Supporting Information

Tetraarylcyclobutadienecyclopentadienylcobalt Complexes: Synthesis, Electronic Spectra, Magnetic Circular Dichroism, Linear Dichroism and TD DFT Calculations

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Measurements. Melting points were determined with a Laboratory Devices MEL-TEMP II apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were acquired with Varian VXR 300S, Varian Unity Inova 400 or Varian Unity Inova 500 spectrometers and referenced to residual ^{1}H and ^{13}C present in the deuterated solvents. All NMR spectra were recorded at room temperature. IR spectra were recorded with Nicolet Avatar 320 FT-IR or Nicolet Nexus 670 FT-IR spectrometers. GC-MS spectra were measured with an HP GC/MS 5988A instrument with a fused silica capillary column (cross-linked 5% phenylmethylsilicone). Electron impact (EI) mass spectra were recorded on a Kratos MS-25 Mass Spectrometer and chemical ionization (CI) mass spectra were recorded on an API QSTAR Pulsar Mass Spectrometer. Fast-atom bombardment (FAB) mass spectra measurements were conducted with a Fisons Instruments VG autospec instrument. ESI spectra were acquired with a Hewlett-Packard 59987A Electrospray instrument connected to a HP 5989B Mass Spectrometer, a VG 7070 EQ-HF Hybrid Tandem Mass spectrometer or a API QSTAR Pulsar Mass Spectrometer. Elemental Analyses were performed by Desert Analytics, Tucson, AZ, and Galbraith Laboratories, Knoxville, TN. UV-Vis spectra were measured on an HP 8452A Diode Array spectrophotometer or an Olis RSM 1000 spectrometer and baseline corrected. Magnetic circular dischroism (MCD) measurements were performed with a JASCO J-720 spectropolarimeter equipped with a 1.504 T JASCO electromagnet.

Methods of Calculation. All DFT geometry optimizations were performed with the B3LYP method as implemented in ADF[1] using the TZP internal basis set of Slater type orbitals. Vertical excitation energies were calculated with the TD-DFT method (B3LYP/DZP), MCD B terms at the B3LYP/DZP level.

Optimized geometries at the B3LYP/TZP level.

1:

C	-0.556163	-1.096208	3.318335
C	0.850273	-0.837101	3.338996
C	1.038277	0.580313	3.347257
C	-0.251275	1.197059	3.331791
C	-1.236764	0.161564	3.313847
Co	-0.004171	0.002481	1.559339
C	-1.030168	0.062318	-0.202048
C	-2.476637	0.129775	-0.459360
C	-2.997110	1.098389	-1.338445
C	-4.359384	1.126614	-1.643714
C	-5.228350	0.187811	-1.083747
C	-4.722845	-0.781666	-0.210716
C	-3.364666	-0.809579	0.100024
C	-0.052162	-1.033785	-0.195501
C	1.044522	-0.055631	-0.189075
C	2.492927	-0.129791	-0.432057
C	3.017563	-1.109656	-1.296330
C	4.382455	-1.147192	-1.588125
C	5.250449	-0.206839	-1.029145
C	4.741101	0.773413	-0.170614
C	3.380178	0.810551	0.126788
C	0.065767	1.040922	-0.195703
C	0.135599	2.488567	-0.444285
C	1.121883	3.016085	-1.299297
C	1.154249	4.380192	-1.595731
C	0.202072	5.244342	-1.051152
C	-0.785607	4.731851	-0.202958
C	-0.817656	3.371888	0.099145
C	-0.123919	-2.480983	-0.447334
C	-1.087593	-2.998997	-1.333473
C	-1.121210	-4.362137	-1.633901
C	-0.192735	-5.234475	-1.061925
C	0.771006	-4.731613	-0.181164
C	0.803935	-3.372484	0.125119
H	6.309982	-0.233545	-1.261111
H	5.406390	1.510433	0.267783
H	4.764115	-1.907270	-2.262460
H	2.350057	-1.833829	-1.750906
H	2.991345	1.573886	0.792417
H	1.855166	2.351510	-1.743404
H	1.919721	4.764138	-2.262621
H	0.224952	6.303189	-1.286689
H	-1.532519	5.393896	0.223466
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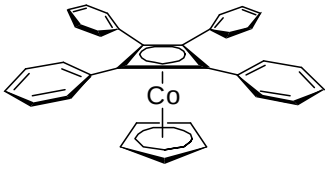
H	-2.328363	1.820757	-1.794090



1

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H	-1.868424	-4.738870	-2.325179
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H	1.498381	-5.400569	0.267592
H	1.553831	-2.988414	0.808586
H	-2.307106	0.304245	3.268730
H	-0.443446	2.260119	3.306453
H	1.988951	1.093347	3.346974
H	1.634637	-1.579897	3.334092
H	-1.019257	-2.071893	3.285877

17d:

C	-0.129092	0.939924	3.064100
C	0.699657	1.937442	2.519767
C	0.082673	2.881120	1.680827
C	-1.289383	2.786961	1.439588
N	-2.077190	1.838999	1.958977
C	-1.487174	0.935920	2.754440
C	2.148610	1.969291	2.760788
C	3.208595	0.949841	2.752899
C	4.227656	2.010444	2.783329
C	5.681221	2.063563	2.580169
C	6.340228	1.131572	1.760550
C	7.716022	1.254380	1.555137
N	8.470123	2.220301	2.091177
C	7.839966	3.112793	2.867932
C	6.475039	3.080253	3.142364
Co	3.168038	1.958388	4.526739
C	3.166799	3.028662	2.790258
C	3.121413	4.483637	2.593990
C	4.067459	5.141487	1.789583
C	3.957406	6.519609	1.593449
N	2.990721	7.276665	2.123951
C	2.083306	6.647087	2.883680
C	2.102688	5.279802	3.148534
C	2.010635	2.378943	6.280094
C	2.380412	0.997616	6.271591
C	3.807826	0.922394	6.292292
C	4.320262	2.256397	6.313952
C	3.210160	3.156701	6.306314
C	3.245855	-0.497757	2.508524
C	2.292673	-1.121749	1.685446
C	2.391041	-2.493403	1.444078
N	3.351755	-3.275650	1.948213
C	4.264776	-2.678903	2.727386
C	4.257768	-1.320690	3.035908
H	5.045456	-3.320310	3.129919
H	1.658735	-2.981328	0.804907
H	1.494695	-0.549479	1.225819
H	5.026596	-0.906463	3.678909
H	5.791900	0.331817	1.275391
H	8.231192	0.538462	0.918771
H	8.458784	3.897612	3.296911
H	6.032887	3.834086	3.784593
H	4.869341	4.590837	1.310690
H	4.684430	7.034229	0.969323
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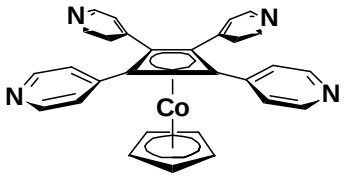

17d

H	-1.772697	3.511779	0.788476
H	-2.133990	0.166535	3.169781
H	0.280733	0.180368	3.720782
H	3.267580	4.235815	6.290431
H	5.364874	2.532831	6.308093
H	4.394739	0.015556	6.277951
H	1.702484	0.156995	6.242232
H	1.001460	2.764155	6.249551

