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Supporting Material for: Electronic structure, absorption spectra and oxidation dynamics in polyynes and dicyanopolyynes

Lazaros Chalkopiadis,[a] Konstantinos Lambropoulos,[a], Constantinos Simserides*[a]

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This is Supporting Material for: Electronic structure, absorption spectra and oxidation dynamics in polyynes and dicyanopolyynes. The matlab code for TB with all valence orbitals can be found in `http://users.uoa.gr/~csimseri/All_Vallence_Orbitals.zip`. The zip contains also some auxiliary files, including geometries.

1 Polyynes

Figure S1 presents the molecular eigenstates of *polnsl* molecules with $n = 2,4,6,8,10$. Eigenenergies together with *character*, i.e., analysis of molecular states into atomic valence states.

Fig. S2 shows a snapshot, for the initial 3 femtoseconds, of the time-dependent probabilities at C_1, C_3 and C_6 orbitals, for initial placement of the hole at $2s$ orbital of C_1, in *pol6sl*. The $2p_x$ and $2p_z$ time-dependent probabilities remain zero. An sp path is activated in this case: only $2s$ and $2p_y$ orbitals have significant probabilities. In Fig. S3 we show the same quantities for the time interval from 7 to 10 femtoseconds.

Table S1 shows Löwdin Population Analysis, at the B3LYP/STO-3G level of theory, for *pol-n-sl* molecules with $n = 2,4,6,8,10$. Table S2 shows Löwdin Population Analysis (shell charges), for the ground state (GS) and localised hole state (LHS), at carbon atom C_1 of *pol-n-sl* molecules with $n = 2,4,6,8,10$, at the B3LYP/ STO-3G level of theory. The difference between GS and LHS is also shown.

Table S1 Löwdin Population Analysis at the B3LYP/STO-3G level of theory for *pol-n-sl* molecules with $n = 2,4,6,8,10$.

atom	neutral	*pol2sl*	*pol4sl*	*pol6sl*	*pol8sl*	*pol10sl*
C1	6	6.08	6.06	6.05	6.05	6.05
C2	6	6.08	6.03	6.03	6.03	6.02
C3	6	-	6.03	6.01	6.01	6.00
C4	6	-	6.06	6.01	6.01	6.01
C5	6	-	-	6.03	6.01	6.01
C6	6	-	-	6.05	6.01	6.01
C7	6	-	-	-	6.03	6.01
C8	6	-	-	-	6.05	6.00
C9	6	-	-	-	-	6.02
C10	6	-	-	-	-	6.05
H_{n+1}	1	0.92	0.91	0.91	0.91	0.90
H_{n+2}	1	0.92	0.91	0.91	0.91	0.90

Table S2 Löwdin Population Analysis (shell charges), for the ground state (GS) and the localised hole state (LHS), at carbon atom C_1 of *pol-n-sl* molecules with $n = 2,4,6,8,10$, B3LYP/ STO-3G level of theory. The difference between GS and LHS is also shown.

Molecule	Löwdin Population Analysis			
	State	"$1s$"	"$2s$"	"$2p''$
pol2sl	GS	1.99	1.05	3.05
	LHS	1.99	0.97	2.12
	GS−LHS	0.00	0.08	0.93
pol4sl	GS	1.99	1.05	3.02
	LHS	1.99	0.98	2.09
	GS−LHS	0.00	0.07	0.93
pol6sl	GS	1.99	1.06	3.01
	LHS	1.99	0.99	2.08
	GS−LHS	0.00	0.07	0.93
pol8sl	GS	1.99	1.06	3.00
	LHS	1.99	0.99	2.07
	GS−LHS	0.00	0.07	0.93
pol10sl	GS	1.99	1.06	3.00
	LHS	1.99	0.99	2.08
	GS−LHS	0.00	0.07	0.92

[a] Department of Physics, National and Kapodistrian University of Athens, Panepistimiopolis, Zografos GR-15784, Athens, Greece.

