Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2019

SUPPORTING INFORMATION FOR:

Hypsochromic solvent shift of the charge separation band in ionic donor-acceptor $Li^+@C_{60}\subset$[10]CPP

Anton J. Stasyuk,[a*] Olga A. Stasyuk,[a] Miquel Solà,[a*] and Alexander A. Voityuk [a,b*]

Abstract: Donor-acceptor dyads with C_{60} as electron acceptor and a cycloparaphenylene (CPP) unit assembled *via* non-covalent interactions as electron donor have been reported in the literature. In this work, we study computationally using the DFT/TDDFT approach the photoinduced electron transfer (PET) in CPP-based donor–acceptor supramolecule $C_{60}\subset$[10]CPP and $Li^+@C_{60}\subset$[10]CPP. As it is well known, the energy of charge separated (CS) states generated in donor-acceptor systems by PET is significantly stabilized by polar environment. Based on the analysis of initial and final states after PET in various fullerene complexes, we find a system, $Li^+@C_{60}\subset$[10]CPP, that shows anomalous solvent effects, *i.e.*, destabilization of charge separated states by polar medium. To our knowledge, this is the first example of fullerene based systems where a hypsochromic shift of the CS band is demonstrated. As the CS reaction in the $Li^+@C_{60}\subset$[10]CPP complex is found to occur in the inverted Marcus regime, in spite of that the CS reaction rate becomes faster with increasing solvent polarity of the environment.

DOI: 10.1039/x0xx00000x

Table of Contents

Theoretical calculation methodology

General.

Geometry optimizations were performed employing the DFT BLYP[1, 2] exchange−correlation functional with Ahlrichs' Def2-SVP basis set.[3, 4] and using the resolution of identity approximation (RI, alternatively termed density fitting)[5, 6] implemented in the TURBOMOLE 7.0 program.[7] Electronic structures calculations and vertical excitation energies were calculated using TDA formalism[8] with the range-separated functional from Handy and coworkers' CAM-B3LYP[9] using Gaussian 16 (rev. A03)[10] and Ahlrichs' Def2-SVP basis set.[3, 4] The empirical dispersion D3 correction with Becke–Johnson damping,[11, 12] was employed. To prevent the generation of the solvent accessible surface inside the fullerene molecule at the stage of geometry optimization using the Turbomol program, we applied a keyword *use_contcav* whereas ghost atoms Bq were introduced inside the fullerene cage when performing Gaussian calculations. To visualize molecular structures and frontier molecular orbitals, we used the program Chemcraft 1.8.[13]

Analysis of excited states.

The quantitative analysis of exciton delocalization and charge transfer in the donor-acceptor complexes was carried out using a tool suggested recently by Plasser et al.[14, 15] A key quantity is the parameter Ω:

$$\Omega(\mathrm{A},\mathrm{B}) = \frac{1}{2}\sum_{\alpha\in\mathrm{A},\,\beta\in\mathrm{B}}\left[\left(\mathrm{SP}^{0\mathrm{i}}\right)_{\alpha\beta}\left(\mathrm{P}^{0\mathrm{i}}\mathrm{S}\right)_{\alpha\beta} + \mathrm{P}^{0\mathrm{i}}_{\alpha\beta}\left(\mathrm{SP}^{0\mathrm{i}}\mathrm{S}\right)_{\alpha\beta}\right] \quad (1)$$

$$\mathrm{X}(\mathrm{F}_\mathrm{i}) = \sum_{\mathrm{A}\in\mathrm{F}_\mathrm{i}}\Omega(\mathrm{A},\mathrm{A}) \quad (2)$$

$$\Delta\mathrm{q}(\mathrm{CT}^{\mathrm{F}_\mathrm{i}\to\mathrm{F}_\mathrm{j}}) = \sum_{\mathrm{A}\in\mathrm{F}_\mathrm{i},\mathrm{B}\in\mathrm{F}_\mathrm{j}}\Omega(\mathrm{A},\mathrm{B}) + \Omega(\mathrm{B},\mathrm{A}) \quad (3)$$

$$\Delta\mathrm{q}(\mathrm{CS}^{\mathrm{F}_\mathrm{i}\to\mathrm{F}_\mathrm{j}}) = \sum_{\mathrm{A}\in\mathrm{F}_\mathrm{i},\mathrm{B}\in\mathrm{F}_\mathrm{j}}\Omega(\mathrm{A},\mathrm{B}) - \Omega(\mathrm{B},\mathrm{A}) \quad (4)$$

