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

Electronic Supplementary Information for

Non-Aufbau orbital ordering and spin density modulation in high-spin donor–acceptor conjugated polymers

Md Abdus Sabuj, Obinna Muoh, Md Masrul Huda, and Neeraj Rai*

Dave C. Swalm School of Chemical Engineering, and Center for Advanced Vehicular Systems, Mississippi State University, Mississippi State, MS 39762, USA.

E-mail: neerajrai@che.msstate.edu

Table S1: Electronic properties calculated with HF and different grids with UB3LYP, performed on a dimer ($N = 2$) of CPDS-CBBT. HF calculations are performed on the UB3LYP optimized geometry. Energy values are provided in eV, and y_0 is a dimensionless quantity

Theory	Grid	ΔE_{ST}	HOMO	LUMO	E_{g}	y_0	$<S^2>$
HF	-	-0.681	-7.59	1.45	9.04	1.000	7.432
B3LYP	Fine	-5.4×10^{-4}	-4.64	-3.37	1.27	0.974	1.083
	UltraFine	-5.3×10^{-4}	-4.64	-3.37	1.27	0.974	1.083
	SuperFine	-5.3×10^{-4}	-4.64	-3.37	1.27	0.974	1.083

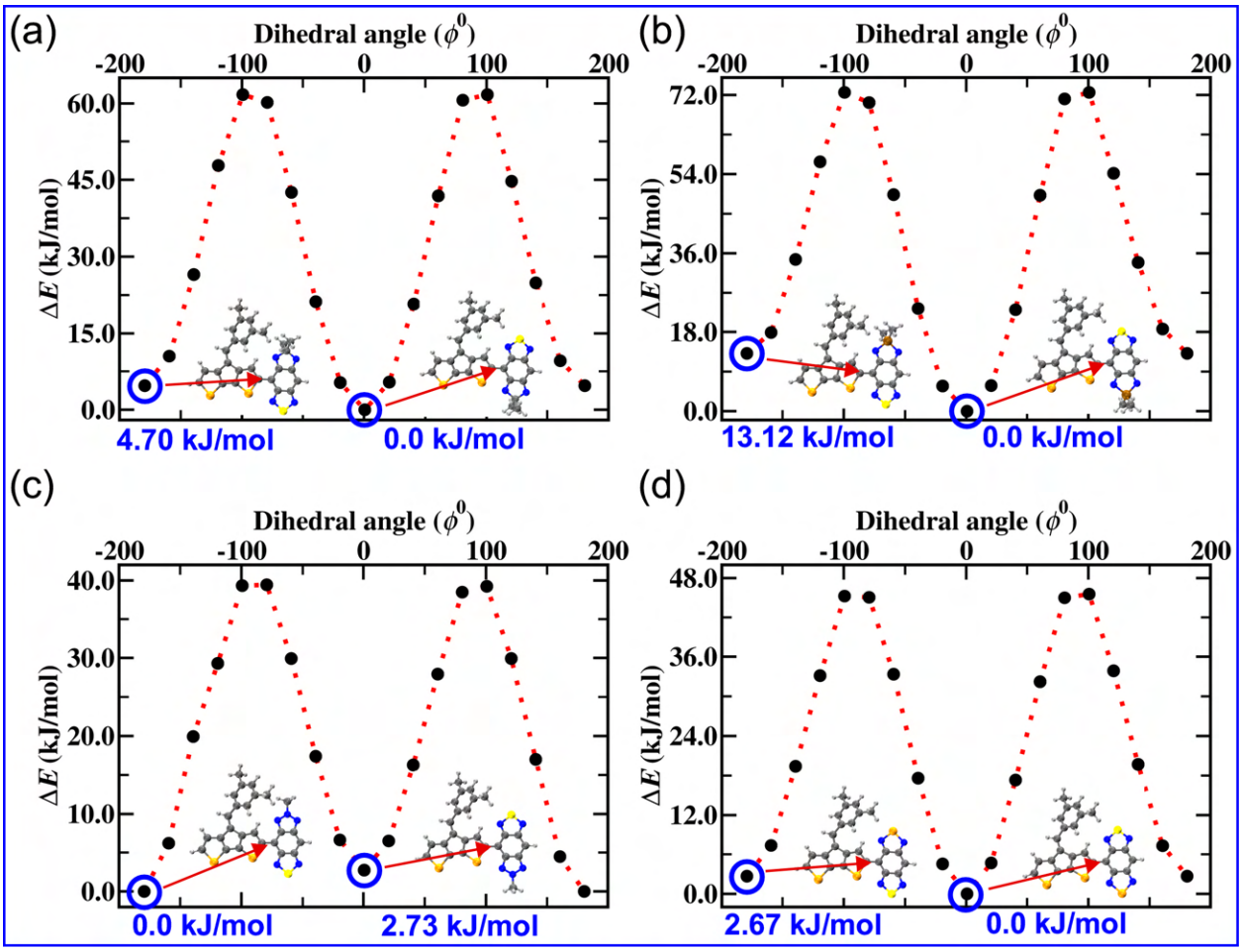
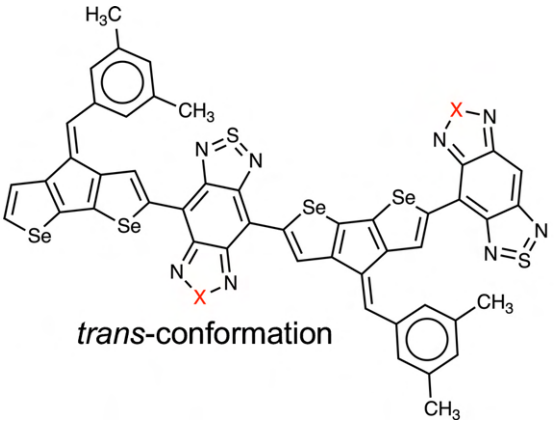


Figure S1: Dihedral scan along the annular bond connecting a donor and acceptor units of the (a) CPDS-CBBT, (b) CPDS-SiBBT, (c) CPDS-NBBT, and (d) CPDS-SeBBT ($N = 1$) polymers in their singlet closed-shell state ($S = 0$).



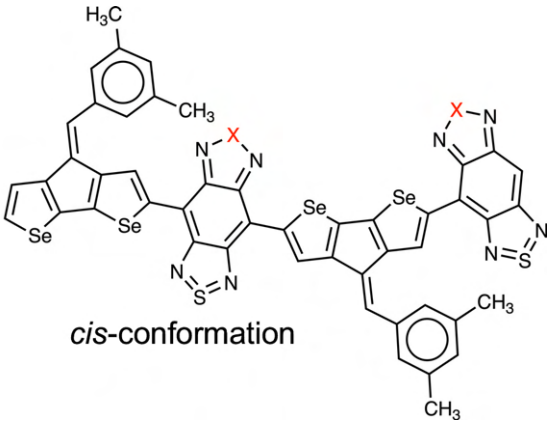


Table S2: Stability energy and singlet-triplet energy gap of the polymers ($N = 2$) with different orientations of the thiadiazole units.

Oligomer ($N = 2$)	Stability Energy (kcal/mol)		ΔE_{ST} (eV)	
	trans-	*cis-*	*trans-*	*cis-*
CPDS-CBBT	0.00	+0.68	-5.33 $\times 10^{-4}$	-5.96 $\times 10^{-4}$
CPDS-SiBBT	0.00	+0.22	+3.90 $\times 10^{-4}$	+3.62 $\times 10^{-4}$
CPDS-NBBT	0.00	+0.80	-2.13 $\times 10^{-1}$	-2.17 $\times 10^{-1}$
CPDS-SeBBT	+0.25	0.00	-1.86 $\times 10^{-2}$	-1.85 $\times 10^{-2}$

Table S3: Electronic properties computed at (U)B3LYP/6-31G(d,p) level of theory and basis set for the CPDS-CBBT, CPDS-SiBBT, CPDS-NBBT, and CPDS-SeBBT polymers, provided as a function of chain length (N). The singlet–triplet energy gap (ΔE_{ST}), population (P_{T}) of the triplet ($S = 1$) state at room temperature, energy of the FMOs, energetic difference between the FMOs (E_{g}), and diradical character index (y_0). Energy values are provided in eV, and y_0 is a dimensionless quantity.

Polymer	N	ΔE_{ST}	P_{T}	HOMO	LUMO	E_{g}	y_0
CPDS-CBBT	1	-9.23×10^{-2}	9.35	−4.79	−3.25	1.55	0.617
	2	-5.33×10^{-4}	74.63	−4.64	−3.37	1.27	0.974
	3	$+7.07 \times 10^{-6}$	75.00	−4.60	−3.40	1.20	0.998
	4	$+2.72 \times 10^{-7}$	75.00	−4.58	−3.41	1.17	1.000
	5	0.00×10^{-0}	75.00	−4.57	−3.42	1.16	1.000
	6	0.00×10^{-0}	75.00	−4.57	−3.42	1.15	1.000
	7	0.00×10^{-0}	75.00	−4.57	−3.42	1.14	1.000
	8	0.00×10^{-0}	75.00	−4.57	−3.43	1.14	1.000
CPDS-SiBBT	1	-2.33×10^{-2}	55.99	−4.78	−3.42	1.37	0.787
	2	$+3.90 \times 10^{-4}$	75.27	−4.69	−3.49	1.20	0.999
	3	-8.44×10^{-6}	74.99	−4.66	−3.52	1.14	1.000
	4	0.00×10^{-0}	75.00	−4.64	−3.53	1.11	1.000
	5	0.00×10^{-0}	75.00	−4.63	−3.54	1.09	1.000
	6	0.00×10^{-0}	75.00	−4.63	−3.54	1.08	1.000
	7	0.00×10^{-0}	75.00	−4.62	−3.55	1.08	1.000
	8	0.00×10^{-0}	75.00	−4.62	−3.55	1.07	1.000
CPDS-NBBT	1	-6.57×10^{-1}	0.00	−4.80	−2.89	1.91	0.000
	2	-2.13×10^{-1}	0.12	−4.35	−3.11	1.24	0.193
	3	-7.49×10^{-2}	16.08	−4.22	−3.16	1.05	0.610
	4	-2.78×10^{-2}	51.93	−4.15	−3.19	0.96	0.838
	5	-1.05×10^{-2}	67.08	−4.11	−3.21	0.90	0.938
	6	-4.01×10^{-3}	72.14	−4.09	−3.22	0.87	0.977
	7	-1.53×10^{-3}	73.93	−4.07	−3.23	0.85	0.991
	8	-5.82×10^{-4}	74.60	−4.07	−3.23	0.85	0.997
CPDS-SeBBT	1	-2.62×10^{-1}	0.02	−4.89	−3.28	1.61	0.244
	2	-1.86×10^{-2}	60.27	−4.60	−3.45	1.16	0.832
	3	-1.09×10^{-3}	74.24	−4.52	−3.47	1.05	0.971
	4	-5.88×10^{-5}	74.96	−4.49	−3.48	1.00	0.995
	5	-2.99×10^{-5}	74.99	−4.47	−3.49	0.98	0.999
	6	0.00×10^{-0}	75.00	−4.46	−3.49	0.97	1.000
	7	0.00×10^{-0}	75.00	−4.45	−3.50	0.95	1.000
	8	0.00×10^{-0}	75.00	−4.45	−3.50	0.95	1.000

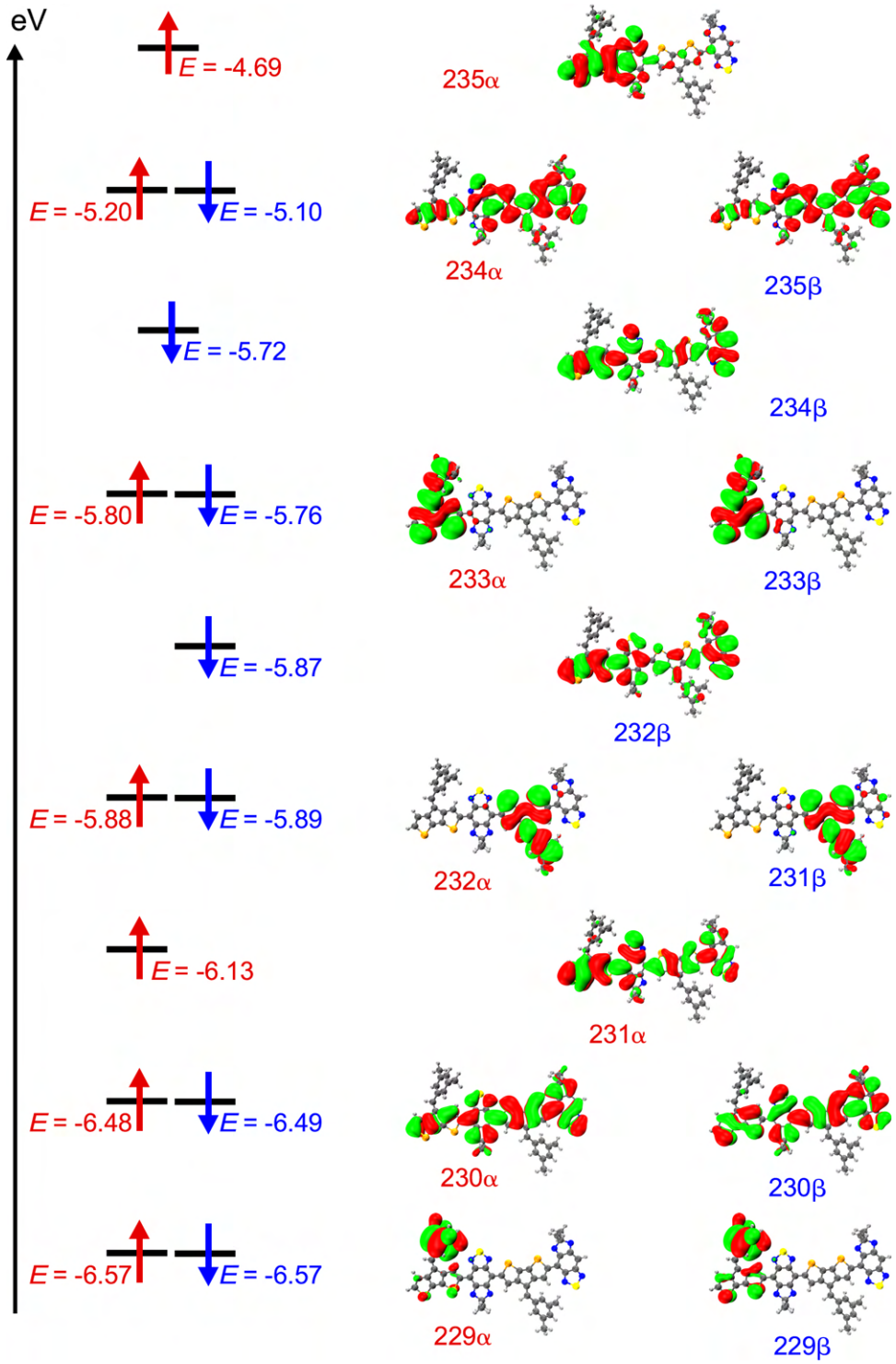


Figure S2: Molecular orbitals (MOs) and their energies at the singlet ($S = 0$) state for CPDS-CBBT dimer ($N = 2$). The green and red surfaces represent positive and negative contributions of the MOs at an isovalue = 0.01 au.

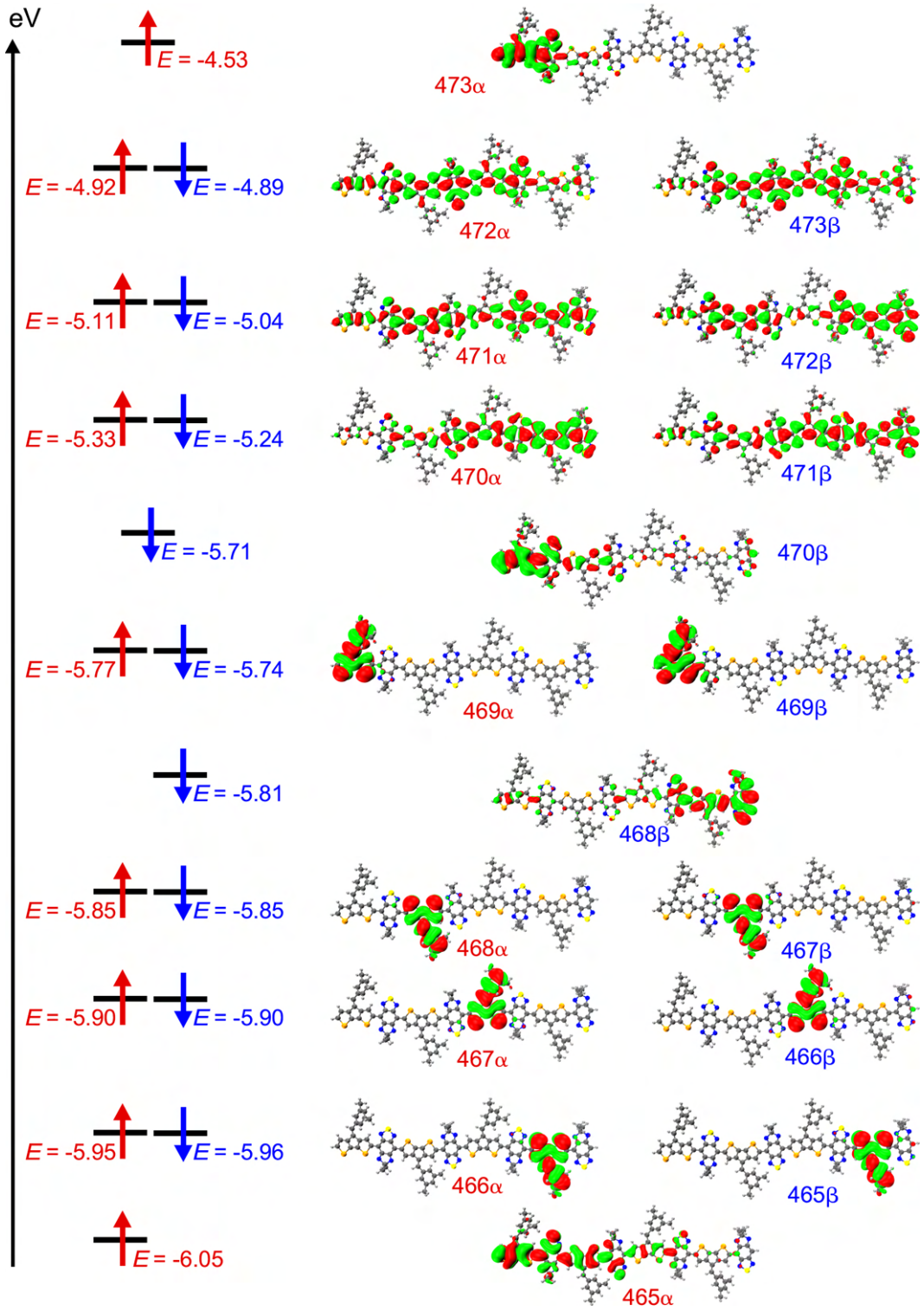


Figure S3: Molecular orbitals (MOs) and their energies at the singlet ($S = 0$) state for CPDS-CBBT tetramer ($N = 4$). The green and red surfaces represent positive and negative contributions of the MOs at an isovalue = 0.01 au.

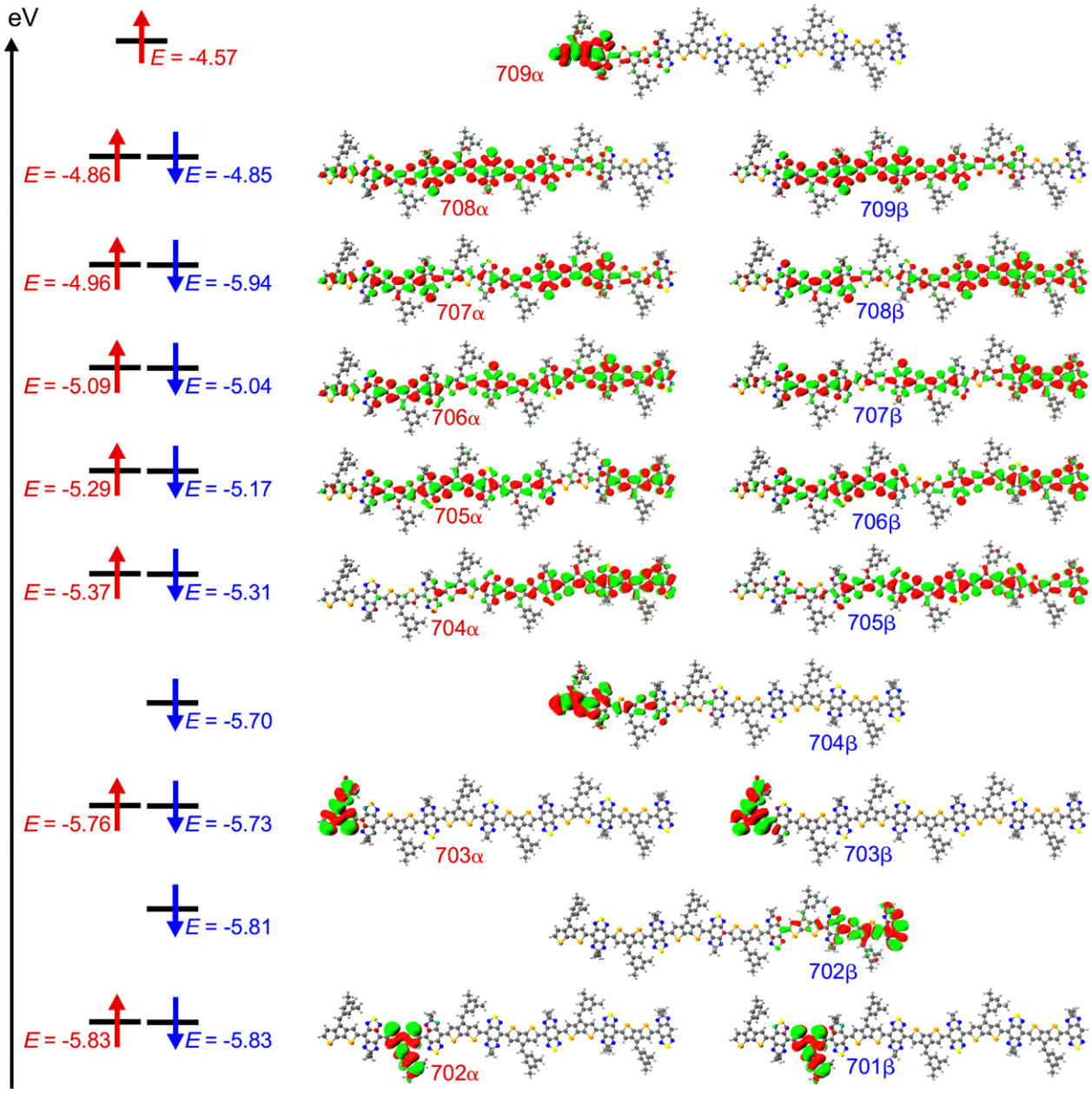


Figure S4: Molecular orbitals (MOs) and their energies at the singlet ($S = 0$) state for CPDS-CBBT hexamer ($N = 6$). The green and red surfaces represent positive and negative contributions of the MOs at an isovalue = 0.01 au.

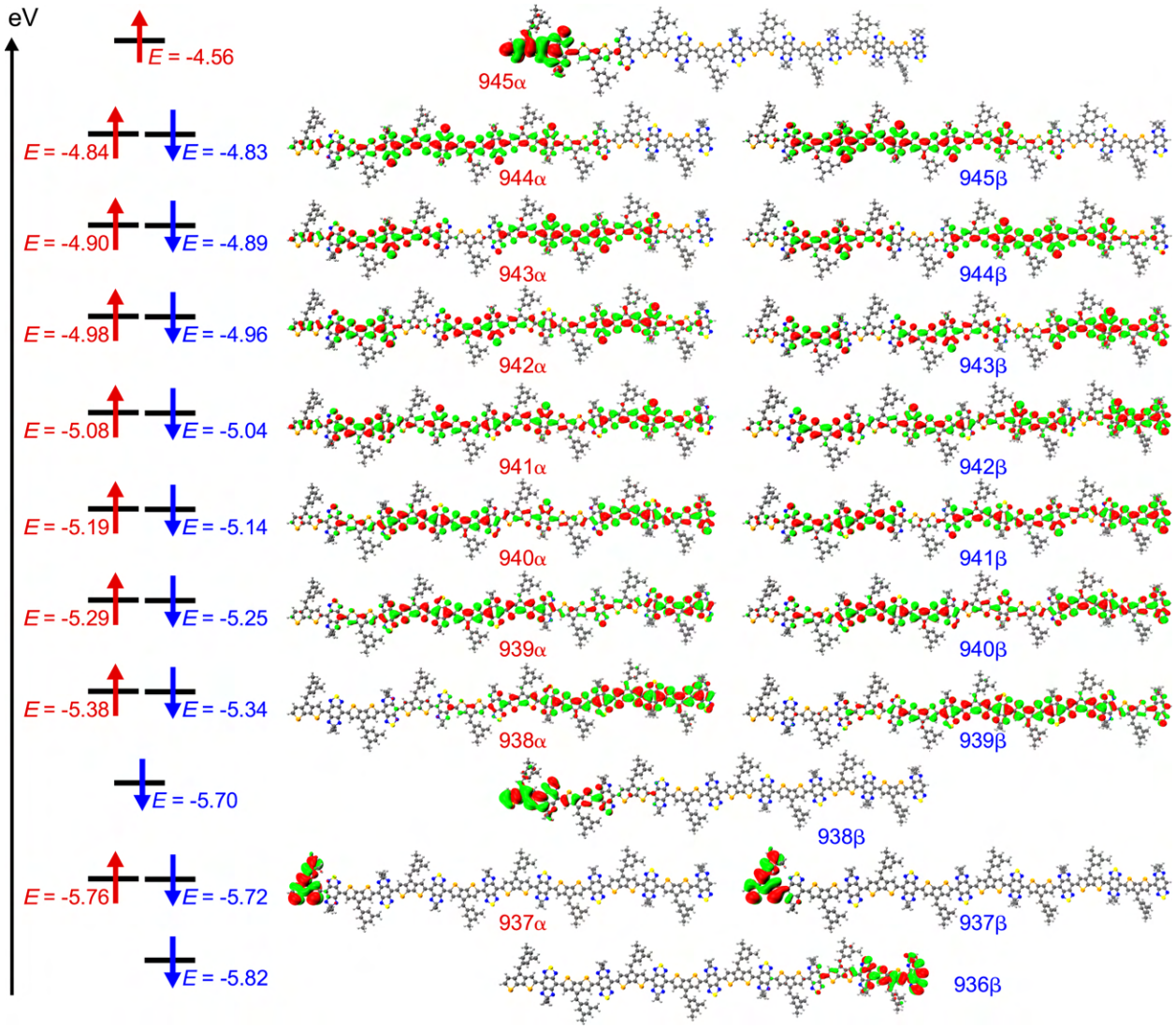


Figure S5: Molecular orbitals (MOs) and their energies at the singlet ($S = 0$) state for CPDS-CBBT octamer ($N = 8$). The green and red surfaces represent positive and negative contributions of the MOs at an isovalue = 0.01 au.

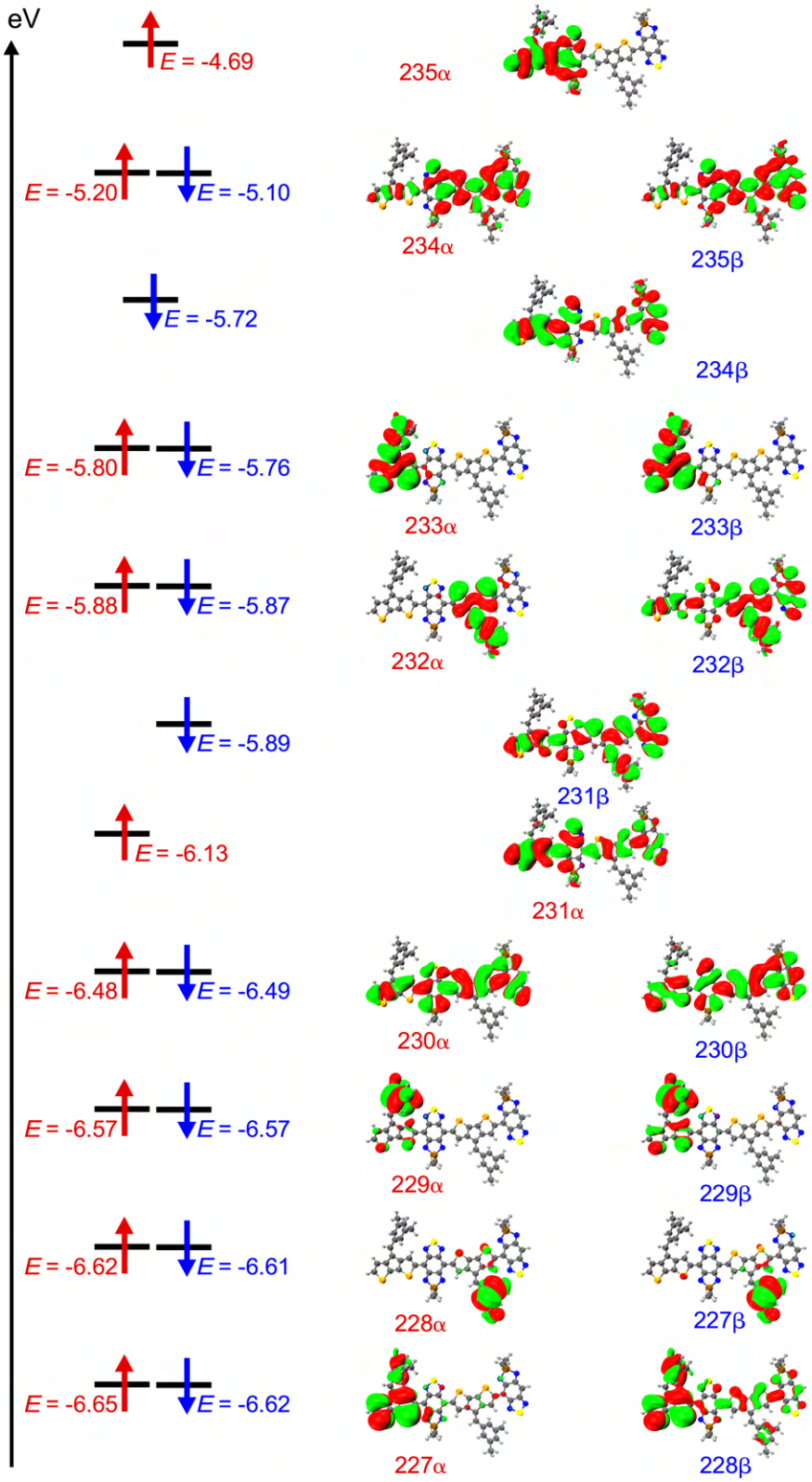


Figure S6: Molecular orbitals (MOs) and their energies at the singlet ($S = 0$) state for CPDS-SiBBT dimer ($N = 2$). The green and red surfaces represent positive and negative contributions of the MOs at an isovalue = 0.01 au.

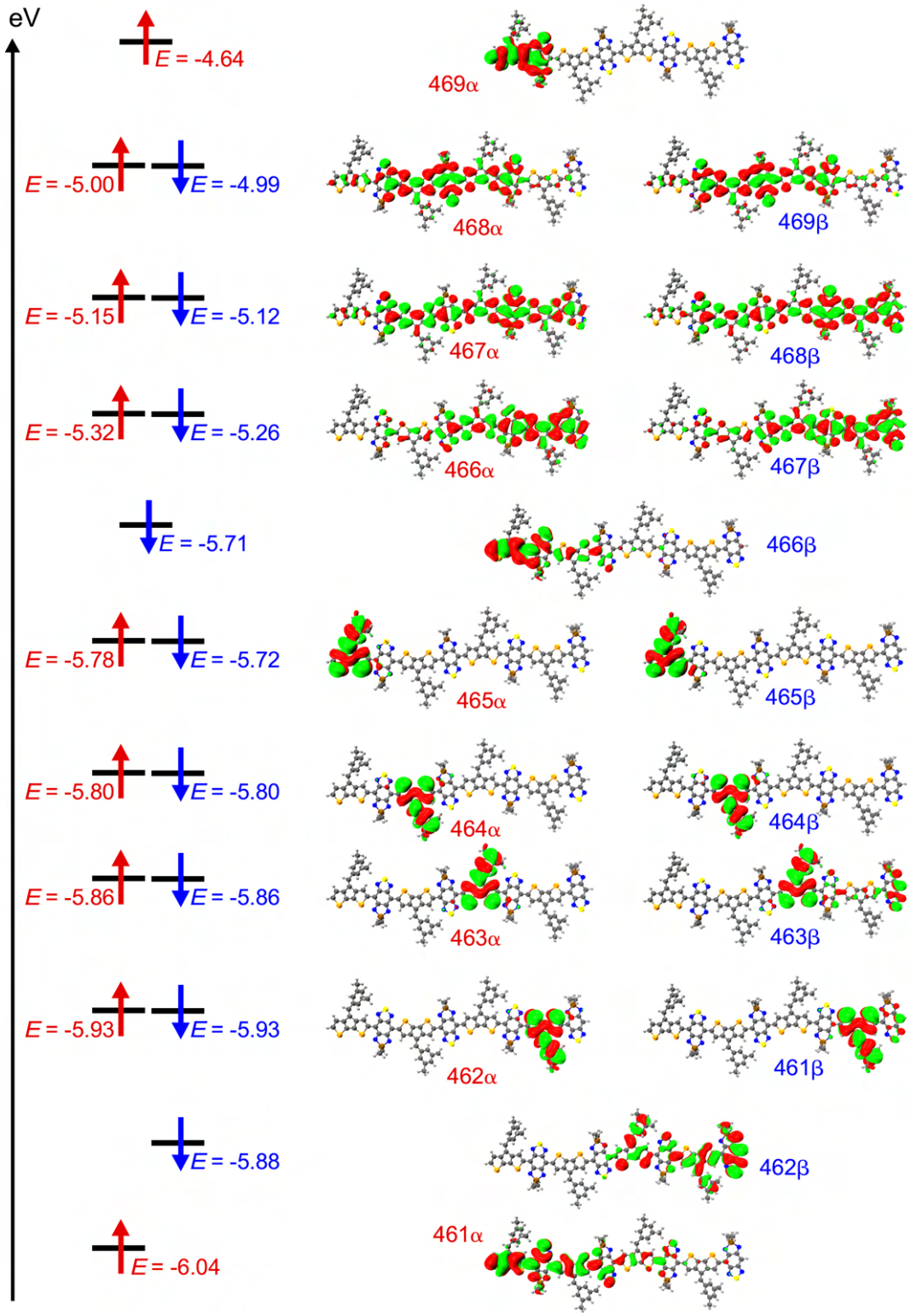


Figure S7: Molecular orbitals (MOs) and their energies at the singlet ($S = 0$) state for CPDS-SiBBT tetramer ($N = 4$). The green and red surfaces represent positive and negative contributions of the MOs at an isovalue = 0.01 au.

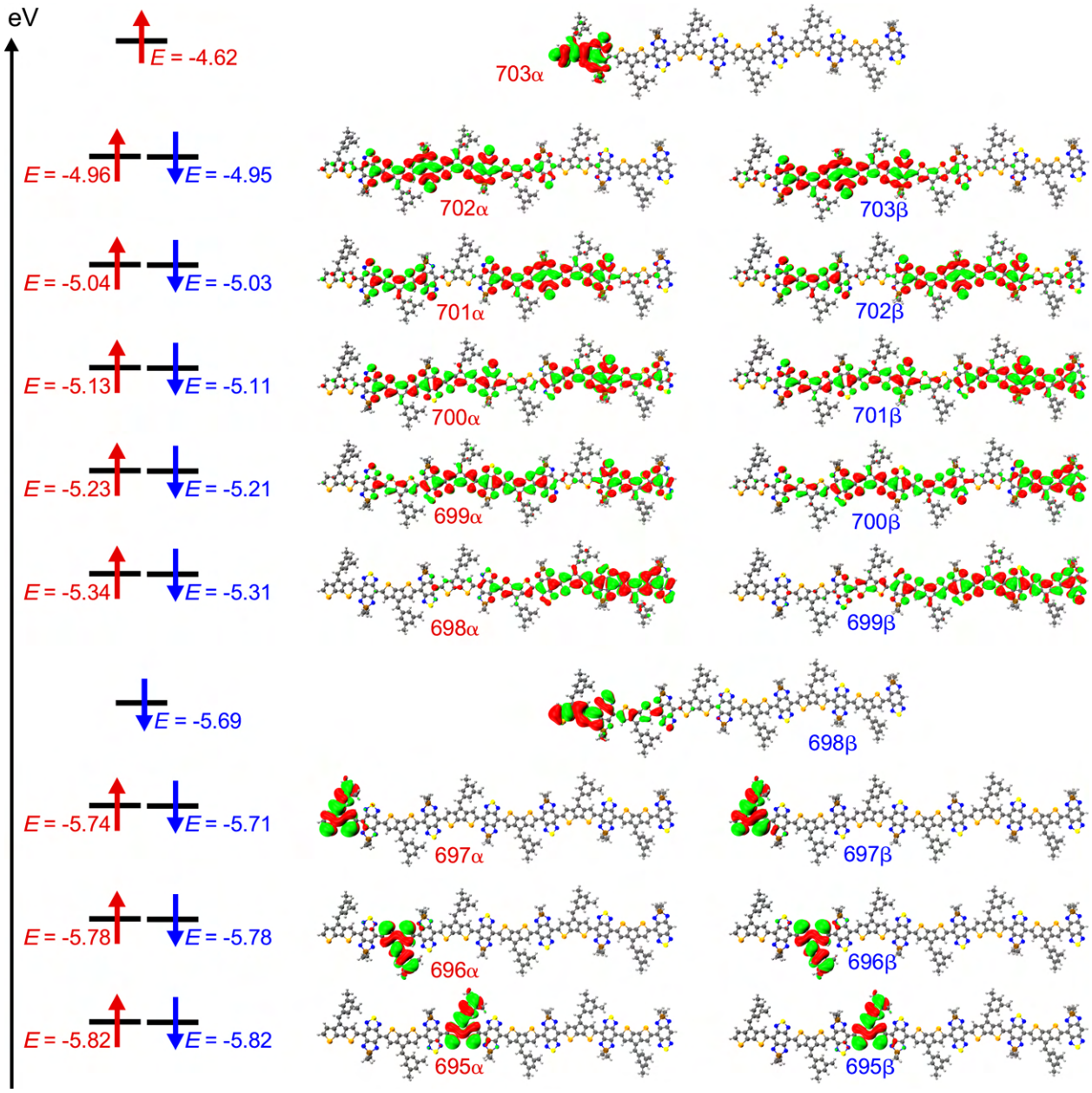


Figure S8: Molecular orbitals (MOs) and their energies at the singlet ($S = 0$) state for CPDS-SiBBT hexamer ($N = 6$). The green and red surfaces represent positive and negative contributions of the MOs at an isovalue = 0.01 au.

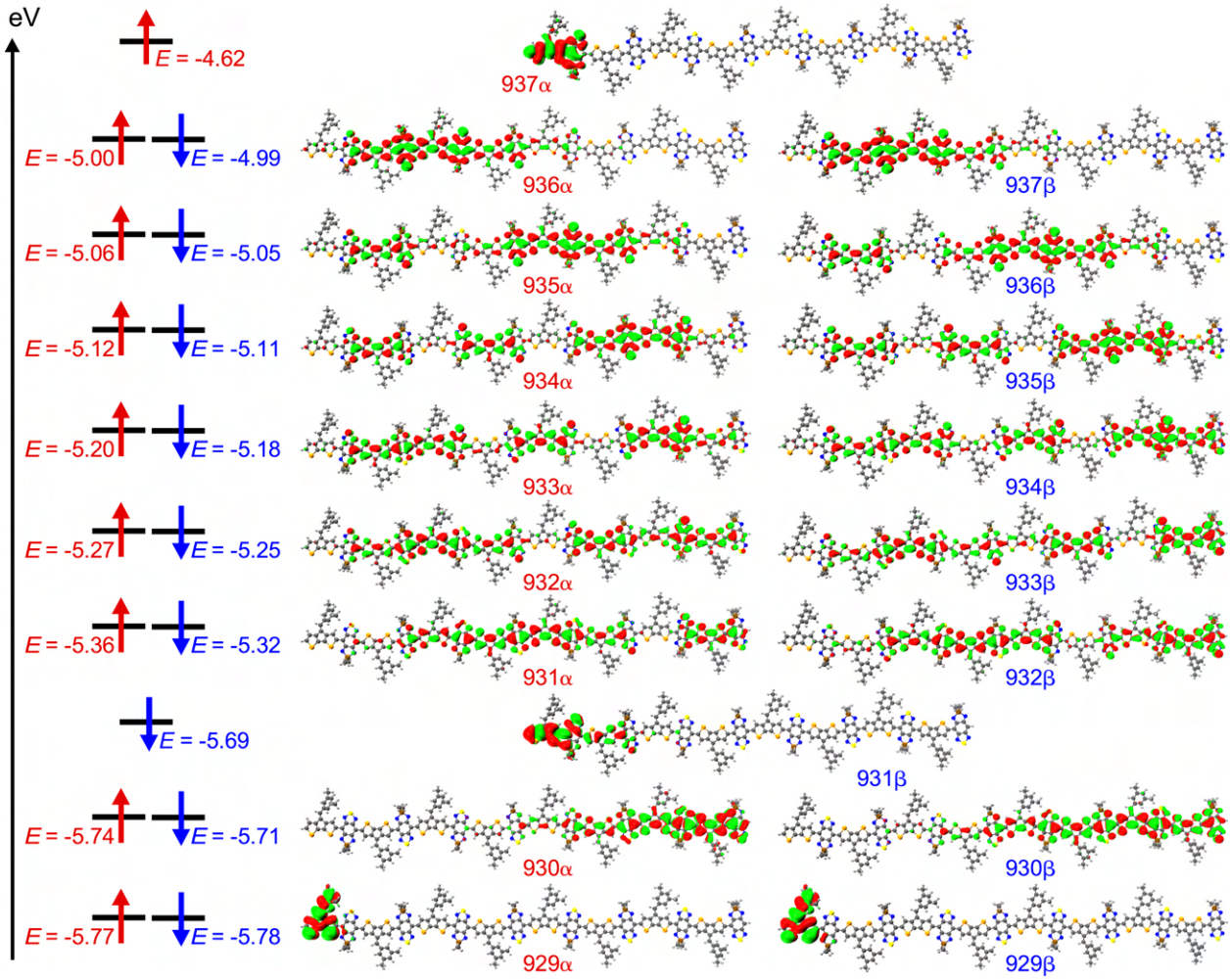


Figure S9: Molecular orbitals (MOs) and their energies at the singlet ($S = 0$) state for CPDS-SiBBT octamer ($N = 8$). The green and red surfaces represent positive and negative contributions of the MOs at an isovalue = 0.01 au.

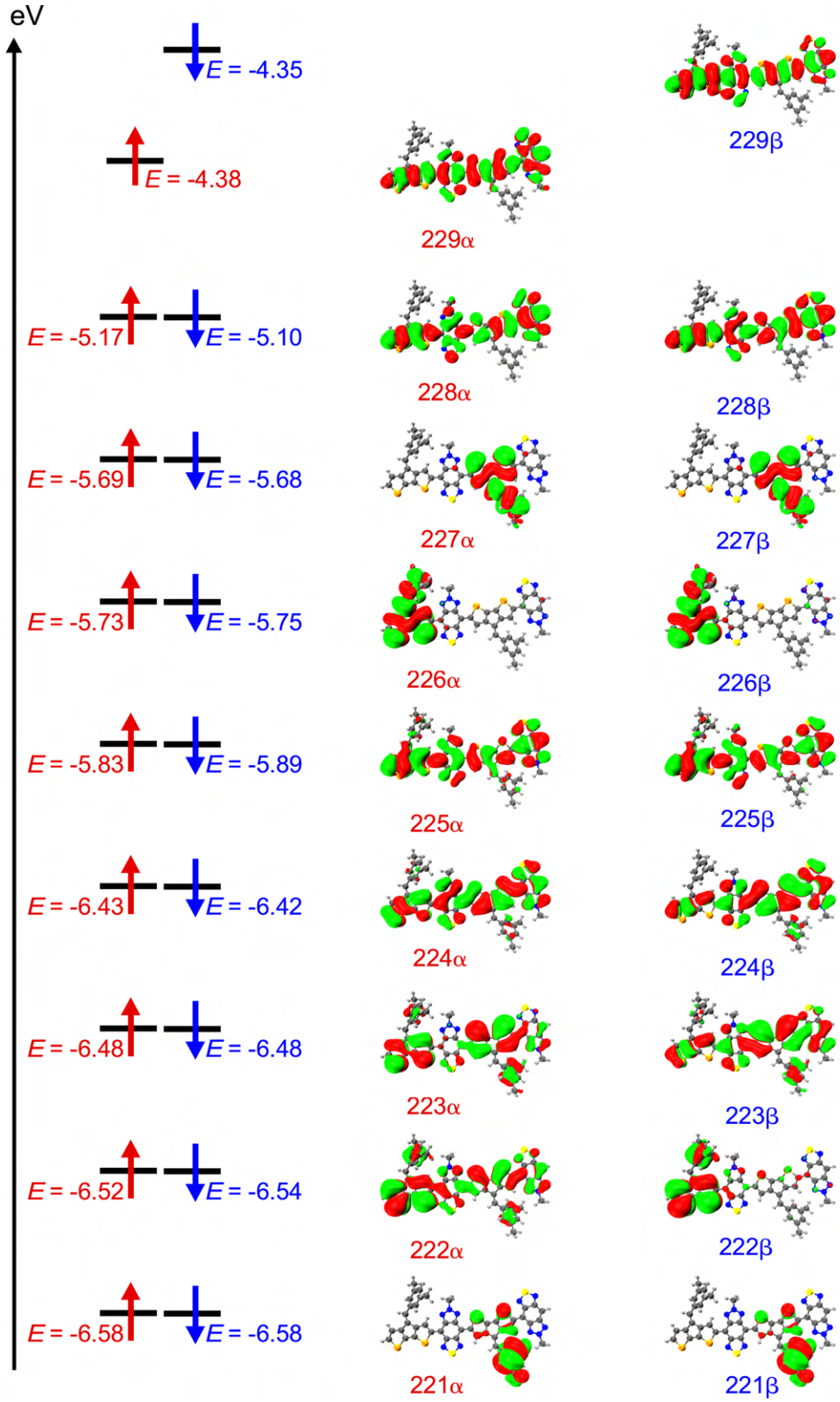


Figure S10: Molecular orbitals (MOs) and their energies at the singlet ($S = 0$) state for CPDS-NBBT dimer ($N = 2$). The green and red surfaces represent positive and negative contributions of the MOs at an isovalue = 0.01 au.

