Supporting Information for

Ab initio Study of Charge Transfer Transitions in Complexes of Tetracyanoethylene with Aromatic Compounds

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Table of Contents

Table S1. MP2 and CCSD association energies ΔE (kcal/mol) for the benzene/TCNE complex in the ground state using SCS, SOS and F12 approaches.[a,b]

Method	ΔE
MP2/cc-pVTZ	-14.10
SCS-MP2/ cc-pVTZ	-10.17
SOS-MP2/cc-pVTZ	-8.20
SOS-MP2/cc-pVTZ optim. geom.	-8.99
MP2-F12/cc-pVDZ-F12	-14.15
SCS-MP2-F12/cc-pVDZ-F12	-9.97
SOS-MP2-F12/cc-pVDZ-F12	-7.88
CCSD/cc-pVTZ	-6.38
CCSD(T)/cc-pVTZ	-8.82
CCSD(F12)/cc-pVDZ-F12	-6.18
CCSD(F12*)/cc-pVDZ-F12	-6.18
CCSD(F12*)(T)/cc-pVDZ-F12	-8.56

[a] For the definition of methods and basis sets see the main text.

[b] If not stated differently, the MP2/cc-pVTZ geometry is used.

Table S2. MP2 and CCSD association energies ΔE (kcal/mol) for the naphtalene/TCNE complex in the ground state using the SCS, SOS and F12 approaches.[a,b]

Method	ΔE
MP2/cc-pVTZ'	-18.15
SCS-MP2/cc-pVTZ'	-12.69
SOS-MP2/cc-pVTZ'	-9.95
SOS-MP2/cc-pVTZ' optimized	-11.10
MP2-F12/cc-pVDZ-F12	-18.19
SCS-MP2-F12/cc-pVDZ-F12	-12.32
SOS-MP2-F12/cc-pVDZ-F12	-9.38

[a] For the definition of methods and basis sets see the main text.

[b] If not stated differently, the MP2/cc-pVTZ' geometry is used.

Table S3. MP2 and CCSD association energies ΔE (kcal/mol) for the perpendicular complex anthracene/TCNE in the ground state using the SCS, SOS and F12 approaches.[a,b]

Method	ΔE
MP2/cc-pVTZ'	-25.84
SCS-MP2/cc-pVTZ'	-15.61
SOS-MP2/cc-pVTZ'	-10.49
SOS-MP2/cc-pVTZ' optimized	-13.47
MP2-F12/cc-pVDZ-F12	-26.09
SCS-MP2-F12//cc-pVDZ-F12	-15.25
SOS-MP2-F12/cc-pVDZ-F12	-9.83

[a] For the definition of methods and basis sets see the main text.

[b] If not stated differently, the MP2/cc-pVTZ' geometry is used.

Table S4. Vertical excitation energies ΔE_{exc} (eV) in the benzene/TCNE complex, oscillator strengths and charge transfer (q(CT) in e units) using the ADC(2) method and the cc-pVTZ basis computed for two excited states per irreducible representation.

State	ΔE_{exc}	f [b]	q(CT)
1^1A_2	3.229	0.000	0.953
2^1A_1	3.283	0.086	0.934
1^1B_2	4.852	0.322	0.044
1^1B_1	5.276	0.001	0.088
2^1B_1	5.501	0.000	0.035
2^1B_2	5.812	0.000	0.158
2^1A_2	5.910	0.000	0.025
3^1A_1	6.130	0.003	0.032

Table S5. Vertical excitation energies ΔE_{exc} (eV) in the naphthalene/TCNE complex, oscillator strengths and charge transfer (q(CT) in e units) using the ADC(2) method and the cc-pVTZ' basis.

State	ΔE_{exc}	f [b]	q(CT)
2^1A	2.149	0.008	0.959
3^1A	2.958	0.072	0.932
4^1A	4.077	0.028	0.896
5^1A	4.397	0.004	0.075
6^1A	4.635	0.036	0.160
7^1A	4.759	0.178	0.197
8^1A	5.191	0.086	0.631
9^1A	5.367	0.009	0.930

Table S6. Vertical excitation energies ΔE_{exc} (eV) in the perpendicular anthracene/TCNE complex, oscillator strengths and charge transfer (q(CT) in e units) using the ADC(2) method and the cc-pVTZ' basis computed for two excited states per irreducible representation.

