Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information for

Linker-Dependent Symmetry Breaking Charge Separation in 9,10-Bis(phenylethynyl)anthracene Dimers

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Content

1. DFT-calculated ground state of *o-/m-/p-dimer*

Figure S1 shows the optimized ground-state geometry for o-dime, m-dimer and p-dimer. Table S1 shows the distance between the centers of the two chromophores.

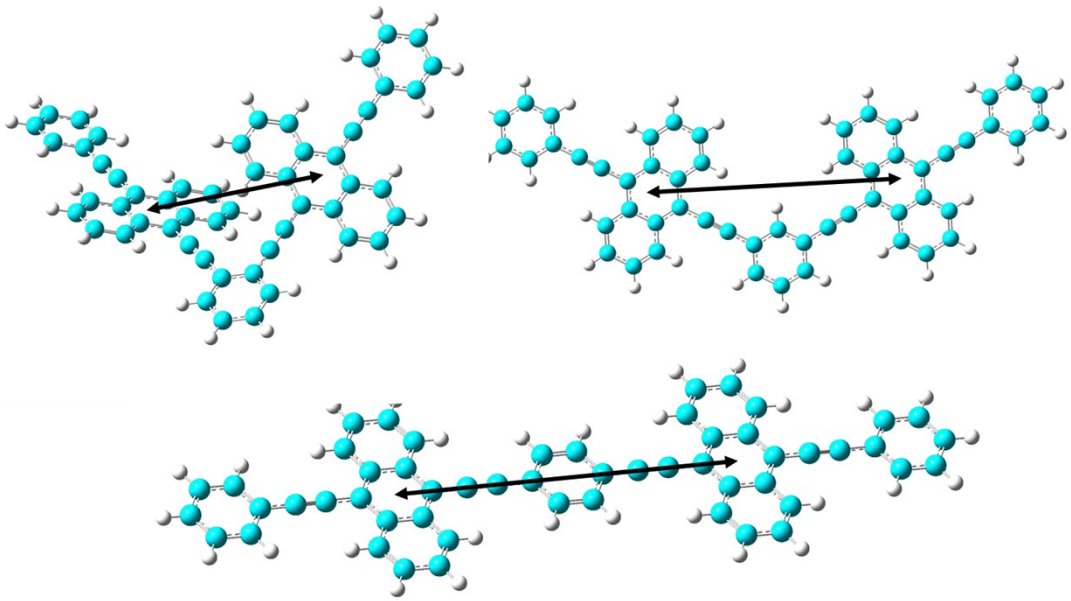

Figure S1. Optimized ground-state geometry for *o-dimer*, *m-dimer* and *p-dimer*.

Table S1. The distance between the centers of the two BPEA units in these three dimers.

	o-dimer	***m-dimer***	***p-dimer***
d(Å)	**7.**47	11.97	13.80

Table S2. The Davydov splitting energy of the three dimers calculated by the TD-DFT method.

	o-dimer	***m-dimer***	***p-dimer***
Energy(eV)	0.2915	0.1644	0.3489

2. Fluorescence dynamic of *o-/m-/p-monomer* and *o-/m-/p-dimer*

The fluorescence lifetime of *o-/m-/p-monomer* and *o-/m-/p-dimer* in different solvents and PS film are shown in Figure S2. The lifetime of fluorescence and fluorescence quantum yield of *o-/m-/p-monomer* in THF and PS film are shown in the Table S2.

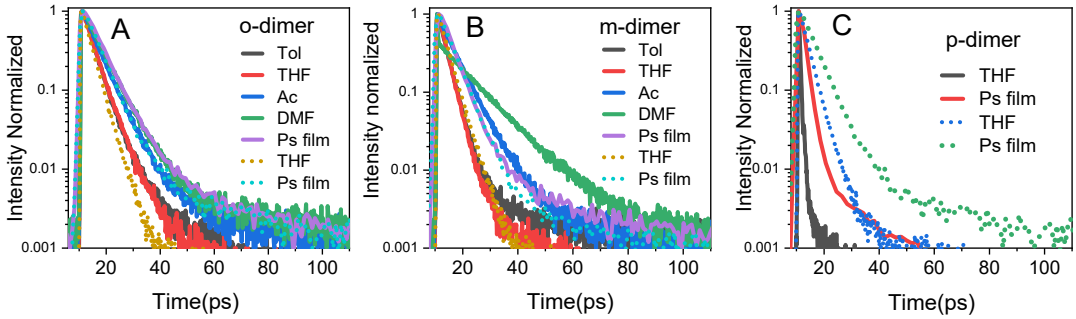

Figure S2. Time-resolved fluorescence decay of *o-dimer* (A), *m-dimer* (B) and *p-dimer* (C) as well as their corresponding monomers. The excitation wavelength is 440 nm. The monitored wavelength is the maximum fluorescence peak.