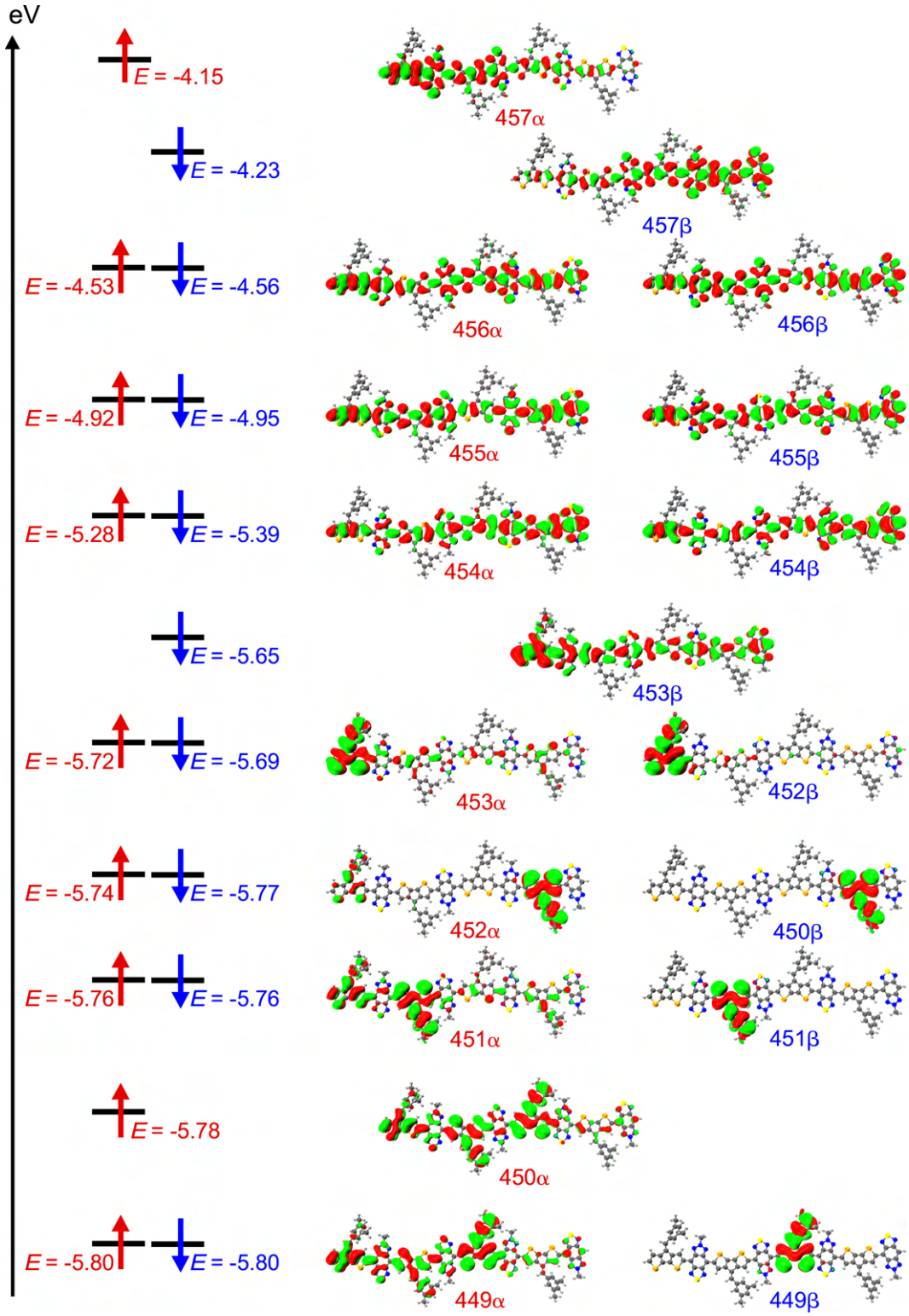


Figure S11: Molecular orbitals (MOs) and their energies at the singlet ($S = 0$) state for CPDS-NBBT tetramer ($N = 4$). The green and red surfaces represent positive and negative contributions of the MOs at an isovalue = 0.01 au.

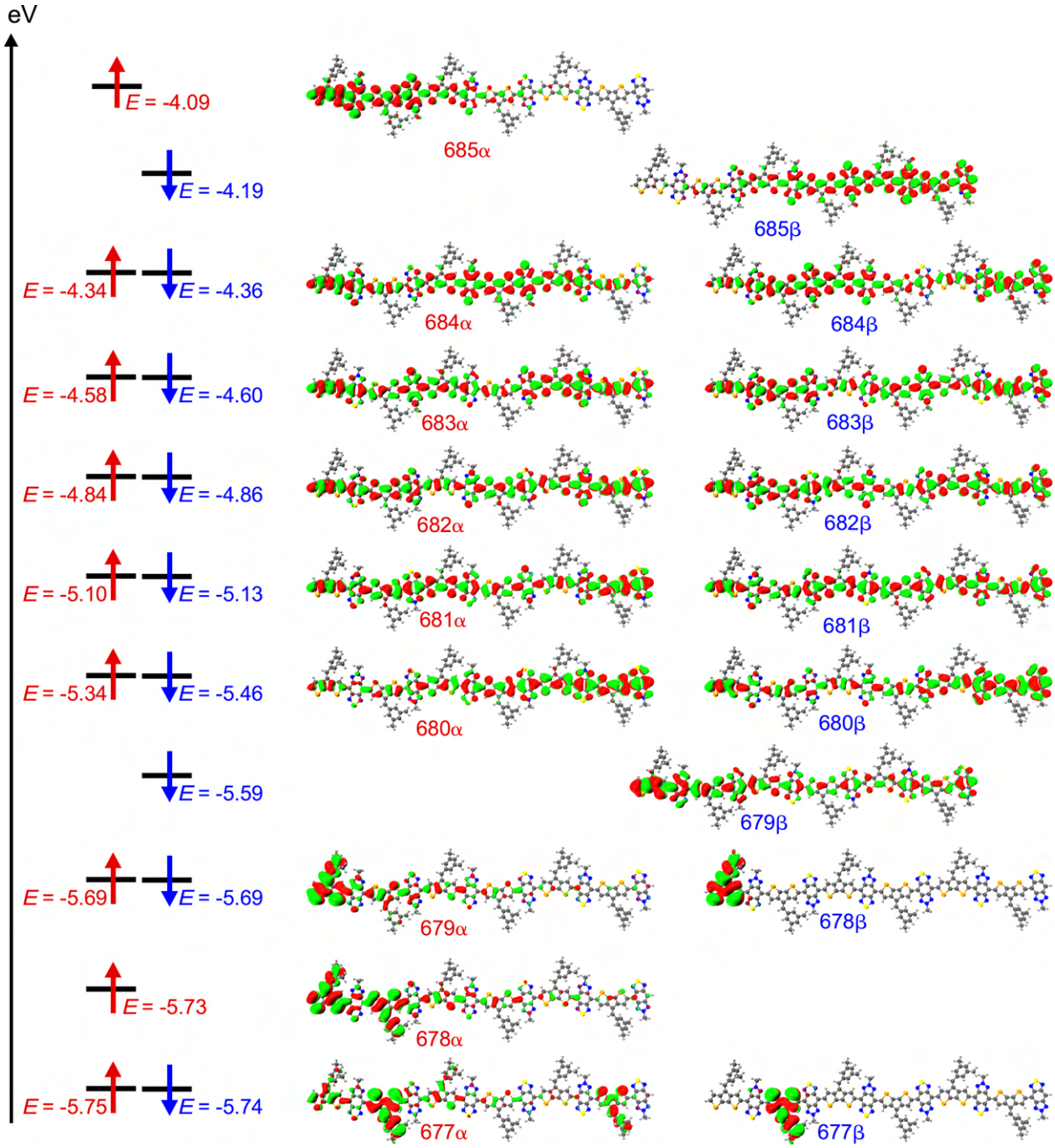


Figure S12: Molecular orbitals (MOs) and their energies at the singlet ($S = 0$) state for CPDS-NBBT hexamer ($N = 6$). The green and red surfaces represent positive and negative contributions of the MOs at an isovalue = 0.01 au.

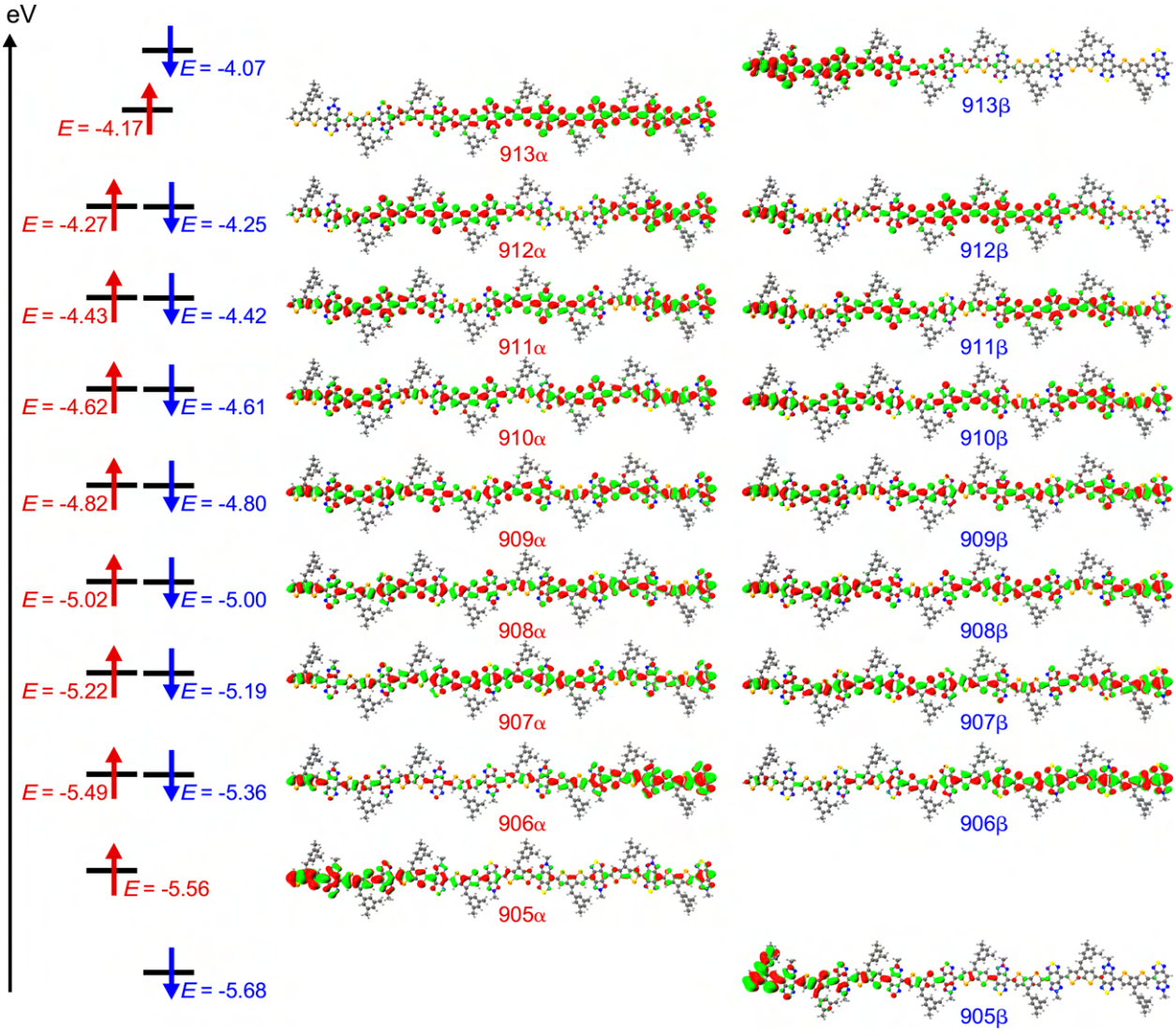


Figure S13: Molecular orbitals (MOs) and their energies at the singlet ($S = 0$) state for CPDS-NBBT octamer ($N = 8$). The green and red surfaces represent positive and negative contributions of the MOs at an isovalue = 0.01 au.

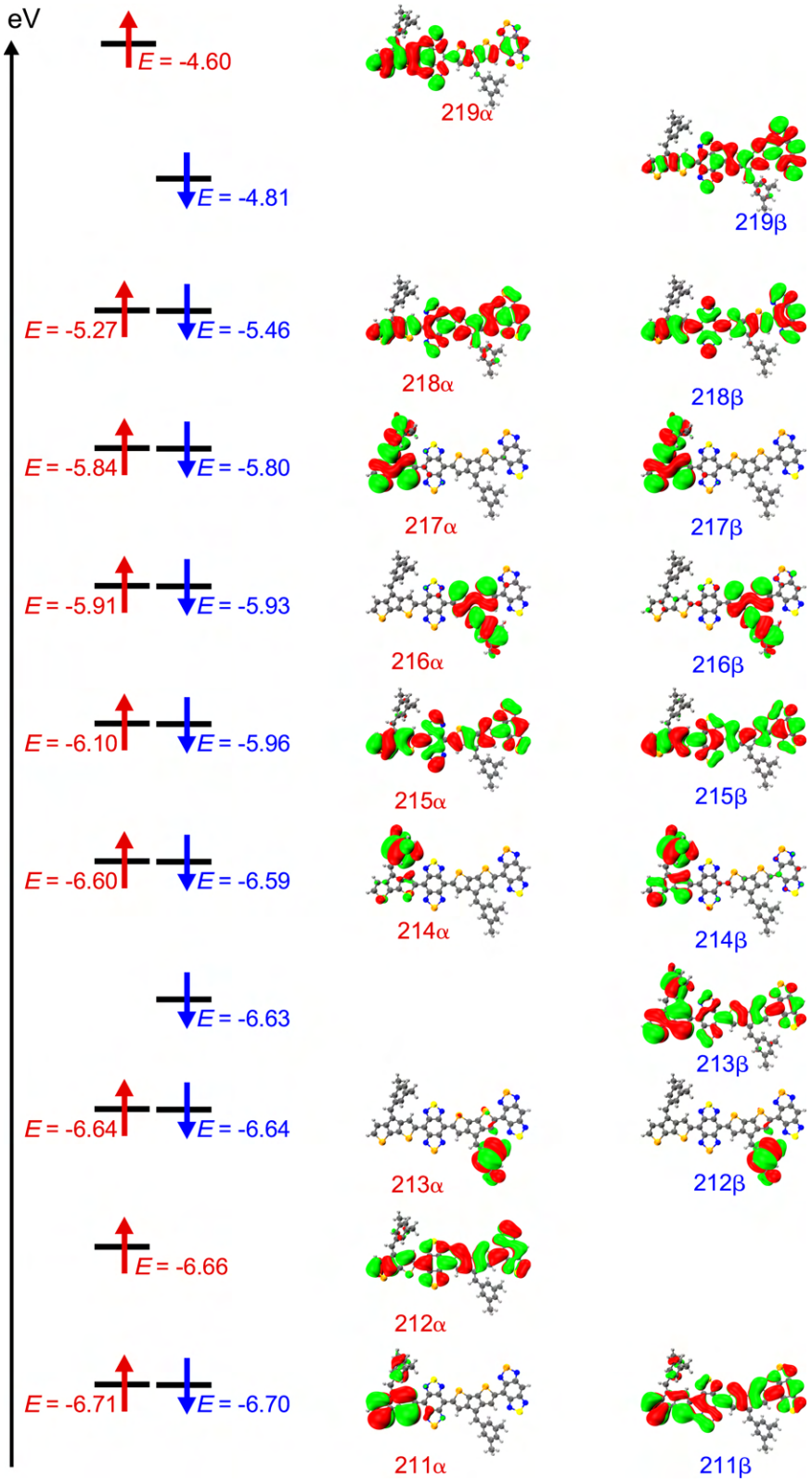


Figure S14: Molecular orbitals (MOs) and their energies at the singlet ($S = 0$) state for CPDS-SeBBT dimer ($N = 2$). The green and red surfaces represent positive and negative contributions of the MOs at an isovalue = 0.01 au.

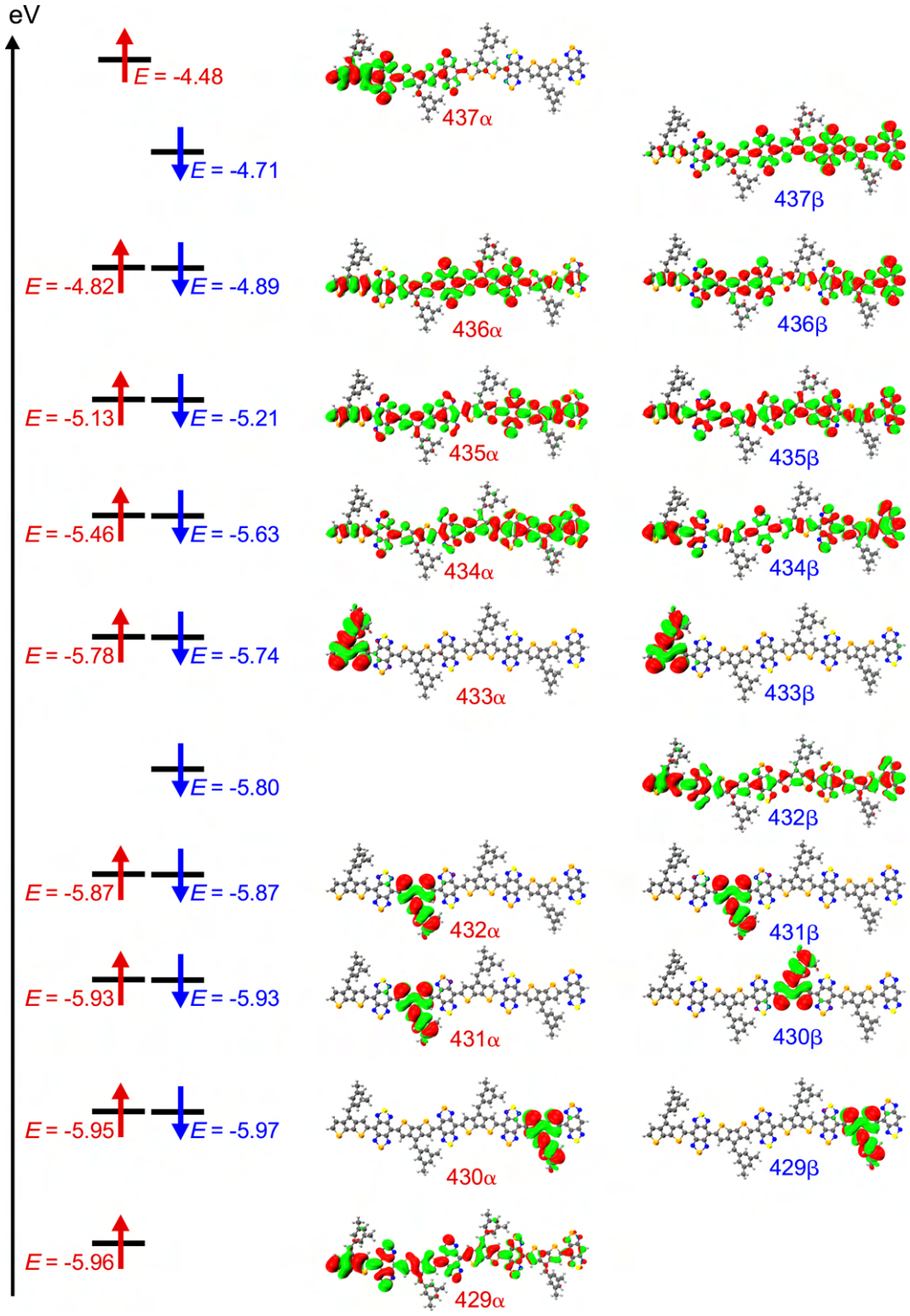


Figure S15: Molecular orbitals (MOs) and their energies at the singlet ($S = 0$) state for CPDS-SeBBT tetramer ($N = 4$). The green and red surfaces represent positive and negative contributions of the MOs at an isovalue = 0.01 au.

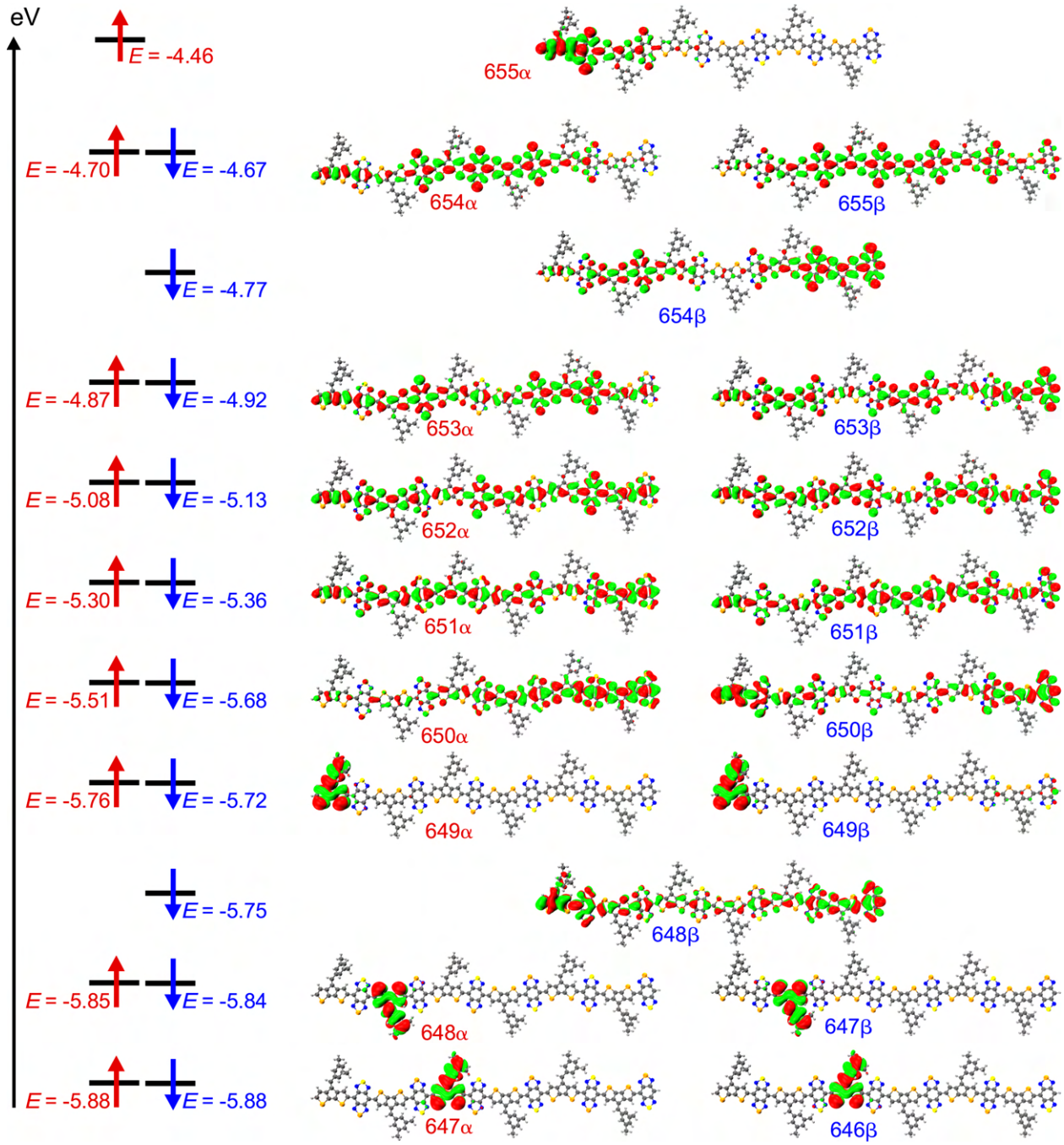


Figure S16: Molecular orbitals (MOs) and their energies at the singlet ($S = 0$) state for CPDS-SeBBT hexamer ($N = 6$). The green and red surfaces represent positive and negative contributions of the MOs at an isovalue = 0.01 au.

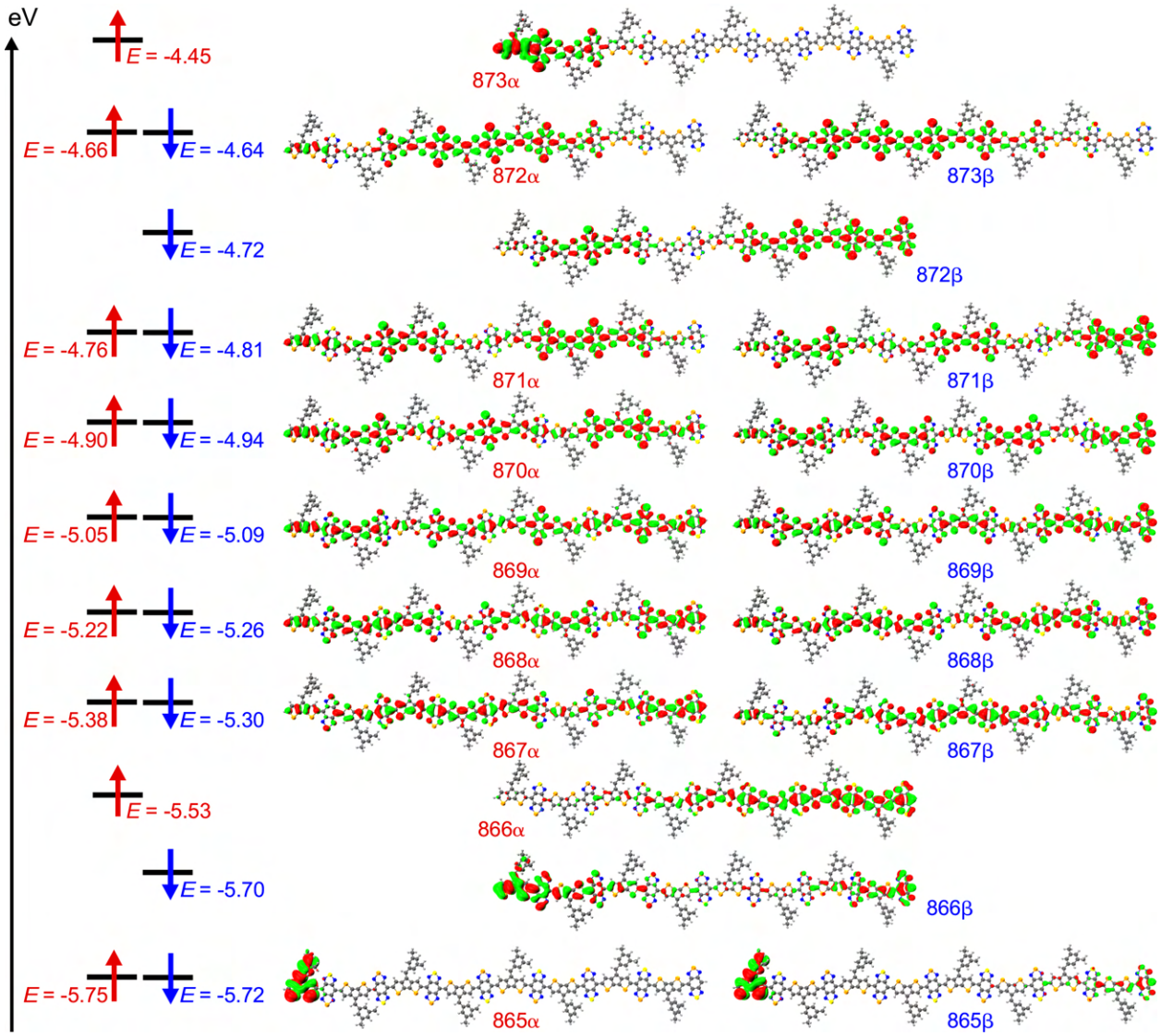


Figure S17: Molecular orbitals (MOs) and their energies at the singlet ($S = 0$) state for CPDS-SeBBT octamer ($N = 8$). The green and red surfaces represent positive and negative contributions of the MOs at an isovalue = 0.01 au.

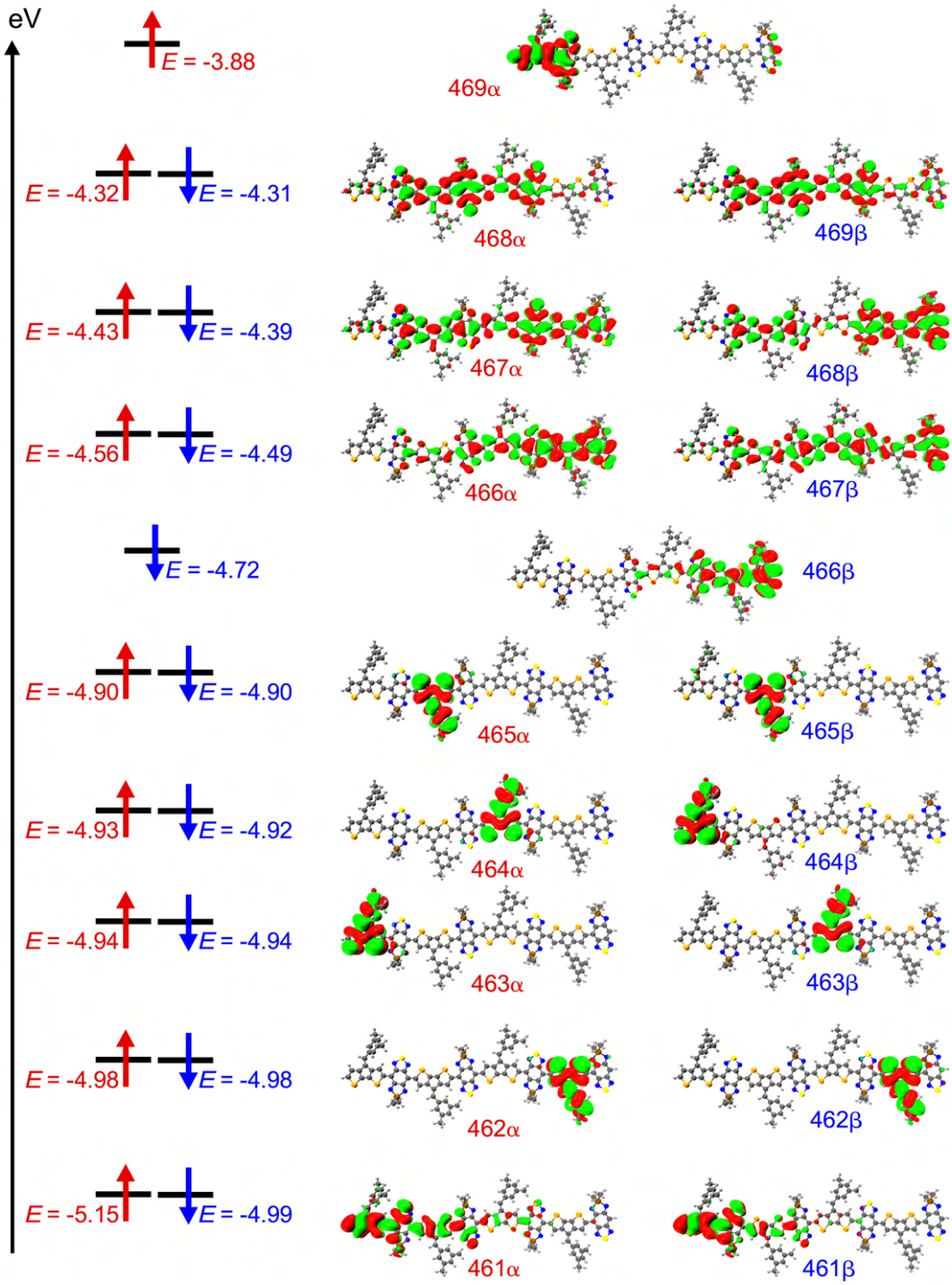


Figure S18: Molecular orbitals (MOs) and their energies at the singlet ($S = 0$) state for CPDS-SiBBT tetramer ($N = 4$) at UBLYP/6-31G(d,p) level of theory and basis set. The green and red surfaces represent positive and negative contributions of the MOs at an isovalue = 0.01 au.

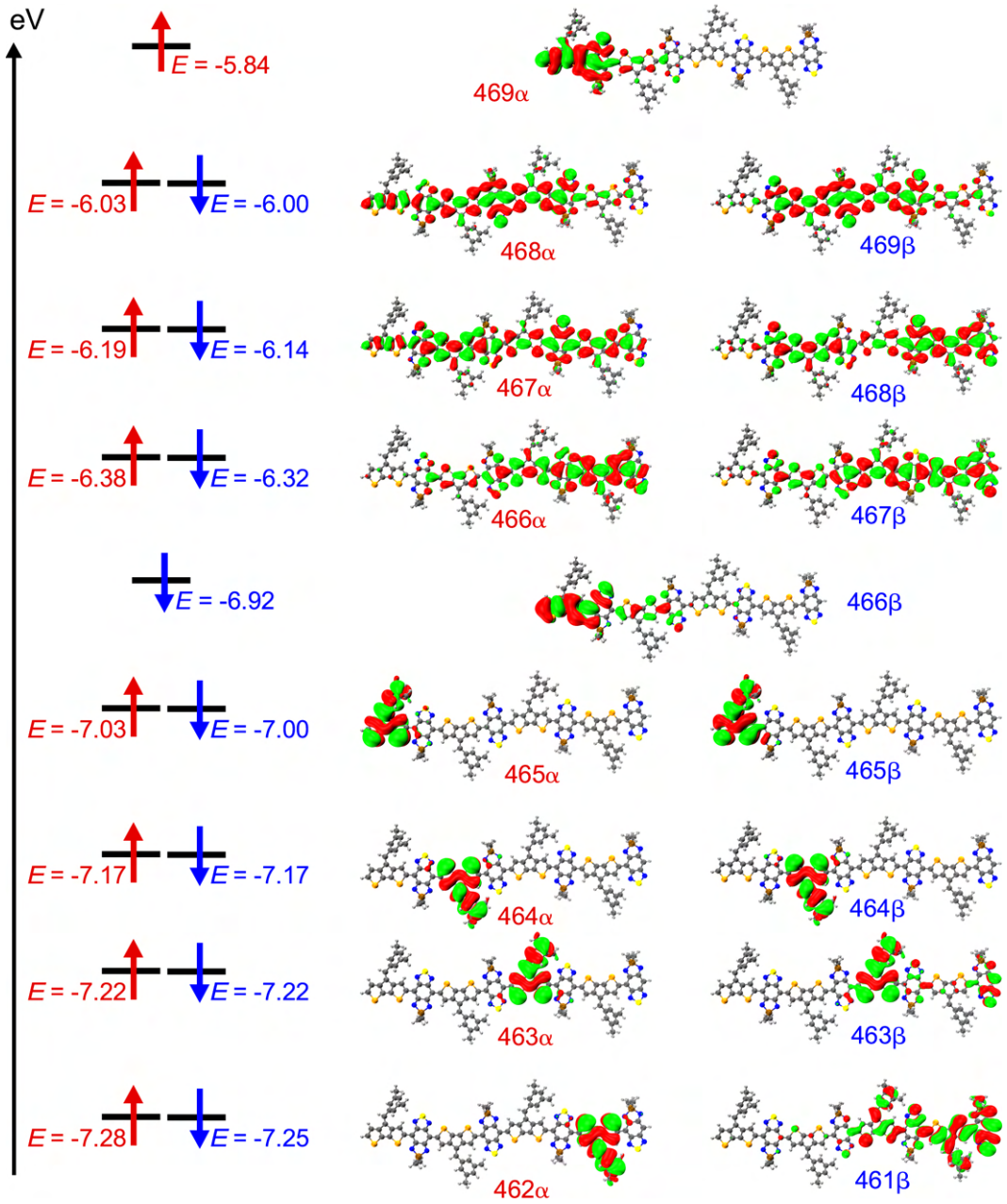


Figure S19: Molecular orbitals (MOs) and their energies at the singlet ($S = 0$) state for CPDS-SiBBT tetramer ($N = 4$) at UCAM-B3LYP/6-31G(d,p) level of theory and basis set. The green and red surfaces represent positive and negative contributions of the MOs at an isovalue = 0.01 au.

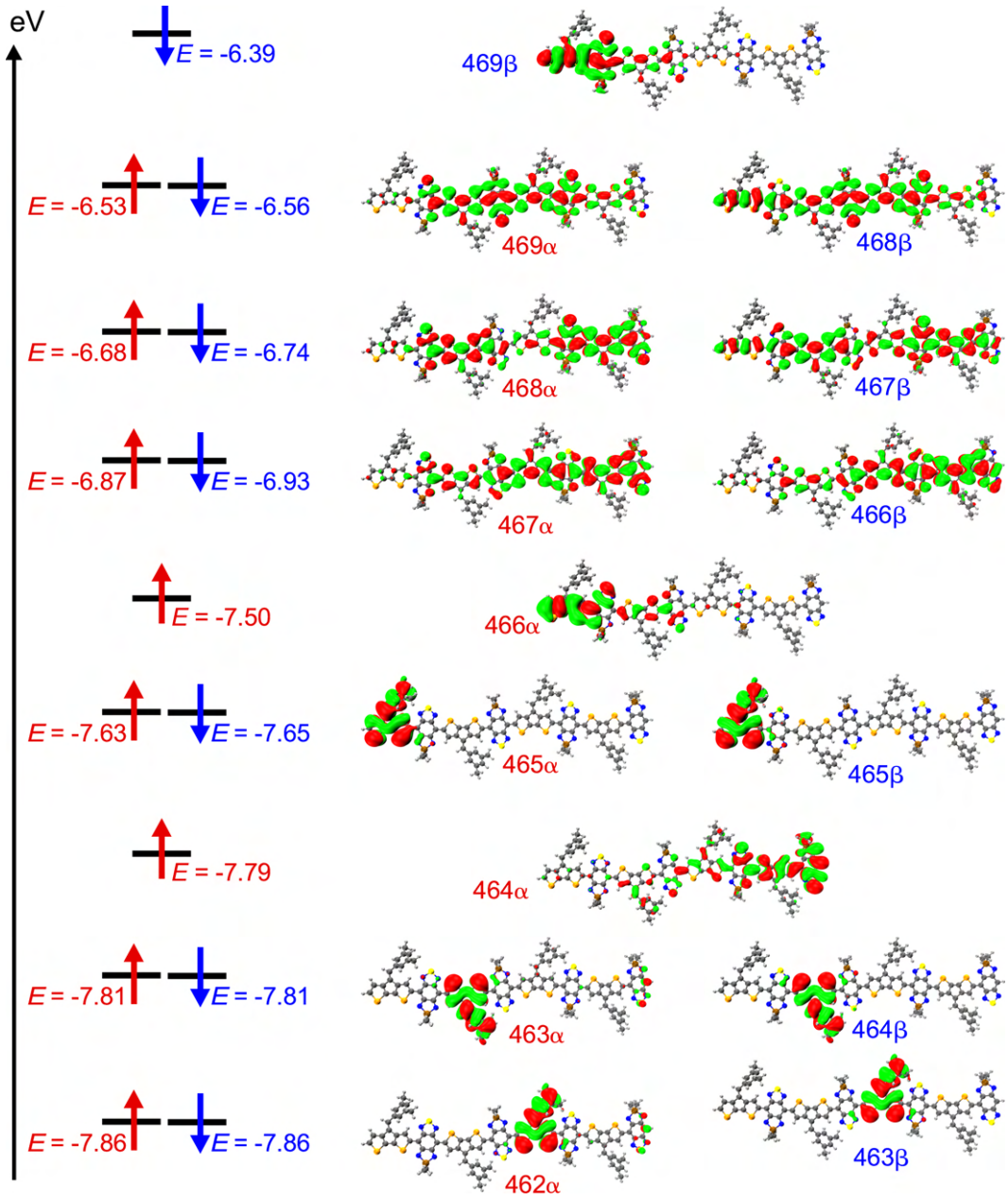


Figure S20: Molecular orbitals (MOs) and their energies at the singlet ($S = 0$) state for CPDS-SiBBT tetramer ($N = 4$) at ωB97X-D/6-31G(d,p) level of theory and basis set. The green and red surfaces represent positive and negative contributions of the MOs at an isovalue = 0.01 au.

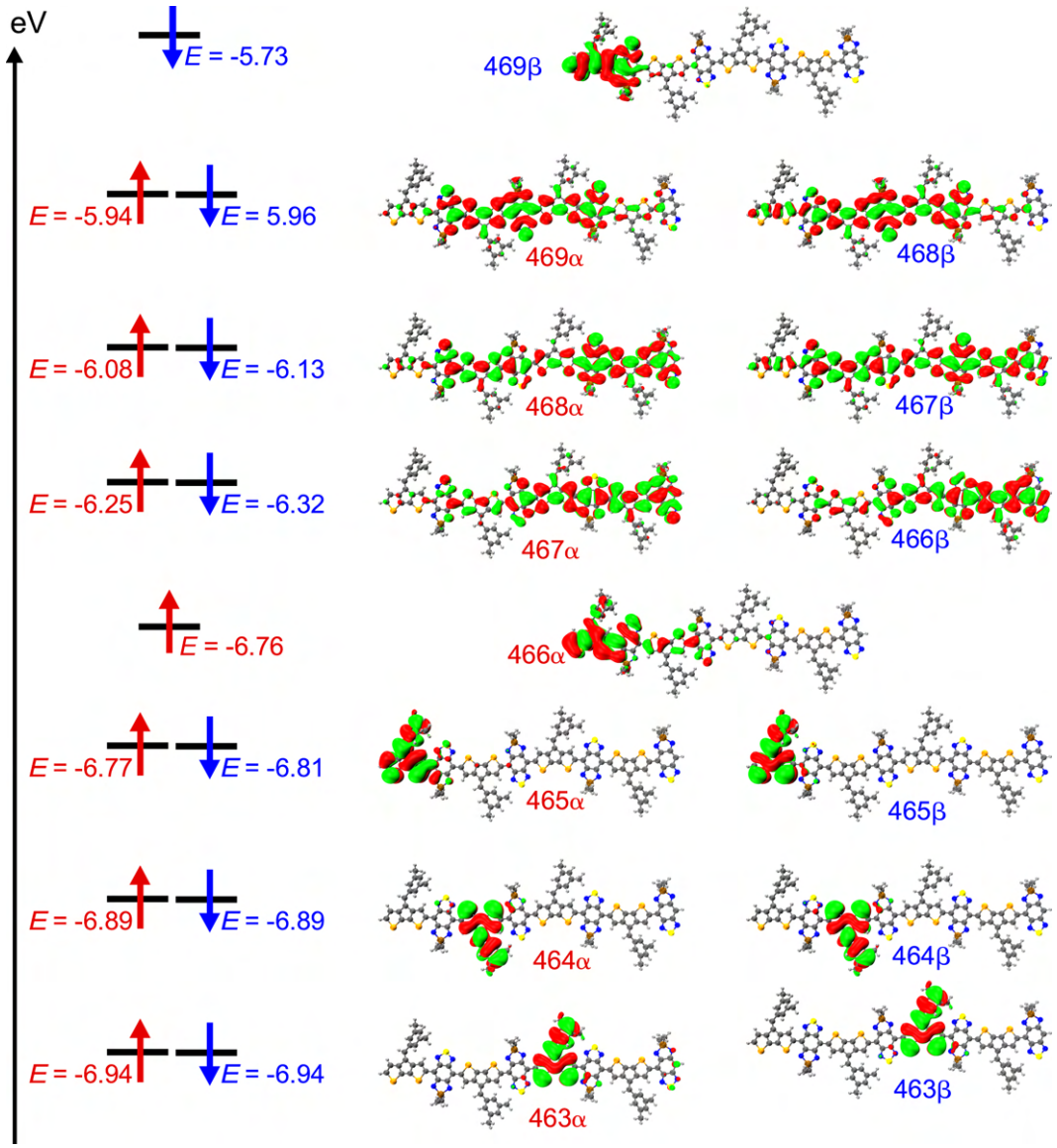


Figure S21: Molecular orbitals (MOs) and their energies at the singlet ($S = 0$) state for CPDS-SiBBT tetramer ($N = 4$) at ULC-ωHPBE/6-31G(d,p) level of theory and basis set. The green and red surfaces represent positive and negative contributions of the MOs at an isovalue = 0.01 au.

