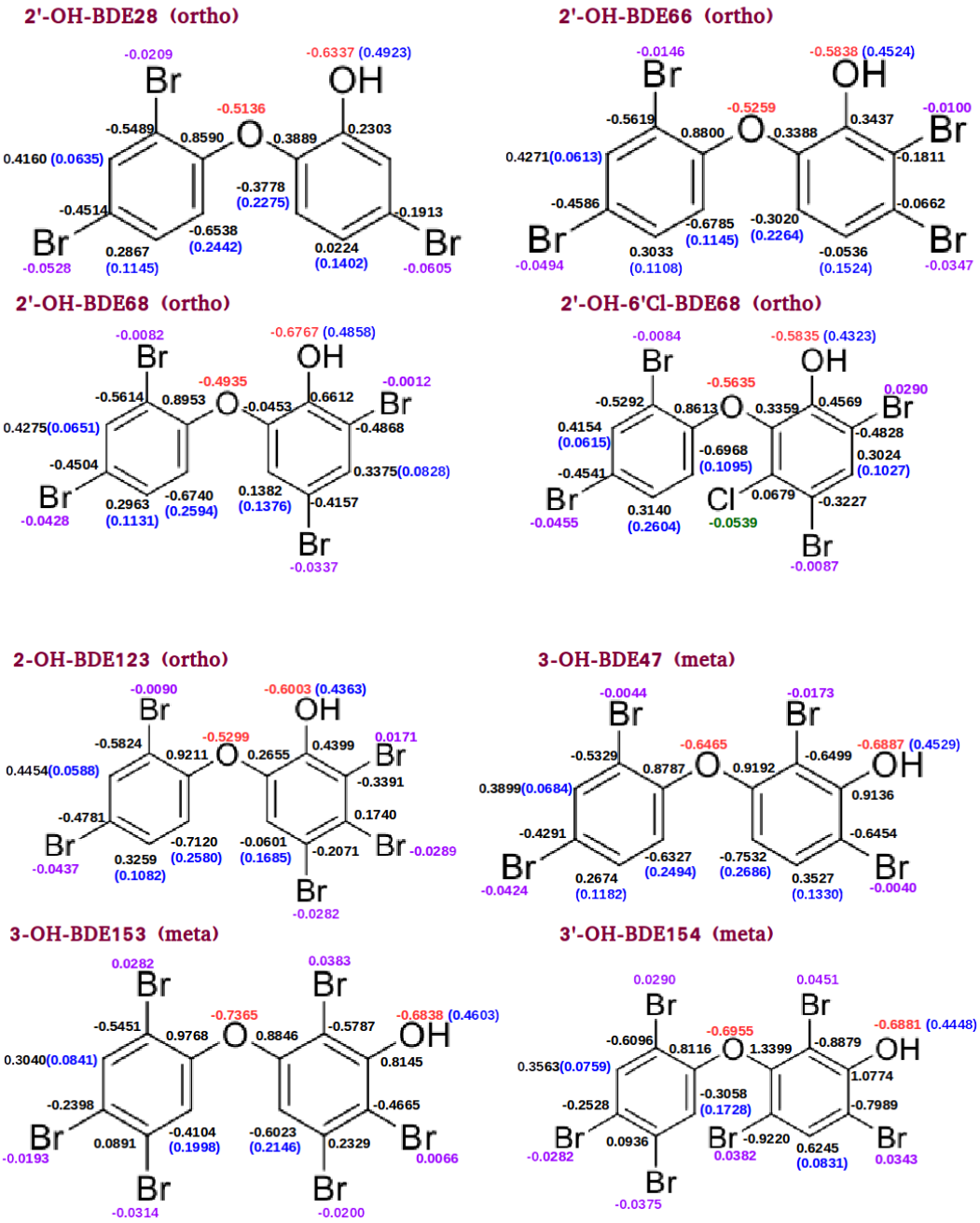

Figure S1. OH-PBDE molecules and their partial charges. Charges for hydrogen atoms are given in parenthesis

