Electronic Supplementary Information

From $C_{60}Ph_5Cl$ to $C_{60}Ph_6$: Fully phenylated C_{60} derivative rendering superior organic photovoltaic performance

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Contents

1) Separation and Characterization for $C_{60}Ph_6$.

Table S1 Reaction of $C_{60}Cl_6$ with benzene in selected solvent[a].

Entry	Solvent	**Result**
1	CH_2Cl_2	complicate
2	$CHCl_3$	complicate
3	DCE	complicate
4	TCE	complicate
5	*o*-DCB	mainly $C_{60}Ph_5Cl$
6	$PhNO_2$	$C_{60}Ph_5Cl$ + $C_{60}Ph_6$

[a]All reactions were carried out with 0.05 mmol $C_{60}Cl_6$, 0.2 ml dry benzene and 0.5mmol $FeCl_3$ in the selected solvent at 80 °C for 1h.

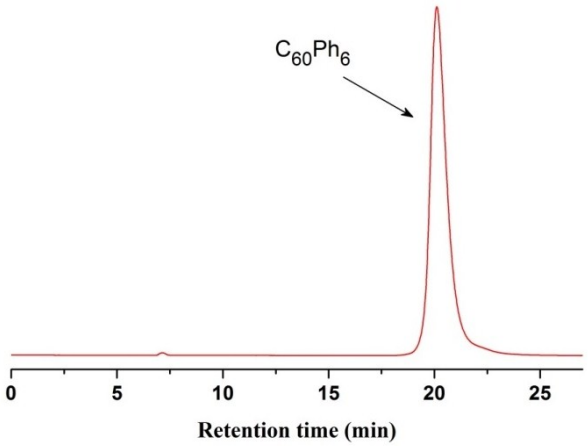

Figure S1. HPLC chromatogram of purified $C_{60}Ph_6$.

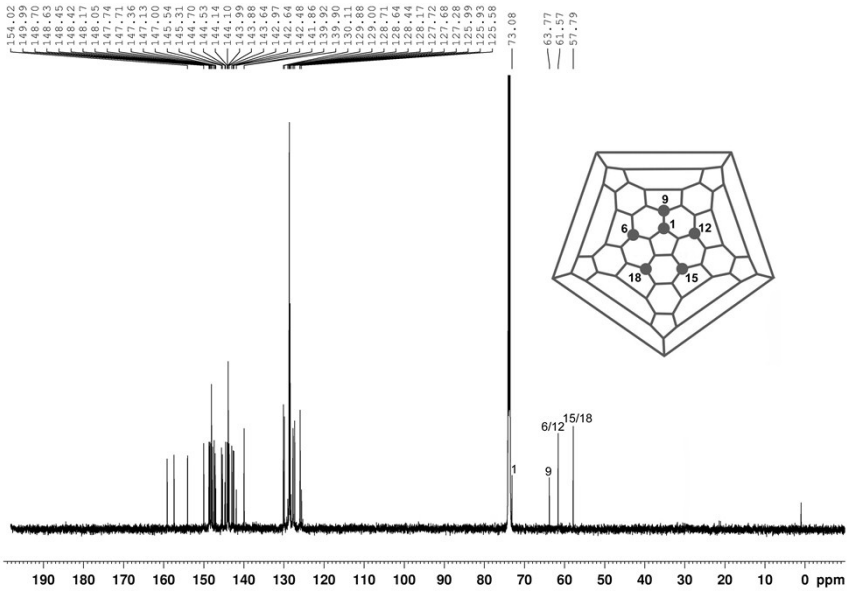

Figure S2. ^{13}C-NMR spectrum of $C_{60}Ph_6$.

