Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

SUPPORTING INFORMATION: Conformational changes of β-carotene and zeaxanthin inmmersed in a model membrane through atomistic molecular dynamics simulations

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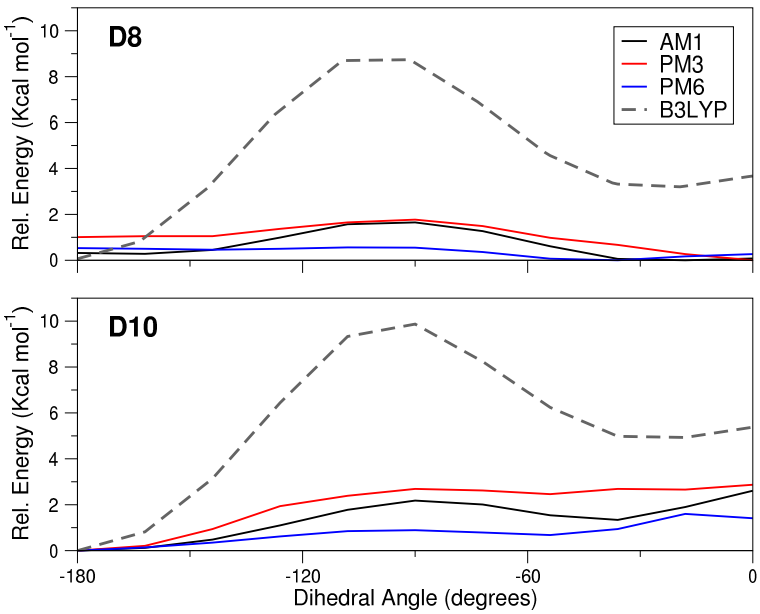

Figure S.1: Potential energy plots generated by the scan around the dihedral defined by atoms C7C8C9C10 (D8) and C9C10C11C12 (D10) of β-carotene using different semiempirical methods (AM1, PM3 and PM6) and a DFT calculation (B3LYP/6-31G(d)). Atom labeling correspond to that in Figure 1 in the paper. Note the significant differences in the energy barriers and location of minima obtained from semiempirical methods as compare with the DFT calculation.

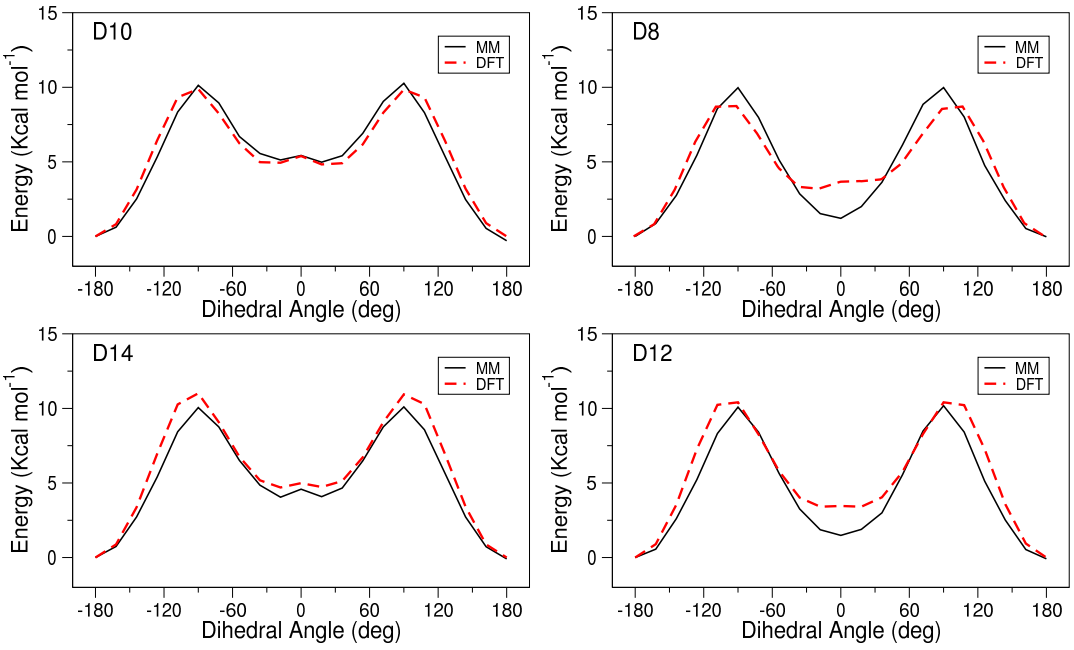

Figure S.2: Potential energy plots for dihedrals asociated to single bonds calculated using the parameters for β-carotene derived in this work.

