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

Electric Field Controlled Uphill Electron Migration along α-Helical Oligopeptides

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1. Comparisons of Calculated Results Using Different Methods on Anionic Structures

Table SI. Calculated energies, dipole moments and LUMO energies of the neutral α-helical oligopeptides with different chain lengths using the RB3LYP and UB3LYP

α-helical	E_{app}	Methods	Energy (a.u.)	Dipole moment (Debye)	LUMO energy (a.u.)
n=5	30	RB3LYP	-1288.719621	22.437	-0.02903
		UB3LYP	-1288.719621	22.437	-0.02903
	40	RB3LYP	-1288.728533	23.0824	-0.02301
		UB3LYP	-1288.728533	23.0824	-0.02301
n=9	30	RB3LYP	-2120.857821	39.042	-0.03523
		UB3LYP	-2120.857821	39.042	-0.03523
	40	RB3LYP	-2120.873282	40.1215	-0.03839
		UB3LYP	-2120.873282	40.1215	-0.03839
n=15	30	RB3LYP	-3369.061793	69.1844	-0.02852
		UB3LYP	-3369.061793	69.1844	-0.02852
	40	RB3LYP	-3369.089365	71.0192	-0.03749
		UB3LYP	-3369.089365	71.0192	-0.03749

Table SII. Calculated energies, dipole moments and SOMO energies of the anionic α-helical oligopeptides with different chain lengths using the RB3LYP and UB3LYP

α-helical	E_{app}	Methods	Energy (a.u.)	Dipole moment (Debye)	SOMO energy (a.u.)
n=5	30	RB3LYP	-1288.717428	23.3681	0.02894
		UB3LYP	-1288.717863	23.4632	0.02899
	40	RB3LYP	-1288.729666	37.5028	0.02924
		UB3LYP	-1288.729676	37.4994	0.02769
n=9	30	RB3LYP	-2120.864835	48.1231	0.02045
		UB3LYP	-2120.86485	48.112	0.01741
	40	RB3LYP	-2120.88811	71.8388	0.02294
		UB3LYP	-2120.888123	71.8572	0.01557

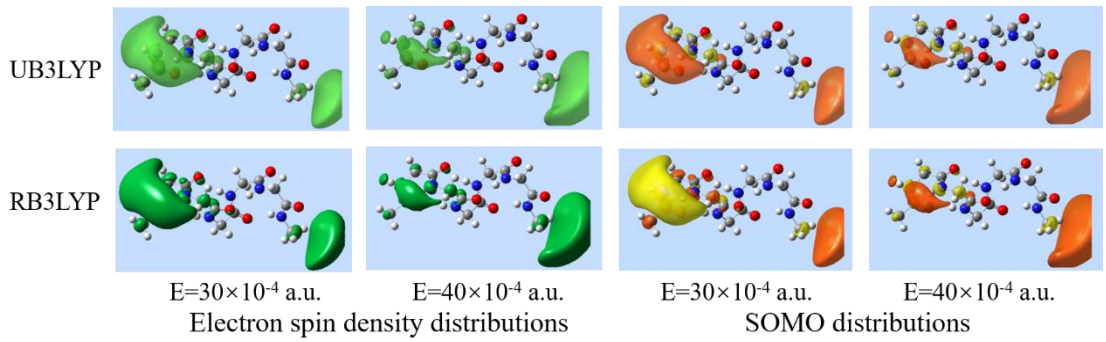


Figure S1. Electron spin density and SOMO distributions of the anionic α-helical oligopeptide 5 (residue unit number is 5) in two E_{app} using the RB3LYP and UB3LYP functionals.

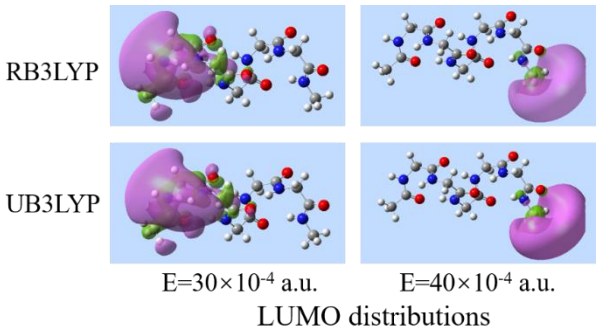


Figure S2. LUMO distributions of the neutral α-helical oligopeptide 5 (residue unit number is 5) in two E_{app} using the RB3LYP and UB3LYP functionals.

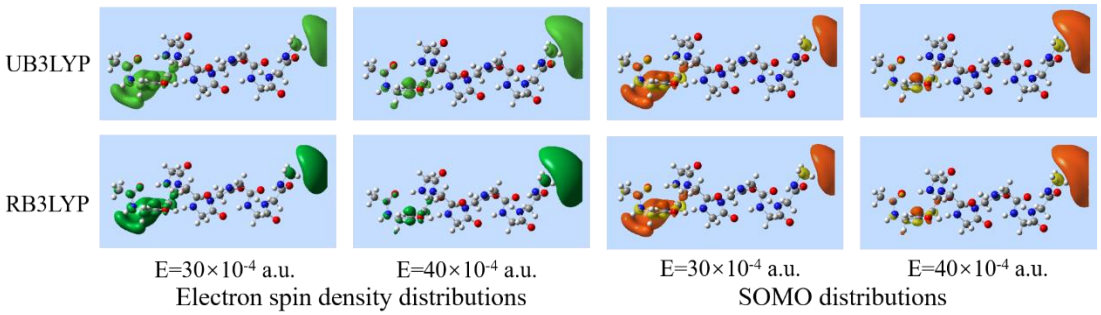


Figure S3. Electron spin density and SOMO distributions of the anionic α-helical oligopeptide 9 (residue unit number is 9) in two E_{app} using the RB3LYP and UB3LYP functionals.