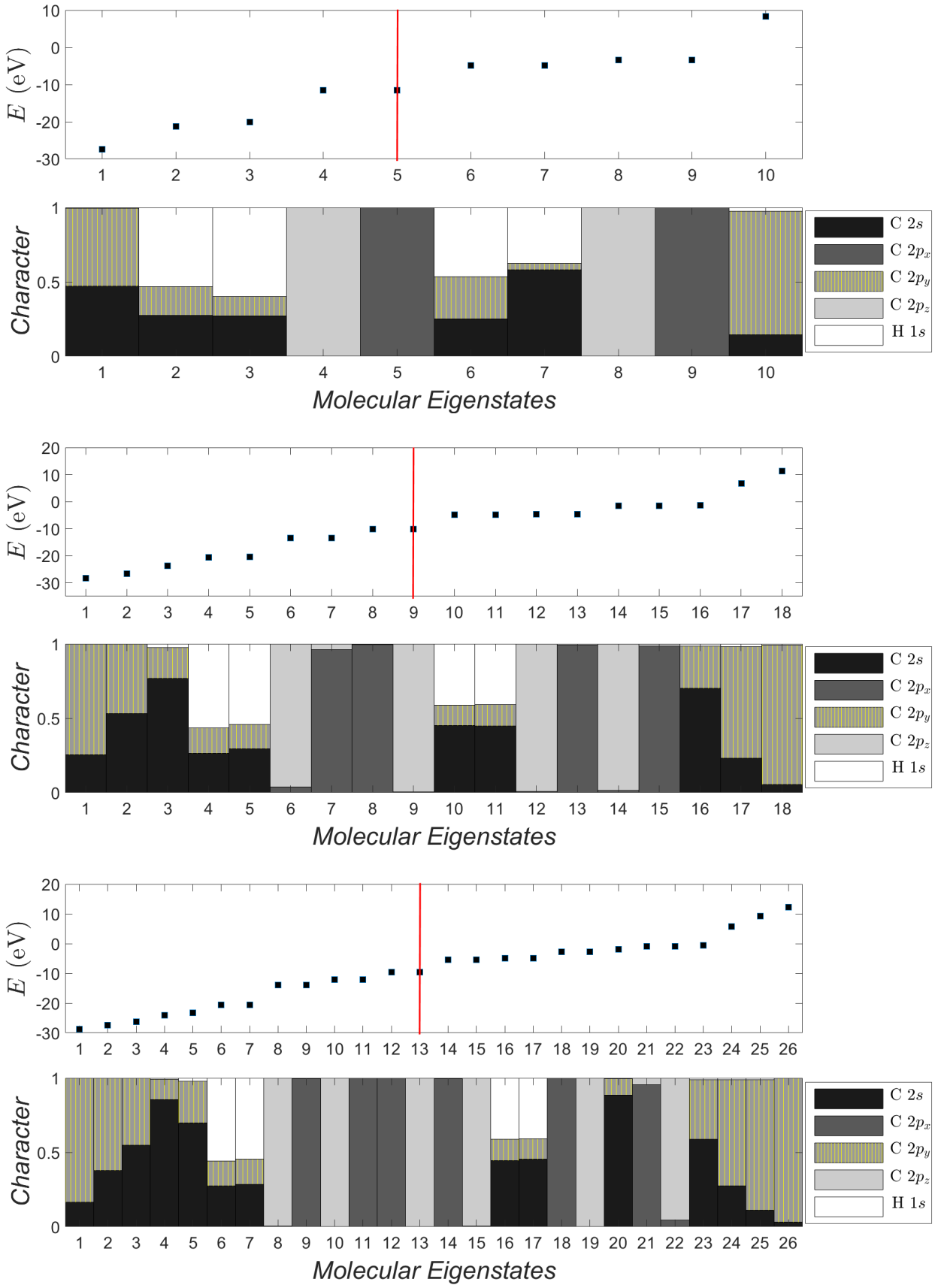


Fig. S1 Molecular eigenstates of *polnsl* molecules with $n = 2,4,6$. Eigenenergies together with *character*, i.e., analysis of molecular states into atomic valence states.