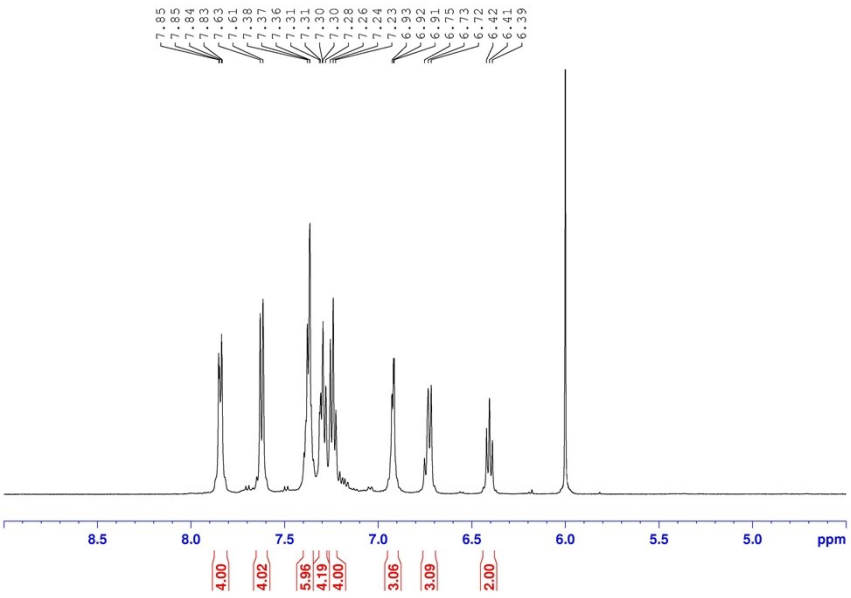

Figure S3. ^{1}H-NMR spectrum of $C_{60}Ph_6$.

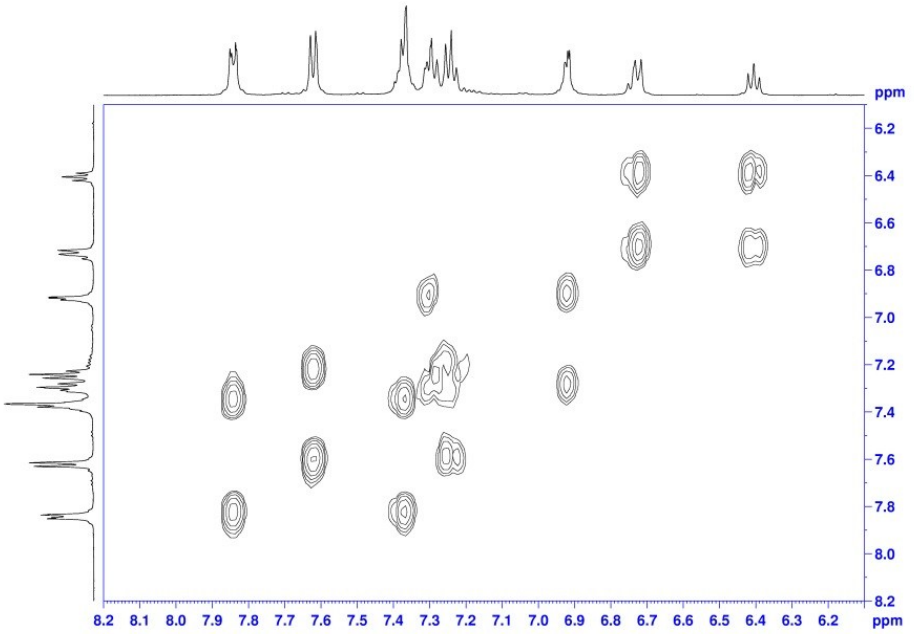

Figure S4. ^{1}H-^{1}H COSY spectrum of $C_{60}Ph_6$.