where A and B are atoms, F_i and F_j are fragments, α and β are atomic orbitals, $\mathbf{P}^{0i}$ is the transition density matrix for the $\psi_0 \rightarrow \psi_i$ excitation, and S is the overlap matrix. $X(F_i)$ is the extent of exciton localization on the fragment F_i. $\Delta q(CT^{F_i \to F_j})$ is the total amount of the electron density transferred between fragments F_i and F_j in the $\psi_0 \rightarrow \psi_i$ excitation. $\Delta q(CS^{F_i \to F_j})$) is a measure of the charge separation between fragments F_i and F_j. Note that in the situation when when charge transfer $(F_i \to F_j)$ is equal to the back transfer $(F_j \to F_i)$ there is no charge separation between the fragments, $\mathrm{CS}^{\mathrm{F}_\mathrm{i}\to\mathrm{F}_\mathrm{j}}$ is equal to zero.

Solvent Effects.

The equilibrium solvation energy E_S^{eq} in a medium with dielectric constant ε was estimated using a COSMO-like polarizable continuum model (CPCM) in the monopole approximation.[16]

$$E_S^{eq}(Q,\varepsilon) = -\frac{1}{2} f(\varepsilon) Q^{+} D Q \quad , \qquad (5)$$

where $f(\varepsilon)$ is the dielectric scaling factor, $f(\varepsilon)=(\varepsilon-1)/\varepsilon$, **Q** is the vector of *n* atomic charges in the molecular system, and **D** is the *n* x *n* symmetric matrix determined by the shape of the boundary surface between solute and solvent; $\mathbf{D=B^{+}A^{-1}B}$, where the *m* x *m* matrix **A** describes electrostatic interaction between *m* surface charges and the *m* x *n* **B** matrix describes the interaction of the surface charges with *n* atomic charges of the solute. Atomic charges in the excited state ψ_i, were calculated using Eqs. 1-4.

Electron transfer rates.

The rate of the nonadiabatic ET, k_{ET}, can be expressed in terms of the electronic coupling squared, V^2, and the Franck-Condon Weighted Density of states (FCWD):

$$k_{ET} = \frac{2\pi}{\hbar^2} V^2 \, (FCWD) \qquad (6)$$

that accounts for the overlap of vibrational states of donor and acceptor and can be approximately estimated using the classical Marcus equation:[17]

$$(FCWD) = (4\pi\lambda kT)^{-1/2} \exp\left[-(\Delta G^0 + \lambda)^2 / 4\lambda kT\right] \qquad (7)$$

where λ is the reorganization energy and ΔG^0 is the standard Gibbs energy change of the process. The fragment charge difference (FCD)[18, 19] method was employed to calculate the electronic couplings in this work.

Interaction energies and superadditivity.

Interaction energies were calculated directly from electronic energies of particular CNOs and the electronic energies of individual fragments from which this object consists. For $Li^{+}@C_{60}\subset$[10]CPP interaction energy can be expressed as follows:

$$E_{int} = E_{Li@C_{60}\subset[10]CPP} - \left(E_{Li} + E_{C_{60}} + E_{[10]CPP}\right) \qquad (8)$$

Conclusions about superadditive E_{SA} nature of the interactions between individual layers in $Li^{+}@C_{60}\subset$[10]CPP were made based on energy differences between sum of individual $Li^{+}@C_{60}$ and $C_{60}\subset$[10]CPP interactions and total interaction energy for the system

$$E_{SA} = E_{int}^{Li@C_{60}\subset[10]CPP} - \left(E_{int}^{Li@C_{60}} + E_{int}^{C_{60}\subset[10]CPP}\right) \qquad (9)$$