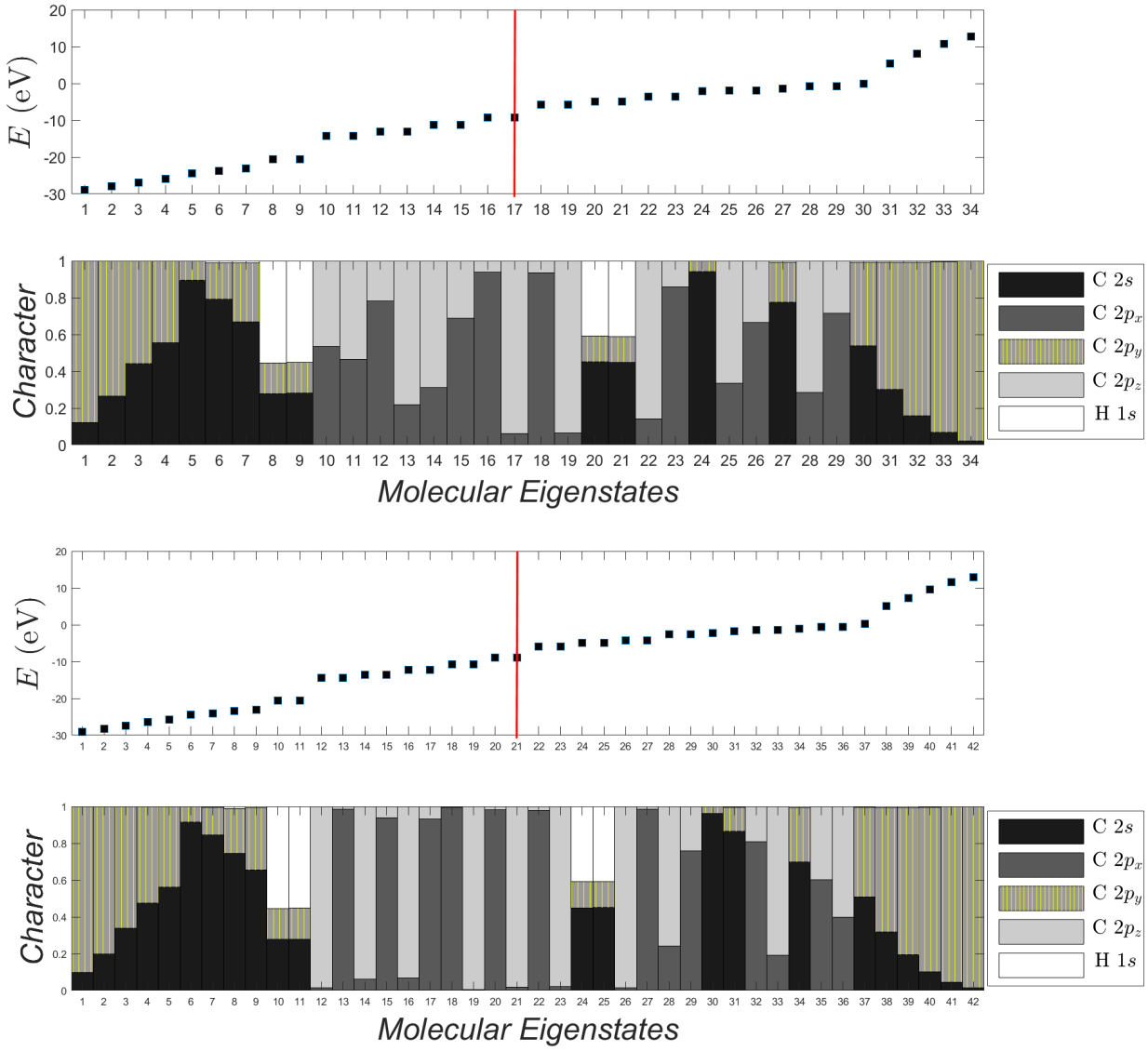
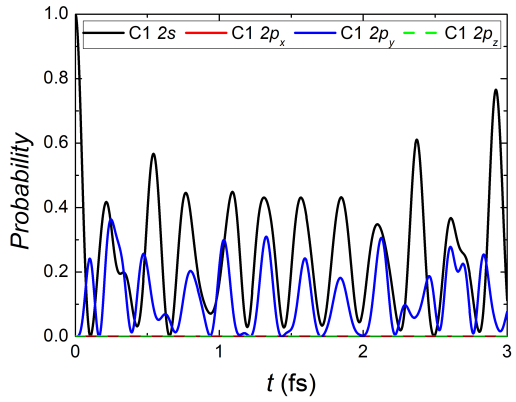
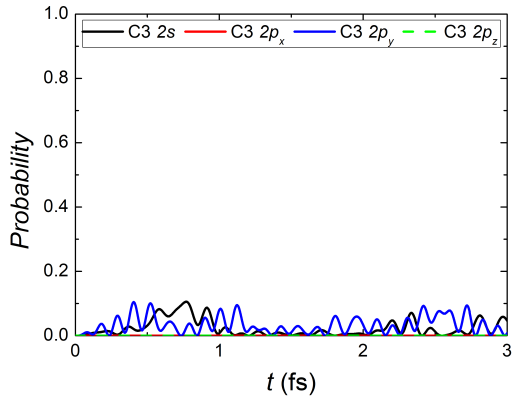