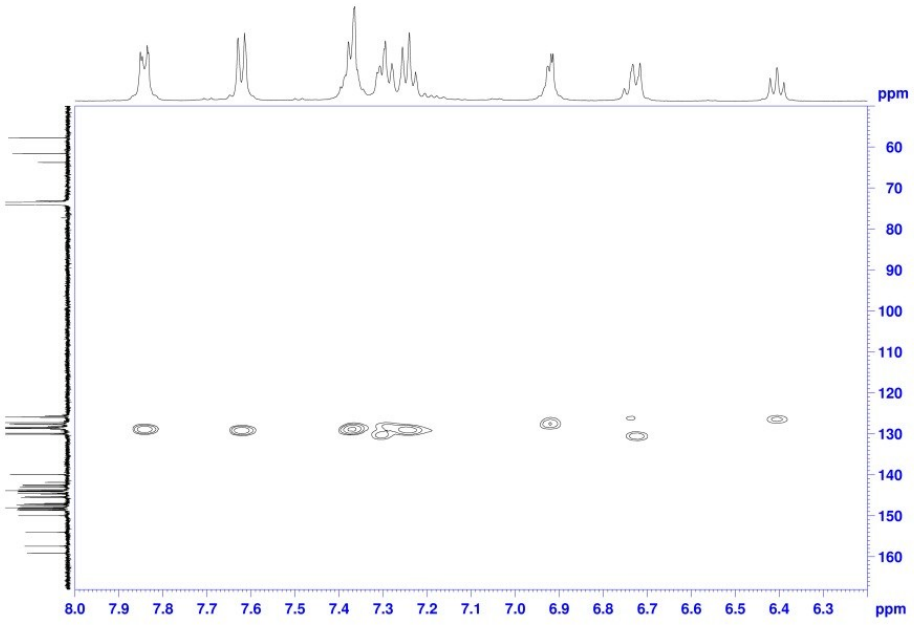

Figure S5. HSQC spectrum of $C_{60}Ph_6$.

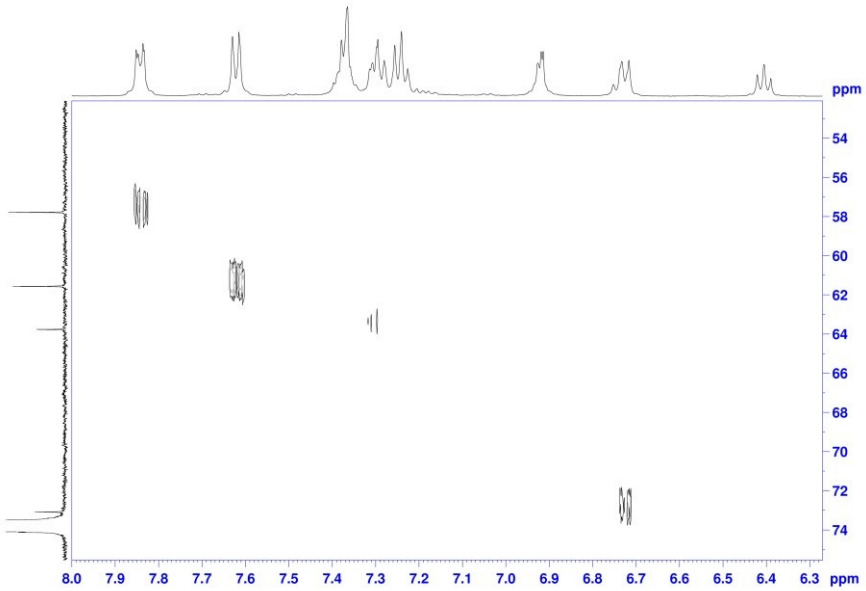

Figure S6. HMBC spectrum of $C_{60}Ph_6$.

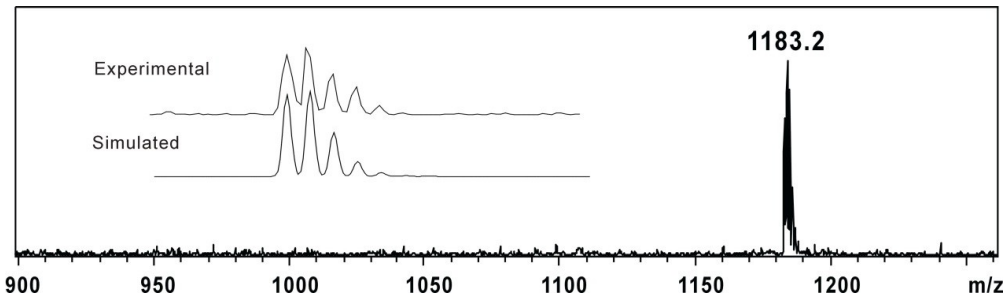

Figure S7. APCI-MS spectrum of purified $C_{60}Ph_6$.

