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Supporting Information for

Electrochemical control of the switching process of photochromic dimethyldihydropyrene derivatives

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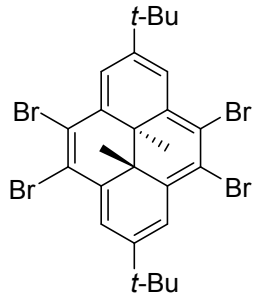
1. Synthetic procedure

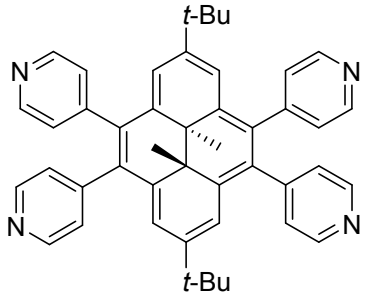
4,5,9,10-tetrabromo-2,7-di-tert-butyl-trans-10b,10c-dimethyl-10b,10c-dihydropyrene



A solution of Br_2 (2,05g, 12,8 mmol) in CCl_4 (160ml) was added dropwise to a solution of dihydropyrene[1] (1,10 g, 3,2 mmol) in CCl_4 (200mL) at 0°C over 1h. The mixture was stirred for an additional 1h and then poured into ice-water. The mixture was extracted with CH_2Cl_2 (300 mL) and the organic layer was washed with water, dried ($MgSO_4$), and concentrated. Recristallisation in hexane yielded (2.01 g, 95%) as green crystals.

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.96 (4H, s), 1.71 (18H, s, t-Bu), -3.50 (6H, s, $-CH_3$); ^{13}C NMR (126 MHz, CD_3CN) δ/ppm: 125.24, 31.92, 14.49; HRMS: m/z calc. for $C_{26}H_{28}Br_4$ 655.8925, found: 659.8942.

2,7-di-tert-butyl-4,5,9,10-(4-pyridyl)-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene

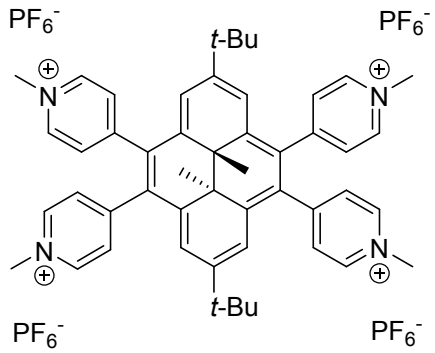


A round bottom flask was filled under an argon atmosphere with 4,5,9,10-tetrabromo-2,7-di-tertbutyl-trans-10b,10c-dimethyl-10b,10c-dihydropyrene (0.100 g, 0.2 mmol), 4-pyridinylboronic acid (100 mg, 0.82 mmol) and freshly distilled THF (6 mL). A degassed aqueous solution (2 mL) of sodium carbonate (200mg, 1.9 mmol) and tetrakis-triphenylphosphine-palladium (70 mg, 0.06 mmol) were added into the flask and the resulting mixture was heated to reflux under stirring for 48 h. After cooling down the mixture to room temperature, the solvent was evaporated under reduced pressure until dryness. The solid

residue was dissolved in CH_2Cl_2 (50 mL) and the solution is washed with water (3 x 50 mL). The organic phase was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The crude solid product was purified by column chromatography on silica gel using cyclohexane as eluent. After having eluted the first fraction which was the unreacted tetrabromide derivatives, the polarity of the eluent was gradually increased up to methanol: ethyl acetate 20:80 (vol:vol) to afford as a dark brown solid (yield 80%, 137 mg).

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ/ ppm: 8.75 (d, 4H), 8.56 (d, 4H), 8.24 (s, 4H), 7.66 (d, 4H), 7.15 (d, 4H), 1.38 (s, 18H, t-Bu), -3.29 (s, 6H, $-CH_3$); ^{13}C NMR (126 MHz, CD_3CN) δ/ppm: 149.28, 149.15, 148.95, 134.32, 127.23, 126.78, 121.72, 31.57, 15.60; HRMS: m/z: calcd for $C_{46}H_{44}N_4$+H^+ 653.3644 $[M+H]^+$, found 653.3646.

2,7-di-tert-butyl-4,5,9,10-(N-methylpyridin-4-yl)-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene hexafluorophosphate (2_c^{4+})



20 mg of 2,7-di-tert-butyl-4,5,9,10-(4-pyridyl)-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (0.047 mmol) were dissolved in 7 mL of degassed acetonitrile. 2 mL of CH_3I (0.032 mol) was then rapidly added and the solution was refluxed for 5 days. Upon cooling down to room temperature, the precipitate formed (iodide salt) was filtered off, washed with diethyl ether and dissolved in 1-2 mL CH_3OH. The hexafluorophosphate salt of was then precipitated upon addition of a saturated aqueous solution of NH_4PF_6. The brown powder was then collected by filtration, washed with cold water and dried under vacuum (yield 36%, 22 mg).

^{1}H NMR (400 MHz, 298 K, CD_3CN) δ/ppm: 8.76 (d, 4H), 8.53 (d, 4H), 8.40 (d, 4H), 7.74 (d, 4H), 4.38 (s, 12H), 7.34(s, 4H), 1.47 (s, 18H), -3.23 (s, 6H); ^{13}C NMR (100 MHz, CD_3CN) δ/ppm: 131.81, 123.89, 31.37, 15.81; HRMS: m/z: calcd for $C_{50}H_{56}F_{24}N_4P_4$: 1147.3430 $[M-PF_6]^+$, found 1147.3384 $[M-PF_6]^+$.