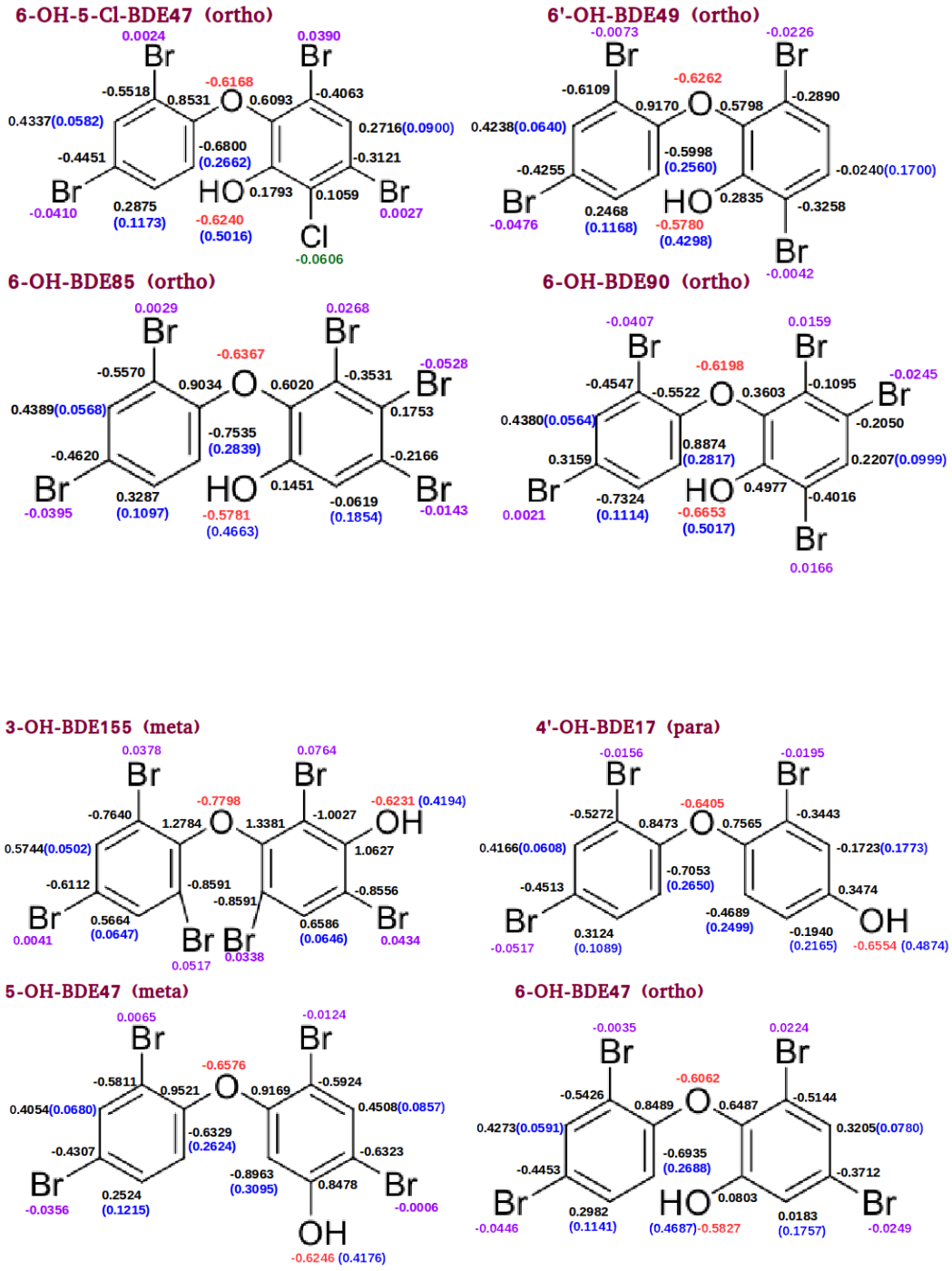

Figure S1, cont: OH-PBDE molecules and their partial charges

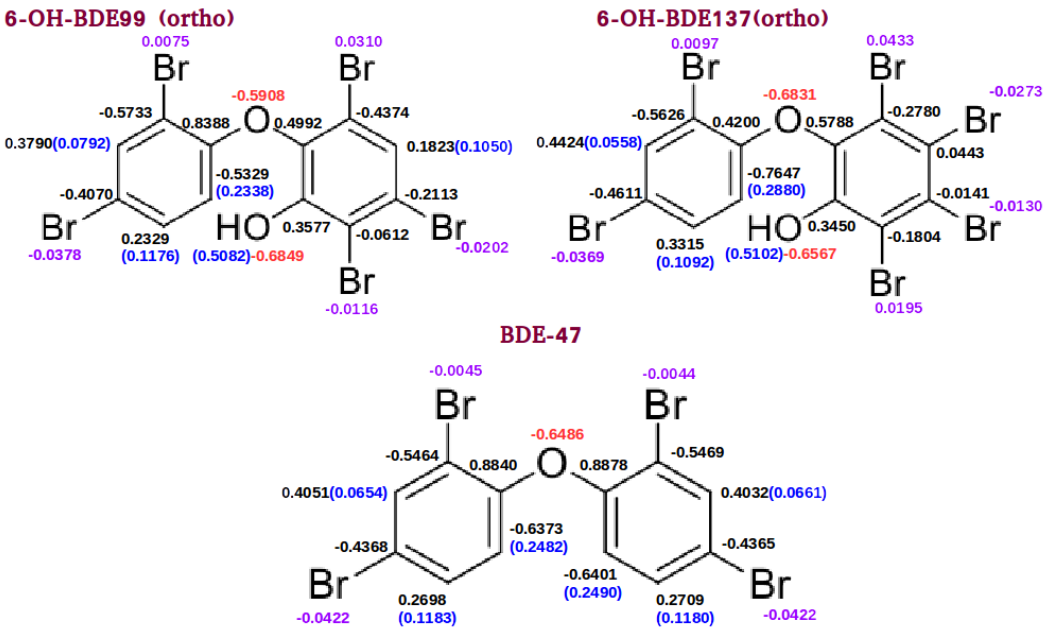

Figure S1, cont: OH-PBDE molecules and their partial charges

Information from quantum mechanical calculations. Reference molecules.

Table S1. Calculated values for reference molecules at B3LYP/6-31+G(d,p) level of theory. E_0 is electron energy of the optimized conformation, $ZPVE$ is zero level vibrational energy, G_{aq} is Gibbs energy, q is the molecular partition function.