Table S3. fluorescence parameters of *o-monomer*, *m-monomer* and *p-monomer* in THF and PS film.

	o-monomer		***m-monomer***		***p-monomer***	
	Φ_F (%)	τ (ns)	Φ_F (%)	τ (ns)	Φ_F (%)	τ (ns)
THF	100	3.68	100	3.45	100	3.11
Ps film	100	5.17	100	4.75	100	6.08

3. Femtosecond transient absorption spectra of *o-/m-/p-monomer* in THF

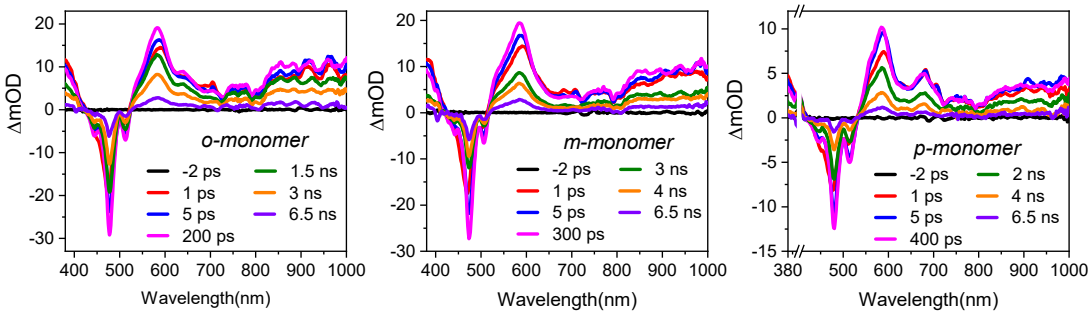

Figure S3. Femtosecond transient absorption spectra of *o-monomer* (A), *m-monomer* (B), *p-monomer* (C) in THF following the excitation at 400 nm.