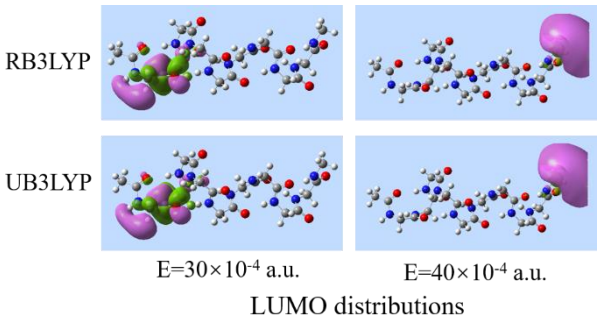


Figure S4. LUMO distributions of the neutral α-helical oligopeptide 9 (residue unit number is 9) in two E_{app} using the RB3LYP and UB3LYP functionals.

Note: From Tables S I and S II, Figures S1-S4, we find the RB3LYP and UB3LYP results are similar. In this work, we use RB3LYP and UB3LYP to calculate the neutral and anionic structures, respectively.

2. Electric Field Effects on the Structure of α-Helical Oligopeptides

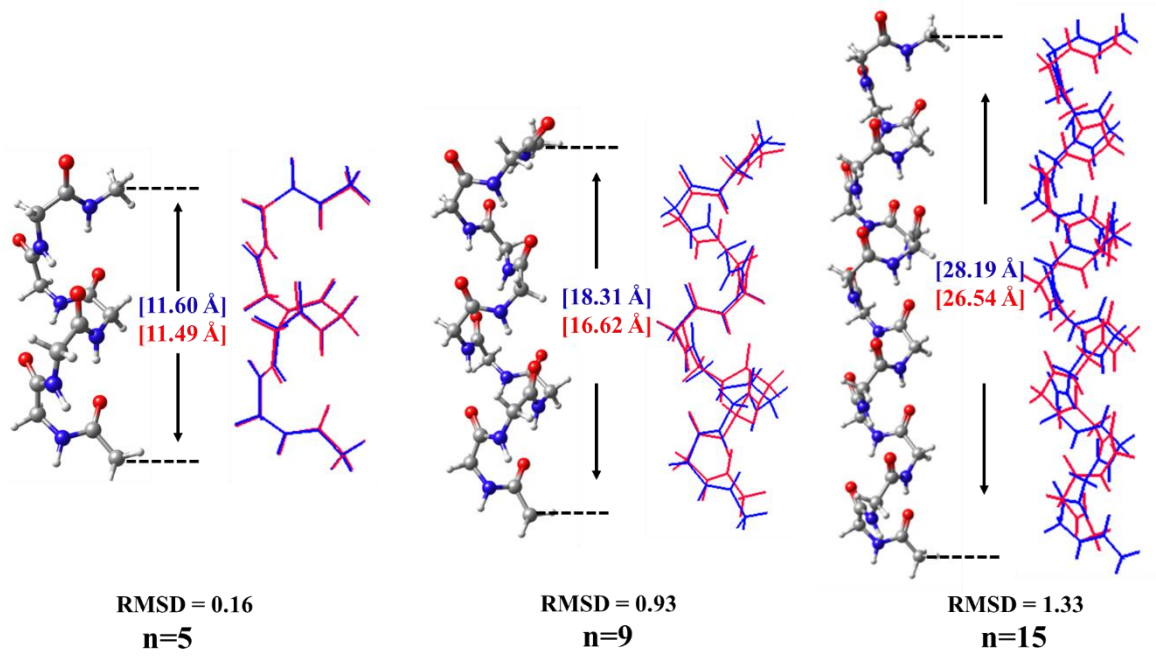


Figure S5. Overlap of the neutral α-helical oligopeptides in the absence of E_{app} and in E_{app}= 60 x 10-4 a.u. Blue and red represent the structure was optimized in the absence of E_{app} and in the presence of E_{app}, respectively. The numbers in the square brackets denote the distance between N-terminal and C-terminal. RMSD (root mean square deviation) reflects the deviations between the two structures.