Species	$E_0(a.u)$	$ZPVE(a.u)$	$G_{aq}(a.u)$	q
2-Bromo-Phenol	-2878.62726079	0.095144	-2878.564207	5.759E+14
2-Bromo-Phenol$^-$	-2878.15423193	0.08167	-2878.104631	5.631E+14
3-Bromo-Phenol	-2878.62958242	0.094512	-2878.567367	7.170E+14
3-Bromo-Phenol$^-$	-2878.15750249	0.081626	-2878.107893	5.326E+14
4-Bromo-Phenol	-2878.6290749	0.094766	-2878.56651	6.480E+14
4-Bromo-Phenol$^-$	-2878.15568953	0.081559	-2878.106254	5.971E+14
24-Bromo-Phenol	-5449.75366477	0.08581	-5449.703039	1.525E+16
24-Bromo-Phenol$^-$	-5449.28412692	0.072723	-5449.246307	1.134E+16
26-Bromo-Phenol	-5449.74974073	0.08556	-5449.699219	1.309E+16
26-Bromo-Phenol$^-$	-5449.28224569	0.072467	-5449.245129	1.820E+16
35-Bromo-Phenol	-5449.75581734	0.085333	-5449.705616	1.444E+16
35-Bromo-Phenol$^-$	-5449.28783577	0.072113	-5449.250764	1.311E+16
246-Bromo-Phenol	-8020.87518744	0.076142	-8020.836957	2.744E+17
246-Bromo-Phenol$^-$	-8020.41208322	0.063391	-8020.386287	1.959E+17
Penta-Bromo-Phenol	-13163.1141654	0.05911	-13163.097623	3.797E+19
Penta-Bromo-Phenol$^-$	-13162.6551324	0.046426	-13162.651414	4.402E+19

Table S2. Calculated values for reference molecules at B3LYP/6-311++G(d,p) level of theory. E_0 is electron energy of the optimized conformation, $ZPVE$ is zero level vibrational energy, G_{aq} is Gibbs energy, q is the molecular partition function.

Species	$E_0(a.u)$	$ZPVE(a.u)$	$G_{aq}(a.u)$	q
2-Bromo-Phenol	-2881.10899677	0.093707	-2881.047709	8.160E+14
2-Bromo-Phenol$^-$	-2880.63762817	0.080761	-2880.589192	7.390E+14
3-Bromo-Phenol	-2881.11169899	0.093583	-2881.05059	8.656E+14
3-Bromo-Phenol$^-$	-2880.64073701	0.080514	-2880.592522	7.192E+14
4-Bromo-Phenol	-2881.11149496	0.093697	-2881.050222	8.206E+14
4-Bromo-Phenol$^-$	-2880.63890924	0.080527	-2880.590767	7.871E+14
24-Bromo-Phenol	-5454.65040441	0.083774	-5454.602406	2.854E+16
24-Bromo-Phenol$^-$	-5454.18249118	0.070884	-5454.147073	2.057E+16
26-Bromo-Phenol	-5454.64626698	0.083534	-5454.598367	2.457E+16
26-Bromo-Phenol$^-$	-5454.18102092	0.070649	-5454.144773	6.658E+15
35-Bromo-Phenol	-5454.65295075	0.083547	-5454.605085	2.582E+16
35-Bromo-Phenol$^-$	-5454.18625275	0.070353	-5454.151515	2.408E+16
246-Bromo-Phenol	-8028.18522198	0.073182	-8028.150936	7.781E+17
246-Bromo-Phenol$^-$	-8027.72445397	0.060744	-8027.702174	4.920E+17
Penta-Bromo-Phenol	-13175.2423588	0.051856	-13175.235265	3.884E+20
Penta-Bromo-Phenol$^-$	-13174.7864955	0.039403	-13174.790547	9.722E+19

Table S3. Calculated values for reference molecules at MP2/6-31+G(d,p) level of theory. E_0 is electron energy of the optimized conformation, $ZPVE$ is zero level vibrational energy, G_{aq} is Gibbs energy, q is the molecular partition function.

Species	$E_0(a.u)$	$ZPVE(a.u)$	$G_{aq}(a.u)$	q
2-Bromo-Phenol	-2874.91796014	0.094559	-2875.946749	7.629E+14
2-Bromo-Phenol$^-$	-2874.43575393	0.080362	-2875.486528	4.593E+14
3-Bromo-Phenol	-2874.92062511	0.093952	-2875.949798	1.120E+15
3-Bromo-Phenol$^-$	-2874.43945775	0.080726	-2875.49029	1.267E+15
4-Bromo-Phenol	-2874.92043461	0.094083	-2875.948699	9.809E+14
4-Bromo-Phenol$^-$	-2874.43822095	0.080342	-2875.486925	2.266E+14
24-Bromo-Phenol	-5444.24544706	0.084809	-5445.398197	2.137E+16
24-Bromo-Phenol$^-$	-5443.76708498	0.071459	-5444.941442	2.696E+16
26-Bromo-Phenol	-5444.23993271	0.084458	-5445.394839	1.998E+16
26-Bromo-Phenol$^-$	-5443.7642736	0.071178	-5444.939431	7.755E+15
35-Bromo-Phenol	-5444.24770101	0.084738	-5445.400381	1.906E+16
35-Bromo-Phenol$^-$	-5443.77060484	0.071222	-5444.945389	2.163E+16
246-Bromo-Phenol	-8013.56616336	0.074883	-8014.845246	4.437E+17
246-Bromo-Phenol$^-$	-8013.09557304	0.061964	-8014.394811	4.630E+17
Penta-Bromo-Phenol	-13152.1995734	0.057166	-13153.738384	5.282E+19
Penta-Bromo-Phenol$^-$	-13151.7338773	0.044424	-13153.292788	7.698E+19