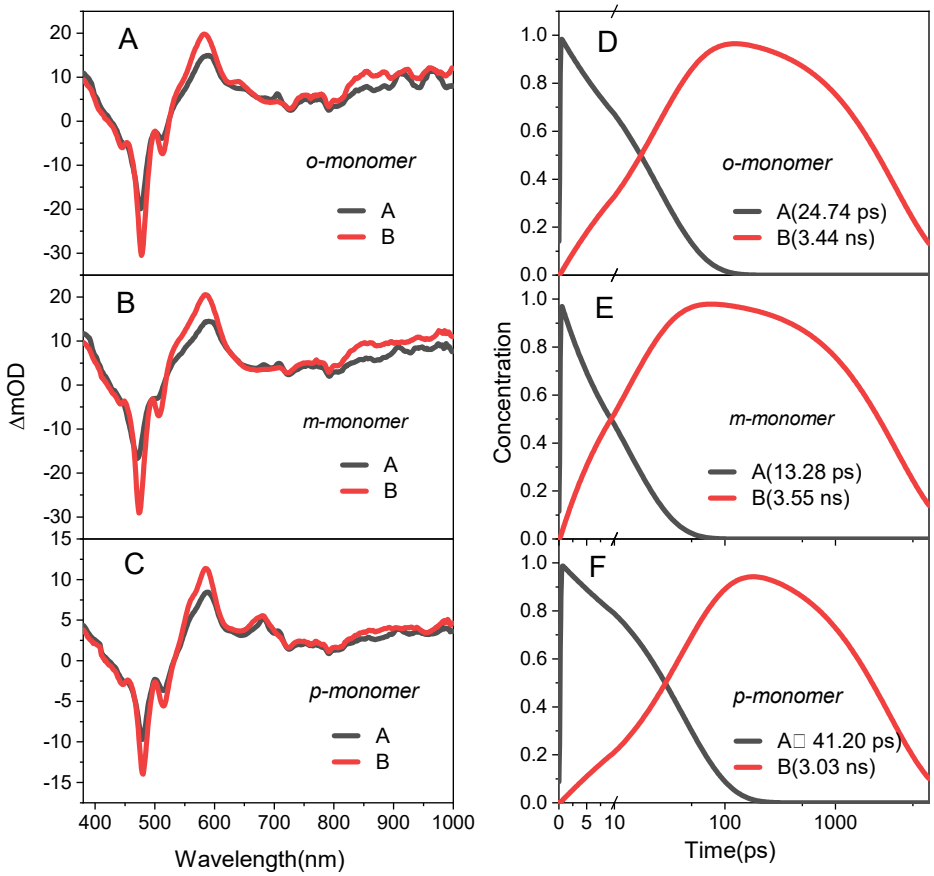

Figure S4. EADSs from global analysis and concentrations of transient species for *o-monomer* (A, D), *m-monomer* (B, E) and *p-monomer* (C, F) in THF.

4. Absorption spectra of dimer$^{\cdot+}$ and dimer$^{\cdot-}$

To produce the cation and anion of BPEA derivatives, electron transfer experiment was conducted by adding the reductant N,N-dimethylaniline (DMA) or oxidant tetracyanoethylene (TCNE) to the acetone solution of *o-monomer*, *m-dimer* and *p-dimer*.[1] The electron transfer process was measured by femtosecond (A-C) and nanosecond transient absorption (D-E) spectra (Figure S5).

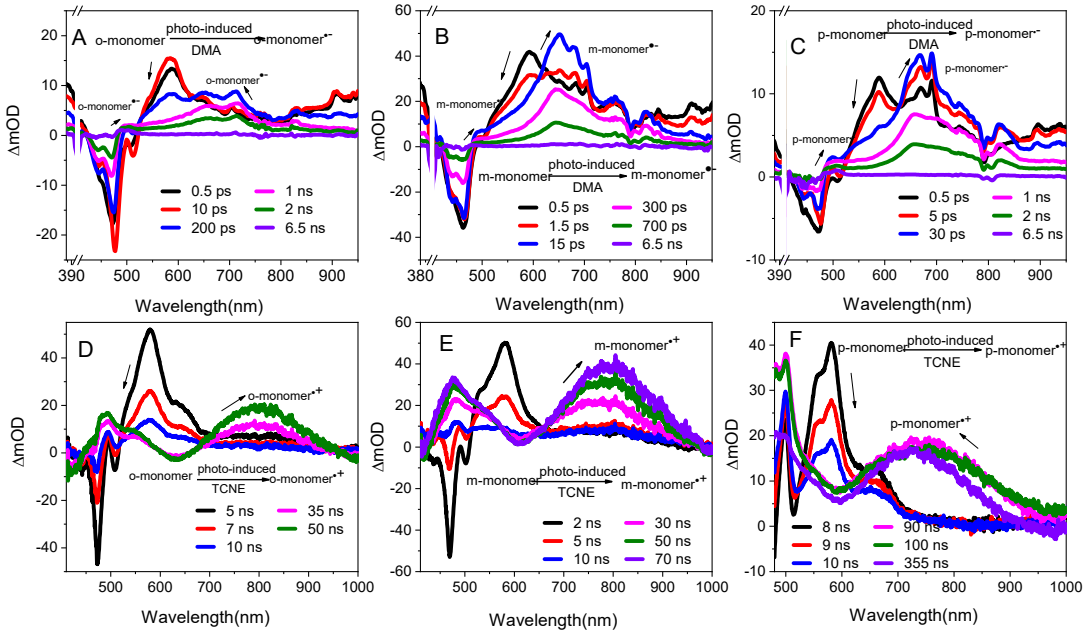

Figure S5. Absorption spectra of anion (*o-/m-/p-monomer*$^{\cdot-}$) and cation (*o-/m-/p-monomer*$^{\cdot+}$) in acetone.