3. LUMO Distributions of Different α-Helical Oligopeptides

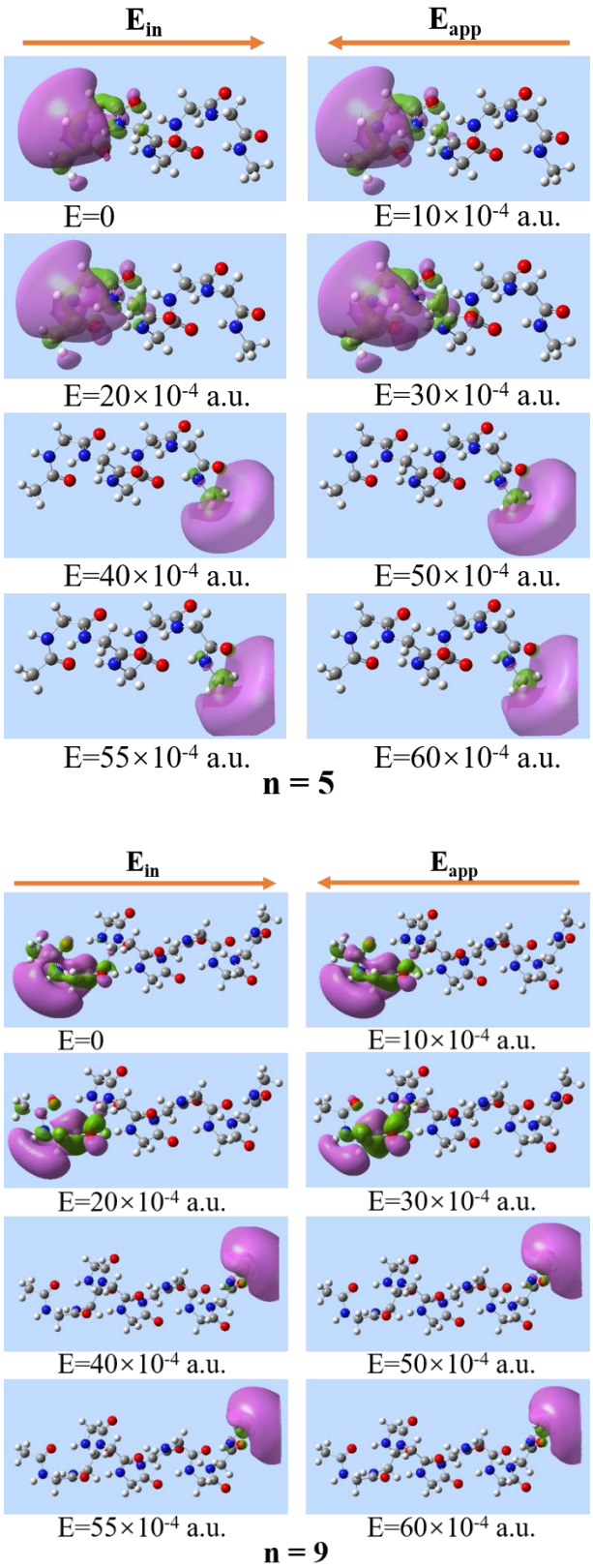


Figure S6. LUMO distributions of α-helical oligopeptides with different chain lengths (the number of residue units, n) along with E_{app}.

4. Spin Density Distributions of Different α-Helical Oligopeptides

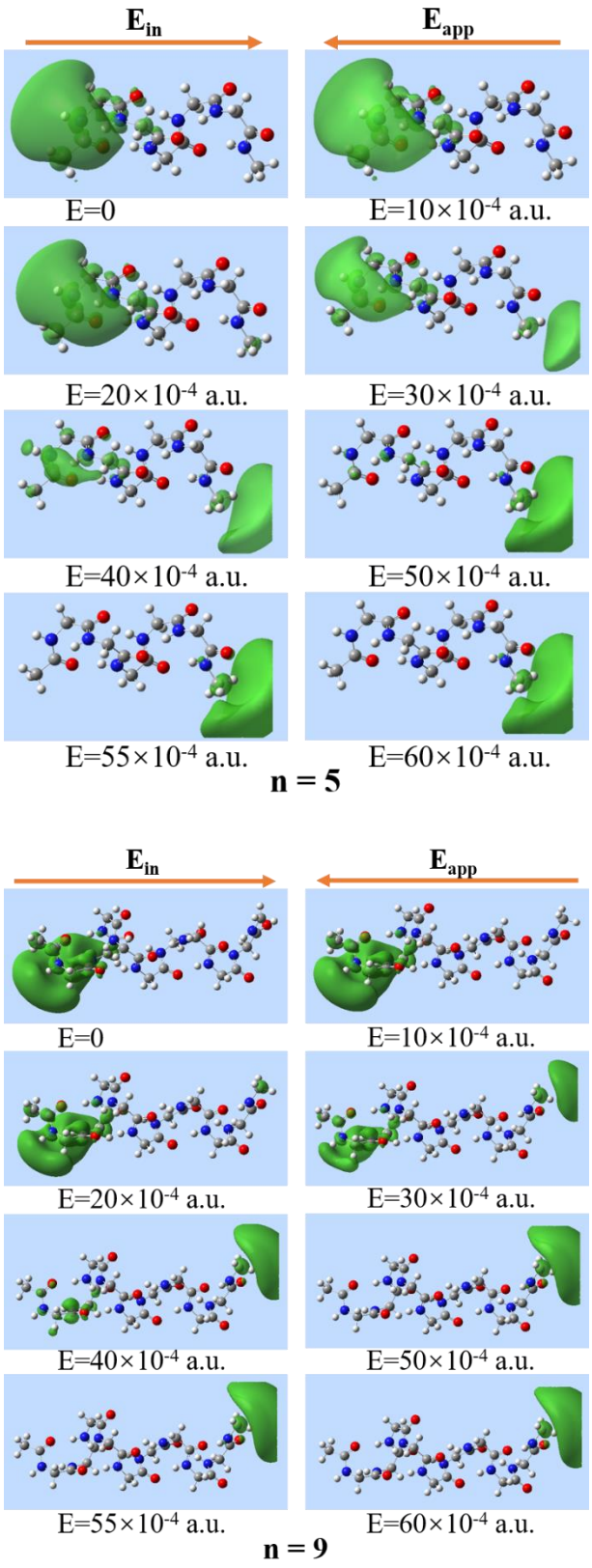


Figure S7. Spin density distributions of α-helical peptides with different chain lengths (the number of residue units, n) along with E_{app}.

5. Spin Densities of Each Residue in Different α-Helical Oligopeptides in Different Strength Electric Fields

Table S III. Spin density variations of each residue in peptide 5 with residue number n=5 in different strength E_{app}

Residue order	Electric field strength (10^{-4} a.u.)												
	0	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**	**50**	**55**	**60**
1	0.67	0.60	0.53	0.45	0.36	0.27	0.19	0.13	0.09	0.05	0.03	0.01	0.00
2	0.37	0.44	0.51	0.58	0.54	0.49	0.45	0.40	0.34	0.26	0.16	0.06	0.03
3	-0.03	-0.03	-0.03	-0.02	-0.01	-0.01	-0.02	-0.02	-0.02	-0.02	-0.02	-0.01	-0.01
4	0.00	0.00	-0.01	-0.01	-0.03	-0.03	-0.04	-0.04	-0.04	-0.04	-0.04	-0.04	-0.04
5	0.00	0.00	0.00	-0.01	0.14	0.29	0.41	0.53	0.64	0.75	0.87	0.99	1.02

Table S IV. Spin density variations of each residue in peptide 9 with residue number n=9 in different strength E_{app}