2. Additional NMR data

Figure S1: ^{1}H NMR spectrum for $\mathbf{2_c^{4+}}$, $\mathbf{2_c}$

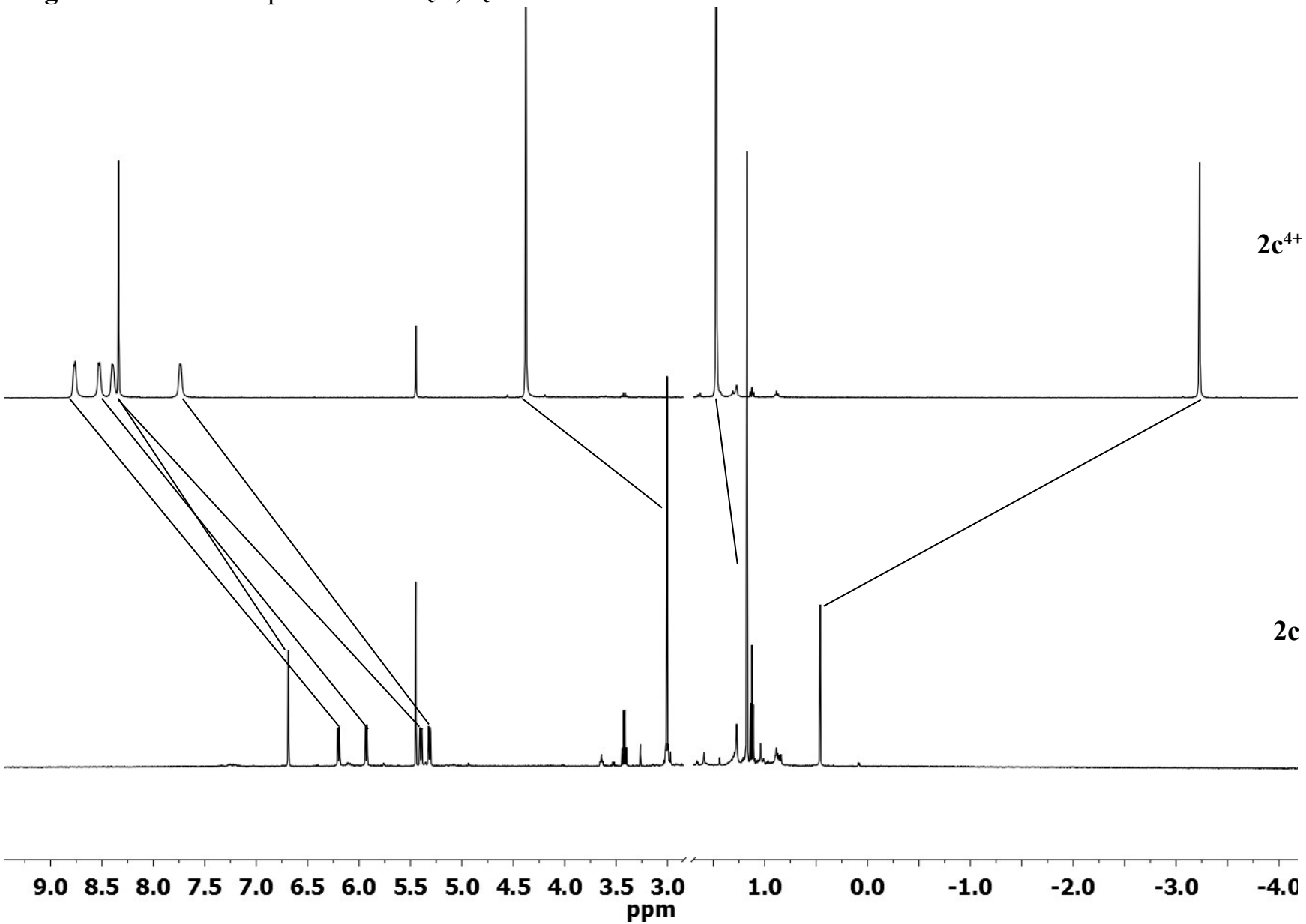
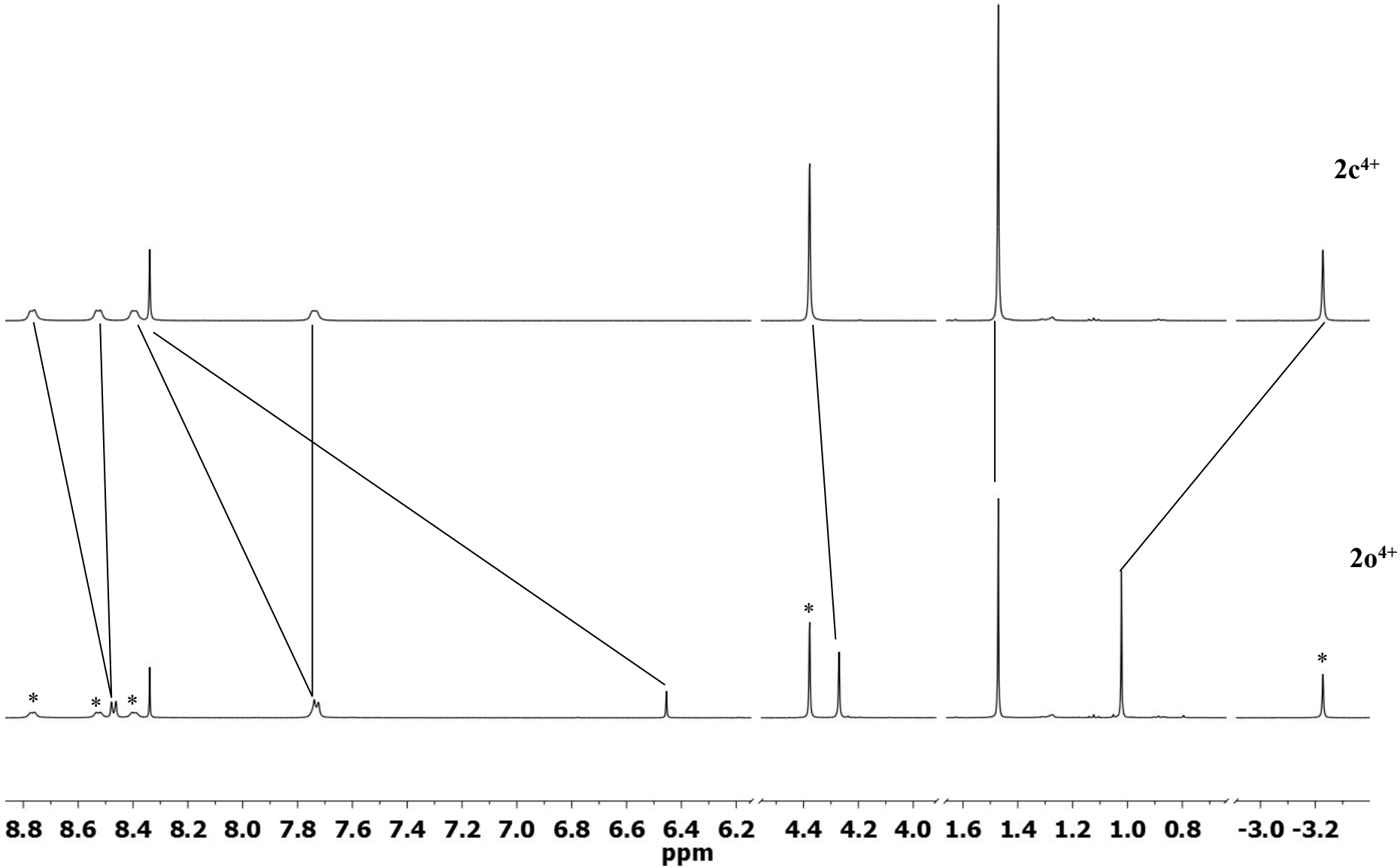


Figure S2: ^{1}H NMR spectrum for $\mathbf{2_c^{4+}}$, $\mathbf{2_o^{4+}}$ (CD3CN) (* residual peaks of $\mathbf{2_c^{4+}}$)



3. Additional Electrochemical data

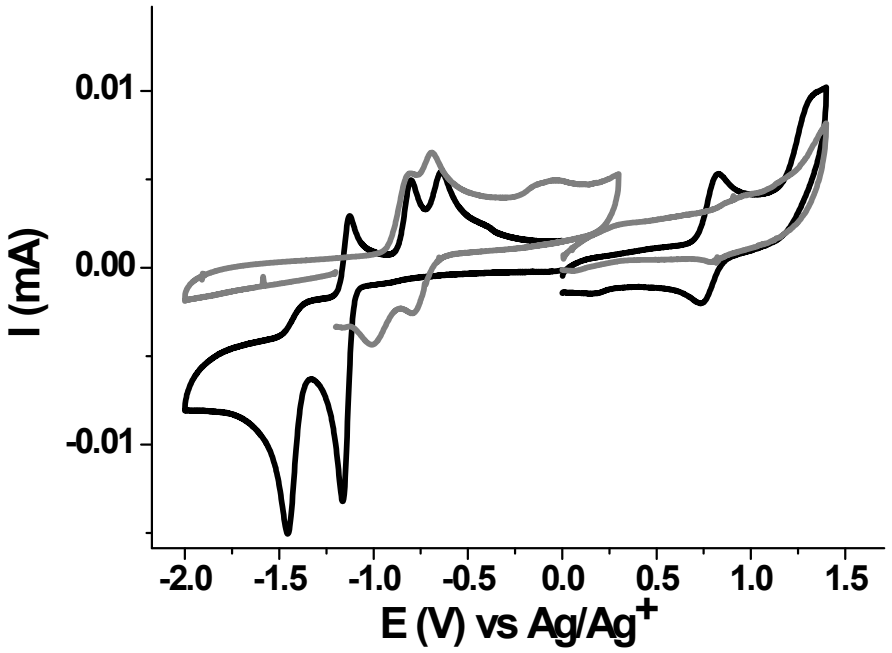


Figure S3. Cyclic voltammograms of (a)$\mathbf{2_c}^{4+}$ (black) and $\mathbf{2_c}$ (gray) ;1mM in CH_3CN + 0.1 M $TBAPF_6$; 0.1 $V.s^{-1}$; WE : glassy carbon

4. Computational details

Density functional theory (DFT) has been used to perform calculations of closed-shell and open-shell species for isolated model systems of the bispyridinium- (**1**) and tetrapyridinium-appended (**2**) dimethyldihydropyrene derivatives in different redox states. The model systems were obtained by simply replacing the bulky *tert*-butyl groups by hydrogen atoms in order to reduce the computational cost. Geometry optimizations were carried out for the closed-ring ($\mathbf{1_c}^{2+}$ and $\mathbf{2_c}^{4+}$) and open-ring ($\mathbf{1_o}^{2+}$ and $\mathbf{2_o}^{4+}$) isomers of the compounds and for the closed-ring ($\mathbf{1_c}$ and $\mathbf{2_c}$) and open-ring ($\mathbf{1_o}$ and $\mathbf{2_o}$) isomers of the fully reduced-compounds. Open-shell triplet (diradical) and quintet (tetraradical) species were computed with unrestricted DFT. Open-shell singlet (diradical) species were obtained using broken-symmetry DFT calculations. To account for the spin contamination, spin-projected energies were computed with the approximated spin-correction procedure proposed by Yamaguchi and coworkers.[1,2] All these geometry optimizations were performed with the B3LYP functional[3] and the corresponding optimized Cartesian coordinates and energies are collected in Table S1. The main resonance structures were derived using the information from these optimized geometries and the Mulliken spin densities for open-shell species (Figures S4 and S5). Absorption spectra were computed at the time-dependent DFT (TD-DFT) level using the CAM-B3LYP functional (Figures S6 and S7).[4] The triplet-ζ plus polarization functions 6-311G(d,p) was used throughout.[5] All calculations were performed with Gaussian 09.[6]

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[6] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2009.