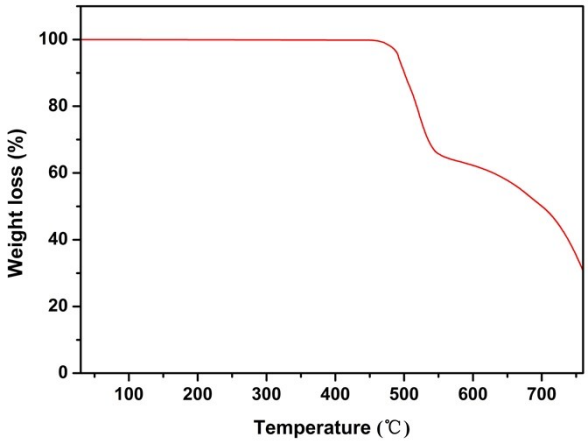

Figure S8. Thermogravimetric analysis (TGA) (10 ^{o}C/min) for $C_{60}Ph_6$.

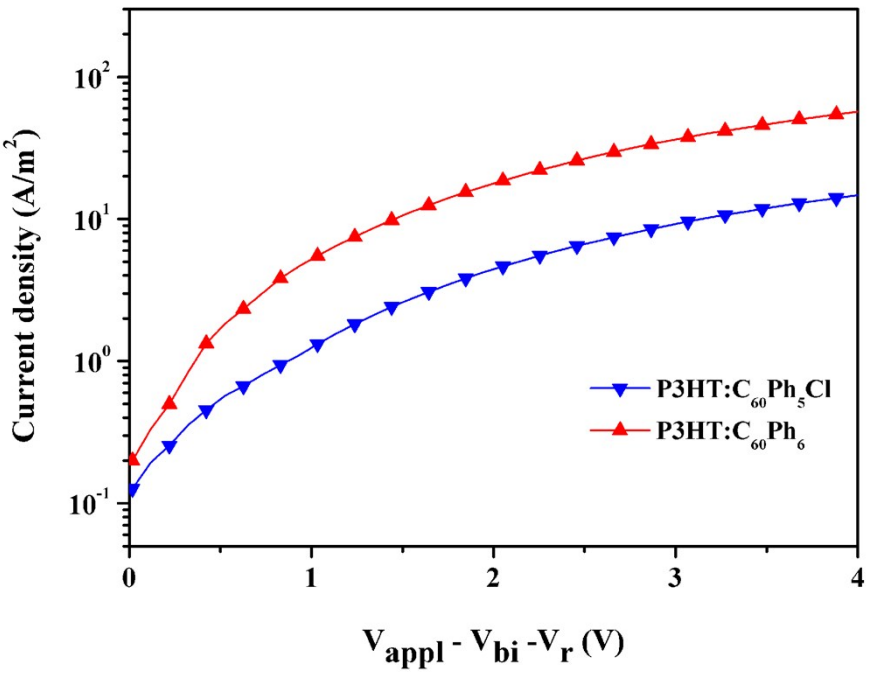

Figure S9. Measured space-charge limited *J–V* characteristics of the P3HT: $C_{60}Ph_6$ and P3HT: $C_{60}Ph_5Cl$ blend devices under dark conditions for electron-only devices.