Table S4. Calculated values for reference molecules at MP2/aug-cc-pVDZ level of theory. E_0 is electron energy of the optimized conformation, $ZPVE$ is zero level vibrational energy, G_{aq} is Gibbs energy, q is the molecular partition function.

Species	$E_0(a.u)$	$ZPVE(a.u)$	$G_{aq}(a.u)$	q
2-Bromo-Phenol	-2877.41004354	0.093826	-2878.502343	7.397E+14
2-Bromo-Phenol$^-$	-2876.92886641	0.08063	-2878.046639	7.159E+14
3-Bromo-Phenol	-2877.41306956	0.093258	-2878.505181	9.977E+14
3-Bromo-Phenol$^-$	-2876.93232684	0.080472	-2878.049406	7.328E+14
4-Bromo-Phenol	-2877.41307491	0.093538	-2878.504164	8.648E+14
4-Bromo-Phenol$^-$	-2876.93094792	0.080435	-2878.046646	3.944E+14
24-Bromo-Phenol	-5449.21191021	0.083366	-5450.460502	2.942E+16
24-Bromo-Phenol$^-$	-5448.73445478	0.070738	-5450.007092	2.022E+16
26-Bromo-Phenol	-5449.20650836	0.083096	-5450.457942	2.620E+16
26-Bromo-Phenol$^-$	-5448.73197203	0.070471	-5450.005861	6.886E+15
35-Bromo-Phenol	-5449.21458318	0.08322	-5450.462775	2.804E+16
35-Bromo-Phenol$^-$	-5448.73805795	0.070156	-5450.011681	2.575E+16
246-Bromo-Phenol	-8021.00567146	0.072553	-8022.414086	8.196E+17
246-Bromo-Phenol$^-$	-8020.53608205	0.060479	-8021.966451	4.754E+17
Penta-Bromo-Phenol	-13164.5764409	0.050906	-13166.31626	1.689E+20
Penta-Bromo-Phenol$^-$	-13164.1128336	0.039433	-13165.875276	8.809E+20

Information from quantum mechanical calculations. OH-PBDE molecules.

Table S5. Calculated values for neutral and anionic forms of OH-PBDE molecules at B3LYP/6-31+G(d,p) level of theory. E_0 is electron energy of the optimized conformation, $ZPVE$ is zero level vibrational energy, G_{aq} is Gibbs energy, q is the molecular partition function.

Species	$E_0(a.u)$	$ZPVE(a.u)$	$G_{aq}(a.u)$	q
2-OH-BDE28	-8327.16452745	0.161023	-8327.050131	2.797E+21
2-O-BDE28	-8326.6972451	0.148091	-8326.595984	3.472E+21
2-OH-BDE66	-10898.286086	0.150982	-10898.183892	2.757E+22
2-O-BDE66	-10897.8196796	0.138322	-10897.730155	2.787E+22
2-OH-BDE68	-10898.288862	0.150363	-10898.187627	3.958E+22
2-O-BDE68	-10897.8240471	0.138444	-10897.734584	3.383E+22
2-OH-6-Cl-BDE68	-11357.8737428	0.141891	-11357.782367	1.720E+23
2-O-6-Cl-BDE68	-11357.4135836	0.129064	-11357.335155	1.953E+23
3-OH-BDE155	-16040.5330862	0.13105	-16040.456291	9.024E+24
3-O-BDE155	-16040.0717407	0.118048	-16040.007744	7.272E+24
6-OH-BDE47	-10898.2904935	0.151112	-10898.188464	3.770E+22
6-O-BDE47	-10897.8212507	0.136985	-10897.733135	3.008E+22
2-OH-BDE123	-13469.4094683	0.141907	-13469.320005	1.326E+24
2-O-BDE123	-13468.9471071	0.129141	-13468.869729	6.446E+23
3-OH-BDE153	-16040.534892	0.131934	-16040.457468	1.182E+25
3-O-BDE153	-16040.0760688	0.119216	-16040.011071	8.680E+24
3-OH-BDE154	-16040.5376622	0.131582	-16040.46067	1.287E+25
3-O-BDE154	-16040.0777065	0.118786	-16040.013675	1.532E+25
6-OH-BDE85	-13469.4110802	0.142055	-13469.320571	5.119E+23
6-O-BDE85	-13468.9492521	0.129221	-13468.871438	4.420E+23
6-OH-BDE90	-13469.4094047	0.141816	-13469.31944	7.073E+23
6-O-BDE90	-13468.9510302	0.129033	-13468.873378	4.303E+23
3-OH-BDE47	-10898.2875725	0.151483	-10898.184855	2.695E+22
3-O-BDE47	-10897.8233665	0.138307	-10897.733736	2.454E+22
4-OH-BDE17	-8327.16648879	0.160804	-8327.052288	2.730E+21
4-O-BDE17	-8326.69603092	0.147875	-8326.594383	1.832E+21
5-OH-BDE47	-10898.2899564	0.151079	-10898.187869	3.426E+22
5-O-BDE47	-10897.8223113	0.13877	-10897.732868	4.880E+22
6-OH-5-Cl-BDE47	-11357.8749243	0.141311	-11357.784739	3.285E+23
6-O-5-Cl-BDE47	-11357.4182239	0.128708	-11357.34003	1.717E+23
6-OH-BDE137	-16040.5327996	0.132346	-16040.454323	6.000E+24
6-O-BDE137	-16040.0731255	0.119519	-16040.007628	7.050E+24
6-OH-BDE49	-10898.286495	0.151132	-10898.184165	2.801E+22
6-O-BDE49	-10897.8259582	0.138404	-10897.736266	2.546E+22
6-OH-BDE99	-13469.4059231	0.140278	-13469.317367	6.170E+23
6-O-BDE99	-13468.9467707	0.127619	-13468.87064	4.821E+23