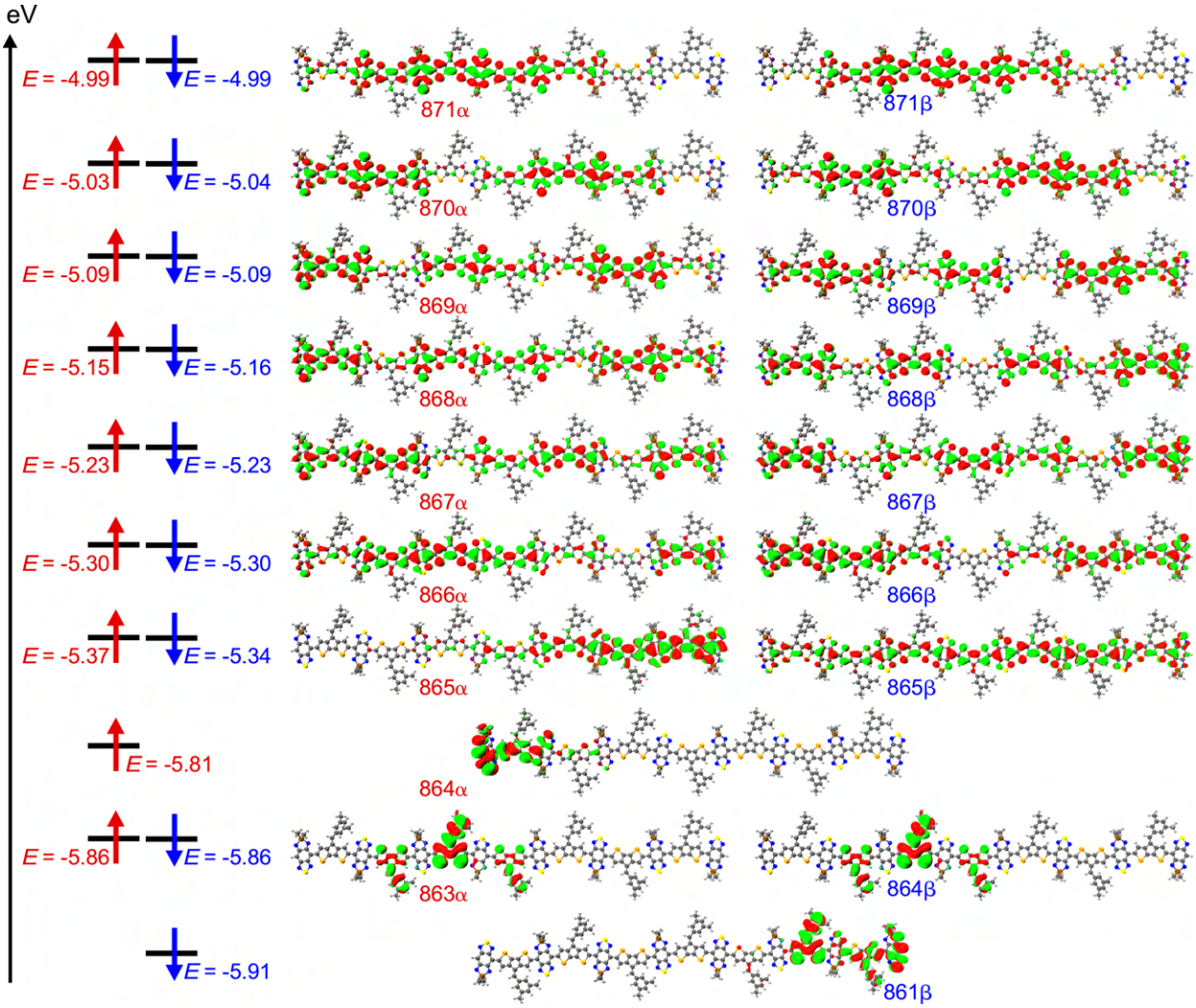


Figure S22: Molecular orbitals (MOs) and their energies at the singlet ($S = 0$) state for CPDS-SiBBT heptamer ($N = 7$) with acceptor end units. The green and red surfaces represent positive and negative contributions of the MOs at an isovalue = 0.01 au.

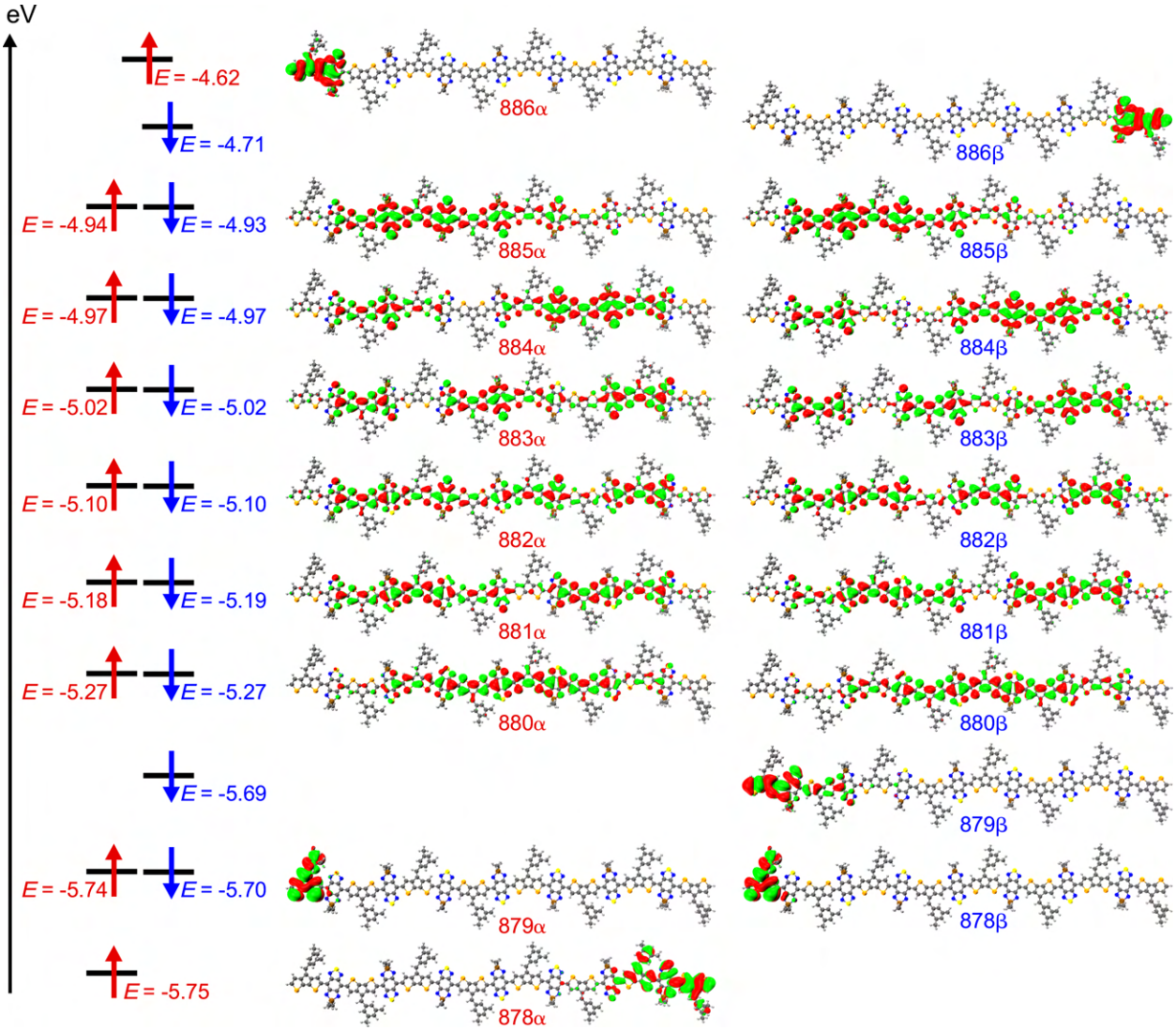


Figure S23: Molecular orbitals (MOs) and their energies at the singlet ($S = 0$) state for CPDS-SiBBT heptamer ($N = 7$) with donor end units. The green and red surfaces represent positive and negative contributions of the MOs at an isovalue = 0.01 au.

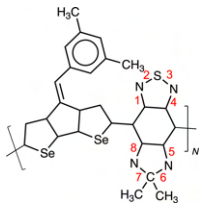


Table S4: Bond lengths of the auxiliary rings of CPDS-CBBT octamer ($N = 8$).

Repeat Unit 1			Repeat Unit 2		
Bond Index	Singlet (Å)	Triplet (Å)	Bond Index	Singlet (Å)	Triplet (Å)
1	1.32922	1.32922	1	1.32556	1.32556
2	1.65834	1.65835	2	1.65889	1.65888
3	1.66249	1.66248	3	1.66012	1.66012
4	1.32391	1.32391	4	1.32489	1.32489
5	1.29513	1.29512	5	1.29533	1.29533
6	1.46814	1.46814	6	1.46737	1.46737
7	1.46764	1.46764	7	1.46856	1.46856
8	1.29882	1.29882	8	1.29460	1.29460
Repeat Unit 3			Repeat Unit 4		
Bond Index	Singlet (Å)	Triplet (Å)	Bond Index	Singlet (Å)	Triplet (Å)
1	1.32552	1.32552	1	1.32550	1.32549
2	1.65877	1.65877	2	1.65874	1.65874
3	1.66007	1.66007	3	1.66005	1.66005
4	1.32495	1.32495	4	1.32497	1.32496
5	1.29537	1.29537	5	1.29537	1.29537
6	1.46730	1.46730	6	1.46726	1.46726
7	1.46868	1.46868	7	1.46868	1.46868
8	1.29450	1.29450	8	1.29446	1.29446
Repeat Unit 5			Repeat Unit 6		
Bond Index	Singlet (Å)	Triplet (Å)	Bond Index	Singlet (Å)	Triplet (Å)
1	1.32552	1.32552	1	1.32556	1.32555
2	1.65870	1.65870	2	1.65867	1.65867
3	1.66002	1.66002	3	1.65995	1.65995
4	1.32496	1.32496	4	1.32491	1.32492
5	1.29535	1.29535	5	1.29527	1.29527
6	1.46728	1.46729	6	1.46733	1.46733
7	1.46868	1.46868	7	1.46860	1.46860
8	1.29446	1.29446	8	1.29449	1.29449
Repeat Unit 7			Repeat Unit 8		
Bond Index	Singlet (Å)	Triplet (Å)	Bond Index	Singlet (Å)	Triplet (Å)
1	1.32574	1.32575	1	1.32514	1.32517
2	1.65849	1.65849	2	1.66683	1.66681
3	1.65956	1.65956	3	1.64781	1.64779
4	1.32480	1.32480	4	1.33875	1.33878
5	1.29504	1.29504	5	1.31187	1.31188
6	1.46752	1.46752	6	1.46887	1.46888
7	1.46837	1.46837	7	1.47550	1.47551
8	1.29459	1.29459	8	1.29494	1.29493

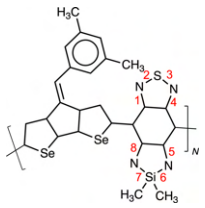


Table S5: Bond lengths of the auxiliary rings of CPDS-SiBBT octamer ($N = 8$).

Repeat Unit 1			Repeat Unit 2		
Bond Index	Singlet (Å)	Triplet (Å)	Bond Index	Singlet (Å)	Triplet (Å)
1	1.32827	1.32828	1	1.32547	1.32547
2	1.65833	1.65833	2	1.65907	1.65907
3	1.66200	1.66200	3	1.66010	1.66010
4	1.32402	1.32402	4	1.32479	1.32479
5	1.29543	1.29543	5	1.29523	1.29523
6	1.77101	1.77101	6	1.77072	1.77072
7	1.77250	1.77250	7	1.77481	1.77481
8	1.30146	1.30146	8	1.29742	1.29742
Repeat Unit 3			Repeat Unit 4		
Bond Index	Singlet (Å)	Triplet (Å)	Bond Index	Singlet (Å)	Triplet (Å)
1	1.32542	1.32542	1	1.32540	1.32540
2	1.65892	1.65892	2	1.65886	1.65886
3	1.66005	1.66005	3	1.66002	1.66002
4	1.32487	1.32487	4	1.32489	1.32489
5	1.29527	1.29527	5	1.29528	1.29528
6	1.77048	1.77048	6	1.77042	1.77042
7	1.77535	1.77535	7	1.77552	1.77552
8	1.29717	1.29716	8	1.29708	1.29708
Repeat Unit 5			Repeat Unit 6		
Bond Index	Singlet (Å)	Triplet (Å)	Bond Index	Singlet (Å)	Triplet (Å)
1	1.32541	1.32541	1	1.32545	1.32545
2	1.65883	1.65883	2	1.65879	1.65879
3	1.65999	1.65999	3	1.65992	1.65992
4	1.32488	1.32488	4	1.32485	1.32485
5	1.29523	1.29524	5	1.29511	1.29511
6	1.77049	1.77049	6	1.77077	1.77077
7	1.77553	1.77553	7	1.77542	1.77542
8	1.29707	1.29707	8	1.29708	1.29708
Repeat Unit 7			Repeat Unit 8		
Bond Index	Singlet (Å)	Triplet (Å)	Bond Index	Singlet (Å)	Triplet (Å)
1	1.32559	1.32559	1	1.32486	1.32486
2	1.65865	1.65865	2	1.66866	1.66866
3	1.65967	1.65967	3	1.64731	1.64731
4	1.32470	1.32470	4	1.33856	1.33856
5	1.29468	1.29468	5	1.31206	1.31206
6	1.77165	1.77165	6	1.78418	1.78418
7	1.77495	1.77495	7	1.78207	1.78207
8	1.29718	1.29718	8	1.29780	1.29780

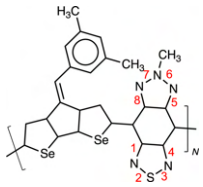


Table S6: Bond lengths of the auxiliary rings of CPDS-NBBT octamer ($N = 8$).

Repeat Unit 1

Bond Index	Singlet (Å)	Triplet (Å)
1	1.33412	1.33410
2	1.65016	1.65021
3	1.65050	1.65054
4	1.33107	1.33103
5	1.34594	1.34591
6	1.32723	1.32725
7	1.32938	1.32940
8	1.35024	1.35021

Repeat Unit 2

Bond Index	Singlet (Å)	Triplet (Å)
1	1.32841	1.32838
2	1.65541	1.65547
3	1.65379	1.65385
4	1.32867	1.32863
5	1.34357	1.34353
6	1.32855	1.32857
7	1.33138	1.33140
8	1.34545	1.34540

Repeat Unit 3

Bond Index	Singlet (Å)	Triplet (Å)
1	1.32746	1.32741
2	1.65622	1.65629
3	1.65422	1.65428
4	1.32834	1.32830
5	1.34321	1.34316
6	1.32874	1.32877
7	1.33170	1.33173
8	1.34470	1.34465

Repeat Unit 4

Bond Index	Singlet (Å)	Triplet (Å)
1	1.32732	1.32727
2	1.65632	1.65639
3	1.65425	1.65432
4	1.32829	1.32824
5	1.34317	1.34313
6	1.32874	1.32877
7	1.33172	1.33175
8	1.34457	1.34453

Repeat Unit 5

Bond Index	Singlet (Å)	Triplet (Å)
1	1.32734	1.32730
2	1.65627	1.65634
3	1.65414	1.65421
4	1.32833	1.32828
5	1.34321	1.34317
6	1.32866	1.32868
7	1.33174	1.33177
8	1.34459	1.34455

Repeat Unit 6

Bond Index	Singlet (Å)	Triplet (Å)
1	1.32754	1.32750
2	1.65602	1.65608
3	1.65366	1.65372
4	1.32874	1.32870
5	1.34354	1.34350
6	1.32835	1.32838
7	1.33167	1.33170
8	1.34478	1.34473

Repeat Unit 7

Bond Index	Singlet (Å)	Triplet (Å)
1	1.32854	1.32850
2	1.65459	1.65465
3	1.65120	1.65125
4	1.33159	1.33155
5	1.34562	1.34559
6	1.32710	1.32712
7	1.33098	1.33101
8	1.34602	1.34598

Repeat Unit 8

Bond Index	Singlet (Å)	Triplet (Å)
1	1.33588	1.33586
2	1.64840	1.64844
3	1.63854	1.63857
4	1.34783	1.34782
5	1.36012	1.36011
6	1.32213	1.32214
7	1.32923	1.32925
8	1.35390	1.35387

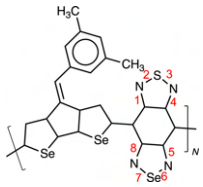


Table S7: Bond lengths of the auxiliary rings of CPDS-SeBBT octamer ($N = 8$).

Repeat Unit 1			Repeat Unit 2		
Bond Index	Singlet (Å)	Triplet (Å)	Bond Index	Singlet (Å)	Triplet (Å)
1	1.33155	1.33155	1	1.32722	1.32722
2	1.65451	1.65450	2	1.65552	1.65552
3	1.65904	1.65903	3	1.65735	1.65735
4	1.32558	1.32558	4	1.32613	1.32614
5	1.31854	1.31854	5	1.31888	1.31888
6	1.81313	1.81313	6	1.81156	1.81156
7	1.81039	1.81040	7	1.81263	1.81263
8	1.32276	1.32277	8	1.31816	1.31816
Repeat Unit 3			Repeat Unit 4		
Bond Index	Singlet (Å)	Triplet (Å)	Bond Index	Singlet (Å)	Triplet (Å)
1	1.32716	1.32716	1	1.32715	1.32715
2	1.65549	1.65550	2	1.65545	1.65545
3	1.65733	1.65733	3	1.65729	1.65729
4	1.32616	1.32616	4	1.32617	1.32617
5	1.31891	1.31892	5	1.31891	1.31891
6	1.81152	1.81152	6	1.81148	1.81148
7	1.81262	1.81263	7	1.81259	1.81259
8	1.31809	1.31809	8	1.31808	1.31808
Repeat Unit 5			Repeat Unit 6		
Bond Index	Singlet (Å)	Triplet (Å)	Bond Index	Singlet (Å)	Triplet (Å)
1	1.32718	1.32718	1	1.32726	1.32726
2	1.65542	1.65542	2	1.65534	1.65534
3	1.65725	1.65725	3	1.65711	1.65711
4	1.32614	1.32614	4	1.32606	1.32606
5	1.31888	1.31889	5	1.31880	1.31880
6	1.81141	1.81141	6	1.81126	1.81126
7	1.81254	1.81255	7	1.81246	1.81246
8	1.31811	1.31811	8	1.31819	1.31819
Repeat Unit 7			Repeat Unit 8		
Bond Index	Singlet (Å)	Triplet (Å)	Bond Index	Singlet (Å)	Triplet (Å)
1	1.32754	1.32754	1	1.32954	1.32954
2	1.65511	1.65511	2	1.65925	1.65925
3	1.65627	1.65628	3	1.64465	1.64466
4	1.32624	1.32624	4	1.34195	1.34195
5	1.31908	1.31909	5	1.33731	1.33732
6	1.81047	1.81047	6	1.80200	1.80200
7	1.81229	1.81229	7	1.82029	1.82030
8	1.31843	1.31843	8	1.31965	1.31965

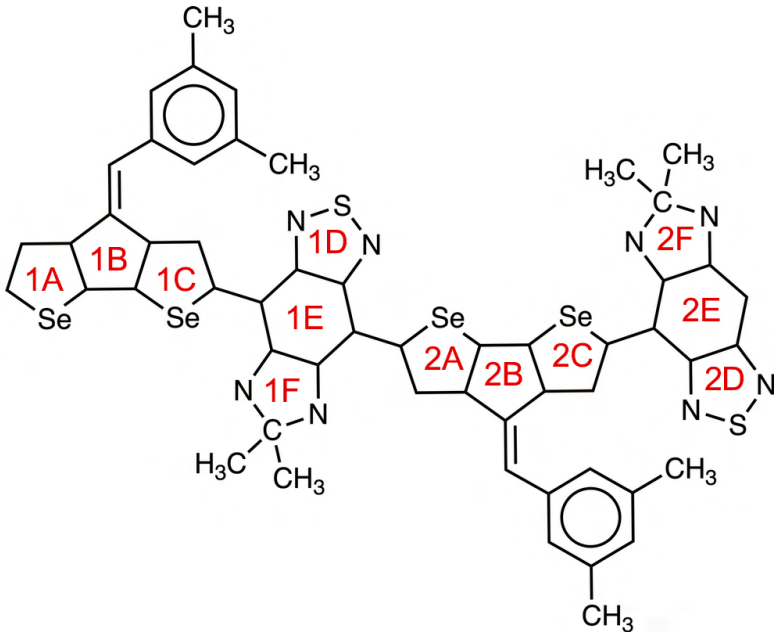


Table S8: Calculated $\mathrm{NICS}_{\mathrm{iso}}(1)$ (ppm) of CPDS-CBBT dimer ($N = 2$) in the singlet and triplet states.

Ring index	singlet ($S = 0$)	triplet ($S = 1$)	Ring index	singlet ($S = 0$)	triplet ($S = 1$)
1A	-7.1029	-7.1021	2A	-3.4418	-3.4277
1B	-0.6162	-0.6263	2B	-1.4897	-1.4950
1C	-4.8502	-4.8615	2C	-3.4675	-3.4671
1D	-9.0363	-9.0965	2D	-9.0611	-9.0607
1E	-0.3340	-0.3752	2E	-0.8937	-0.8893
1F	-5.5152	-5.4611	2F	-5.6785	-5.6642

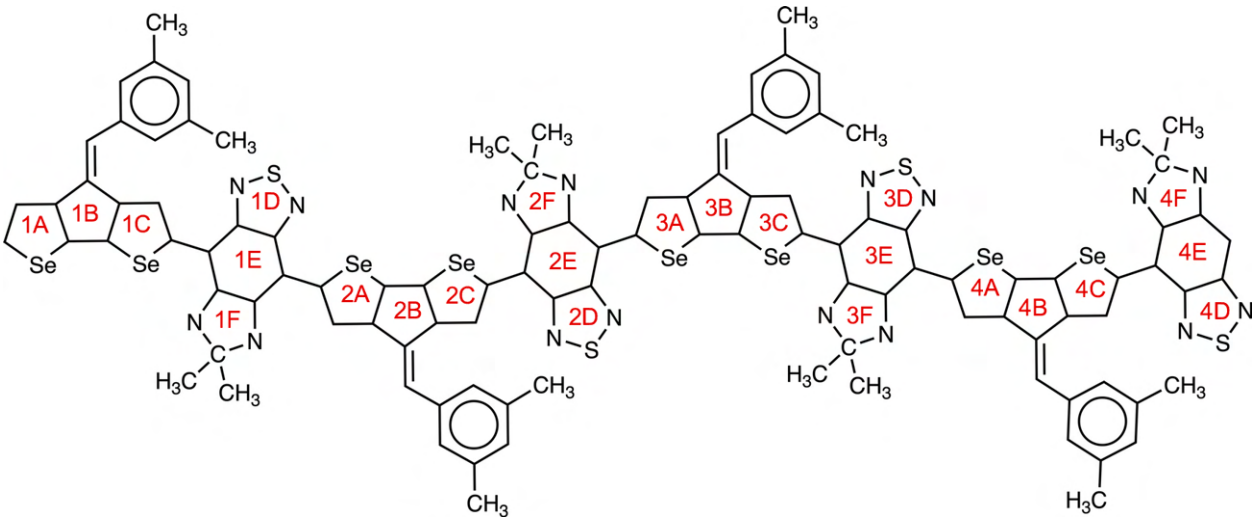


Table S9: Calculated $NICS_{iso}(1)$ (ppm) of CPDS-CBBT tetramer ($N = 4$) in the singlet and triplet states.

Ring index	singlet ($S = 0$)	triplet ($S = 1$)	Ring index	singlet ($S = 0$)	triplet ($S = 1$)
1A	-7.0275	-7.0207	2A	-3.5651	-3.5641
1B	-0.1390	-0.1365	2B	-2.0258	-2.0251
1C	-4.5249	-4.5246	2C	-3.8185	-3.8206
1D	-8.9402	-8.9459	2D	-9.3655	-9.3569
1E	-0.2750	-0.2777	2E	-0.2577	-0.2624
1F	-5.4331	-5.4334	2F	-5.4637	-5.4681
3A	-3.4994	-3.5008	4A	-3.4679	-3.4709
3B	-1.4892	-1.4878	4B	-1.9996	-1.9980
3C	-3.3760	-3.3793	4C	-3.8873	-3.8907
3D	-9.2532	-9.2537	4D	-9.1937	-9.1851
3E	-0.1856	-0.1883	4E	-0.9377	-0.9380
3F	-5.4238	-5.4318	4F	-5.6718	-5.6809

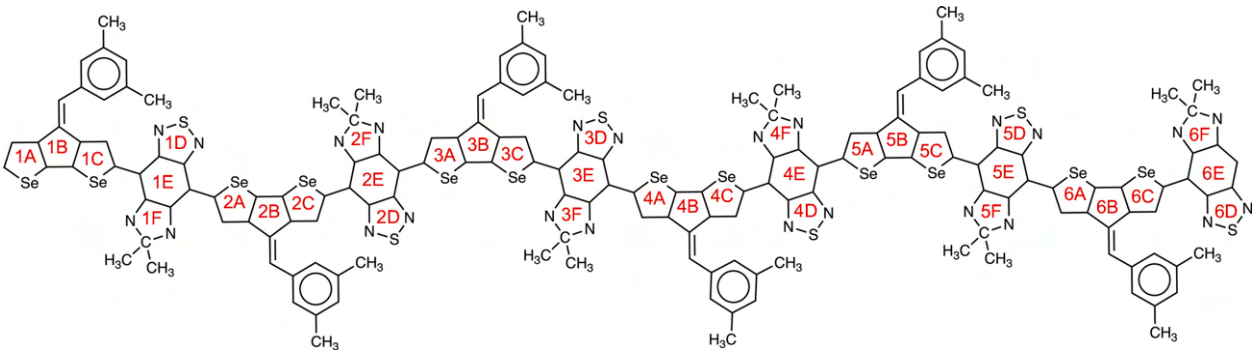


Table S10: Calculated $NICS_{iso}(1)$ (ppm) of CPDS-CBBT hexamer ($N = 6$) in the singlet and triplet states.

Ring index	singlet ($S = 0$)	triplet ($S = 1$)	Ring index	singlet ($S = 0$)	triplet ($S = 1$)
1A	-7.1549	-7.1622	2A	-3.5320	-3.5350
1B	-0.5328	-0.5410	2B	-1.4946	-1.4946
1C	-4.9090	-4.9135	2C	-3.3898	-3.3891
1D	-9.0705	-9.0705	2D	-9.2272	-9.2298
1E	-0.3775	-0.3779	2E	-0.1914	-0.1970
1F	-5.4640	-5.4664	2F	-5.4219	-5.4231
3A	-3.5949	-3.5921	4A	-3.5260	-3.5273
3B	-2.0036	-2.0035	4B	-1.4802	-1.4847
3C	-3.7898	-3.7893	4C	-3.3550	-3.3557
3D	-9.3671	-9.3678	4D	-9.2378	-9.2421
3E	-0.2516	-0.2541	4E	-0.1758	-0.1821
3F	-5.4503	-5.4520	4F	-5.3950	-5.3974
5A	-3.5288	-3.5303	6A	-3.4270	-3.4273
5B	-2.0016	-2.0054	6B	-1.4895	-1.4882
5C	-3.7831	-3.7838	6C	-3.4422	-3.4424
5D	-9.3735	-9.3721	6D	-9.0718	-9.0700
5E	-0.2460	-0.2464	6E	-0.8863	-0.8856
5F	-5.4735	-5.4733	6F	-5.6325	-5.6320

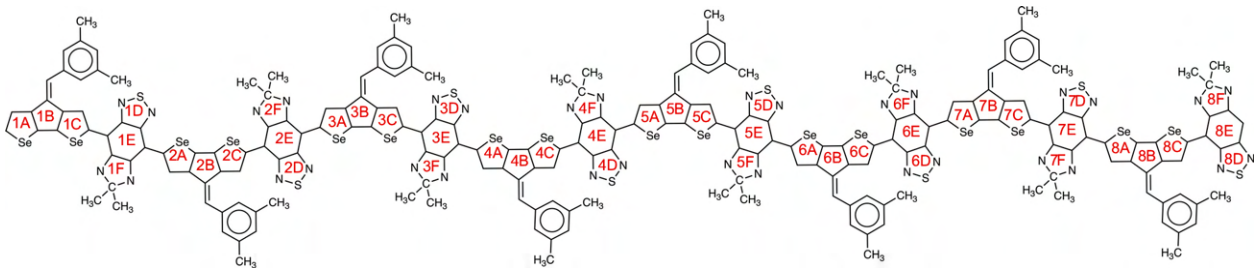


Table S11: Calculated $NICS_{iso}(1)$ (ppm) of CPDS-CBBT octamer ($N = 8$) in the singlet and triplet states.

Ring index	singlet ($S = 0$)	triplet ($S = 1$)	Ring index	singlet ($S = 0$)	triplet ($S = 1$)
1A	-7.0595	-7.0600	2A	-3.6181	-3.6161
1B	-0.1116	-0.1084	2B	-2.0120	-2.0142
1C	-4.5490	-4.5459	2C	-3.7977	-3.7960
1D	-8.9389	-8.9388	2D	-9.3701	-9.3716
1E	-0.2957	-0.2905	2E	-0.2698	-0.2725
1F	-5.4801	-5.4755	2F	-5.4881	-5.4825
3A	-3.5526	-3.5576	4A	-3.5982	-3.5997
3B	-1.4816	-1.4849	4B	-2.0052	-2.0031
3C	-3.3728	-3.3755	4C	-3.7694	-3.7684
3D	-9.2442	-9.2385	4D	-9.3649	-9.3612
3E	-0.1812	-0.1810	4E	-0.2549	-0.2527
3F	-5.4267	-5.4242	4F	-5.4543	-5.4524
5A	-3.5351	-3.5333	6A	-3.5525	-3.5534
5B	-1.4848	-1.4827	6B	-2.0035	-2.0057
5C	-3.3402	-3.3407	6C	-3.7783	-3.7879
5D	-9.2337	-9.2330	6D	-9.3599	-9.3547
5E	-0.1829	-0.1780	6E	-0.2473	-0.2457
5F	-5.3958	-5.3940	6F	-5.4389	-5.4351
7A	-3.4793	-3.4801	8A	-3.4259	-3.4247
7B	-1.4869	-1.4921	8B	-2.0013	-2.0016
7C	-3.3408	-3.3414	8C	-3.8699	-3.8748
7D	-9.2442	-9.2450	8D	-9.1719	-9.1664
7E	-0.1783	-0.1787	8E	-0.9566	-0.9512
7F	-5.3880	-5.3903	8F	-5.6744	-5.6748

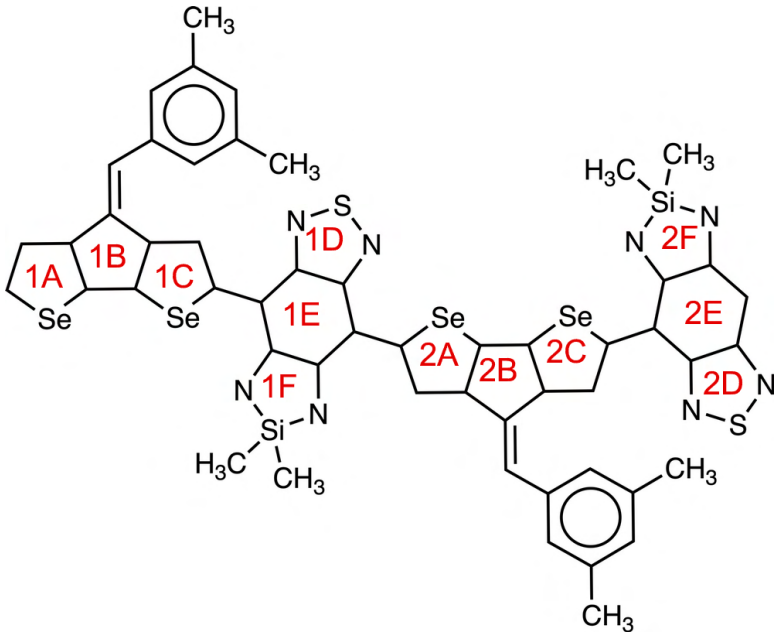


Table S12: Calculated $NICS_{iso}(1)$ (ppm) of CPDS-SiBBT dimer ($N = 2$) in the singlet and triplet states.

Ring index	singlet ($S = 0$)	triplet ($S = 1$)	Ring index	singlet ($S = 0$)	triplet ($S = 1$)
1A	-6.9906	-6.9880	2A	-3.3728	-3.3727
1B	-0.6016	-0.6016	2B	-1.5075	-1.5074
1C	-4.1456	-4.1496	2C	-3.0227	-3.0243
1D	-9.0021	-9.0376	2D	-8.7546	-8.7229
1E	0.3689	0.3319	2E	0.3704	0.3993
1F	-2.9289	-2.9316	2F	-2.8343	-2.8282

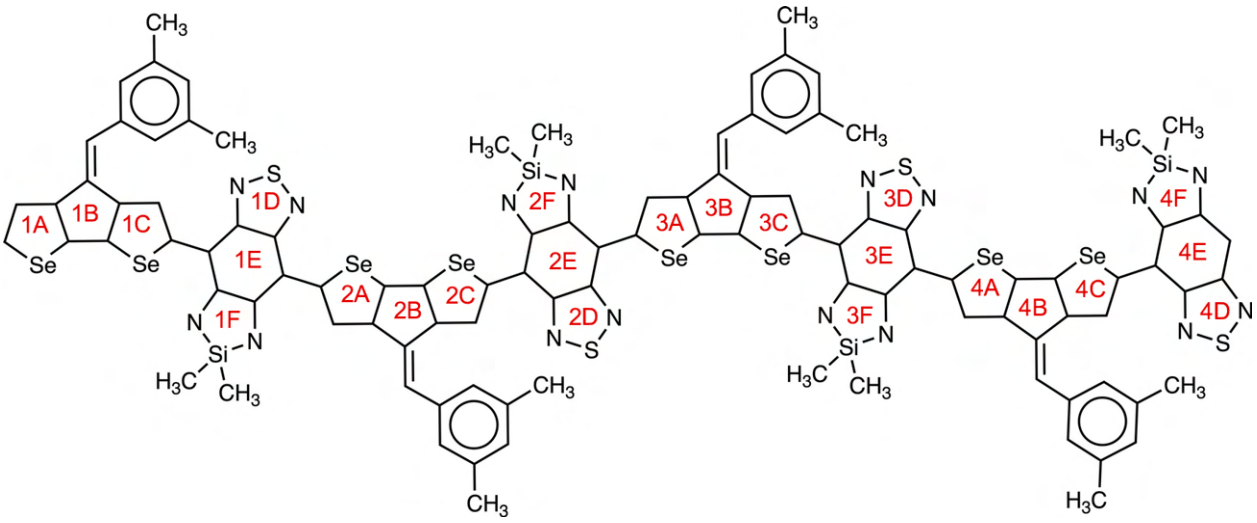


Table S13: Calculated $NICS_{iso}(1)$ of CPDS-SiBBT tetramer ($N = 4$) in the singlet and triplet states.

Ring index	singlet ($S = 0$)	triplet ($S = 1$)	Ring index	singlet ($S = 0$)	triplet ($S = 1$)
1A	-7.0441	-7.0374	2A	-3.4372	-3.4367
1B	-0.5585	-0.5620	2B	-1.4750	-1.4763
1C	-4.1853	-4.1863	2C	-2.8886	-2.8868
1D	-9.0252	-9.0248	2D	-9.1552	-9.1551
1E	0.3342	0.3348	2E	0.4218	0.4237
1F	-2.8994	-2.9002	2F	-2.8252	-2.8244
3A	-3.4588	-3.4562	4A	-3.3770	-3.3774
3B	-1.9995	-2.0033	4B	-1.4855	-1.4843
3C	-3.3201	-3.3196	4C	-2.9759	-2.9755
3D	-9.3133	-9.3134	4D	-8.7702	-8.7709
3E	0.3531	0.3524	4E	0.3888	0.3905
3F	-2.8989	-2.8987	4F	-2.8535	-2.8515

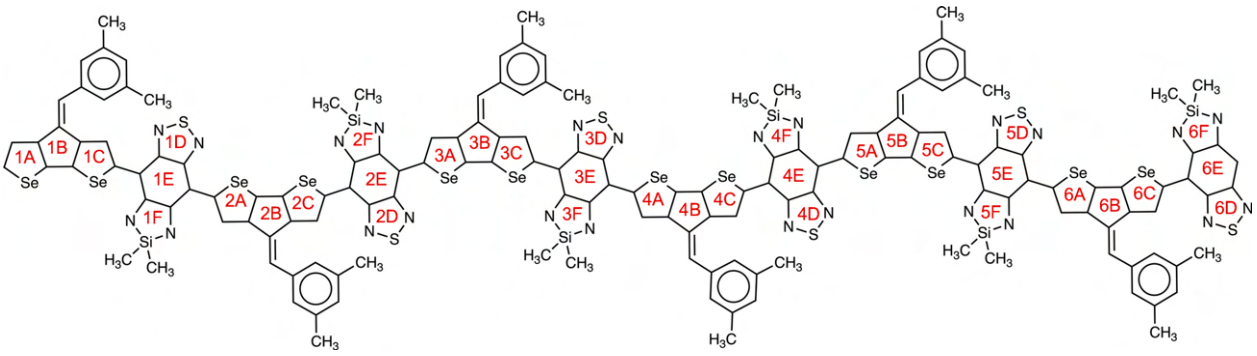


Table S14: Calculated $NICS_{iso}(1)$ (ppm) of CPDS-SiBBT hexamer ($N = 6$) in the singlet and triplet states.

Ring index	singlet ($S = 0$)	triplet ($S = 1$)	Ring index	singlet ($S = 0$)	triplet ($S = 1$)
1A	-7.0694	-6.9663	2A	-3.4533	-3.5023
1B	-0.5624	-0.1254	2B	-1.4785	-2.0219
1C	-4.1698	-3.7545	2C	-2.8712	-3.3164
1D	-9.0255	-8.8924	2D	-9.1388	-9.2758
1E	0.3287	0.4185	2E	0.4182	0.3367
1F	-2.9105	-2.8559	2F	-2.8283	-2.8756
3A	-3.4961	-3.4576	4A	-3.4584	-3.4832
3B	-1.9981	-1.4522	4B	-1.4615	-1.9959
3C	-3.2851	-2.8262	4C	-2.8265	-3.2949
3D	-9.2913	-10.3233	4D	-9.1614	-9.2871
3E	0.3398	0.4245	4E	0.4350	0.3526
3F	-2.8716	-2.8216	4F	-2.8172	-2.8634
5A	-3.4517	-3.4328	6A	-3.3611	-3.3667
5B	-2.0011	-1.4648	6B	-1.4876	-2.0154
5C	-3.3081	-2.8365	6C	-2.9639	-3.4390
5D	-9.2976	-9.1780	6D	-8.7826	-8.8806
5E	0.8887	0.4384	6E	0.3699	0.3040
5F	-2.8905	-2.8511	6F	-2.8781	-2.9015

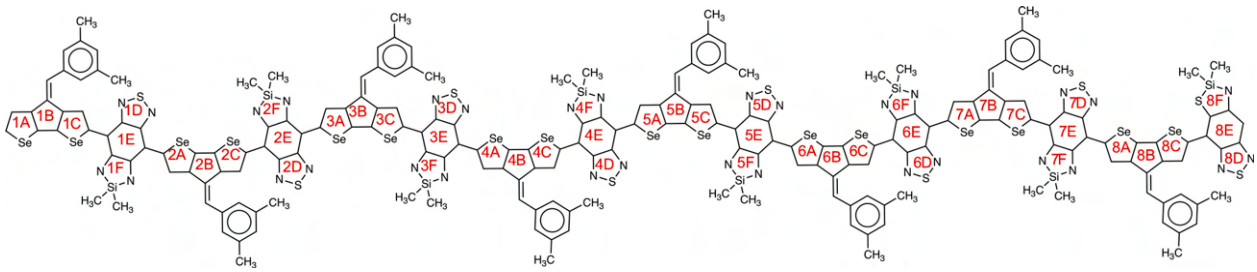


Table S15: Calculated $NICS_{iso}(1)$ (ppm) of CPDS-SiBBT octamer ($N = 8$) in the singlet and triplet states.

Ring index	singlet ($S = 0$)	triplet ($S = 1$)	Ring index	singlet ($S = 0$)	triplet ($S = 1$)
1A	-7.0801	-7.0792	2A	-3.4668	-3.4678
1B	-0.5603	-0.5604	2B	-1.4819	-1.4780
1C	-4.1476	-4.1489	2C	-2.8724	-2.8691
1D	-9.0301	-9.0332	2D	-9.1402	-9.1404
1E	0.3217	0.3195	2E	0.4187	0.4122
1F	-2.9145	-2.9146	2F	-2.8349	-2.8365
3A	-3.5158	-3.5173	4A	-3.4786	-3.4756
3B	-2.0033	-2.0038	4B	-1.4537	-1.4536
3C	-3.2769	-3.2749	4C	-2.8050	-2.8053
3D	-9.2946	-9.2927	4D	-9.1524	-9.1574
3E	0.3318	0.3329	4E	0.4273	0.4242
3F	-2.8716	-2.8696	4F	-2.8235	-2.8234
5A	-3.4985	-3.4987	6A	-3.4598	-3.4645
5B	-1.9941	-1.9938	6B	-1.4605	-1.4613
5C	-3.2649	-3.2650	6C	-2.8168	-2.8184
5D	-9.2825	-9.2867	6D	-9.1613	-9.1612
5E	0.3447	0.3461	6E	0.4381	0.4392
5F	-2.8711	-2.8706	6F	-2.8141	-2.8125
7A	-3.4368	-3.4351	8A	-3.3566	-3.3614
7B	-1.9949	-1.9931	8B	-1.4906	-1.4932
7C	-3.3113	-3.3068	8C	-2.9641	-2.9612
7D	-9.2964	-9.2977	8D	-8.7831	-8.7791
7E	0.3596	0.3595	8E	0.3650	0.3627
7F	-2.8842	-2.8840	8F	-2.9031	-2.9053

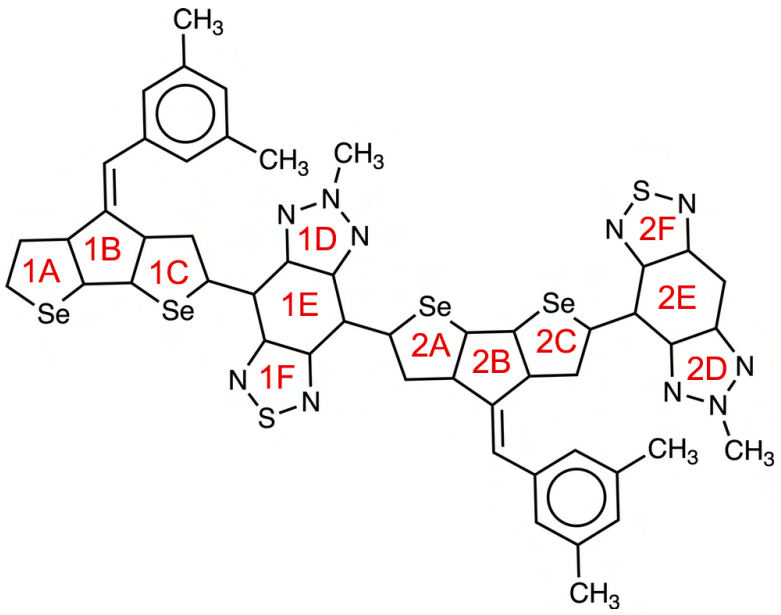


Table S16: Calculated $NICS_{iso}(1)$ (ppm) of CPDS-NBBT dimer ($N = 2$) in the singlet and triplet states.

Ring index	singlet ($S = 0$)	triplet ($S = 1$)	Ring index	singlet ($S = 0$)	triplet ($S = 1$)
1A	-7.3675	-7.0998	2A	-5.1534	-3.8109
1B	0.0341	-0.2406	2B	-0.1901	-1.0769
1C	-5.8014	-5.3262	2C	-5.1755	-4.1698
1D	-12.2704	-11.0936	2D	-12.8503	-12.0539
1E	-6.2482	-1.8055	2E	-8.7026	-5.9152
1F	-12.2188	-9.4115	2F	-12.9600	-11.3093

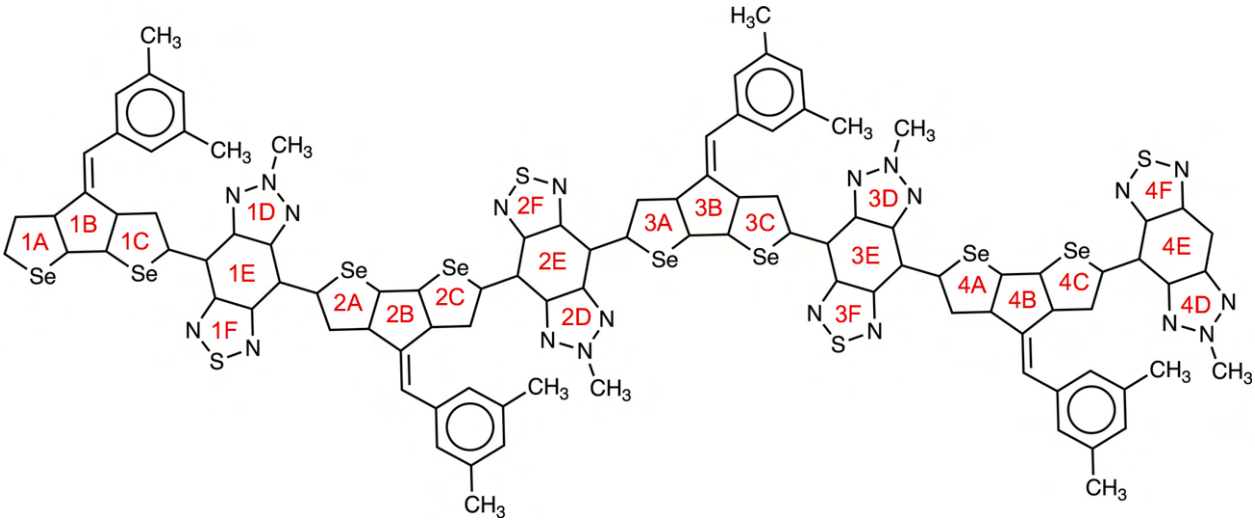


Table S17: Calculated $NICS_{iso}(1)$ (ppm) of CPDS-NBBT tetramer ($N = 4$) in the singlet and triplet states.