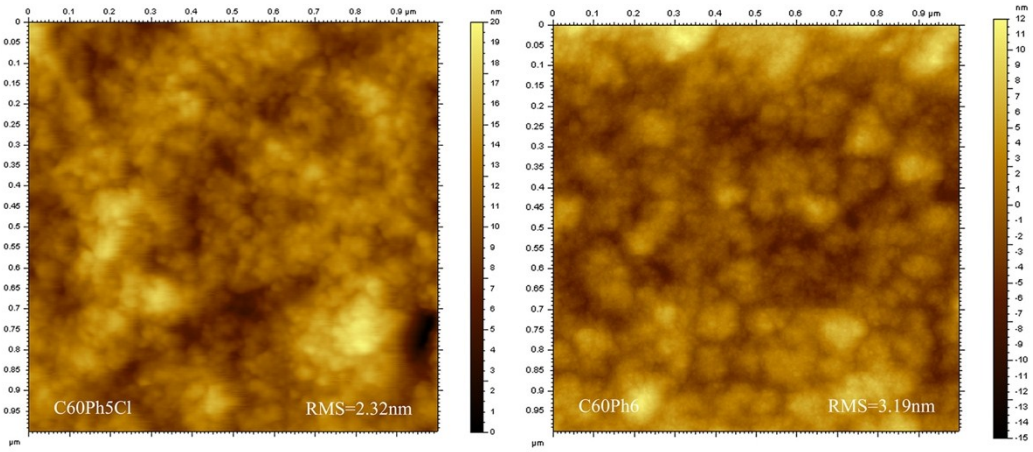

Figure S10. Tapping mode AFM phase images of P3HT/$C_{60}Ph_5Cl$ and P3HT/$C_{60}Ph_6$ films.

2) X-ray crystallographic data for $C_{60}Ph_6$.

Single crystals of $C_{60}Ph_6$ suitable for X-ray diffraction studies were obtained by solvent evaporation from its toluene solution. The diffraction data of compound $C_{60}Ph_6$ were collected on a Bruker Smart Apex-2000 CCD diffractometer using a graphite-monochromated Mo Kα (λ = 0.71073 A) radiation with a ω scan mode at 293 K. Data integration, scaling and empirical absorption correction were carried out using Oxford CrysAlisPro Gemini Ultra System program (Oxford Diffraction, 2009). The structure was solved by direct methods with SHELXS-97 program and refined using Full-matrix least-squares method with SHELXL-97 program based on F^2 [S1, S2]. CCDC 1009636 ($C_{60}Ph_6$) contains the supplementary crystallographic data for this paper. These data, summarized in Table S2, can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S2 Crystal data and structure refinement for $C_{60}Ph_6$.

Chemical formula	$C_{96}H_{30}$
Formula weight	1183.20
Temperature (K)	293
Radiation, wavelength	Mo Kα， 0.71073
Crystal color	red
Crystal size (mm)	0.20 × 0.13 × 0.12
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	22.965(4)
b (Å)	26.334(5)
c (Å)	19.819(4)
Alpha (deg)	90.00
Beta (deg)	110.524(4)
Gamma (deg)	90.00
Cell volume (Å^3)	11225(4)
Z	8
Data/parameters	18506/1730
F(000)	4848
Goodness-of-fit on F^2	1.014

θ range for data collection (deg)	3.02-25.00
Reflections with $I>2\sigma(I)$	9107
R indices (all data)	R_1=0.1839, ωR_2=0.2954
Final R indices[$I>2\sigma(I)$]	R_1=0.1030, ωR_2=0.2533

3) Computational Details.

All DFT (density functional theory) calculations were carried out using the Gaussian 09 program [S3]. All structures were optimized with no constraints of freedom by using the hybrid density functional B3LYP [S4, S5] in combination with double-ζ basis set plus polarization (DZP), i.e., the 6-31+G(d) basis set [S6] for C and Cl. Solvent effects were taken into account by the PCM method [S7] with $PhNO_2$ (ε = 34.8) as solvent.

Cartesian Coordinates, Total Electronic Energies (Etotal, in Hartree)

$[C_{60}Cl_5]^+$(A) E_{total} = -4586.82800

C	-0.58493900	-0.53846600	0.19869200
C	0.92436600	-0.43474700	-0.02890800
C	1.61976400	0.76825700	-0.03859100
C	0.97668400	2.13130000	0.21854700
C	-0.47992100	2.02359800	-0.09707900
C	-1.19425100	0.77383600	-0.13799100
C	-0.99883400	-1.54578400	-0.87619400
C	0.16898300	-2.17851700	-1.40365800
C	1.34672500	-1.49888900	-0.88410300
C	2.48929500	-1.37082700	-1.68668800
C	2.76884700	0.92822400	-0.88525600
C	1.64600400	2.99571500	-0.85820000
C	0.95676500	3.88997700	-1.64889000
C	-0.56099700	4.09932900	-1.54859300
C	-1.16009500	2.89977100	-0.90410100
C	-2.36980800	2.20178500	-1.43696300
C	-2.38254500	0.92432700	-0.93675400
C	-3.09649200	-0.22097100	-1.57807100
C	-2.11730100	-1.39016000	-1.68585700
C	0.18248400	-2.70226200	-2.70415200