5. Optimized structures

Table S1. B3LYP/6-311G(d,p) Cartesian coordinates and energy for closed-shell singlet of $\mathbf{1_c^{2+}}$.

N	0.010211166607	-0.169372380826	6.854752432196
C	0.053459107812	-0.207276446759	4.052384778434
C	0.878389846306	-0.975809299371	6.198744576308
H	1.539325484307	-1.572186026354	6.813028977899
C	0.018137785190	-0.110641228676	8.336048969218
H	0.687810716492	0.684650344158	8.665794424487
H	0.357025716898	-1.066629398764	8.728732516670
H	-0.991992507250	0.084356815454	8.690094335324
C	-0.152206261689	3.077423364566	-0.081573953865
H	-0.120527202898	3.942032244781	-0.735929333784
C	-0.062012320552	3.254812223062	1.293391276996
C	-0.076348982381	0.854449204765	1.749000464954
C	0.138782907423	-1.575284306769	2.008591620830
H	0.107293871052	-2.444049527818	2.657608150218
C	0.055635030635	-0.290367966255	2.583182580399
C	0.018902801758	2.169595607601	2.180291267597
H	0.221750698359	2.387346890492	3.221482438951
C	0.914641924131	-1.015168809830	4.824247980275
H	1.637256250290	-1.663966001690	4.348111706972
C	-1.954492884064	0.315346137712	0.245642633662
H	-2.488373967898	1.198185523085	0.600082434246
H	-2.217136480924	-0.527992835046	0.884673399488
H	-2.291839193528	0.100310883890	-0.769250575197
C	-0.410175021144	0.597111398991	0.273501275873
C	-0.840565904938	0.615117628376	6.148558299721
H	-1.525662726898	1.220953391507	6.726117543741
C	-0.836201785240	0.616828308950	4.773295884011
H	-1.559873917799	1.233474773767	4.259183392119
C	-0.199743685980	1.796763743870	-0.636217811420
N	-0.010211166607	0.169372380826	-6.854752432196
C	-0.053459107812	0.207276446759	-4.052384778434
C	-0.878389846306	0.975809299371	-6.198744576308
H	-1.539325484307	1.572186026354	-6.813028977899
C	-0.018137785190	0.110641228676	-8.336048969218
H	-0.687810716492	-0.684650344158	-8.665794424487
H	-0.357025716898	1.066629398764	-8.728732516670
H	0.991992507250	-0.084356815454	-8.690094335324
C	0.152206261689	-3.077423364566	0.081573953865
H	0.120527202898	-3.942032244781	0.735929333784
C	0.062012320552	-3.254812223062	-1.293391276996
C	0.076348982381	-0.854449204765	-1.749000464954
C	-0.138782907423	1.575284306769	-2.008591620830
H	-0.107293871052	2.444049527818	-2.657608150218
C	-0.055635030635	0.290367966255	-2.583182580399
C	-0.018902801758	-2.169595607601	-2.180291267597
H	-0.221750698359	-2.387346890492	-3.221482438951
C	-0.914641924131	1.015168809830	-4.824247980275
H	-1.637256250290	1.663966001690	-4.348111706972
C	1.954492884064	-0.315346137712	-0.245642633662
H	2.488373967898	-1.198185523085	-0.600082434246
H	2.217136480924	0.527992835046	-0.884673399488
C	0.410175021144	-0.597111398991	-0.273501275873
C	0.840565904938	-0.615117628376	-6.148558299721
H	1.525662726898	-1.220953391507	-6.726117543741
C	0.836201785240	-0.616828308950	-4.773295884011
H	1.559873917799	-1.233474773767	-4.259183392119
C	0.199743685980	-1.796763743870	0.636217811420
H	2.291839193528	-0.100310883890	0.769250575197
H	0.016822409127	4.259382101916	1.691824150350
H	-0.016822409127	-4.259382101916	-1.691824150350

B3LYP energy:

$E(S_0)$ = -1269.326147 a.u.

Table S1 (continued). B3LYP/6-311G(d,p) Cartesian coordinates and energy for closed-shell singlet of $\mathbf{1_o^{2+}}$.

N	-0.090120600545	-0.150088095123	-6.768181651477
C	-0.243453035296	0.112603646888	-3.979896258879
C	2.930676535324	0.569383057076	0.187165330417
H	3.638198743803	0.835188877816	0.965060684403
C	1.860222163860	-0.290436006235	0.491038175495
C	-1.152442209301	0.762793129191	-4.844056383505
H	-1.925271481342	1.413343858638	-4.458768812879
C	-0.319675132326	0.198872205231	-2.515820814541
C	1.991837952981	0.985894775036	-1.972792805474
H	1.969175347935	1.586550897716	-2.875658782913
C	0.765071986679	-0.651869202619	-4.605325291822
H	1.508450474328	-1.168799200780	-4.013994981688
C	0.947343891276	0.082514112203	-1.713133279775
C	-1.536530582799	0.419214909665	-1.922620770689
H	-2.402882725423	0.457888738964	-2.577538559925
C	-1.058567723106	0.614440308927	-6.206771972125
H	-1.737900794171	1.106492418193	-6.889688311559
C	1.002132841717	-0.719440791571	-0.554549923933
C	0.251807337081	-2.019422886550	-0.448152452004
H	-0.038603212553	-2.265293322768	0.571141695064
H	0.932182645876	-2.812837162056	-0.779498113076
H	-0.627126123579	-2.061503297010	-1.087673712629
C	0.813960144932	-0.773251520550	-5.973620700656
H	1.565066395964	-1.368173081941	-6.475375579744
C	3.038625533888	1.150235349563	-1.071305858007
C	0.016435309133	-0.251493601570	-8.243035559363
H	-0.979043599773	-0.189209847277	-8.677372569830
H	0.460587894247	-1.210044305155	-8.502278691032
H	0.638771796525	0.560363164608	-8.621653881813
N	0.090120600545	0.150088095123	6.768181651477
C	0.243453035296	-0.112603646888	3.979896258879
C	-2.930676535324	-0.569383057076	-0.187165330417
H	-3.638198743803	-0.835188877816	-0.965060684403
C	-1.860222163860	0.290436006235	-0.491038175495
C	1.152442209301	-0.762793129191	4.844056383505
H	1.925271481342	-1.413343858638	4.458768812879
C	0.319675132326	-0.198872205231	2.515820814541
C	-1.991837952981	-0.985894775036	1.972792805474
H	-1.969175347935	-1.586550897716	2.875658782913
C	-0.765071986679	0.651869202619	4.605325291822
H	-1.508450474328	1.168799200780	4.013994981688
C	-0.947343891276	-0.082514112203	1.713133279775
C	1.536530582799	-0.419214909665	1.922620770689
H	2.402882725423	-0.457888738964	2.577538559925
C	1.058567723106	-0.614440308927	6.206771972125
H	1.737900794171	-1.106492418193	6.889688311559
C	-1.002132841717	0.719440791571	0.554549923933
C	-0.251807337081	2.019422886550	0.448152452004
H	0.038603212553	2.265293322768	-0.571141695064
H	-0.932182645876	2.812837162056	0.779498113076
H	0.627126123579	2.061503297010	1.087673712629
C	-0.813960144932	0.773251520550	5.973620700656
H	-1.565066395964	1.368173081941	6.475375579744
C	-3.038625533888	-1.150235349563	1.071305858007
C	-0.016435309133	0.251493601570	8.243035559363
H	0.979043599773	0.189209847277	8.677372569830
H	-0.460587894247	1.210044305155	8.502278691032
H	-0.638771796525	-0.560363164608	8.621653881813
H	-3.869718239627	-1.803607419686	1.304950779287
H	3.869718239627	1.803607419686	-1.304950779287

B3LYP energy:

$E(S_0)$ = -1269.298891 a.u.

Table S1 (continued). B3LYP/6-311G(d,p) Cartesian coordinates and energy for closed-shell singlet of **1$_c$**.