Fig. S1 Molecular eigenstates of *polnsl* molecules with $n = 8, 10$. Eigenenergies together with *character*, i.e., analysis of molecular states into atomic valence states.





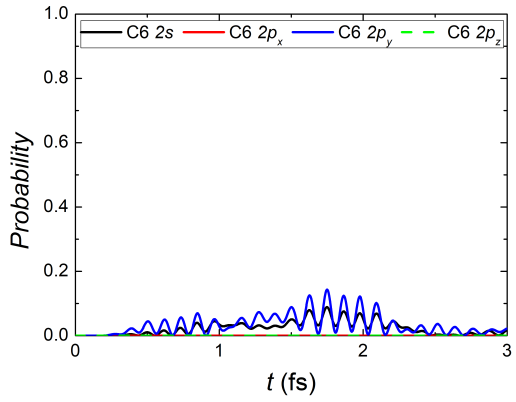
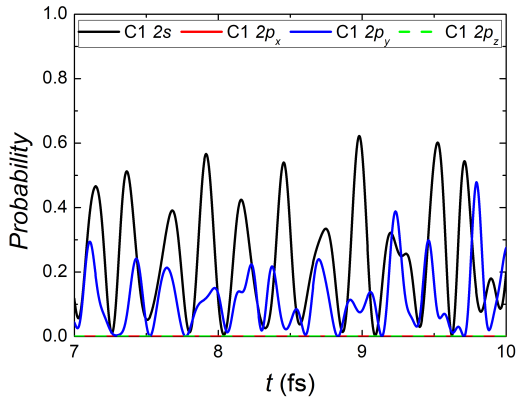
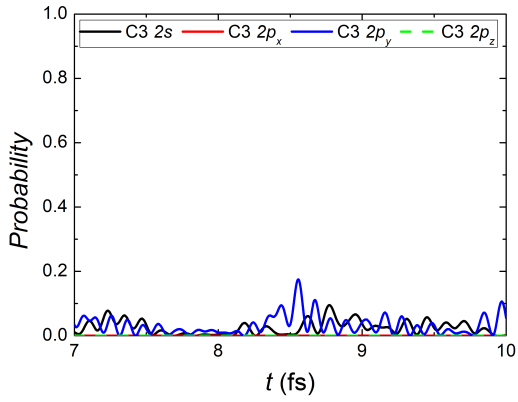


Fig. S2 A snapshot, for the initial 3 femtoseconds, of the time-dependent probabilities at C_1, C_3 and C_6 orbitals, for initial placement of the hole at $2s$ orbital of C_1, in *pol6sl*. The $2p_x$ and $2p_z$ time-dependent probabilities remain zero. An sp path is activated in this case: only $2s$ and $2p_y$ orbitals have significant probabilities.