C	-0.98528100	-2.55319000	C	1.36928200	4.09470800
	-3.53944800			-3.00887500	
C	-2.10396500	-1.88535700	C	2.50700800	3.46289000
	-3.03430300			-3.52549600	
C	-2.84086300	-0.95746800	C	3.68092300	1.43275800
	-3.87618300			-3.53441200	
C	-3.33398100	0.11965000	C	3.68224600	0.12901300
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	-2.66346700			-5.18018200	
C	-2.10405400	3.43570100	C	1.61144500	-1.39980300
	-3.51768500			-5.70114500	
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	-3.01921200			-6.53906300	
C	2.78118500	2.28896300	C	-0.51119600	-0.47129600
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	-5.68945900			-6.52496100	
C	2.49684800	2.94105900	C	-2.09477300	2.91518800
	-4.87880400			-4.84873300	
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	-5.69794100			-5.69630400	
C	1.61440500	0.79285100	C	-2.41810200	-0.72842600
	-6.53138100			-5.18769800	
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	-6.52589000			-5.70436600	
C	-0.97637200	3.08003700	C	-0.53973300	-2.30823900
	-5.67588300			-4.89968600	
C	0.19224200	3.75456500	C	0.91137000	-2.30482100
	-5.16027100			-4.89737400	
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C	2.48949900	-1.88883100	-3.03469000
C	3.23376900	2.53537700	-2.69471800
C	3.21885200	-0.12526100	-1.68561400
C	0.91714000	2.00402800	-6.53621600
Cl	-1.03537700	5.64752700	-0.69085200
Cl	-4.60734600	3.58622500	-2.26624700
Cl	-4.63868200	-0.70027600	-0.71293700
Cl	-1.05462500	-1.02390700	1.90297600
Cl	1.31576200	2.73571900	1.91442300

$[C_{60}Cl_5]^+$(B) E_{total} = -4586.85032

C	-0.56772800	-0.54111500	0.20035900
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C	0.96174200	2.08891600	0.24624600
C	-0.51393700	1.97853800	0.00016600
C	-1.16857800	0.80292400	-0.09401200
C	-0.98196900	-1.53002400	-0.88713100
C	0.18407200	-2.18405500	-1.41054700
C	1.36479100	-1.52192200	-0.88243300
C	2.50561500	-1.39306800	-1.67997500
C	2.77191800	0.89942700	-0.85928500
C	1.61059700	2.91706700	-0.86769600
C	0.90224600	3.81112000	-1.68031000
C	-0.52277600	3.78620100	-1.70973200
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C	0.19278400	3.78243700	C	0.92221900	-2.28518700
	-5.17130600			-4.89409800	
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C	3.66713600	1.43999200	C	3.22357600	-0.14308800
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C	3.66168600	0.13016300	C	0.91926600	2.02073100
	-3.03211000			-6.53855700	
C	3.22584600	-0.96267900	Cl	-2.00468100	4.30658300
	-3.87752400			0.46811400	
C	2.79605200	-0.70736700	Cl	-4.63160700	3.64416600
	-5.18548100			-2.41465000	

Cl	-4.59182200	-0.62844400	-0.66381200
Cl	-1.03091600	-1.11302300	1.87766600
Cl	1.38017300	2.82620200	1.87509400