Ring index	singlet ($S = 0$)	triplet ($S = 1$)	Ring index	singlet ($S = 0$)	triplet ($S = 1$)
1A	-7.3132	-7.2806	2A	-4.2485	-4.0231
1B	-0.0387	-0.0597	2B	-0.9602	-1.1369
1C	-5.6722	-5.6207	2C	-4.1431	-3.9221
1D	-11.7753	-11.6415	2D	-11.4075	-11.2786
1E	-4.0498	-3.5085	2E	-2.6816	-1.9923
1F	-10.9784	-10.6481	2F	-10.4970	-10.1020
3A	-4.1509	-3.8973	4A	-4.5634	-4.3871
3B	-1.5980	-1.8241	4B	-0.6239	-0.7476
3C	-4.5109	-4.2857	4C	-4.7724	-4.6510
3D	-11.6452	-11.5003	4D	-12.5545	-12.4673
3E	-3.2354	-2.6041	4E	-7.4612	-7.1359
3F	-10.6837	-10.3255	4F	-12.2621	-12.0764

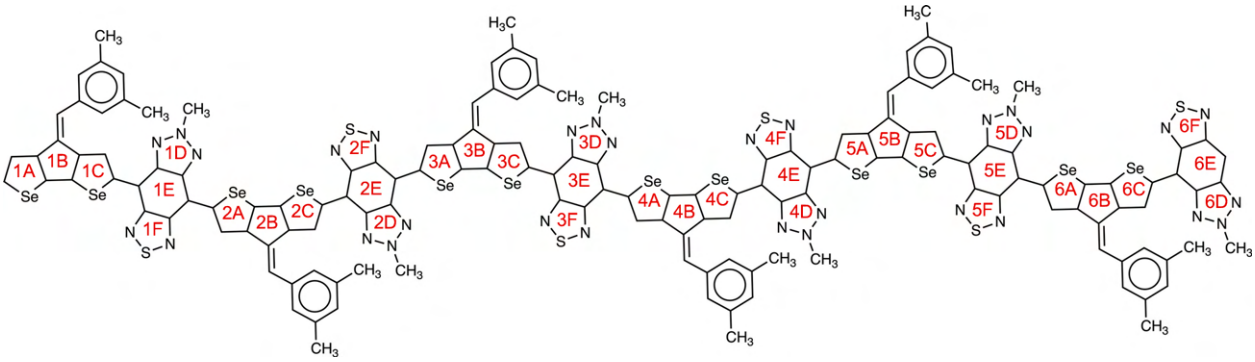


Table S18: Calculated $\mathrm{NICS}_{\mathrm{iso}}(1)$ (ppm) of CPDS-NBBT hexamer ($N = 6$) in the singlet and triplet states.

Ring index	singlet ($S = 0$)	triplet ($S = 1$)	Ring index	singlet ($S = 0$)	triplet ($S = 1$)
1A	-7.2808	-7.2805	2A	-4.1540	-4.1272
1B	-0.0607	-0.0599	2B	-1.0412	-1.0689
1C	-5.6377	-5.6281	2C	-4.0249	-3.9949
1D	-11.7263	-11.7064	2D	-11.3269	-11.3093
1E	-3.8133	-3.7332	2E	-2.3099	-2.2121
1F	-10.8256	-10.7748	2F	-10.2878	-10.2375
3A	-3.9987	-3.9612	4A	-3.8847	-3.8431
3B	-1.7896	-1.8227	4B	-1.2866	-1.3186
3C	-4.2799	-4.2485	4C	-3.8517	-3.8155
3D	-11.5117	-11.4891	4D	-11.3477	-11.3365
3E	-2.2543	-2.1503	4E	-2.1799	-2.0752
3F	-10.2813	-10.2238	4F	-10.2718	-10.2198
5A	-3.9984	-3.9669	6A	-4.4912	-4.4704
5B	-1.7298	-1.7598	6B	-0.6917	-0.7080
5C	-4.4214	-4.3925	6C	-4.7397	-4.7142
5D	-11.5902	-11.5782	6D	-12.5116	-12.5108
5E	-2.9301	-2.8541	6E	-7.3704	-7.3235
5F	-10.5341	-10.4818	6F	-12.2027	-12.1649

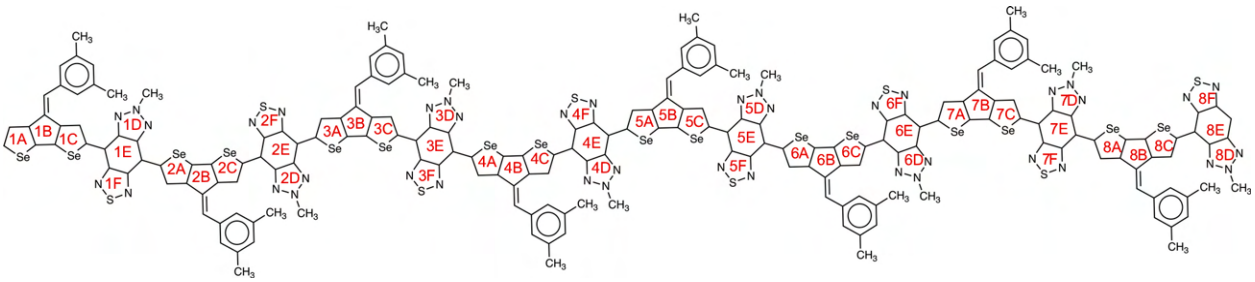


Table S19: Calculated $NICS_{iso}(1)$ (ppm) of CPDS-NBBT octamer ($N = 8$) in the singlet and triplet states.

Ring index	singlet ($S = 0$)	triplet ($S = 1$)	Ring index	singlet ($S = 0$)	triplet ($S = 1$)
1A	-7.2768	-7.2837	2A	-4.1407	-4.1351
1B	-0.0719	-0.0765	2B	-1.0455	-1.0492
1C	-5.6295	-5.6315	2C	-3.9880	-3.9814
1D	-11.7364	-11.7288	2D	-11.3160	-11.3052
1E	-3.7883	-3.7737	2E	-2.2707	-2.2538
1F	-10.7974	-10.7920	2F	-10.2553	-10.2522
3A	-3.9990	-3.9941	4A	-3.8665	-3.8596
3B	-1.8093	-1.8164	4B	-1.3136	-1.3190
3C	-4.2368	-4.2380	4C	-3.7924	-3.7845
3D	-11.5010	-11.5068	4D	-11.3173	-11.3165
3E	-2.1915	-2.1762	4E	-2.0165	-1.9995
3F	-10.2346	-10.2251	4F	-10.2016	-10.1910
5A	-3.9293	-3.9302	6A	-3.8712	-3.8577
5B	-1.8554	-1.8604	6B	-1.3145	-1.3197
5C	-4.2429	-4.2405	6C	-3.8357	-3.8266
5D	-11.5102	-11.5112	6D	-11.3485	-11.3430
5E	-2.1668	-2.1478	6E	-2.1299	-2.1168
5F	-10.2494	-10.2439	6F	-10.2545	-10.2398
7A	-3.9757	-3.9738	8A	-4.4699	-4.4707
7B	-1.7427	-1.7460	8B	-0.7048	-0.7018
7C	-4.4314	-4.4316	8C	-4.7364	-4.7345
7D	-11.6083	-11.6133	8D	-12.5074	-12.5099
7E	-2.9022	-2.8970	8E	-7.3377	-7.3519
7F	-10.5166	-10.5110	8F	-12.1823	-12.1771

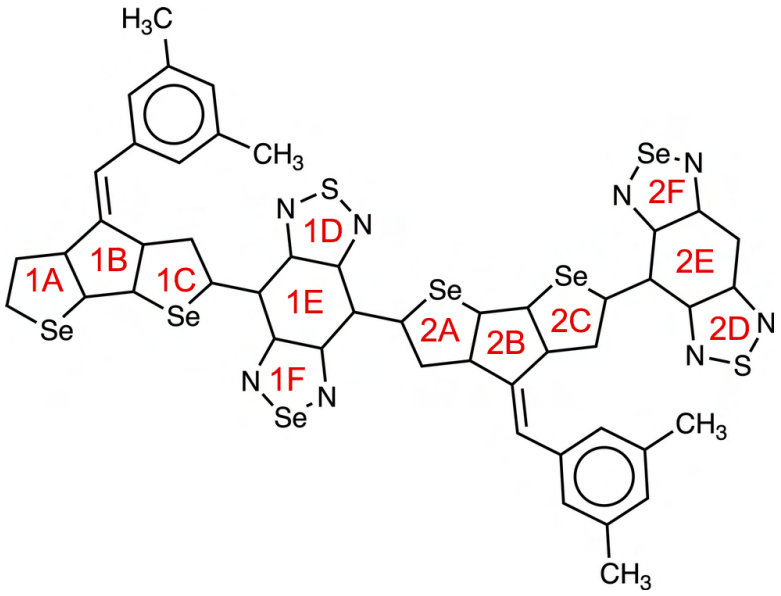


Table S20: Calculated $NICS_{iso}(1)$ (ppm) of CPDS-SeBBT dimer ($N = 2$) in the singlet and triplet states.

Ring index	singlet ($S = 0$)	triplet ($S = 1$)	Ring index	singlet ($S = 0$)	triplet ($S = 1$)
1A	-7.1044	-7.0596	2A	-3.5023	-3.3597
1B	-0.4674	-0.5090	2B	-1.1993	-1.2890
1C	-4.8710	-4.8683	2C	-3.5612	-3.4377
1D	-9.8487	-9.4314	2D	-10.4939	-10.3167
1E	-1.6298	-1.0642	2E	-3.5126	-3.1268
1F	-9.6049	-9.0452	2F	-9.9291	-9.6486

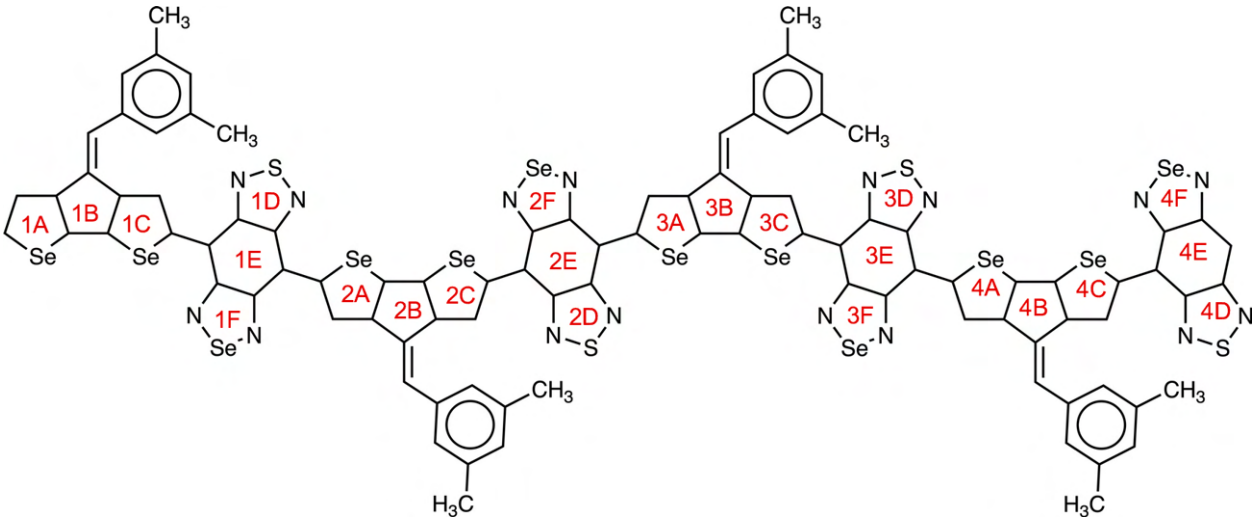


Table S21: Calculated $NICS_{iso}(1)$ (ppm) of CPDS-SeBBT tetramer ($N = 4$) in the singlet and triplet states.

Ring index	singlet ($S = 0$)	triplet ($S = 1$)	Ring index	singlet ($S = 0$)	triplet ($S = 1$)
1A	-7.0540	-7.0566	2A	-3.4910	-3.4914
1B	-0.0204	-0.0243	2B	-1.8702	-1.8675
1C	-4.5280	-4.5264	2C	-3.7381	-3.7370
1D	-9.4703	-9.4698	2D	-9.7382	-9.7379
1E	-1.2087	-1.2129	2E	-0.8816	-0.8704
1F	-9.1912	-9.1904	2F	-9.3308	-9.3297
3A	-3.4438	-3.4391	4A	-3.4745	-3.4741
3B	-1.3522	-1.3555	4B	-1.7526	-1.7547
3C	-3.3024	-3.3039	4C	-3.9660	-3.9632
3D	-9.6494	-9.6475	4D	-10.5312	-10.5253
3E	-0.8793	-0.8813	4E	-3.3846	-3.3698
3F	-9.3169	-9.3175	4F	-9.8601	-9.8566

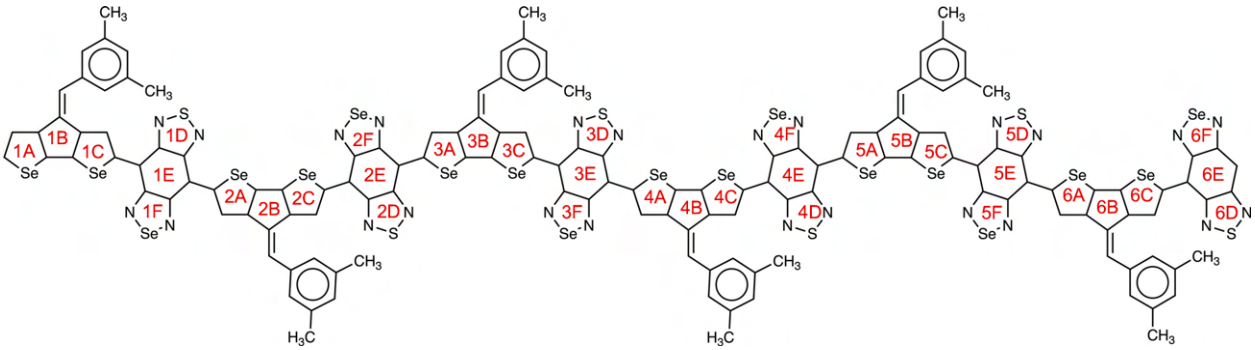


Table S22: Calculated $NICS_{iso}(1)$ (ppm) of CPDS-SeBBT hexamer ($N = 6$) in the singlet and triplet states.

Ring index	singlet ($S = 0$)	triplet ($S = 1$)	Ring index	singlet ($S = 0$)	triplet ($S = 1$)
1A	-7.0575	-7.0537	2A	-3.5268	-3.5248
1B	-0.0129	-0.0115	2B	-1.8696	-1.8687
1C	-4.5228	-4.5270	2C	-3.6951	-3.6975
1D	-9.4662	-9.4645	2D	-9.7405	-9.7412
1E	-1.2281	-1.2225	2E	-0.8755	-0.8748
1F	-9.1687	-9.1710	2F	-9.2996	-9.3001
3A	-3.4946	-3.4918	4A	-3.5138	-3.5185
3B	-1.3499	-1.3526	4B	-1.8684	-1.8713
3C	-3.2635	-3.2656	4C	-3.7297	-3.7309
3D	-9.6147	-9.6153	4D	-9.7357	-9.7374
3E	-0.8103	-0.8084	4E	-0.8663	-0.8748
3F	-9.2518	-9.2525	4F	-9.3406	-9.3471
5A	-3.4471	-3.4448	6A	-3.4681	-3.4666
5B	-1.3572	-1.3581	6B	-1.7559	-1.7588
5C	-3.3030	-3.3028	6C	-3.9762	-3.9755
5D	-9.6508	-9.6518	6D	-10.5014	-10.5056
5E	-0.8762	-0.8770	6E	-3.3787	-3.3847
5F	-9.3210	-9.3250	6F	-9.8668	-9.8594

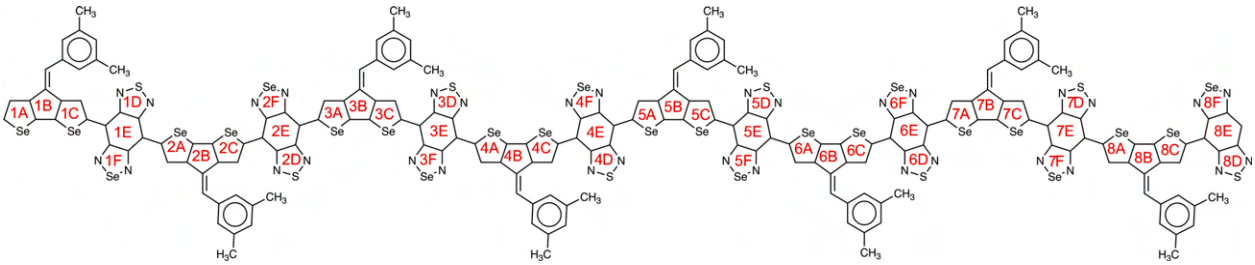


Table S23: Calculated $NICS_{iso}(1)$ (ppm) of CPDS-SeBBT octamer ($N = 8$) in the singlet and triplet states.

Ring index	singlet ($S = 0$)	triplet ($S = 1$)	Ring index	singlet ($S = 0$)	triplet ($S = 1$)
1A	-7.0610	-7.0628	2A	-3.5495	-3.5506
1B	-0.0091	-0.0086	2B	-1.8699	-1.8713
1C	-4.5221	-4.5207	2C	-3.6753	-3.6744
1D	-9.4578	-9.4615	2D	-9.7501	-9.7493
1E	-1.2225	-1.2243	2E	-0.8764	-0.8748
1F	-9.1626	-9.1602	2F	-9.2933	-9.2858
3A	-3.5136	-3.5115	4A	-3.5468	-3.5465
3B	-1.3510	-1.3450	4B	-1.8711	-1.8723
3C	-3.2561	-3.2537	4C	-3.6856	-3.6887
3D	-9.6095	-9.6098	4D	-9.7422	-9.7418
3E	-0.7999	-0.7990	4E	-0.8697	-0.8690
3F	-9.2391	-9.2306	4F	-9.3144	-9.3205
5A	-3.5002	-3.5006	6A	-3.5164	-3.5156
5B	-1.3535	-1.3551	6B	-1.8694	-1.8699
5C	-3.2536	-3.2540	6C	-3.7447	-3.7463
5D	-9.6126	-9.6133	6D	-9.7403	-9.7443
5E	-0.8018	-0.8052	6E	-0.8718	-0.8717
5F	-9.2661	-9.2694	6F	-9.3557	-9.3550
7A	-3.4413	-3.4401	8A	-3.4542	-3.4570
7B	-1.3658	-1.3624	8B	-1.7550	-1.7575
7C	-3.3006	-3.3010	8C	-3.9918	-3.9917
7D	-9.6522	-9.6526	8D	-10.5035	-10.5041
7E	-0.8737	-0.8789	8E	-3.4190	-3.4224
7F	-9.3364	-9.3331	8F	-9.8831	-9.8841

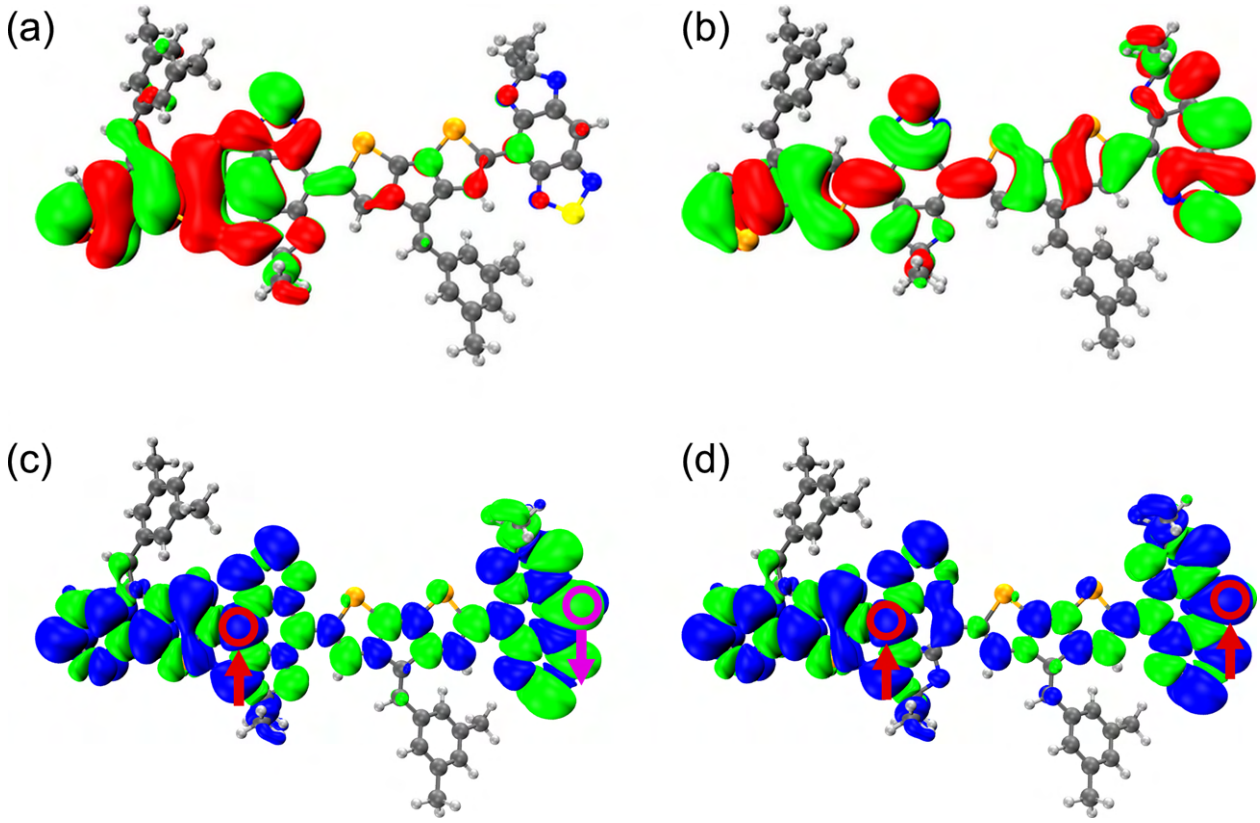


Figure S24: Optimized ground-state geometric structures for the CPDS-CBBT dimer ($N = 2$) and pictorial representations of the SOMOs with spin density distribution. (a) α-SOMO and (b) β-SOMO-1 of the open-shell singlet ($S = 0$), (c) spin density distribution of the singlet and (d) triplet states ($S = 1$). The green and red surfaces represent positive and negative signs of the MO at isovalue = 0.01 au, respectively. The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are indicated with up (alpha spin) and down (beta spin) arrows and open circles, respectively. Color codes for the atoms are: gray for C, blue for N, and yellow for S.

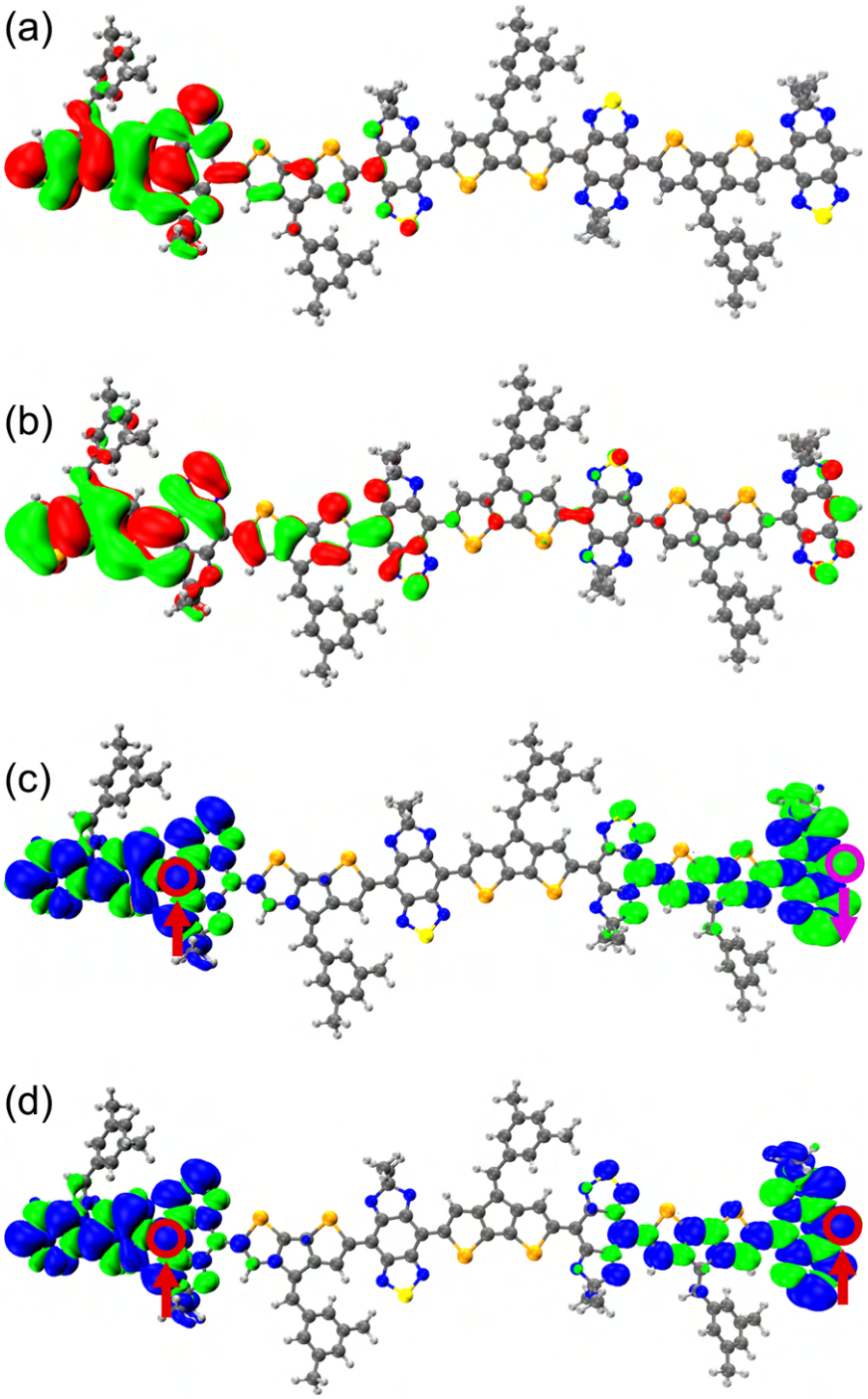


Figure S25: Optimized ground-state geometric structures for the CPDS-CBBT tetramer ($N = 4$) and pictorial representations of the SOMOs with spin density distribution. (a) α-SOMO and (b) β-SOMO-3 of the open-shell singlet ($S = 0$), (c) spin density distribution of the singlet and (d) triplet states ($S = 1$). The green and red surfaces represent positive and negative signs of the MO at isovalue = 0.01 au, respectively. The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are indicated with up (alpha spin) and down (beta spin) arrows and open circles, respectively. Color codes for the atoms are: gray for C, blue for N, and yellow for S.

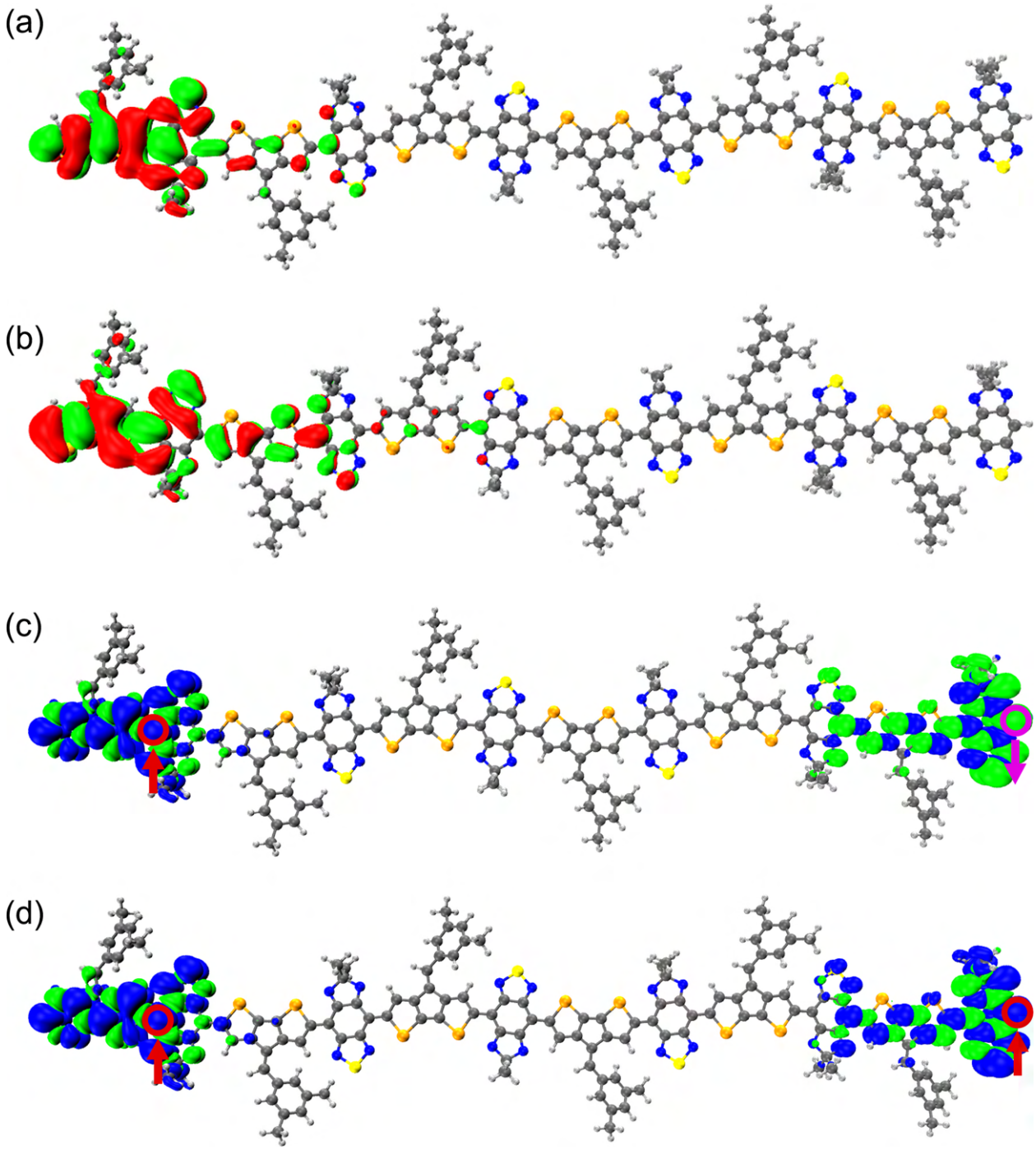


Figure S26: Optimized ground-state geometric structures for the CPDS-CBBT hexamer ($N = 6$) and pictorial representations of the SOMOs with spin density distribution. (a) α-SOMO and (b) β-SOMO-4 of the open-shell singlet ($S = 0$), (c) spin density distribution of the singlet and (d) triplet states ($S = 1$). The green and red surfaces represent positive and negative signs of the MO at isovalue = 0.01 au, respectively. The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are indicated with up (alpha spin) and down (beta spin) arrows and open circles, respectively. Color codes for the atoms are: gray for C, blue for N, and yellow for S.

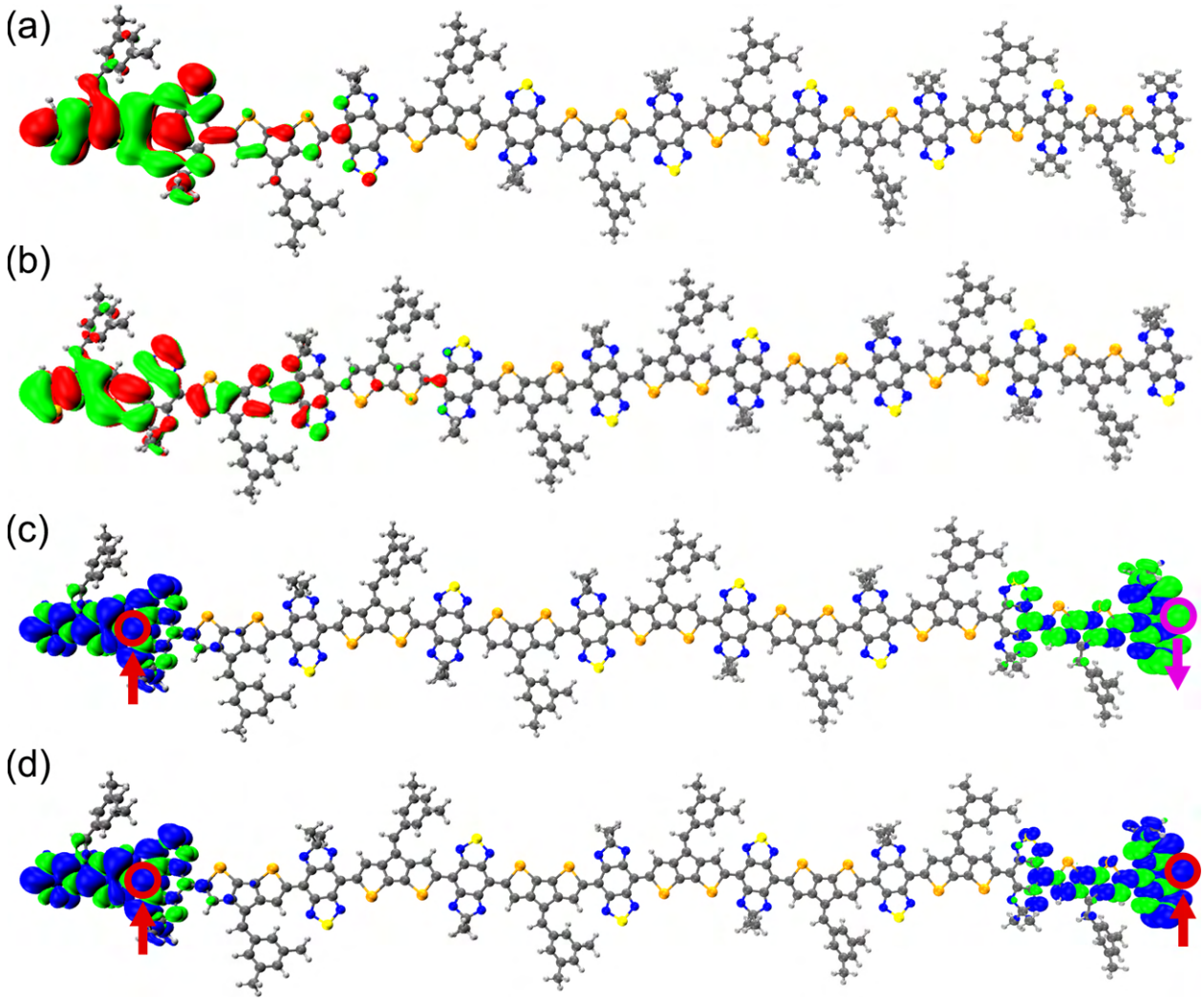


Figure S27: Optimized ground-state geometric structures for the CPDS-CBBT octamer ($N = 8$) and pictorial representations of the SOMOs with spin density distribution. (a) α-SOMO and (b) β-SOMO-8 of the open-shell singlet ($S = 0$), (c) spin density distribution of the singlet and (d) triplet states ($S = 1$). The green and red surfaces represent positive and negative signs of the MO at isovalue = 0.01 au, respectively. The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are indicated with up (alpha spin) and down (beta spin) arrows and open circles, respectively. Color codes for the atoms are: gray for C, blue for N, and yellow for S.

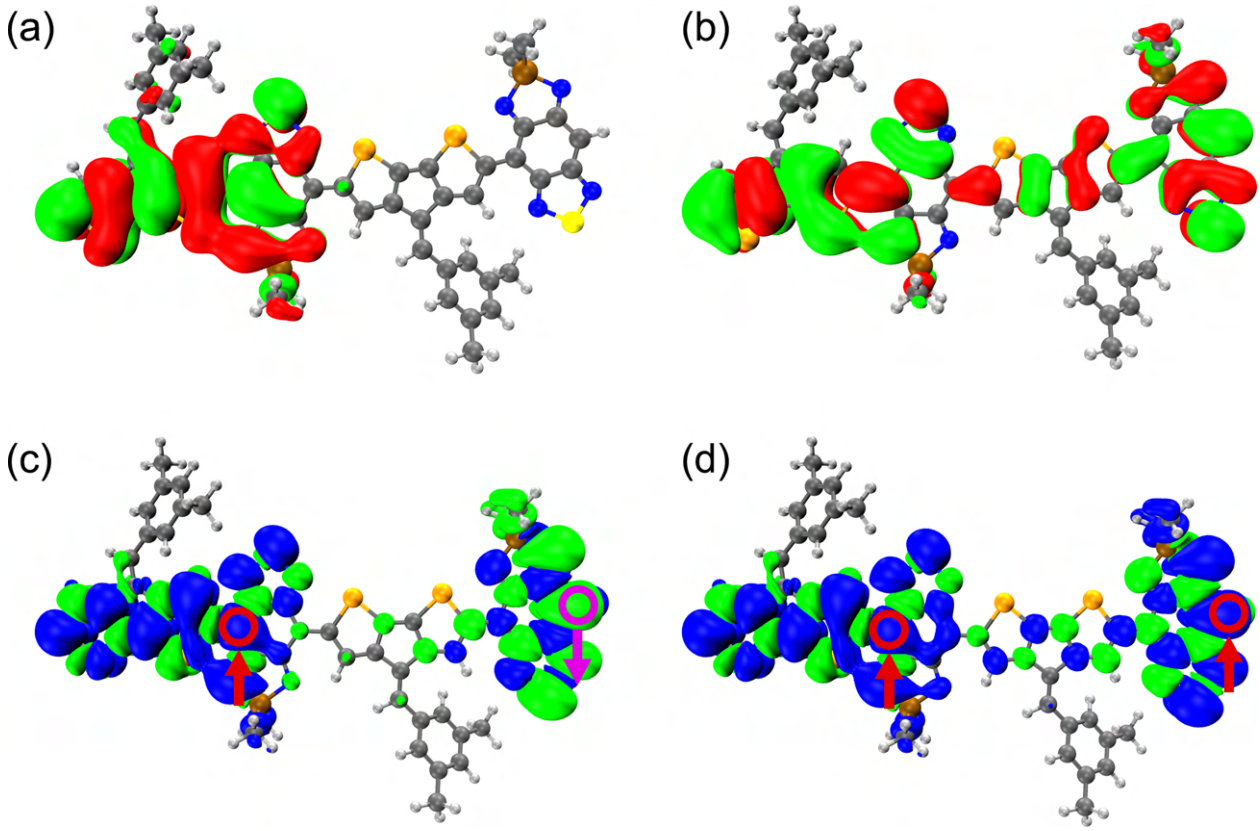


Figure S28: Optimized ground-state geometric structures for the CPDS-SiBBT dimer ($N = 2$) and pictorial representations of the SOMOs with spin density distribution. (a) α-SOMO and (b) β-SOMO-1 of the open-shell singlet ($S = 0$), (c) spin density distribution of the singlet and (d) triplet states ($S = 1$). The green and red surfaces represent positive and negative signs of the MO at isovalue = 0.01 au, respectively. The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are indicated with up (alpha spin) and down (beta spin) arrows and open circles, respectively. Color codes for the atoms are: gray for C, blue for N, and yellow for S.

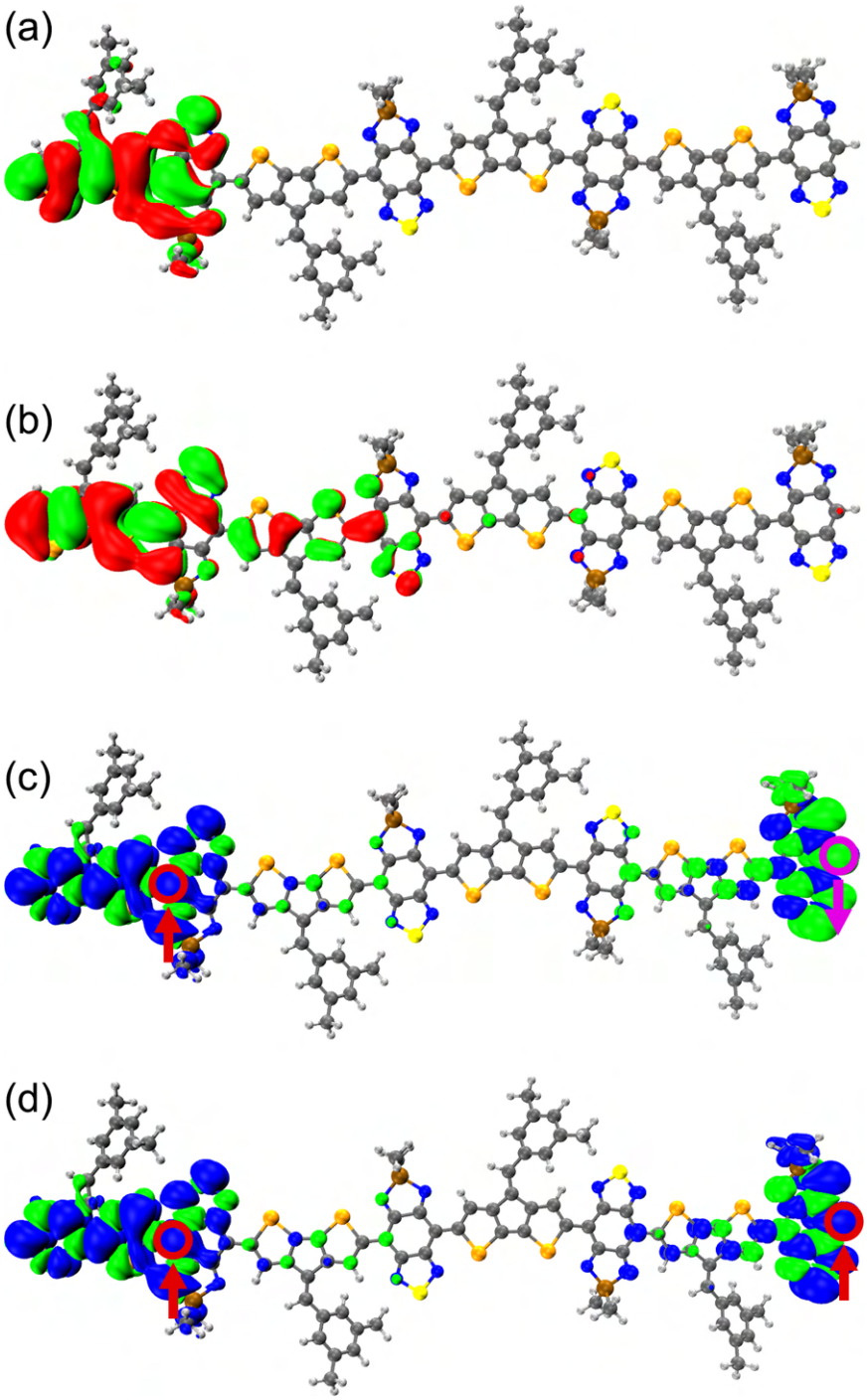


Figure S29: Optimized ground-state geometric structures for the CPDS-SiBBT tetramer ($N = 4$) and pictorial representations of the SOMOs with spin density distribution. (a) α-SOMO and (b) β-SOMO-3 of the open-shell singlet ($S = 0$), (c) spin density distribution of the singlet and (d) triplet states ($S = 1$). The green and red surfaces represent positive and negative signs of the MO at isovalue = 0.01 au, respectively. The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are indicated with up (alpha spin) and down (beta spin) arrows and open circles, respectively. Color codes for the atoms are: gray for C, blue for N, and yellow for S.