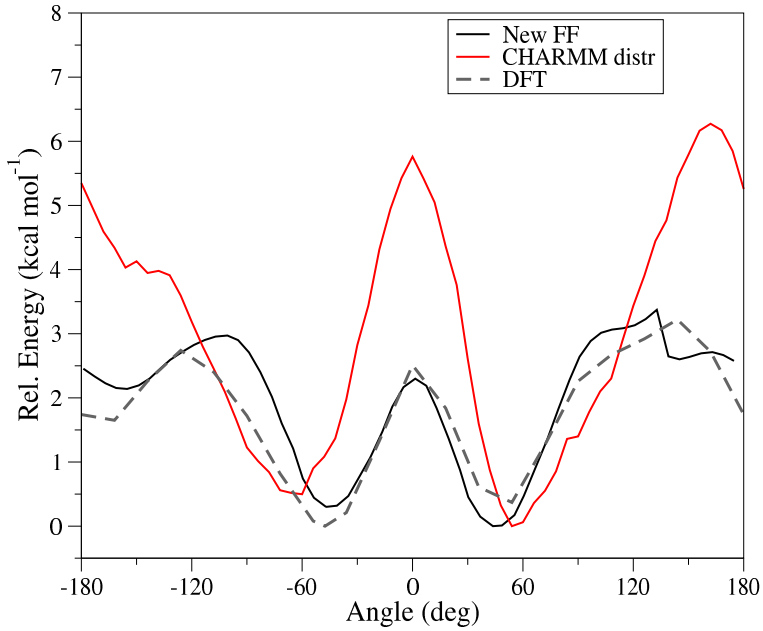

Figure S.3: Potential energy plots for the dihedrals D6 of β-carotene using the force fields paramters derived in this work (NewnFF) and with those from the original CHARMM27 FF distribution (CHARMM distr). The energy plot computed at B3LYP/6-31G(d) is included for comparison.

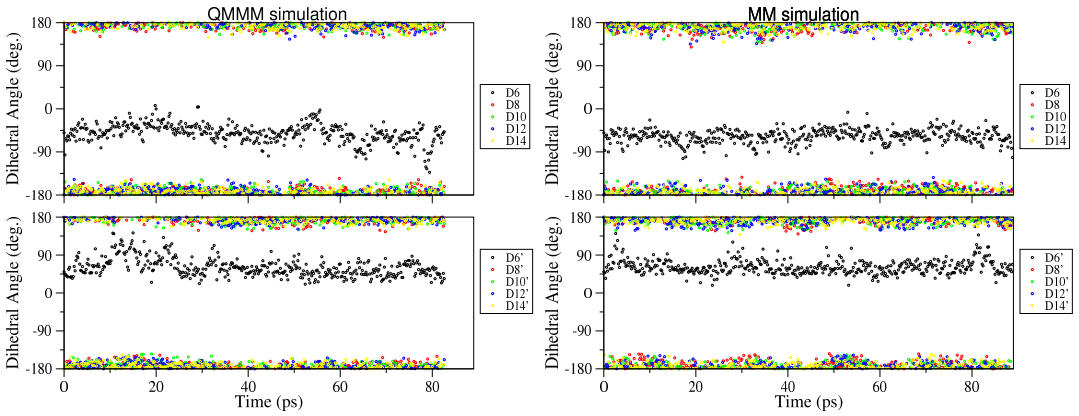

Figure S.4: Evolution of the dihedral angles of β-carotene along an NVE simulaton of this molecule in water using a QMMM (left) and a MM (right) level to compute the potential. The QMMM approach consisted in B3LYP/3-21G for β-carotene (QM part) and CHARMM27+TIP3P for water and water-carotene interactions within an ONIOM scheme. The MM calculation used the parameters derived in this paper for β-carotene and TIP3P for water.