$[C_{60}Cl_5]^+$(C) E_{total} = -4586.84693

C	-0.56866700	-0.53686900	0.19254900
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C	1.62926900	0.73814600	-0.00198600
C	0.95889200	2.10150700	0.23769300
C	-0.50578700	1.99473200	-0.05133400
C	-1.17255500	0.80377100	-0.11379000
C	-0.98224400	-1.53221900	-0.88998200
C	0.18352000	-2.18547700	-1.41226000
C	1.36252100	-1.51993700	-0.88432900
C	2.49934600	-1.39099400	-1.68543800
C	2.76134100	0.90778000	-0.87331000
C	1.59431100	2.94540700	-0.86446200
C	0.90079900	3.82729500	-1.65651000
C	-0.58909300	4.15125200	-1.55269000
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C	-2.42492400	2.27863800	-1.38653500
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C	0.18926000	-2.71075800	-2.70829500
C	-0.97878500	-2.55358500	-3.53986700
C	-2.09361200	-1.88470900	-3.03378000
C	-2.83916600	-0.96447800	-3.88073700
C	-3.31052300	0.11199400	-3.06856400
C	-3.29944600	1.40845200	-3.55471200
C	-2.82572500	2.50667300	-2.70675600
C	-2.11839500	3.45337500	-3.53517200
C	-0.98900300	4.09366300	-3.03278600
C	2.74642200	2.25859800	-1.39723600
C	1.34509000	3.09420000	-5.69056700
C	2.47788500	2.93752100	-4.87646800
C	3.21437300	1.69010500	-4.88791700

C	2.78198300	0.63646200	C	-2.41996800	0.62683300
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C	1.60675700	0.79646600	C	-2.41012300	-0.72381300
	-6.54569500			-5.19533100	
C	-0.54821700	2.00012700	C	-1.23635700	-1.40193900
	-6.55614200			-5.71179700	
C	-1.00035700	3.09052900	C	-0.53461000	-2.29851000
	-5.70660800			-4.90132900	
C	0.17596300	3.75286200	C	0.91550900	-2.30135400
	-5.17002400			-4.90373800	
C	0.16777200	4.23223700	C	1.36423200	-2.55757600
	-3.84897900			-3.54595100	
C	1.33808100	4.06442700	C	2.49505500	-1.90887000
	-3.00674100			-3.04495000	
C	2.47819000	3.44605400	C	3.20716100	2.51767400
	-3.51832400			-2.68906700	
C	3.66612500	1.42765600	C	3.21835500	-0.14059000
	-3.53214900			-1.68172000	
C	3.66741800	0.12438900	C	0.90349500	2.00284800
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C	3.21471800	-0.96966400	Cl	-0.79150400	5.89451600
	-3.88066600			-1.04230600	
C	2.78580300	-0.72021000	Cl	-2.21573700	3.89304600
	-5.19272700			0.78456900	
C	1.61439400	-1.39949300	Cl	-4.58163200	-0.53736300
	-5.71301000			-0.65336500	
C	0.88581400	-0.46327400	Cl	-1.04411400	-1.08826700
	-6.55127600			1.87322100	
C	-0.51289000	-0.46571300	Cl	1.26892700	2.76973300
	-6.55370600			1.91608400	
C	-1.24393600	0.78970500	$[C_{60}Cl_5]^+$(D)	E_{total} = -4586.84071	
	-6.55961700		C	-0.54863700	-0.52050700
C	-2.11862800	2.93406300		0.19582000	
	-4.89560500		C	0.96328900	-0.45278000
C	-2.84564100	1.67453400		0.00923300	
	-4.90074800				