16a:

C	0.782611	-3.397451	0.390169
C	-0.137137	-2.479544	-0.148115
C	-1.094357	-2.994696	-1.040523
C	-1.123449	-4.341759	-1.393623
C	-0.175921	-5.256820	-0.879383
C	0.768438	-4.744600	0.044145
C	-0.060433	-1.037349	0.126241
C	1.039761	-0.061476	0.130524
C	0.063460	1.038503	0.123228
C	0.139654	2.480801	-0.149764
C	1.117058	3.003403	-1.015472
C	1.146967	4.351258	-1.365792
C	0.180631	5.259762	-0.875652
C	-0.786145	4.739762	0.019896
C	-0.801268	3.392077	0.363098
Co	-0.008256	0.001739	1.882688
C	-1.036122	0.062438	0.119000
C	-2.477243	0.136319	-0.161917
C	-2.992667	1.097153	-1.050138
C	-4.338626	1.123505	-1.407869
C	-5.252105	0.169532	-0.902896
C	-4.739436	-0.779673	0.015420
C	-3.393482	-0.791225	0.365959
C	-0.560466	-1.093275	3.652544
C	0.846082	-0.836167	3.671123
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C	-0.252721	1.199089	3.662355
C	-1.239244	0.165020	3.646997
C	2.482626	-0.141410	-0.138950
C	3.000570	-1.110114	-1.017281
C	4.348600	-1.143536	-1.366238
C	5.262278	-0.189610	-0.861486
C	4.747194	0.766964	0.047721
C	3.399040	0.785611	0.389383
N	6.600375	-0.176307	-1.257245
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H	4.681069	-1.912657	-2.052075
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H	3.043437	1.543543	1.079615
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H	1.923332	4.687497	-2.041540
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H	-1.539071	5.388393	0.449741
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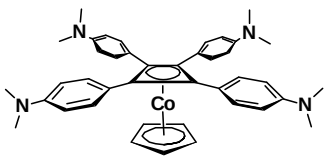

16a

H	-5.392535	-1.521240	0.458029
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H	-1.825285	-2.325133	-1.481158
H	-1.883740	-4.672219	-2.090197
N	-0.157239	-6.593650	-1.279143
H	1.504114	-5.399076	0.494503
H	1.530394	-3.044095	1.092548
H	-2.309455	0.309239	3.603678
H	-0.443783	2.262369	3.637486
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H	-7.243267	-1.730294	-0.608417
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C	-1.285588	-7.123077	-2.028750
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H	1.715309	-7.253248	-0.566085
H	0.358814	-7.638224	0.515105
H	-1.087689	-8.164407	-2.284096
H	-2.232323	-7.078949	-1.466936
H	-1.423070	-6.576409	-2.966538
C	7.547798	0.648242	-0.524300
C	7.130979	-1.312761	-1.993622
H	8.530705	0.560815	-0.987966
H	7.260603	1.703430	-0.563472
H	7.638857	0.358785	0.534905
H	8.173072	-1.118180	-2.248433
H	7.084835	-2.253566	-1.422080
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C	1.310152	7.135219	-1.990016
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H	-1.728996	7.245996	-0.607009
H	-0.403386	7.633086	0.511075
H	1.113195	8.176004	-2.248306
H	2.241517	7.095127	-1.402766
H	1.476108	6.591585	-2.924925

16b:

C	0.733190	-3.293879	0.375056
C	-0.163804	-2.424159	-0.271865
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C	-1.086942	-4.375128	-1.423811
C	-0.168778	-5.247270	-0.790240
C	0.734455	-4.662096	0.134038
C	-0.101209	-0.966655	-0.092734
Co	-0.138711	0.183169	1.611661
C	-0.020977	1.485100	3.322911
C	-1.287523	0.823685	3.310382
C	-1.050010	-0.584847	3.395745
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C	0.998778	0.487776	3.415030
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C	1.271235	4.380316	-1.613525
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C	-0.889016	3.445489	-0.105606
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O	1.295508	7.045671	-2.244916
C	-2.515607	0.164555	-0.490669
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O	-7.039436	0.974623	-2.397741
C	0.992695	0.004913	-0.110350
C	2.448927	-0.102546	-0.278194
C	3.007376	-1.119155	-1.074584
C	4.375771	-1.197562	-1.313495
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C	4.712329	0.764474	0.051992
C	3.343227	0.828119	0.281674
N	6.632757	-0.291059	-1.039872
C	7.190725	-1.442421	-1.733080
C	0.688837	-7.490677	-0.270007
C	7.540566	0.586812	-0.317050
O	-0.606988	7.401302	-1.238450
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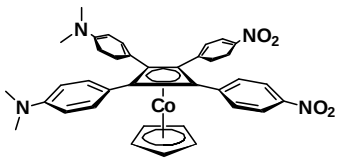
H	1.446834	-5.278959	0.666927



16b

H	-1.809926	-4.760676	-2.131229
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H	4.742551	-2.001623	-1.938686
H	5.348542	1.507360	0.515961
H	2.956981	1.620409	0.914865
H	1.978083	2.358665	-1.590812
H	2.093396	4.760855	-2.205714
H	-1.601484	5.483293	-0.156309
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H	-2.367381	1.832391	-1.859826
H	-4.770863	1.817775	-2.473690
H	-5.432040	-1.530598	0.119538
H	-3.030035	-1.519895	0.758993
H	0.138934	2.551130	3.244110
H	2.064723	0.664021	3.422609
H	0.860539	-1.747792	3.516949
H	-1.803900	-1.358652	3.400997
H	-2.254675	1.299451	3.234264
H	0.603320	-8.506235	-0.655262
H	1.743869	-7.203414	-0.330558
H	0.397869	-7.500482	0.791166
H	-0.990460	-8.253560	-2.023761
H	-2.190619	-7.089681	-1.430273
H	-1.226589	-6.731530	-2.879310
H	8.554692	0.433129	-0.684520
H	7.286797	1.638910	-0.482405
H	7.536102	0.400103	0.767446
H	8.258730	-1.286844	-1.882483
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H	6.734557	-1.566836	-2.720540

18:

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C	0.789442	-4.706279	-0.263424
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C	1.040815	-0.048426	-0.368256
C	0.058631	1.036617	-0.372389
C	0.129757	2.488329	-0.567033
C	1.103313	3.046817	-1.404451
C	1.145984	4.417091	-1.637271
C	0.221862	5.283020	-1.052368
C	-0.755378	4.723777	-0.222245
C	-0.800616	3.359002	0.020177
Co	-0.014029	-0.017515	1.336426
C	-1.030547	0.056050	-0.383366
C	-2.473132	0.131499	-0.582821
C	-3.054270	1.138056	-1.367589
C	-4.413069	1.185372	-1.584241
N	-5.258055	0.250487	-1.050491
C	-4.712348	-0.748030	-0.284341
C	-3.360657	-0.816107	-0.047376
C	-0.570013	-1.121449	3.044503
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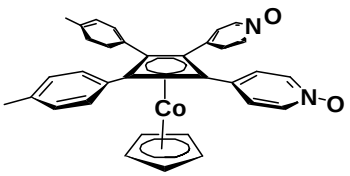
C	-0.242204	1.157458	3.080986
C	-1.233561	0.137363	3.057888
C	2.493133	-0.116650	-0.558017
C	3.058689	-1.082455	-1.399446
C	4.431413	-1.126349	-1.619357
C	5.292441	-0.208772	-1.018034
C	4.725440	0.764701	-0.188267
C	3.358935	0.810750	0.041170
C	6.782564	-0.271425	-1.234753
H	5.367318	1.497636	0.289108
H	4.836197	-1.884242	-2.281300
H	2.418162	-1.795694	-1.902065
H	2.952119	1.574298	0.691917
H	1.825209	2.401780	-1.888287
H	1.909158	4.816962	-2.296204
C	0.284606	6.770826	-1.284668
H	-1.491034	5.369565	0.245504
H	-1.564039	2.959465	0.676171
H	-2.438876	1.898751	-1.827554
H	-4.910538	1.934452	-2.181071
O	-6.518700	0.304462	-1.256279



18

H	-5.438684	-1.444582	0.105709
H	-2.993865	-1.618386	0.578843
H	-1.873193	-2.469454	-1.829474
H	-1.889731	-4.942319	-2.160774
O	-0.246858	-6.529851	-1.220962
H	1.494225	-5.423322	0.128949
H	1.648883	-2.972618	0.580582
H	-2.300872	0.292001	3.032318
H	-0.424210	2.220381	3.076732
H	1.988701	1.032547	3.088524
H	1.608355	-1.628407	3.050845
H	-1.044290	-2.089967	3.016619
H	-0.714333	7.207008	-1.349194
H	0.806267	7.275149	-0.465082
H	0.818303	7.007212	-2.206564
H	7.214116	0.727363	-1.329126
H	7.282210	-0.761875	-0.393394
H	7.030045	-0.834377	-2.135959

Table S1. TDDFT (B3LYP/DZP) calculated vertical transitions in **17d**.

	$\tilde{\nu}$/cm^{-1}	f	B term[a]	dominant configurations[b]	polarization
1	17 735	0.0020	1.8050	**3→-1, 4→-2**	*x,y*
2	17 749	0.0021	1.8163	**3→-2, 4→-1**	
3	21 045	0.0032	-2.9795	**4→-1**, 3→-2, 10→-1	*x,y*
4	21 075	0.0032	-2.9250	**4→-2**, 10→-2, 3→-1	
5	23 144	0.0001	-1.0861	**1→-2, 2→-1**	*x,y*
6	24 574	0.0000	-0.8043	**2→-1, 1→-2**	
7	25 945	0.0001	-0.3220	**1→-1, 2→-2**	*z*
8	26 922	0.0034	-1.4966	**10→-1**, 16→-1, 4→-1	*x,y*
9	26 943	0.0032	-1.2386	**10→-2**, 16→-2, 4→-2	
10	31 071	0.1690	-34.3605	**2→-2, 1→-1, 4→-3**	*z*
11	31 281	0.1720	27.8620	**1→-3**	*x,y*
12	31 322	0.1668	28.2417	**2→-3**	
13	32 077	0.0075	-0.7695	**3→-3**	*z*
14	34 749	0.0008	0.8533	**5→-1**, 6→-2, 8→-3	*z*
15	34 803	0.0032	0.4072	**6→-2**	*z*
16	34 941	0.0012	0.4707	**7→-1**, 8→-1, 5→-3	*x,y*
17	34 997	0.0012	0.4055	**8→-2, 7→-2**, 6→-3	
18	35 571	0.2277	-9.6997	**4→-3**, 2→-2, 1→-1	*z*
19	35 698	0.0068	-0.4248	**15→-1, 14→-2**	*z*
20	36 530	0.0747	2.2367	**1→-4**, 1→-5	*x,y*
21	36 569	0.0711	4.8496	**2→-4**	
22	36 846	0.0427	1.6939	**1→-5**, 1→-4, 9→-1	*x,y*
23	36 884	0.0409	3.1861	**2→-5**, 2→-4, 9→-2, 7→-2	
24	36 971	0.0003	0.5029	**5→-2, 6→-1**	*x,y*
25	37 053	0.0016	0.6472	**6→-1, 5→-2**	
26	37 395	0.0037	0.3559	**8→-1, 7→-1**, 1→-5	*x,y*
27	37 403	0.0037	0.4606	**7→-2**, 8→-2, 2→-5	
28	37 546	0.0001	-1.2808	11→-1, 12→-2, 15→-2, 14→-1, 1→-7	*z*
29	37 706	0.0062	4.7315	**12→-2**, 11→-1, 2→-6, 1→-7	*z*
30	37 978	0.0001	-1.2078	15→-1, 14→-2, 11→-2, 12→-1	*z*
31	38 077	0.0272	-1.4882	**9→-1**, 1→-5	*z*
32	38 096	0.0018	0.5135	15→-2, 14→-1, 2→-6	*z*
33	38 105	0.0274	-0.7369	**9→-2**, 2→-5	*z*
34	38 563	0.0018	-0.9419	**11→-2, 12→-1**	*z*
35	38 695	0.0000	0.4902	12→-1, 11→-2, 15→-1, 14→-2	*z*
36	39 303	0.0000	-0.7793	**3→-4**	*z*
37	39 427	0.0114	0.6414	**13→-1**, 5→-3	*x,y*
38	39 447	0.0005	1.2437	**1→-6**	*z*
39	39 472	0.0112	2.8744	**13→-2**, 6→-3	*x,y*
40	39 524	0.0001	-2.4408	**2→-7**, 1→-7, 2→-6	*z*
41	39 600	0.0032	-1.9150	**7→-3**	*z*
42	39 672	0.0016	0.3562	**8→-3**, 2→-7	*z*
43	39 687	0.0070	1.5313	**5→-3, 13→-1**	*z*
44	39 730	0.0065	-0.4790	**6→-3**, 13→-2	*z*
45	40 059	0.0238	-6.5571	**1→-7, 11→-1**	*x,y*

46	40 079	0.0174	-4.7030	**2→-6, 12→-2**	
47	40 124	0.0005	-0.3882	**4→-4, 10→-3**	*z*
48	40.376	0.0003	1.8450	**4→-4**, 10→-3	*z*
49	40 653	0.0951	-20.8244	**16→-1**, 10→-1	*x,y*
50	40 672	0.0137	-3.2023	**3→-5**	*z*

[a] In units of 10^{-5} $D^2\beta_e/cm^{-1}$. [b] Dominant configurations with weight more than 10% (bold: weight more than 25%). 1 = HOMO, -1 = LUMO, 2 = HOMO-1, -2 = LUMO+1, etc.

Figure S1. The B3LYP/DZP frontier orbitals of **17d**.