Table S6. Calculated values for neutral and anionic forms of OH-PBDE molecules at B3LYP/6-311++G(d,p) level of theory. E_0 is electron energy of the optimized conformation, $ZPVE$ is zero level vibrational energy, G_{aq} is Gibbs energy, q is the molecular partition function.

Species	$E_0(a.u)$	$ZPVE(a.u)$	$G_{aq}(a.u)$	q	pK_a
2-OH-BDE28	-8334.53420056	0.157775	-8334.424245	9.894E+21	8.42
2-O-BDE28	-8334.06798246	0.144847	-8333.970394	5.462E+21	
2-OH-BDE66	-10908.0679391	0.147473	-10907.971455	2.838E+23	7.09
2-O-BDE66	-10907.6046674	0.134526	-10907.520487	1.437E+23	
2-OH-BDE68	-10908.0716356	0.147819	-10907.974164	1.438E+23	6.68
2-O-BDE68	-10907.6083564	0.134799	-10907.524093	1.757E+23	
2-OH-6-Cl-BDE68	-11367.6838219	0.138102	-11367.597442	6.174E+23	4.51
2-O-6-Cl-BDE68	-11367.224137	0.124915	-11367.152102	2.96E+24	
2-OH-BDE123	-13481.6018326	0.136977	-13481.519157	9.480E+24	6.16
2-O-BDE123	-13481.1410424	0.124235	-13481.070223	3.709E+24	
3-OH-BDE47	-10908.0668281	0.147354	-10907.970289	2.362E+23	6.85
3-O-BDE47	-10907.604126	0.134573	-10907.51986	1.378E+23	
3-OH-BDE153	-16055.1364886	0.126288	-16055.066969	1.293E+26	4.96
3-O-BDE153	-16054.6783168	0.113691	-16054.62064	5.817E+25	
3-OH-BDE154	-16055.1367931	0.126504	-16055.066617	8.108E+25	4.08
3-O-BDE154	-16054.6788241	0.113733	-16054.622197	1.850E+26	
3-OH-BDE155	-16055.129157	0.126201	-16055.058608	3.961E+25	5.17
3-O-BDE155	-16054.6698634	0.113573	-16054.611817	3.470E+25	
4-OH-BDE17	-8334.53208405	0.157525	-8334.422325	9.351E+21	9.79
4-O-BDE17	-8334.06239464	0.144481	-8333.965493	7.680E+21	
5-OH-BDE47	-10908.0689584	0.147016	-10907.972827	2.543E+23	5.52
5-O-BDE47	-10907.6053763	0.134241	-10907.525275	7.987E+24	
6-OH-BDE47	-10908.0703915	0.147195	-10907.974173	2.802E+23	9.98
6-O-BDE47	-10907.6012707	0.133883	-10907.518025	1.958E+23	
6-OH-5-Cl-BDE47	-11367.6819923	0.13723	-11367.59819	3.757E+24	3.71
6-O-5-Cl-BDE47	-11367.2268125	0.124879	-11367.154572	1.629E+24	
6-OH-BDE49	-10908.066546	0.147173	-10907.969732	1.458E+23	5.16
6-O-BDE49	-10907.6070257	0.134569	-10907.522964	1.705E+23	
6-OH-BDE85	-13481.6002696	0.136666	-13481.517492	6.120E+24	5.77
6-O-BDE85	-13481.1400481	0.124029	-13481.069404	3.592E+24	
6-OH-BDE90	-13481.6004486	0.136825	-13481.516781	2.823E+24	3.64
6-O-BDE90	-13481.1438318	0.12414	-13481.073319	4.644E+24	
6-OH-BDE99	-13481.5950386	0.136406	-13481.511742	2.684E+24	4.08
6-O-BDE99	-13481.1376038	0.123771	-13481.067317	3.992E+24	
6-OH-BDE137	-16055.1316728	0.126481	-16055.061216	5.882E+25	3.86
6-O-BDE137	-16054.6740757	0.113729	-16054.617282	1.543E+26	