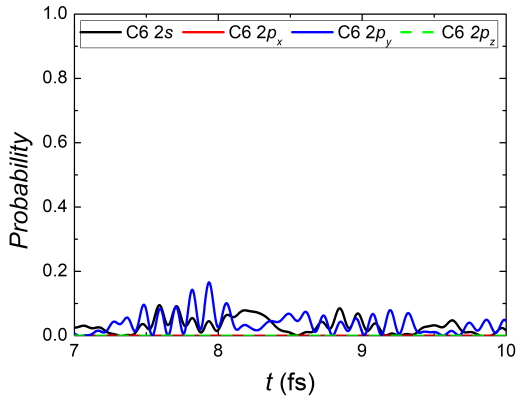


Fig. S3 A snapshot, for the time interval from 7 to 10 femtoseconds, of the time-dependent probabilities at C_1, C_3 and C_6 orbitals, for initial placement of the hole at $2s$ orbital of C_1, in *pol6sl*. The $2p_x$ and $2p_z$ time-dependent probabilities remain zero. An sp path is activated in this case: only $2s$ and $2p_y$ orbitals have significant probabilities.

2 Dicyanopolyynes

Figure S4 shows the molecular states of *dicyano-n-polyynes* with $n = 2,4,6,8,10$. Eigenenergies and *character*, i.e., analysis of molecular states into atomic valence states.

Table S3 shows the Löwdin Population Analysis, at the B3LYP/STO-3G level of theory, for *dicyano-n-polyynes* molecules with $n = 2,4,6,8,10$. Table S4 shows the Löwdin Population Analysis (shell charges), for ground state (GS) and localised hole state (LHS), at nitrogen atom N_1 of *dicyano-n-polyynes* with $n = 2,4,6,8,10$, B3LYP/ STO-3G level of theory. The difference between GS and LHS is also shown.

Table S3 Löwdin Population Analysis, at the B3LYP/STO-3G level of theory for *dicyano-n-polyynes* with $n = 2,4,6,8,10$.

atom	neutral	*dicyano2*	*dicyano4*	*dicyano6*	*dicyano8*	*dicyano10*
N1	7	7.04	7.05	7.06	7.06	7.07
C2	6	5.96	5.96	5.97	5.97	5.97
C3	6	5.96	5.98	5.99	6.00	6.00
C4	6	-	5.98	5.98	5.98	5.98
C5	6	-	5.96	5.98	5.99	5.99
C6	6	-	-	5.99	5.99	5.99
C7	6	-	-	5.97	5.98	5.99
C8	6	-	-	-	6.00	5.99
C9	6	-	-	-	5.97	5.98
C10	6	-	-	-	-	6.00
C11	6	-	-	-	-	5.97
N_{n+2}	7	7.04	7.06	7.06	7.06	7.07

Table S4 Löwdin Population Analysis (shell charges), for the ground state (GS) and the localised hole state (LHS), at nitrogen atom N_1 of *dicyano-n-polyynes* molecules with $n = 2,4,6,8,10$, B3LYP/ STO-3G level of theory. The difference between GS and LHS is also shown.

molecule	Löwdin Population Analysis			
	State	"1s"	"2s"	"2p"
dicyano2	GS	2.00	1.69	3.35
	LHS	2.00	1.67	2.37
	GS - LHS	0.00	0.02	0.98
dicyano4	GS	2.00	1.69	3.36
	LHS	2.00	1.52	2.53
	GS - LHS	0.00	0.17	0.83
dicyano6	Gs	2.00	1.69	3.37
	LHs	2.00	1.56	2.50
	GS - LHS	0.00	0.13	0.87
dicyano8	GS	2.00	1.69	3.37
	LHS	2.00	1.57	2.49
	GS - LHS	0.00	0.12	0.88
dicyano10	GS	2.00	1.69	3.37
	LHS	2.00	1.58	2.48
	GS - LHS	0.00	0.11	0.89