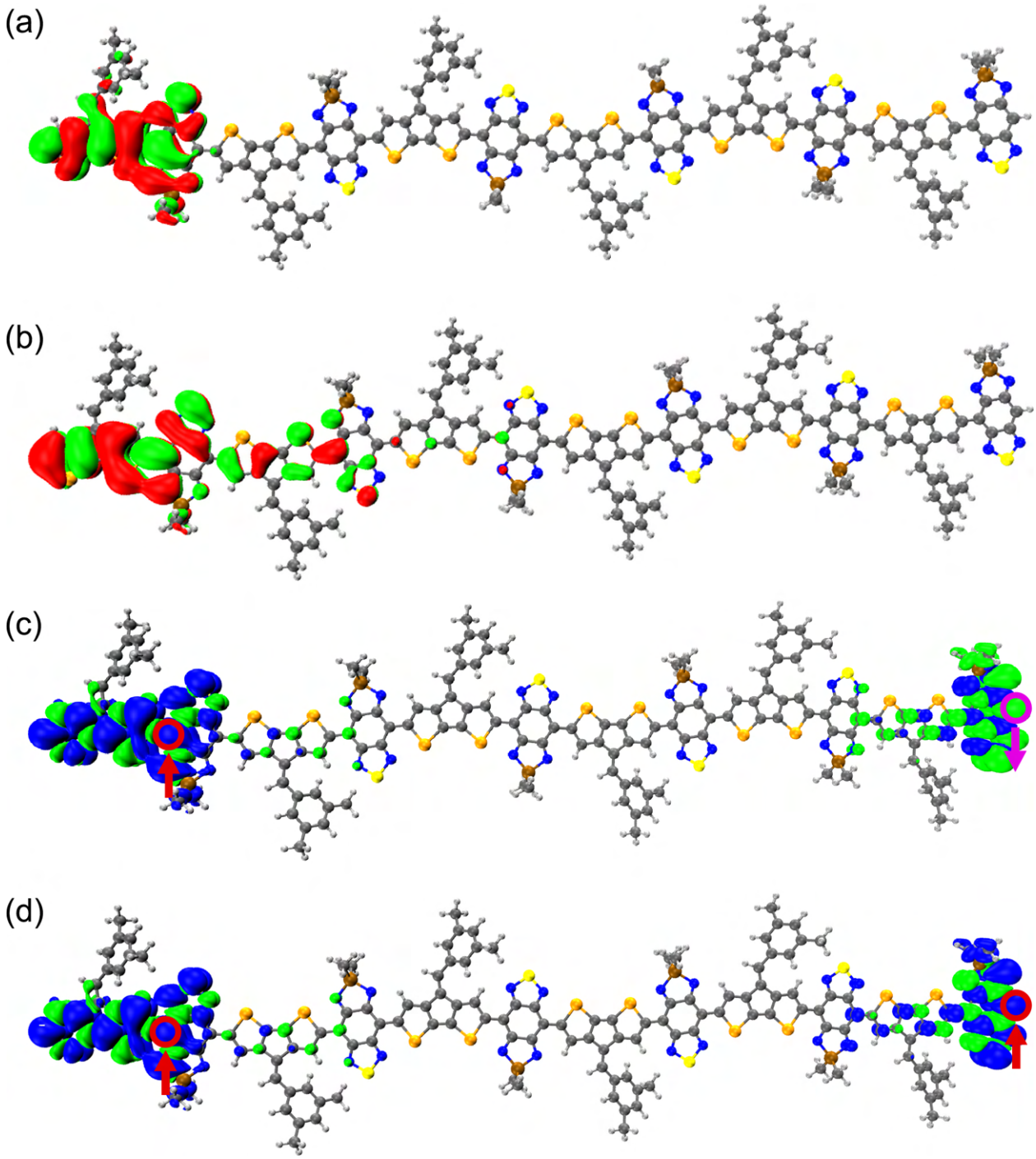


Figure S30: Optimized ground-state geometric structures for the CPDS-SiBBT hexamer ($N = 6$) and pictorial representations of the SOMOs with spin density distribution. (a) α-SOMO and (b) β-SOMO-5 of the open-shell singlet ($S = 0$), (c) spin density distribution of the singlet and (d) triplet states ($S = 1$). The green and red surfaces represent positive and negative signs of the MO at isovalue = 0.01 au, respectively. The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are indicated with up (alpha spin) and down (beta spin) arrows and open circles, respectively. Color codes for the atoms are: gray for C, blue for N, and yellow for S.

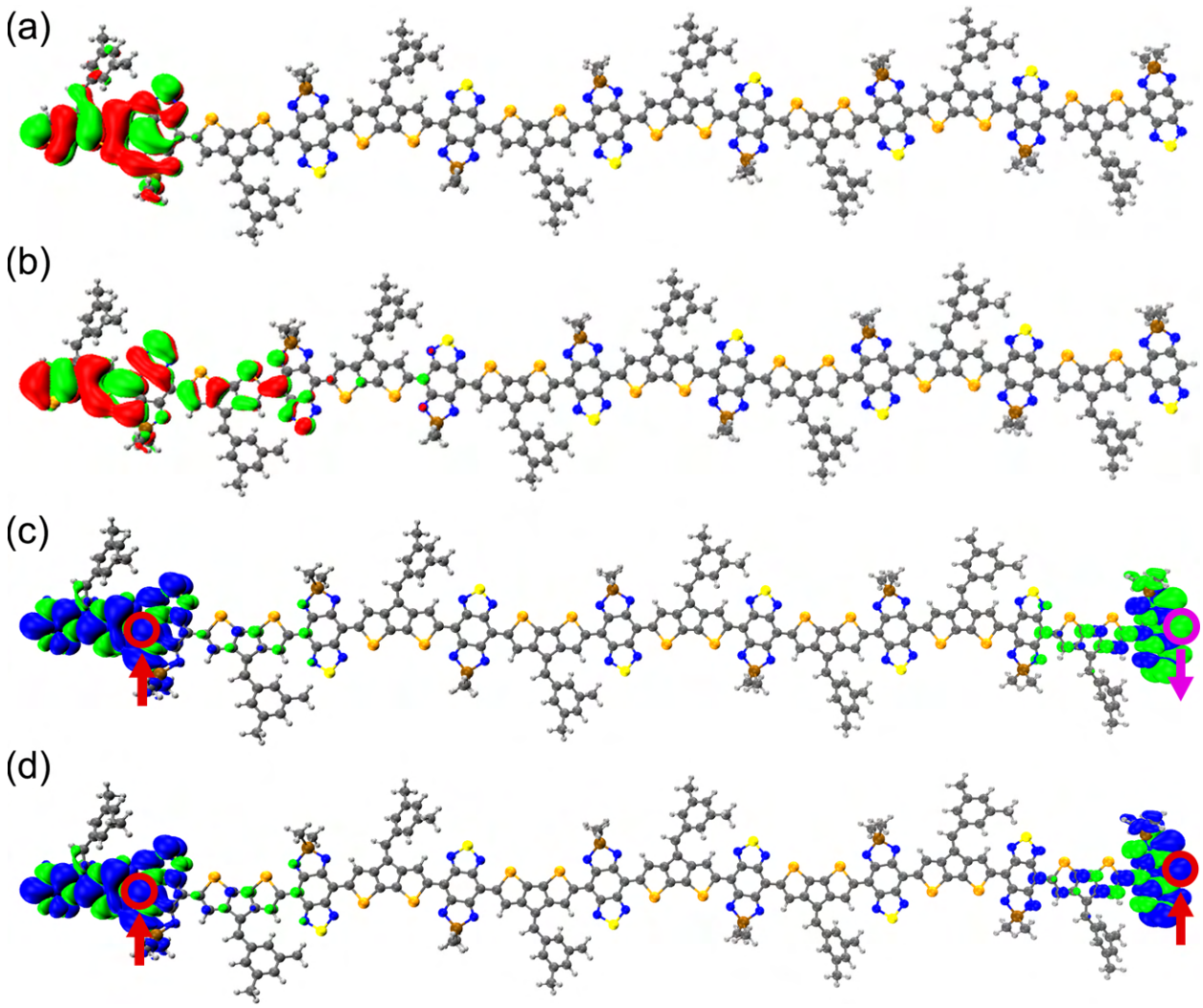


Figure S31: Optimized ground-state geometric structures for the CPDS-SiBBT octamer ($N = 8$) and pictorial representations of the SOMOs with spin density distribution. (a) α-SOMO and (b) β-SOMO-6 of the open-shell singlet ($S = 0$), (c) spin density distribution of the singlet and (d) triplet states ($S = 1$). The green and red surfaces represent positive and negative signs of the MO at isovalue = 0.01 au, respectively. The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are indicated with up (alpha spin) and down (beta spin) arrows and open circles, respectively. Color codes for the atoms are: gray for C, blue for N, and yellow for S.

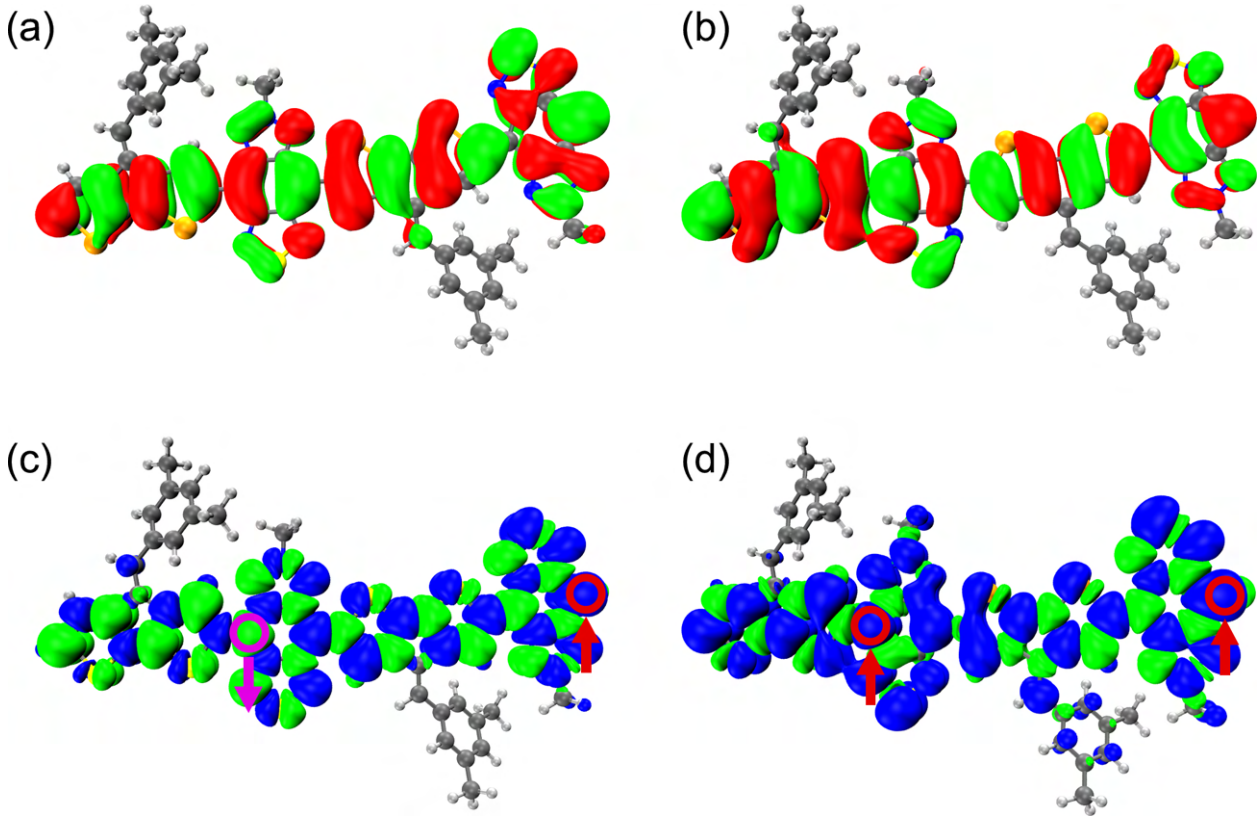


Figure S32: Optimized ground-state geometric structures for the CPDS-NBBT dimer ($N = 2$) and pictorial representations of the SOMOs with spin density distribution. (a) α-SOMO and (b) β-SOMO of the open-shell singlet ($S = 0$), (c) spin density distribution of the singlet and (d) triplet states ($S = 1$). The green and red surfaces represent positive and negative signs of the MO at isovalue = 0.01 au, respectively. The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are indicated with up (alpha spin) and down (beta spin) arrows and open circles, respectively. Color codes for the atoms are: gray for C, blue for N, yellow for S, and orange for Se.

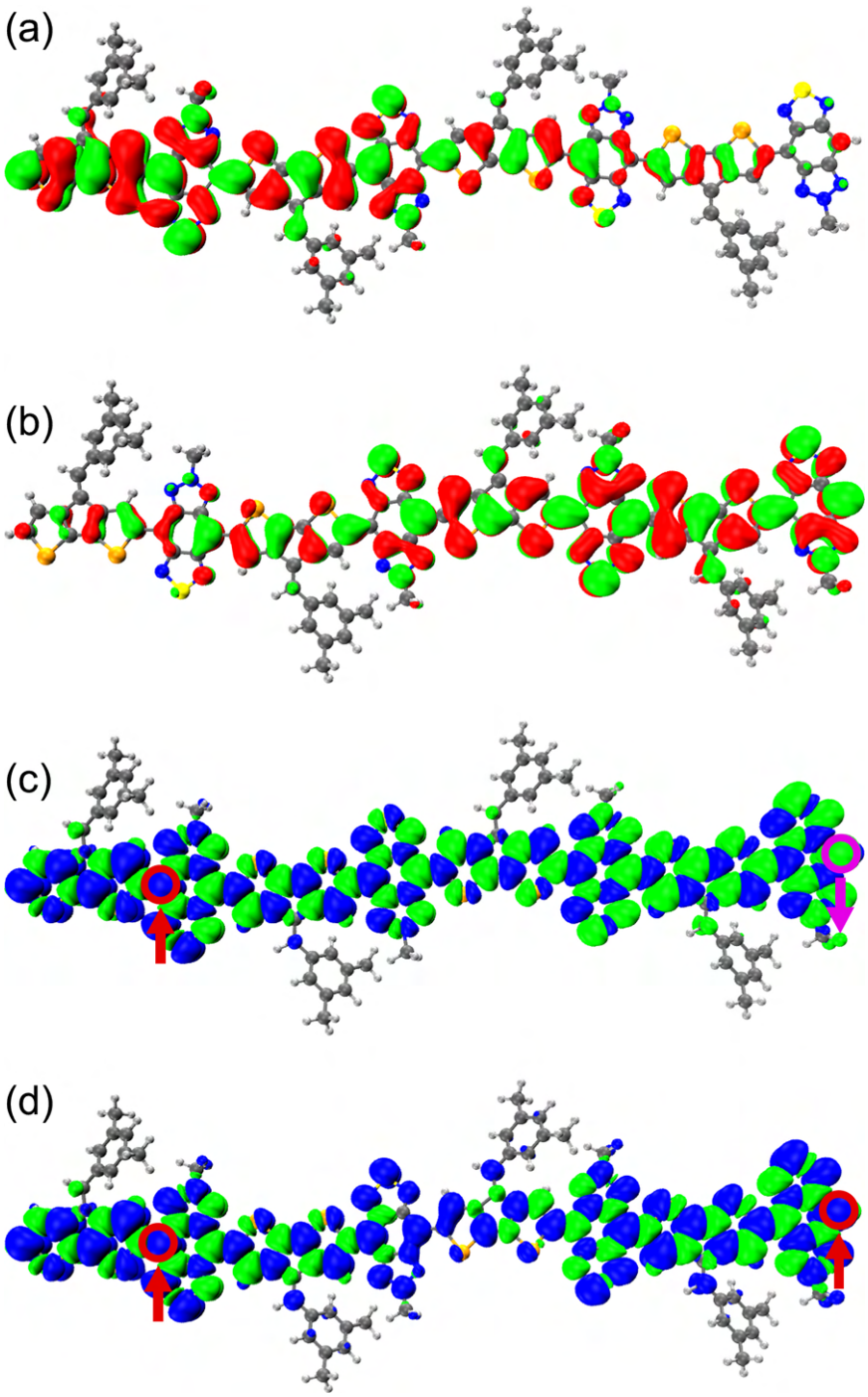


Figure S33: Optimized ground-state geometric structures for the CPDS-NBBT tetramer ($N = 4$) and pictorial representations of the SOMOs with spin density distribution. (a) α-SOMO and (b) β-SOMO of the open-shell singlet ($S = 0$), (c) spin density distribution of the singlet and (d) triplet states ($S = 1$). The green and red surfaces represent positive and negative signs of the MO at isovalue = 0.01 au, respectively. The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are indicated with up (alpha spin) and down (beta spin) arrows and open circles, respectively. Color codes for the atoms are: gray for C, blue for N, yellow for S, and orange for Se.

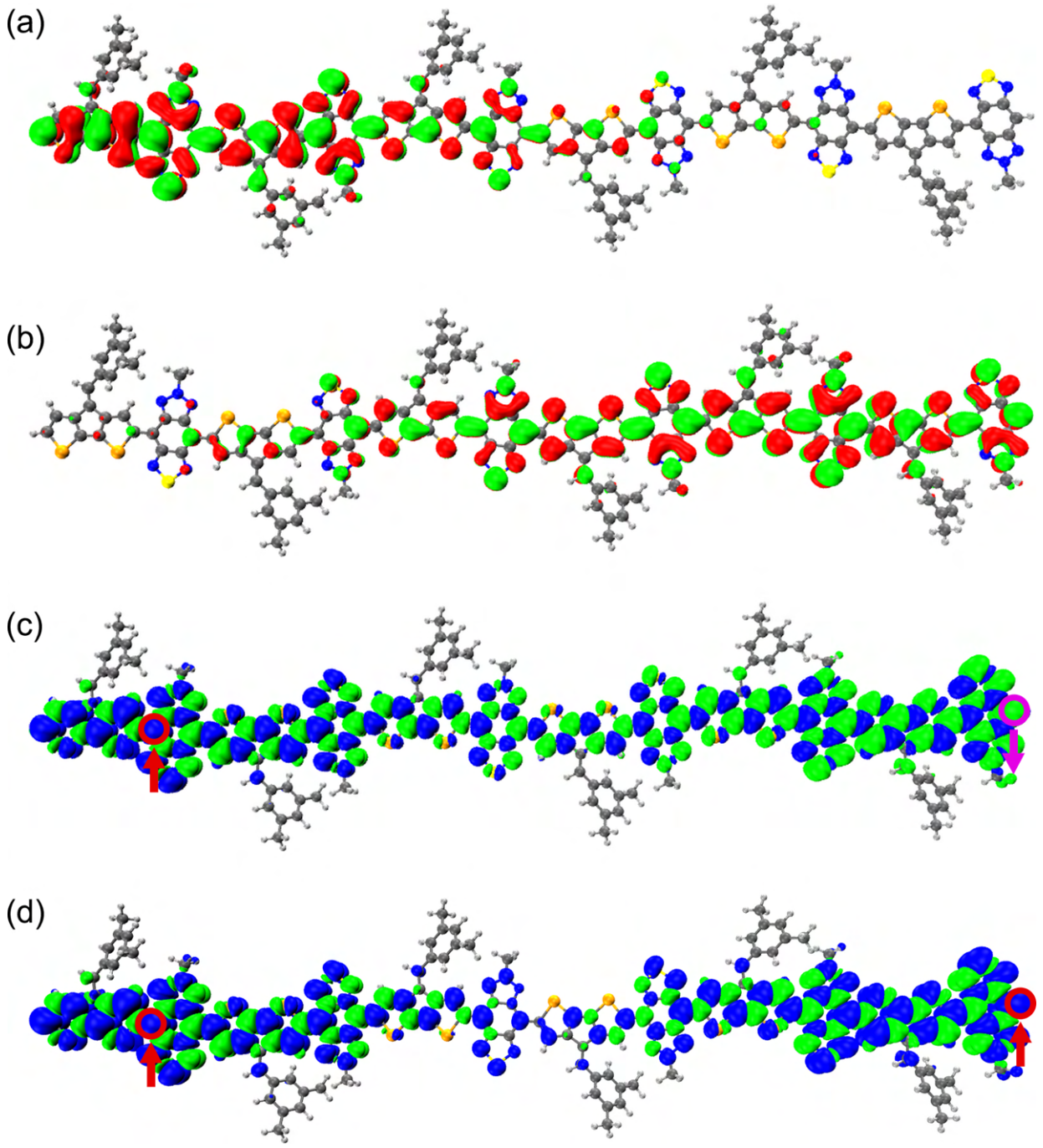


Figure S34: Optimized ground-state geometric structures for the CPDS-NBBT hexdamer ($N = 6$) and pictorial representations of the SOMOs with spin density distribution. (a) α-SOMO and (b) β-SOMO of the open-shell singlet ($S = 0$), (c) spin density distribution of the singlet and (d) triplet states ($S = 1$). The green and red surfaces represent positive and negative signs of the MO at isovalue = 0.01 au, respectively. The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are indicated with up (alpha spin) and down (beta spin) arrows and open circles, respectively. Color codes for the atoms are: gray for C, blue for N, yellow for S, and orange for Se.

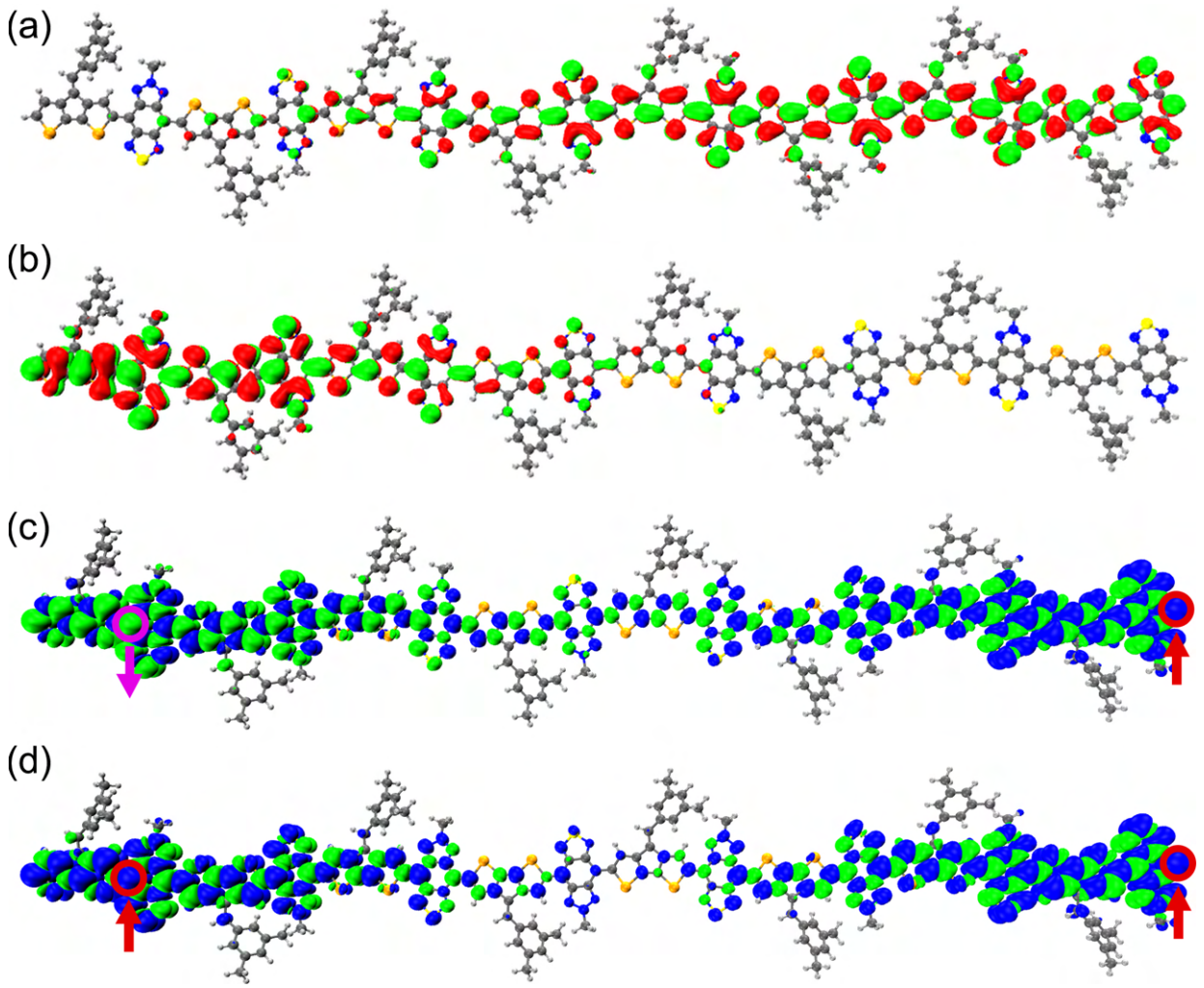


Figure S35: Optimized ground-state geometric structures for the CPDS-NBBT octamer ($N = 8$) and pictorial representations of the SOMOs with spin density distribution. (a) α-SOMO-1 and (b) β-SOMO of the open-shell singlet; (c) spin density distribution of the singlet ($S = 0$) and (d) triplet ($S = 1$) states. The green and red surfaces represent positive and negative signs of the MO at isovalue = 0.01 au, respectively. The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are highlighted with open circles (red: up-spin and purple: down-spin).

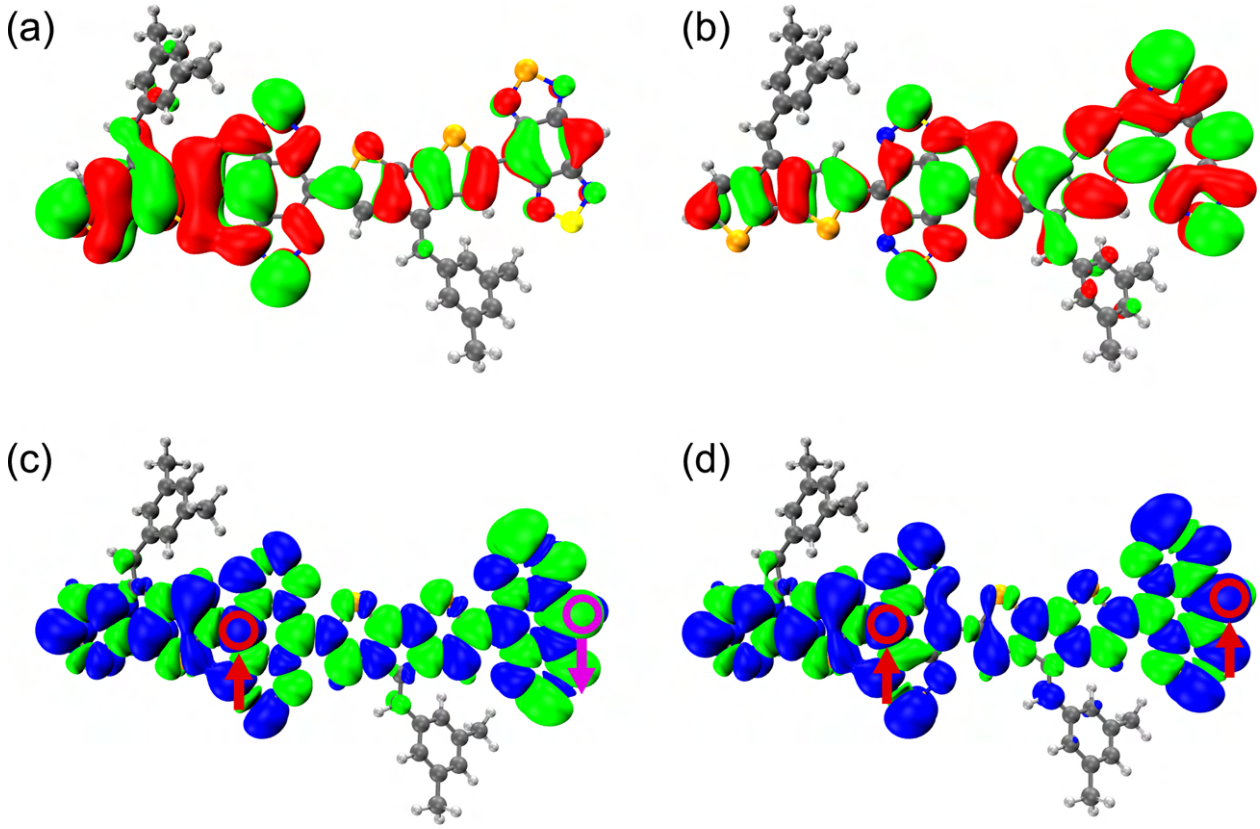


Figure S36: Optimized ground-state geometric structures for the CPDS-SeBBT dimer ($N = 2$) and pictorial representations of the SOMOs with spin density distribution. (a) α-SOMO and (b) β-SOMO of the open-shell singlet ($S = 0$), (c) spin density distribution of the singlet and (d) triplet states ($S = 1$). The green and red surfaces represent positive and negative signs of the MO at isovalue = 0.01 au, respectively. The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are indicated with up (alpha spin) and down (beta spin) arrows and open circles, respectively. Color codes for the atoms are: gray for C, blue for N, and yellow for S.

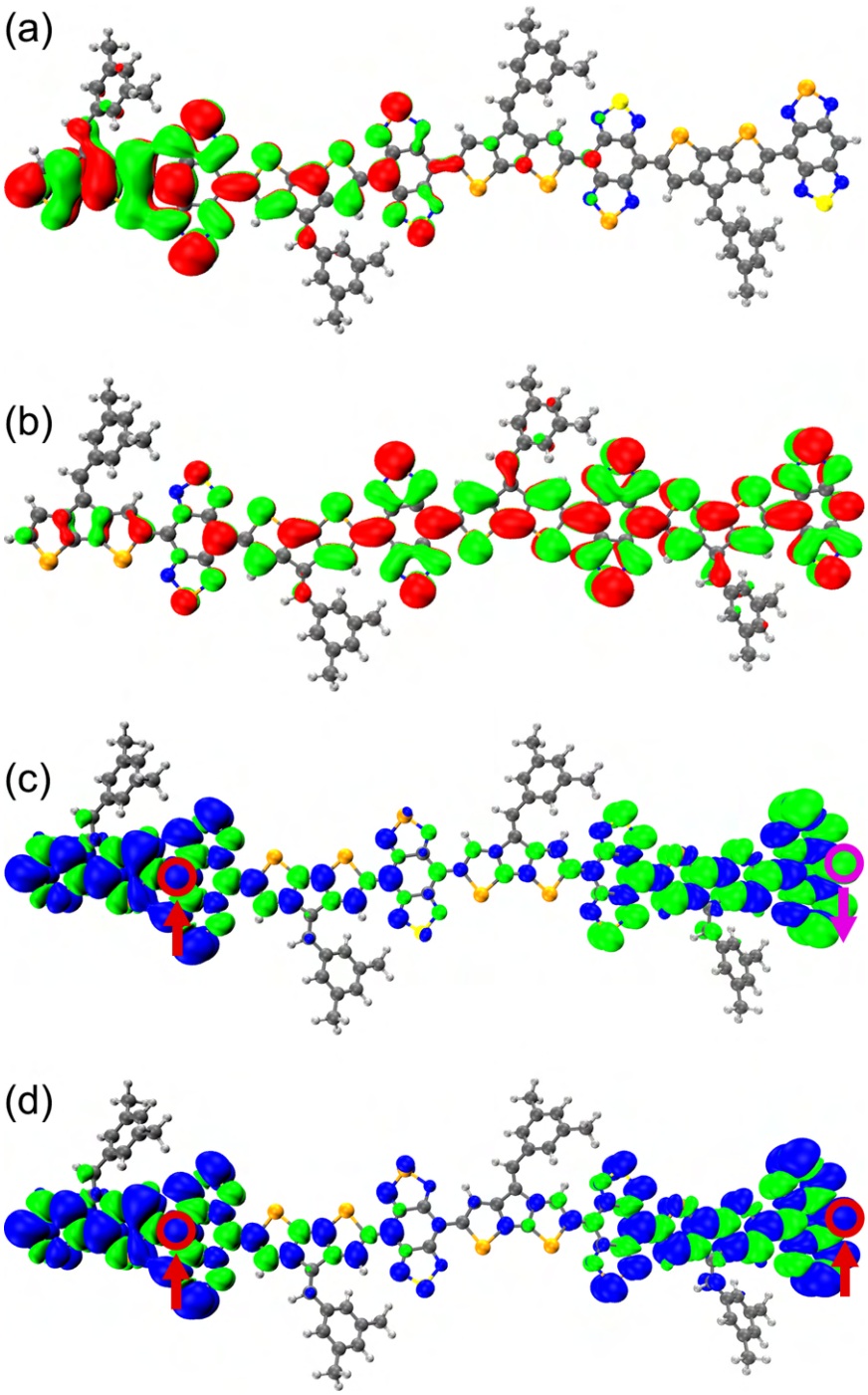


Figure S37: Optimized ground-state geometric structures for the CPDS-SeBBT tetramer ($N = 4$) and pictorial representations of the SOMOs with spin density distribution. (a) α-SOMO and (b) β-SOMO of the open-shell singlet ($S = 0$), (c) spin density distribution of the singlet and (d) triplet states ($S = 1$). The green and red surfaces represent positive and negative signs of the MO at isovalue = 0.01 au, respectively. The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are indicated with up (alpha spin) and down (beta spin) arrows and open circles, respectively. Color codes for the atoms are: gray for C, blue for N, and yellow for S.

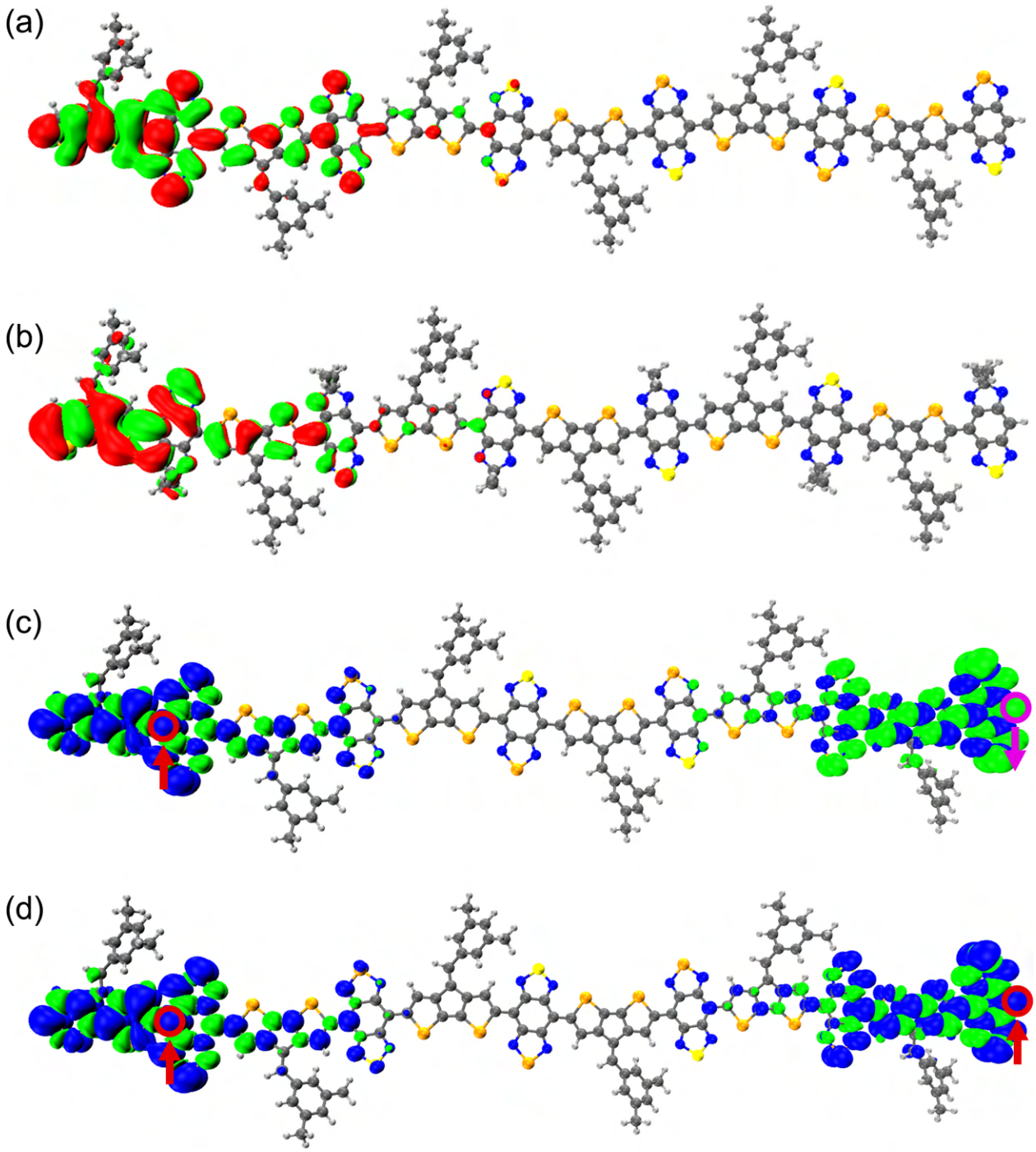


Figure S38: Optimized ground-state geometric structures for the CPDS-SeBBT hexamer ($N = 6$) and pictorial representations of the SOMOs with spin density distribution. (a) α-SOMO and (b) β-SOMO-1 of the open-shell singlet ($S = 0$), (c) spin density distribution of the singlet and (d) triplet states ($S = 1$). The green and red surfaces represent positive and negative signs of the MO at isovalue = 0.01 au, respectively. The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are indicated with up (alpha spin) and down (beta spin) arrows and open circles, respectively. Color codes for the atoms are: gray for C, blue for N, and yellow for S.

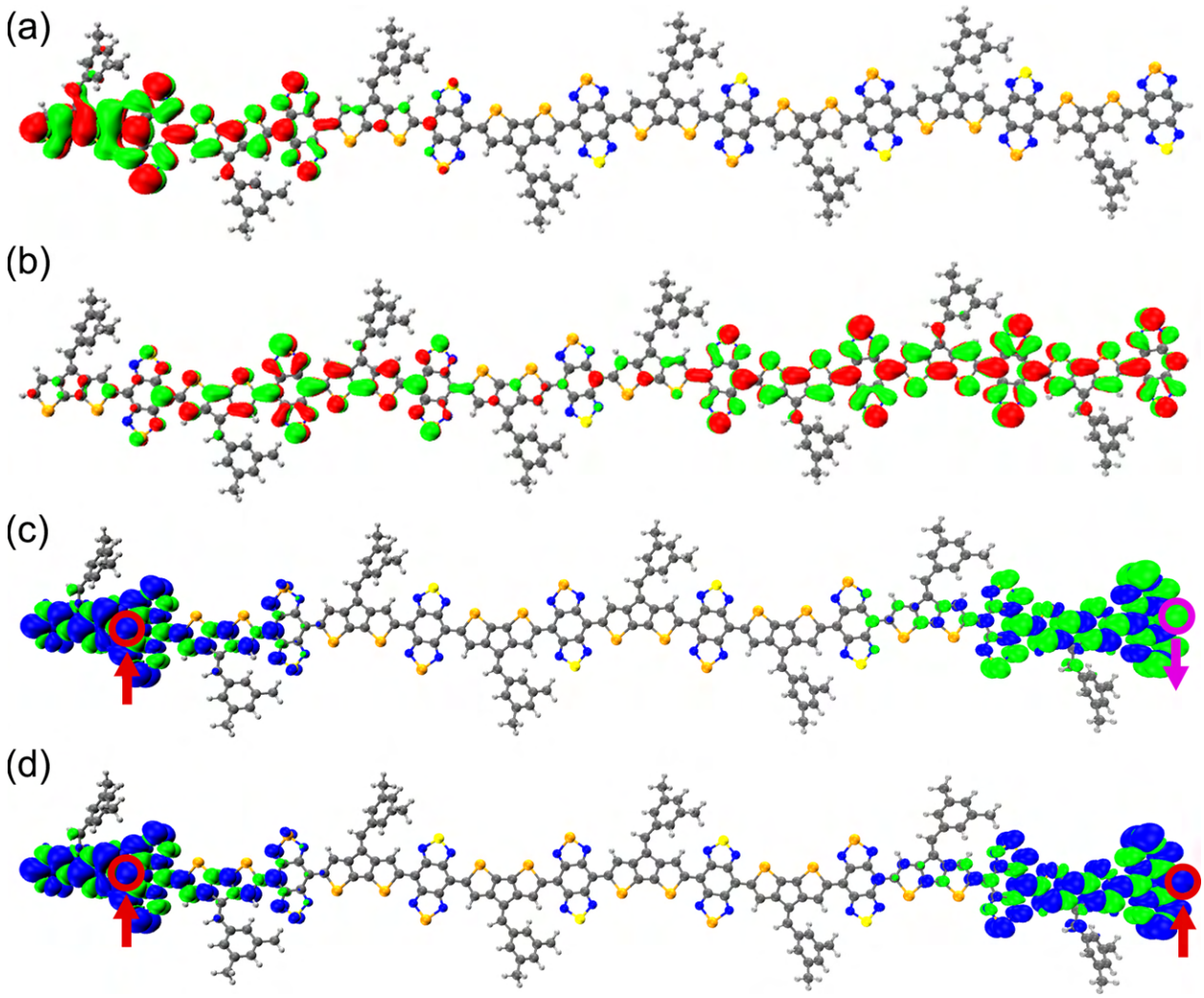


Figure S39: Optimized ground-state geometric structures for the CPDS-SeBBT octamer ($N = 8$) and pictorial representations of the SOMOs with spin density distribution. (a) α-SOMO and (b) β-SOMO-1 of the open-shell singlet ($S = 0$), (c) spin density distribution of the singlet and (d) triplet states ($S = 1$). The green and red surfaces represent positive and negative signs of the MO at isovalue = 0.01 au, respectively. The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are indicated with up (alpha spin) and down (beta spin) arrows and open circles, respectively. Color codes for the atoms are: gray for C, blue for N, and yellow for S.

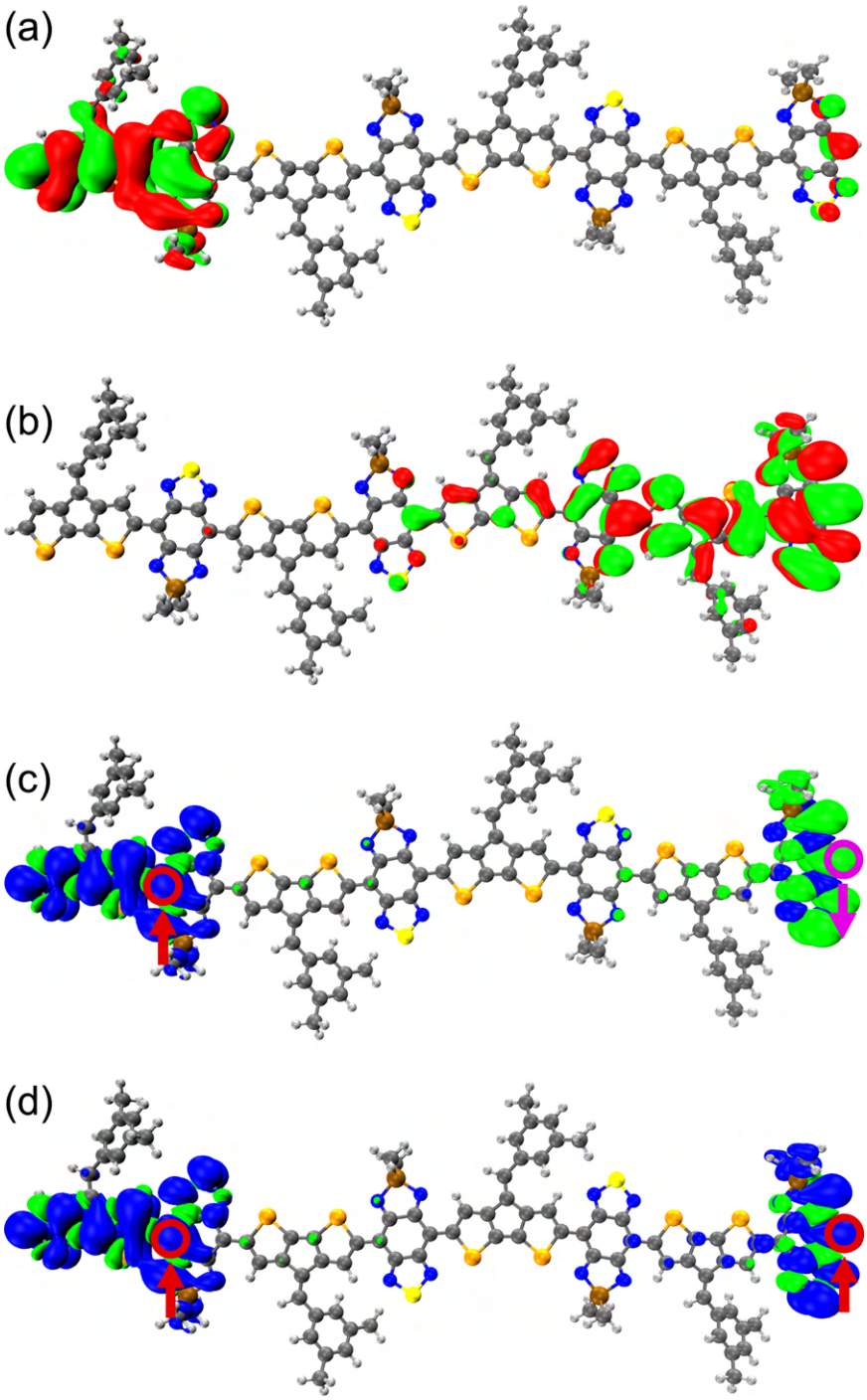


Figure S40: Optimized ground-state geometric structures for the CPDS-SiBBT tetramer ($N = 4$) and pictorial representations of the SOMOs with spin density distribution at UBLYP/6-31G(d,p) level of theory and basis set. (a) α-SOMO and (b) β-SOMO-3 of the open-shell singlet ($S = 0$), (c) spin density distribution of the singlet and (d) triplet states ($S = 1$). The green and red surfaces represent positive and negative signs of the MO at isovalue = 0.01 au, respectively. The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are indicated with up (alpha spin) and down (beta spin) arrows and open circles, respectively. Color codes for the atoms are: gray for C, blue for N, and yellow for S.