Information from metadynamics simulations

Evolution of collecive variables in metadynamics simulations

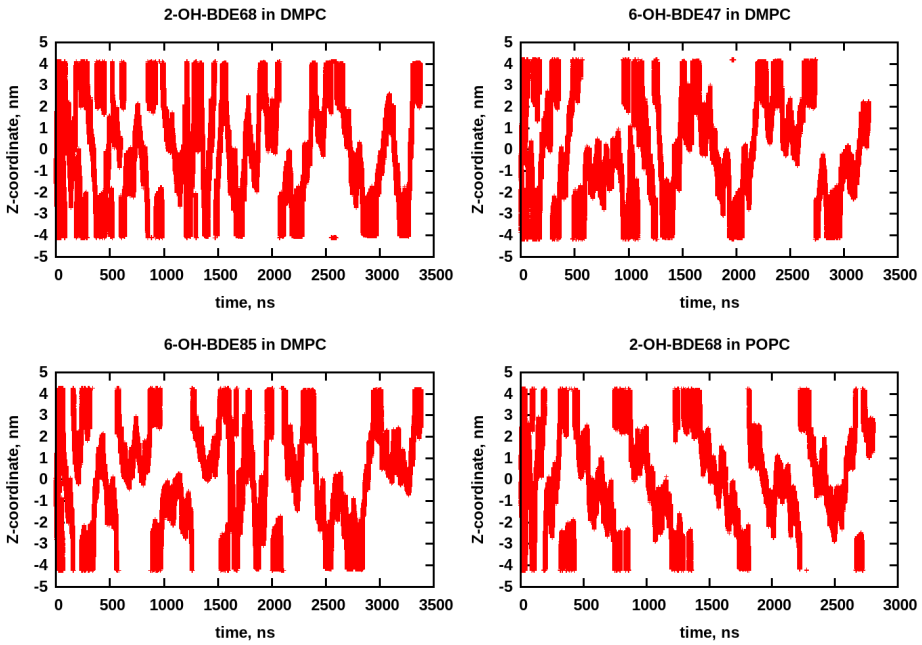

Figure S2. Evolution of collective variable (distance between the solute center of mass and membrane middle plane) in metadynamics simulations.

Conformational and orientational properties of selected OH-PBDE molecules

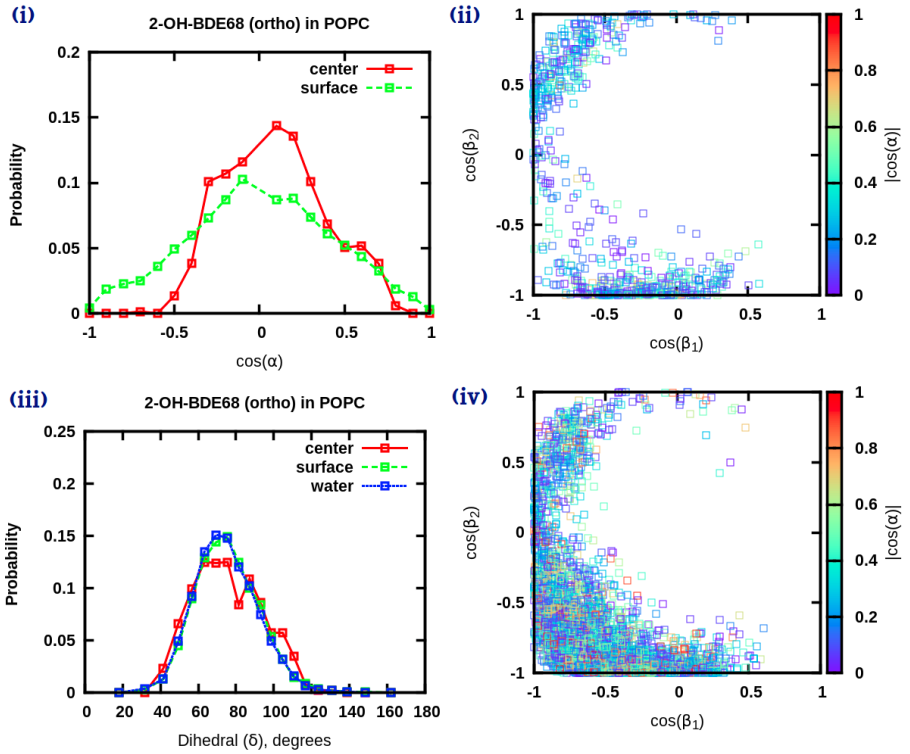

Figure S3. Distributions of dihedrals in 2'-OH-BDE68 (ortho) and angles between the selected vector and a normal to the membrane consisting of POPC lipids. (a) Probability distribution of cosine of angle (α) between normal to the membrane and the molecular vector. (c) Probability distribution of dihedral δ. (b,d) Distribution map of cosines for two dihedrals (β_1 and β_2). Each point corresponds to a trajectory frame and is coloured according to the absolute value of cosine of the angle α between the molecular vector and the normal to the membrane (α). (b): for molecules located in the centre of the membrane, (d): for molecules located at the bilayer surface.