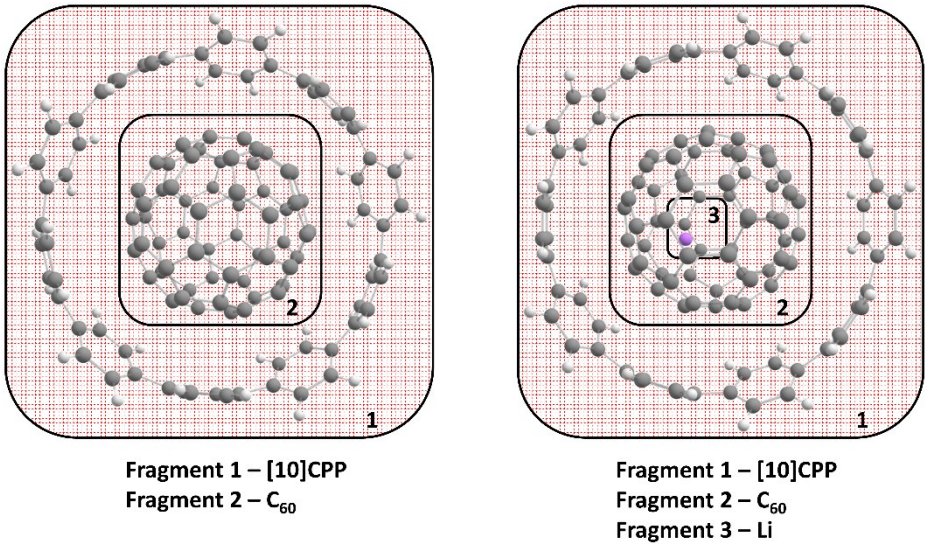

Figure S1. Fragmentation scheme for C_{60}⊂[10]CPP and Li^+@C_{60}⊂[10]CPP systems.

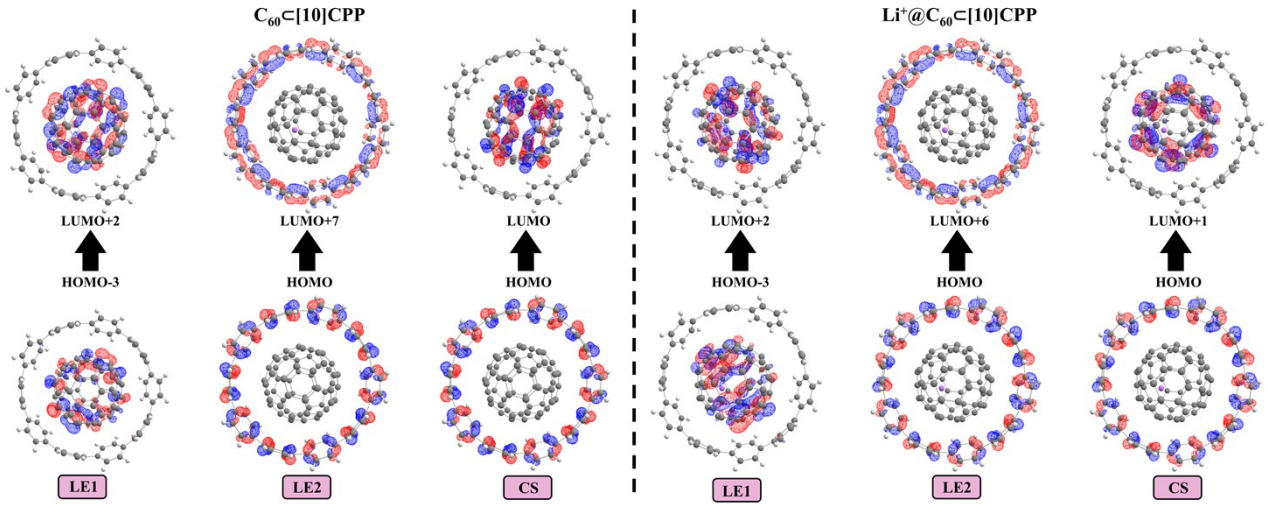

Figure S2. Frontier molecular orbitals representing lowest-lying singlet LE1 and LE2 and CS state correspondinf to [10]CPP → C60 transition in C_{60}⊂[10]CPP (left) and Li^+@C_{60}⊂[10]CPP (right) systems.

Table S1. Individual fragments, C_{60}⊂[10]CPP and Li^+@C_{60}⊂[10]CPP systems SCF energies, interaction energies (ΔE_{int}, kcal/mol) between fragments and superadditivity (ΔE_{SA}, kcal/mol) obtained at CAM-B3LYP-D3(BJ)/Def2-SVP level of theory.

Fragment/System	SCF Energy	ΔE_{int}[a]	ΔE_{SA}[b]
Li+	-7.26077	n/a	n/a
C60	-2283.46496		
[10]CPP	-2307.59850		
Li+@C60	-2290.77468	-30.71	
C_{60}⊂[10]CPP	-4591.14855	-53.78	
Li^+@C_{60}⊂[10]CPP	-4598.47529	-94.78	-10.68

[a] Calculates accordingly Eq.8 [b] Calculates accordingly Eq.9

Table S2. Root-mean-squared deviation (RMSD)[a] of atomic positions for Li^+@C_{60}⊂[10]CPP optimized at (COSMO)BLYP/Def2-SVP level of theory in the gas-phase (GAS) as well as in selected solvents: toluene (TOL), diisopropyl ether (DIPE), diethyl ether (DEE), fluorobenzene (FBNZ), tetrahydrofuran (THF), dichloromethane (DCM), and benzonitrile (BZN).

