SUPPORTING INFORMATION

Cyclohepta[def]fluorene as a Bistable Molecule: First Principles Studies on its Electronic Structure and the Effects of Benzo-Extension, Substitution and Solvation

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Authors: Robert Toews, Andreas Koehn

Institution: Institute for Theoretical Chemistry, University of Stuttgart

Contact: toews@theochem.uni-stuttgart.de,

koehn@theochem.uni-stuttgart.de

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S1 Active Orbitals of Cyclohepta[def]fluorene and Benzo-Extended Systems

All active orbitals were generated by a CAS(10,10)-CASSCF/def2-TZVPP calculation averaging over 2 singlet states and one triplet state. The active orbitals are ordered according to increasing energy and for each orbital the respective orbital index is shown.

S1.1 Active Orbitals of Cyclohepta[def]fluorene 1

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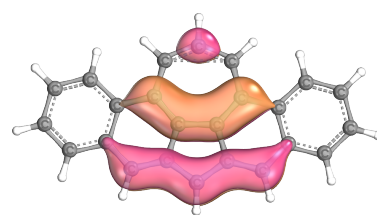
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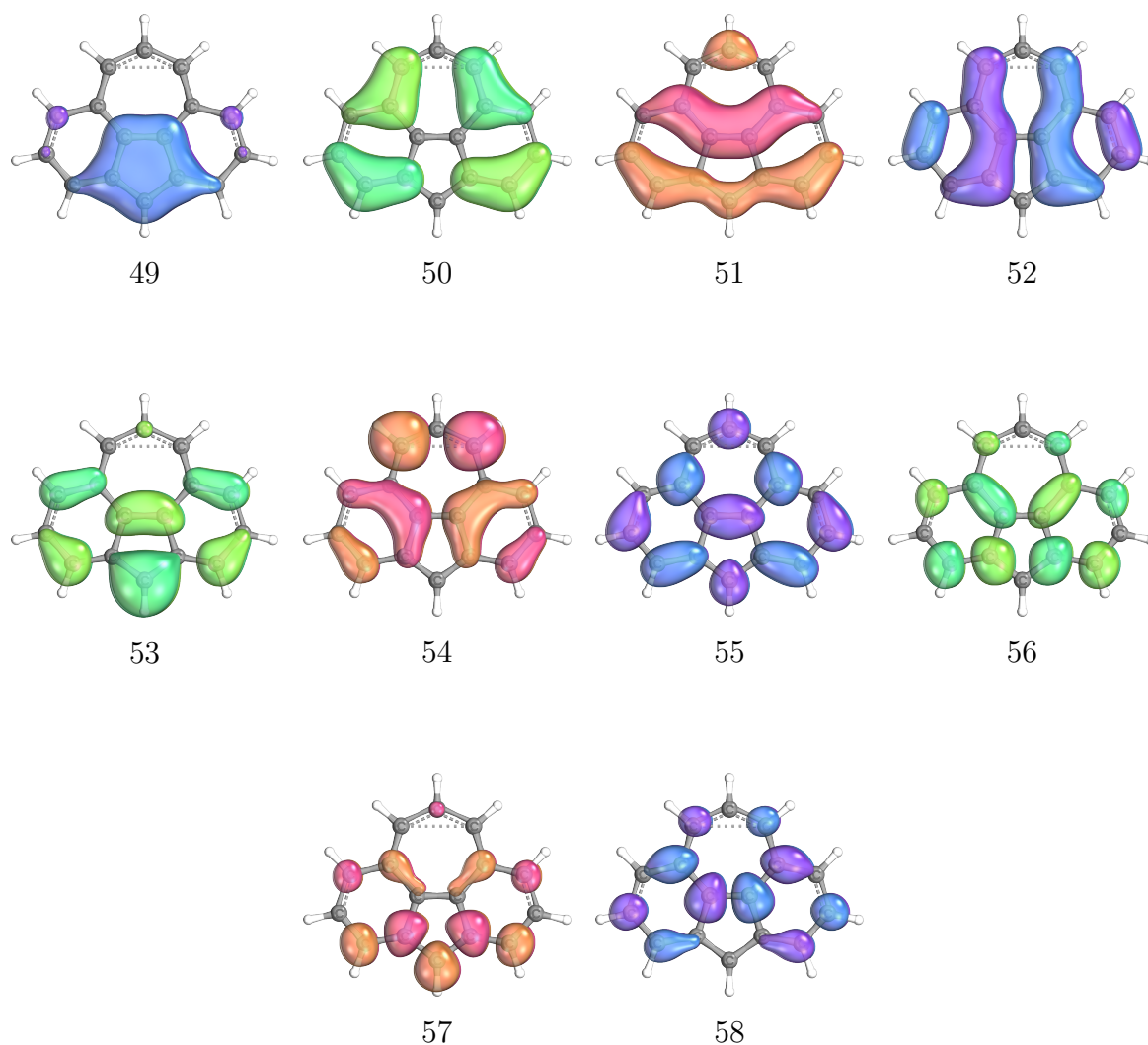
S1.2 Active Orbitals of Derivative 2