Residue order	Electric field strength (10^{-4} a.u.)												
	0	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**	**50**	**55**	**60**
1	1.41	1.41	1.41	1.34	1.02	0.79	0.10	0.07	0.07	0.06	0.00	0.00	0.00
2	-0.27	-0.30	-0.34	-0.35	-0.26	-0.20	0.37	0.26	0.13	0.01	0.00	0.00	0.00
3	0.01	0.00	0.01	0.06	0.02	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00
4	-0.01	-0.01	-0.02	-0.06	-0.03	-0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00	0.01	0.01	0.03	0.03	0.03	0.01	0.01	0.00	0.00
6	0.00	0.00	0.00	0.00	0.02	0.02	-0.01	0.00	0.02	0.03	0.03	0.02	0.02
7	0.00	0.00	0.00	0.02	0.02	0.02	0.01	0.01	0.00	0.00	-0.01	-0.02	-0.02
8	0.00	0.00	0.00	-0.01	0.14	0.24	-0.02	-0.02	-0.03	-0.04	-0.04	-0.04	-0.04
9	-0.14	-0.10	-0.06	-0.01	0.07	0.13	0.50	0.64	0.78	0.93	1.01	1.03	1.04

Table S V. Spin density variations of each residue in peptide 15 with residue number n=15 in different strength E_{app}

Residue order	Electric field strength (10^{-4} a.u.)												
	0	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**	**50**	**55**	**60**
1	0.53	0.44	0.36	0.27	0.18	0.10	0.01	0.00	0.00	0.00	0.00	0.00	0.00
2	0.49	0.47	0.44	0.34	0.20	0.06	0.01	0.00	0.00	0.00	0.00	0.00	0.00
3	-0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00
5	0.00	0.01	0.02	0.02	0.02	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.00
6	0.00	0.04	0.07	0.07	0.07	0.07	0.06	0.03	0.00	0.00	0.00	0.00	0.00
7	0.00	0.02	0.04	0.05	0.05	0.05	0.05	0.02	0.00	0.00	0.00	0.00	0.00
8	0.00	0.01	0.05	0.04	0.03	0.04	0.03	0.02	0.00	0.00	0.00	0.00	0.00
9	0.00	0.00	0.00	0.02	0.02	0.03	0.03	0.02	0.01	0.00	0.00	0.00	0.00
10	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00
12	0.00	0.00	0.00	0.01	0.01	0.02	0.03	0.05	0.05	0.04	0.03	0.02	0.02
13	0.00	0.00	0.00	0.01	0.02	0.02	0.02	0.02	0.01	0.00	-0.01	-0.02	-0.02
14	0.00	0.00	0.00	0.00	-0.01	-0.02	-0.03	-0.05	-0.07	-0.07	-0.07	-0.08	-0.08
15	0.00	0.00	0.00	0.14	0.37	0.57	0.74	0.88	0.99	1.03	1.05	1.07	1.08

6. SOMO Distributions of Different α-Helical Oligopeptides

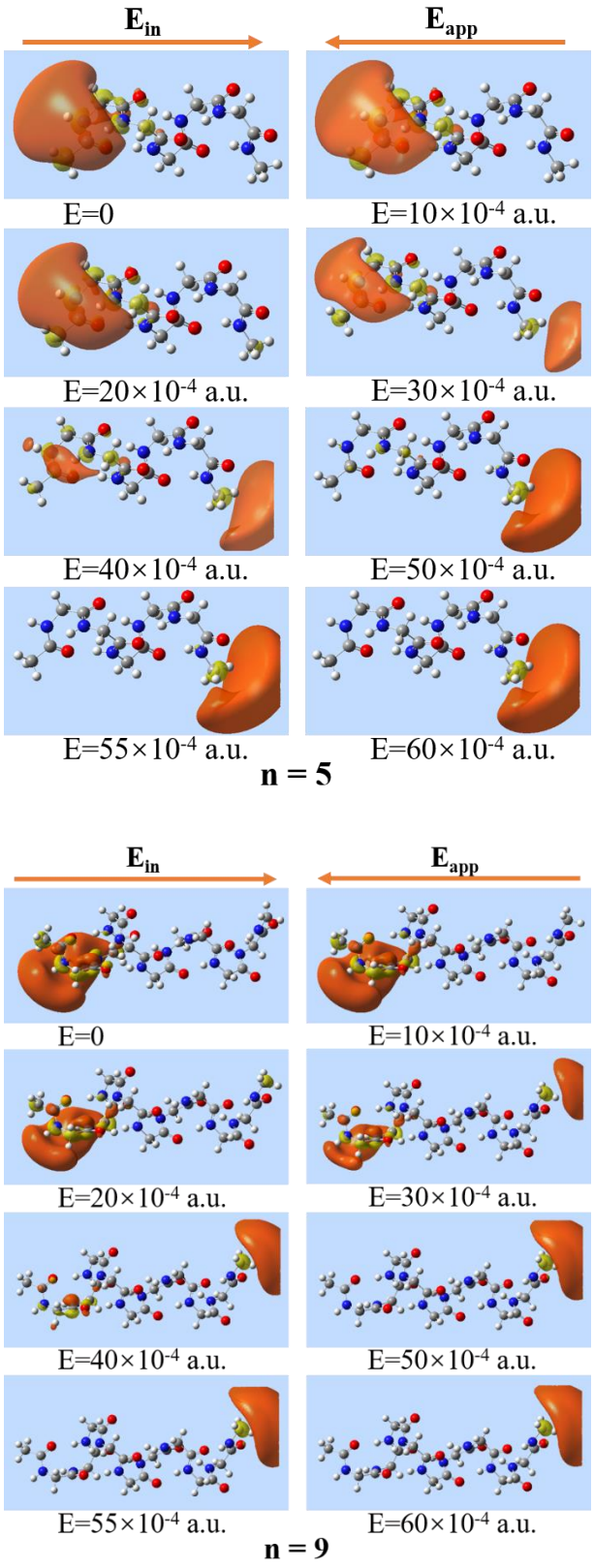
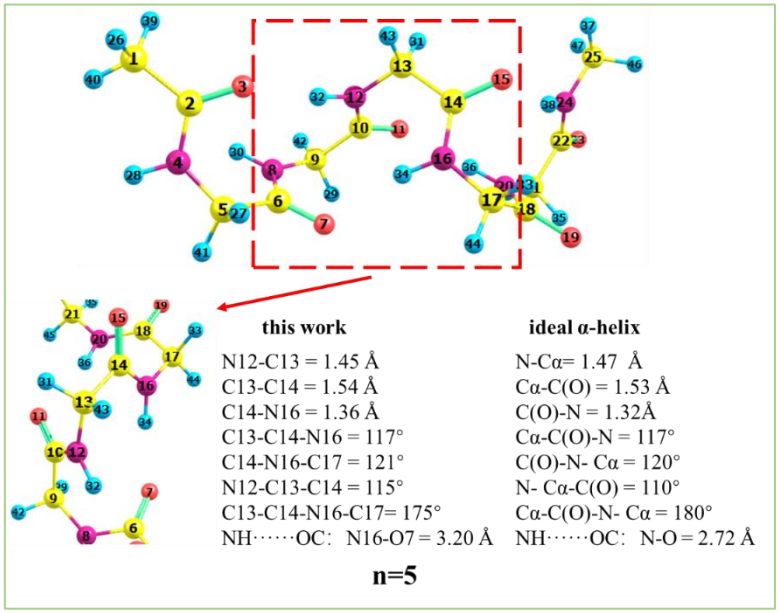