As shown in Figure S5A, with the increase of the time, the singlet absorption band at 580 nm was decreased in *o-monomer*, accompanied by the rise of two new bands at ~650 and ~710 nm. Similarly, as the singlet state absorption intensity decreased in *m-monomer* and *p-monomer* (Figure S5B-S5C), a broad absorption band from 500 nm to 800 nm was emerged, with the band at ~660 nm as the main peak. These new bands are close to the anion of EBPEA derivatives based on the previous report.[2] So these new bands were ascribed to the anion of BPEA derivatives. When the oxidant tetracyanoethylene (TCNE) was added, two new broad bands (414-600 nm and 617-1000 nm) were observed, which was ascribed to the cation of BPEA derivatives.

5. Single-wavelength dynamics of *o-dimer*，*m-dimer* and *p-dimer*

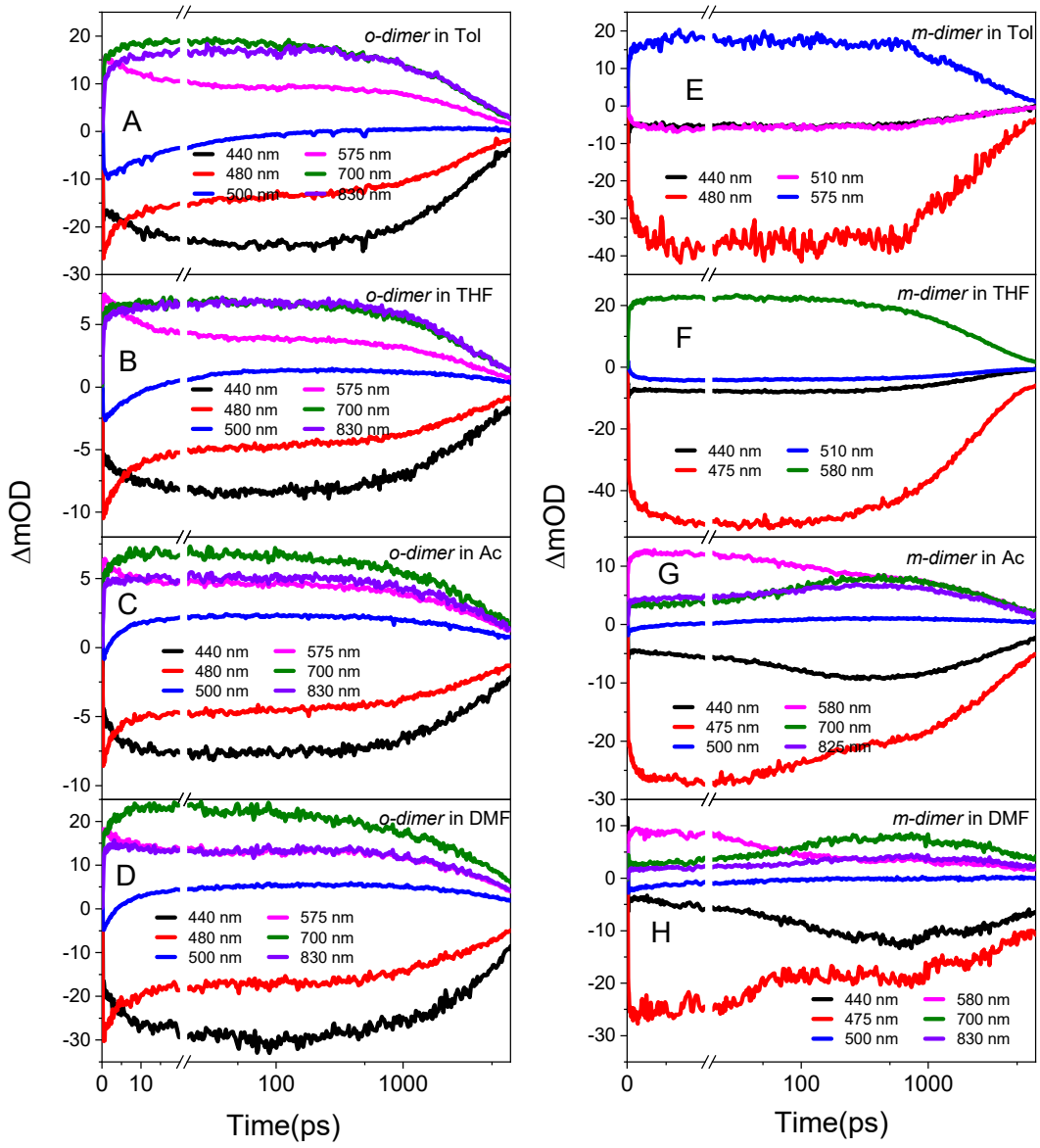

Figure S6. Single-wavelength dynamics probed at different wavelengths for *o-dimer* (A-C) and *m-dimer* (E-H) in Tol, THF, Ac, and DMF.