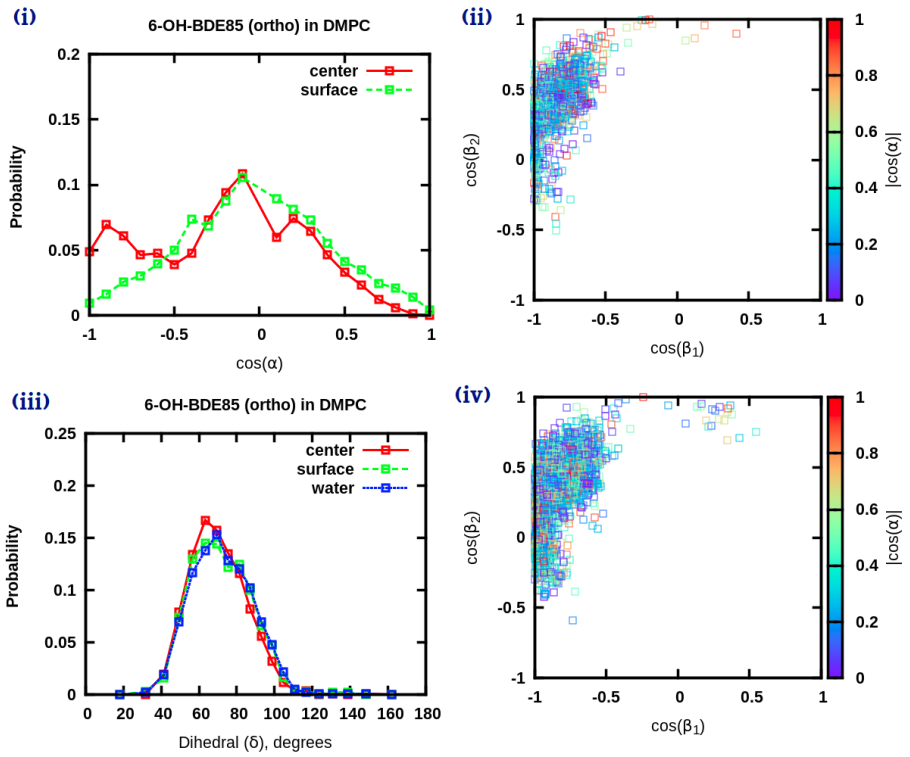

Figure S4. Distributions of dihedrals in 6-OH-BDE85 (ortho) and angles between the selected vector and a normal to the membrane consisting of POPC lipids. Notations the same as in Figure S3.

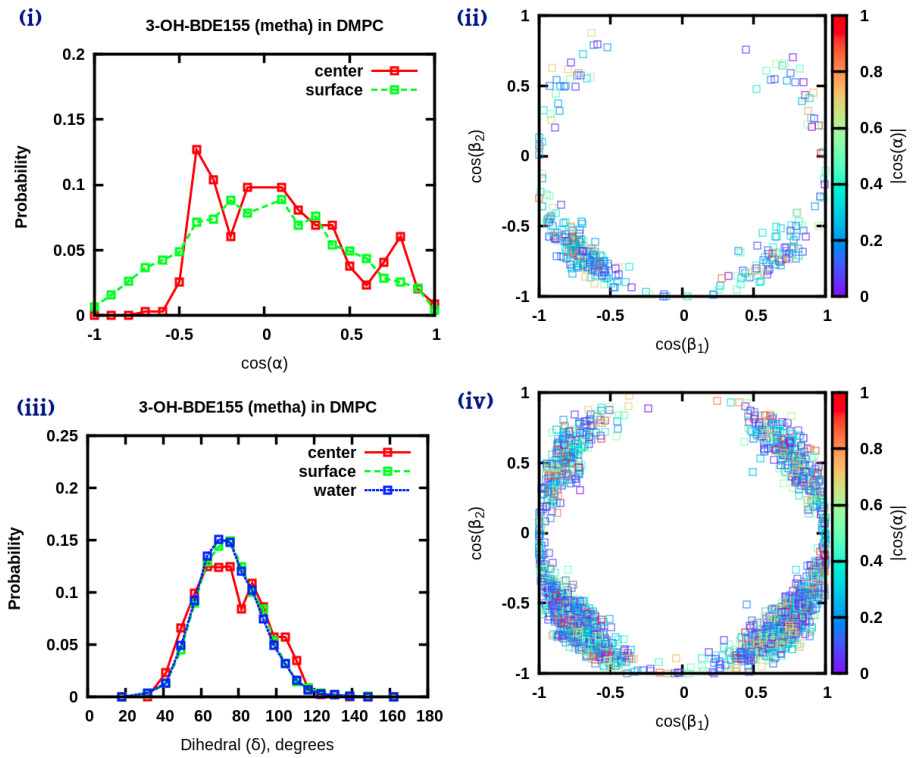

Figure S5. Distributions of dihedrals in 3-OH-BDE155 (ortho) and angles between the selected vector and a normal to the membrane consisting of POPC lipids. Notations the same as in Figure S3.

