Supporting Information

Poly(cyclopenta[*c*]selenophene): a new polyselenophene

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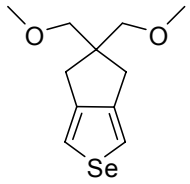
General: Tetrahydrofuran was distilled from sodium/benzophenone under an atmosphere of dry nitrogen. Melting point was recorded on BÜCHI Melting Point B-545 and was uncorrected. NMR spectra was recorded on a 500 MHz spectrometer (Bruker) as a solution in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard, chemical shifts (δ) are reported in parts per million. Columns were prepared with silica gel (60-120 mesh and 230-400 mesh, Merck). Acetonitrile (AcCN, Merck) was distilled from P_2O_5 (Spectrochem, India) under dry nitrogen atmosphere. Tetrabutylamonium perchlorate, (TBAPC, Sigma-Aldrich) was used as received. Ferrocene powder (Sigma-Aldrich) was used to establish an electrochemical reference. Non-aqueous Ag/AgCl wire was prepared by dipping silver wire in a solution of $FeCl_3$ and HCl.

Electrochemistry and Spectroelectrochemistry : Electrochemical studies were carried out with a Princeton Applied Research 263A potentiostat and CH instrument 400A using platinum(Pt) disk electrode (dia. 1.6mm) as the working electrode, a platinum wire as counter electrode, and an AgCl coated Ag wire, which was directly dipped in the electrolyte solution, as the reference electrode. Under these conditions, a Fc/Fc+ standard was calibrated to be +0.34 V. Pt disk electrodes were polished with alumina, water, acetone and was dried with nitrogen gas before use to remove any incipient oxygen. The electrolyte used was 0.1 M TBAPC in AcCN. Films were electrodeposited in 0.1 M TBAPC in AcCN by cyclic voltammetry (CV) between -0.2 and 1.45 V at 50 mV/s for 10 cycles terminated at 1.2 V (stable oxidized state). CPS (**1**) was electropolymerized on indium tin oxide (ITO) coated glass as a working electrode. Before examining the optical properties of PCPS films, the films were rinsed with acetonitrile. UV-vis-NIR spectra were recorded on a HITACHI U-4100 UV-vis-NIR spectrophotometer. In spectrochemical measurements, the working electrode was an ITO-coated glass slide, the counter electrode was a platinum wire, and Ag/AgCl was used as the pseudoreference electrode. Under these conditions, the Fc/Fc+ standard was calibrated to be +0.34 V.

Synthesis: All reactions were carried out under nitrogen. 1,7-Bis(trimethylsilyl)-4,4-bis(methoxymethyl)-1,6-heptadiyne was prepared in 4 steps from diethyl malonate , following the sequence reported by Tamao *et al*.[1]

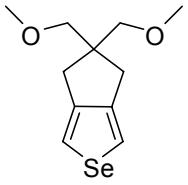
Synthesis of Cyclopenta[*c*]selenophene-$(CH_2OMe)_2$:



To Cp_2ZrCl_2 (946 mg, 3.234 mmol) in 40 mL of dry THF was added *n*-BuLi (4.3 mL, 6.776 mmol, 1.6 M solution in hexane) at -78°C. After the solution was stirred for about 30 mins, 4,4-bis(methoxymethyl)-1,7-bis(trimethylsilyl)hepta-1,6-diyne (1 g, 3.080 mmol) in 10 mL of dry THF was added drop wise. The resulting solution was allowed to warm to room temperature, and stirred for additional 2 hrs. The color of the solution changed from pale yellow to orange. $SeCl_2$ (4.62 mmol, Se = 364 mg, SO_2Cl_2 = 375 µl) in 5mL dry THF was added slowly via syringe while maintaining the temperature at 0°C and the solution was stirred for overnight at room temperature. The reaction was quenched by pouring the resulting solution into 3N HCl, stirred for 30 mins and the resulting mixture was filtered through celite pad and filtrate was extracted with diethylether. The organic layer was washed with water, brine, and water and then dried over Na_2SO_4. The volatile material was then removed and the resulting dark reddish brown liquid was subjected to column chromatography (230-400 silica gel, hexane:ethylacetate = 95:5) to give CPS **1** (290 mg, yield = 36%) as a colorless liquid which solidified when kept in refrigerator for one day. mp 56°C; IR (KBr, cm^{-1}) : 3448, 2923, 2872, 2370, 1458, 1195, 1109, 957, 790, 752; δ_H (500 MHz; $CDCl_3$; Me_4Si) 7.31 (s, 2H, selenyl-H, $^2J_{77Se\text{-}C\text{-}H}$ = 49 Hz), 2.44 (s, 4H, CH_2), 3.27(s, 10H, OCH_2 & OCH_3). δ_C (125 MHz; $CDCl_3$; Me_4Si) 148.98, 118.6 ($^1J_{77Se\text{-}C}$ = 110 Hz), 75.99, 59.27, 54.48, 34.28. HRMS (EI+): calculated for $C_{11}H_{16}O_2Se$, 260.0316; found 260.0310.

1 S. Yamaguchi, R. Z. Jin, Y. Itami, T. Goto and K. Tamao, *J. Am. Chem. Soc.* 1999, **121**, 10420-10421.

NMR Spectra of CPS:



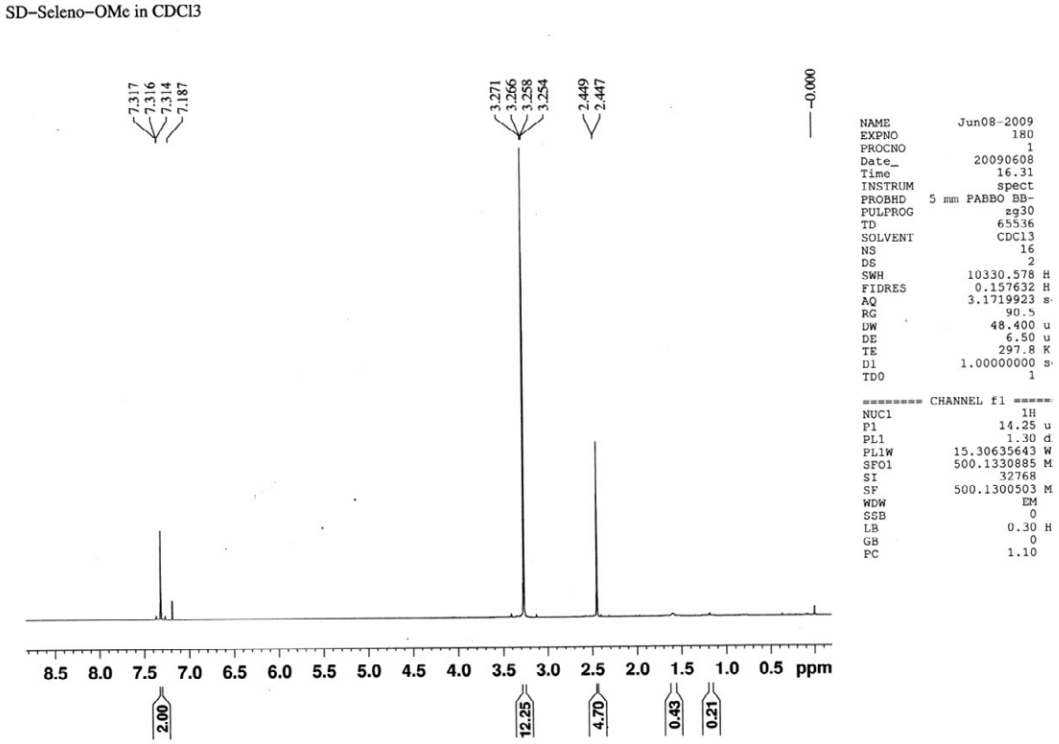


Figure S1. ^{1}H spectra of CPS 1.