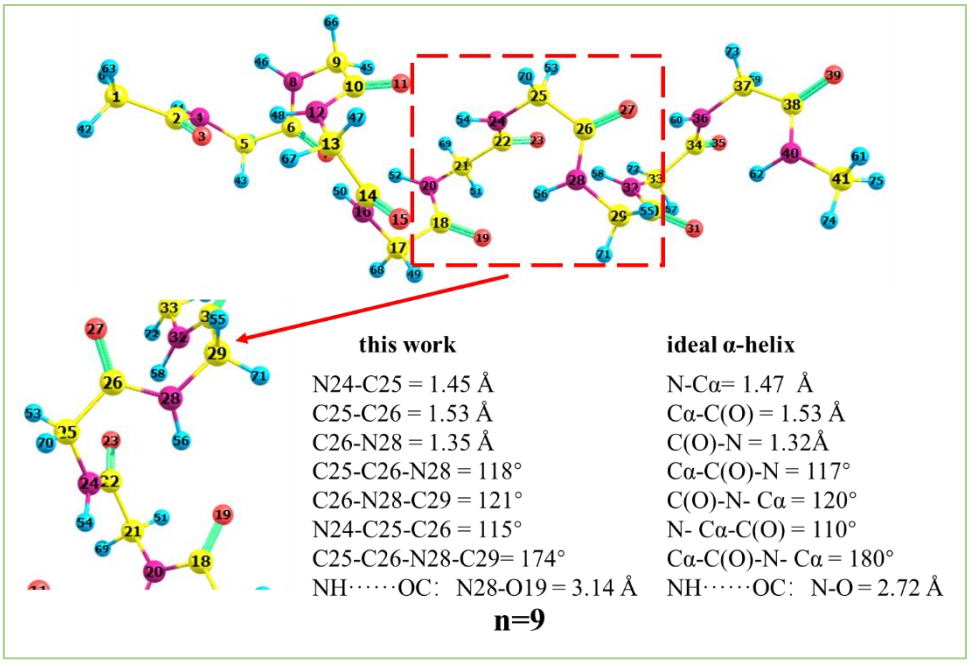
Figure S8. SOMO distributions of α-helical peptides with different chain lengths (the number of residue units, n) along with E_{app}.

7. Comparison of the Peptides in This Work and Ideal α-Helix



this work	ideal α-helix
N12-C13 = 1.45 Å	N-Cα= 1.47 Å
C13-C14 = 1.54 Å	Cα-C(O) = 1.53 Å
C14-N16 = 1.36 Å	C(O)-N = 1.32Å
C13-C14-N16 = 117°	Cα-C(O)-N = 117°
C14-N16-C17 = 121°	C(O)-N- Cα = 120°
N12-C13-C14 = 115°	N- Cα-C(O) = 110°
C13-C14-N16-C17= 175°	Cα-C(O)-N- Cα = 180°
NH·····OC: N16-O7 = 3.20 Å	NH·····OC: N-O = 2.72 Å

n=5



this work	ideal α-helix
N24-C25 = 1.45 Å	N-Cα= 1.47 Å
C25-C26 = 1.53 Å	Cα-C(O) = 1.53 Å
C26-N28 = 1.35 Å	C(O)-N = 1.32Å
C25-C26-N28 = 118°	Cα-C(O)-N = 117°
C26-N28-C29 = 121°	C(O)-N- Cα = 120°
N24-C25-C26 = 115°	N- Cα-C(O) = 110°
C25-C26-N28-C29= 174°	Cα-C(O)-N- Cα = 180°
NH·····OC: N28-O19 = 3.14 Å	NH·····OC: N-O = 2.72 Å