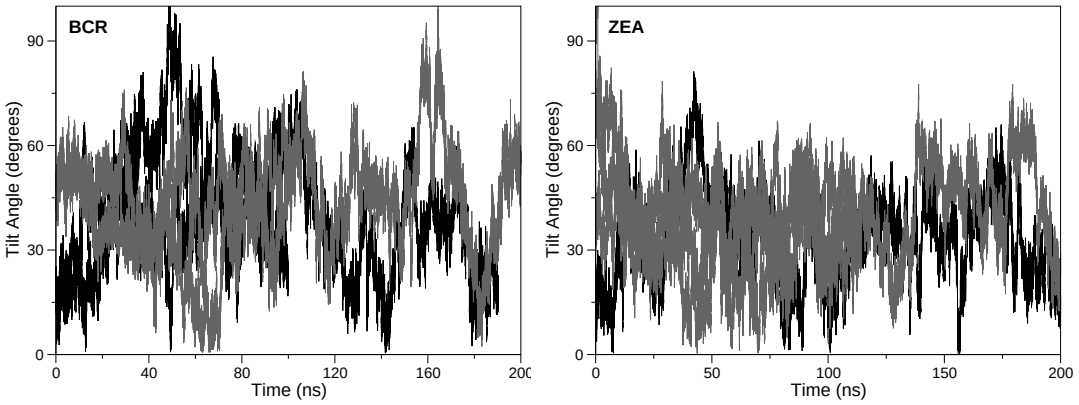

Figure S.5: Variation of the tilt angle for the carotenoid chain along the after-equilibration simulations of β-carotene (**BCR**) and zeaxanthin (**ZEA**) embedded in the DMPC bilayer, started originally from both parallel (black) and perpendicular (gray) orientations of the carotenoids with respect to the membrane normal axis.

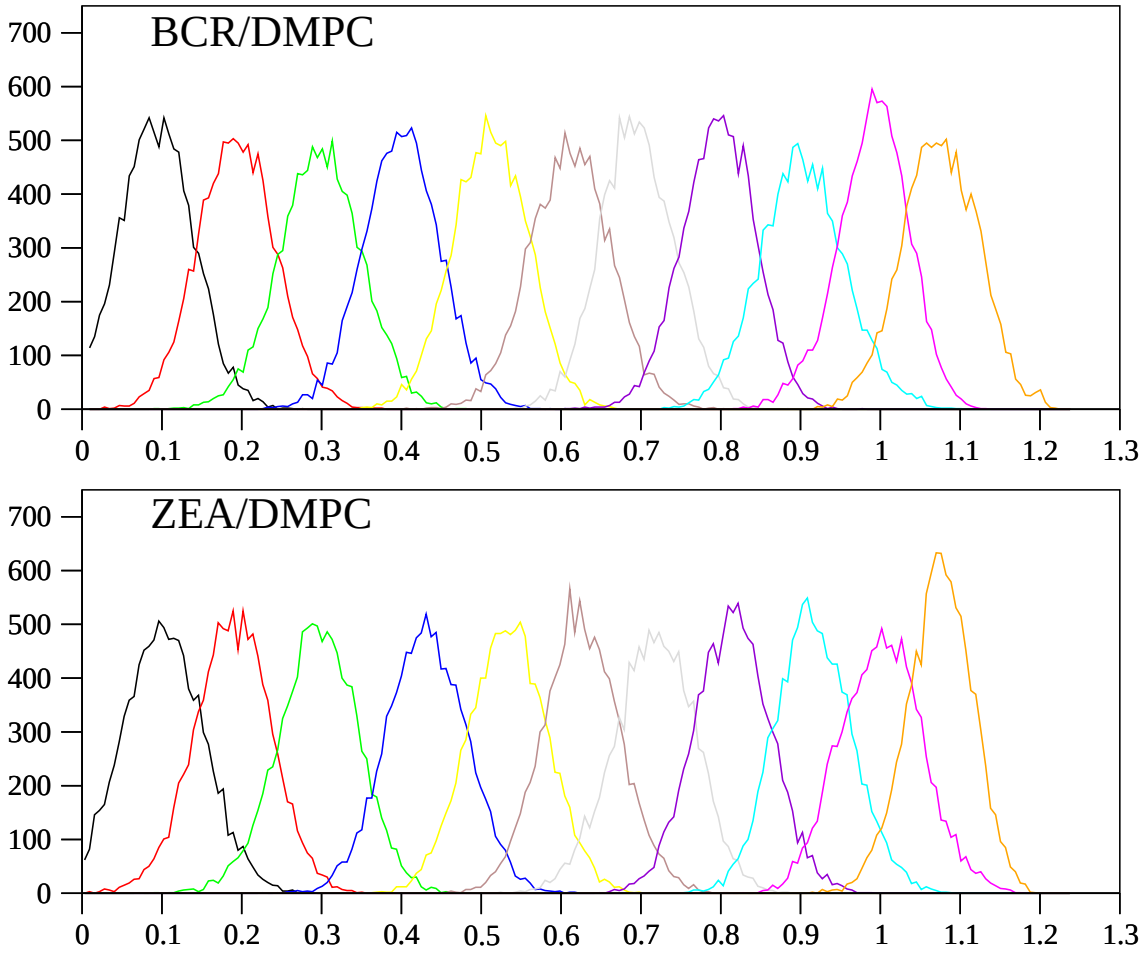

Figure S.6: Histograms corresponding to all windows sampled for the computaion of the potential of mean force through the umbrella sampling technique.