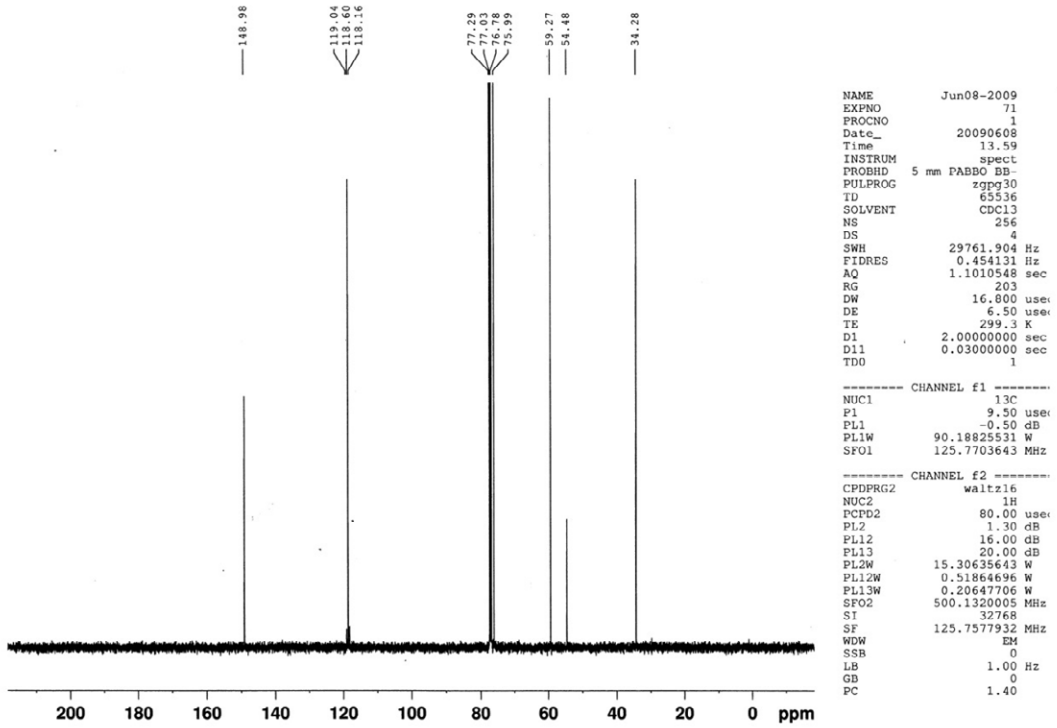


Figure S2. ^{13}C spectra of CPS 1.

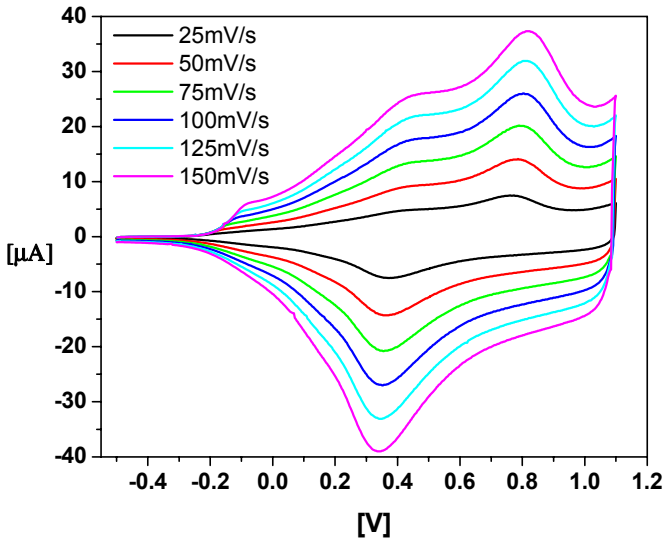


Figure S3. Cyclic voltammetry of PCPS produced in monomer-free acetonitrile.