Li^+@C_{60}⊂[10]CPP								
RMSD	GAS	TOL	DIPE	DEE	FBNZ	THF	DCM	BZN
GAS	0	0.0003	0.0005	0.0006	0.0007	0.0007	0.0008	0.0008
TOL		0	0.0003	0.0004	0.0004	0.0005	0.0005	0.0007
DIPE			0	<0.0001	0.0001	0.0002	0.0002	0.0004
DEE				0	<0.0001	0.0001	0.0002	0.0003
FBNZ					0	<0.0001	0.0001	0.0002
THF						0	<0.0001	0.0002
DCM							0	0.0001
BZN								0

[a] RMSD was minimized for all atoms for geometries obtained with denoted level of theory using Chemcraft software v. 1.80

Table S3. Relative energies (Ex, eV) and solvation energies (Esolv, eV) for the ground state and lowest-lying singlet LE1, LE2 and CS states calculated for C_{60}⊂[10]CPP and Li^+@C_{60}⊂[10]CPP in toluene (TOL), diisopropyl ether (DIPE), diethyl ether (DEE), fluorobenzene (FBNZ), tetrahydrofuran (THF), dichloromethane (DCM), and benzonitrile (BZN).

	Supramolecule						
	C_{60}⊂[10]CPP						
	TOL	DIPE	DEE	FBNZ	THF	DCM	BZN
	Ground state (GS)						
E_{rel}^{solv}	0.00	0.00	0.00	0.00	0.00	0.00	0.00
E_{solv}	-0.45	-0.60	-0.68	-0.75	-0.83	-0.86	-0.99
	LE1 (Fullerene)						
E_x	2.49	2.49	2.49	2.49	2.49	2.49	2.49
E_{solv}	-0.45	-0.60	-0.68	-0.76	-0.83	-0.87	-0.99
	LE2 ([10]CPP)						
E_x	3.46	3.46	3.46	3.46	3.46	3.46	3.46
E_{solv}	-0.45	-0.59	-0.67	-0.75	-0.82	-0.86	-0.98
	CS ([10]CPP → Fullerene)						
E_x	2.63	2.60	2.59	2.57	2.56	2.56	2.54
E_{solv}	-0.58	-0.76	-0.85	-0.94	-1.03	-1.07	-1.21
	Li^+@C_{60}⊂[10]CPP						
	TOL	DIPE	DEE	FBNZ	THF	DCM	BZN
	Ground state (GS)						
E_x	0.00	0.00	0.00	0.00	0.00	0.00	0.00
E_{solv}	-1.00	-1.32	-1.49	-1.66	-1.83	-1.91	-2.19
	LE1 (Fullerene)						
E_x	2.50	2.51	2.51	2.52	2.52	2.52	2.53
E_{solv}	-0.97	-1.29	-1.46	-1.62	-1.78	-1.86	-2.13
	LE2 ([10]CPP)						
E_x	3.40	3.41	3.42	3.42	3.43	3.43	3.44
E_{solv}	-0.96	-1.28	-1.45	-1.60	-1.70	-1.84	-2.11
	CS ([10]CPP → Fullerene)						
E_x	1.87	1.93	1.97	2.00	2.04	2.06	2.13
E_{solv}	-0.816	-1.11	-1.25	-1.37	-1.50	-1.57	-1.78