N	-0.098615196023	-0.219212299395	6.898878059627
C	0.106390988088	-0.223047612829	4.030012869803
C	0.578084990245	-1.219730323995	6.230145362390
H	1.038674541384	-1.972067786077	6.857403516112
C	-0.020747349401	-0.098741874615	8.345467151122
H	0.848723050930	0.489910343382	8.663520796366
H	0.046811495946	-1.091613653298	8.792492712554
H	-0.924610248021	0.383564645097	8.721930678021
C	-0.424152225860	3.078029048927	-0.088465001663
H	-0.544535805636	3.920532851577	-0.763705319307
C	-0.163390037800	3.280064950148	1.228960668677
C	-0.043998025225	0.874389927417	1.743295306805
C	0.410725769337	-1.547814850065	1.987772270110
H	0.429808945532	-2.433095635649	2.614838767537
C	0.188842394366	-0.273958651814	2.627086098072
C	0.084774655150	2.176246572892	2.120261535405
H	0.420543095234	2.415470501115	3.121449010002
C	0.667898755645	-1.255953712465	4.879553477056
H	1.231001562628	-2.069401585339	4.444756548811
C	-1.946740812262	0.063686626259	0.360772300195
H	-2.578268241030	0.869476885716	0.742517746153
H	-2.051700831559	-0.801131556797	1.017996431059
H	-2.301471979996	-0.207366356544	-0.636013779546
C	-0.469683911595	0.553934945844	0.299430343930
C	-0.679292607727	0.776436972352	6.134557368504
H	-1.239978795153	1.519902983079	6.686667642557
C	-0.589249416202	0.799582914250	4.783402291473
H	-1.122039862010	1.580295614608	4.261821778141
C	-0.442961322591	1.755921438512	-0.639485550837
N	0.098615196023	0.219212299395	-6.898878059627
C	-0.106390988088	0.223047612829	-4.030012869803
C	-0.578084990245	1.219730323995	-6.230145362390
H	-1.038674541384	1.972067786077	-6.857403516112
C	0.020747349401	0.098741874615	-8.345467151122
H	-0.848723050930	-0.489910343382	-8.663520796366
H	-0.046811495946	1.091613653298	-8.792492712554
H	0.924610248021	-0.383564645097	-8.721930678021
C	0.424152225860	-3.078029048927	0.088465001663
H	0.544535805636	-3.920532851577	0.763705319307
C	0.163390037800	-3.280064950148	-1.228960668677
C	0.043998025225	-0.874389927417	-1.743295306805
C	-0.410725769337	1.547814850065	-1.987772270110
H	-0.429808945532	2.433095635649	-2.614838767537
C	-0.188842394366	0.273958651814	-2.627086098072
C	-0.084774655150	-2.176246572892	-2.120261535405
H	-0.420543095234	-2.415470501115	-3.121449010002
C	-0.667898755645	1.255953712465	-4.879553477056
H	-1.231001562628	2.069401585339	-4.444756548811
C	1.946740812262	-0.063686626259	-0.360772300195
H	2.578268241030	-0.869476885716	-0.742517746153
H	2.051700831559	0.801131556797	-1.017996431059
C	0.469683911595	-0.553934945844	-0.299430343930
C	0.679292607727	-0.776436972352	-6.134557368504
H	1.239978795153	-1.519902983079	-6.686667642557
C	0.589249416202	-0.799582914250	-4.783402291473
H	1.122039862010	-1.580295614608	-4.261821778141
C	0.442961322591	-1.755921438512	0.639485550837
H	2.301471979996	0.207366356544	0.636013779546
H	-0.090431366538	4.288409127640	1.622429467616
H	0.090431366538	-4.288409127640	-1.622429467616

B3LYP energy:

$E(S_0)$ = -1269.747213 a.u.

Table S1 (continued). Unrestricted B3LYP/6-311G(d,p) Cartesian coordinates and energy for open-shell triplet of $\mathbf{1_c}$.

N	-0.059434623750	-0.228318263056	6.912516572365
C	0.032429989003	-0.228673858291	4.059414815028
C	0.789297607669	-1.087213683835	6.221258000867
H	1.406583338207	-1.730185193289	6.833900963295
C	0.078163303281	-0.051452221404	8.346146079384
H	0.845988623796	0.692162459661	8.599687556566
H	0.348207998278	-1.002054934620	8.809438630189
H	-0.873923637081	0.274921875292	8.768815100067
C	-0.218287701411	3.076155089542	-0.063995322469
H	-0.201304164384	3.941152141790	-0.720783372490
C	-0.119244812168	3.249208051597	1.309646328446
C	-0.088022351905	0.841891771378	1.756752348430
C	0.157026074175	-1.576942072577	1.998256481042
H	0.123381019957	-2.451227342809	2.641721957474
C	0.049788854479	-0.301126944533	2.601764442848
C	-0.016269029977	2.157130042028	2.190721839362
H	0.183742036044	2.363153276883	3.234636403459
C	0.825923577502	-1.109441047327	4.861723596680
H	1.508845102648	-1.802261361204	4.386042028586
C	-1.958269361848	0.258583351633	0.239502994616
H	-2.510658061014	1.122000503106	0.616100149433
H	-2.193327084551	-0.602776845221	0.866506457590
H	-2.291201287859	0.055096496662	-0.779673828983
C	-0.426487025671	0.583902227673	0.277687375953
C	-0.849161830939	0.642369201411	6.166318856586
H	-1.511286139887	1.279041616035	6.737593404532
C	-0.817733861864	0.647649894231	4.806368958849
H	-1.498654134052	1.310094612945	4.289157817385
C	-0.243095422933	1.796046817070	-0.630114120437
N	0.059434623750	0.228318263056	-6.912516572365
C	-0.032429989003	0.228673858291	-4.059414815028
C	-0.789297607669	1.087213683835	-6.221258000867
H	-1.406583338207	1.730185193289	-6.833900963295
C	-0.078163303281	0.051452221404	-8.346146079384
H	-0.845988623796	-0.692162459661	-8.599687556566
H	-0.348207998278	1.002054934620	-8.809438630189
H	0.873923637081	-0.274921875292	-8.768815100067
C	0.218287701411	-3.076155089542	0.063995322469
H	0.201304164384	-3.941152141790	0.720783372490
C	0.119244812168	-3.249208051597	-1.309646328446
C	0.088022351905	-0.841891771378	-1.756752348430
C	-0.157026074175	1.576942072577	-1.998256481042
H	-0.123381019957	2.451227342809	-2.641721957474
C	-0.049788854479	0.301126944533	-2.601764442848
C	0.016269029977	-2.157130042028	-2.190721839362
H	-0.183742036044	-2.363153276883	-3.234636403459
C	-0.825923577502	1.109441047327	-4.861723596680
H	-1.508845102648	1.802261361204	-4.386042028586
C	1.958269361848	-0.258583351633	-0.239502994616
H	2.510658061014	-1.122000503106	-0.616100149433
H	2.193327084551	0.602776845221	-0.866506457590
C	0.426487025671	-0.583902227673	-0.277687375953
C	0.849161830939	-0.642369201411	-6.166318856586
H	1.511286139887	-1.279041616035	-6.737593404532
C	0.817733861864	-0.647649894231	-4.806368958849
H	1.498654134052	-1.310094612945	-4.289157817385
C	0.243095422933	-1.796046817070	0.630114120437
H	2.291201287859	-0.055096496662	0.779673828983
H	-0.046798697820	4.253081365084	1.714467183553
H	0.046798697820	-4.253081365084	-1.714467183553

Unrestricted B3LYP energy:

E(triplet) = -1269.729179 a.u.
$\langle S^2 \rangle = 2.02316$

Table S1 (continued). Broken-symmetry B3LYP/6-311G(d,p) Cartesian coordinates and energy for open-shell singlet of $\mathbf{1_o}$.