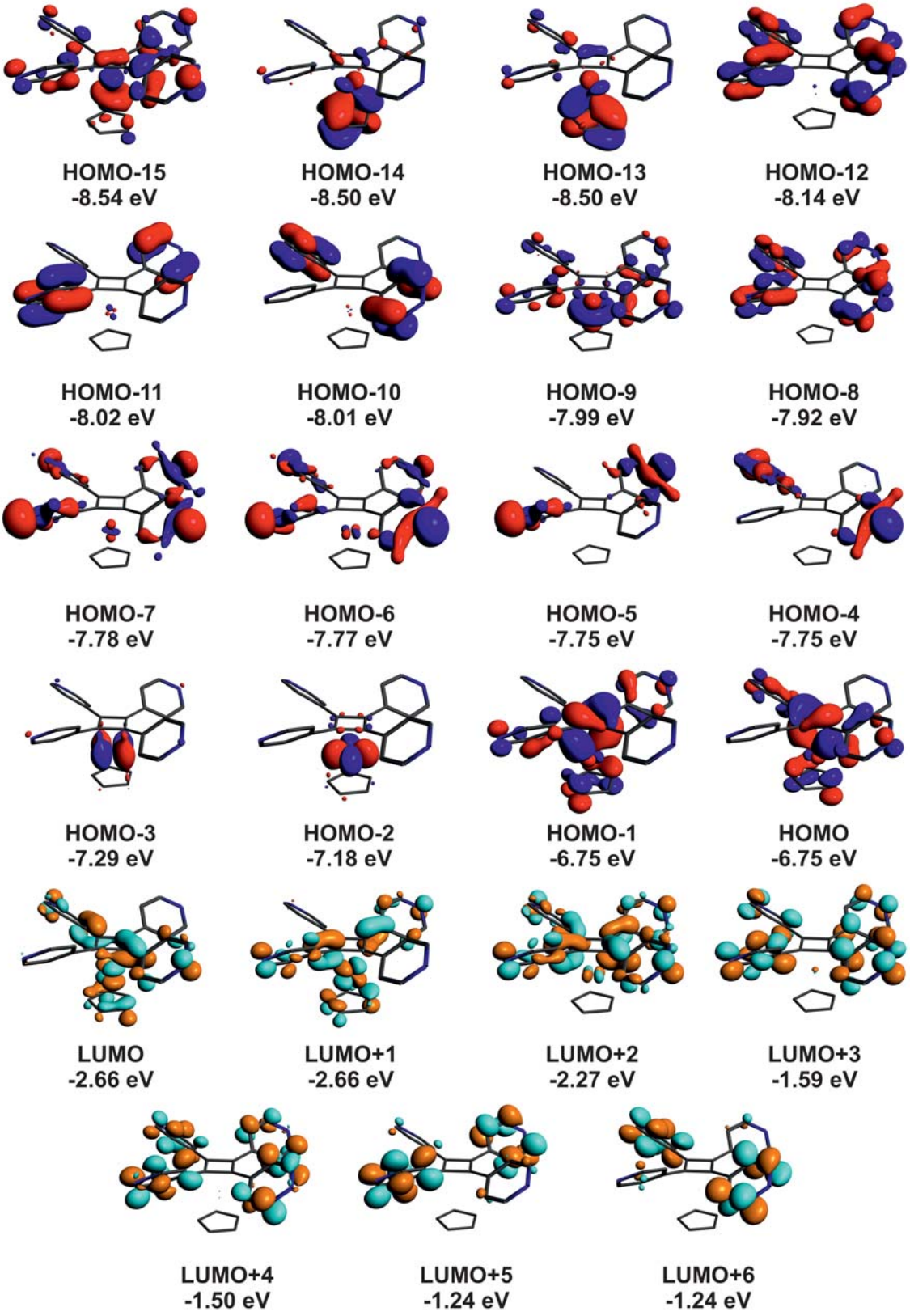


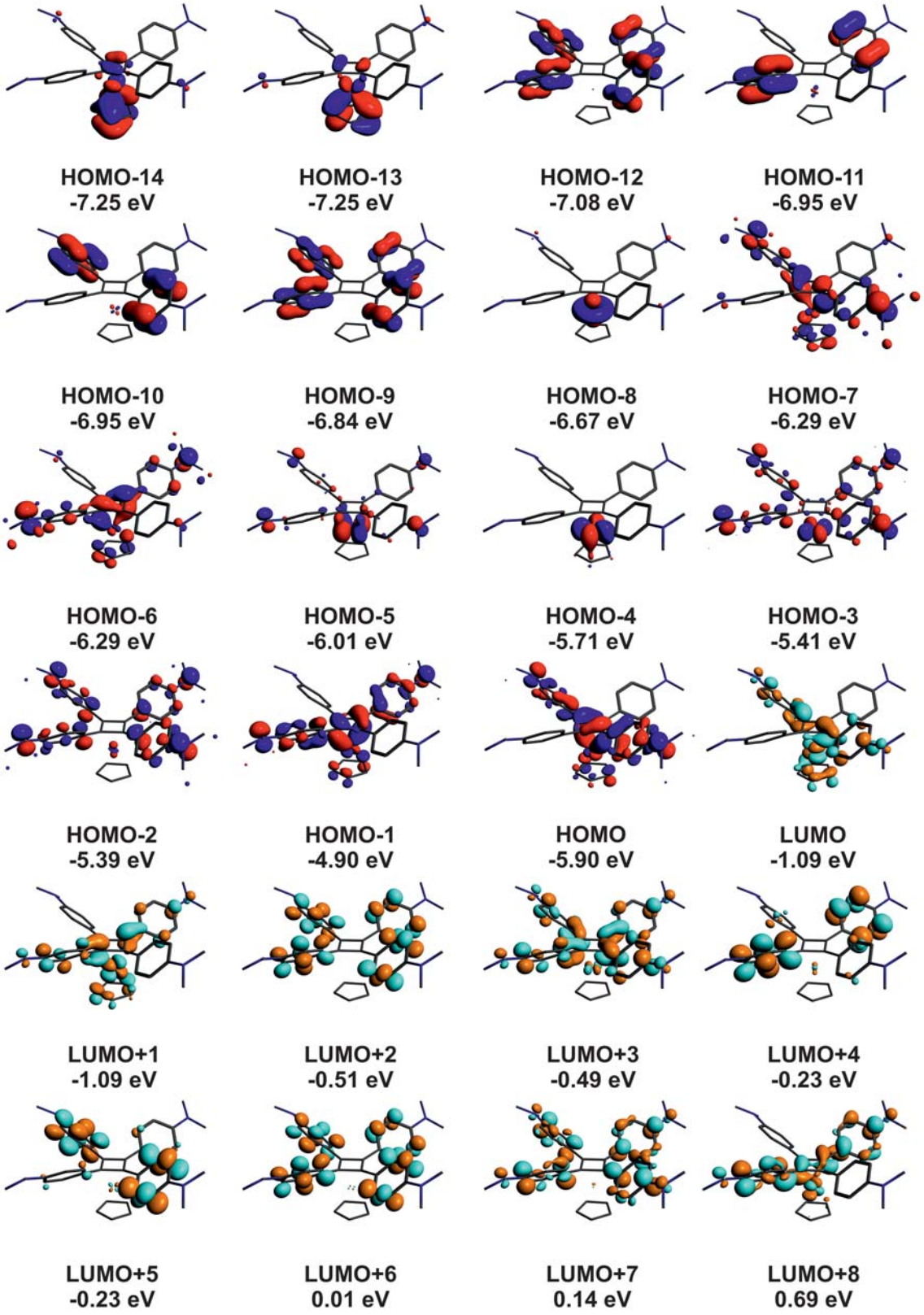
Table S2. TDDFT (B3LYP/DZP) calculated vertical transitions in **16a**.