Cartesian coordinates

C_{60}⊂[10]CPP

Gas-phase. BLYP-D3(BJ)/def2-SVP

Atom	X	Y	Z
6	4.808559694	-5.300201099	1.251449780
6	5.718952441	-4.238668212	1.294444889
6	5.940224541	-3.415832449	0.160797629
6	5.342122537	-3.818481873	-1.058227309
6	4.426387057	-4.874164336	-1.099110991
6	4.069489736	-5.583771162	0.074467630
1	4.626189382	-5.886220204	2.162655491
1	6.231451897	-4.009564108	2.238842491
1	5.483595495	-3.210338080	-1.960794632
1	3.879450436	-5.060104630	-2.031996483
6	6.533224199	-2.061039842	0.269723558
6	6.337479889	-1.307562884	1.453150245
6	7.076387965	-1.382353359	-0.850941848
6	6.514911375	0.078933299	1.463385959
1	5.904973872	-1.789480763	2.339256227
6	7.252791372	0.005716775	-0.840883224
1	7.317859906	-1.946813125	-1.762097431
6	6.893690085	0.779801773	0.291038233
1	6.221213921	0.640936032	2.358880331
1	7.626883228	0.506554490	-1.744556476
6	2.798511012	-6.347610533	0.101267792
6	2.212910108	-6.885758967	-1.073331294
6	1.991721377	-6.305686955	1.264908864
6	0.846462131	-7.182147536	-1.128662311
1	2.826849468	-7.019321981	-1.974631458
6	0.627871673	-6.610509637	1.212479550
1	2.401235092	-5.889413073	2.193877147
1	0.412004021	-7.538183396	-2.072926544
1	0.013169283	-6.424973683	2.102726099
6	6.627943128	2.236612918	0.205464185
6	6.093108074	2.771863830	-0.992152069
6	6.613249902	3.070982705	1.352244337
6	5.405283633	3.989567040	-0.995252498
1	6.082708490	2.159792426	-1.903074552
6	5.925495781	4.289738591	1.348914597
1	7.096837576	2.729200792	2.277780151
6	5.219703972	4.727667506	0.199091952
1	4.875186574	4.291817455	-1.907768750
1	5.880357765	4.883648252	2.272195444
6	4.103331329	5.701094355	0.280420158
6	3.306839055	5.733516862	1.452119689
6	3.618286685	6.397892091	-0.855109793
6	2.019519079	6.277456694	1.436385782
1	3.641781330	5.199108781	2.350440128
6	2.328349593	6.940815347	-0.871304553
1	4.240878737	6.464915049	-1.758194042
6	1.466248146	6.814072591	0.247293430
1	1.384145344	6.153272074	2.322364505
1	1.961459248	7.424597298	-1.787346528
6	-0.005868236	6.952895164	0.131516504
6	-0.641936407	6.594789345	-1.082125963
6	-0.838016257	7.176345752	1.258242446
6	-2.006914299	6.293768592	-1.120611023

Li^+@C_{60}⊂[10]CPP

Gas-phase. BLYP-D3(BJ)/def2-SVP

Atom	X	Y	Z
6	3.257130623	-6.454954878	1.360288741
6	4.430898973	-5.696828545	1.412720195
6	4.882156496	-4.971059697	0.280961264
6	4.208735960	-5.189849829	-0.946236617
6	3.037523474	-5.949664178	-0.999200637
6	2.485882749	-6.524335174	0.172773995
1	2.905509974	-6.966581711	2.266654111
1	4.979777043	-5.623693320	2.361570301
1	4.533123137	-4.653885614	-1.847648771
1	2.475562454	-5.990382831	-1.941077749
6	5.809417434	-3.822765216	0.400509367
6	5.813180022	-3.058369996	1.592111601
6	6.497326615	-3.286850759	-0.718192524
6	6.296799075	-1.747315111	1.605618453
1	5.307253309	-3.441619329	2.487416692
6	6.982970307	-1.975668678	-0.704180950
1	6.606992283	-3.890427558	-1.629316905
6	6.801100232	-1.141354027	0.428229512
1	6.161927206	-1.145429153	2.512624030
1	7.466443963	-1.574661871	-1.605047251
6	1.056286296	-6.910400960	0.182460194
6	0.374179800	-7.310420538	-0.994425686
6	0.270700554	-6.620505633	1.324941184
6	-1.019412782	-7.232664713	-1.079962871
1	0.950132982	-7.636368954	-1.871051498
6	-1.122854103	-6.546635807	1.241035597
1	0.759802976	-6.321574011	2.260768265
1	-1.514540084	-7.495990307	-2.024650284
1	-1.686634598	-6.190524817	2.112954170
6	6.858052289	0.335510012	0.337065924
6	6.550381344	0.970604593	-0.892951153
6	6.956277766	1.158270805	1.487186221
6	6.192914734	2.320859448	-0.940478331
1	6.471394429	0.371894944	-1.808922592
6	6.595430392	2.507710492	1.440315842
1	7.273082309	0.722652528	2.444412496
6	6.121929655	3.098647741	0.240269314
1	5.841697917	2.740451675	-1.892090103
1	6.637345752	3.104557837	2.360993602
6	5.342504198	4.358049028	0.241582721
6	4.570511607	4.693256320	1.380188881
6	5.128065596	5.115943894	-0.937796779
6	3.512438683	5.600746011	1.291607932
1	4.714251451	4.142026274	2.318010321
6	4.068609959	6.024747852	-1.027138158
1	5.768099219	4.950394707	-1.814686750
6	3.178591010	6.216204673	0.059314958
1	2.858017018	5.734545410	2.161882151
1	3.895733138	6.555901156	-1.973186310
6	1.816538460	6.768910111	-0.119476211
6	1.145313471	6.558714312	-1.348758341
6	1.047062557	7.246506871	0.971765463
6	-0.248096244	6.637007199	-1.430241732