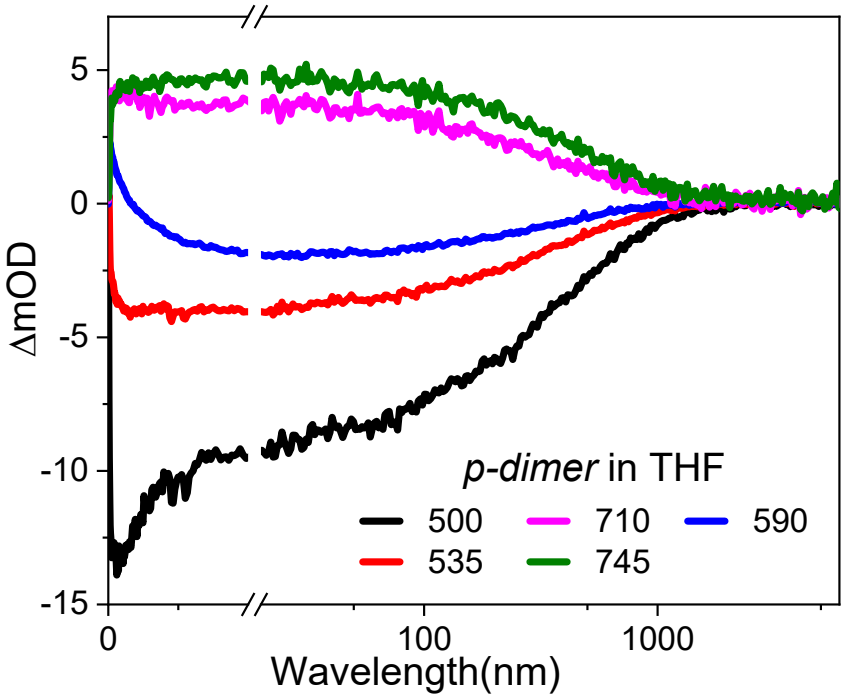

Figure S7. Single-wavelength dynamics probed at different wavelengths for *p-dimer* in THF.

6. Coordinates of the Optimized Geometries

Table S4. Geometry-optimized atomic coordinates for o-dimer.
There were zero imaginary frequencies

Atom Type	X	Y	Z
0 1			
C	-0.69858300	7.67710500	-0.03377200
C	0.69899000	7.67709900	0.03357200
C	1.39298500	6.47304900	0.06210600
C	0.71287400	5.23984800	0.02589400
C	-0.71249300	5.23985600	-0.02584200
C	-1.39259100	6.47305800	-0.06219100
H	-1.24525800	8.61543200	-0.05911500
H	1.24567600	8.61542200	0.05881400
H	2.47778600	6.46560400	0.10132900
H	-2.47739100	6.46561700	-0.10142900
C	1.45408300	4.02753000	0.01789900
C	-1.45373800	4.02755200	-0.01777200
C	2.13424400	3.01619600	-0.02440300
C	-2.13396200	3.01626400	0.02458700
C	2.92611600	1.84073500	-0.09179900
C	2.44363200	0.69994600	-0.79305700