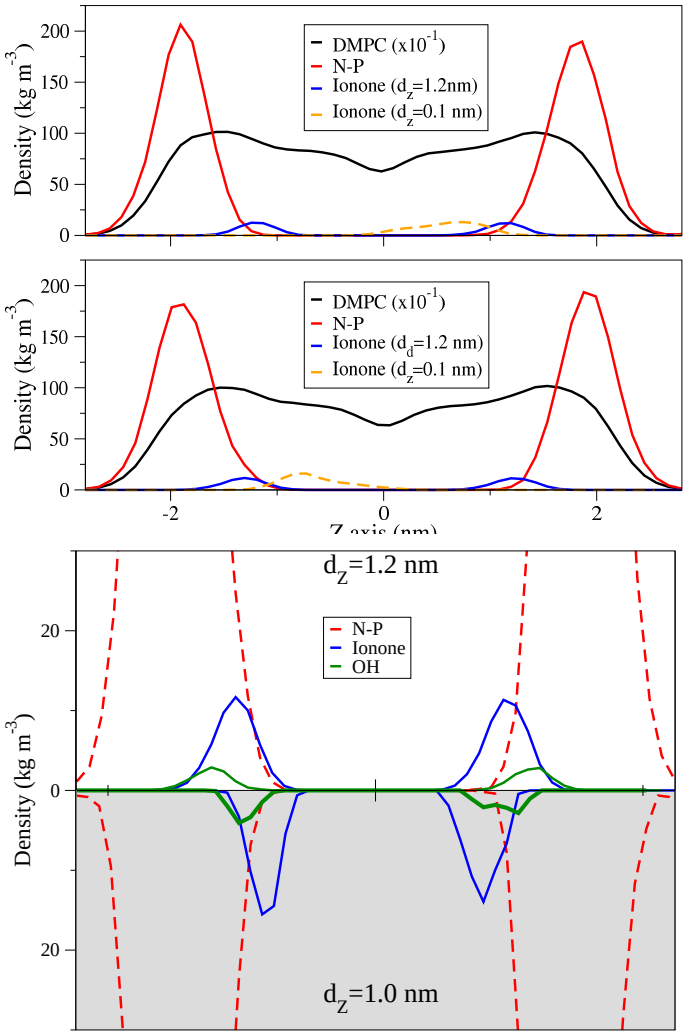

Figure S.7: Density profiles showing: (top) the location of the membrane (DMPC), the polar heads (P-N) and the β-ionone rings in the first and last sampling windows in umbrella sampling; and (down) a focuss on the last ($d_z = 1.2\,\mathrm{nm}$) and 10th windows ($d_z = 1.0\,\mathrm{nm}$) for zeaxanthin also showing the location of the hidroxyl groups; the nature of the overlapping distributions on each case is responsible for the relative stability of each one (see PMF in the text).