N	-0.117642310807	-0.196198524711	-6.823747278069
C	-0.226628537809	0.104917964989	-3.982396922554
C	2.957499366169	0.475377772269	0.146795392814
H	3.676146705483	0.731176298725	0.919625868336
C	1.841825922090	-0.313651337412	0.493358834637
C	-1.246729012525	0.611081932184	-4.868415205529
H	-2.092423643943	1.156382721349	-4.472201560382
C	-0.311421651398	0.175490604031	-2.553055004348
C	2.032228787719	0.879310677244	-2.026419537322
H	2.023196996002	1.458228491187	-2.942995961064
C	0.870327784192	-0.525725043376	-4.660183923938
H	1.688595320608	-0.936459164688	-4.084140147642
C	0.949467657879	0.032417276321	-1.740770653069
C	-1.532171119877	0.427639690859	-1.921111910534
H	-2.409188173599	0.424018881768	-2.562121234609
C	-1.168247509605	0.468506056376	-6.214287995216
H	-1.919939581184	0.866619025802	-6.883355940274
C	0.977981997653	-0.737711559990	-0.556562016787
C	0.171354226264	-2.006355461713	-0.433652107371
H	-0.309316996784	-2.131250813699	0.534601489931
H	0.860776775349	-2.850494678440	-0.561734620344
H	-0.584373807987	-2.080659465697	-1.213950770007
C	0.911093185199	-0.659408642583	-6.011324164626
H	1.726795595519	-1.150975633739	-6.524173350261
C	3.088186641212	1.014286357850	-1.126052288129
C	0.033912328789	-0.185684306376	-8.268221763780
H	-0.949736517170	-0.164486186397	-8.739358704753
H	0.545917300621	-1.094197465359	-8.591140964203
H	0.608686630460	0.682375789233	-8.616412749167
N	0.117642310807	0.196198524711	6.823747278069
C	0.226628537809	-0.104917964989	3.982396922554
C	-2.957499366169	-0.475377772269	-0.146795392814
H	-3.676146705483	-0.731176298725	-0.919625868336
C	-1.841825922090	0.313651337412	-0.493358834637
C	1.246729012525	-0.611081932184	4.868415205529
H	2.092423643943	-1.156382721349	4.472201560382
C	0.311421651398	-0.175490604031	2.553055004348
C	-2.032228787719	-0.879310677244	2.026419537321
H	-2.023196996002	-1.458228491187	2.942995961064
C	-0.870327784192	0.525725043376	4.660183923938
H	-1.688595320608	0.936459164688	4.084140147642
C	-0.949467657879	-0.032417276321	1.740770653069
C	1.532171119877	-0.427639690859	1.921111910534
H	2.409188173599	-0.424018881768	2.562121234609
C	1.168247509605	-0.468506056376	6.214287995216
H	1.919939581184	-0.866619025802	6.883355940274
C	-0.977981997653	0.737711559990	0.556562016787
C	-0.171354226264	2.006355461713	0.433652107371
H	0.309316996784	2.131250813699	-0.534601489931
H	-0.860776775349	2.850494678440	0.561734620344
H	0.584373807987	2.080659465697	1.213950770007
C	-0.911093185199	0.659408642583	6.011324164626
H	-1.726795595519	1.150975633739	6.524173350261
C	-3.088186641212	-1.014286357850	1.126052288129
C	-0.033912328789	0.185684306376	8.268221763780
H	0.949736517170	0.164486186397	8.739358704753
H	-0.545917300621	1.094197465359	8.591140964203
H	-0.608686630460	-0.682375789233	8.616412749167
H	-3.947615147674	-1.626702597423	1.376190459627
H	3.947615147674	1.626702597423	-1.376190459627

Broken-symmetry B3LYP energy:

E(BS) = -1269.711658 a.u.
$\langle S^2 \rangle$ = 1.05842

E(triplet) = -1269.711083 a.u.
$\langle S^2 \rangle$ = 2.05489

Table S1 (continued). Unrestricted B3LYP/6-311G(d,p) Cartesian coordinates and energy for open-shell triplet of $\mathbf{1_o}$.

N	-0.121236275697	-0.201955075556	-6.823893278472
C	-0.227226890664	0.110376857701	-3.983790219838
C	2.949357159265	0.475418356363	0.152332366460
H	3.663796373061	0.730307572990	0.929271527996
C	1.837387176988	-0.321453634363	0.489780933806
C	-1.249384898208	0.611431349882	-4.870515696469
H	-2.095786332530	1.156803329286	-4.475976315488
C	-0.310858349611	0.185067199528	-2.553432770168
C	2.030258111703	0.890363723865	-2.020514376597
H	2.020473973928	1.475192315883	-2.933300896483
C	0.869192023121	-0.521590369417	-4.659551680033
H	1.688645748457	-0.928499198230	-4.082361447623
C	0.950072587203	0.037074104353	-1.742105730541
C	-1.526923568912	0.446618217542	-1.919307447361
H	-2.404991602321	0.455218479179	-2.558778057349
C	-1.171845036501	0.463802037436	-6.215870274376
H	-1.924756826433	0.858426283268	-6.885667314361
C	0.978053691382	-0.741248906517	-0.564366010063
C	0.166118864874	-2.007251957533	-0.448496310430
H	-0.342441931703	-2.120714730380	0.506737412060
H	0.856600013153	-2.854223369132	-0.547611229405
H	-0.567807892297	-2.087589730707	-1.248929072856
C	0.909288929711	-0.661168253488	-6.010430474350
H	1.724940942303	-1.153950586445	-6.522067921744
C	3.082765819532	1.023016865323	-1.117156005100
C	0.030478027544	-0.194965906826	-8.268283976910
H	-0.953029967642	-0.169917616933	-8.739469343030
H	0.538182980133	-1.106540081962	-8.589553111966
H	0.609451620610	0.669678341572	-8.618141335434
N	0.121236275697	0.201955075556	6.823893278472
C	0.227226890664	-0.110376857701	3.983790219838
C	-2.949357159265	-0.475418356363	-0.152332366460
H	-3.663796373061	-0.730307572990	-0.929271527996
C	-1.837387176988	0.321453634363	-0.489780933806
C	1.249384898208	-0.611431349882	4.870515696469
H	2.095786332530	-1.156803329286	4.475976315488
C	0.310858349611	-0.185067199528	2.553432770168
C	-2.030258111703	-0.890363723865	2.020514376597
H	-2.020473973928	-1.475192315883	2.933300896483
C	-0.869192023121	0.521590369417	4.659551680033
H	-1.688645748457	0.928499198230	4.082361447623
C	-0.950072587203	-0.037074104353	1.742105730541
C	1.526923568912	-0.446618217542	1.919307447361
H	2.404991602321	-0.455218479179	2.558778057349
C	1.171845036501	-0.463802037436	6.215870274376
H	1.924756826433	-0.858426283268	6.885667314361
C	-0.978053691382	0.741248906517	0.564366010063
C	-0.166118864874	2.007251957533	0.448496310430
H	0.342441931703	2.120714730380	-0.506737412060
H	-0.856600013153	2.854223369132	0.547611229405
H	0.567807892297	2.087589730707	1.248929072856
C	-0.909288929711	0.661168253488	6.010430474350
H	-1.724940942303	1.153950586445	6.522067921744
C	-3.082765819532	-1.023016865323	1.117156005100
C	-0.030478027544	0.194965906826	8.268283976910
H	0.953029967642	0.169917616933	8.739469343030
H	-0.538182980133	1.106540081962	8.589553111966
H	-0.609451620610	-0.669678341572	8.618141335434
H	-3.940961314142	-1.639929102058	1.360374986033
H	3.940961314142	1.639929102058	-1.360374986033

Unrestricted B3LYP energy:

E(triplet) = -1269.711129 a.u.
$\langle S^2 \rangle = 2.05445$

Table S1 (continued). B3LYP/6-311G(d,p) Cartesian coordinates and energy for closed-shell singlet of $\mathbf{2_c}^{4+}$.