1	-0.037168851	6.407277477	-1.978536935	1	1.705708580	6.197677764	-2.220709425
6	-2.205171146	6.881526330	1.217653262	6	-0.346418941	7.326394572	0.889347582
1	-0.394506422	7.536829817	2.196722260	1	1.544491625	7.506029431	1.916398515
6	-2.803177697	6.342091681	0.049795605	6	-1.031587667	6.932501432	-0.288024629
1	-2.426897146	5.876509818	-2.044639959	1	-0.739896991	6.335241060	-2.363890698
1	-2.810117622	7.019282858	2.124364820	1	-0.919024889	7.650412778	1.768814629
6	-4.077930513	5.585378098	0.088485643	6	-2.464024037	6.555481427	-0.277872788
6	-4.426255528	4.873770290	1.263331911	6	-3.021062981	5.989557920	0.895606834
6	-4.829246053	5.308935417	-1.082467133	6	-3.235177191	6.485538613	-1.465712908
6	-5.342713304	3.818356255	1.226295946	6	-4.191618775	5.228272547	0.842477078
1	-3.870293070	5.054800977	2.191880430	1	-2.463684158	6.035396743	1.839654059
6	-5.742845775	4.250283610	-1.120696452	6	-4.407795999	5.724875877	-1.518740128
1	-4.651825089	5.896942624	-1.993342366	1	-2.882311169	6.995195270	-2.372469853
6	-5.951924285	3.421610825	0.010970194	6	-4.858593246	5.000287633	-0.386180430
1	-5.472716152	3.202604520	2.125504343	1	-4.517660510	4.695886381	1.745302555
1	-6.265185102	4.026500741	-2.061052310	1	-4.955231165	5.650339430	-2.468239952
6	-6.539720557	2.065274479	-0.102056717	6	-5.774532216	3.842844559	-0.505757506
6	-6.345149677	1.321476626	-1.292014533	6	-5.766153035	3.074364552	-1.694789367
6	-7.075493513	1.376026758	1.015416139	6	-6.464063484	3.305972349	0.611529067
6	-6.515617274	-0.065140915	-1.311687834	6	-6.246846631	1.761896664	-1.708002689
1	-5.922702144	1.812542637	-2.177900199	1	-5.254022281	3.456145540	-2.587188402
6	-7.248601066	-0.012295193	0.994593227	6	-6.945443794	1.993081664	0.598317656
1	-7.314125562	1.932756030	1.932165550	1	-6.577424805	3.910220683	1.521444060
6	-6.889657680	-0.776328781	-0.144244287	6	-6.760629501	1.158911134	-0.533147232
1	-6.223007468	-0.619355216	-2.212349205	1	-6.103069788	1.156880963	-2.611635723
1	-7.619415835	-0.520662102	1.895346724	1	-7.431273581	1.592762089	1.498136685
6	-6.622191093	-2.233238547	-0.073979014	6	-6.824811311	-0.317296497	-0.442682303
6	-6.095626187	-2.783562025	1.120157046	6	-6.525808414	-0.956569602	0.787549903
6	-6.597841234	-3.051477228	-1.232402336	6	-6.926541990	-1.138627006	-1.594043062
6	-5.406350414	-4.000512323	1.111708100	6	-6.172145110	-2.307747016	0.833345998
1	-6.091919461	-2.183449844	2.038999120	1	-6.452083132	-0.360466309	1.705794813
6	-5.908273988	-4.268798600	-1.240818753	6	-6.568736680	-2.488419639	-1.549039580
1	-7.073111030	-2.696935464	-2.157278404	1	-7.245392070	-0.700826547	-2.549527241
6	-5.212138140	-4.721861197	-0.091512399	6	-6.096094372	-3.081622812	-0.349777112
1	-4.880969941	-4.314263025	2.022968280	1	-5.827098184	-2.731253984	1.785494914
1	-5.852703185	-4.848784994	-2.172462391	1	-6.614376671	-3.085181739	-2.469860531
6	-4.097056138	-5.695427432	-0.177638130	6	-5.312654239	-4.338071412	-0.353086763
6	-3.288403366	-5.708659605	-1.341578908	6	-4.534863024	-4.665465681	-1.490222014
6	-3.627866676	-6.415802719	0.949201976	6	-5.101262453	-5.099070290	0.824212281
6	-2.004388688	-6.259610822	-1.322884215	6	-3.476966101	-5.573815927	-1.401682722
1	-3.612692510	-5.156097125	-2.232733547	1	-4.675518500	-4.108852688	-2.425102055
6	-2.340536840	-6.964133744	0.969139337	6	-4.042238826	-6.008533283	0.913519200
1	-4.260794234	-6.497670672	1.843992051	1	-5.744602973	-4.938008175	1.699412373
6	-1.466311059	-6.820191313	-0.138000656	6	-3.149903370	-6.196752212	-0.171531399
1	-1.360056902	-6.124141035	-2.201042358	1	-2.819185160	-5.704224158	-2.270088304
1	-1.984423340	-7.465933400	1.879528397	1	-3.871902620	-6.543422211	1.857502735
6	0.004010903	-6.963849753	-0.008502173	6	-1.790755374	-6.754755748	0.009902824
6	0.642865294	-3.151772634	1.680343659	6	1.400289546	-2.753203558	1.782659860
6	-0.812547747	-3.073683156	1.768796216	6	0.007713960	-3.169075460	1.632211547
6	1.447007399	-2.296400452	2.456233917	6	1.718806385	-1.668684785	2.621285782
6	-1.413941643	-2.134426311	2.628681912	6	-1.012689917	-2.495226444	2.331980003
6	-2.583542743	-1.379837898	2.183913285	6	-2.278821574	-2.187050190	1.666417095
6	-1.357057890	-3.292991744	0.431463770	6	-0.199442251	-3.560668694	0.240604314
6	-2.482540510	-2.566306740	0.003836204	6	-1.424113048	-3.273569367	-0.400614303
6	-3.104005325	-1.589837881	0.894064066	6	-2.485983665	-2.572485804	0.325435835
6	2.973954930	-1.937983630	0.532616940	6	3.336688947	-0.805682451	0.950736254
6	2.139504968	-2.826863247	-0.270085206	6	2.999714803	-1.926545380	0.077528953
6	2.635725861	-1.677828225	1.871689017	6	2.707401324	-0.679407715	2.201310237
6	0.997168944	-3.421712858	0.291103800	6	2.053174132	-2.883034816	0.484445995