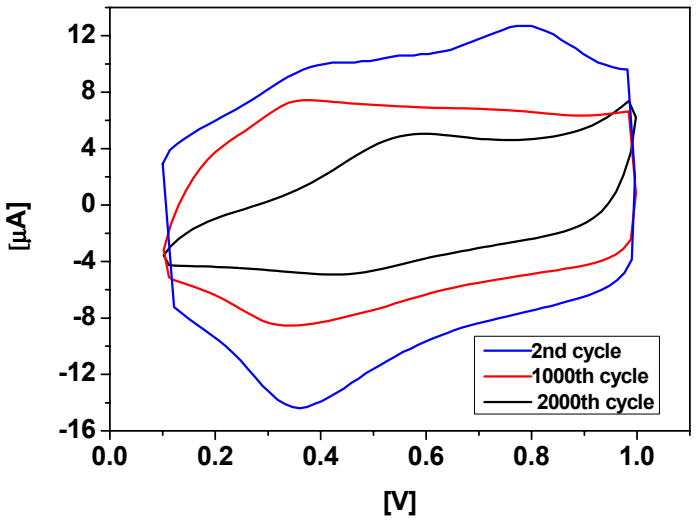


Figure S4. CV of PCPS film after 2nd, 1000th and 2000th cycle in monomer free acetonitrile and 0.1M TBAPC cycled between 0.1 and 1.0 V. After 1000th and 2000th cycles 30 and 60% reduction in the charges have been observed, respectively.

Ref. 23.

Gaussian 03, Revision E.01. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, 2007.

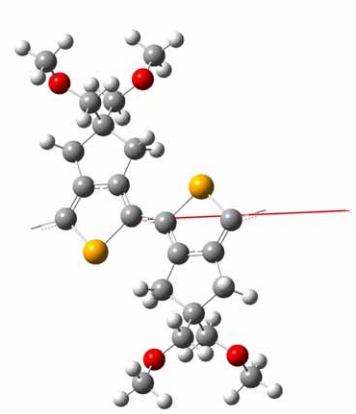
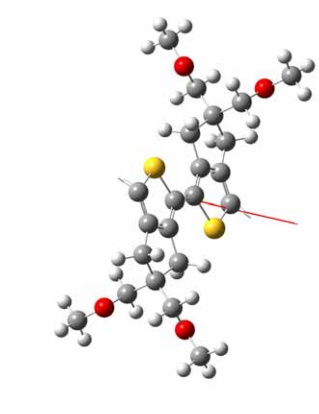
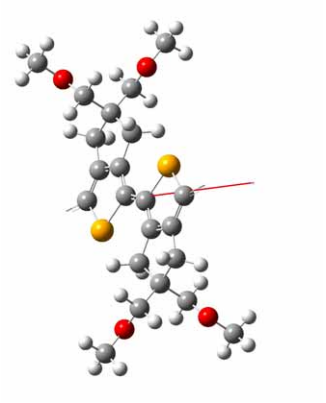
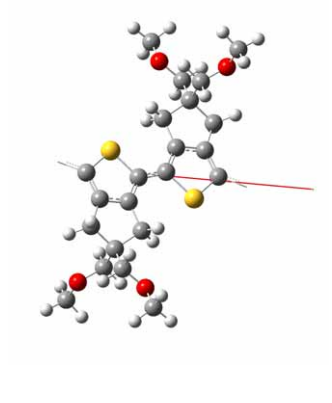
PCPS	PCPT
	
	

Figure S5. Optimized structures of PCPS and PCPT (two views).