n=9

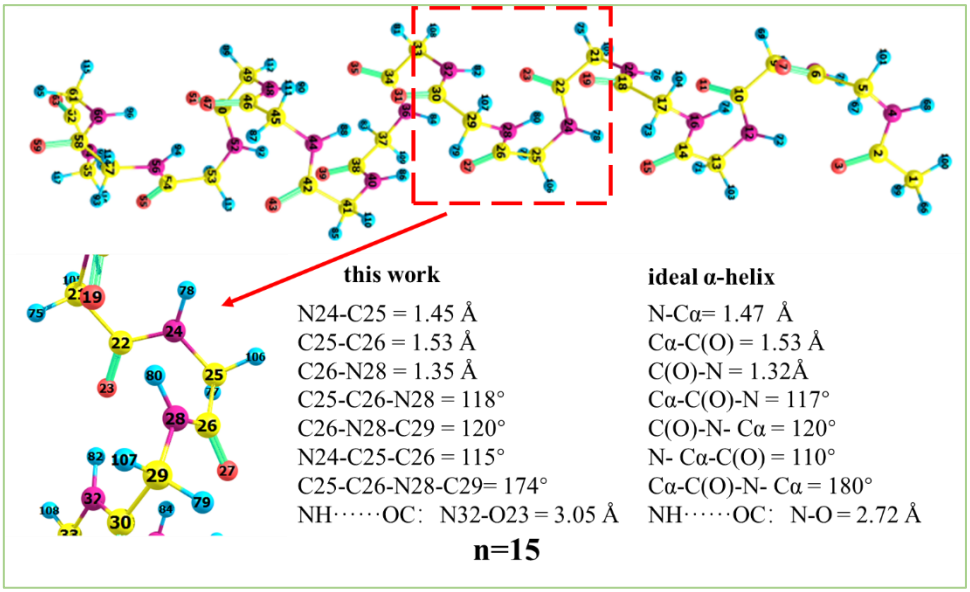


Figure S9. Geometric structure parameters comparisons of the α-helical peptides with different chain lengths (the number of residue units, n) in this work and the ideal helixes. Atomic display: C-yellow, H-blue, O-red, N-pink. The ideal data from the work of Pauling and coworkers.[1-2]

References:

1. Pauling, L.; Corey, R. B.; Branson, H. R. The Structure of Proteins: Two Hydrogen-Bonded Helical Configurations of the Polypeptide Chain. *Proc. Natl. Acad. Sci.* 1951, *37*, 205–211.
2. Pauling, L.; Corey, R. B. Atomic Coordinates and Structure Factors for Two Helical Configurations of Polypeptide Chains. *Proc. Natl. Acad. Sci.* 1951, *37*, 235–240.

8. Behaviors of Free Amino and Carboxyl Groups at Terminus of α-Helical Oligopeptides (NH_2-(CO-CH_2-NH)$_n$-COOH) in the Applied Electric Field

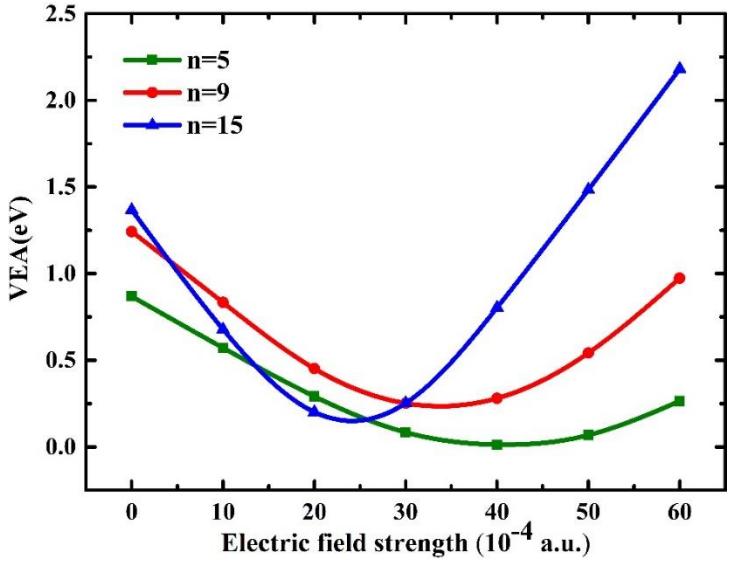


Figure S10. The variations of vertical electron affinities (VEAs) of α-helical oligopeptides with different chain lengths (n denotes the number of residue) with the increase of E_{app}. VEA = E_n – E_a, where E_n and E_a represent the total energies of a neutral structure and its corresponding anion in the same E_{app}, respectively.

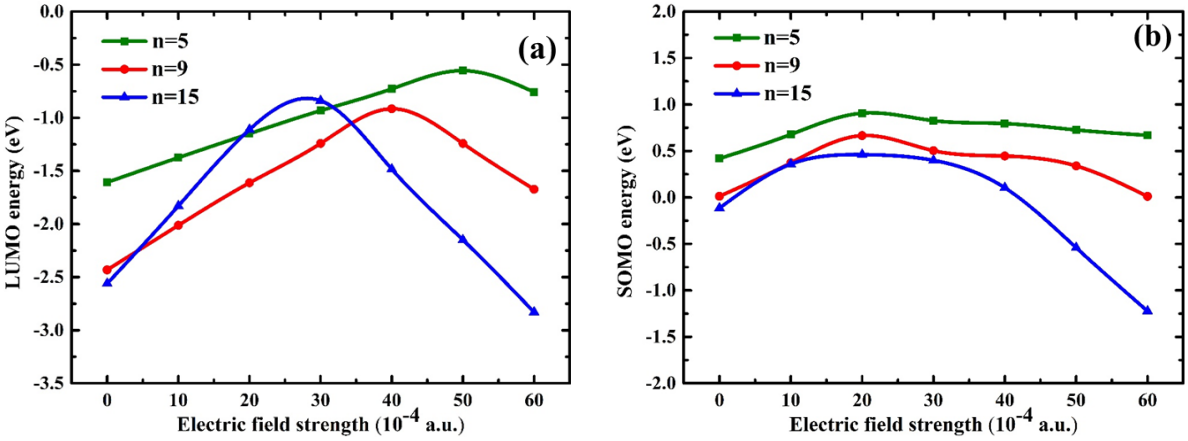


Figure S11. The variations of frontier molecular orbital energies of α-helical oligopeptides with different chain lengths (n denotes the number of residues) with the increase of E_{app}. (**a**) the LUMO energies, and (**b**) the SOMO energies.