6	-0.237954811	-3.511909020	-0.479896136	6	1.066515577	-3.384626282	-0.467589635
6	2.090878025	-2.294816721	-1.627611764	6	3.003973523	-1.438887791	-1.297371938
6	0.899820943	-2.378788740	-2.373549141	6	2.055603974	-1.923431768	-2.217803138
6	-0.286847327	-3.000458323	-1.789579118	6	1.067316942	-2.912265800	-1.793626362
6	3.190857444	0.726516029	1.572238221	6	2.464103841	1.769838238	1.861738172
6	3.543019153	0.453294314	0.182668909	6	3.118998738	1.638648276	0.564418637
6	2.744235703	-0.320228646	2.400734357	6	2.262710455	0.631172746	2.664886588
6	3.438299647	-0.853947467	-0.326530041	6	3.546504089	0.374583513	0.119225063
6	2.894822555	-1.075856632	-1.662947999	6	3.338778101	-0.016506938	-1.270493780
6	3.107088596	1.589241786	-0.622051669	6	2.467124193	2.561194294	-0.361523865
6	2.584513795	1.378038323	-1.910825006	6	2.269645725	2.186253648	-1.701189167
6	2.474099757	0.020836147	-2.439619232	6	2.711993534	0.871894602	-2.162819153
6	0.992781506	1.156474068	3.363111201	6	-0.019121572	1.416883971	3.251146390
6	1.458711381	2.244137281	2.505518070	6	0.189093563	2.599026864	2.420576533
6	1.623269978	-0.101006466	3.311398714	6	0.998088232	0.451909366	3.371309064
6	2.538232729	2.032892368	1.625874056	6	1.407292372	2.770473845	1.736688137
6	2.485226724	2.565775097	0.267664699	6	1.409094171	3.261140251	0.362398240
6	0.289277398	2.998584225	2.060778843	6	-1.073406900	2.909728363	1.756142232
6	0.240196633	3.510035374	0.751140556	6	-1.071845357	3.380040074	0.431224797
6	1.358742163	3.290878210	-0.160502942	6	0.191948574	3.558811359	-0.276496137
6	-0.581103466	-1.242507028	3.431289245	6	-0.678863096	-1.373401310	3.205597504
6	-1.235508848	0.062111455	3.483383372	6	-1.733494866	-0.372511311	3.081293878
6	0.822620150	-1.322060713	3.345922269	6	0.661741502	-0.968029133	3.344877535
6	-0.462777962	1.239441152	3.449351321	6	-1.408736716	0.996737627	3.101157171
6	-0.897809610	2.376791103	2.643994783	6	-2.061568130	1.919891162	2.176314849
6	-2.473295398	-0.022453616	2.712726170	6	-2.723022294	-0.872318007	2.130108428
6	-2.893447400	1.073789467	1.934641473	6	-3.348505043	0.017291447	1.235678532
6	-2.089327648	2.292450264	1.898891175	6	-3.017861437	1.440728429	1.261543844
6	-0.642239753	3.150892390	-1.408677735	6	-1.406140292	2.746944108	-1.817614775
6	-0.995599540	3.420376687	-0.019085132	6	-2.058908776	2.875919960	-0.518707749
6	-2.137703071	2.824842314	0.541566222	6	-3.013861328	1.927816188	-0.112899861
6	-1.445886401	2.296145370	-2.185918008	6	-1.730132865	1.670007506	-2.663890946
6	0.582426965	1.240700351	-3.158681667	6	0.667219674	1.371402301	-3.236255540
6	1.414843669	2.132159859	-2.355451977	6	1.003984907	2.493343476	-2.364920259
6	0.813198504	3.072126171	-1.496911494	6	-0.014975779	3.166690788	-1.666456713
6	-0.821275161	1.320682683	-3.074834821	6	-0.673353838	0.969571186	-3.386875872
6	-0.991936057	-1.158296595	-3.092133497	6	0.011519739	-1.418048626	-3.291195159
6	0.463751113	-1.240786987	-3.177875981	6	1.402628043	-1.000788330	-3.142338610
6	1.236494697	-0.063609182	-3.210428658	6	1.722171468	0.369625560	-3.111606224
6	-1.622465351	0.099666855	-3.040873105	6	-1.006728302	-0.451785354	-3.411152817
6	-3.188238824	-0.727124742	-1.300575812	6	-2.480176756	-1.776597867	-1.903121175
6	-2.535550490	-2.033370444	-1.353913869	6	-1.421309807	-2.779934067	-1.777991320
6	-1.456566716	-2.245875806	-2.233761028	6	-0.196591906	-2.599355228	-2.457213172
6	-2.742884245	0.319574014	-2.129803419	6	-2.271039615	-0.630560143	-2.701896465
6	-2.972139171	1.936662763	-0.261776853	6	-3.347838850	0.807506989	-0.987835576
6	-3.437257446	0.852815344	0.597550037	6	-3.554692916	-0.373829360	-0.155492504
6	-3.541129196	-0.454405007	0.088741321	6	-3.137187925	-1.645503987	-0.603225804
6	-2.634500261	1.677448643	-1.601151066	6	-2.717501294	0.680538932	-2.239435935
				3	-0.843143185	-0.981124415	-0.245444125