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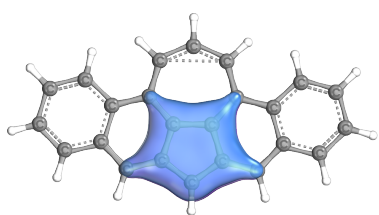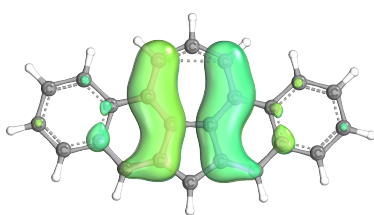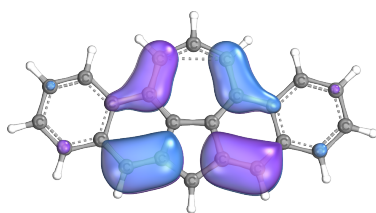
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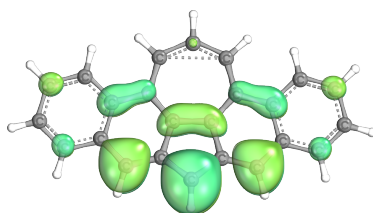
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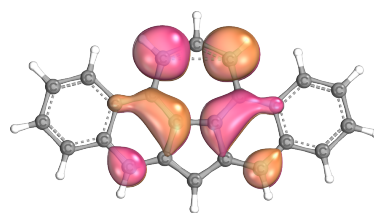
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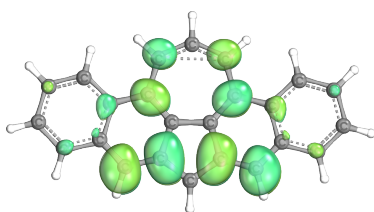
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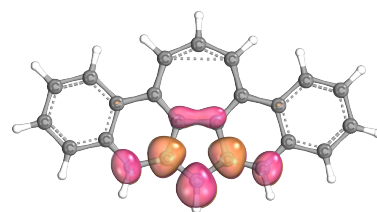
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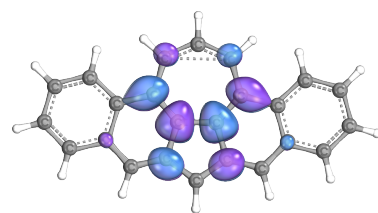
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S1.3 Active Orbitals of Derivative 3