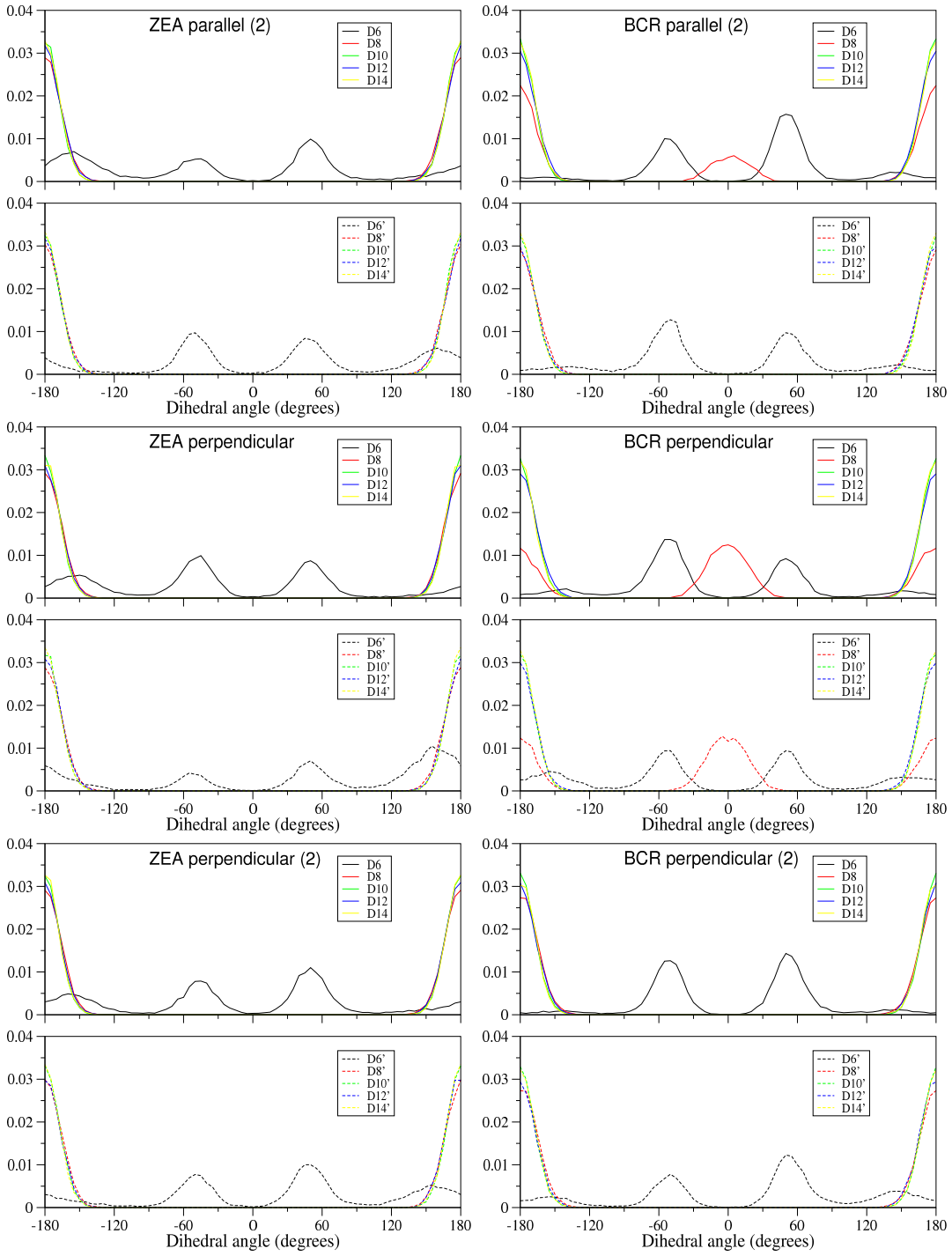

Figure S.8a: Dihedral distribution associated to single bonds along the conjugated chain: D6, D8, D10, D12 and D14, and the symmetric D6', D8', D10', D12' and D14', obtained with a 100 ns simulation of β-carotene (BCR) and zeaxanthin (ZEA) embeded in a DMPC bilayer, initially placed with either a parallel or a perpendicular arrangement with respect to the axis normal to the DMPC membrane as indicated on the plots.