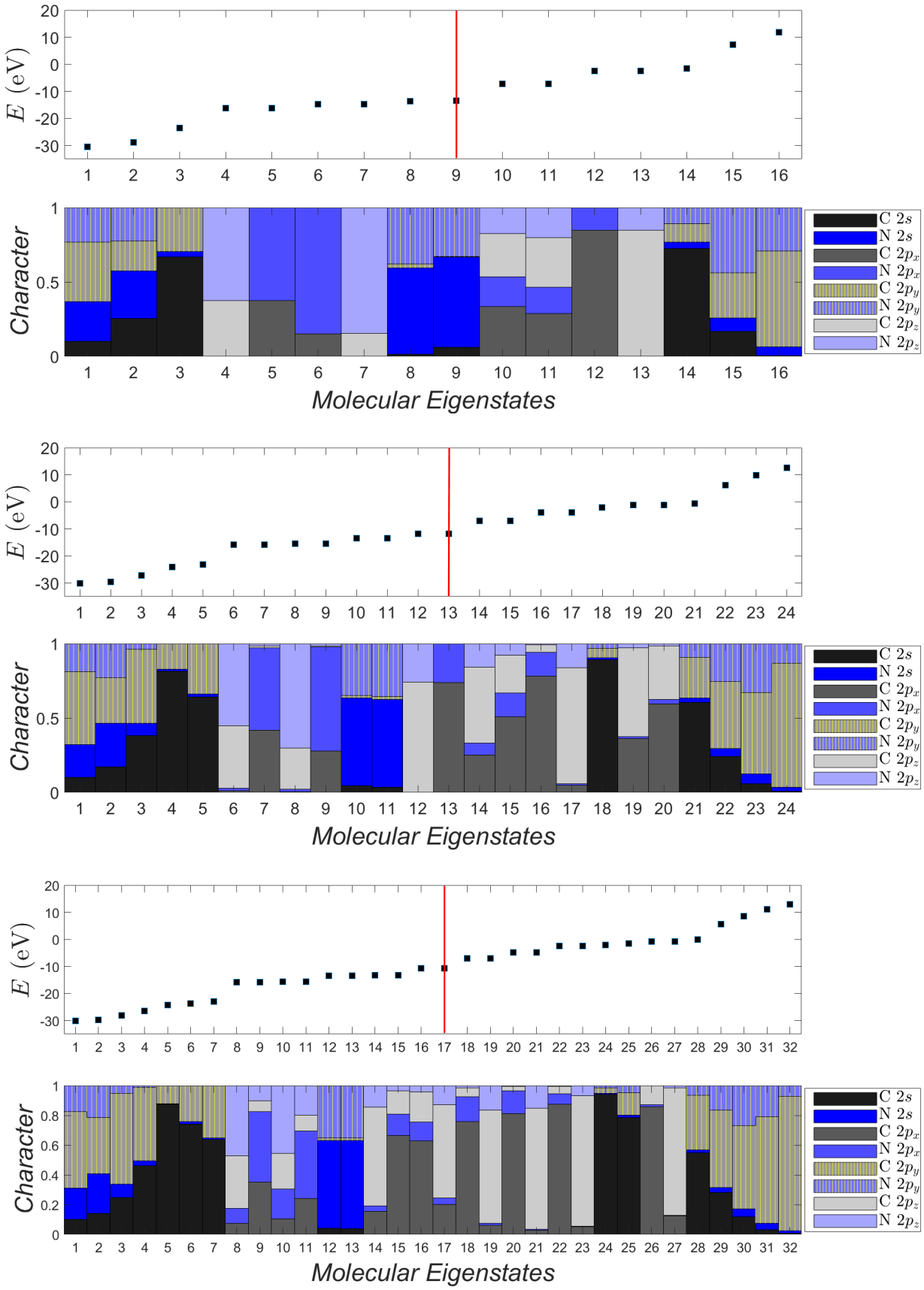


Fig. S4 Molecular eigenstates of *dicyano-n-polyynes* with $n = 2, 4, 6$. Eigenenergies and *character*, i.e., analysis of molecular states into atomic valence states.