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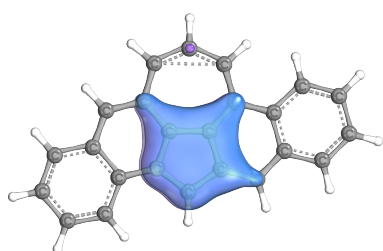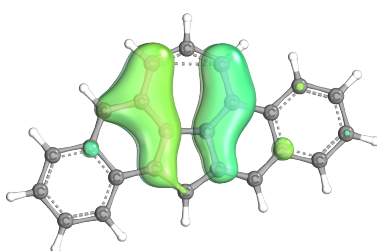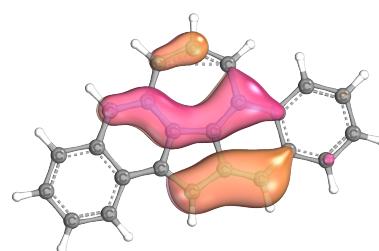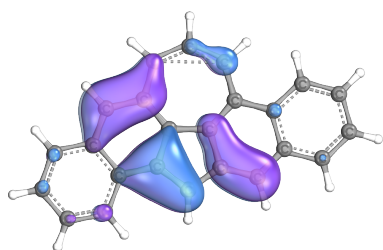
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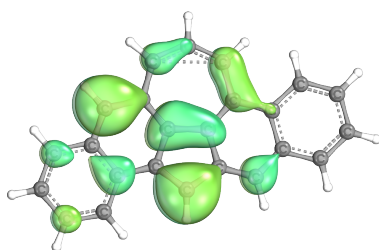
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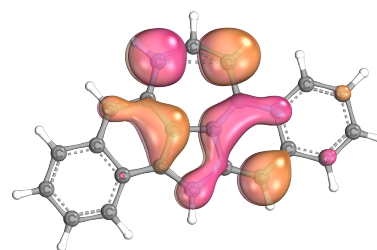
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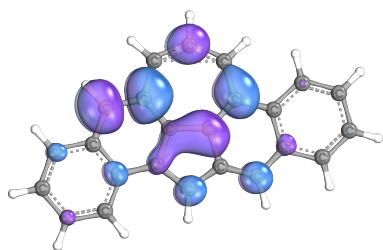
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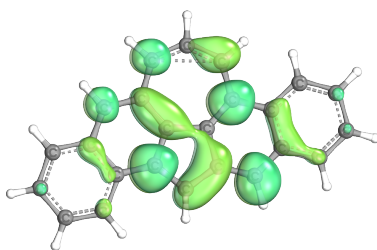
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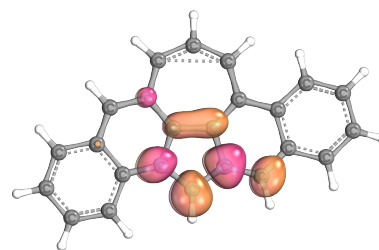
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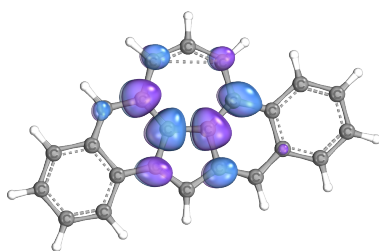
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S1.4 Active Orbitals of Derivative 4

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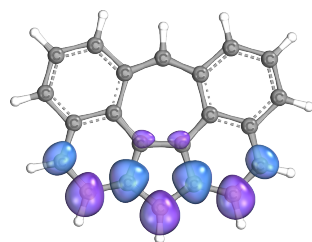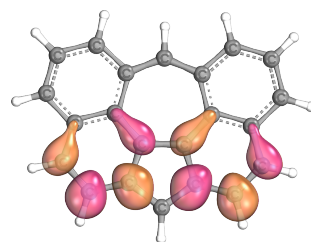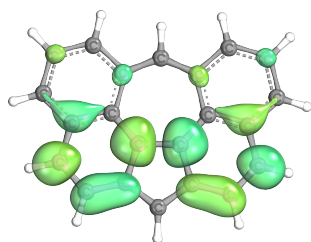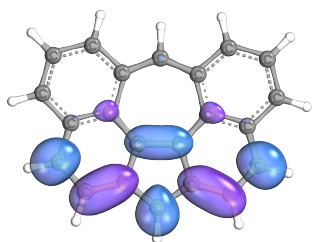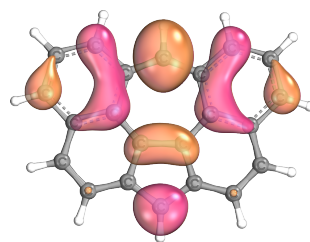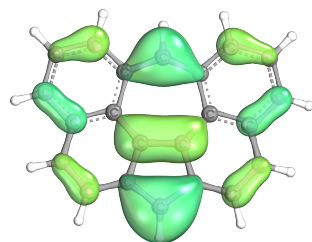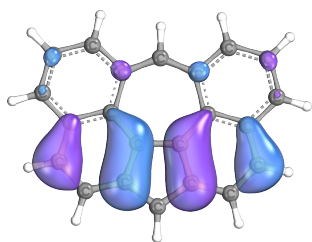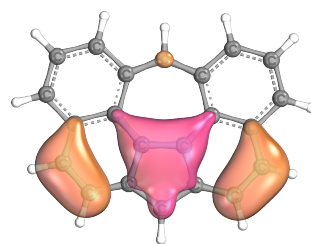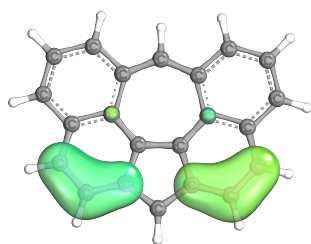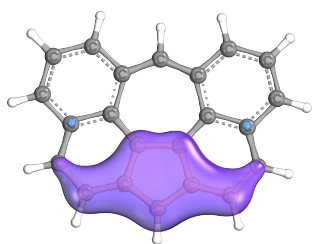
S2 Configuration Analysis of Cyclohepta[def]fluorene and Benzo-Extended Systems

All CASSCF wave functions were obtained with a CAS(10,10), a def2-TZVPP basis set and by averaging over two singlet states and one triplet state. The order of the occupations corresponds to the order of the orbitals from section **S1**.