C	4.20545600	1.81218400	0.53143300
C	1.16969100	0.70200700	-1.43609400
C	3.25277600	-0.48662600	-0.87113000
C	5.01372000	0.62571400	0.45358500
C	4.71471700	2.93806200	1.24492400
C	0.71561600	-0.40038900	-2.11321400
H	0.56204500	1.59839300	-1.37608400
C	2.74339600	-1.61219300	-1.58451200
C	4.53177000	-0.51631900	-0.24667000
C	6.29092100	0.62868100	1.08948600
H	4.09838000	3.82874000	1.30570800
C	5.94791700	2.90272600	1.84321800
C	1.51286300	-1.57325300	-2.18799000
H	-0.25936400	-0.37872200	-2.59161200
H	3.35686600	-2.50501800	-1.63996200
C	6.74772000	1.73162900	1.76386700
H	6.89686800	-0.26880700	1.02671100
H	6.31578100	3.77182500	2.38177600
H	1.14399900	-2.44215100	-2.72616400
H	7.72381200	1.71159100	2.24084200
C	-2.92592700	1.84085800	0.09194400
C	-2.44377400	0.70018100	0.79360700
C	-4.20505800	1.81227600	-0.53171700
C	-1.17008100	0.70230000	1.43713600
C	-3.25302200	-0.48632500	0.87161800
C	-5.01342700	0.62587200	-0.45392600
C	-4.71400400	2.93805600	-1.24558900
C	-0.71633100	-0.39998600	2.11465400
H	-0.56235600	1.59863400	1.37716300
C	-2.74397200	-1.61178300	1.58540700
C	-4.53179600	-0.51605700	0.24671400
C	-6.29040600	0.62880100	-1.09027300
H	-4.09759800	3.82869000	-1.30631700
C	-5.94699800	2.90268600	-1.84430600
C	-1.51366700	-1.57279300	2.18934800
H	0.25845500	-0.37827800	2.59344600
H	-3.35750700	-2.50456700	1.64079200
C	-6.74689900	1.73165100	-1.76502100
H	-6.89643000	-0.26863800	-1.02754300
H	-6.31461900	3.77170900	-2.38315200
H	-1.14505300	-2.44161000	2.72782300
H	-7.72282400	1.71158300	-2.24233700
C	-5.32909100	-1.68684700	0.32249300
C	5.32895500	-1.68718100	-0.32248900

C	6.01391400	-2.69367800	-0.38760300
C	-6.01416700	-2.69326700	0.38754300
C	6.81253600	-3.86918100	-0.46465400
C	6.35238500	-5.00582800	-1.16168100
C	8.07895900	-3.91971100	0.15429100
C	7.13675500	-6.15301400	-1.23452500
H	5.37869400	-4.97436200	-1.64091900
C	8.85606400	-5.07148000	0.07593500
H	8.43998100	-3.04869700	0.69258700
C	8.38985000	-6.19153100	-0.61738800
H	6.76926900	-7.02102900	-1.77517800
H	9.82979900	-5.09582200	0.55766100
H	8.99943400	-7.08893900	-0.67650200
C	-6.81285000	-3.86873500	0.46449200
C	-8.07919900	-3.91921000	-0.15461000
C	-6.35283700	-5.00539800	1.16158200
C	-8.85636400	-5.07094600	-0.07634900
H	-8.44011900	-3.04818000	-0.69294800
C	-7.13726600	-6.15254800	1.23433100
H	-5.37920500	-4.97397200	1.64094200
C	-8.39028400	-6.19101400	0.61703500
H	-9.83004000	-5.09524600	-0.55819600
H	-6.76988600	-7.02057800	1.77503300
H	-8.99991300	-7.08839600	0.67607600

Table S5. Geometry-optimized atomic coordinates for m-dimer.

There were zero imaginary frequencies

Atom Type	X	Y	Z
0 1			
C	1.20992900	4.54496200	-0.00003700
C	0.00000600	5.23398700	-0.00002700
C	-1.20991900	4.54496700	-0.00001000
C	-1.22316200	3.13402200	-0.00000200
C	0.00000000	2.44114600	-0.00001200
C	1.22316600	3.13401700	-0.00003000
H	2.15155200	5.08459600	-0.00005000
H	0.00000800	6.32039600	-0.00003300
H	-2.15154100	5.08460400	-0.00000500
H	-0.00000100	1.35654500	-0.00000500
C	2.45583100	2.42169200	-0.00004000
C	-2.45583100	2.42170300	0.00001200
C	-3.51422700	1.81703700	0.00001500
C	3.51422800	1.81702800	-0.00004300
C	4.74600600	1.11334000	-0.00004100
C	4.75048200	-0.31002800	0.00007100