Conformation of the hydroxyl group

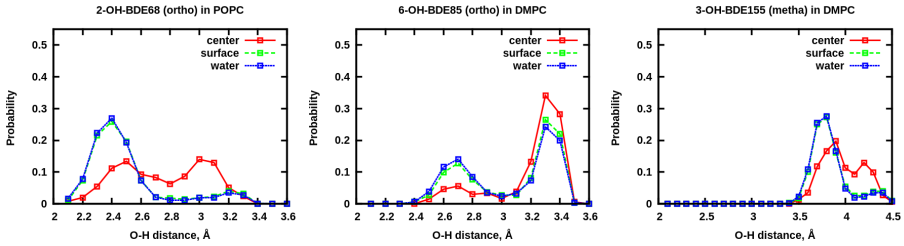

Figure S6. Distribution of distances between hydrogen of hydroxyl group and oxygen of the ether link for 2'-OH-BDE68 (ortho) in POPC membrane, and for 6-OH-BDE85 (ortho) and 3-OH-BDE155 (meta) in DMPC membrane, in the membrane interior, at the surface and in the water phase.

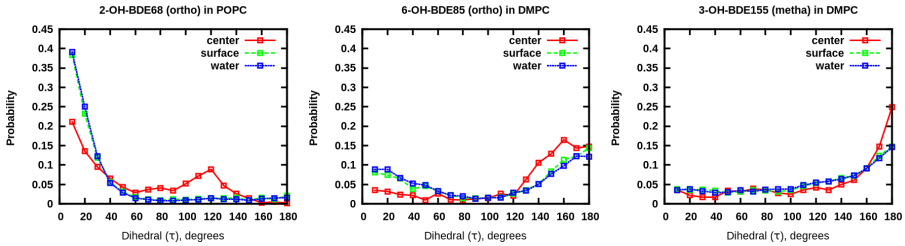

Figure S7. Distribution of the hydroxyl group torsion angle τ (see definition in the Figure 3 of the main text) in the membrane interior, at the surface and in the water phase.

Radial Distribution Functions

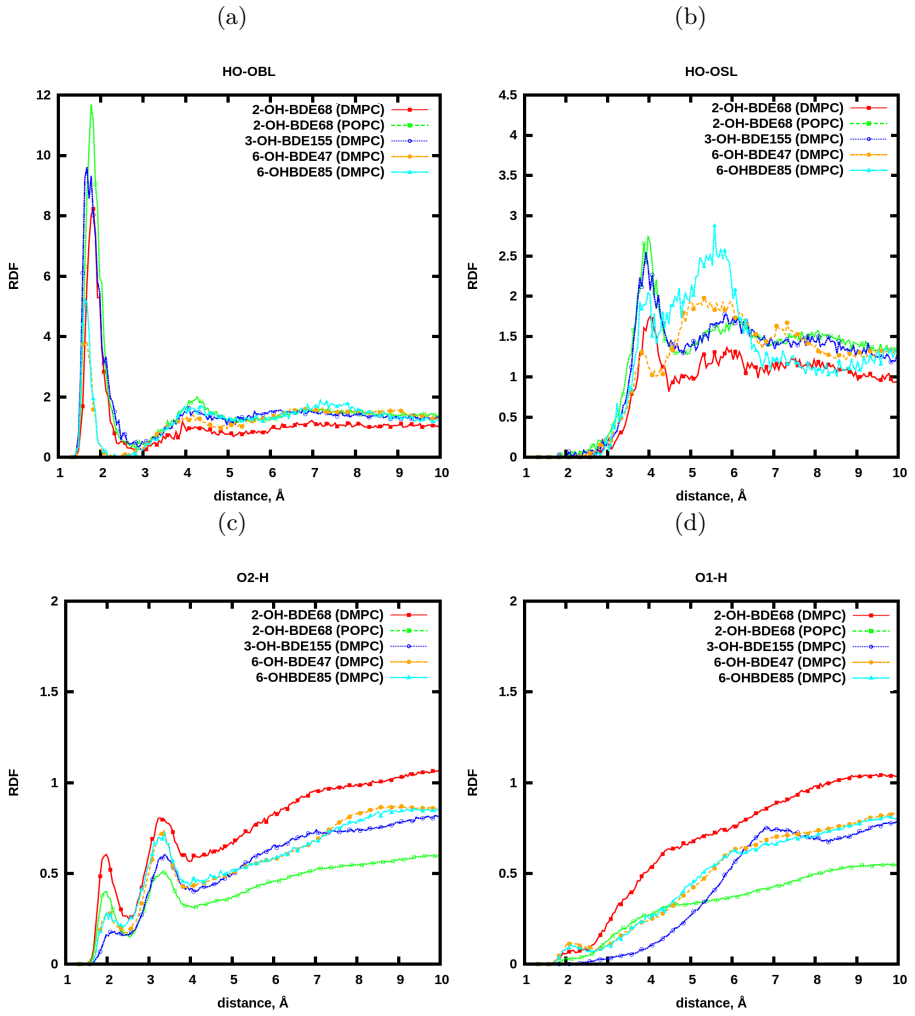

Figure S8. Radial distribution functions. (a) - between hydrogen of the hydroxyl group of OH-PBDE (HO) and carbonyl oxygen of lipids (OBL); (b): between hydrogen of the hydroxyl group of OH-PBDE (HO) and ester oxygen of lipids (OSL); (c): between oxygen of the hydroxyl group of OH-PBDE and water hydrogen (H); (d): between oxygen of the ether link (O1) of OH-PBDE and water hydrogen (H)