S2.1 Configuration Analysis of Cyclohepta[def]fluorene 1

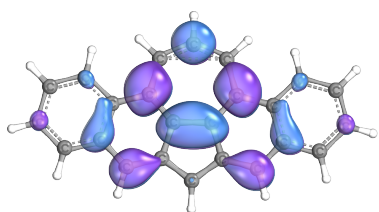For T_0 in the triplet geometry, the Slater determinant $|2222aa0000\rangle$ has a CI coefficient of $C_0 = 0.902$ and we can thus represent this state by a single Slater determinant. The unpaired electrons in T_0 occupy orbitals 53 and 54, *cf.* subsection **S1.1**. If we superimpose both orbitals, we get an idea of the spin distribution in T_0, which basically resembles the Clar structure of **1**.

The CI coefficients for the singlet states S_0, S_1 and S_2 are shown in Table S1. These coefficients refer to geometries where the respective singlet state has a lower energy. This means that the coefficients for S_0 belong to the singlet geometry and the coefficients for S_1 ad S_2 belong to the triplet geometry. S_0 is closed-shell and can be represented by a single Slater determinant.

Table S1: CI coefficients for selected configurations of **1** contained in the CASSCF wave functions of the singlet states S_0, S_1 and S_2. The coefficients refer either to the singlet geometry (s) or the triplet geometry (t).

		$S_0^{(s)}$	$S_1^{(t)}$	$S_2^{(t)}$
A	2222200000	0.852	0.000	-0.021
B	2222ab0000	0.005	0.630	0.000
C	2222ba0000	-0.005	-0.630	0.000
D	2222020000	-0.067	0.000	0.439
E	222a2b0000	-0.126	0.000	-0.266
F	222b2a0000	0.126	0.000	0.266
G	2222b0a000	-0.128	0.000	0.244
H	2222a0b000	0.128	0.000	-0.244

S_1 is an open-shell singlet state with two leading Slater determinants. These determinants differ only in the spins of the unpaired electrons. The unpaired electrons in S_1 occupy the orbitals 53 and 54, which are the same as for T_0. The spin distribution of S_1 is therefore similar to T_0 with both unpaired electrons having opposite spins. Looking

at the coefficients for S_2, there are several Slater determinants that contribute. One significant contribution arises from the closed-shell determinant $|2222202000\rangle$. All other major contributions come from determinants with unpaired electrons. Analogous to S_1, these determinants appear in pairs with the determinants in a pair differing only in the spins of the unpaired electrons. Considering the leading open-shell determinants, the orbitals in subsection **S1.1** occupied by unpaired electrons suggest that these electrons are distributed over the entire π-system. Since the overall contribution of the open-shell determinants is greater than that of the closed-shell determinant, we propose that S_2 has open-shell character.

For the singlet geometry, we have a coupling coefficient of $C_{02}^{\mathrm{(mix)}} = 0.187$ between S_0 and S_2. This means that electron correlation induces a coupling between these two states.

S2.2 Configuration Analysis of Derivative 2

We can represent T_0 by a single Slater determinant, since the CI coefficient of the determinant $|2222aa0000\rangle$ is $C_0 = 0.892$ for the triplet geometry.

Considering the CI coefficients of the singlet states in Table, we have a similar situation as for **1**, *cf.* subsection **S2.1**. By analogy, we can therefore transfer our assignments from **1** to **2**.

Also for **2**, a strong coupling between S_0 and S_2 occurs with a coupling coefficient of $C_{02}^{\mathrm{(mix)}} = 0.308$ (singlet geometry).

Table S2: CI coefficients for selected configurations of **2** contained in the CASSCF wave functions of the singlet states S_0, S_1 and S_2. The coefficients refer either to the singlet geometry (s) or the triplet geometry (t).