	$\tilde{\nu}$/cm^{-1}	f	B term[a]	dominant configurations[b]	polarization[c]
1	18 010	0.0046	3.3083	**5→-1**, 4→-1, 5→-2, 6→-2	*x,y*
2	18 012	0.0047	3.3130	**5→-2**, 4→-2, 5→-1, 6→-1	
3	21 240	0.0112	-3.8193	6→-1, 4→-1, 5→-2, 9→-1	*x,y*
4	21 248	0.0116	-3.9529	6→-2, 4→-2, 5→-1, 9→-2	
5	21 331	0.0007	-0.3334	**1→-2, 2→-1**	*mixed*
6	23 106	0.0000	0.8973	**2→-1, 1→-2**	*mixed*
7	24 270	0.0000	2.3260	**1→-1, 2→-2**	*x,y*
8	26 821	0.0165	-3.5308	**9→-2**, 3→-2	*x,y*
9	26 827	0.0165	-3.5232	**9→-1**, 3→-1	
10	29 899	0.2090	2.3169	**2→-2, 1→-1**	*z*
11	30 789	0.0166	7.0758	**1→-4, 3→-1**	*x,y*
12	30 799	0.0142	6.1309	**2→-4, 3→-2**	
13	30 890	0.0169	10.6723	**1→-3**, 2→-4	*x,y*
14	30 903	0.0183	10.4780	**2→-3**	
15	31 494	0.5391	4.3162	**1→-4, 3→-1**, 2→-3	*x,y*
16	31 499	0.5410	5.4771	**2→-4, 3→-2**	
17	32 840	0.1355	16.4656	**6→-1, 4→-1**	*x,y*
18	32 845	0.1342	16.3973	**6→-2, 2→-2**	
19	33 072	0.0492	-9.3644	**1→-6, 2→-5**	*z*
20	33 130	0.0005	-0.6280	**2→-5, 1→-6**	*z*
21	33 149	0.0029	-0.5139	**1→-5, 2→-6**	*z*
22	33 219	0.0001	-1.8394	**2→-6, 1→-5**	*mixed*
23	34 360	0.0209	3.3124	**5→-4, 4→-4**	*z*
24	34 935	0.0025	5.0995	**1→-7**	*x,y*
25	34 951	0.0025	5.0597	**2→-7**	
26	35 200	0.0000	-1.9546	**4→-3**	*mixed*
27	35 441	0.0048	0.5545	**3→-3**	*z*
28	35 771	0.0000	0.3942	**3→-4**	*mixed*
29	35 938	0.0190	6.1065	4→-4, 5→-4, 7→-1, 8→-2	*z*
30	36 142	0.0004	1.8301	**7→-1, 8→-2**	*mixed*
31	36 240	0.0647	11.2130	**8→-2**, 7→-1, 4→-4	*z*
32	36 433	0.3903	-1.0232	**1→-8**	*x,y*
33	36 450	0.3890	-2.6411	**2→-8**	
34	36 819	0.0001	0.8976	**7→-2, 8→-1**	*x,y*
35	36 866	0.0000	-1.9311	**5→-3**	*x,y*
36	37 326	0.0159	-0.4921	**4→-5**	*x,y*
37	37 329	0.0167	-0.6033	**4→-6**	
38	37 627	0.0514	-6.5168	**3→-5**, 4→-5	*x,y*
39	37 637	0.0511	-	**3→-6**, 4→-6	
40	37 847	0.0697	-	14→-1, 15→-1	*z*
41	38 333	0.0662	-	**8→-1, 7→-2**	*z*
42	39 088	0.0001	-	**6→-4, 5→-5**	*x,y*
43	39 102	0.0003	-	**5→-6**, 6→-4, 3→-7	*mixed*
44	39 107	0.0001	-	**5→-5, 5→-6**	*x,y*
45	39 127	0.0001	-	**3→-7**, 6→-3, 5→-6	*mixed*

46	39 162	0.0058	-	**4→-7**	*z*
47	39 562	0.0001	-	**1→-9, 2→-10**	*mixed*
48	39 682	0.0000	-	**6→-3, 3→-7**	*x,y*
49	39 869	0.0000	-	**1→-10, 2→-9**	*x,y*
50	40 227	0.0018	-	**2→-10, 1→-9**	*z*

[a]In units of 10^{-5} $D^2\beta_e/cm^{-1}$. [b] Dominant configurations with weight more than 10% (bold: weight more than 25%). 1 = HOMO, -1 = LUMO, 2 = HOMO-1, -2 = LUMO+1, etc. [c]Polarization is marked *z* if transition dipole moment vector in *z* direction is more then 3 times larger then in perpendicular (*x*,*y*) direction, if more then 3 times smaller the polarization is marked *x*,*y*, otherwise the polarization is *mixed*.

Figure S2. The B3LYP/DZP frontier orbitals of **16a**. Isosurface value = 0.04, except for Rydberg (diffuse) orbitals (LUMO+10 - LUMO+14), where the value is 0.015.