State	ΔE_{exc}	f [b]	q(CT)
2^1A_1	2.113	0.180	0.787
1^1A_2	3.028	0.000	0.862
1^1B_2	3.200	0.043	0.837
1^1B_1	3.485	0.029	0.138
2^1B_2	3.952	0.023	0.089
3^1A_1	4.390	0.039	0.790
2^1B_1	4.435	0.181	0.511
2^1A_2	4.537	0.000	0.062

Table S7. Vertical excitation energies ΔE_{exc} (eV) in the parallel anthracene/TCNE complex, oscillator strengths and charge transfer (q(CT) in e) using the ADC(2) method and the cc-pVTZ' basis computed for two excited states per irreducible representation.

State	ΔE_{exc}	f [b]	q(CT)
1^1A_2	1.396	0.000	0.962
2^1A_1	2.741	0.055	0.944
1^1B_1	3.098	0.000	0.946
2^1B_1	3.533	0.062	0.019
1^1B_2	3.865	0.002	0.043
2^1A_2	4.189	0.000	0.909
2^1B_2	4.353	0.027	0.618
3^1A_1	5.544	0.002	0.060

Cartesian coordinates (Å) for the benzene/TCNE complex using the SOS-MP2/cc-pVTZ method.

C	1.2110846	-0.6981203	-1.4794736
C	1.2110846	0.6981203	-1.4794736
C	0.0000000	1.3962037	-1.4774858
C	0.0000000	-1.3962037	-1.4774858
C	-1.2110846	-0.6981203	-1.4794736
C	-1.2110846	0.6981203	-1.4794736
H	2.1477495	-1.2395298	-1.4797761
H	2.1477495	1.2395298	-1.4797761
H	0.0000000	2.4786562	-1.4828159
H	0.0000000	-2.4786562	-1.4828159
H	-2.1477495	-1.2395298	-1.4797761
H	-2.1477495	1.2395298	-1.4797761
C	0.0000000	-0.6808318	1.7449264
C	0.0000000	0.6808318	1.7449264
C	1.2259346	1.4265404	1.7650182
C	1.2259346	-1.4265404	1.7650182
C	-1.2259346	-1.4265404	1.7650182
C	-1.2259346	1.4265404	1.7650182
N	2.2112424	2.0542879	1.8019191
N	-2.2112424	2.0542879	1.8019191
N	2.2112424	-2.0542879	1.8019191
N	-2.2112424	-2.0542879	1.8019191

Cartesian coordinates (Å) for the naphtalene/TCNE complex using the SOS-MP2/cc-pVTZ' method.

C	-0.8132765	1.3997778	-1.1760326
C	0.4290626	0.7051305	-1.1273827
C	0.4272715	-0.7199503	-1.1476725
C	-0.8163526	-1.4074761	-1.2100446
C	-2.0026655	-0.7103398	-1.2449051
C	-2.0011454	0.7094615	-1.2297611
C	1.6716816	1.3943891	-1.0626215
C	2.8549064	0.6954277	-1.0208372
C	2.8524770	-0.7225674	-1.0423934
C	1.6668540	-1.4149107	-1.1056356
H	-0.8087069	2.4879208	-1.1669701
H	-0.8158262	-2.4955269	-1.2280710
H	-2.9485500	-1.2449484	-1.2944869
H	-2.9451048	1.2477404	-1.2616332
H	1.6705469	2.4825920	-1.0493348
H	3.8006671	1.2287241	-0.9679653
H	3.7958788	-1.2606852	-1.0029733
H	1.6615462	-2.5028488	-1.1183161
C	-1.2826655	-0.4356756	1.9822943
C	-0.2568426	0.4601600	2.0222939
C	1.1057224	0.0270876	2.1346591
C	-1.0300139	-1.8475221	2.0211078
C	-2.6503467	-0.0041216	1.9460395
C	-0.5010379	1.8743574	2.0191879
N	2.2180654	-0.3060600	2.2743738
N	-0.6769215	3.0298062	2.0394955
N	-0.8344156	-2.9989230	2.0701597
N	-3.7708086	0.3289806	1.9474258

Cartesian coordinates (Å) for the anthracene/TCNE (perp.) complex using the SOS-MP2/cc-pVTZ’ method.