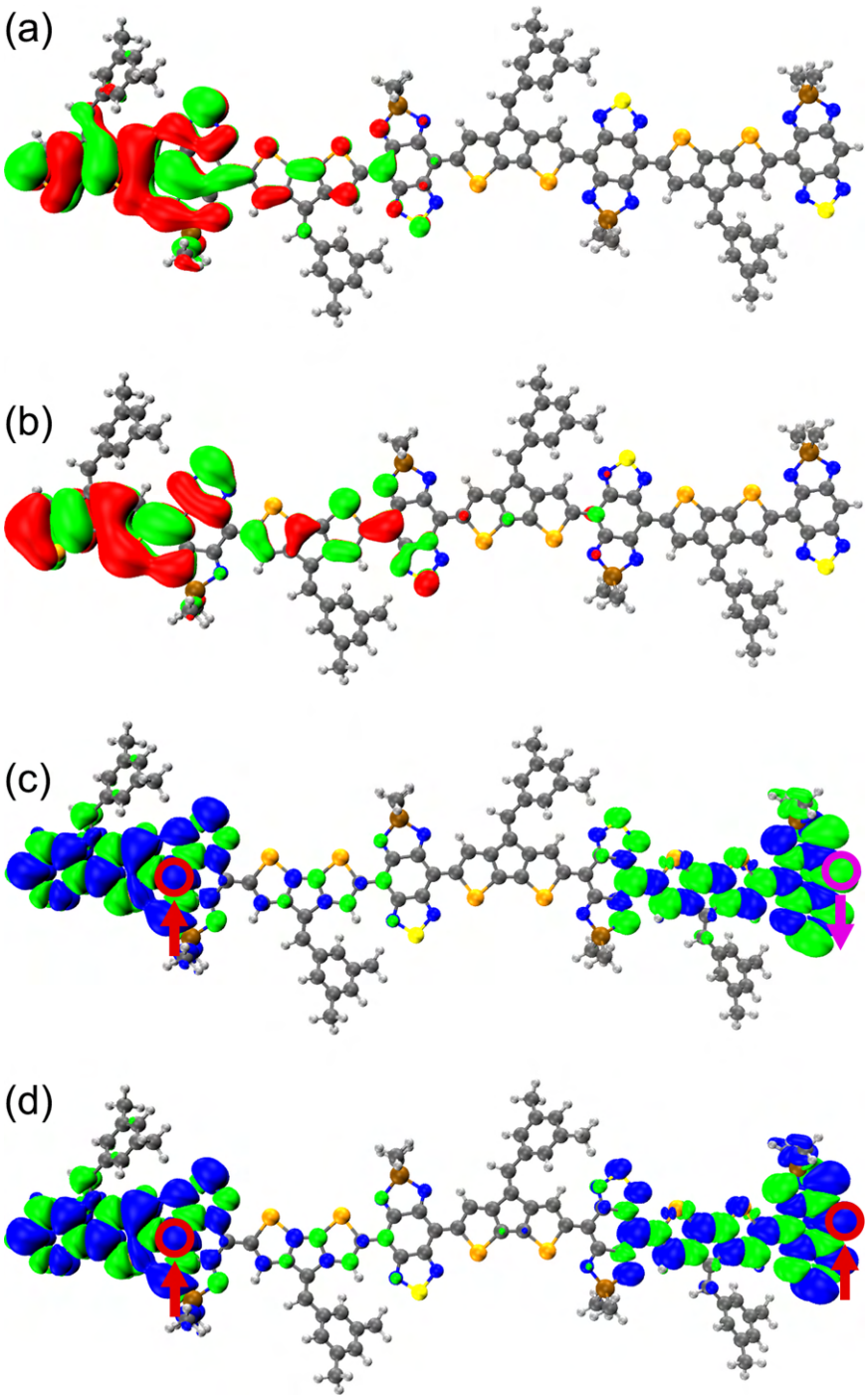


Figure S41: Optimized ground-state geometric structures for the CPDS-SiBBT tetramer ($N = 4$) and pictorial representations of the SOMOs with spin density distribution at UCAM-B3LYP/6-31G(d,p) level of theory and basis set. (a) α-SOMO and (b) β-SOMO-3 of the open-shell singlet ($S = 0$), (c) spin density distribution of the singlet and (d) triplet states ($S = 1$). The green and red surfaces represent positive and negative signs of the MO at isovalue = 0.01 au, respectively. The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are indicated with up (alpha spin) and down (beta spin) arrows and open circles, respectively. Color codes for the atoms are: gray for C, blue for N, and yellow for S.

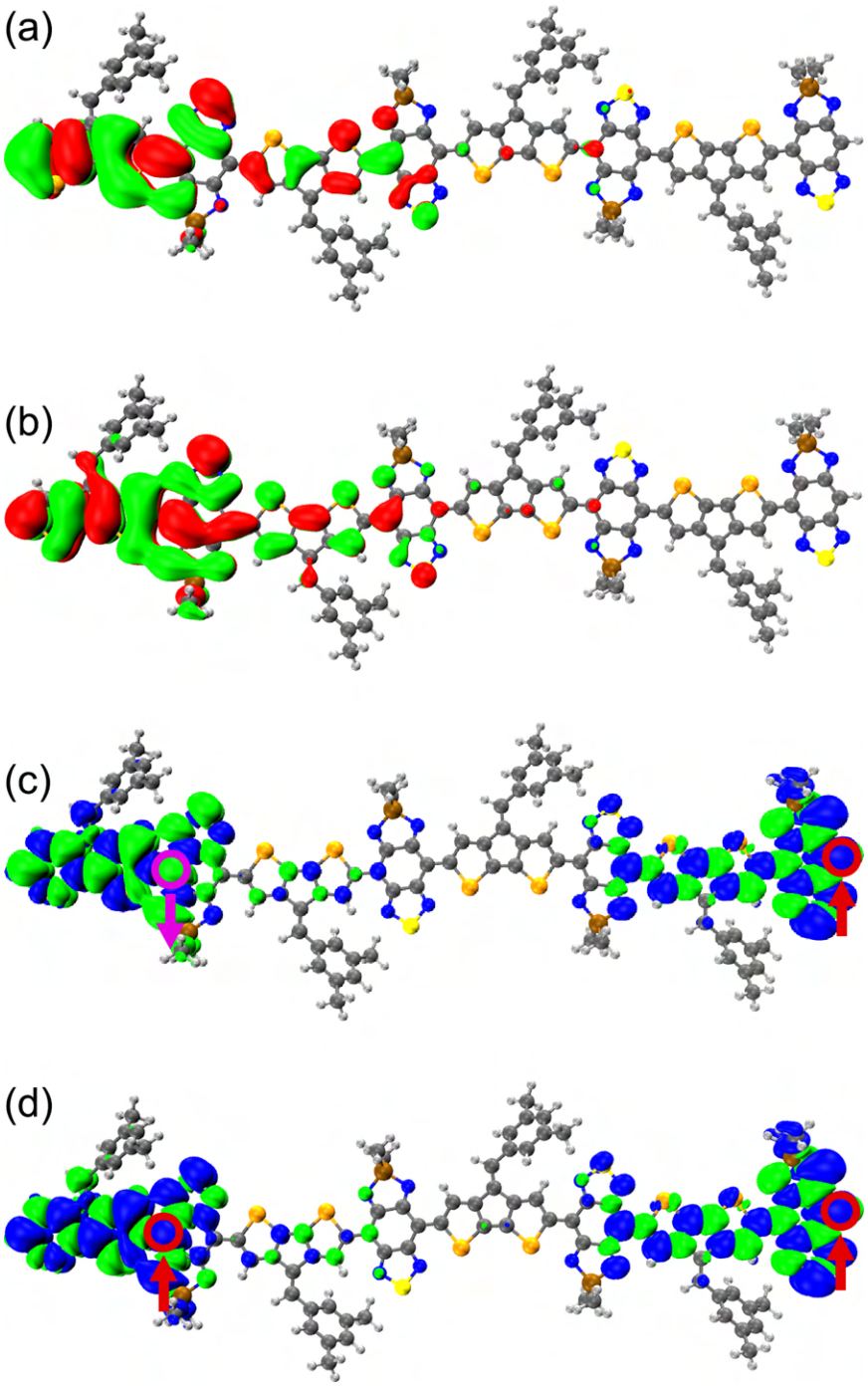


Figure S42: Optimized ground-state geometric structures for the CPDS-SiBBT tetramer ($N = 4$) and pictorial representations of the SOMOs with spin density distribution at ωB97X-D/6-31G(d,p) level of theory and basis set. (a) α-SOMO-3 and (b) β-SOMO of the open-shell singlet ($S = 0$), (c) spin density distribution of the singlet and (d) triplet states ($S = 1$). The green and red surfaces represent positive and negative signs of the MO at isovalue = 0.01 au, respectively. The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are indicated with up (alpha spin) and down (beta spin) arrows and open circles, respectively. Color codes for the atoms are: gray for C, blue for N, and yellow for S.

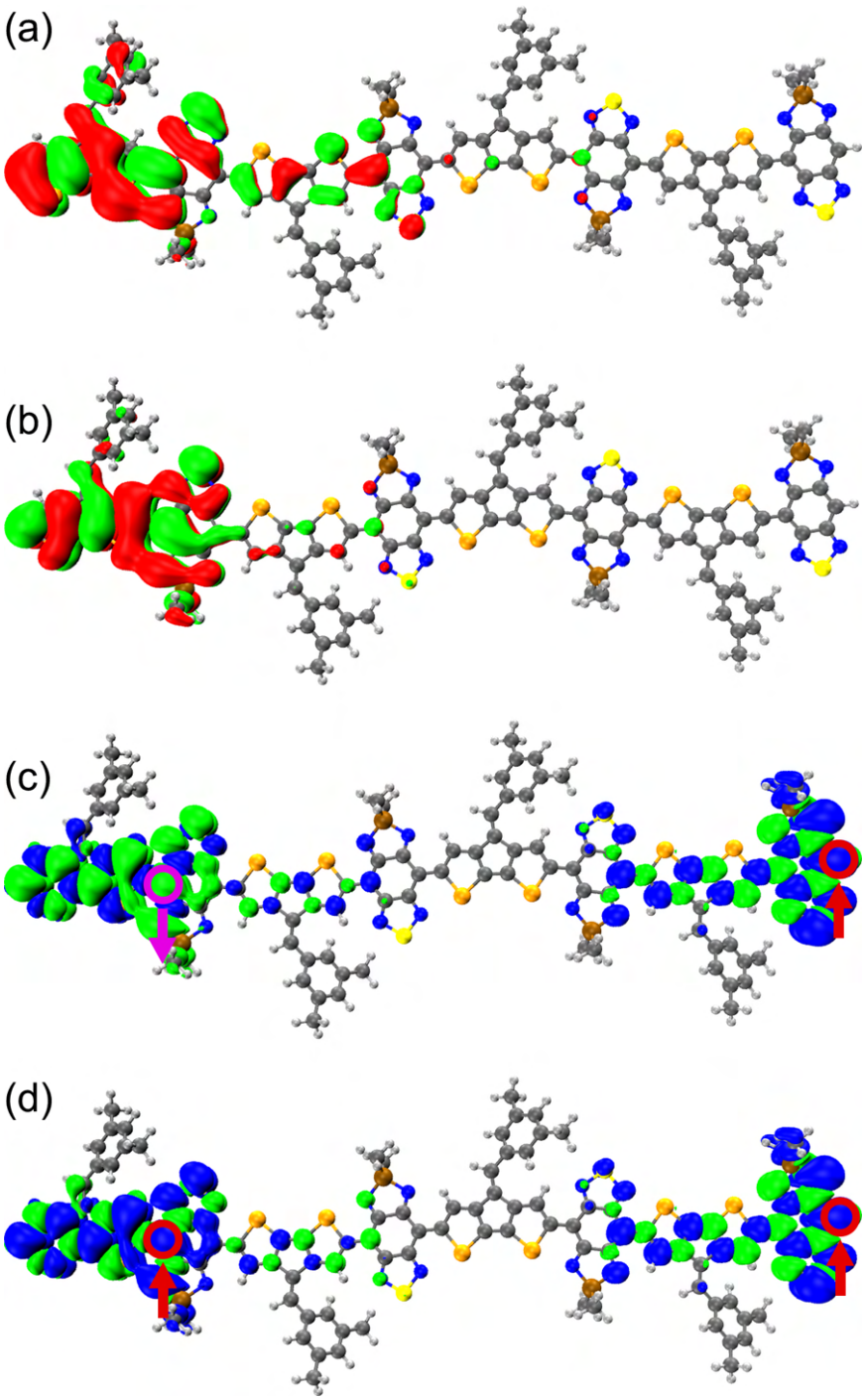


Figure S43: Pictorial representations of the SOMOs with spin density distribution for CPDS-SiBBT tetramer ($N = 4$) at ULC-ωHPBE level of theory and 6-31G(d,p) basis set. (a) α-SOMO-3 and (b) β-SOMO of the open-shell singlet ($S = 0$), (c) spin density distribution of the singlet and (d) triplet states ($S = 1$). The green and red surfaces represent positive and negative signs of the MO at isovalue = 0.01 au, respectively. The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are indicated with up (alpha spin) and down (beta spin) arrows and open circles, respectively. Color codes for the atoms are: gray for C, blue for N, and yellow for S.

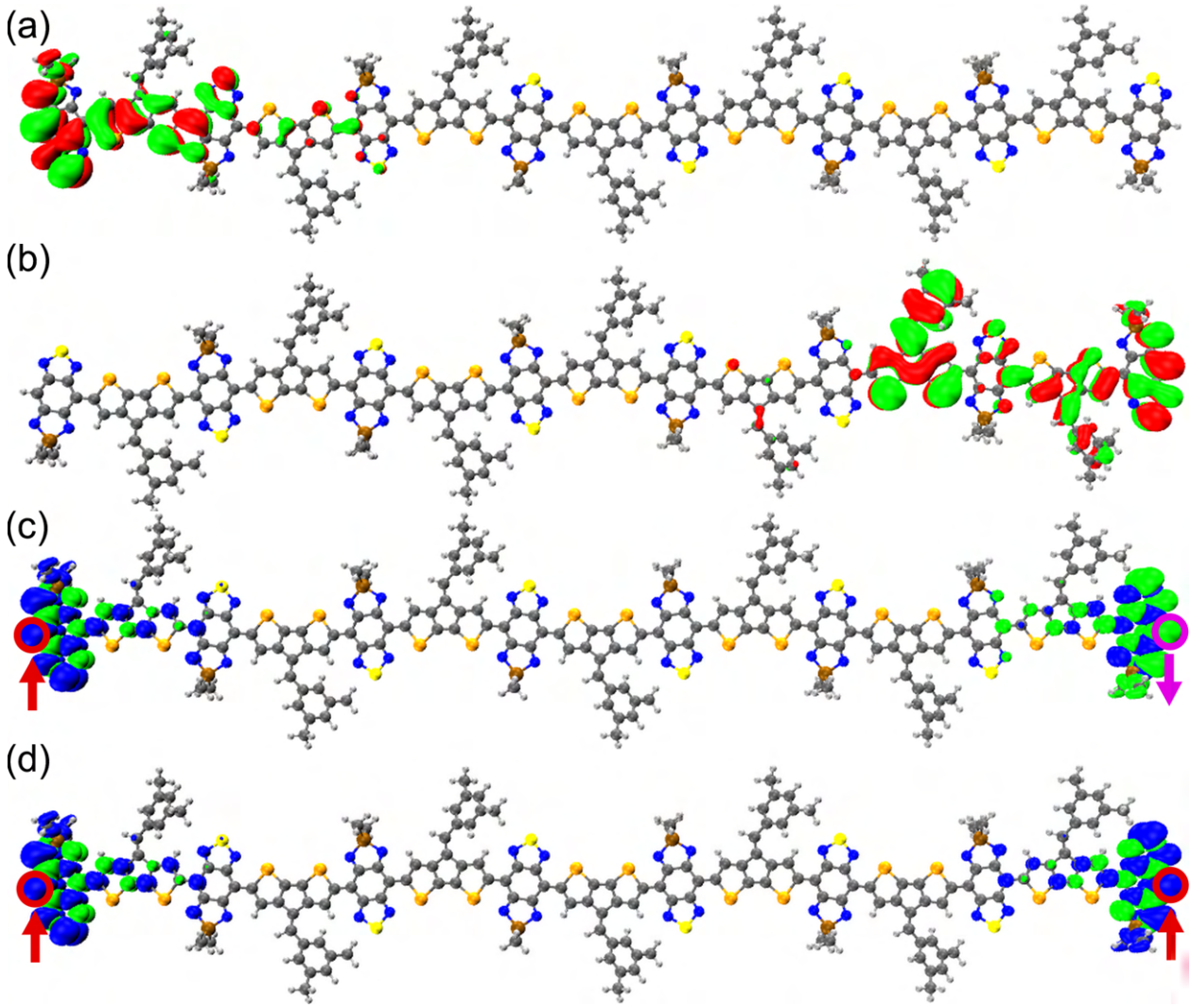


Figure S44: Optimized ground-state geometric structures for the CPDS-SiBBT heptamer ($N = 7$) with end acceptor units and pictorial representations of the SOMOs with spin density distribution. (a) α-SOMO-7 and (b) β-SOMO-13 of the open-shell singlet ($S = 0$), (c) spin density distribution of the singlet and (d) triplet states ($S = 1$). The green and red surfaces represent positive and negative signs of the MO at isovalue = 0.01 au, respectively. The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are indicated with up (alpha spin) and down (beta spin) arrows and open circles, respectively. Color codes for the atoms are: gray for C, blue for N, and yellow for S.

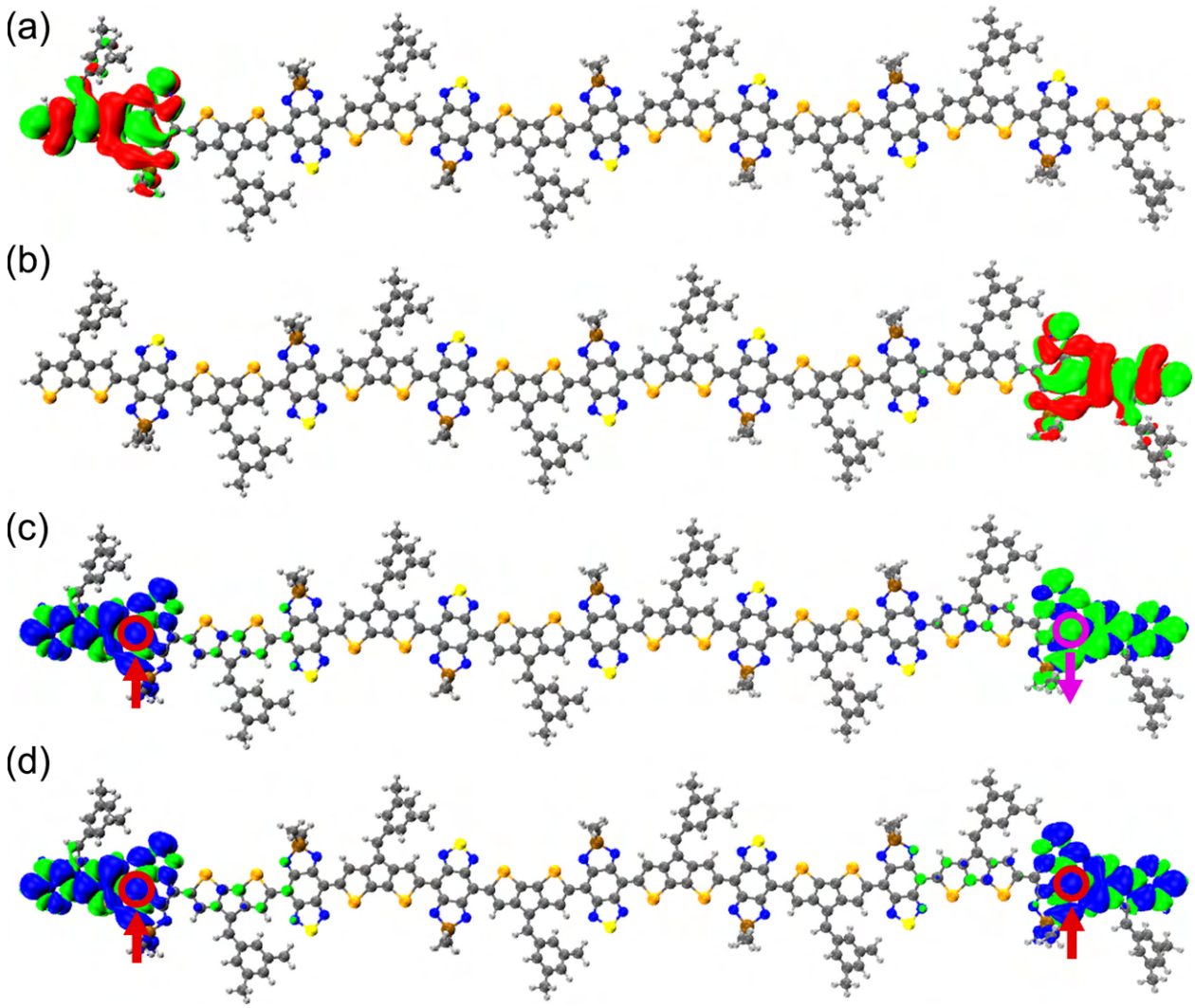


Figure S45: Optimized ground-state geometric structures for the CPDS-SiBBT heptamer ($N = 7$) with end donor units and pictorial representations of the SOMOs with spin density distribution. (a) α-SOMO and (b) β-SOMO of the open-shell singlet ($S = 0$), (c) spin density distribution of the singlet and (d) triplet states ($S = 1$). The green and red surfaces represent positive and negative signs of the MO at isovalue = 0.01 au, respectively. The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are indicated with up (alpha spin) and down (beta spin) arrows and open circles, respectively. Color codes for the atoms are: gray for C, blue for N, and yellow for S.

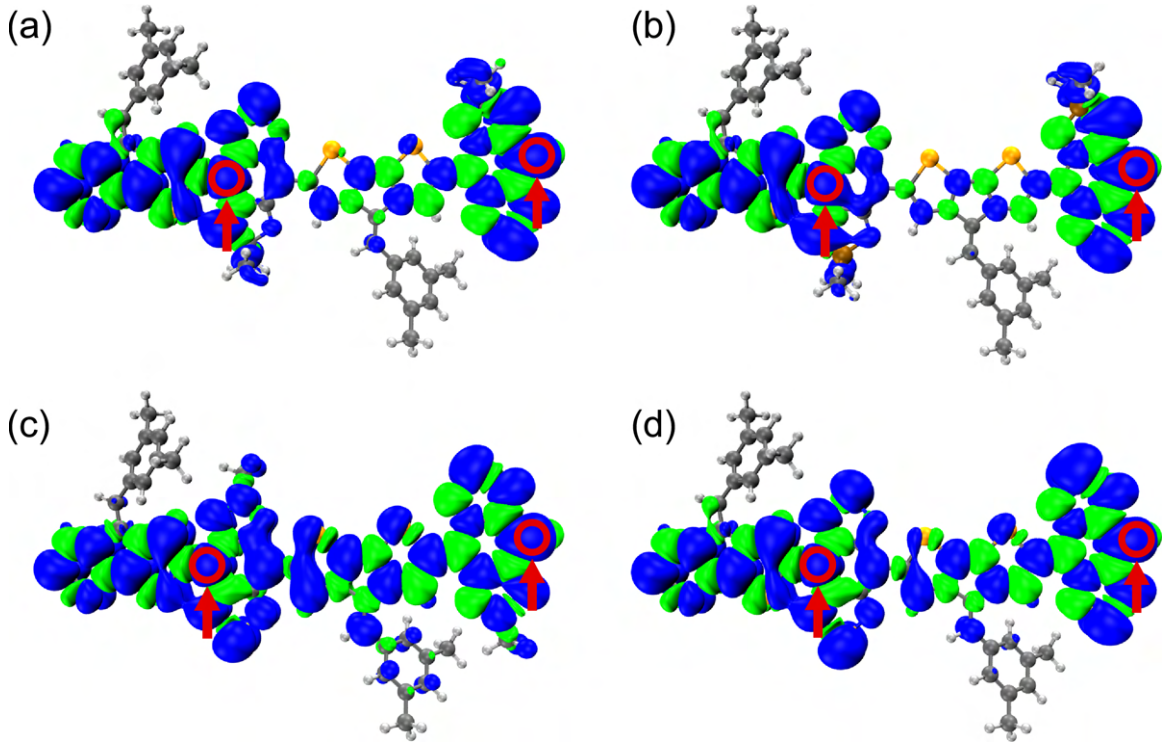


Figure S46: Spin density distributions of the (a) CPDS-CBBT, (b) CPDS-SiBBT, (c) CPDS-NBBT, and (d) CPDS-SeBBT ($N = 2$) polymers in their triplet state ($S = 1$). The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are highlighted with open circles.

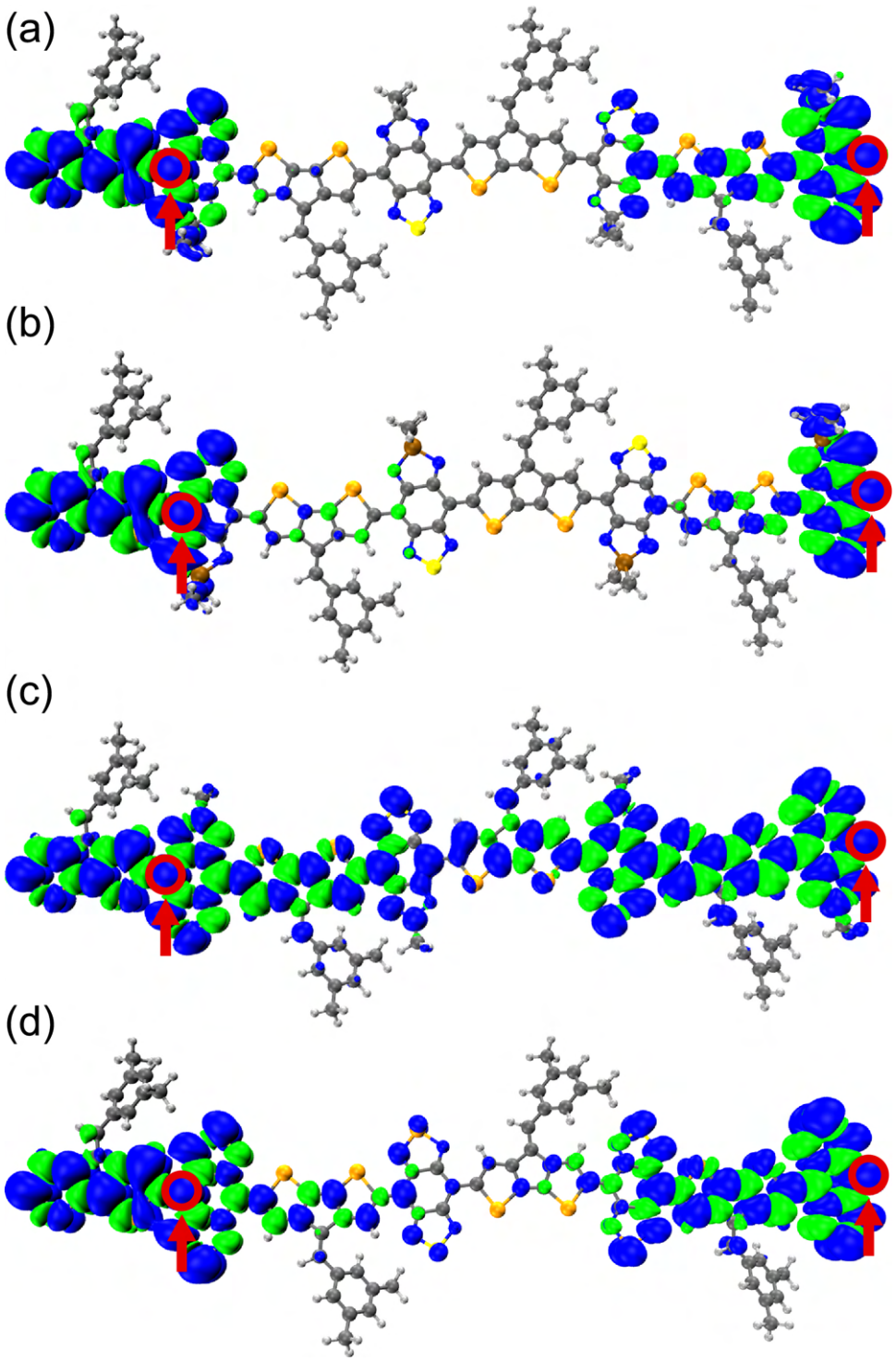


Figure S47: Spin density distributions of the (a) CPDS-CBBT, (b) CPDS-SiBBT, (c) CPDS-NBBT, and (d) CPDS-SeBBT ($N = 4$) polymers in their triplet state ($S = 1$). The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are highlighted with open circles.

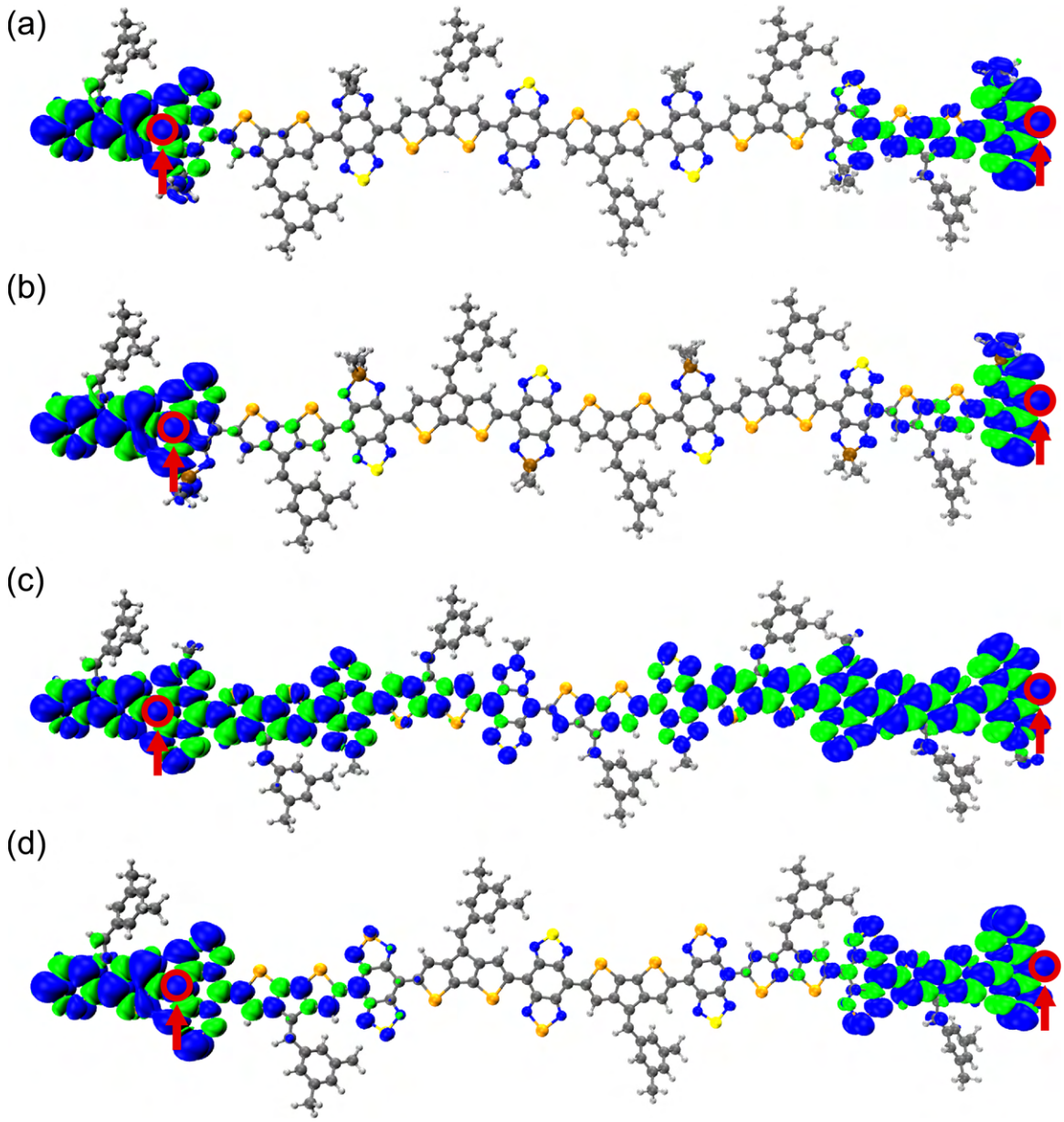


Figure S48: Spin density distributions of the (a) CPDS-CBBT, (b) CPDS-SiBBT, (c) CPDS-NBBT, and (d) CPDS-SeBBT ($N = 6$) polymers in their triplet state ($S = 1$). The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons are highlighted with open circles.

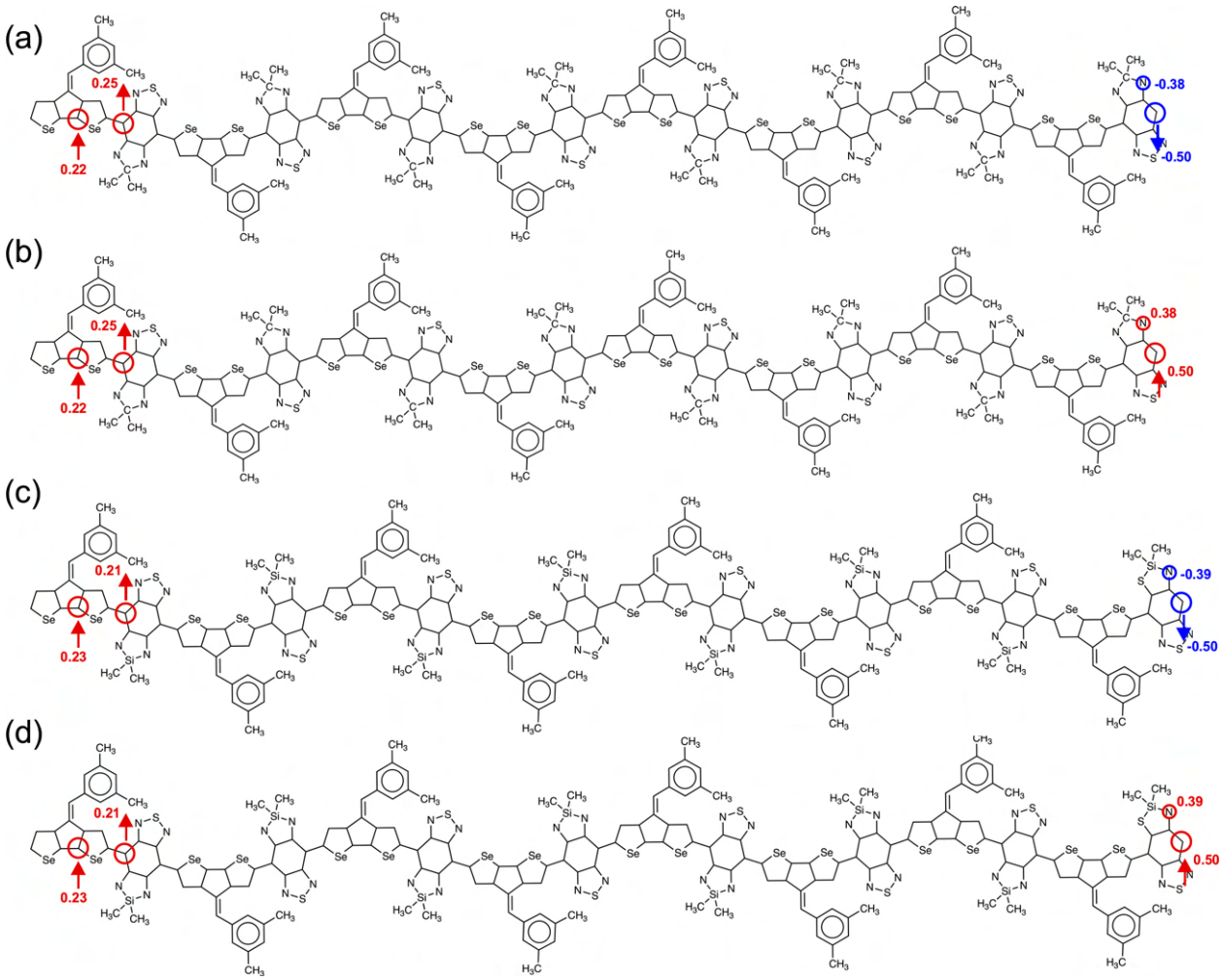


Figure S49: Spin values of the unpaired electrons for CPDS-CBBT ($N = 8$) in the (a) singlet ($S = 0$) and (b) triplet ($S = 1$) states, and for CPDS-SiBBT ($N = 8$) in the (c) singlet ($S = 0$) and (d) triplet ($S = 1$) states. Color code: Red is for spin-up and Blue is for spin-down.

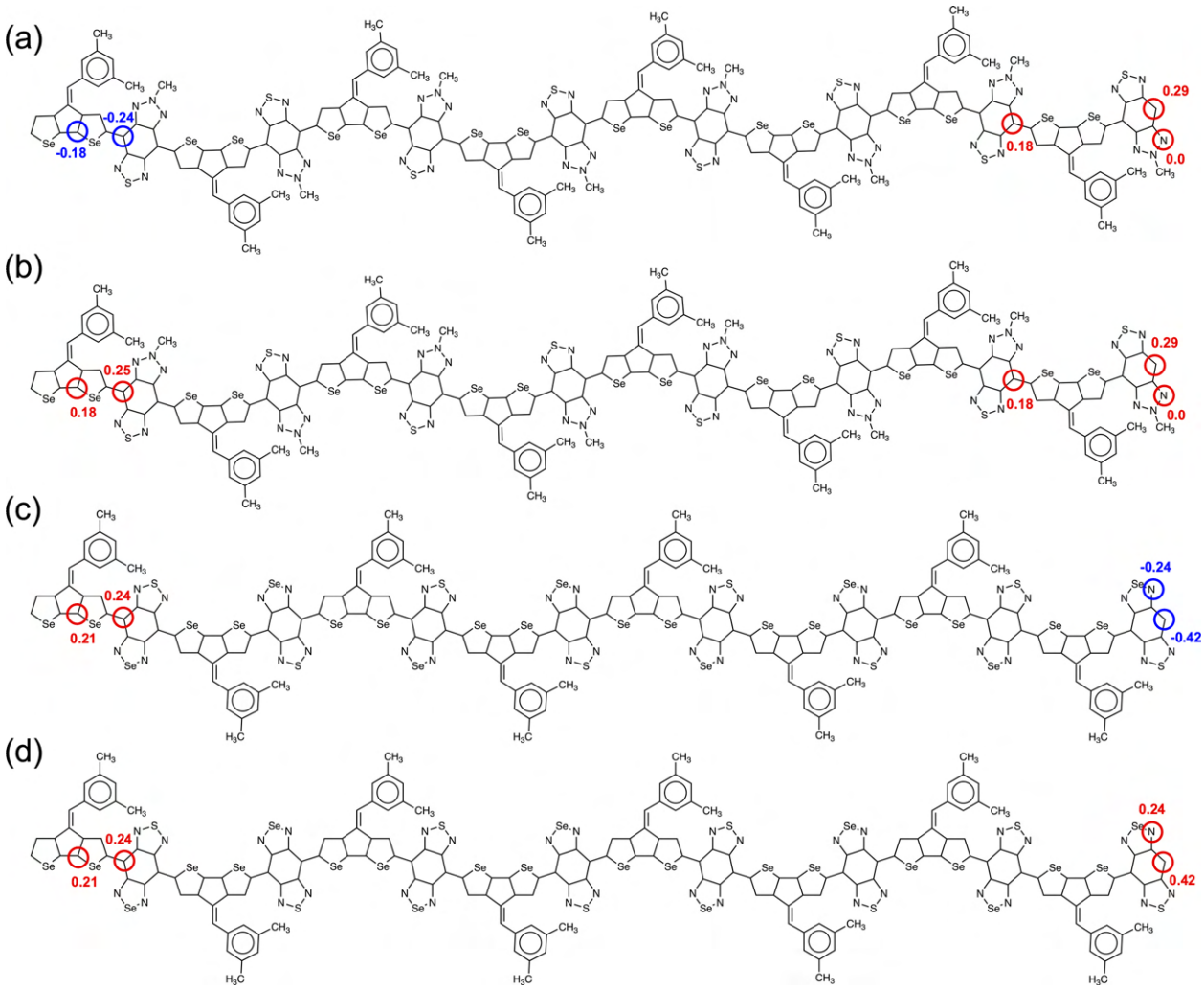


Figure S50: Spin values of the unpaired electrons for CPDS-NBBT ($N = 8$) in the (a) singlet ($S = 0$) and (b) triplet ($S = 1$) states, and for CPDS-SeBBT ($N = 8$) in the (c) singlet ($S = 0$) and (d) triplet ($S = 1$) states. Color code: Red is for spin-up and Blue is for spin-down.

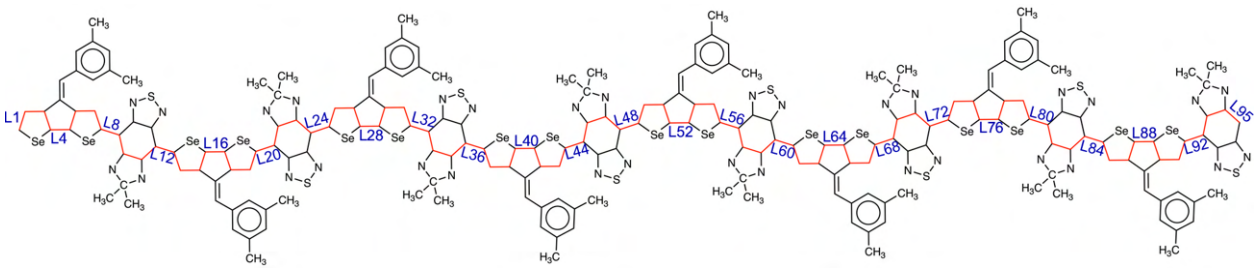


Table S24: Calculated bond lengths (Å) of CPDS-CBBT octamer ($N = 8$) in the singlet and triplet states.

Bond index	singlet ($S = 0$)	triplet ($S = 1$)	Bond index	singlet ($S = 0$)	triplet ($S = 1$)
1	1.37033	1.37032	49	1.43656	1.436560
2	1.42095	1.42096	50	1.36734	1.36734
3	1.40139	1.40139	51	1.44630	1.44630
4	1.41909	1.41911	52	1.37197	1.37197
5	1.41986	1.41986	53	1.45450	1.45450
6	1.39418	1.39419	54	1.37052	1.37052
7	1.41528	1.41527	55	1.43742	1.43742
8	1.40777	1.40777	56	1.38808	1.38808
9	1.44354	1.44354	57	1.45012	1.45011
10	1.49301	1.49301	58	1.49330	1.49330
11	1.46070	1.46070	59	1.46020	1.46020
12	1.38695	1.38695	60	1.38746	1.38746
13	1.43680	1.43679	61	1.43661	1.43662
14	1.36711	1.36711	62	1.36732	1.36732
15	1.44652	1.44653	63	1.44632	1.44633
16	1.37197	1.37197	64	1.37194	1.37194
17	1.45426	1.45426	65	1.45445	1.45446
18	1.37075	1.37076	66	1.37059	1.37059
19	1.43722	1.43723	67	1.43739	1.43739
20	1.38840	1.38841	68	1.38816	1.38816
21	1.44984	1.44985	69	1.45004	1.45004
22	1.49332	1.49332	70	1.49327	1.49327
23	1.46028	1.46028	71	1.46038	1.46038
24	1.38739	1.38739	72	1.38725	1.38725
25	1.43663	1.43663	73	1.43675	1.43675
26	1.36727	1.36727	74	1.36718	1.36717
27	1.44633	1.44633	75	1.44648	1.44648
28	1.37199	1.37200	76	1.37196	1.37195
29	1.45442	1.45443	77	1.45434	1.45433
30	1.37058	1.37058	78	1.37070	1.37070
31	1.43735	1.43735	79	1.43719	1.43719
32	1.38816	1.38816	80	1.38845	1.38845
33	1.45005	1.45005	81	1.44980	1.44980
34	1.49331	1.49331	82	1.49326	1.49327
35	1.46017	1.46018	83	1.46091	1.46091
36	1.38751	1.38751	84	1.38680	1.38680
37	1.43658	1.43658	85	1.43704	1.43704
38	1.36735	1.36735	86	1.36702	1.36703
39	1.44628	1.44628	87	1.44655	1.44654
40	1.37195	1.37195	88	1.37252	1.37253
41	1.45448	1.45448	89	1.45354	1.45354
42	1.37055	1.37055	90	1.37204	1.37205
43	1.43744	1.43744	91	1.43514	1.43513
44	1.38808	1.38807	92	1.39118	1.39118
45	1.45012	1.45011	93	1.45250	1.45252
46	1.49329	1.49329	94	1.48662	1.48662
47	1.46015	1.46015	95	1.41289	1.41288
48	1.38752	1.38751			

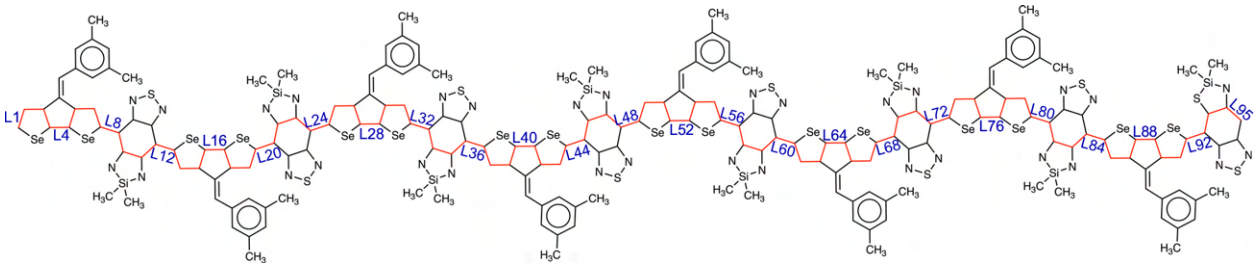


Table S25: Calculated bond lengths (Å) of CPDS-SiBBT octamer ($N = 8$) in the singlet and triplet states.