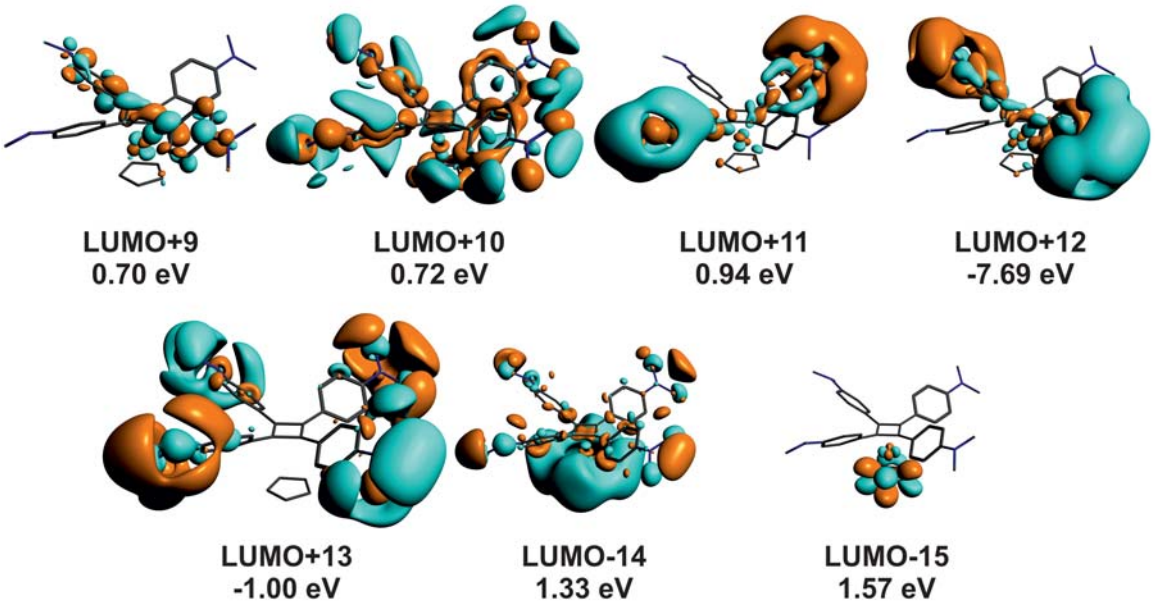

LUMO+9
0.70 eV
LUMO+10
0.72 eV
LUMO+11
0.94 eV
LUMO+12
-7.69 eV
LUMO+13
-1.00 eV
LUMO-14
1.33 eV
LUMO-15
1.57 eV

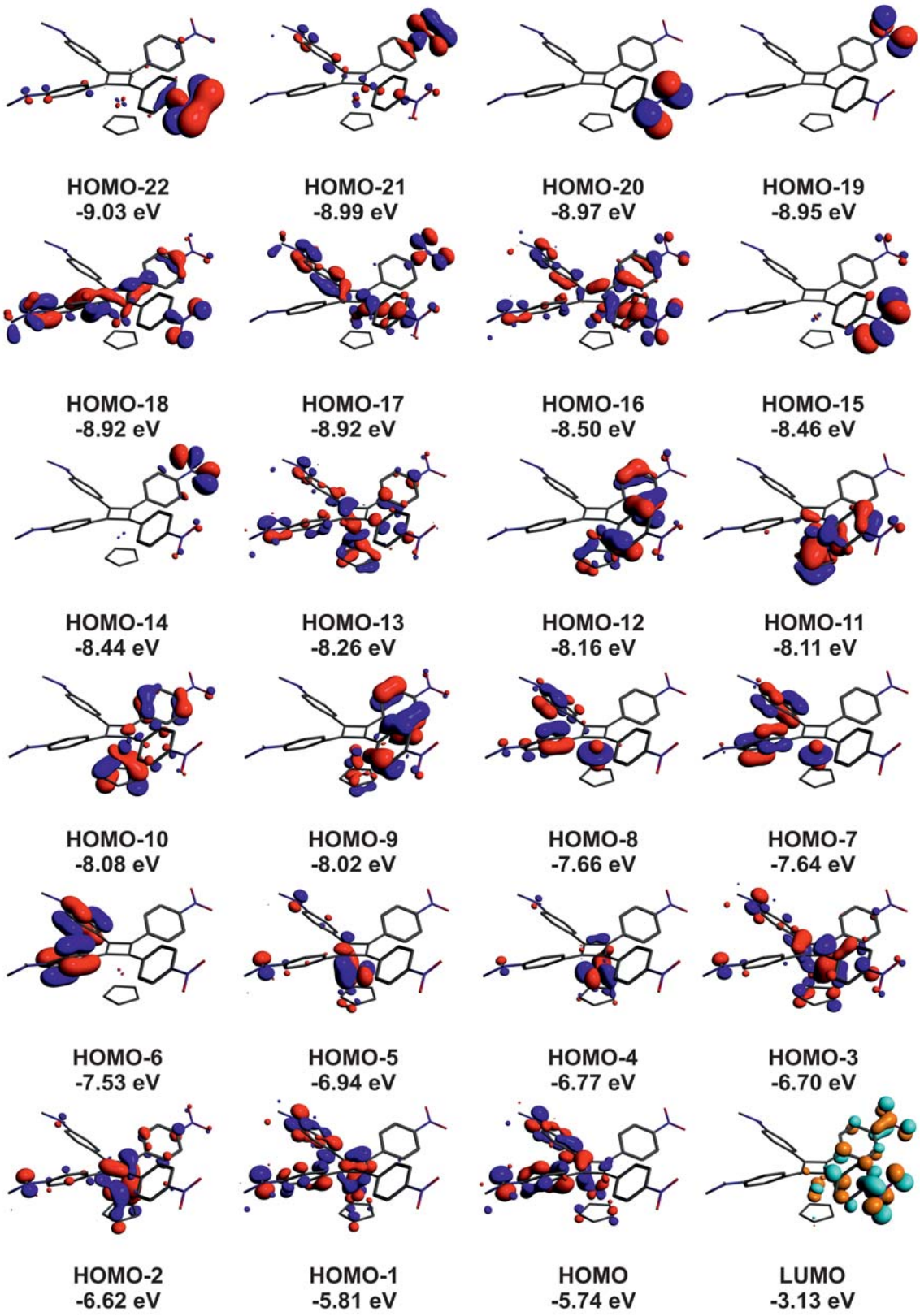
Table S3. TDDFT (B3LYP/DZP) calculated vertical transitions in **16b**.

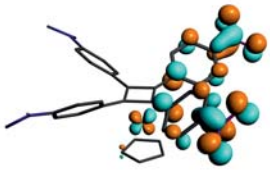
	$\tilde{\nu}$/cm^{-1}	f	B term[a]	dominant configurations[b]	polarization[c]
1	16 528	0.0042	4.6721	5→-3, 2→-2, 5→-1	*x,y*
2	16 728	0.0013	0.5568	2→-1, 5→-4, 5→-2, 6→-3	*mixed*
3	17 170	0.0057	1.3058	**1→-1**	*x,y*
4	17 803	0.0121	4.7613	**1→-2, 2→-1**	*x,y*
5	18 387	0.0154	-0.5020	**2→-2**	*x,y*
6	18 845	0.0239	-1.4310	**1→-2**, 2→-1	*mixed*
7	20 533	0.0572	-11.5150	2→-2, 6→-2, 6→-4, 3→-2	*x,y*
8	20 767	0.0884	-7.2136	2→-1, 6→-1, 6→-3	*mixed*
9	23 269	0.0006	2.1172	4→-1, 1→-3	*x,y*
10	24 172	0.0053	0.8915	**3→-1**, 4→-2, 1→-4	*x,y*
11	24 611	0.0473	-0.3358	4→-1, 1→-3	*x,y*
12	25 084	0.0134	-4.2202	1→-4, 2→-3, 3→-2	*x,y*
13	25 408	0.0094	-2.5443	2→-4, 1→-3, 4→-1, 5→-2	*x,y*
14	26 178	0.0991	6.1836	**4→-1**, 3→-1, 6→-1	*mixed*
15	26 352	0.0034	2.6606	6→-1, 3→-2, 5→-1	*x,y*
16	26 755	0.3093	-10.6846	**4→-2**, 3→-1, 3→-2	*x,y*
17	27 065	0.2821	-4.1116	**2→-4**, 6→-2, 3→-2, 4→-2	*x,y*
18	27 559	0.0008	0.4642	5→-3, 5→5, 3→-3, 6→-2	*mixed*
19	28 148	0.0060	1.1166	**5→-2**, 5→-4, 6→-1	*x,y*
20	29 218	0.0021	-1.8654	5→-3, 6→-1, 3→-4, 6→-3	*mixed*
21	29 592	0.0163	-0.4876	**6→-2**, 5→-4, 6→-4, 3→-4	*mixed*
22	29 921	0.1840	14.9272	2→-3, 1→-4, 2→-4, 1→-3	*mixed*
23	30 546	0.0035	-1.1164	**1→-5**	*mixed*
24	30 678	0.0016	-0.8051	**15→-2, 15→-1**	*mixed*
25	30 685	0.0020	-0.7657	**16→-1, 16→-2**	*mixed*
26	30 971	0.0531	-4.0507	**2→-5**	*mixed*
27	32 069	0.0002	1.6175	**7→-1**	*mixed*
28	32 508	0.0071	2.1350	**4→-3**, 4→-4, 1→-6	*x,y*
29	32 524	0.0016	1.5399	**7→-2**, 9→-1, 8→-1	*mixed*
30	32 663	0.0023	0.6966	**1→-6**	*x,y*
31	32 823	0.0575	12.3292	**2→-6, 1→-7**, 4→-4	*x,y*
32	32 949	0.1133	-2.5476	**1→-7, 2→-6**	*x,y*
33	33 192	0.0400	1.3361	4→-4, 6→-3, 3→-3, 2→-6	*mixed*
34	33 446	0.0300	1.3434	**8→-1, 7→-2**, 9→-1, 2→-7	*x,y*
35	33 512	0.1328	13.1920	**2→-7**	*x,y*
36	33 805	0.0073	-1.3412	**8→-2, 1→-8**, 9→-2	*mixed*
37	33 867	0.0141	0.6069	6→-4, 3→-4, 6→-3	*mixed*
38	34 089	0.0267	-2.2189	**1→-8**, 8→-2, 9→-2	*mixed*
39	34 327	0.0143	-1.6563	**11→-1**, 10→-1, 12→-2	*x,y*
40	34 405	0.0285	-0.2957	**2→-8**, 10→-2	*x,y*
41	34 613	0.0359	5.0571	**10→-1**, 13→-2	*mixed*
42	34 764	0.0005	1.7159	**10→-2**, 2→-8, 11→-1	*mixed*
43	34 968	0.0245	-3.7687	9→-1, 8→-1, 9→-3, 8→-3	*x,y*
44	35 195	0.0076	-2.2507	12→-1, 9→-2, 11→-2	*mixed*
45	35 306	0.0006	2.1214	**22→-2, 22→-1**, 18→-2, 18→-1	*x,y*