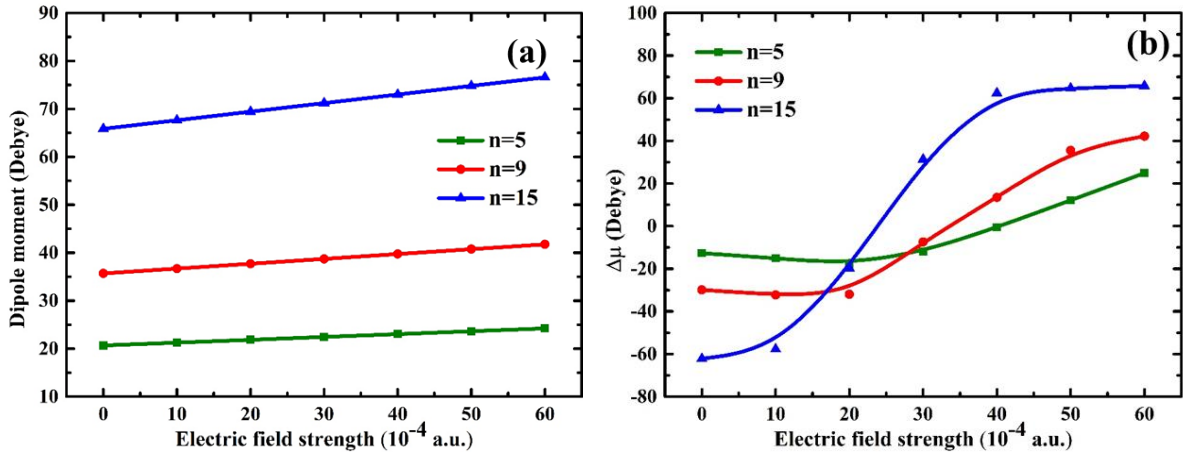
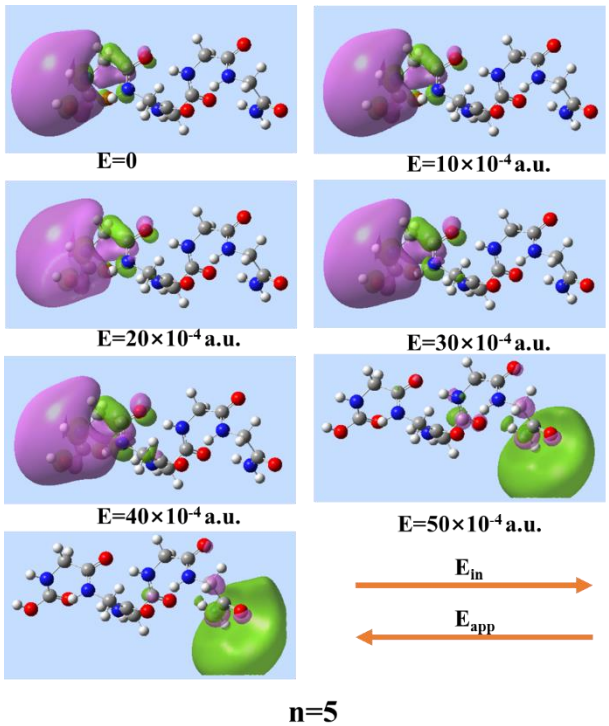


Figure S12. Variations of dipole moments of α-helical oligopeptides with different chain lengths (n denotes the number of residue) in E_{app}. (**a**) neutral peptides, and (**b**) the difference (Δμ) between the anionic and neutral peptides: $\Delta\mu = \mu_a - \mu_n$, where μ_n and μ_a represent the dipole moments of a neutral structure and its corresponding anion in the same E_{app}, respectively.