Bond index	singlet ($S = 0$)	triplet ($S = 1$)	Bond index	singlet ($S = 0$)	triplet ($S = 1$)
1	1.37085	1.37085	49	1.43670	1.43670
2	1.42028	1.42028	50	1.36706	1.36706
3	1.40294	1.40294	51	1.44609	1.44609
4	1.41726	1.41725	52	1.37243	1.37243
5	1.42204	1.42204	53	1.45418	1.45418
6	1.39195	1.39194	54	1.37070	1.37070
7	1.41795	1.41795	55	1.43772	1.43772
8	1.40761	1.40762	56	1.39162	1.39162
9	1.44795	1.44795	57	1.45355	1.45355
10	1.54422	1.54422	58	1.54599	1.54599
11	1.47092	1.47092	59	1.46963	1.46963
12	1.39148	1.39147	60	1.39257	1.39257
13	1.43726	1.43726	61	1.43675	1.43675
14	1.36658	1.36658	62	1.36703	1.36703
15	1.44646	1.44646	63	1.44613	1.44613
16	1.37242	1.37242	64	1.37242	1.37242
17	1.45383	1.45383	65	1.45415	1.45415
18	1.37105	1.37105	66	1.37075	1.37074
19	1.43731	1.43731	67	1.43767	1.43767
20	1.39220	1.39220	68	1.39171	1.39171
21	1.45291	1.45291	69	1.45346	1.45346
22	1.54595	1.54595	70	1.54598	1.54598
23	1.46986	1.46986	71	1.46990	1.46990
24	1.39239	1.39239	72	1.39234	1.39234
25	1.43683	1.43683	73	1.43690	1.43690
26	1.36695	1.36695	74	1.36690	1.36690
27	1.44616	1.44616	75	1.44626	1.44626
28	1.37246	1.37246	76	1.37242	1.37242
29	1.45407	1.45407	77	1.45402	1.45402
30	1.37080	1.37080	78	1.37089	1.37089
31	1.43760	1.43760	79	1.43746	1.43746
32	1.39176	1.39176	80	1.39204	1.39204
33	1.45339	1.45339	81	1.45311	1.45311
34	1.54597	1.54598	82	1.54603	1.54603
35	1.46962	1.46962	83	1.47077	1.47077
36	1.39259	1.39259	84	1.39149	1.39149
37	1.43672	1.43672	85	1.43754	1.43754
38	1.36704	1.36704	86	1.36639	1.36639
39	1.44609	1.44609	87	1.44680	1.44680
40	1.37243	1.37243	88	1.37224	1.37223
41	1.45417	1.45417	89	1.45386	1.45386
42	1.37072	1.37072	90	1.37149	1.37148
43	1.43771	1.43771	91	1.43641	1.43641
44	1.39163	1.39163	92	1.39318	1.39318
45	1.45354	1.45354	93	1.45844	1.45844
46	1.54598	1.54598	94	1.53065	1.53065
47	1.46957	1.46957	95	1.41852	1.41852
48	1.39263	1.39263			

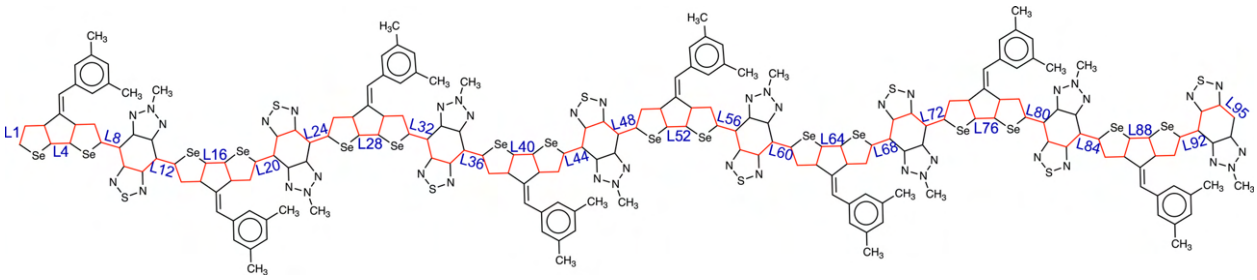


Table S26: Calculated bond lengths (Å) of CPDS-NBBT octamer ($N = 8$) in the singlet and triplet states.

Bond index	singlet ($S = 0$)	triplet ($S = 1$)	Bond index	singlet ($S = 0$)	triplet ($S = 1$)
1	1.36931	1.36932	49	1.43165	1.43179
2	1.42243	1.42243	50	1.37088	1.37075
3	1.39750	1.39752	51	1.44118	1.44135
4	1.42642	1.42640	52	1.37677	1.37659
5	1.41104	1.41107	53	1.44840	1.44856
6	1.40097	1.40094	54	1.37287	1.37274
7	1.40569	1.40573	55	1.43271	1.43286
8	1.41838	1.41833	56	1.39013	1.38997
9	1.43572	1.43576	57	1.44840	1.44849
10	1.43082	1.43079	58	1.42588	1.42583
11	1.43528	1.43533	59	1.44288	1.44297
12	1.40184	1.40173	60	1.39114	1.39099
13	1.42283	1.42292	61	1.43145	1.43159
14	1.37789	1.37780	62	1.37104	1.37091
15	1.43343	1.43355	63	1.44090	1.44106
16	1.38490	1.38477	64	1.37725	1.37707
17	1.44191	1.44203	65	1.44790	1.44806
18	1.37739	1.37729	66	1.37333	1.37321
19	1.42809	1.42821	67	1.43213	1.43227
20	1.39470	1.39458	68	1.39087	1.39072
21	1.44642	1.44650	69	1.44783	1.44792
22	1.42663	1.42659	70	1.42617	1.42613
23	1.44176	1.44184	71	1.44219	1.44227
24	1.39261	1.39247	72	1.39284	1.39270
25	1.43031	1.43044	73	1.42979	1.42991
26	1.37194	1.37182	74	1.37267	1.37256
27	1.44001	1.44016	75	1.43853	1.43867
28	1.37794	1.37777	76	1.38038	1.38022
29	1.44746	1.44762	77	1.44476	1.44489
30	1.37349	1.37336	78	1.37620	1.37610
31	1.43209	1.43224	79	1.42857	1.42869
32	1.39070	1.39055	80	1.39522	1.39510
33	1.44820	1.44829	81	1.44451	1.44458
34	1.42597	1.42593	82	1.42816	1.42813
35	1.44279	1.44288	83	1.43769	1.43776
36	1.39119	1.39103	84	1.40410	1.40401
37	1.43147	1.43162	85	1.41934	1.41941
38	1.37099	1.37087	86	1.38312	1.38305
39	1.44106	1.44122	87	1.42415	1.42422
40	1.37689	1.37670	88	1.39897	1.39888
41	1.44835	1.44852	89	1.42802	1.42809
42	1.37285	1.37273	90	1.39210	1.39206
43	1.43270	1.43285	91	1.40925	1.40929
44	1.39008	1.38992	92	1.42058	1.42053
45	1.44845	1.44855	93	1.42963	1.42966
46	1.42585	1.42581	94	1.44267	1.44266
47	1.44295	1.44304	95	1.39839	1.39841
48	1.39098	1.39082			

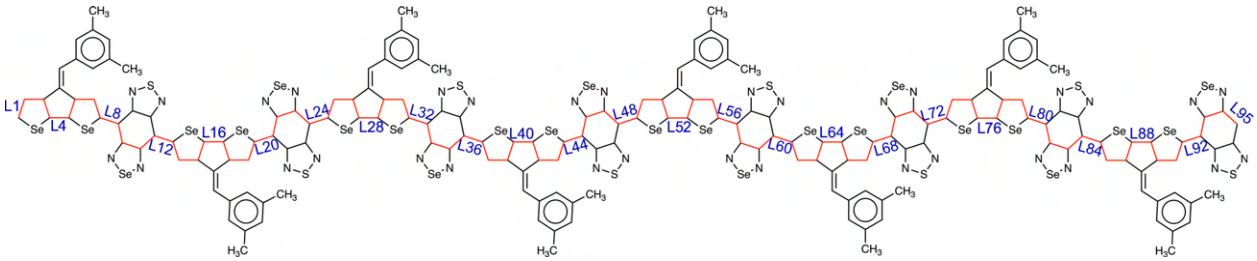


Table S27: Calculated bond lengths (Å) of CPDS-SeBBT octamer ($N = 8$) in the singlet and triplet states.

Bond index	singlet ($S = 0$)	triplet ($S = 1$)	Bond index	singlet ($S = 0$)	triplet ($S = 1$)
1	1.37006	1.37006	49	1.43483	1.43483
2	1.42137	1.42138	50	1.36904	1.36904
3	1.40040	1.40040	51	1.44261	1.44261
4	1.42063	1.42063	52	1.37435	1.37435
5	1.41694	1.41694	53	1.45108	1.45108
6	1.39594	1.39593	54	1.37194	1.37194
7	1.41377	1.41377	55	1.43650	1.43650
8	1.41465	1.41465	56	1.39339	1.39340
9	1.44790	1.44790	57	1.45631	1.45631
10	1.46163	1.46163	58	1.46041	1.46041
11	1.44946	1.44945	59	1.45071	1.45072
12	1.39416	1.39416	60	1.39339	1.39339
13	1.43421	1.43420	61	1.43490	1.43491
14	1.36936	1.36936	62	1.36895	1.36895
15	1.44234	1.44234	63	1.44270	1.44270
16	1.37476	1.37477	64	1.37435	1.37435
17	1.45073	1.45073	65	1.45103	1.45103
18	1.37218	1.37218	66	1.37200	1.37200
19	1.43625	1.43625	67	1.43641	1.43641
20	1.39367	1.39367	68	1.39353	1.39353
21	1.45619	1.45619	69	1.45620	1.45619
22	1.46050	1.46050	70	1.46034	1.46034
23	1.45065	1.45065	71	1.45091	1.45091
24	1.39348	1.39348	72	1.39310	1.39309
25	1.43483	1.43483	73	1.43512	1.43512
26	1.36903	1.36903	74	1.36878	1.36878
27	1.44259	1.44259	75	1.44290	1.44290
28	1.37439	1.37439	76	1.37436	1.37435
29	1.45104	1.45104	77	1.45081	1.45081
30	1.37196	1.37196	78	1.37225	1.37225
31	1.43647	1.43647	79	1.43609	1.43609
32	1.39340	1.39340	80	1.39406	1.39406
33	1.45632	1.45632	81	1.45572	1.45572
34	1.46047	1.46047	82	1.46027	1.46027
35	1.45063	1.45063	83	1.45082	1.45082
36	1.39353	1.39353	84	1.39436	1.39436
37	1.43480	1.43480	85	1.43364	1.43364
38	1.36905	1.36905	86	1.37036	1.37036
39	1.44258	1.44258	87	1.44036	1.44036
40	1.37437	1.37437	88	1.37861	1.37861
41	1.45110	1.45110	89	1.44649	1.44649
42	1.37192	1.37192	90	1.37704	1.37704
43	1.43651	1.43651	91	1.42928	1.42928
44	1.39336	1.39335	92	1.40292	1.40291
45	1.45634	1.45634	93	1.45400	1.45400
46	1.46044	1.46044	94	1.46899	1.46899
47	1.45065	1.45064	95	1.40927	1.40928
48	1.39350	1.39350			

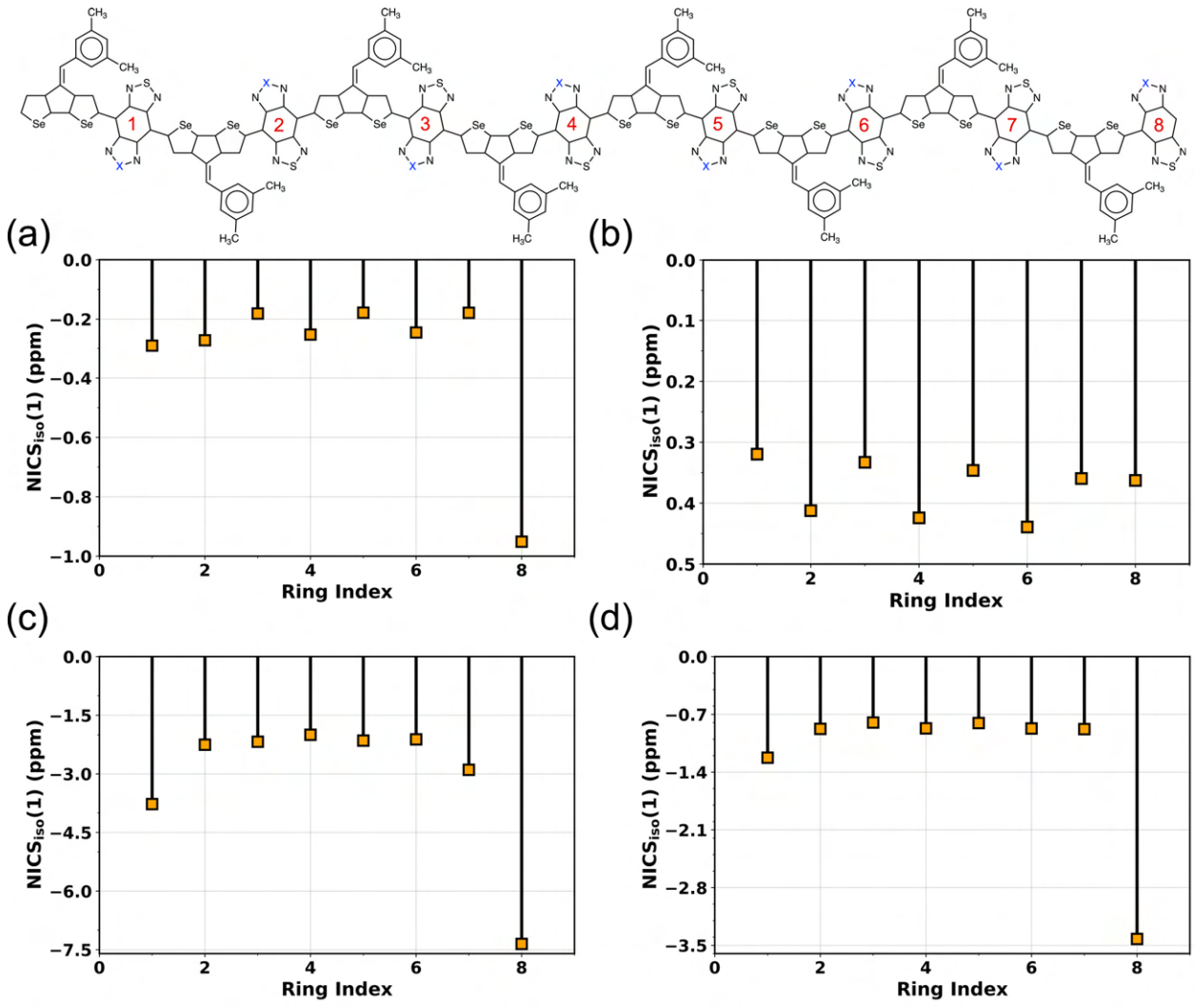


Figure S51: Calculated NICS$_{iso}$(1) (ppm) of the benzenoid rings along the (a) CPDS-CBBT, (b) CPDS-SiBBT, (c) CPDS-NBBT, and (d) CPDS-SeBBT polymer backbones in their singlet state.

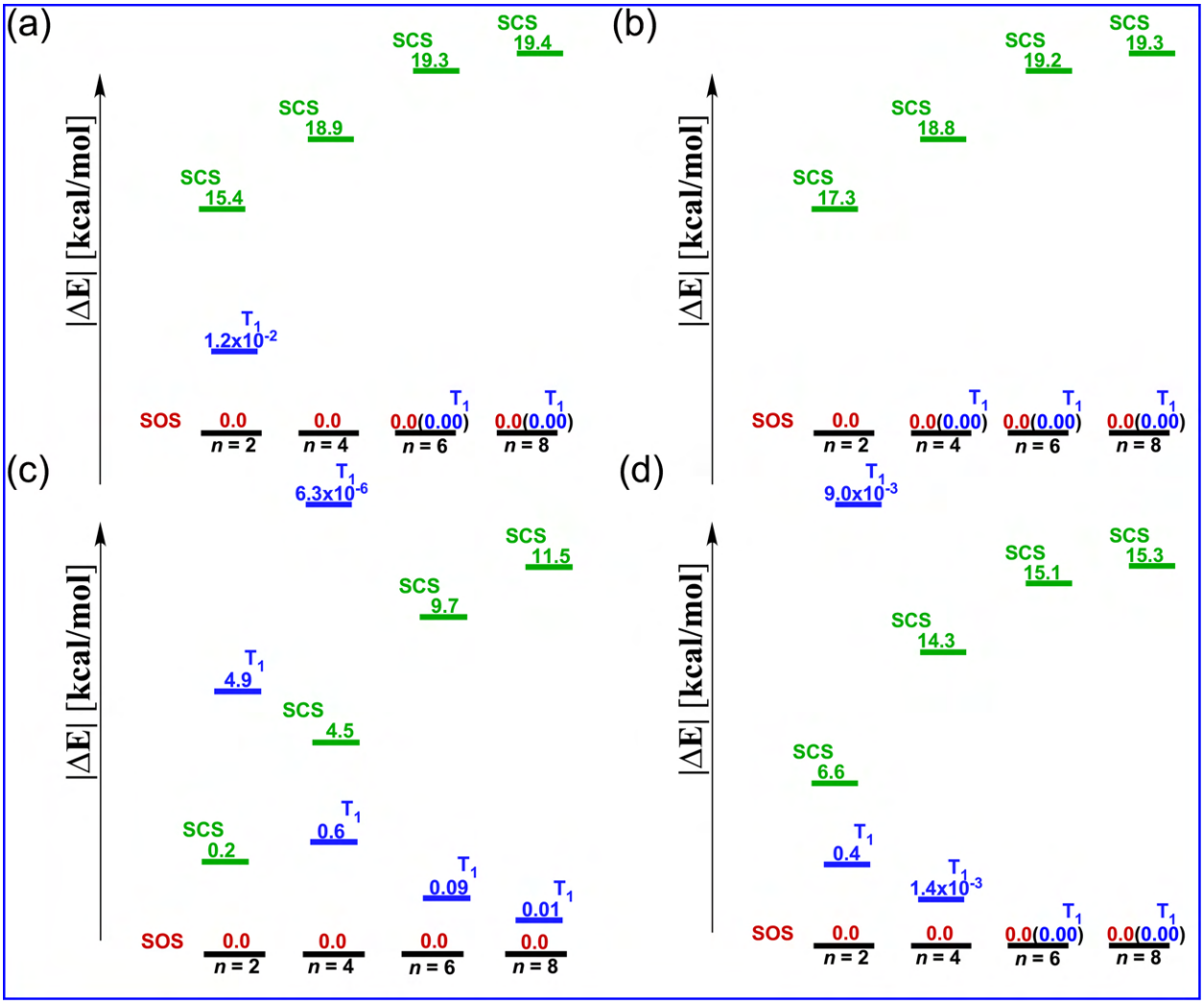


Figure S52: Energy diagrams of the (a) CPDS-CBBT, (b) CPDS-SiBBT, (c) CPDS-NBBT, and (d) CPDS-SeBBT polymers as a function of oligomer chain lengths. Energy values are provided with reference to the singlet open-shell (SOS) and compared with the singlet closed-shell (SCS) and triplet (T_1) states.

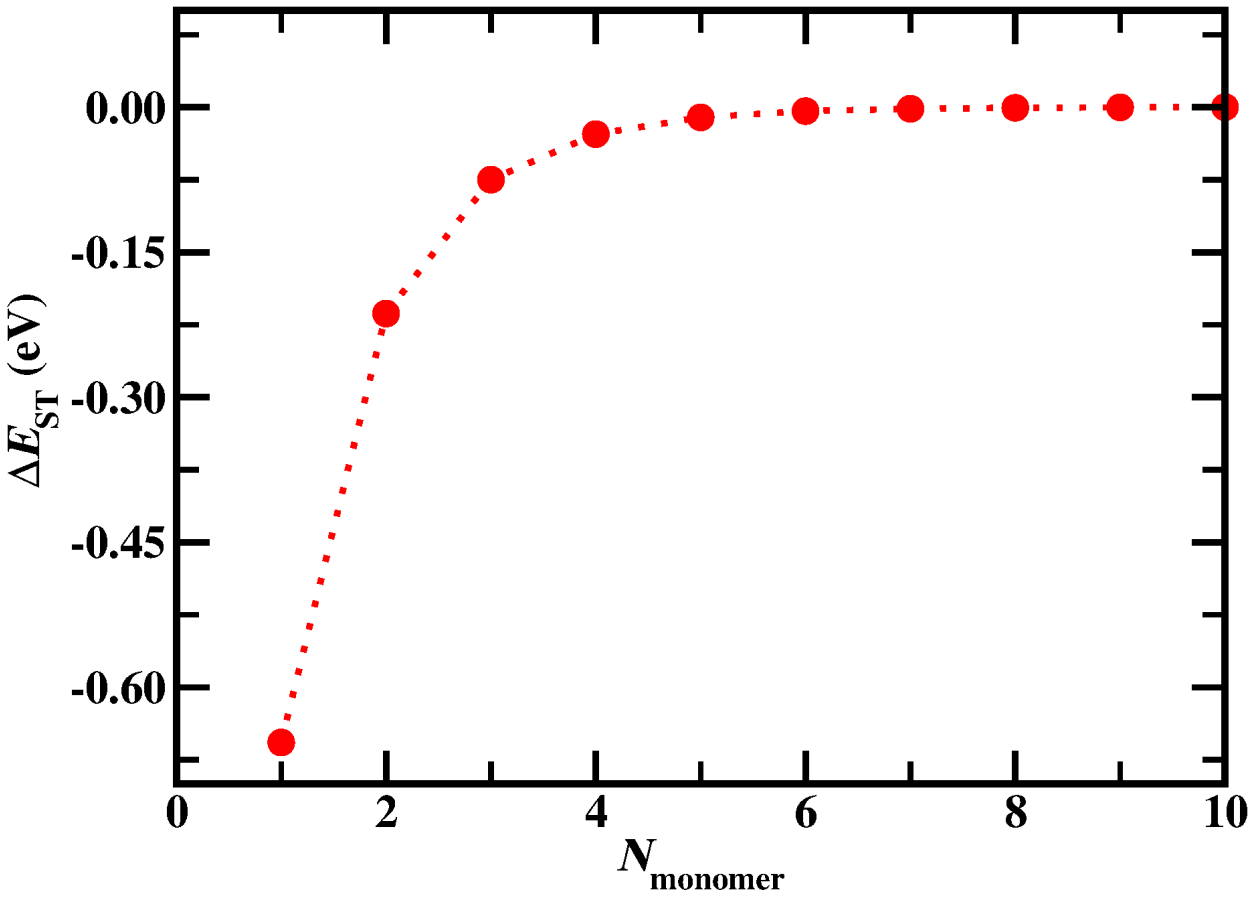


Figure S53: Calculated ΔE_{ST} of the CPDS-NBBT polymer as a function of N showing as N increases, ΔE_{ST} decreases. From extrapolation of these data, an inflection point is achieved at $N = 9$ (shown with the vertical line).

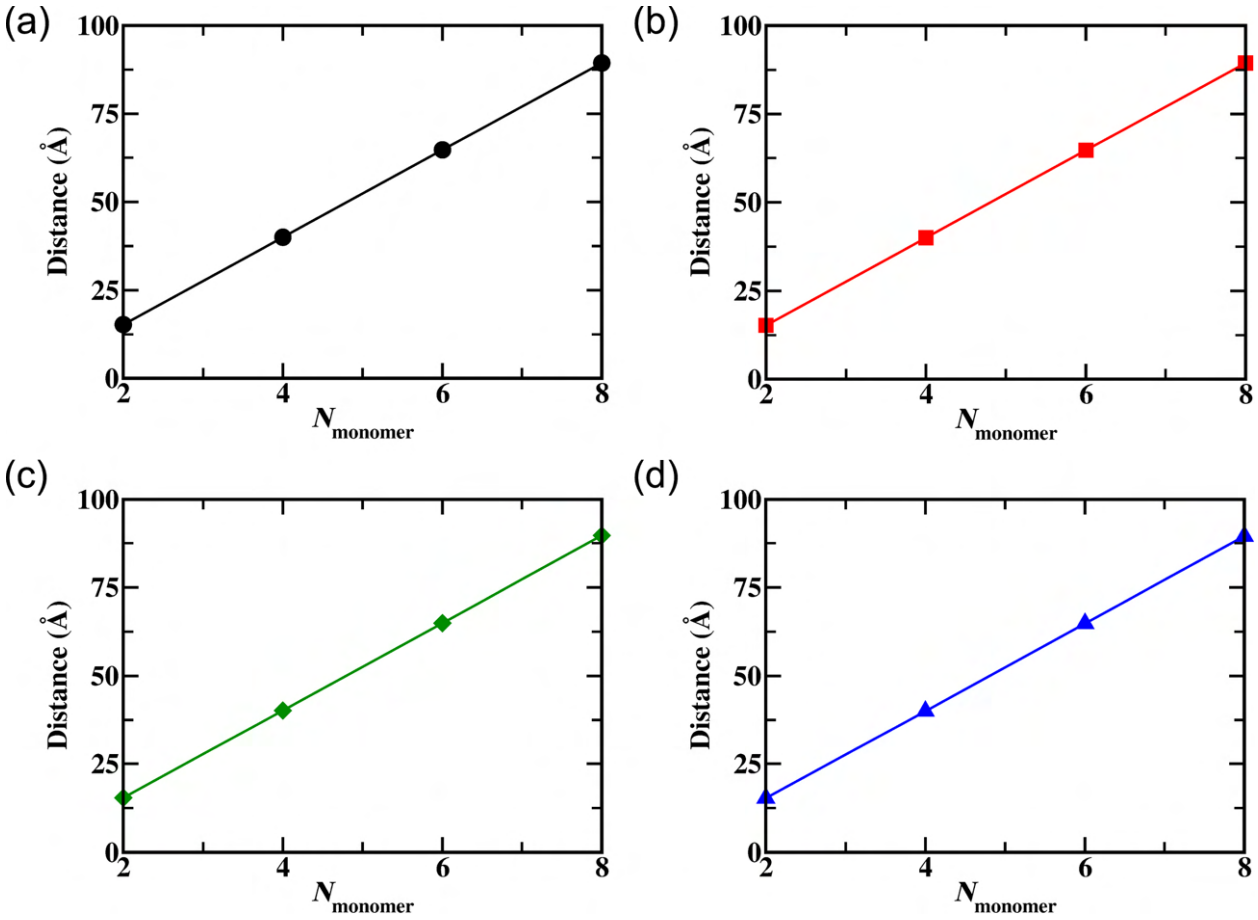


Figure S54: Separation between the unpaired electrons as a function of polymer chain length for (a) CPDS-CBBT, (b) CPDS-SiBBT, (c) CPDS-NBBT, and (d) CPDS-SeBBT in the singlet state ($S = 0$). As a greater number of monomer units are added to the polymer backbone, a rapid increase in the distance between the unpaired electrons is observed.

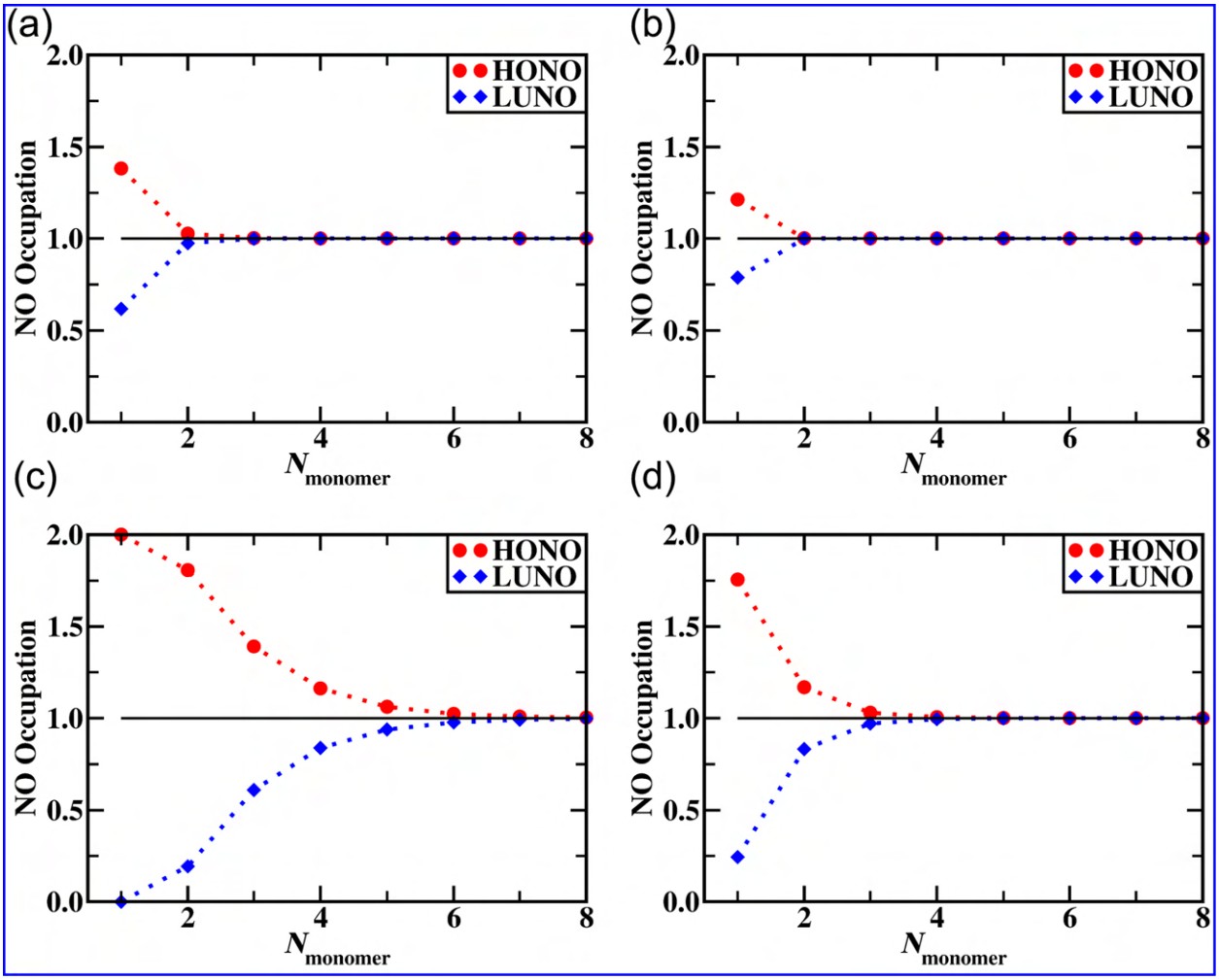


Figure S55: Calculated occupation numbers of the highest occupied natural orbital (HONO) and lowest unoccupied natural orbital (LUNO) of (a) CPDS-CBBT, (b) CPDS-SiBBT, (c) CPDS-NBBT, and (d) CPDS-SeBBT polymers, obtained as a function of oligomer length (N). As more monomers are added to the polymer chain, the HONO decreases, while increasing the LUNO. Both the HONO and LUNO reaches to the saturation (indicated with the solid black lines) for a larger repeat unit, indicating the bond dissociation limit.

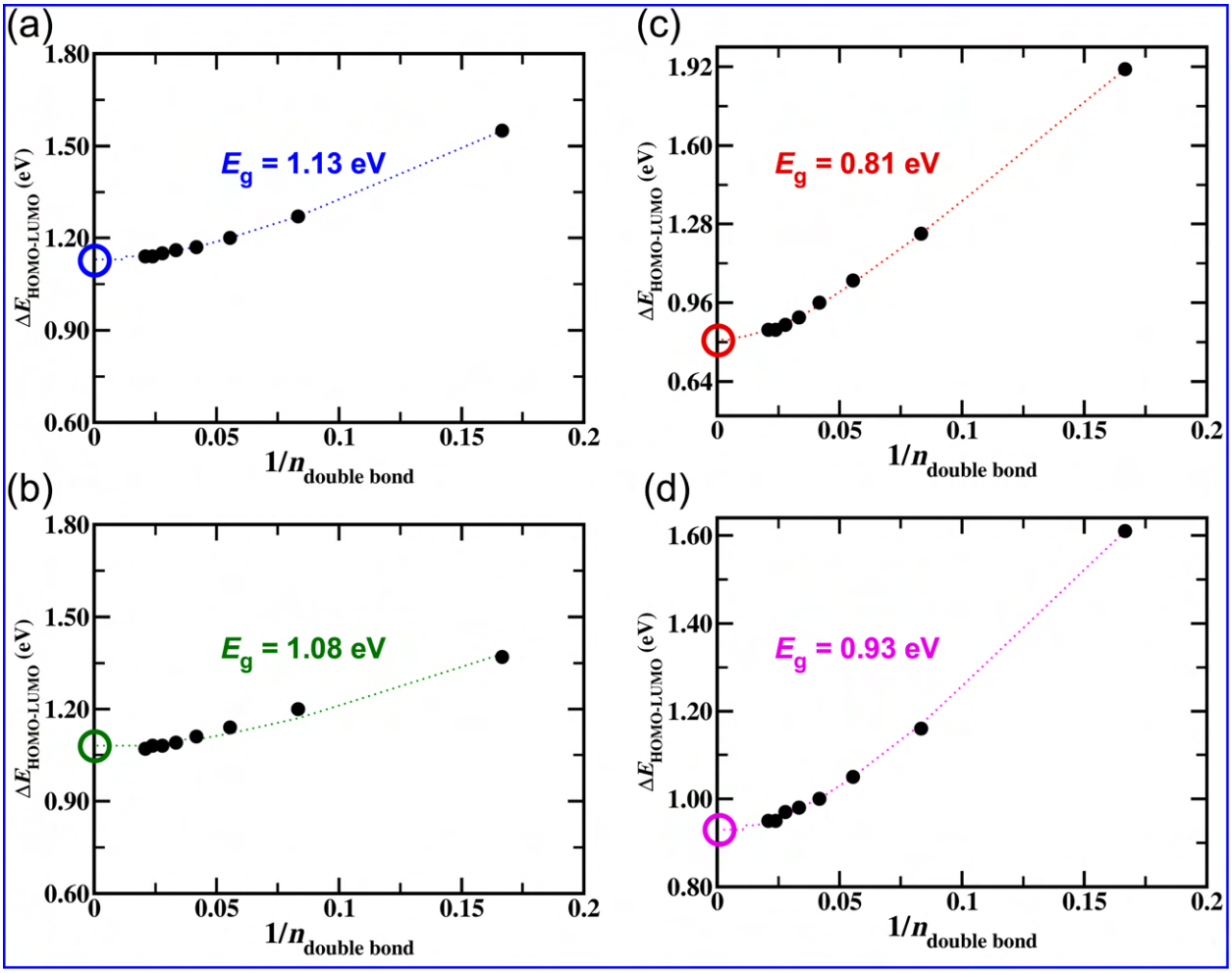


Figure S56: Calculated HOMO–LUMO energy gaps as a function of double bonds (n) of (a) CPDS-CBBT, (b) CPDS-SiBBT, (c) CPDS-NBBT, and (d) CPDS-SeBBT polymers. The predicted electrochemical bandgap (E_g) is obtained by extrapolation of the calculated HOMO–LUMO gaps to the polymer chain limit ($n \rightarrow \infty$) using Kuhn model.[1] The calculated HOMO–LUMO gaps are indicated in black filled circles and extrapolated trend is shown in dashed lines.

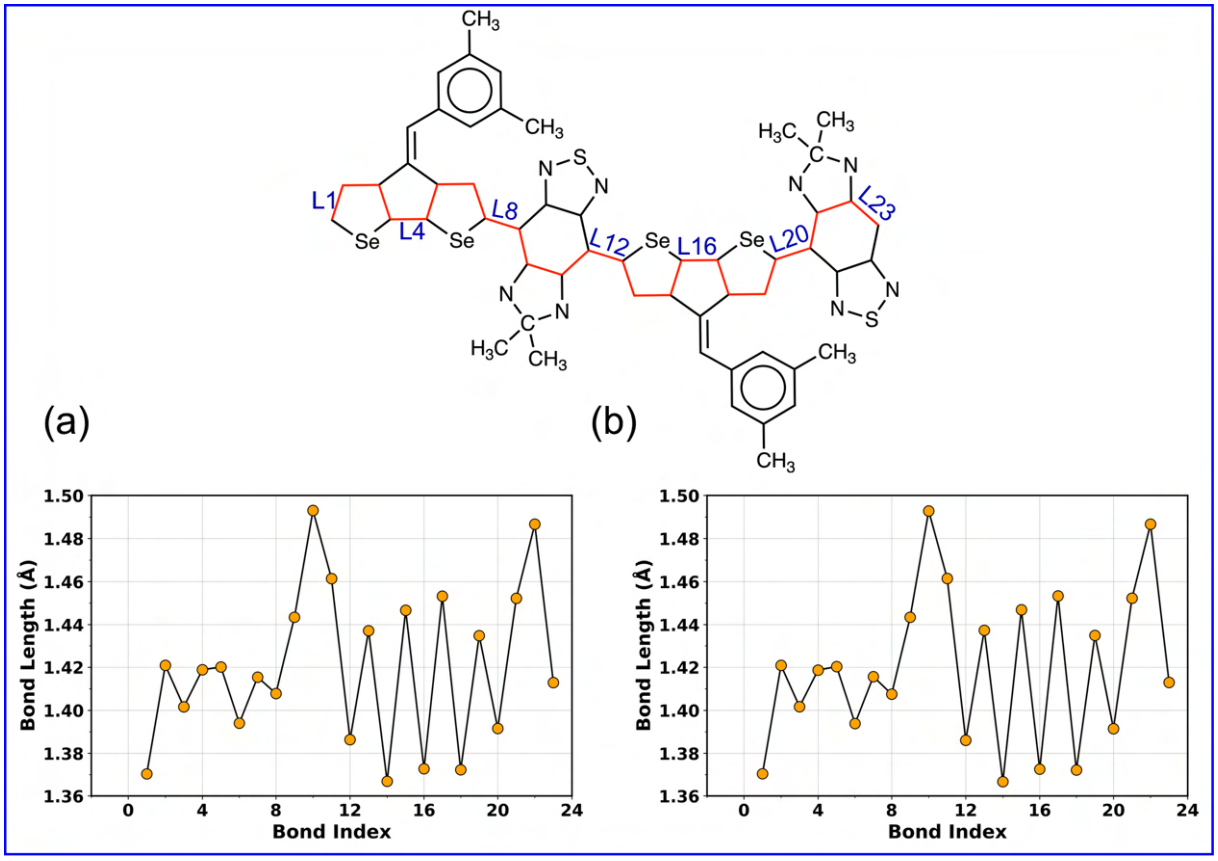


Figure S57: Calculated bond lengths (Å) of the CPDS-CBBT dimer ($N = 2$) for (a) singlet ($S = 0$) and (b) triplet states ($S = 1$).

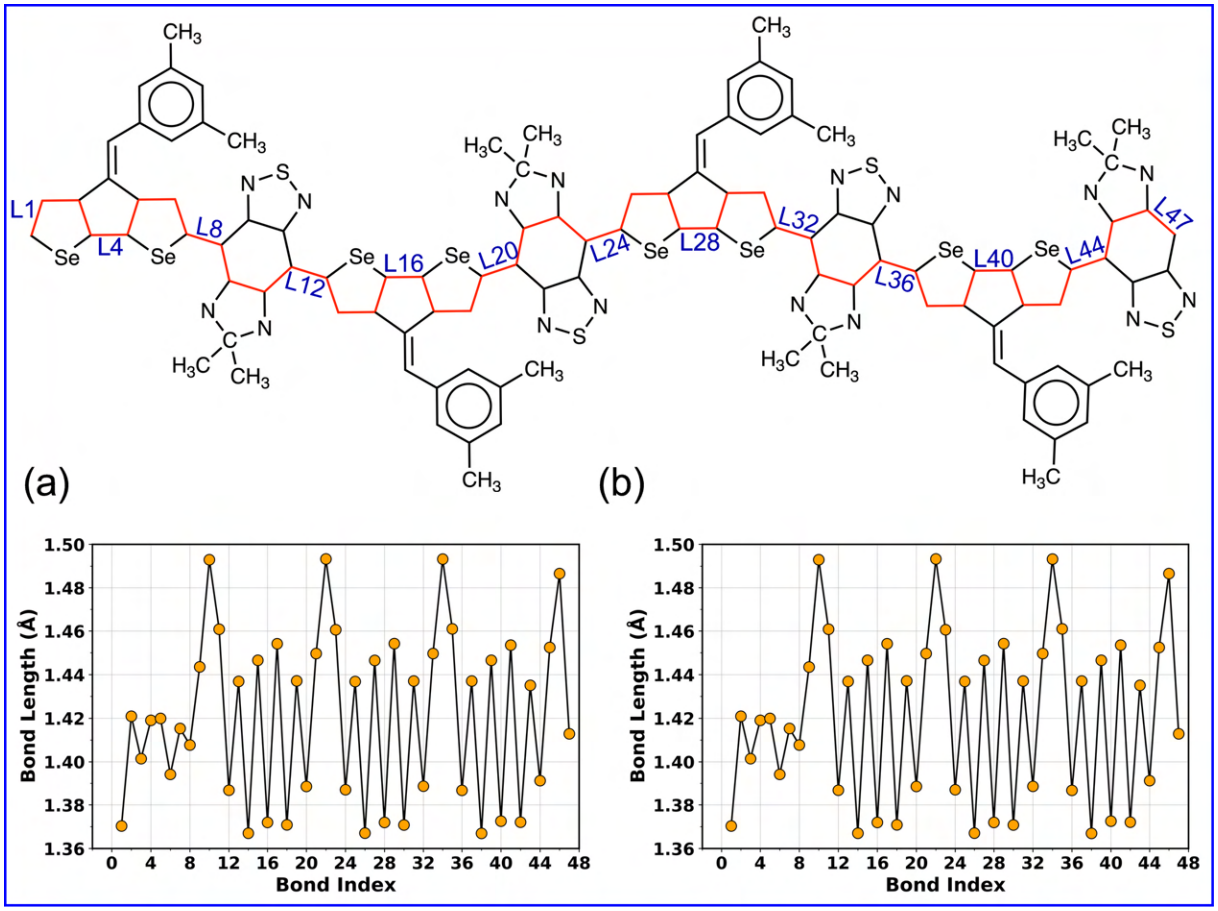


Figure S58: Calculated bond lengths (Å) of the CPDS-CBBT tetramer ($N = 4$) for (a) singlet ($S = 0$) and (b) triplet states ($S = 1$).

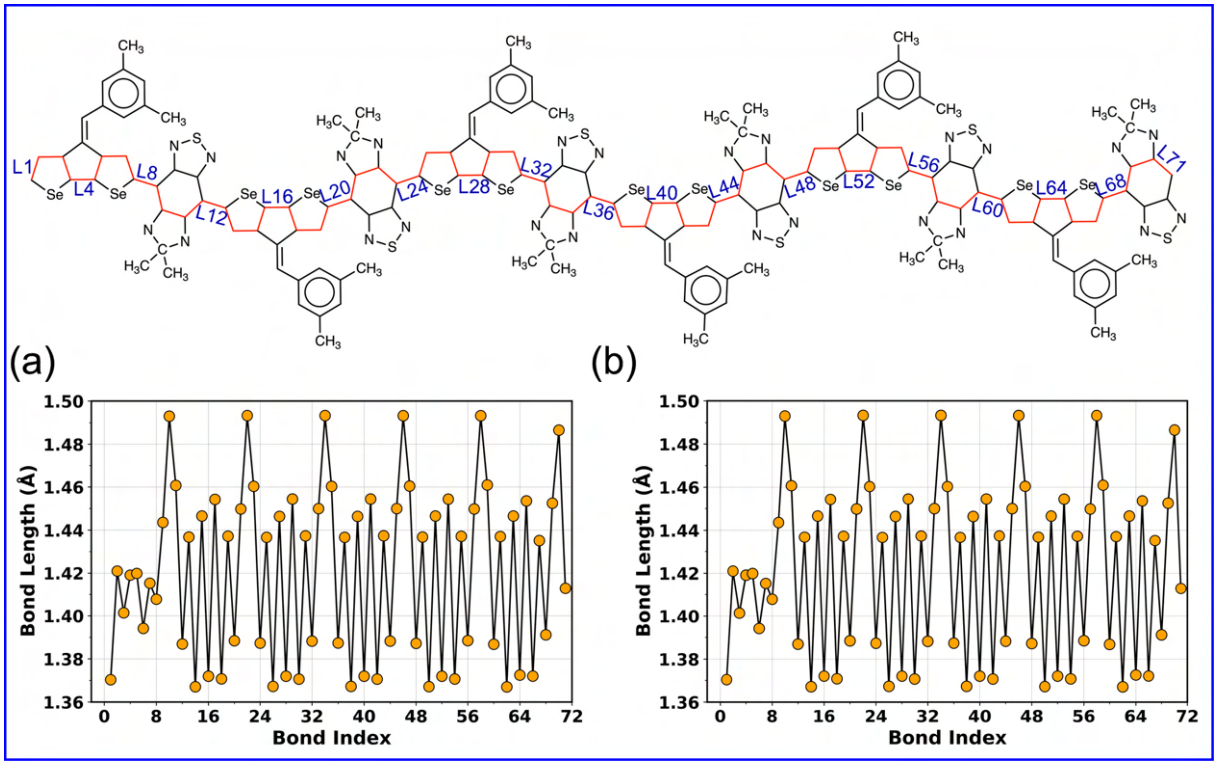


Figure S59: Calculated bond lengths (Å) of the CPDS-CBBT hexamer ($N = 6$) for (a) singlet ($S = 0$) and (b) triplet states ($S = 1$).