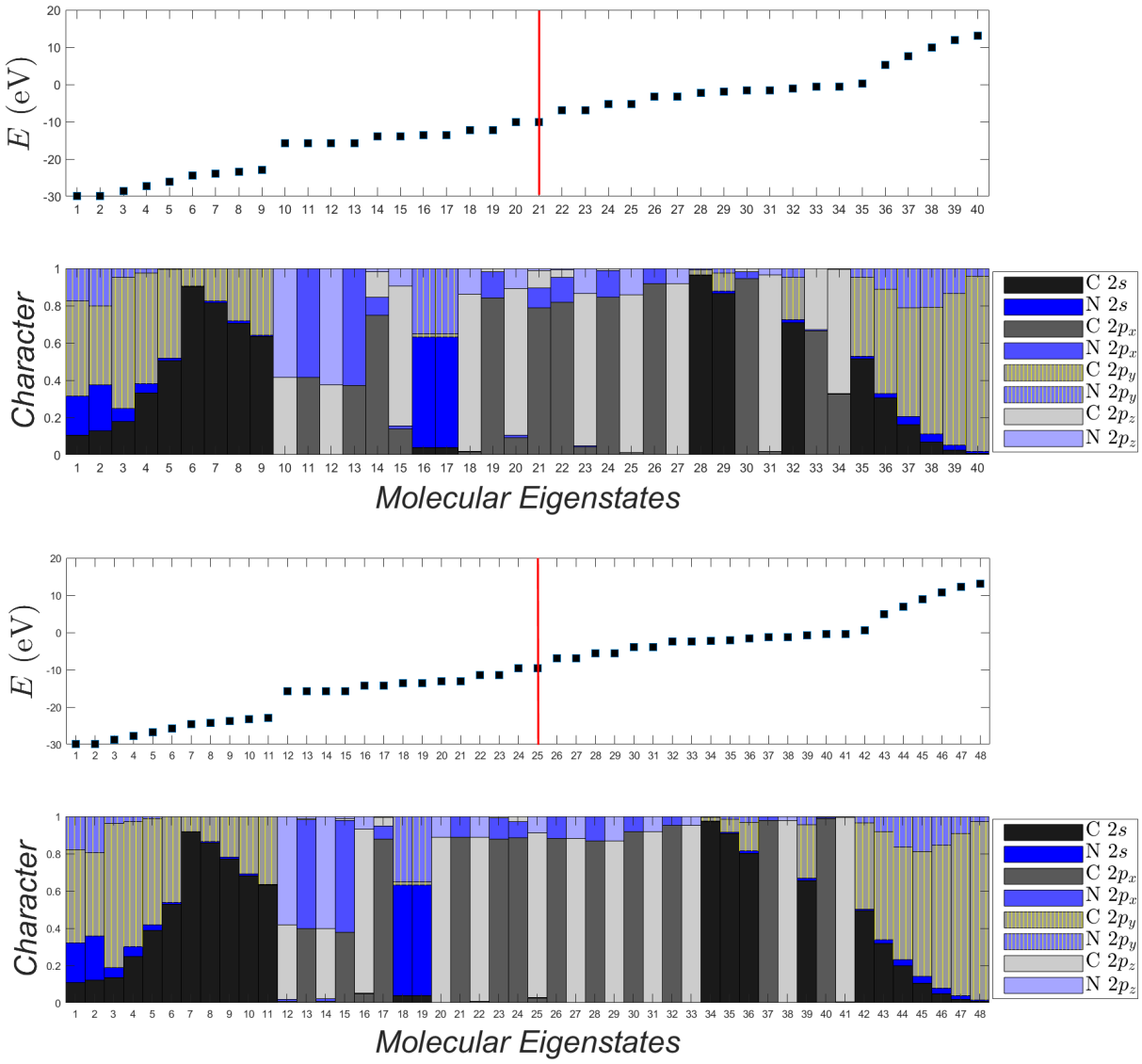


Fig. S4 Molecular eigenstates of *dicyano-n-polyynes* with $n = 8, 10$. Eigenenergies and *character*, i.e., analysis of molecular states into atomic valence states.

3 Comparison of polyynes to dicyanopolyynes

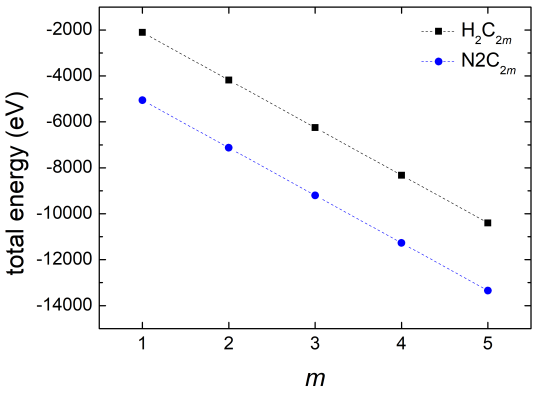


Fig. S5 Total DFT energies of the polyynes (H_2C_{2m}) and dicyanopolyynes (N_2C_{2m}, bottom), $n = 1,2,\ldots,5$, at the B3LYP/cc-pVTZ level of theory.