46	35 348	0.0011	-0.6952	**23→-1, 23→-2**	*mixed*
47	35 494	0.0646	-0.7460	**12→-2**, 12→-1	*x,y*
48	35 734	0.0138		11→-2, 12→-1	*mixed*
49	36 065	0.0056		**1→-9**	*mixed*
50	36 296	0.1310		4→-3, 3→-4	*mixed*

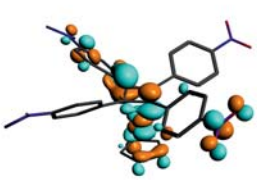
[a] In units of 10^{-5} $D^2\beta_e/cm^{-1}$. [b] Dominant configurations with weight more than 10% (bold: weight more than 25%). 1 = HOMO, -1 = LUMO, 2 = HOMO-1, -2 = LUMO+1, etc. [c] Polarization is marked *z* if transition dipole moment vector in *z* direction is more then 3 times larger then in perpendicular (*x*,*y*) direction, if more then 3 times smaller the polarization is marked *x*,*y*, otherwise the polarization is *mixed*.

Figure S3. The B3LYP/DZP frontier orbitals of **16b**.

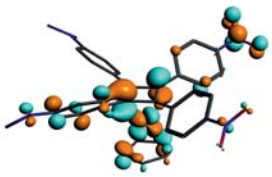




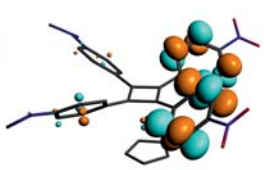
LUMO+1
-3.06 eV



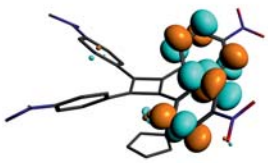
LUMO+2
-1.90 eV



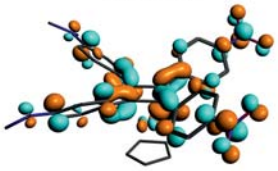
LUMO+3
-1.90 eV



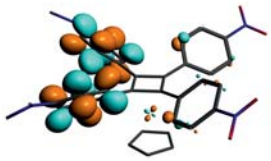
LUMO+4
-1.46 eV



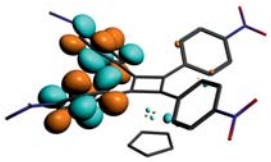
LUMO+5
-1.20 eV



LUMO+6
-1.18 eV



LUMO+7
-0.96 eV



LUMO+8
-0.70 eV

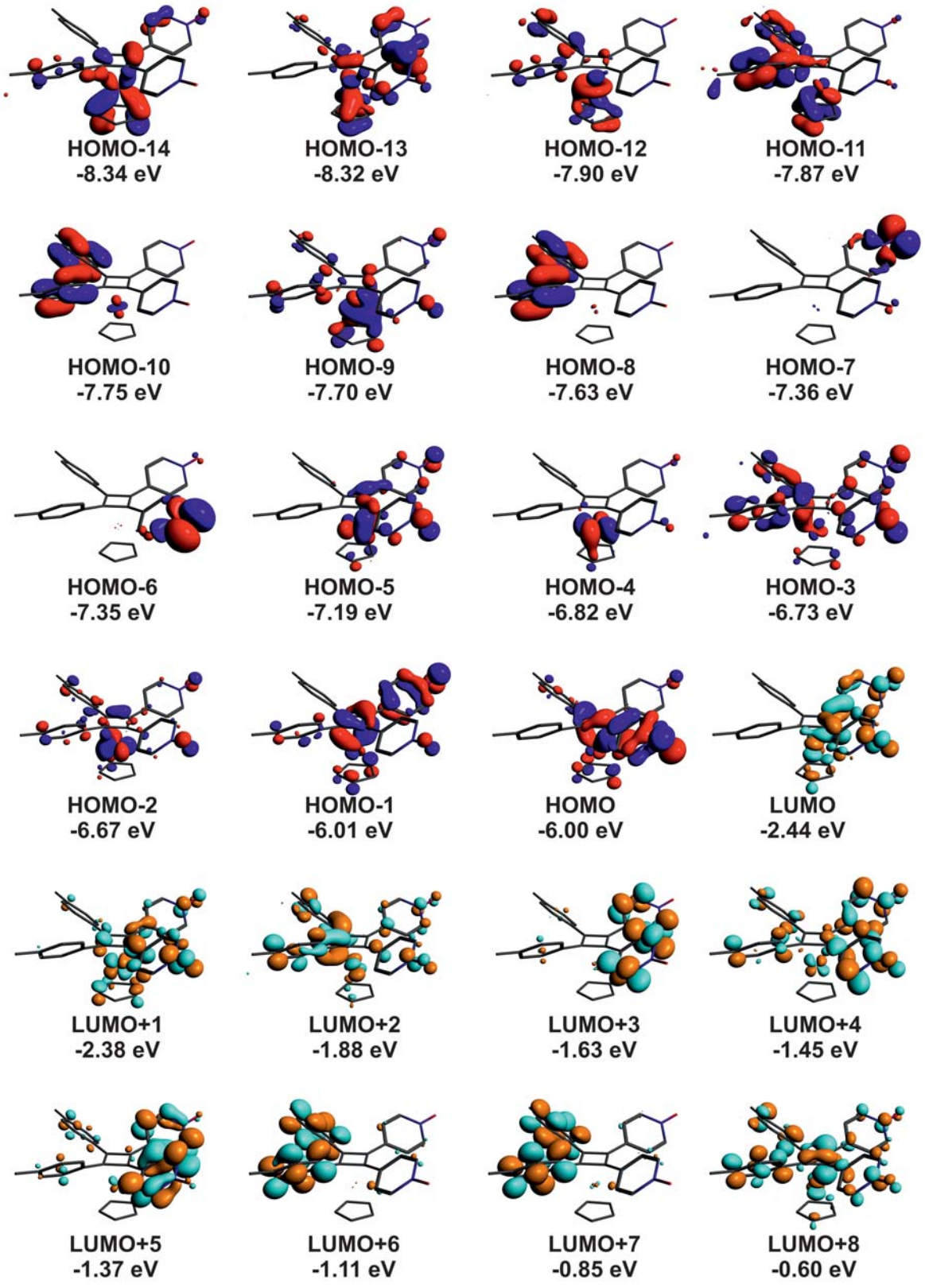
Table S4. TDDFT (B3LYP/DZP) calculated vertical transitions in **18**.