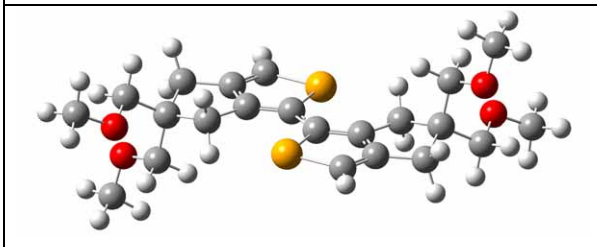
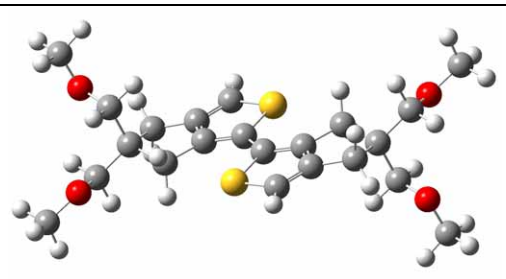
2CPS	2CPT
	

Figure S6. Optimized structures of dimers of CPS and CPT.

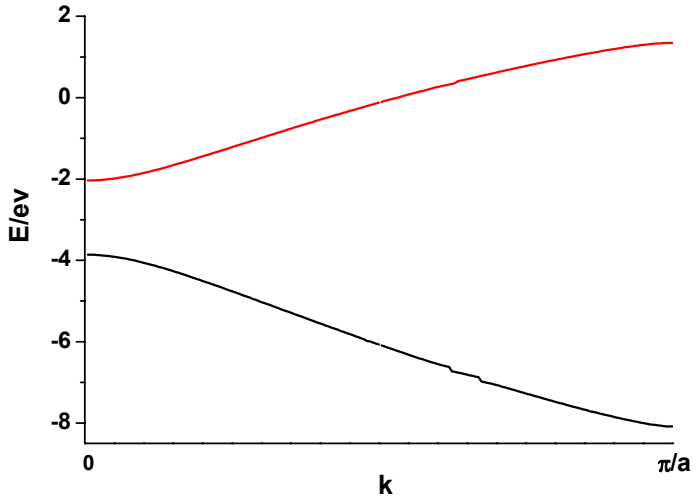


Figure S7. Band structures of PCPS for the valence band (highest occupied crystal orbital, HOCO) and conduction band (lowest unoccupied crystal orbital, LUCO) at PBC/B3LYP/6-31G(d)

Table S1. Relative Energies of dimers and polymer of CPS and CPT

Polymer	Absolute energy at PBC/B3LYP/6-31G(d)
PCPS	-5954.8082594
PCPT	-1952.4164182
Dimer	Absolute energy at B3LYP/6-31G(d)
2CPS	-5955.9818986
2CPT	-1953.6026653

Table S2. Coordinates for optimized geometry of PCPS at PBC/B3LYP/6-31G(d).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.361174	0.159413	0.000000
2	6	0	2.737322	1.390686	-0.072011
3	6	0	1.321052	1.391455	-0.071747
4	6	0	0.696828	0.159954	-0.000072
5	6	0	3.280795	2.793456	-0.176788
6	1	0	4.051516	3.023528	0.567040
7	1	0	3.743910	2.963862	-1.160509
8	6	0	2.032789	3.712695	0.034018
9	6	0	0.780725	2.796460	-0.172203
10	1	0	0.308833	2.983297	-1.146316
11	1	0	0.007267	3.010392	0.576924
12	34	0	2.029114	-1.194779	0.108437
13	34	0	-2.029159	1.194600	-0.107066
14	6	0	-3.361214	-0.159618	0.001222
15	6	0	-0.696863	-0.160147	0.001260
16	6	0	-2.737354	-1.390891	0.073084
17	6	0	-1.321084	-1.391655	0.072794
18	6	0	-3.280798	-2.793694	0.177620
19	6	0	-0.780767	-2.796683	0.172972
20	6	0	-2.032812	-3.712829	-0.033701
21	1	0	-3.743659	-2.964369	1.161413
22	1	0	-4.051676	-3.023590	-0.566094
23	1	0	-0.007178	-3.010434	-0.576063
24	1	0	-0.309072	-2.983775	1.147133
25	6	0	2.055382	4.882639	-0.951736
26	1	0	2.945849	5.505129	-0.773015
27	1	0	2.114997	4.494490	-1.983854
28	6	0	2.009470	4.236247	1.478750
29	1	0	1.125089	4.875256	1.620294
30	1	0	1.933369	3.386053	2.178503
31	6	0	-2.055347	-4.883328	0.951390
32	1	0	-2.114933	-4.495772	1.983734
33	1	0	-2.945798	-5.505748	0.772355
34	6	0	-2.009524	-4.235571	-1.478727
35	1	0	-1.933419	-3.384991	-2.178005
36	1	0	-1.125163	-4.874522	-1.620639
37	8	0	-0.874853	-5.649980	0.787491
38	8	0	-3.193302	-4.972013	-1.733230
39	8	0	3.193228	4.972854	1.732857
40	8	0	0.874912	5.649434	-0.788325
41	6	0	-0.826643	-6.772589	1.639729
42	1	0	-1.667147	-7.461060	1.455694
43	1	0	0.112118	-7.294591	1.435133
44	1	0	-0.847696	-6.479822	2.702336
45	6	0	-3.244347	-5.491788	-3.043693
46	1	0	-3.213095	-4.691664	-3.800897
47	1	0	-2.410842	-6.185284	-3.239990
48	1	0	-4.188624	-6.034556	-3.140107
49	6	0	3.244249	5.493366	3.043028