N	0.200171248163	3.029944642130	6.105937772825
C	0.023542353457	1.481296925860	3.785154783473
C	1.247434896131	2.267669055573	5.719390579753
H	2.135700390178	2.319305098430	6.335453831243
C	0.315406199749	3.908726712881	7.305839607463
H	0.652886149388	4.897079156586	6.991579508068
H	1.032442667439	3.473175647967	7.997755600033
H	-0.657699188605	3.981634874897	7.786769689173
C	-0.088459577134	2.821988664541	-1.220069264821
H	0.027565869677	3.413255816530	-2.118509726769
C	-0.093262737257	3.496288005900	0.000000000000
C	-0.151906115871	1.432055639302	1.291301593117
C	0.045935200688	-0.708256015271	2.504373131863
C	-0.045935200688	0.708256015271	2.504373131863
C	-0.088459577134	2.821988664541	1.220069264821
H	0.027565869677	3.413255816530	2.118509726769
C	1.180329841004	1.487123550953	4.580130689589
H	2.055508988795	0.916485457565	4.298717439055
C	-1.961226796225	0.363169677763	0.000000000000
H	-2.506955976061	1.307554882555	0.000000000000
H	-2.258164337520	-0.203518607621	0.883113483325
H	-2.258164337520	-0.203518607621	-0.883113483325
C	-0.418440168719	0.649089063593	0.000000000000
C	-0.938030341211	3.034058230975	5.374942515739
H	-1.743477689267	3.659302671467	5.738142643509
C	-1.047258040067	2.279326549695	4.222860026058
H	-1.974901423299	2.321843929619	3.666720634459
C	-0.151906115871	1.432055639302	-1.291301593117
N	-0.200171248163	-3.029944642130	-6.105937772825
C	-0.023542353457	-1.481296925860	-3.785154783473
C	-1.247434896131	-2.267669055573	-5.719390579753
H	-2.135700390178	-2.319305098430	-6.335453831243
C	-0.315406199749	-3.908726712881	-7.305839607463
H	-0.652886149388	-4.897079156586	-6.991579508068
H	-1.032442667439	-3.473175647967	-7.997755600033
H	0.657699188605	-3.981634874897	-7.786769689173
C	0.088459577134	-2.821988664541	1.220069264821
H	-0.027565869677	-3.413255816530	2.118509726769
C	0.093262737257	-3.496288005900	0.000000000000
C	0.151906115871	-1.432055639302	-1.291301593117
C	-0.045935200688	0.708256015271	-2.504373131863
C	0.045935200688	-0.708256015271	-2.504373131863
C	0.088459577134	-2.821988664541	-1.220069264821
H	-0.027565869677	-3.413255816530	-2.118509726769
C	-1.180329841004	-1.487123550953	-4.580130689589
H	-2.055508988795	-0.916485457565	-4.298717439055
C	1.961226796225	-0.363169677763	0.000000000000
H	2.506955976061	-1.307554882555	0.000000000000
H	2.258164337520	0.203518607621	-0.883113483325
C	0.418440168719	-0.649089063593	0.000000000000
C	0.938030341211	-3.034058230975	-5.374942515739
H	1.743477689267	-3.659302671467	-5.738142643509
C	1.047258040067	-2.279326549695	-4.222860026058
H	1.974901423299	-2.321843929619	-3.666720634459
C	0.151906115871	-1.432055639302	1.291301593117
H	2.258164337520	0.203518607621	0.883113483325
H	-0.026579057287	4.577739659719	0.000000000000
H	0.026579057287	-4.577739659719	0.000000000000
N	-0.200171248163	-3.029944642130	6.105937772825
C	-0.023542353457	-1.481296925860	3.785154783473
C	-1.247434896131	-2.267669055573	5.719390579753
H	-2.135700390178	-2.319305098430	6.335453831243
C	-0.315406199749	-3.908726712881	7.305839607463
H	-0.652886149388	-4.897079156586	6.991579508068
H	-1.032442667439	-3.473175647967	7.997755600033
H	0.657699188605	-3.981634874897	7.786769689173
C	-1.180329841004	-1.487123550953	4.580130689589
H	-2.055508988795	-0.916485457565	4.298717439055
C	0.938030341211	-3.034058230975	5.374942515739
H	1.743477689267	-3.659302671467	5.738142643509
C	1.047258040067	-2.279326549695	4.222860026058
H	1.974901423299	-2.321843929619	3.666720634459
N	0.200171248163	3.029944642130	-6.105937772825
C	0.023542353457	1.481296925860	-3.785154783473
C	-0.938030341211	3.034058230975	-5.374942515739
H	-1.743477689267	3.659302671467	-5.738142643509
C	0.315406199749	3.908726712881	-7.305839607463
H	-0.657699188605	3.981634874897	-7.786769689173
H	0.652886149388	4.897079156586	-6.991579508068
H	1.032442667439	3.473175647967	-7.997755600033
C	-1.047258040067	2.279326549695	-4.222860026058
H	-1.974901423299	2.321843929619	-3.666720634459
C	1.247434896131	2.267669055573	-5.719390579753
H	2.135700390178	2.319305098430	-6.335453831243
C	1.180329841004	1.487123550953	-4.580130689589
H	2.055508988795	0.916485457565	-4.298717439055

B3LYP energy:

$E(S_0)$ = -1842.688470 a.u.

Table S1 (continued). B3LYP/6-311G(d,p) Cartesian coordinates and energy for closed-shell singlet of $\mathbf{2_o}^{4+}$.

N	-3.192638675052	0.056714062119	5.948920481085
C	-1.502991016478	-0.005839626330	3.722979557743
C	-2.240131885605	1.001295087024	5.796090649470
H	-2.194893579805	1.769893614273	6.556453074824
C	-4.133368598207	0.108286835072	7.105393380721
H	-5.093046005671	0.499417461058	6.766044198460
H	-3.718712308454	0.758242292328	7.871769866558
H	-4.257702662917	-0.896231996198	7.506041245971
C	-2.432129498331	1.174677860525	-1.192504716437
H	-2.706356422554	1.670355889452	-2.116066211105
C	-2.967409199551	1.643000189359	0.000000000000
C	-1.506009022167	0.117080745856	1.209348981663
C	0.686984576644	0.026405873064	2.468195852064
C	-0.686984576644	-0.026405873064	2.468195852064
C	-2.432129498331	1.174677860525	1.192504716437
H	-2.706356422554	1.670355889452	2.116066211105
C	-1.386540027010	0.987995503086	4.707065144593
H	-0.660693158630	1.785104844377	4.618135733040
C	-0.697440671412	-1.975752364087	0.000000000000
H	-1.569090813851	-2.640848193657	0.000000000000
H	-0.112924195936	-2.222048957463	0.884016899339
H	-0.112924195936	-2.222048957463	-0.884016899339
C	-1.211521501489	-0.561607592389	0.000000000000
C	-3.329701891693	-0.920881862109	5.021002749175
H	-4.112011676745	-1.647733261466	5.198113273192
C	-2.516048748617	-0.964294312535	3.908280028087
H	-2.679856362924	-1.749681232496	3.182017412277
C	-1.506009022167	0.117080745856	-1.209348981663
N	3.192638675052	-0.056714062119	-5.948920481085
C	1.502991016478	0.005839626330	-3.722979557743
C	2.240131885605	-1.001295087024	-5.796090649470
H	2.194893579805	-1.769893614273	-6.556453074824
C	4.133368598207	-0.108286835072	-7.105393380721
H	5.093046005671	-0.499417461058	-6.766044198460
H	3.718712308454	-0.758242292328	-7.871769866558
H	4.257702662917	0.896231996198	-7.506041245971
C	2.432129498331	-1.174677860525	1.192504716437
H	2.706356422554	-1.670355889452	2.116066211105
C	2.967409199551	-1.643000189359	0.000000000000
C	1.506009022167	-0.117080745856	-1.209348981663
C	-0.686984576644	-0.026405873064	-2.468195852064
C	0.686984576644	0.026405873064	-2.468195852064
C	2.432129498331	-1.174677860525	-1.192504716437
H	2.706356422554	-1.670355889452	-2.116066211105
C	1.386540027010	-0.987995503086	-4.707065144593
H	0.660693158630	-1.785104844377	-4.618135733040
C	0.697440671412	1.975752364087	0.000000000000
H	1.569090813851	2.640848193657	0.000000000000
H	0.112924195936	2.222048957463	-0.884016899339
C	1.211521501489	0.561607592389	0.000000000000
C	3.329701891693	0.920881862109	-5.021002749175
H	4.112011676745	1.647733261466	-5.198113273193
C	2.516048748617	0.964294312535	-3.908280028087
H	2.679856362924	1.749681232496	-3.182017412277
C	1.506009022167	-0.117080745856	1.209348981663
H	0.112924195936	2.222048957463	0.884016899339
H	-3.707390944042	2.433192717394	0.000000000000
H	3.707390944042	-2.433192717394	0.000000000000
N	3.192638675052	-0.056714062119	5.948920481085
C	1.502991016478	0.005839626330	3.722979557743
C	2.240131885605	-1.001295087024	5.796090649470
H	2.194893579805	-1.769893614273	6.556453074824
C	4.133368598207	-0.108286835072	7.105393380721
H	5.093046005671	-0.499417461058	6.766044198460
H	3.718712308454	-0.758242292328	7.871769866558
H	4.257702662917	0.896231996198	7.506041245971
C	1.386540027010	-0.987995503086	4.707065144593
H	0.660693158630	-1.785104844377	4.618135733040
C	3.329701891693	0.920881862109	5.021002749175
H	4.112011676745	1.647733261466	5.198113273192
C	2.516048748617	0.964294312535	3.908280028087
H	2.679856362924	1.749681232496	3.182017412277
N	-3.192638675052	0.056714062119	-5.948920481085
C	-1.502991016478	-0.005839626330	-3.722979557743
C	-3.329701891693	-0.920881862109	-5.021002749175
H	-4.112011676745	-1.647733261466	-5.198113273193
C	-4.133368598207	0.108286835072	-7.105393380721
H	-4.257702662917	-0.896231996198	-7.506041245971
H	-5.093046005671	0.499417461058	-6.766044198460
H	-3.718712308454	0.758242292328	-7.871769866558
C	-2.516048748617	-0.964294312535	-3.908280028087
H	-2.679856362924	-1.749681232496	-3.182017412277
C	-2.240131885605	1.001295087024	-5.796090649470
H	-2.194893579805	1.769893614273	-6.556453074824
C	-1.386540027010	0.987995503086	-4.707065144593
H	-0.660693158630	1.785104844377	-4.618135733040

B3LYP energy:

$E(S_0)$ = -1842.655842 a.u.