Results at different levels of theory converge nicely as we increase the basis set. A comparison of the total DFT energies of polyynes (H_2C_{2m}) and dicyanopolyynes (N_2C_{2m}) is shown in Fig. S5.

The HOMO and LUMO orbital energies of the dicyanopolyynic series (N_2C_{2m}), $m = 1,2,\ldots,5$, can be used to obtain the HOMO-LUMO gap. In Fig. S7, we use the largest of the basis sets used, cc-pVTZ, to illustrate the variation of the HOMO-LUMO gap increasing m.

HOMO-LUMO gaps of polyynes (H_2C_{2m}) and dicyanopolyynes (N_2C_{2m}), $n = 1,2,\ldots,5$, at the B3LYP/cc-pVTZ level of theory. Total DFT energies of the polyynes (H_2C_{2m}) and dicyanopolyynes (N_2C_{2m}, bottom), $n = 1,2,\ldots,5$, at the B3LYP/cc-pVTZ level of theory.

Contributions (one-electron terms, Coulomb repulsion, exchange correlation, nuclear repulsion) to the total DFT energies of the polyynic series ($C_{2m}H_2$, top) and the dicyanopolyynic series ($C_{2m}N_2$, bottom), for $n = 1,2,\ldots,5$, using the cc-pVTZ basis set.

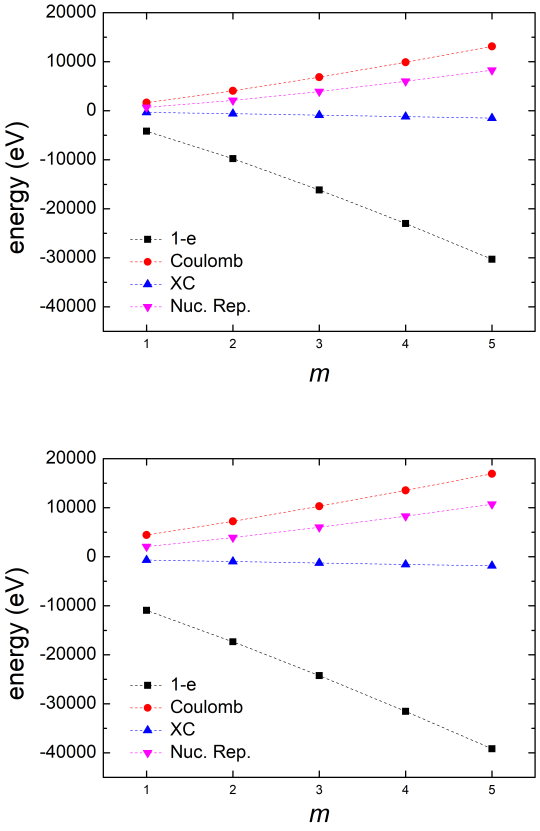


Fig. S6 Contributions (one-electron terms, Coulomb repulsion, exchange correlation, nuclear repulsion) to the total DFT energies of the polyynic series ($C_{2m}H_2$, top) and the dicyanopolyynic series ($C_{2m}N_2$, bottom), for $n = 1,2,\ldots,5$, using the cc-pVTZ basis set.

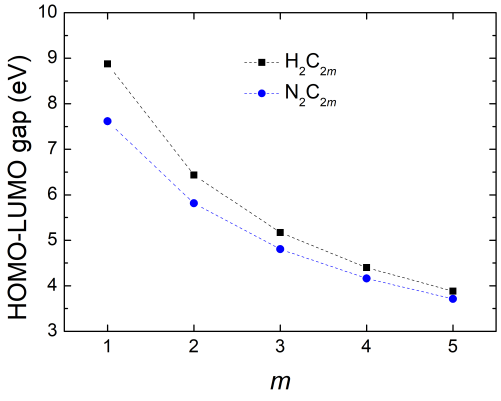


Fig. S7 HOMO-LUMO gaps of polyynes (H_2C_{2m}) and dicyanopolyynes (N_2C_{2m}), $n = 1,2,\ldots,5$, at the B3LYP/cc-pVTZ level of theory.