50	1	0	2.410723	6.186948	3.238933
51	1	0	3.213015	4.693664	3.800682
52	1	0	4.188511	6.036213	3.139145
53	6	0	0.826811	6.771579	-1.641178
54	1	0	-0.111949	7.293725	-1.436944
55	1	0	1.667325	7.460118	-1.457442
56	1	0	0.847944	6.478229	-2.703621
57	-2	0	8.116132	0.000000	0.000000
Lengths of translation vectors:			8.116132		

Table S3. Coordinates for optimized geometry of PCPT at PBC/B3LYP/6-31G(d)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.259630	0.196908	0.008094
2	6	0	2.685034	1.453727	-0.052723
3	6	0	1.268786	1.455000	-0.056661
4	6	0	0.692301	0.198603	0.000313
5	6	0	3.225206	2.859277	-0.134863
6	1	0	4.034385	3.070666	0.570163
7	1	0	3.621958	3.066255	-1.140104
8	6	0	1.980206	3.755718	0.169991
9	6	0	0.733388	2.862692	-0.141174
10	1	0	0.340580	3.082291	-1.143390
11	1	0	-0.088767	3.063177	0.554903
12	16	0	1.975052	-1.017113	0.074472
13	16	0	-1.975085	1.017354	-0.068363
14	6	0	-3.259671	-0.196666	-0.002016
15	6	0	-0.692349	-0.198381	0.005691
16	6	0	-2.685083	-1.453494	0.058783
17	6	0	-1.268829	-1.454768	0.062675
18	6	0	-3.225229	-2.859072	0.140734
19	6	0	-0.733443	-2.862486	0.146875
20	6	0	-1.980272	-3.755380	-0.164618
21	1	0	-3.621690	-3.066294	1.146044
22	1	0	-4.034562	-3.070309	-0.564149
23	1	0	0.088721	-3.062806	-0.549237
24	1	0	-0.340692	-3.082365	1.149053
25	6	0	2.004699	5.028659	-0.677905
26	1	0	2.892786	5.629189	-0.426883
27	1	0	2.068626	4.760474	-1.747293
28	6	0	1.950673	4.115839	1.664521
29	1	0	1.065556	4.735759	1.870963
30	1	0	1.872151	3.194934	2.267310
31	6	0	-2.004678	-5.028780	0.682591
32	1	0	-2.068766	-4.761186	1.752117
33	1	0	-2.892632	-5.629284	0.431090
34	6	0	-1.950818	-4.114682	-1.659341
35	1	0	-1.872372	-3.193446	-2.261641