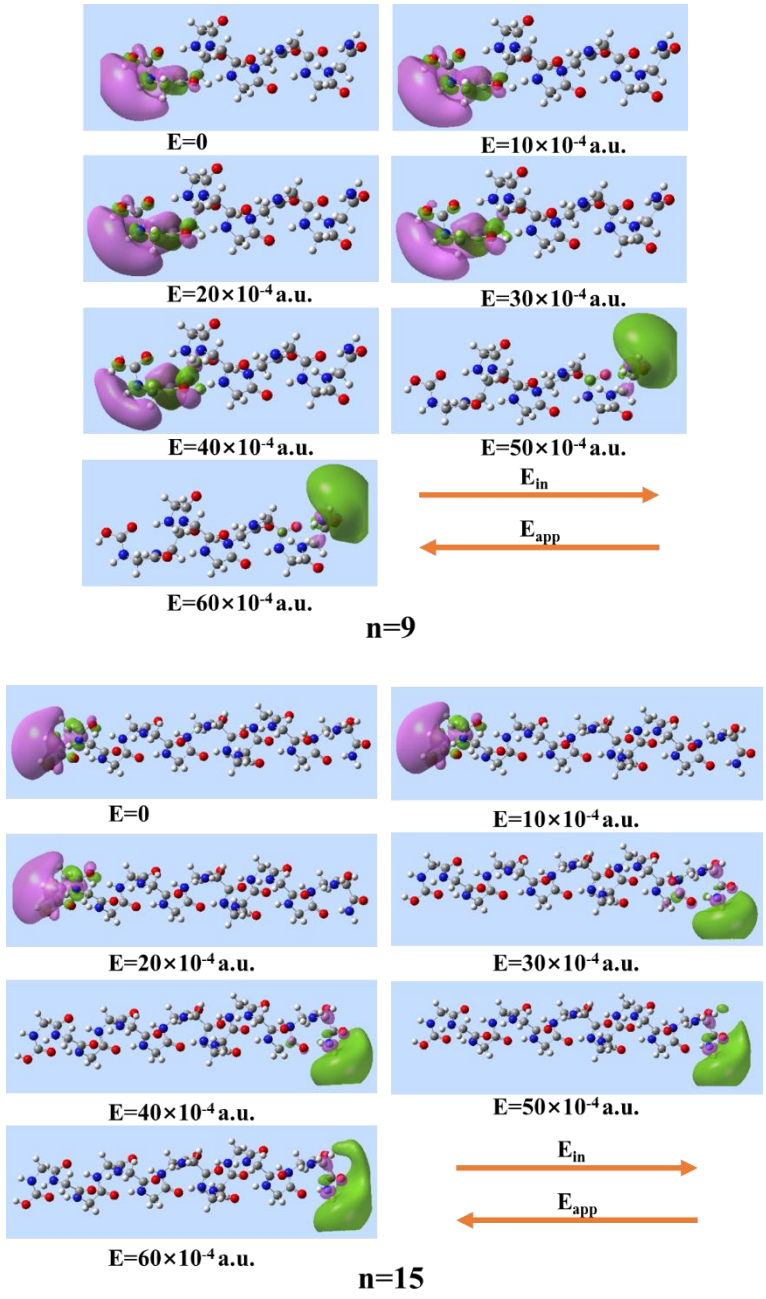
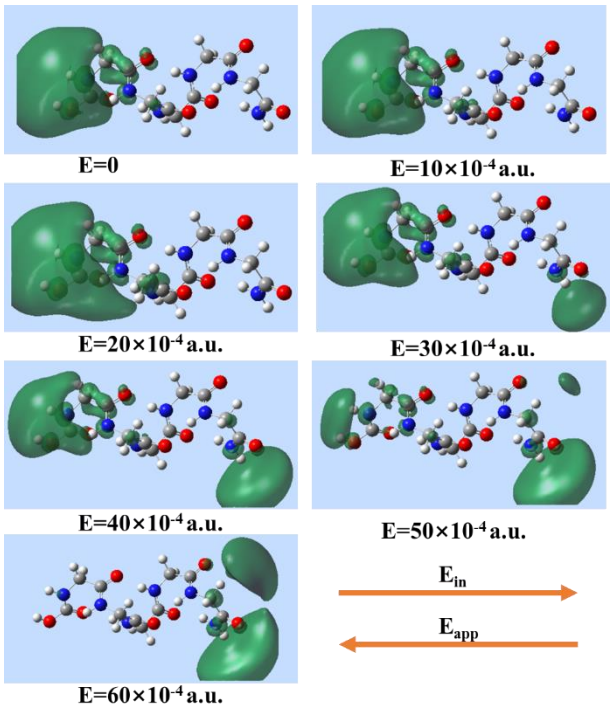
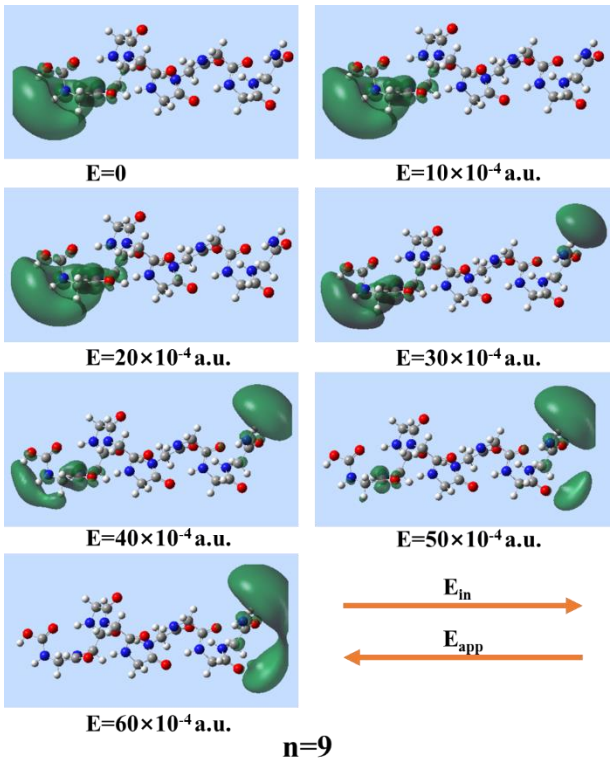


Figure S13. LUMO distributions of α-helical oligopeptides with different chain lengths (the number of residue units, n) along with E_{app}.


E=0
E=10×10⁻⁴ a.u.
E=20×10⁻⁴ a.u.
E=30×10⁻⁴ a.u.
E=40×10⁻⁴ a.u.
E=50×10⁻⁴ a.u.
E=60×10⁻⁴ a.u.
E_in
E_app

n=5


E=0
E=10×10⁻⁴ a.u.
E=20×10⁻⁴ a.u.
E=30×10⁻⁴ a.u.
E=40×10⁻⁴ a.u.
E=50×10⁻⁴ a.u.
E=60×10⁻⁴ a.u.
E_in
E_app

n=9

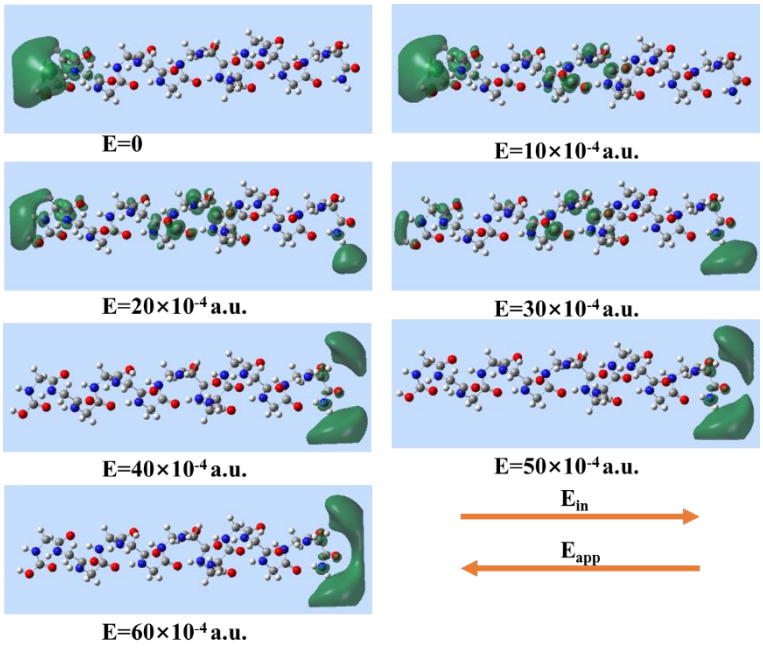


Figure S14. Spin density distributions of α-helical peptides with different chain lengths (the number of residue units, n) along with E_{app}.