C	5.97413900	1.83294700	-0.00014700
C	3.53748200	-1.06120000	0.00017200
C	5.99915400	-1.02296800	0.00008200
C	7.22272700	1.11990000	-0.00013000
C	6.00457800	3.25935400	-0.00027200
C	3.54962500	-2.43214300	0.00027500
H	2.59818600	-0.51878000	0.00016500
C	5.96945800	-2.44936900	0.00019000
C	7.22756700	-0.30361500	-0.00001200
C	8.43603500	1.87058000	-0.00023300
H	5.05999500	3.79253400	-0.00028800
C	7.19131600	3.94588800	-0.00037100
C	4.78305400	-3.13641700	0.00028300
H	2.61355200	-2.98386600	0.00035100
H	6.91446800	-2.98177500	0.00019500
C	8.42470200	3.24151800	-0.00035000
H	9.37484900	1.32732700	-0.00021600
H	7.19065400	5.03246400	-0.00046500
H	4.78394700	-4.22296800	0.00036300
H	9.36090500	3.79299700	-0.00042700
C	-4.74601200	1.11336000	0.00002400
C	-4.75050300	-0.31000800	-0.00010800
C	-5.97413700	1.83298000	0.00015900
C	-3.53751400	-1.06119700	-0.00023600
C	-5.99918300	-1.02293200	-0.00011600
C	-7.22273500	1.11994800	0.00014600
C	-6.00455800	3.25938800	0.00031000
C	-3.54967500	-2.43214000	-0.00035800
H	-2.59821000	-0.51878900	-0.00023300
C	-5.96950900	-2.44933300	-0.00024500
C	-7.22758900	-0.30356800	0.00000400
C	-8.43603300	1.87064600	0.00027500
H	-5.05996800	3.79255500	0.00032400
C	-7.19128600	3.94593800	0.00043500
C	-4.78311400	-3.13639700	-0.00036100
H	-2.61361000	-2.98387500	-0.00045300
H	-6.91452700	-2.98172600	-0.00024600
C	-8.42468100	3.24158400	0.00041600
H	-9.37485400	1.32740700	0.00026000
H	-7.19061000	5.03251300	0.00054900
H	-4.78402200	-4.22294900	-0.00045600
H	-9.36087700	3.79307500	0.00051500
C	8.45929900	-1.00695100	0.00001100
C	-8.45932200	-1.00690100	-0.00002100

C	-9.51805100	-1.61147200	-0.00005200
C	9.51805700	-1.61147200	0.00004000
C	-10.75362200	-2.31780900	-0.00005900
C	-11.97981900	-1.62080500	0.00024500
C	-10.77471200	-3.72810300	-0.00037700
C	-13.18525000	-2.31612700	0.00023100
H	-11.97151100	-0.53514000	0.00049200
C	-11.98520000	-4.41456200	-0.00038800
H	-9.83475300	-4.27143200	-0.00061600
C	-13.19390200	-3.71343500	-0.00008600
H	-14.12229600	-1.76592600	0.00046800
H	-11.98612200	-5.50119200	-0.00063500
H	-14.13703200	-4.25280300	-0.00009700
C	10.75364000	-2.31778700	0.00008000
C	10.77475700	-3.72808100	0.00039200
C	11.97982300	-1.62076000	-0.00018800
C	11.98525800	-4.41451700	0.00043300
H	9.83480800	-4.27142800	0.00060200
C	13.18526800	-2.31605900	-0.00014300
H	11.97149500	-0.53509500	-0.00043000
C	13.19394600	-3.71336700	0.00016800
H	11.98620000	-5.50114700	0.00067400
H	14.12230300	-1.76584000	-0.00035200
H	14.13708600	-4.25271700	0.00020200

Table S6. Geometry-optimized atomic coordinates for p-dimer.