36	1	0	-1.065677	-4.734435	-1.866206
37	8	0	-0.821238	-5.769369	0.437903
38	8	0	-3.132521	-4.820393	-1.998671
39	8	0	3.132402	4.821646	2.003526
40	8	0	0.821407	5.769590	-0.433510
41	6	0	-0.774612	-6.982701	1.154922
42	1	0	-1.613697	-7.646046	0.889751
43	1	0	0.165463	-7.476840	0.894666
44	1	0	-0.799573	-6.814861	2.244265
45	6	0	-3.178541	-5.188784	-3.359462
46	1	0	-3.146516	-4.308202	-4.021395
47	1	0	-2.343062	-5.854348	-3.630310
48	1	0	-4.121456	-5.718743	-3.519702
49	6	0	3.178351	5.190892	3.364094
50	1	0	2.342883	5.856663	3.634467
51	1	0	3.146235	4.310734	4.026585
52	1	0	4.121274	5.720913	3.524088
53	6	0	0.774958	6.982520	-1.151209
54	1	0	-0.165034	7.476945	-0.891202
55	1	0	1.614156	7.645875	-0.886427
56	1	0	0.799867	6.814058	-2.240456
57	-2	0	7.903621	-0.004089	0.023382
Lengths of translation vectors:			7.903657		

Table S4. Coordinates for optimized geometry of dimer of CPT at B3LYP/6-31G(d)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.507735	2.521936	-1.362952
2	6	0	-2.405896	1.529636	-1.104435
3	6	0	-1.827500	0.378763	-0.492122
4	6	0	-0.467017	0.473055	-0.287685
5	6	0	-3.884731	1.336698	-1.322125
6	1	0	-4.494067	2.207393	-1.064316
7	1	0	-4.089931	1.100005	-2.376504
8	6	0	-4.231994	0.115132	-0.409499
9	6	0	-2.884759	-0.664397	-0.225258
10	1	0	-2.819209	-1.496353	-0.940199
11	1	0	-2.815685	-1.116905	0.770412
12	16	0	0.092300	2.052800	-0.860696
13	16	0	-0.092299	-2.052802	0.860690
14	6	0	1.507733	-2.521933	1.362959
15	6	0	0.467017	-0.473054	0.287685
16	6	0	2.405895	-1.529634	1.104437
17	6	0	1.827500	-0.378763	0.492121
18	6	0	3.884731	-1.336696	1.322127
19	6	0	2.884759	0.664397	0.225256
20	6	0	4.231994	-0.115132	0.409500
21	1	0	4.089930	-1.100001	2.376507
22	1	0	4.494066	-2.207391	1.064320
23	1	0	2.815686	1.116903	-0.770416

24	1	0	2.819208	1.496355	0.940195
25	6	0	-5.318168	-0.753597	-1.045975
26	1	0	-6.246947	-0.172271	-1.155596
27	1	0	-4.996029	-1.070014	-2.053859
28	6	0	-4.691631	0.609793	0.971931
29	1	0	-4.921139	-0.256724	1.609728
30	1	0	-3.879428	1.182069	1.451913
31	6	0	5.318167	0.753599	1.045975
32	1	0	4.996028	1.070017	2.053857
33	1	0	6.246946	0.172274	1.155597
34	6	0	4.691632	-0.609795	-0.971929
35	1	0	3.879430	-1.182074	-1.451910
36	1	0	4.921138	0.256721	-1.609728
37	8	0	5.540815	1.890464	0.229593
38	8	0	5.841395	-1.426564	-0.822885
39	8	0	-5.841393	1.426564	0.822888
40	8	0	-5.540816	-1.890463	-0.229595
41	6	0	6.555050	2.733603	0.729451
42	1	0	7.522079	2.210140	0.800885
43	1	0	6.654009	3.570161	0.032381
44	1	0	6.302619	3.128715	1.727136
45	6	0	6.333949	-1.906717	-2.054620
46	1	0	5.587031	-2.524339	-2.579343
47	1	0	6.631723	-1.083619	-2.723807
48	1	0	7.211471	-2.521300	-1.835561
49	6	0	-6.333949	1.906711	2.054626
50	1	0	-6.631725	1.083609	2.723807
51	1	0	-5.587032	2.524329	2.579354
52	1	0	-7.211470	2.521296	1.835567
53	6	0	-6.555051	-2.733602	-0.729455
54	1	0	-6.654010	-3.570160	-0.032386
55	1	0	-7.522079	-2.210138	-0.800888
56	1	0	-6.302619	-3.128712	-1.727140
57	1	0	-1.663870	3.494419	-1.811048
58	1	0	1.663868	-3.494413	1.811059