C	-1.4097052	-2.4753329	-0.9352377
C	-0.7174452	-1.2251617	-0.9258409
C	-1.4018775	0.0000000	-0.9046300
C	-0.7174452	1.2251617	-0.9258409
C	-1.4097052	2.4753329	-0.9352377
C	-0.7129456	3.6542147	-0.9412184
C	0.7129456	3.6542147	-0.9412184
C	1.4097052	2.4753329	-0.9352377
C	0.7174452	1.2251617	-0.9258409
C	1.4018775	0.0000000	-0.9046300
C	0.7174452	-1.2251617	-0.9258409
C	1.4097052	-2.4753329	-0.9352377
C	0.7129456	-3.6542147	-0.9412184
C	-0.7129456	-3.6542147	-0.9412184
H	-2.4973103	-2.4743732	-0.9290344
H	-2.4920693	0.0000000	-0.9061131
H	-2.4973103	2.4743732	-0.9290344
H	-1.2466031	4.6010921	-0.9422127
H	1.2466031	4.6010921	-0.9422127
H	2.4973103	2.4743732	-0.9290344
H	2.4920693	0.0000000	-0.9061131
H	2.4973103	-2.4743732	-0.9290344
H	1.2466031	-4.6010921	-0.9422127
H	-1.2466031	-4.6010921	-0.9422127
C	0.6845069	0.0000000	2.1651351
C	-0.6845069	0.0000000	2.1651351
C	-1.4268130	1.2245374	2.2149711
C	1.4268130	1.2245374	2.2149711
C	1.4268130	-1.2245374	2.2149711
C	-1.4268130	-1.2245374	2.2149711
N	-2.0452828	2.2154080	2.2813769
N	-2.0452828	-2.2154080	2.2813769
N	2.0452828	2.2154080	2.2813769
N	2.0452828	-2.2154080	2.2813769

Cartesian coordinates (Å) for the anthracene/TCNE (parallel) complex using the SOS-MP2/cc-pVTZ’ method. Used the same coordinates twice for para and perp.

C	1.4097777	-2.4762541	-0.9701016
C	0.7183012	-1.2214393	-0.9646530
C	1.4048240	0.0000000	-0.9587938
C	0.7183012	1.2214393	-0.9646530
C	1.4097777	2.4762541	-0.9701016
C	0.7150094	3.6537272	-0.9741965
C	-0.7150094	3.6537272	-0.9741965
C	-1.4097777	2.4762541	-0.9701016
C	-0.7183012	1.2214393	-0.9646530
C	-1.4048240	0.0000000	-0.9587938
C	-0.7183012	-1.2214393	-0.9646530
C	-1.4097777	-2.4762541	-0.9701016
C	-0.7150094	-3.6537272	-0.9741965
C	0.7150094	-3.6537272	-0.9741965
H	2.4975344	-2.4740412	-0.9616939
H	2.4943460	0.0000000	-0.9602782
H	2.4975344	2.4740412	-0.9616939
H	1.2488120	4.6007379	-0.9743069
H	-1.2488120	4.6007379	-0.9743069
H	-2.4975344	2.4740412	-0.9616939
H	-2.4943460	0.0000000	-0.9602782
H	-2.4975344	-2.4740412	-0.9616939
H	-1.2488120	-4.6007379	-0.9743069
H	1.2488120	-4.6007379	-0.9743069
C	0.0000000	-0.6816769	2.2683103
C	0.0000000	0.6816769	2.2683103
C	1.2285377	1.4214392	2.3036375
C	1.2285377	-1.4214392	2.3036375
C	-1.2285377	-1.4214392	2.3036375
C	-1.2285377	1.4214392	2.3036375
N	2.2236298	2.0319513	2.3666953
N	-2.2236298	2.0319513	2.3666953
N	2.2236298	-2.0319513	2.3666953
N	-2.2236298	-2.0319513	2.3666953