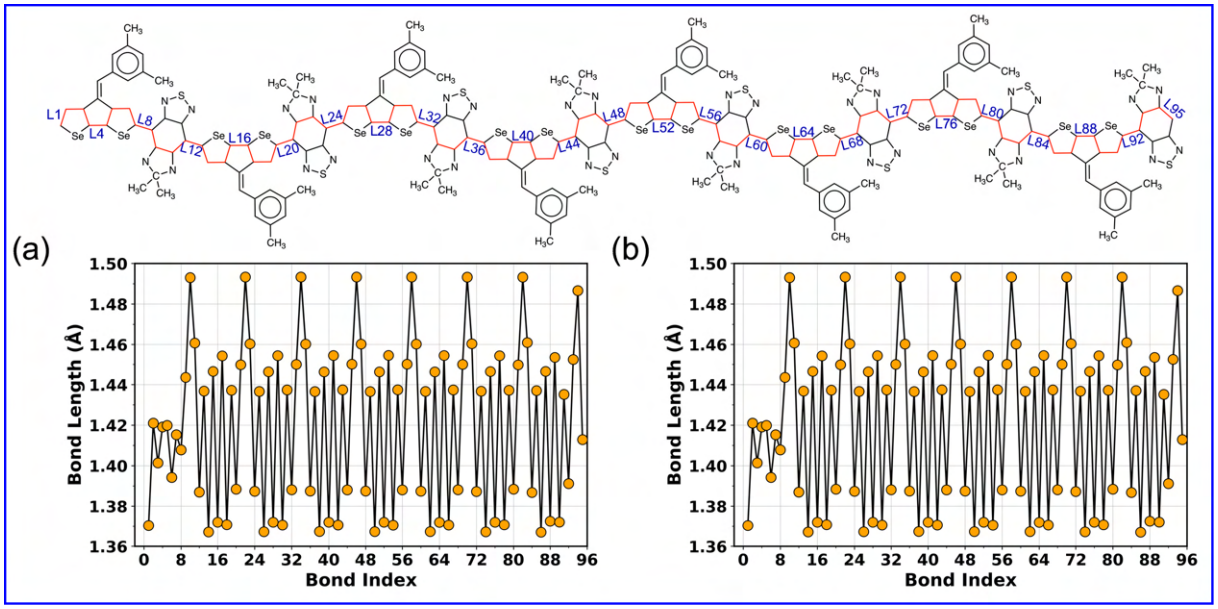


Figure S60: Calculated bond lengths (Å) of the CPDS-CBBT octamer ($N = 8$) for (a) singlet ($S = 0$) and (b) triplet states ($S = 1$).

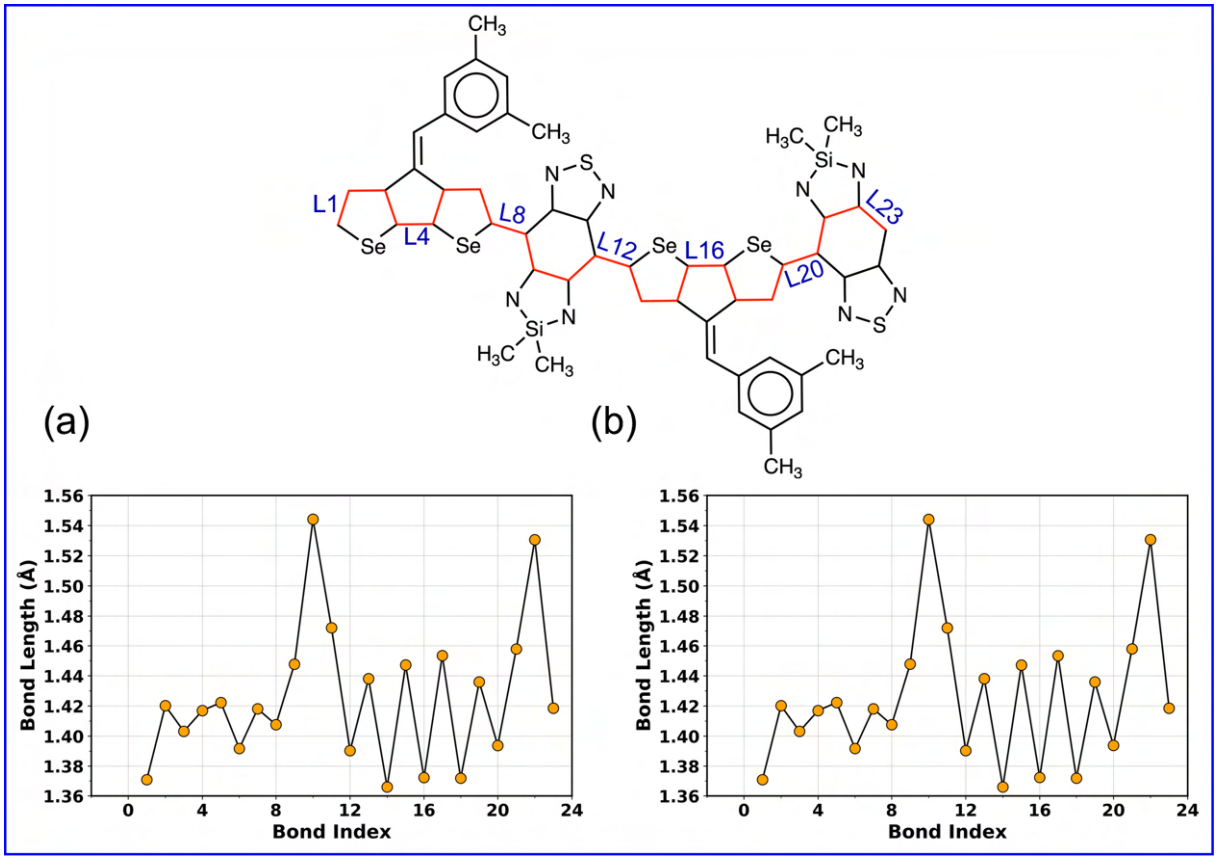


Figure S61: Calculated bond lengths (Å) of the CPDS-SiBBT dimer ($N = 2$) for (a) singlet ($S = 0$) and (b) triplet states ($S = 1$).

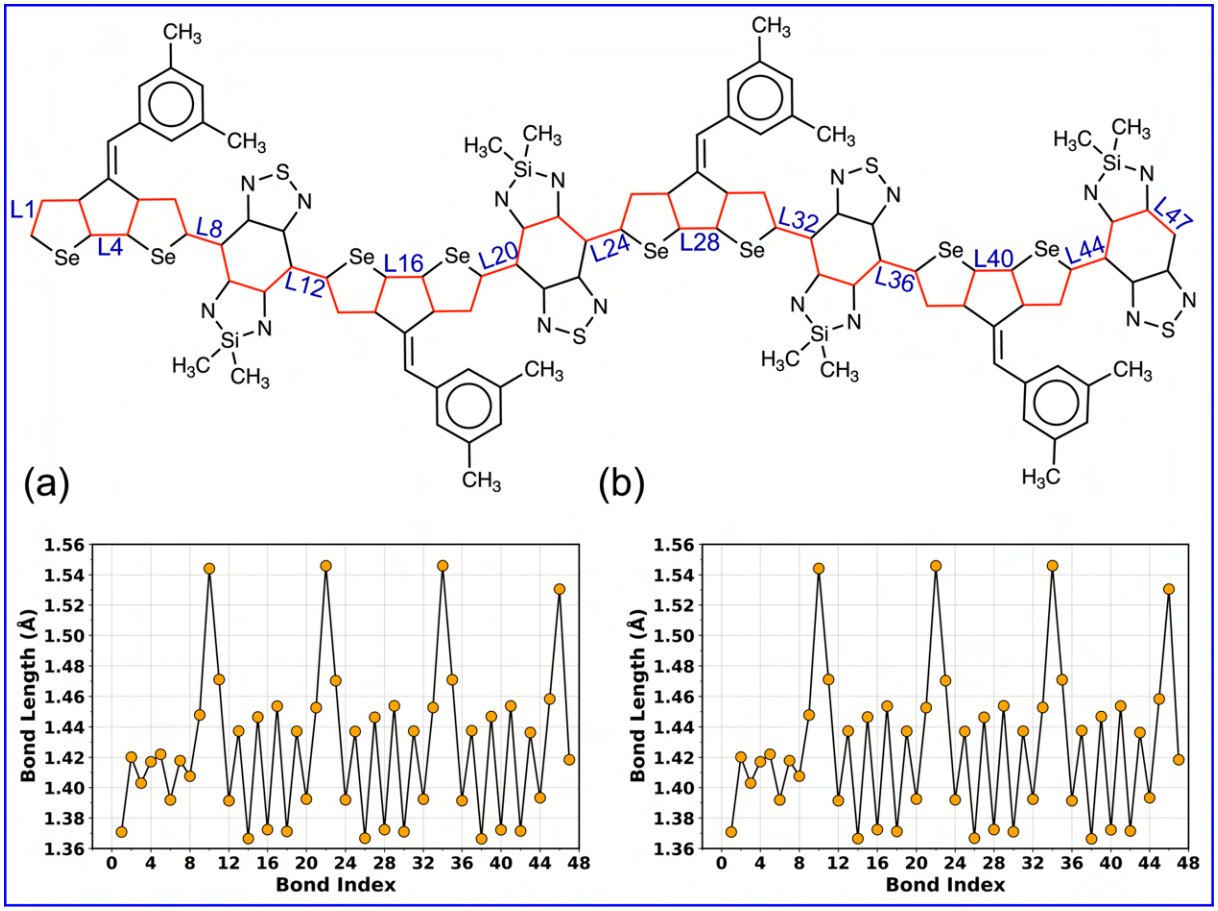


Figure S62: Calculated bond lengths (Å) of the CPDS-SiBBT tetramer ($N = 4$) for (a) singlet ($S = 0$) and (b) triplet states ($S = 1$).

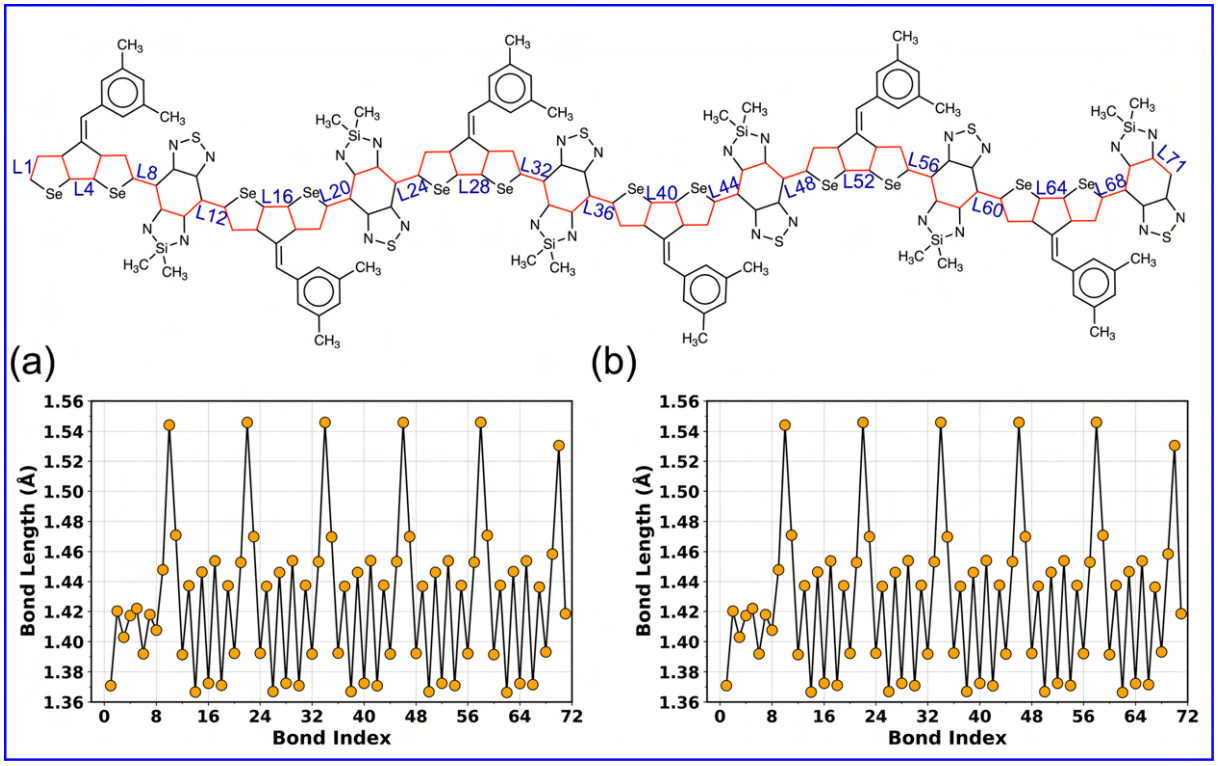


Figure S63: Calculated bond lengths (Å) of the CPDS-SiBBT hexamer ($N = 6$) for (a) singlet ($S = 0$) and (b) triplet states ($S = 1$).

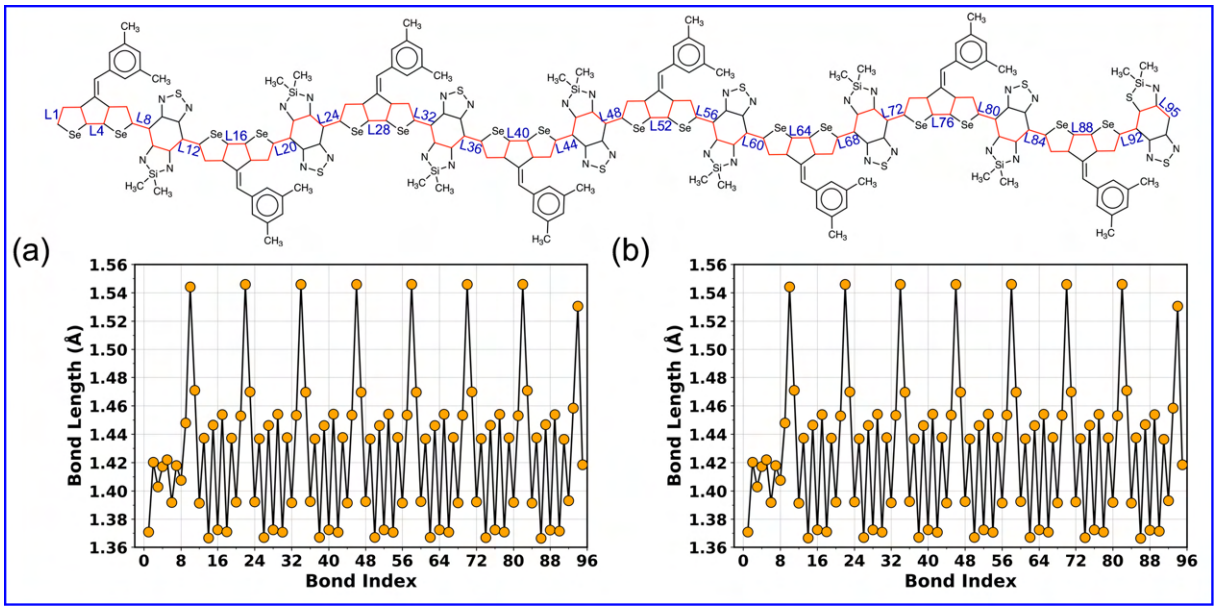


Figure S64: Calculated bond lengths (Å) of the CPDS-SiBBT octamer ($N = 8$) for (a) singlet ($S = 0$) and (b) triplet states ($S = 1$).

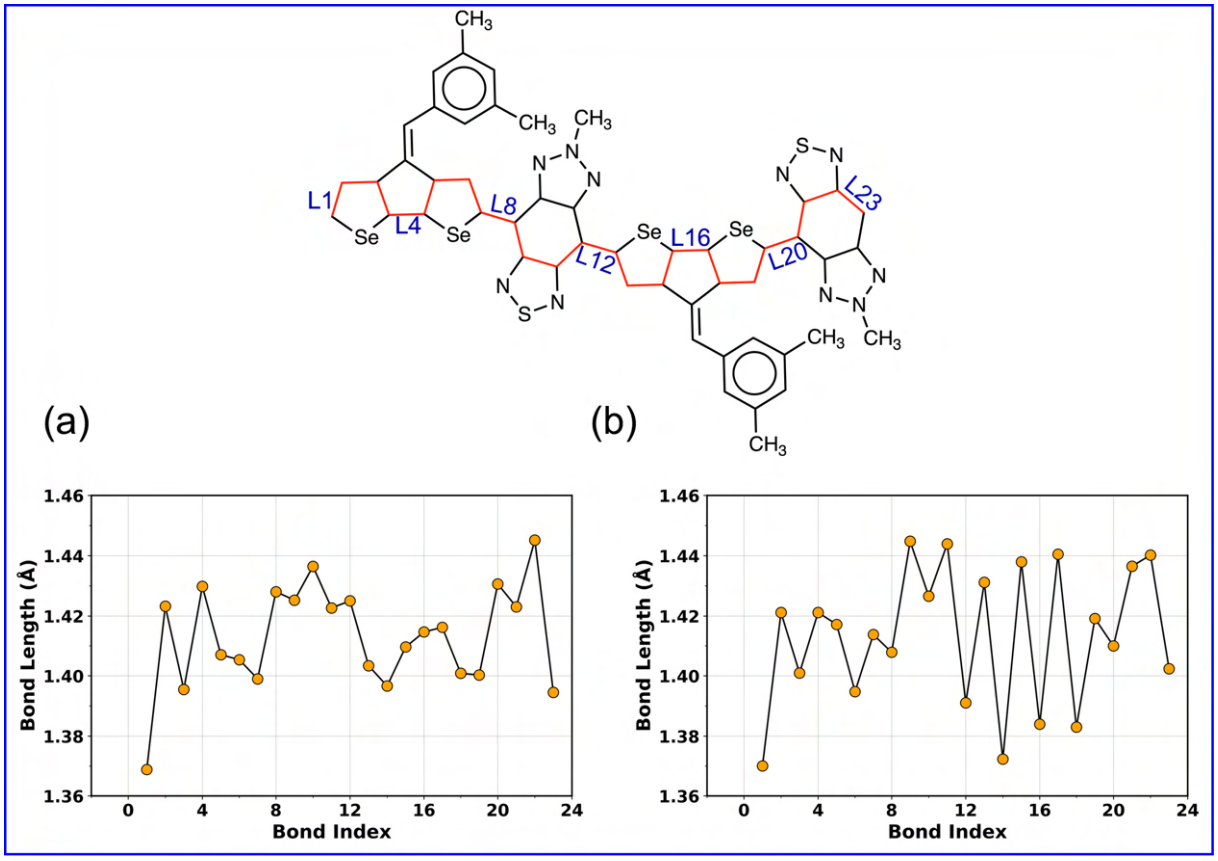


Figure S65: Calculated bond lengths (Å) of the CPDS-NBBT dimer ($N = 2$) for (a) singlet ($S = 0$) and (b) triplet states ($S = 1$).

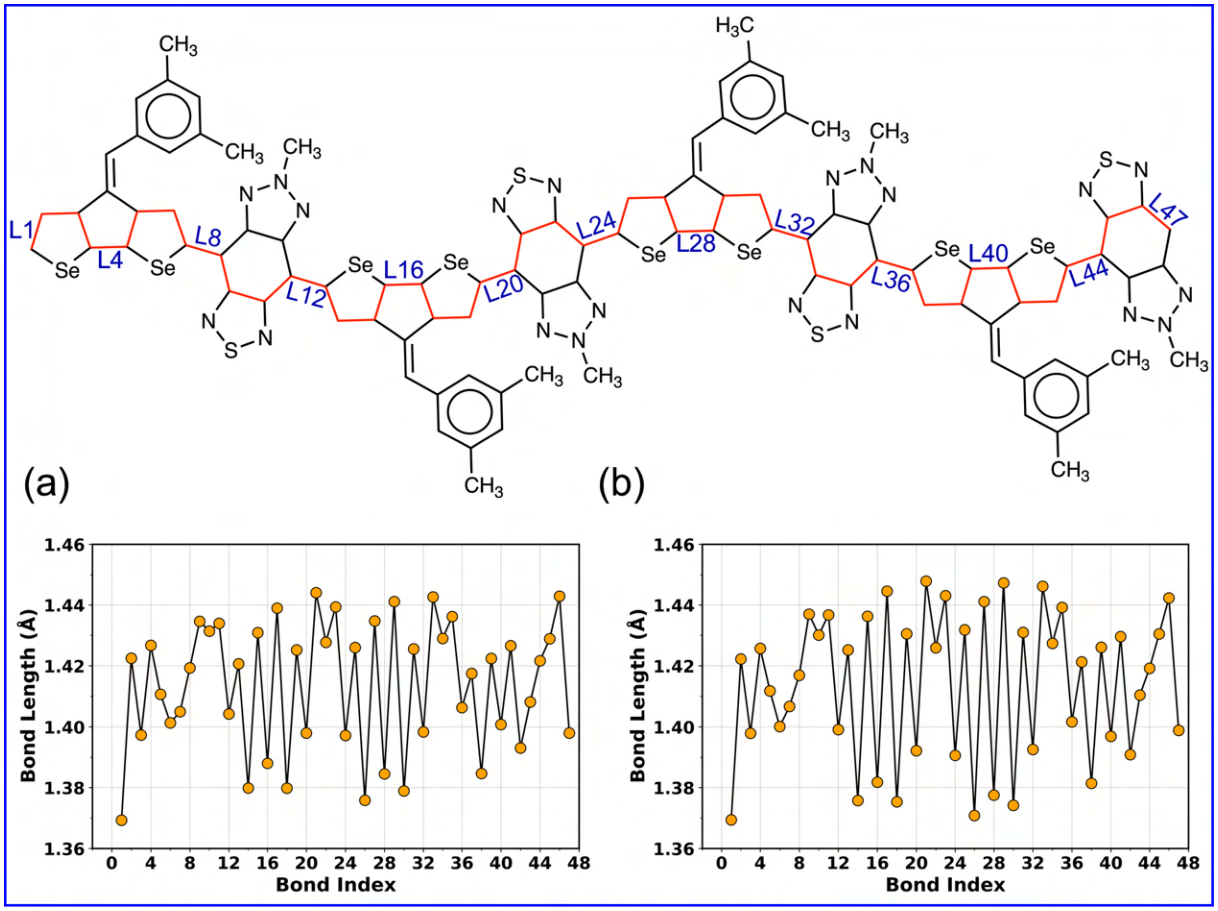


Figure S66: Calculated bond lengths (Å) of the CPDS-NBBT tetramer ($N = 4$) for (a) singlet ($S = 0$) and (b) triplet states ($S = 1$).

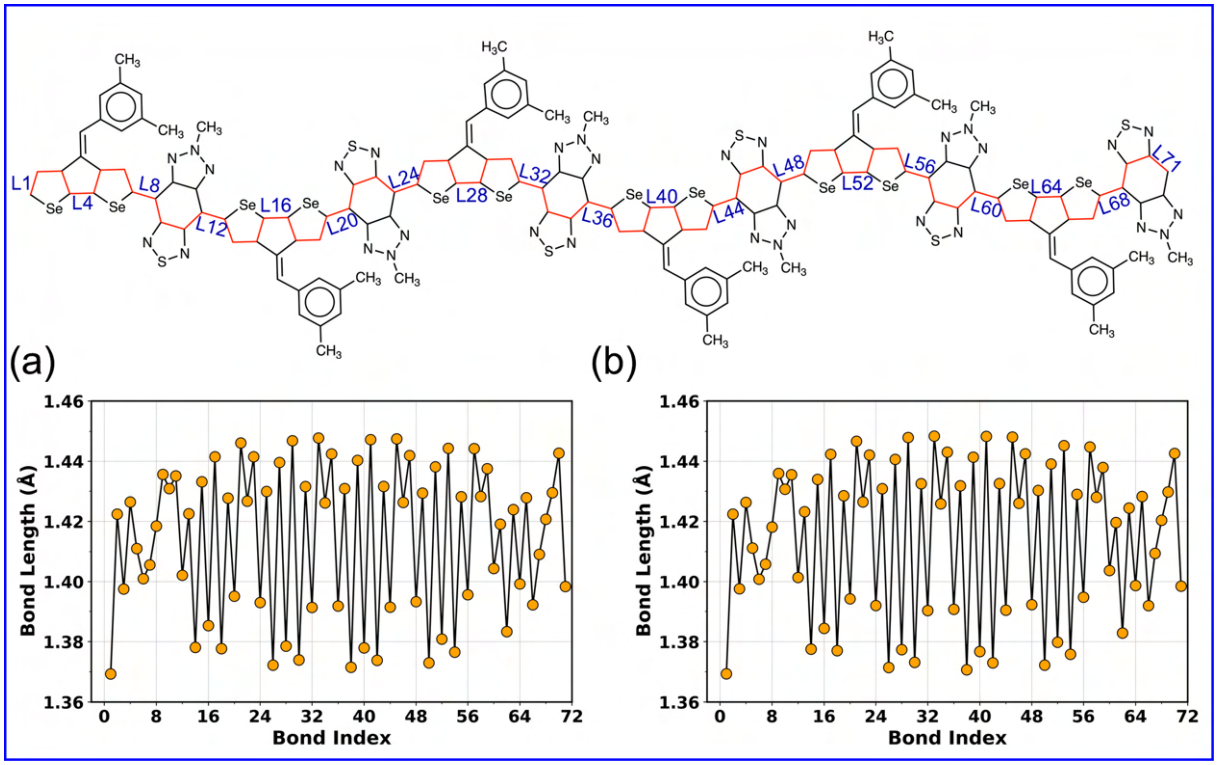


Figure S67: Calculated bond lengths (Å) of the CPDS-NBBT hexamer ($N = 6$) for (a) singlet ($S = 0$) and (b) triplet states ($S = 1$).

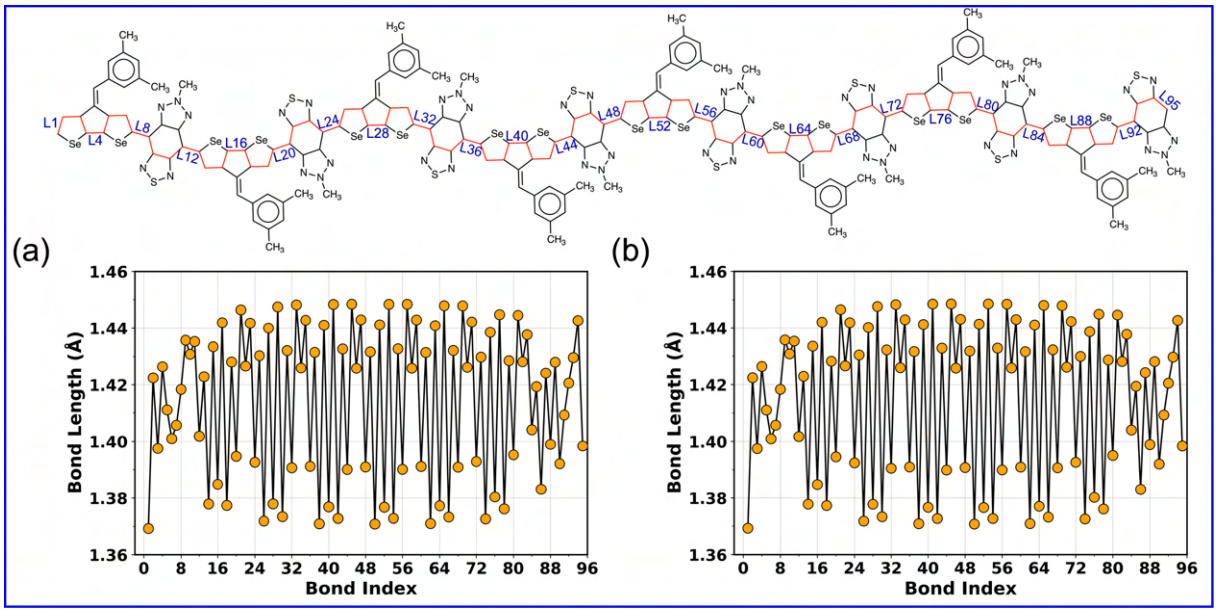


Figure S68: Calculated bond lengths (Å) of the CPDS-NBBT octamer ($N = 8$) for (a) singlet ($S = 0$) and (b) triplet states ($S = 1$).

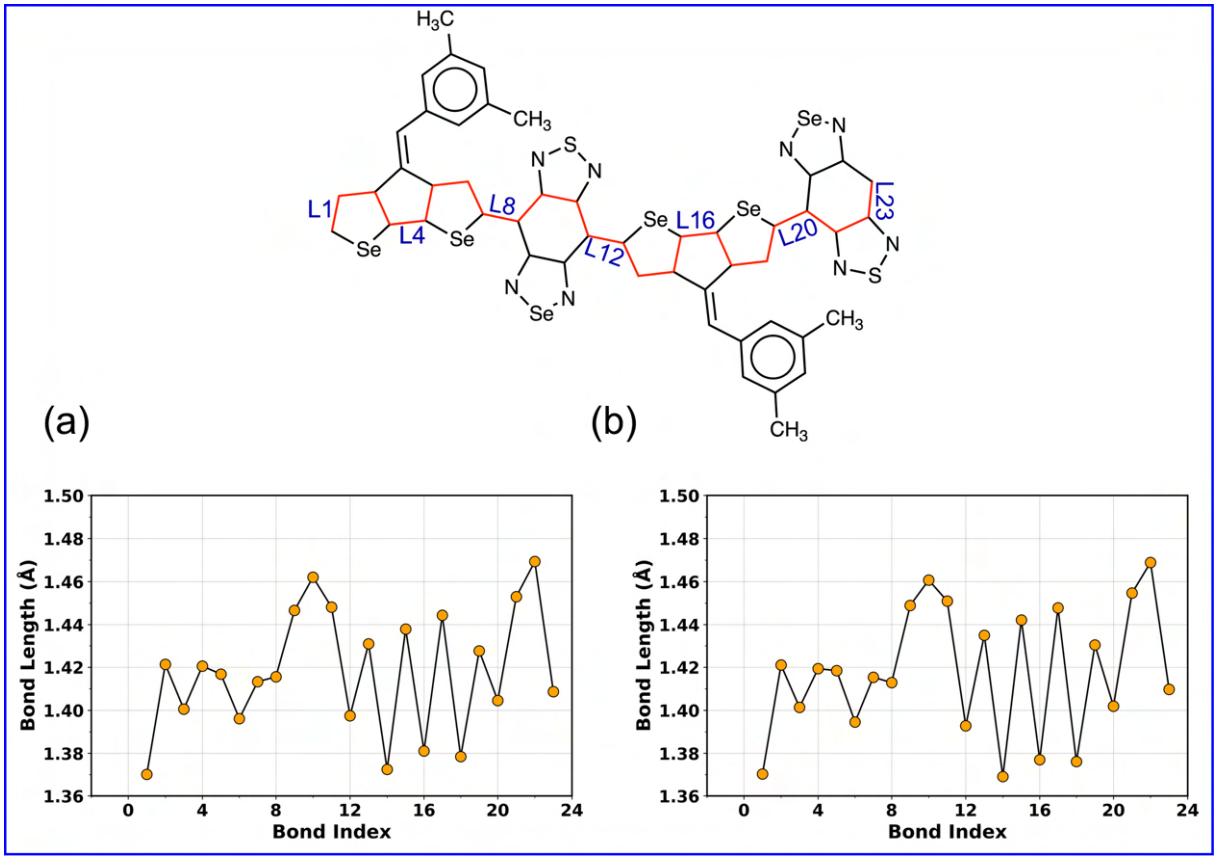


Figure S69: Calculated bond lengths (Å) of the CPDS-SeBBT dimer ($N = 2$) for (a) singlet ($S = 0$) and (b) triplet states ($S = 1$).

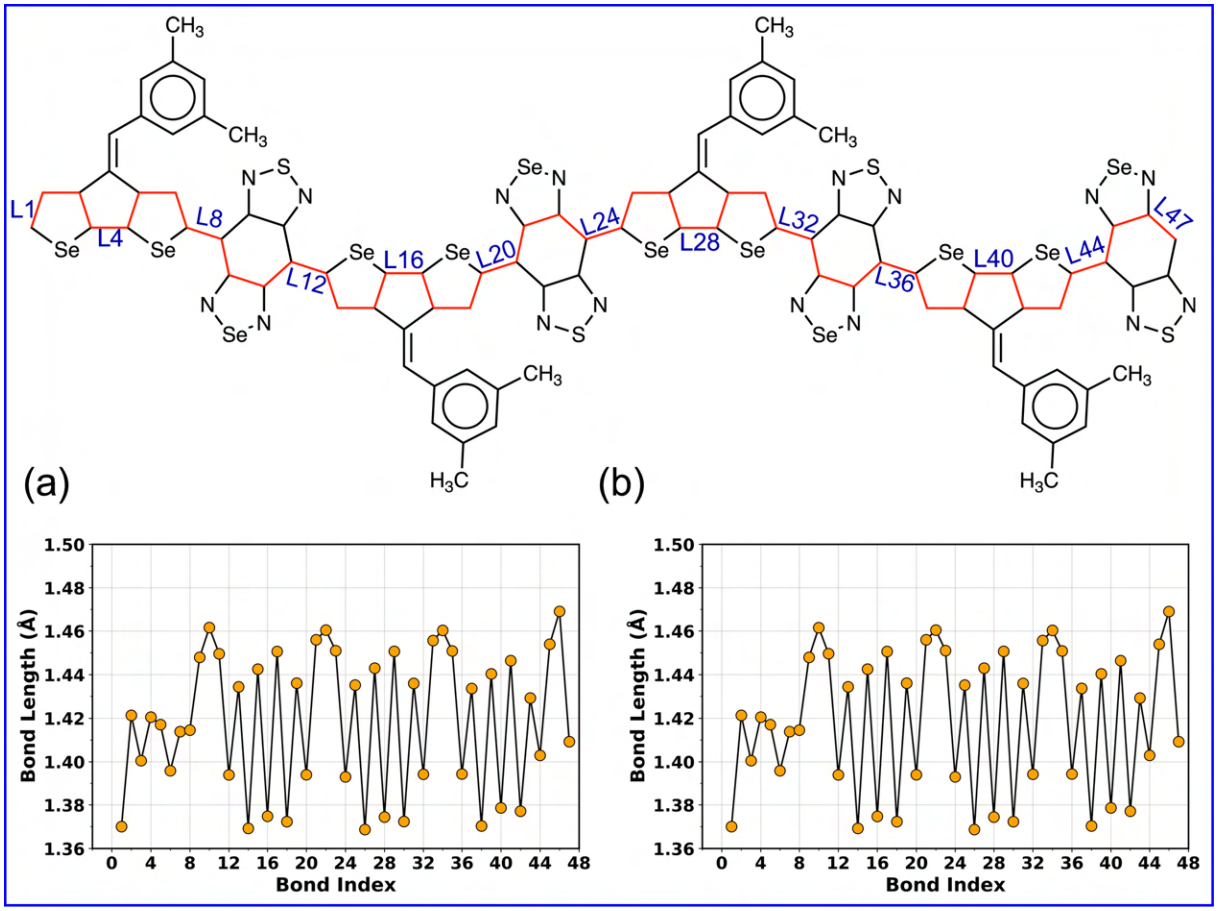


Figure S70: Calculated bond lengths (Å) of the CPDS-SeBBT tetramer ($N = 4$) for (a) singlet ($S = 0$) and (b) triplet states ($S = 1$).

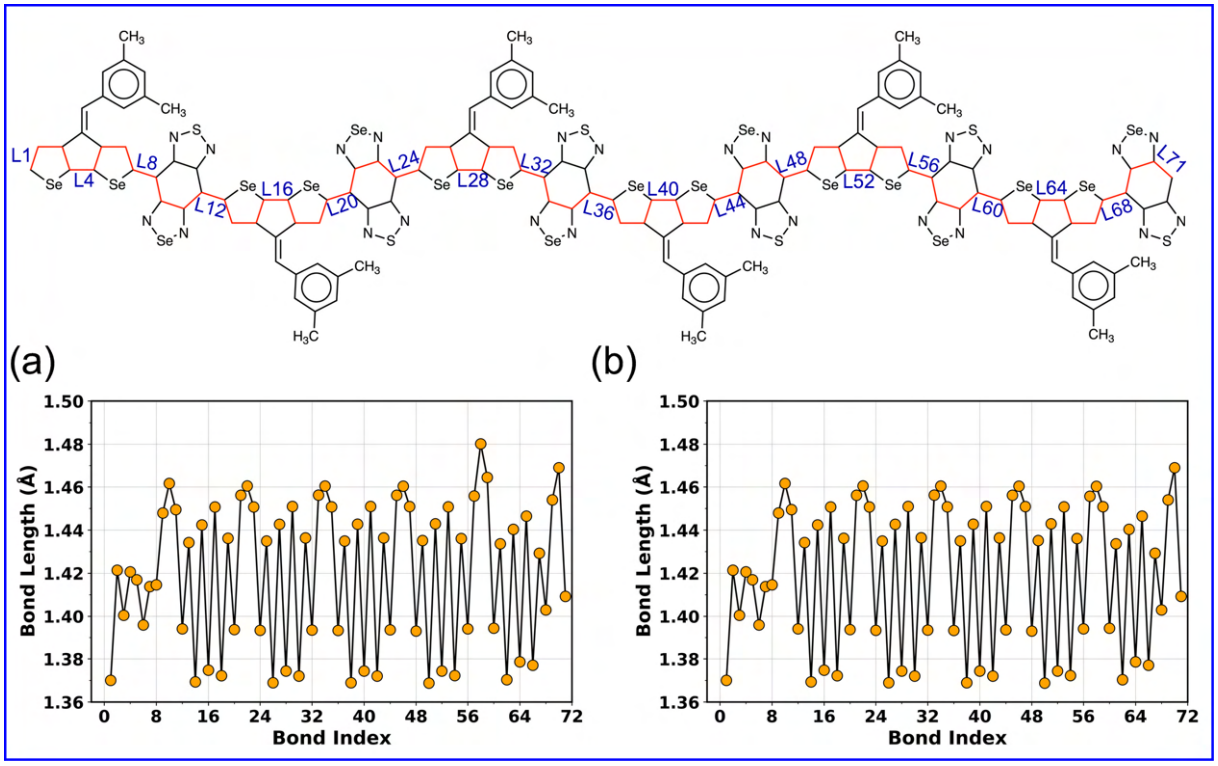


Figure S71: Calculated bond lengths (Å) of the CPDS-SeBBT hexamer ($N = 6$) for (a) singlet ($S = 0$) and (b) triplet states ($S = 1$).

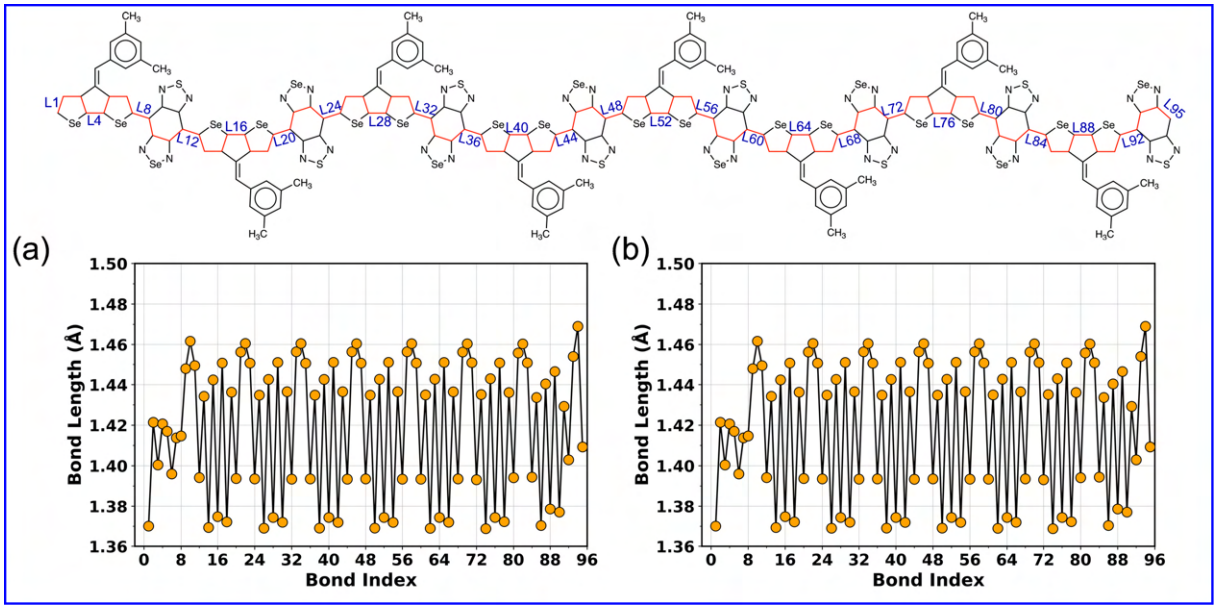


Figure S72: Calculated bond lengths (Å) of the CPDS-SeBBT octamer ($N = 8$) for (a) singlet ($S = 0$) and (b) triplet states ($S = 1$).

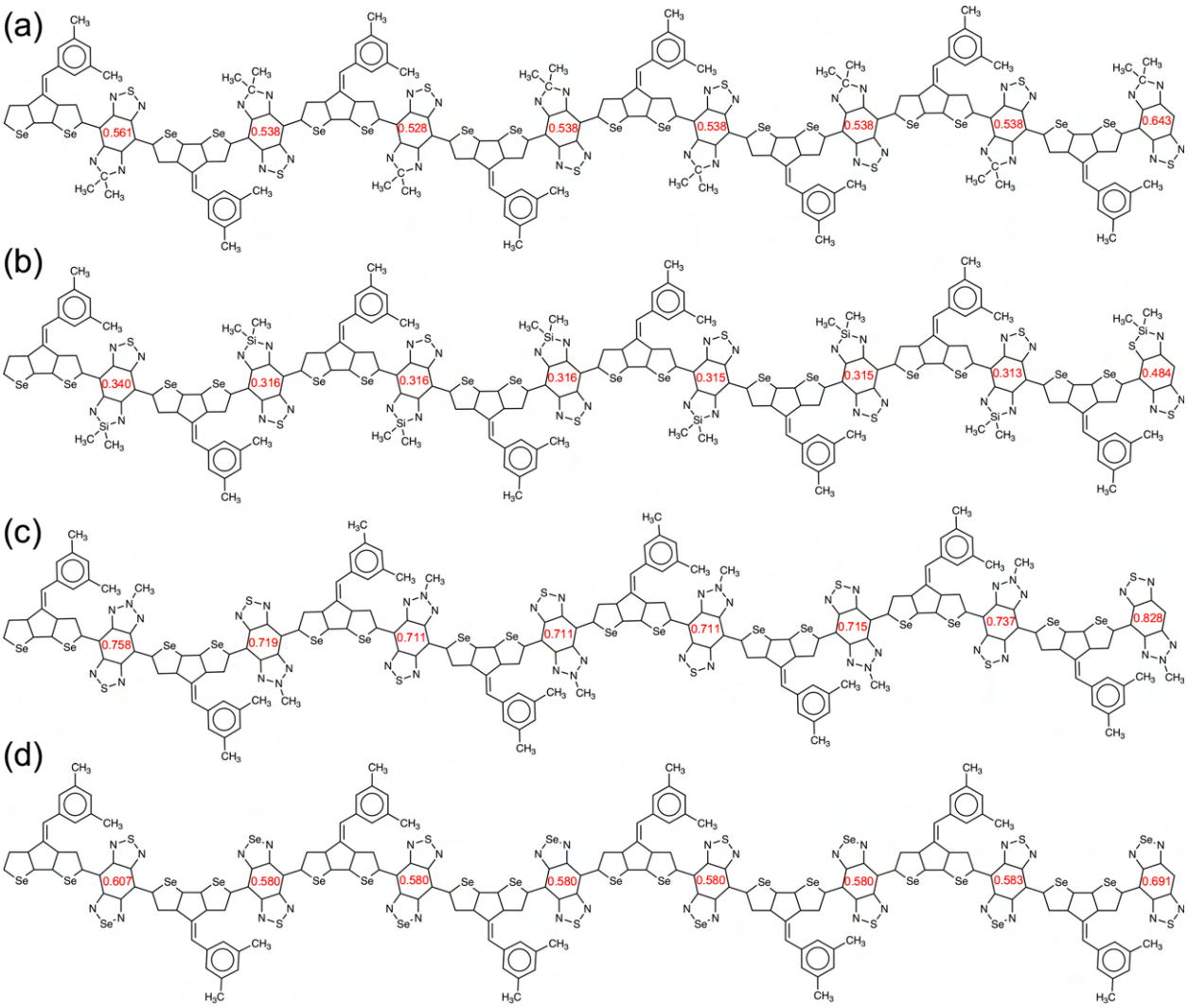


Figure S73: Calculated HOMA values for the octamer ($N = 8$) of (a) CPDS-CBBT, (b) CPDS-SiBBT, (c) CPDS-NBBT, and (d) CPDS-SeBBT polymers in the singlet state.

Literature Cited

(1) Wykes, M.; Milián-Medina, B.; Gierschner, J. Computational engineering of low bandgap copolymers. *Front. in Chem.* **2013**, *1*, 35.