C	1.64440500	0.74151400	C	-0.99396000	-2.56088700
	0.00802400			-3.54791800	
C	0.97655900	2.10995800	C	-2.11475000	-1.90613700
	0.25238600			-3.05157000	
C	-0.49357700	2.00498400	C	-2.85798800	-0.98258000
	-0.02181600			-3.89854400	
C	-1.13699200	0.82387600	C	-3.31278400	0.11924100
	-0.10323500			-3.07290800	
C	-0.95408400	-1.51482800	C	-3.32760600	1.41884800
	-0.89279600			-3.56204600	
C	0.19097100	-2.17997200	C	-3.09650400	2.65323900
	-1.39756800			-2.66587300	
C	1.37614800	-1.51853500	C	-2.11687500	3.44383600
	-0.86608800			-3.51558000	
C	2.50642300	-1.39097800	C	-1.00067900	4.06693300
	-1.67436200			-3.01257200	
C	2.77494700	0.90755300	C	2.75864000	2.25912500
	-0.86940800			-1.39381100	
C	1.60828800	2.94473900	C	1.34895700	3.08218300
	-0.85732600			-5.68608900	
C	0.90434400	3.81325400	C	2.48261700	2.93035700
	-1.65325100			-4.87998000	
C	-0.58640700	4.14704600	C	3.20683300	1.67702800
	-1.54018500			-4.88458600	
C	-1.37697900	3.11815700	C	2.77743900	0.61946500
	-0.62768700			-5.70206000	
C	-2.40909600	2.27382000	C	1.60563800	0.78093400
	-1.38930500			-6.54190400	
C	-2.32573100	0.97618100	C	-0.54655700	1.98880100
	-0.95912200			-6.53527500	
C	-2.78898100	-0.11346000	C	-0.99352600	3.08291000
	-1.74251800			-5.68579700	
C	-2.09248200	-1.36273300	C	0.17554800	3.74784000
	-1.70246200			-5.16169100	
C	0.18712700	-2.69621800	C	0.16503900	4.20239400
	-2.70814400			-3.84128900	

C	1.33717700	4.04653100 -3.00579300	C	-1.24683300	-1.42030100 -5.71733400
C	2.48158000	3.43723300 -3.51960100	C	-0.54637100	-2.31791700 -4.90795500
C	3.66796300	1.41922100 -3.53049700	C	0.90574300	-2.31362000 -4.90181400
C	3.67086100	0.11663500 -3.03491100	C	1.35297000	-2.55993100 -3.53865200
C	3.21719000	-0.97910800 -3.87610500	C	2.48671500	-1.90235900 -3.03623400
C	2.77985700	-0.73179300 -5.18408700	C	3.21343300	2.51224400 -2.68955400
C	1.60444700	-1.41362800 -5.70647300	C	3.22927300	-0.14383100 -1.67497200
C	0.87885400	-0.47710700 -6.54602500	C	0.90364700	1.99066000 -6.53662900
C	-0.51929700	-0.47872300 -6.54934400	Cl	-0.74393000	5.88713100 -1.00485500
C	-1.24684500	0.77962000 -6.54390800	Cl	-2.29898400	3.90260800 0.74049300
C	-2.10461600	2.92024400 -4.86406600	Cl	-4.67344800	3.54120200 -2.34329500
C	-2.85041800	1.67424400 -4.88556500	Cl	-1.07765900	-1.12752900 1.84369800
C	-2.41868800	0.61801100 -5.70609500	Cl	1.34237100	2.77444000 1.92153100
C	-2.42688600	-0.74353400 -5.20149000			

References:

[S1] G.M. Sheldrick, Phase annealing in SHELX-90: direct methods for larger structures, Acta Crystallogr. A., 46 (1990) 467-473.

[S2] G. Sheldrick, SHELXL-97 program for crystal structure solution and refinement; University of Göttingen: Göttingen, Germany, (1997).

[S3] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E.Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A.Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J.Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J.Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A.Montgomery, J.E.P. Jr., F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N.Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E.Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K.Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision B. 01, Gaussian, Inc., Wallingford, CT, (2009).

[S4] A.D. Becke, Density‐functional thermochemistry. III. The role of exact exchange, J. Chem. Phys., 98 (1993) 5648-5652.

[S5] P. Stephens, F. Devlin, C. Chabalowski, M.J. Frisch, Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields, J. Phys. Chem., 98 (1994) 11623-11627.

[S6] W. Hehre, R. Ditchfield, J. Pople, Ab initio calculation of organic compounds, J. Chem. Phys., 56 (1972) 2257-2261.

[S7] J. Tomasi, B. Mennuccia, R. Cammi, Quantum mechanical continuum solvation models, Chem. Rev., 105 (2005) 2999-3094.