Table S5. Coordinates for optimized geometry of dimer of CPS at B3LYP/6-31G(d)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.545019	2.784898	1.006110
2	6	0	2.393858	1.729530	0.878109
3	6	0	1.800298	0.506817	0.433923
4	6	0	0.442241	0.527046	0.213935
5	6	0	3.871449	1.544364	1.124043
6	1	0	4.492527	2.363874	0.751692
7	1	0	4.069907	1.454475	2.202265
8	6	0	4.207319	0.205141	0.392810
9	6	0	2.850164	-0.569625	0.299729
10	1	0	2.770210	-1.318529	1.100080
11	1	0	2.778203	-1.127855	-0.642156
12	34	0	-0.205431	2.287126	0.558208

13	34	0	0.205431	-2.287116	-0.558243
14	6	0	-1.545020	-2.784889	-1.006136
15	6	0	-0.442242	-0.527038	-0.213956
16	6	0	-2.393861	-1.729524	-0.878125
17	6	0	-1.800300	-0.506811	-0.433936
18	6	0	-3.871454	-1.544359	-1.124047
19	6	0	-2.850168	0.569627	-0.299729
20	6	0	-4.207321	-0.205144	-0.392799
21	1	0	-4.069920	-1.454460	-2.202265
22	1	0	-4.492527	-2.363874	-0.751697
23	1	0	-2.778199	1.127857	0.642155
24	1	0	-2.770226	1.318532	-1.100080
25	6	0	5.271310	-0.586910	1.154597
26	1	0	6.210772	-0.013632	1.192046
27	1	0	4.935686	-0.754859	2.193276
28	6	0	4.688480	0.498269	-1.037721
29	1	0	4.911247	-0.450648	-1.547768
30	1	0	3.889522	1.010163	-1.600968
31	6	0	-5.271324	0.586910	-1.154567
32	1	0	-4.935715	0.754867	-2.193250
33	1	0	-6.210786	0.013629	-1.192008
34	6	0	-4.688464	-0.498284	1.037735
35	1	0	-3.889499	-1.010182	1.600968
36	1	0	-4.911227	0.450627	1.547793
37	8	0	-5.476216	1.829583	-0.504779
38	8	0	-5.849040	-1.311644	0.989210
39	8	0	5.849057	1.311627	-0.989190
40	8	0	5.476207	-1.829589	0.504820
41	6	0	-6.471369	2.614536	-1.123861
42	1	0	-7.448874	2.105883	-1.126504
43	1	0	-6.554792	3.542648	-0.551889
44	1	0	-6.208011	2.860064	-2.165749
45	6	0	-6.363157	-1.606283	2.269602
46	1	0	-5.634009	-2.158239	2.884725
47	1	0	-6.650766	-0.692270	2.813467
48	1	0	-7.250521	-2.229198	2.127198
49	6	0	6.363185	1.606259	-2.269578
50	1	0	6.650796	0.692242	-2.813436
51	1	0	5.634044	2.158214	-2.884710
52	1	0	7.250550	2.229171	-2.127169
53	6	0	6.471346	-2.614541	1.123923
54	1	0	6.554773	-3.542658	0.551960
55	1	0	7.448854	-2.105893	1.126575
56	1	0	6.207972	-2.860060	2.165809
57	1	0	-1.772832	-3.794879	-1.320834
58	1	0	1.772831	3.794889	1.320805