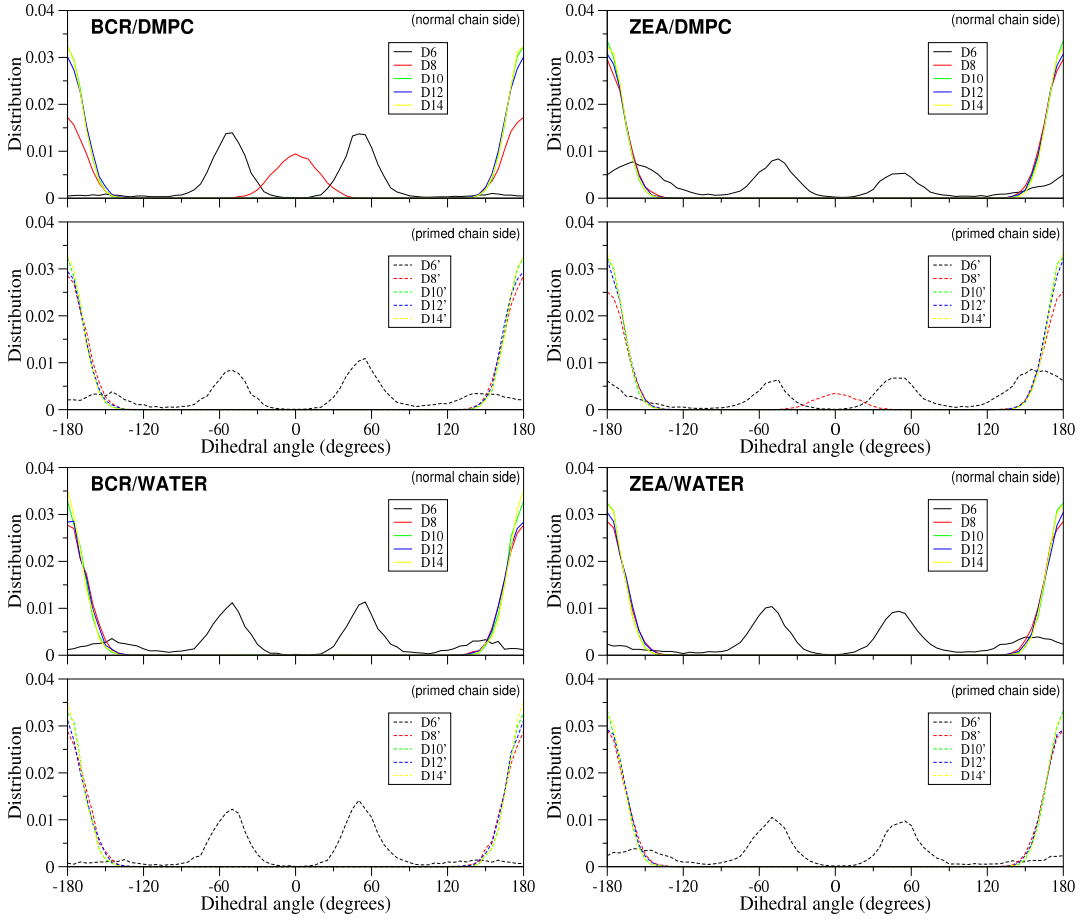

Figure S.8b: Dihedral distribution associated to single bonds along the conjugated chain: D6, D8, D10, D12 and D14, and the symmetric D6', D8', D10', D12' and D14', obtained with a 100 ns simulation of β-carotene (BCR) and zeaxanthin (ZEA) embeded in a DMPC bilayer, initially placed with either a parallel or a perpendicular arrangement with respect to the axis normal to the DMPC membrane as indicated on the plots (dupplicated simulations with respect to Figure S.8a).