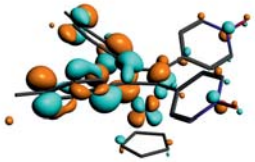
	$\tilde{\nu}$/cm^{-1}	f	B term[a]	dominant configurations[b]	polarization[c]
1	17 611	0.0033	2.1300	**5→-1**, 3→-2, 3→-1, 5→-3	*x,y*
2	17 632	0.0034	2.1201	**5→-2**, 3→-1, 3→-2	
3	20 778	0.0036	-2.1386	3→-2, 5→-1, 6→-2	*x,y*
4	20 817	0.0053	-2.5464	3→-1, 5→-2, 6→-1	
5	21 125	0.0038	-2.5277	**1→-1, 2→-2**	*x,y*
6	22 430	0.0021	0.8547	**2→-1, 1→-2**, 2→-2, 1→-1	*x,y*
7	24 123	0.0339	2.2011	**2→-2, 1→-1**, 1→-2, 2→-1	*x,y*
8	26 392	0.0109	-1.6734	10→-1, 13→-1, 4→-1	*x,y*
9	26 427	0.0168	-1.8506	10→-2, 13→-2, 4→-2	*x,y*
10	28 306	0.2233	6.8915	**1→-3**, 2→-1, 1→-1, 1→-2	*mixed*
11	28 560	0.1227	11.7117	**2→-3**, 1→-3	*x,y*
12	28 971	0.1084	-2.5780	**1→-3**, 1→-2, 2→-3	*mixed*
13	30 227	0.0181	-1.6936	**1→-4**	*mixed*
14	30 317	0.0085	-0.8411	**2→-4**, 1→-4	*x,y*
15	30 574	0.0207	-1.5460	**4→-1**	*mixd*
16	30 748	0.0007	-0.9986	**8→-1**, 7→-2, 8→-2	*mixed*
17	30 864	0.0074	-0.5436	**7→-1**, 7→-2, 4→-1	*x,y*
18	31 476	0.0564	-3.3289	**4→-1**, 6→-1	*x,y*
19	31 517	0.0156	1.1031	**5→-3**, 3→-3	*mixed*
20	31 937	0.0126	-5.2125	**1→-5**, 6→-1	*x,y*
21	32 329	0.0211	-2.9883	**2→-5**, 6→-2, 2→-6	*x,y*
22	32 461	0.0005	2.0947	**1→-6, 2→-6**	*x,y*
23	32 659	0.0138	-5.9655	**2→-6, 1→-6**, 6→-2	*mixed*
24	33 620	0.2355	4.6223	3→-3, 5→-3, 6→-3, 3→-1	*mixed*
25	34 027	0.5496	-0.8859	6→-2, 4→-3, 2→-5	*x,y*
26	34 832	0.0628	2.8678	**1→-7, 4→-3**	*x,y*
27	35 003	0.0122	0.8133	**2→-7**, 4→-3, 1→-7	*mixed*
28	35 132	0.0004	0.9506	**2→-7, 1→-7**, 4→-3	*mixed*
29	35 459	0.3242	7.0305	3→-3, 6→-1, 1→-7	*mixed*
30	35 838	0.0393	0.3909	**3→-4**	*mixed*
31	35 911	0.0076	-0.6256	15→-1, 10→-1	*x,y*
32	36 470	0.0029	0.7703	**3→-5**, 4→-4, 5→-5	*mixed*
33	36 523	0.0108	-1.8083	**4→-4**	*mixed*
34	36 576	0.0003	-0.7058	**7→-1, 7→-2**	*mixed*
35	36 764	0.0008	2.5278	**5→-4**, 8→-2	*mixed*
36	36 800	0.0038	1.0019	**8→-2**, 5→-4, 8→-1, 1→-8	*x,y*
37	36 873	0.0012	1.9372	**1→-8**, 8→-2	*x,y*
38	36 909	0.0023	2.0998	**2→-8**	*mixed*
39	37 125	0.0021	0.3744	**5→-5**	*mixed*
40	37 182	0.0019	0.3838	**6→-3**, 4→-5	*mixed*
41	37 444	0.0016	0.9697	**9→-1**	*mixed*
42	37 637	0.0012	0.9030	5→-5	*mixed*
43	37 823	0.0026	-0.3776	**3→-6**	*mixed*
44	37 906	0.0015	-0.3831	**9→-1**	*mixed*
45	38 052	0.0003	-0.5239	**9→-2**, 1→-8, 4→-6	*x,y*

46	38 118	0.0230	0.3804	2→-9, 1→-9	*x,y*
47	38 291	0.0163	1.0626	**4→-6**, 6→-4	*mixed*
48	38 383	0.0150	-2.3903	**1→-10**, 2→-9	*x,y*
49	38 735	0.0056	-2.4411	**11→-1**, 11→-2	*x,y*
50	38 766	0.0003	-1.4166	**8→-4**, 8→-6	*x,y*

[a] In units of 10^{-5} $D^2\beta_e/cm^{-1}$. [b] Dominant configurations with weight more than 10% (bold: weight more than 25%). 1 = HOMO, -1 = LUMO, 2 = HOMO-1, -2 = LUMO+1, etc. [c] Polarization is marked *z* if transition dipole moment vector in *z* direction is more then 3 times larger then in perpendicular (*x*,*y*) direction, if more then 3 times smaller the polarization is marked *x*,*y*, otherwise the polarization is *mixed*.

Figure S4. The B3LYP/DZP frontier orbitals of **18**.





LUMO+9
-0.53 eV

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