Table S1 (continued). Unrestricted B3LYP/6-311G(d,p) Cartesian coordinates and energy for open-shell quintet of $\mathbf{2_c}$.

N	0.021485427964	2.864477052312	6.265825363560
C	-0.040609953347	1.450340455646	3.789880489485
C	1.036266246651	1.972654002516	5.917745738704
H	1.832840506006	1.865837060525	6.641653725888
C	0.209640680300	3.790035018225	7.365956220182
H	0.768482818977	4.687904686846	7.064948557335
H	0.755496260458	3.296335331781	8.172178194976
H	-0.762156850906	4.101893263386	7.754197729494
C	-0.106407877592	2.816471965498	-1.218961261489
H	0.022724674922	3.389284117728	-2.127808060122
C	-0.093193650903	3.494055845372	0.000000000000
C	-0.186856525447	1.426713167753	1.292847467923
C	0.067034129405	-0.712687359371	2.513596710266
C	-0.067034129405	0.712687359371	2.513596710266
C	-0.106407877592	2.816471965498	1.218961261489
H	0.022724674922	3.389284117728	2.127808060122
C	1.005132691919	1.277415941825	4.749580328957
H	1.812415582253	0.586033775554	4.547017838845
C	-1.965774071728	0.285799951688	0.000000000000
H	-2.540849746249	1.214528567654	0.000000000000
H	-2.237526373986	-0.289137988457	0.887175254597
H	-2.237526373986	-0.289137988457	-0.887175254597
C	-0.441717538760	0.636448850148	0.000000000000
C	-0.997627223257	3.080860369118	5.337036817553
H	-1.760165980915	3.788025677761	5.634444799373
C	-1.036785685803	2.402880153619	4.155541416360
H	-1.871923967945	2.587571905665	3.490907225002
C	-0.186856525447	1.426713167753	-1.292847467923
N	-0.021485427964	-2.864477052312	-6.265825363560
C	0.040609953347	-1.450340455646	-3.789880489485
C	-1.036266246651	-1.972654002516	-5.917745738704
H	-1.832840506006	-1.865837060525	-6.641653725888
C	-0.209640680300	-3.790035018225	-7.365956220182
H	-0.768482818977	-4.687904686846	-7.064948557335
H	-0.755496260458	-3.296335331781	-8.172178194976
H	0.762156850906	-4.101893263386	-7.754197729494
C	0.106407877592	-2.816471965498	1.218961261489
H	-0.022724674922	-3.389284117728	2.127808060122
C	0.093193650903	-3.494055845372	0.000000000000
C	0.186856525447	-1.426713167753	-1.292847467923
C	-0.067034129405	0.712687359371	-2.513596710266
C	0.067034129405	-0.712687359371	-2.513596710266
C	0.106407877592	-2.816471965498	-1.218961261489
H	-0.022724674922	-3.389284117728	-2.127808060122
C	-1.005132691919	-1.277415941825	-4.749580328957
H	-1.812415582253	-0.586033775554	-4.547017838845
C	1.965774071728	-0.285799951688	0.000000000000
H	2.540849746249	-1.214528567654	0.000000000000
H	2.237526373986	0.289137988457	-0.887175254597
C	0.441717538760	-0.636448850148	0.000000000000
C	0.997627223257	-3.080860369118	-5.337036817553
H	1.760165980915	-3.788025677761	-5.634444799373
C	1.036785685803	-2.402880153619	-4.155541416360
H	1.871923967945	-2.587571905665	-3.490907225002
C	0.186856525447	-1.426713167753	1.292847467923
H	2.237526373986	0.289137988457	0.887175254597
H	0.014061023895	4.573791480274	0.000000000000
H	-0.014061023895	-4.573791480274	0.000000000000
N	-0.021485427964	-2.864477052312	6.265825363560
C	0.040609953347	-1.450340455646	3.789880489484
C	-1.036266246651	-1.972654002516	5.917745738704
H	-1.832840506006	-1.865837060525	6.641653725888
C	-0.209640680300	-3.790035018225	7.365956220182
H	-0.768482818977	-4.687904686846	7.064948557335
H	-0.755496260458	-3.296335331781	8.172178194976
H	0.762156850906	-4.101893263386	7.754197729494
C	-1.005132691919	-1.277415941825	4.749580328957
H	-1.812415582253	-0.586033775554	4.547017838845
C	0.997627223257	-3.080860369118	5.337036817553
H	1.760165980915	-3.788025677761	5.634444799373
C	1.036785685803	-2.402880153619	4.155541416360
H	1.871923967945	-2.587571905665	3.490907225002
N	0.021485427964	2.864477052312	-6.265825363560
C	-0.040609953347	1.450340455646	-3.789880489484
C	-0.997627223257	3.080860369118	-5.337036817553
H	-1.760165980915	3.788025677761	-5.634444799373
C	0.209640680300	3.790035018225	-7.365956220182
H	-0.762156850906	4.101893263386	-7.754197729494
H	0.768482818977	4.687904686846	-7.064948557335
H	0.755496260458	3.296335331781	-8.172178194976
C	-1.036785685803	2.402880153619	-4.155541416360
H	-1.871923967945	2.587571905665	-3.490907225002
C	1.036266246651	1.972654002516	-5.917745738704
H	1.832840506006	1.865837060525	-6.641653725888
C	1.005132691919	1.277415941825	-4.749580328957
H	1.812415582253	0.586033775554	-4.547017838845

Unrestricted B3LYP energy:

E(quintet) = -1843.764589 a.u.
$\langle S^2 \rangle = 6.05656$

Table S1 (continued). B3LYP/6-311G(d,p) Cartesian coordinates and energy for closed-shell singlet of **2$_c$**.