There were zero imaginary frequencies

Atom Type	X	Y	Z
0 1			
C	0.69269900	1.21287600	-0.00024800
C	-0.69270600	1.21287300	-0.00003500
C	-1.41701000	0.00004900	0.00007800
C	-0.69270100	-1.21277300	-0.00003100
C	0.69270400	-1.21277000	-0.00024500
C	1.41700900	0.00005500	-0.00035600
H	1.23538800	2.15303300	-0.00033400
H	-1.23539800	2.15302800	0.00004800
H	-1.23539100	-2.15292900	0.00005500
H	1.23539700	-2.15292400	-0.00032800
C	-2.83581000	0.00004400	0.00030200
C	-4.05604900	0.00003300	0.00049300
C	2.83580800	0.00005700	-0.00058100
C	4.05604800	0.00005100	-0.00077000
C	-5.47266000	0.00002200	0.00039200
C	-6.18328800	1.23434500	0.00033500

C	-6.18326800	-1.23431300	0.00036300
C	-5.50267900	2.48790400	0.00036100
C	-7.62089500	1.23398300	0.00024800
C	-7.62087500	-1.23397300	0.00027800
C	-5.50263900	-2.48786100	0.00041800
C	-6.19307300	3.67262700	0.00030300
H	-4.41801100	2.48263300	0.00042600
C	-8.30265700	2.48721100	0.00019100
C	-8.33115300	-0.00000100	0.00022200
C	-8.30261700	-2.48721200	0.00025100
H	-4.41797100	-2.48257300	0.00048200
C	-6.19301400	-3.67259500	0.00038900
C	-7.61323400	3.67235900	0.00021700
H	-5.65373400	4.61589200	0.00032300
H	-9.38729700	2.48057700	0.00012500
C	-7.61317500	-3.67235000	0.00030500
H	-9.38725800	-2.48059500	0.00018700
H	-5.65366000	-4.61585100	0.00043100
H	-8.15299400	4.61536400	0.00017100
H	-8.15292100	-4.61536300	0.00028200
C	5.47266000	0.00003600	-0.00058300
C	6.18326500	-1.23430100	-0.00050800
C	6.18329200	1.23435700	-0.00048000
C	5.50263200	-2.48784700	-0.00061300
C	7.62087200	-1.23396600	-0.00032300
C	7.62089900	1.23399000	-0.00029300
C	5.50268700	2.48791800	-0.00055600
C	6.19300400	-3.67258400	-0.00054200
H	4.41796400	-2.48255600	-0.00075300
C	8.30261000	-2.48720700	-0.00025300
C	8.33115300	0.00000400	-0.00021300
C	8.30266500	2.48721600	-0.00019400
H	4.41801900	2.48265100	-0.00069700
C	6.19308500	3.67263900	-0.00045700
C	7.61316500	-3.67234200	-0.00036000
H	5.65364800	-4.61583800	-0.00062600
H	9.38725100	-2.48059200	-0.00011400
C	7.61324500	3.67236700	-0.00027300
H	9.38730500	2.48057800	-0.00005300
H	5.65374900	4.61590500	-0.00052000
H	8.15290800	-4.61535700	-0.00030500
H	8.15300900	4.61537000	-0.00019600
C	-9.74921300	-0.00001400	0.00014700
C	-10.96847800	-0.00002700	0.00009100

C	9.74921300	-0.00001200	-0.00002400
C	10.96847800	-0.00002800	0.00014400
C	12.39156600	-0.00005100	0.00037300
C	13.11013800	1.21370900	0.00049300
C	13.11009800	-1.21383300	0.00048300
C	14.50169600	1.20855700	0.00071500
H	12.56404900	2.15208200	0.00040800
C	14.50165700	-1.20872700	0.00070600
H	12.56397900	-2.15218800	0.00039200
C	15.20292700	-0.00009600	0.00082300
H	15.04196600	2.15136100	0.00080500
H	15.04189600	-2.15154800	0.00078900
H	16.28938700	-0.00011400	0.00099700
C	-12.39156600	-0.00004200	-0.00006400
C	-13.11013300	1.21372000	-0.00014300
C	-13.11010400	-1.21382200	-0.00014000
C	-14.50169100	1.20857500	-0.00029200
H	-12.56403900	2.15209100	-0.00008400
C	-14.50166300	-1.20870900	-0.00028900
H	-12.56398900	-2.15217900	-0.00008000
C	-15.20292800	-0.00007600	-0.00036600
H	-15.04195700	2.15138100	-0.00035100
H	-15.04190600	-2.15152900	-0.00034500
H	-16.28938800	-0.00008800	-0.00048300

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