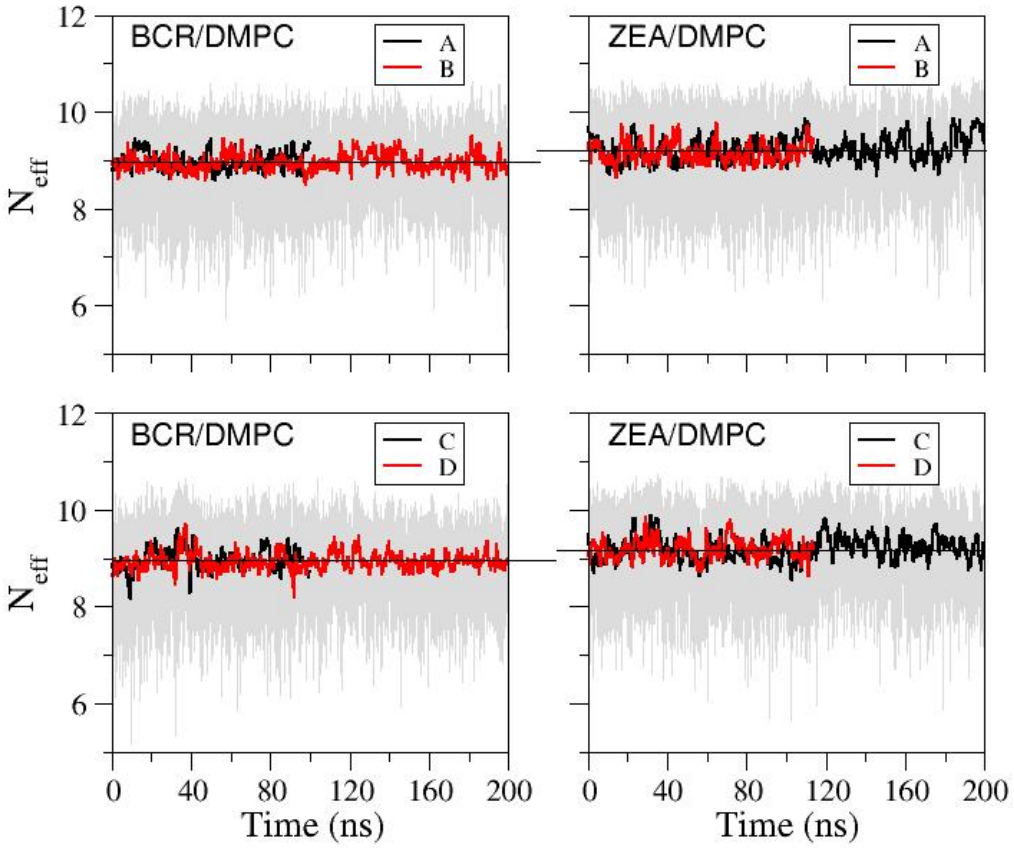

Figure S.9: Evolution of the effective conjugated chain length (computed with protocol described in Section III of the paper) during the simulation time for all the systmes presented in the text. All actual values display a large dispersion (light grey) and for clarity, partial averages taken every 100 points are also included, together with the mean value (orange for DMPC/BCR systems and blue for DMPC/ZAE systems).

Table S.1: Bonded parameters (bonds) employed in this work to describe the interactions of β-carotene and zeaxanthin. In the definition, the atom types that form the bond $(i-j)$ are specified as well as the bond type using the notation: - (single bond) and = (double bond).

Bonds: $V_{ij}^{bond} = k_b(r_{ij} - b_0)^2$		
Definition	b_0 (nm)	k_b (KJ mol^{-1} nm^{-1})
CA=CA*	0.135	255224.0
CA-CA*	0.143	220000.0
CT1-CA#	0.149	192464.0
CT2-CA	0.149	192464.0
CT3-CA	0.149	192464.0
CT2-CT1	0.1538	186188.0
CT2-CT2	0.153	186188.0
CT3-CT1	0.1538	186188.0
CT3-CT2	0.1528	186188.0
HA-CT1	0.1111	258571.2
HA-CT2*	0.110	258571.2
HA-CT3*	0.110	269449.6
HP-CA*	0.109	284512.0
OH1-CT1	0.142	358150.4
OH1-H	0.096	456056.0

*Modified with respect to CHARMM27.

#Add with respect to CHARMM27.

Table S.2: Bonded parameters (angles) employed in this work to describe the interactions of β-carotene and zeaxanthin. In the definition, the atom types that form the angle $(i-j-k)$ are specified as well as the bond type using the notation: - (single bond), = (double bond) and $\simeq$ (parameter used for both single and double bonds).

Angles + UB: $V_{ijk}^{angle} = k_\alpha(\alpha_{ijk} - \alpha_{ijk}^0)^2 + k_{UB}(r_{ik} - r_{ik}^0)^2$				
Definition	α^0 (deg)	k_α (KJ mol^{-1} deg^{-1})	$r_{1,3}^0$ (nm)	k_{UB}
CA=CA-CA*	123.00	334.7200	0.246	29288.0
CT3-CA$\simeq$CA*	124.00	383.2544	0.254	29288.0
HP-CA$\simeq$CA*	120.00	251.04	0.210	18409.6
HP-CA-CT3#	118.00	251.04	0.210	18409.6
HA-CT3-CA	107.50	412.5424	0.0	0.0
CT2-CA$\simeq$CA	122.30	383.2544	0.0	0.0
CT1-CA$\simeq$CA#	122.30	383.2544	0.0	0.0
CT2-CA-CT3#	122.30	383.2544	0.0	0.0
CT2-CT1-CA#	107.50	433.4624	0.0	0.0
CT3-CT1-CA#	107.50	433.4624	0.0	0.0
CT2-CT2-CA#	107.50	433.4624	0.0	0.0
HA-CT2-CA	107.50	412.5424	0.0	0.0
CT2-CT2-CT1	113.50	488.2728	0.2561	9338.688
CT2-CT2-CT2	113.60	488.2728	0.2561	9338.688
CT3-CT1-CT2	114.00	446.4328	0.2561	6694.4
CT3-CT1-CT3	114.00	446.4328	0.2561	6694.4
HA-CT2-CT1	110.10	279.74224	0.2179	18853.104
HA-CT2-CT2	110.10	221.752	0.2179	18853.104
HA-CT2-HA	109.00	297.064	0.1802	4518.72
HA-CT3-CT	110.10	279.74224	0.2179	18853.104
HA-CT3-HA	108.40	297.064	0.1802	4518.72
H-OH1-CT1	106.00	481.16	0.0	0.0
HA-CT1-CT2	110.10	288.696	0.2179	18853.104
HA-CT2-CT1	110.10	279.74224	0.2179	18853.104
OH1-CT1-CT2#	110.10	633.4576	0.0	0.0
OH1-CT1-HA	108.89	384.0912	0.0	0.0
CT2-CT1-CT2#	111.00	446.4328	0.2561	6694.4
CT1-CT2-CA#	107.50	433.4624	0.0	0.0
CT1-CT2-CT#	107.50	433.4624	0.0	0.0

*Modified with respect to CHARMM27.