References

1 A. D. Becke, Phys. Rev. A 1988, **38**, 3098-3100.
2 C. Lee, W. Yang and R. G. Parr, Phys. Rev. B 1988, **37**, 785-789.
3 F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, **7**, 3297-3305.
4 F. Weigend, Phys. Chem. Chem. Phys. 2006, **8**, 1057-1065.
5 K. Eichkorn, O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, Chem. Phys. Lett. 1995, **240**, 283-290.
6 K. Eichkorn, F. Weigend, O. Treutler and R. Ahlrichs, Theor. Chem. Acc. 1997, **97**, 119-124.
7 TURBOMOLE 7.0 2015, a development of the University of Karlsruhe and Forschungszentrum Karlsruhe GmbH 1989–2007, TURBOMOLE GmbH since 2007; available from http://www.turbomole.com.
8 S. Hirata and M. Head-Gordon, Chem. Phys. Lett. 1999, **314**, 291-299.
9 T. Yanai, D. P. Tew and N. C. Handy, Chem. Phys. Lett. 2004, **393**, 51-57.
10 Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
11 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys. 2010, **132**, 154104.
12 S. Grimme, S. Ehrlich and L. Goerigk, J. Comput. Chem. 2011, **32**, 1456-1465.
13 G. A. Zhurko, Chemcraft 1.80 (build 523b) - graphical program for visualization of quantum chemistry computations. (https://chemcraftprog.com).
14 F. Plasser and H. Lischka, J. Chem. Theory Comput. 2012, **8**, 2777-2789.
15 F. Plasser, S. A. Bäppler, M. Wormit and A. Dreuw, J. Chem. Phys. 2014, **141**, 024107.
16 J. Tomasi, B. Mennucci and R. Cammi, Chem. Rev. 2005, **105**, 2999-3093.
17 R. A. Marcus and N. Sutin, Biochim. Biophys. Acta, Rev. Bioenerg. 1985, **811**, 265-322.
18 A. A. Voityuk and N. Rösch, J. Chem. Phys. 2002, **117**, 5607-5616.
19 A. A. Voityuk, Phys. Chem. Chem. Phys. 2012, **14**, 13789-13793.