		$S_0^{(s)}$	$S_1^{(t)}$	$S_2^{(t)}$
A	2222200000	0.807	0.000	-0.004
B	2222ab0000	0.019	0.617	0.000
C	2222ba0000	-0.019	-0.617	0.000
D	2222020000	-0.086	0.000	0.353
E	222a2b0000	-0.004	0.000	0.204
F	222b2a0000	0.004	-0.000	0.204
G	2222b0a000	-0.208	0.000	0.432
H	2222a0b000	0.208	-0.000	-0.432

S2.3 Configuration Analysis of Derivative 3

T_0 can be represented by a single Slater determinant as $|2222aa0000\rangle$ has a CI coefficient of $C_0 = 0.887$ in the triplet state geometry.

Also for **3**, the configurations of the singlet states S_0, S_1 and S_2 are analogous to **1**, *cf.* Table S3. Here, a difference is that the active orbitals in subsection **S1.3** are distorted due to the lowered molecular symmetry.

Another notable difference is in the coupling between electronic states. In **1** and **2**, S_1 is not allowed to couple with S_0 for symmetry reasons. In **3**, such a coupling is allowed and we have a coupling coefficient of $C_{01}^{(\text{mix})} = 0.151$ for the singlet geometry. The strong coupling between S_0 and S_1 also explains smaller dipole moment of S_0, *cf.* the publication.

Table S3: CI coefficients for selected configurations of **3** contained in the CASSCF wave functions of the singlet states S_0, S_1 and S_2. The coefficients refer either to the singlet geometry (s) or the triplet geometry (t).

		$S_0^{(s)}$	$S_1^{(t)}$	$S_2^{(t)}$
A	2222200000	0.824	0.384	0.173
B	2222ab0000	0.181	0.522	0.026
C	2222ba0000	-0.181	-0.522	0.026
D	2222020000	-0.143	-0.106	0.479
E	222a2b0000	-0.079	0.091	0.294
F	222b2a0000	0.079	-0.091	0.294
G	2222b0a000	-0.086	0.020	0.172
H	2222a0b000	0.086	-0.020	-0.172

S2.4 Configuration Analysis of Derivative 4

We discussed that **4** is aromatic by Hückels rule. As a consequence, **4** has in part different configurations for the states S_0, S_1, S_2 and T_0.

T_0 can again be represented by a single Slater determinant, since $|2222aa0000\rangle$ has a CI coefficient of $C_0 = 0.887$ in the triplet state geometry.

According to Table S4, S_0 is also a closed-shell singlet state. S_1 has open-shell character but the two leading determinants are different from those of the foregoing cases. We can look at the orbitals in subsection **S1.4** that are occupied with unpaired electrons. These orbitals suggest that unpaired electrons in **4** are not localized at specific motifs. This is also consistent with the aromatic character of **4**.

Analogous to **1** and **2**, we have a coupling between S_0 and S_2. The coupling coefficient in the singlet geometry is $C_{02}^{(\mathrm{mix})} = 0.2343$.

Table S4: CI coefficients for selected configurations of **4** contained in the CASSCF wave functions of the singlet states S_0, S_1 and S_2. The coefficients refer either to the singlet geometry (s) or the triplet geometry (t).

		$S_0^{(s)}$	$S_1^{(t)}$	$S_2^{(t)}$
A	2222200000	0.850	0.001	0.288
B	2222ab0000	0.148	0.006	0.338
C	2222ba0000	-0.148	-0.006	0.338
D	2222020000	-0.272	-0.004	0.244
E	222a2b0000	-0.000	0.591	0.004
F	222b2a0000	0.000	-0.591	0.004
G	2222b0a000	-0.012	0.000	0.160
H	2222a0b000	0.012	0.000	-0.160

S3 Example Input Files

Example input (1) refers to the TURBOMOLE program package and example inputs (2) and (3) refer to the MOLPRO quantum chemistry package. Next to the input files, additional information such as SCF convergence criteria is provided.