#Add with respect to CHARMM27.

Table S.3: Bonded parameters (dihedrals) employed in this work to describe the interactions of β-carotene and zeaxanthin. In the definition, the atom types that form the dihedral $(i-j-k-l)$ are specified as well as the bond type using the notation: - (single bond) and = (double bond).

Dihedrals: $Vdihed_{ijkl} = k_\theta(1+\cos(n\theta_{ijkl}-\theta^0_{ijkl}))$			
Definition	θ^0 (deg)	k_θ (KJ mol^{-1} deg^{-1})	Mult.(n)
CA=CA-CA=CA*	180.0	5.639	2
HP-CA-CA-HP*	180.0	5.373	2
CA=CA-CA-HP*	180.0	7.409	2
CA=CA-CA-CT3*	180.0	5.665	2
HP-CA-CA-CT3*	180.0	7.067	2
CA-CA=CA-CA*	180.0	23.3467	2
CT2-CA=CA-CT1#	180.0	23.3467	2
CT3-CA=CA-CT1#	180.0	23.3467	2
CT2-CA=CA-CA*	180.0	23.3467	2
CT-CA=CA-CA1#	180.0	23.3467	2
CT3-CA=CA-CA*	180.0	23.3467	2
HP-CA=CA-CA*	180.0	31.6310	2
HP-CA=CA-CT#	180.0	31.6310	2
HP-CA=CA-CT2*	180.0	31.6310	2
HP-CA=CA-CT3*	180.0	31.6310	2
HP-CA=CA-HP*	180.0	18.0749	2
HA-CT3-CA=CA*	180.0	0.494	3
HA-CT3-CA-CA*	0.0	0.494	3
CT2-CT1-CA-CA#	0.0	0.8368	3
CT3-CT1-CA-CA#	0.0	0.8368	3
X-CT1-CT2-CT2*	0.0	0.60	3
X-CT1-CT2-HA*	0.0	0.00	3
X-CT1-CT3-HA*	0.0	0.60	3
X-CT2-CT2-X	0.00	0.81588	3
X-CT2-CA-X	0.00	0.0	6
X-CT3-CA-X	0.00	0.0	6
H-OH1-CT1-CT2#	0.00	5.56472	1
H-OH1-CT1-CT2#	0.00	0.75312	2
H-OH1-CT1-CT2#	0.00	1.33888	3
HA-CT1-CT2-CA	0.00	0.16736	3
X-CT1-OH1-X	0.00	0.58576	3
X-CT1-CT2-CT1#	0.00	0.60	3
X-CT1-CT2-X	0.00	0.8368	3

*Modiffied with respect to CHARMM27.

#Add with respect to CHARMM27.

Table S.4: Partial charges employed to describe the electrostatic interactions for β-carotene and zeaxanthin obtained as described in this work (see text).

Atom	Partial Charge (a.u.)	
	β-Carotene	Zeaxantin
C1	0.500	0.737
C2	-0.230	-0.473
HR21	0.090	0.100
HR22	0.090	0.100
C3	-0.010	0.411
H31	0.090	-0.013
H32	0.090	–
C4	-0.230	-0.348
H41	0.090	0.114
H42	0.090	0.114
C5	0.240	0.392
C6	-0.460	-0.542
C7	0.100	0.123
H7	0.140	0.075
C8	-0.320	-0.356
H8	0.140	0.162
C9	0.240	0.254
C10	-0.320	-0.305
H10	0.140	0.146
C11	0.000	0.003
H11	0.140	0.125
C12	-0.320	-0.348
H12	0.140	0.165
C13	0.240	0.276
C14	-0.320	-0.293
H14	0.140	0.128
C15	-0.100	-0.094
H15	0.140	0.148
C31	-0.460	-0.492
H311	0.090	0.108
H312	0.090	0.108
H313	0.090	0.108
C32	-0.460	-0.492
H321	0.090	0.108
H322	0.090	0.108
H323	0.090	0.108
C33	-0.400	-0.466
H331	0.090	0.119
H332	0.090	0.119
H333	0.090	0.119
C34	-0.280	-0.351
H341	0.090	0.100
H342	0.090	0.100
H343	0.090	0.100
C35	-0.280	-0.321
H351	0.090	0.092
H352	0.090	0.092
H353	0.090	0.092
O1	–	-0.669
HO1	–	0.409