(1) Example input for a geometry optimization of cyclohepta[def]fluorene in the triplet state using a B3LYP/def2-TZVPP level of theory. The threshold for energy convergence in the SCF program was set to 10^{-7} Hartree (standard parameter).

```
$symmetry c1
$redundant    file=coord
$atoms
    basis =def2-TZVPP
    jbas  =def2-TZVPP
$basis    file=basis
$uhfmo_alpha    file=alpha
$uhfmo_beta    file=beta
$uhf
$alpha shells
 a      1-54                              ( 1 )
$beta shells
 a      1-52                              ( 1 )
$scfiterlimit      999
$scfdamp    start=1.000  step=0.050  min=0.100
$scfdump
$scfdiis
$maxcor    500 MiB  per_core
$energy    file=energy
$grad    file=gradient
$dft
    functional   b3-lyp
    gridsize    m3
$scfconv    7
$scforbitalshift  closedshell=.05
$ricore      1000
$rij
$jbas    file=auxbasis
$disp3 bj
$marij
$rundimensions
   natoms=26
```

(2) Example input for a PNO-MS-CASPT2/def2-TZVPP calculation on cyclohepta[*def*]-fluorene in the triplet geometry using a CAS(10,10). The convergence threshold in the CASSCF program was set to 10^{-8} E_h for the energy and to 10^{-5} E_h for the gradient (standard parameters).

```
memory,2000,m
gprint,orbitals,civector
basis=tzvpp
geometry=cycloheptafluorene_b3lyp_tzvpp_t_opt.xyz
charge=0
{df-multi;occ,58;closed,48;wf,,1,2;state,1;wf,,1,0;state,2}
{df-casci;wf,,1,2;state,4;wf,,1,0;state,4;save,cirec=5100.2}
shfpt2=0.3
local,thrpno_occ=1.d-8,thrdist=1.d-6,iext=2
{pno-caspt2,h0=0,coupcor=0,cirec=5100.2,shift=shfpt2;wf,,1,2;state,3
thresh,thrdls=1.d-8}
{pno-caspt2,h0=0,coupcor=0,cirec=5200.2,shift=shfpt2;wf,,1,0;state,3
thresh,thrdls=1.d-8}
```

(3) Example input for a PNO-LCCSD(T)-F12 calculation on cyclohepta[*def*]fluorene in the triplet geometry using a cc-pVDZ-F12 basis set. The convergence threshold for the SCF iterations in the HF program was set to 10^{-8} E_h for the energy and to $3.2 \cdot 10^{-6}$ E_h for the gradient (standard parameters).

```
memory,2000,m
gprint,orbital
geometry=cycloheptafluorene_b3lyp_svp_t_opt.xyz
set,charge=0
basis={
default=vdz-f12
set,jkfit,context=jkfit
default,avtz
set,mp2fit,context=mp2fit
default,avtz
set,ri,context=jkfit
default,avtz}
explicit,ri_basis=ri,df_basis=mp2fit,df_basis_exch=jkfit
gthresh,throvl=1.d-9
{df-hf,basis=jkfit;wf,,1,2}
pno-lccsd(t)-f12
```

S4 Remark on Spin Orbit Coupling

We performed exploratory calculations on the equilibrium geometries of cyclohepta[def]-fluorene **1** for singlet and triplet state to probe the relevance of spin-orbit coupling. Both calculations were performed by setting up a spin-orbit coupling matrix employing the lowest 20 singlet and 15 triplet states as well as the lowest quintet state of a CAS(10,10)-CI expansion. Our results did not indicate any significant contribution of spin orbit coupling to the electronic structure of **1** since all matrix elements were insignificantly small. This result is consistent with **1** being a hydrocarbon. An example input file for the spin-orbit coupling calculation on the triplet geometry of **1** is shown below.

```
memory,2000,m
gprint,orbital
gprint,civector
gdirect
angstrom
basis=svp
geometry=cycloheptafluorene_b3lyp_svp_t_opt.xyz
set,charge=0
{df-multi;
occ,58
closed,48
wf,,1,2;state,1
wf,,1,1;state,2
dm,1}
{df-multi,cas-ci
wf,,1,0;state,20
wf,,1,2;state,15
wf,,1,4;state,1
save,cirec=5100.2}
gexpec,lop
{ci;core,48
hlsmat,als,5100.2,5200.2,5300.2;print,HLS=1,VLS=0}
```

S5 Remark on the Optimised Geometries

The ESI contains XYZ files for all optimised geometries relevant to this publication. The XYZ files are named according to the following scheme:

`number_functional_basis_state_opt.xyz`

`number` indicates the number by which the system is referred to in the publication, `functional` means the density functional and `basis` the basis set used for optimisation. Please note that `svp` stands for the def2-SVP basis set and `tzvpp` for the def2-TZVPP basis set. `state` is either `s` for closed-shell singlet state or `t` for triplet state. `opt` indicates that the geometry is optimised.