N	-0.112397864386	2.996589245756	6.192687216938
C	-0.118538563661	1.469671840406	3.758453876800
C	0.790126428336	1.968143647751	5.984390568122
H	1.510527975226	1.811682054811	6.776876823674
C	0.049371916246	3.915033439778	7.304759663233
H	0.725617198925	4.746218761355	7.062440967988
H	0.450953306398	3.380182538752	8.166955329346
H	-0.921768446258	4.329336489648	7.583552648390
C	0.048519629797	2.780664743867	-1.206735449797
H	0.292986889185	3.317055725968	-2.114043163952
C	0.150534408655	3.468300298083	0.000000000000
C	-0.253756919133	1.424934318849	1.282943438428
C	0.134769066849	-0.721279416984	2.546717032049
C	-0.134769066849	0.721279416984	2.546717032049
C	0.048519629797	2.780664743867	1.206735449797
H	0.292986889185	3.317055725968	2.114043163952
C	0.783527977361	1.213964850537	4.857838345434
H	1.525537480032	0.433838075682	4.769997432955
C	-1.966252842271	0.125650599398	0.000000000000
H	-2.655241721795	0.974829619192	0.000000000000
H	-2.163536490236	-0.480722152012	0.887222915771
H	-2.163536490236	-0.480722152012	-0.887222915771
C	-0.507865513506	0.641704900737	0.000000000000
C	-0.991282873715	3.292013253552	5.158810303939
H	-1.687785419766	4.097128984176	5.354136530231
C	-0.997209286394	2.589875352867	3.998970554845
H	-1.730588350268	2.854795730768	3.249313732071
C	-0.253756919133	1.424934318849	-1.282943438428
N	0.112397864386	-2.996589245756	-6.192687216938
C	0.118538563661	-1.469671840406	-3.758453876800
C	-0.790126428336	-1.968143647751	-5.984390568122
H	-1.510527975226	-1.811682054811	-6.776876823674
C	-0.049371916246	-3.915033439778	-7.304759663233
H	-0.725617198925	-4.746218761355	-7.062440967988
H	-0.450953306398	-3.380182538752	-8.166955329346
H	0.921768446258	-4.329336489648	-7.583552648390
C	-0.048519629797	-2.780664743867	1.206735449797
H	-0.292986889185	-3.317055725968	2.114043163952
C	-0.150534408655	-3.468300298083	0.000000000000
C	0.253756919133	-1.424934318849	-1.282943438428
C	-0.134769066849	0.721279416984	-2.546717032049
C	0.134769066849	-0.721279416984	-2.546717032049
C	-0.048519629797	-2.780664743867	-1.206735449797
H	-0.292986889185	-3.317055725968	-2.114043163952
C	-0.783527977361	-1.213964850537	-4.857838345434
H	-1.525537480032	-0.433838075682	-4.769997432955
C	1.966252842271	-0.125650599398	0.000000000000
H	2.655241721795	-0.974829619192	0.000000000000
H	2.163536490236	0.480722152012	-0.887222915771
C	0.507865513506	-0.641704900737	0.000000000000
C	0.991282873715	-3.292013253552	-5.158810303939
H	1.687785419766	-4.097128984176	-5.354136530231
C	0.997209286394	-2.589875352867	-3.998970554845
H	1.730588350268	-2.854795730768	-3.249313732071
C	0.253756919133	-1.424934318849	1.282943438428
H	2.163536490236	0.480722152012	0.887222915771
H	0.418511601303	4.519205587238	0.000000000000
H	-0.418511601303	-4.519205587238	0.000000000000
N	0.112397864386	-2.996589245756	6.192687216938
C	0.118538563661	-1.469671840406	3.758453876800
C	-0.790126428336	-1.968143647751	5.984390568122
H	-1.510527975226	-1.811682054811	6.776876823674
C	-0.049371916246	-3.915033439778	7.304759663233
H	-0.725617198925	-4.746218761355	7.062440967988
H	-0.450953306398	-3.380182538752	8.166955329346
H	0.921768446258	-4.329336489648	7.583552648390
C	-0.783527977361	-1.213964850537	4.857838345434
H	-1.525537480032	-0.433838075682	4.769997432955
C	0.991282873715	-3.292013253552	5.158810303939
H	1.687785419766	-4.097128984176	5.354136530231
C	0.997209286394	-2.589875352867	3.998970554845
H	1.730588350268	-2.854795730768	3.249313732071
N	-0.112397864386	2.996589245756	-6.192687216938
C	-0.118538563661	1.469671840406	-3.758453876800
C	-0.991282873715	3.292013253552	-5.158810303939
H	-1.687785419766	4.097128984176	-5.354136530231
C	0.049371916246	3.915033439778	-7.304759663233
H	-0.921768446258	4.329336489648	-7.583552648390
H	0.725617198925	4.746218761355	-7.062440967988
H	0.450953306398	3.380182538752	-8.166955329346
C	-0.997209286394	2.589875352867	-3.998970554845
H	-1.730588350268	2.854795730768	-3.249313732071
C	0.790126428336	1.968143647751	-5.984390568122
H	1.510527975226	1.811682054811	-6.776876823674
C	0.783527977361	1.213964850537	-4.857838345434
H	1.525537480032	0.433838075682	-4.769997432955

B3LYP energy:

$E(S_0)$ = -1843.759651 a.u.

Table S1 (continued). B3LYP/6-311G(d,p) Cartesian coordinates and energy for closed-shell singlet of **2_o**.

N	-3.120715857076	0.016584067955	6.066290397500
C	-1.497878928102	-0.050509548213	3.687677784901
C	-1.979902851858	0.790495240213	5.949172396879
H	-1.768467222944	1.440539034780	6.788771262210
C	-4.030794584277	0.193171526798	7.182425793132
H	-4.762037347585	0.993082656035	7.002356602386
H	-3.464757339257	0.436685795438	8.083052841299
H	-4.573821651362	-0.736410244756	7.365531782487
C	-2.603049970951	0.729063091243	-1.188859151941
H	-2.927872518933	1.194113059810	-2.110328212595
C	-3.212553835356	1.093768849960	0.000000000000
C	-1.509872122156	-0.156906840892	1.224200596312
C	0.722309544320	0.130269348458	2.513559112219
C	-0.722309544320	-0.130269348458	2.513559112219
C	-2.603049970951	0.729063091243	1.188859151941
H	-2.927872518933	1.194113059810	2.110328212595
C	-1.184139636764	0.753101238029	4.854918426088
H	-0.318237197797	1.397687864247	4.841643324767
C	-0.331637034375	-2.054293986899	0.000000000000
H	-1.058271687924	-2.877454537223	0.000000000000
H	0.288479876756	-2.172815912936	0.887060699993
H	0.288479876756	-2.172815912936	-0.887060699993
C	-1.102863997779	-0.759962493568	0.000000000000
C	-3.506708471872	-0.715145753877	4.950014665534
H	-4.424483564270	-1.278882011104	5.057423904675
C	-2.765832509286	-0.746406051673	3.818792701865
H	-3.117323710166	-1.358860319553	2.999395922872
C	-1.509872122156	-0.156906840892	-1.224200596312
N	3.120715857076	-0.016584067955	-6.066290397500
C	1.497878928102	0.050509548213	-3.687677784901
C	1.979902851858	-0.790495240213	-5.949172396879
H	1.768467222944	-1.440539034780	-6.788771262210
C	4.030794584277	-0.193171526798	-7.182425793132
H	4.762037347585	-0.993082656035	-7.002356602386
H	3.464757339257	-0.436685795438	-8.083052841299
H	4.573821651362	0.736410244756	-7.365531782487
C	2.603049970951	-0.729063091243	1.188859151941
H	2.927872518933	-1.194113059810	2.110328212595
C	3.212553835356	-1.093768849960	0.000000000000
C	1.509872122156	0.156906840892	-1.224200596312
C	-0.722309544320	-0.130269348458	-2.513559112219
C	0.722309544320	0.130269348458	-2.513559112219
C	2.603049970951	-0.729063091243	-1.188859151941
H	2.927872518933	-1.194113059810	-2.110328212595
C	1.184139636764	-0.753101238029	-4.854918426088
H	0.318237197797	-1.397687864247	-4.841643324767
C	0.331637034375	2.054293986899	0.000000000000
H	1.058271687924	2.877454537223	0.000000000000
H	-0.288479876756	2.172815912936	-0.887060699993
C	1.102863997779	0.759962493568	0.000000000000
C	3.506708471872	0.715145753877	-4.950014665534
H	4.424483564270	1.278882011104	-5.057423904675
C	2.765832509286	0.746406051673	-3.818792701865
H	3.117323710166	1.358860319553	-2.999395922872
C	1.509872122156	0.156906840892	1.224200596312
H	-0.288479876756	2.172815912936	0.887060699993
H	-4.058361690988	1.773307219056	0.000000000000
H	4.058361690988	-1.773307219056	0.000000000000
N	3.120715857076	-0.016584067955	6.066290397500
C	1.497878928102	0.050509548213	3.687677784901
C	1.979902851858	-0.790495240213	5.949172396879
H	1.768467222944	-1.440539034780	6.788771262210
C	4.030794584277	-0.193171526798	7.182425793132
H	4.762037347585	-0.993082656035	7.002356602386
H	3.464757339257	-0.436685795438	8.083052841299
H	4.573821651362	0.736410244756	7.365531782487
C	1.184139636764	-0.753101238029	4.854918426088
H	0.318237197797	-1.397687864247	4.841643324767
C	3.506708471872	0.715145753877	4.950014665534
H	4.424483564270	1.278882011104	5.057423904675
C	2.765832509286	0.746406051673	3.818792701865
H	3.117323710166	1.358860319553	2.999395922872
N	-3.120715857076	0.016584067955	-6.066290397500
C	-1.497878928102	-0.050509548213	-3.687677784901
C	-3.506708471872	-0.715145753877	-4.950014665534
H	-4.424483564270	-1.278882011104	-5.057423904675
C	-4.030794584277	0.193171526798	-7.182425793132
H	-4.573821651362	-0.736410244756	-7.365531782487
H	-4.762037347585	0.993082656035	-7.002356602386
H	-3.464757339257	0.436685795438	-8.083052841299
C	-2.765832509286	-0.746406051673	-3.818792701865
H	-3.117323710166	-1.358860319553	-2.999395922872
C	-1.979902851858	0.790495240213	-5.949172396879
H	-1.768467222944	1.440539034780	-6.788771262210
C	-1.184139636764	0.753101238029	-4.854918426088
H	-0.318237197797	1.397687864247	-4.841643324767

B3LYP energy:

$E(S_0)$ = -1843.785805 a.u.

6. Electronic structures

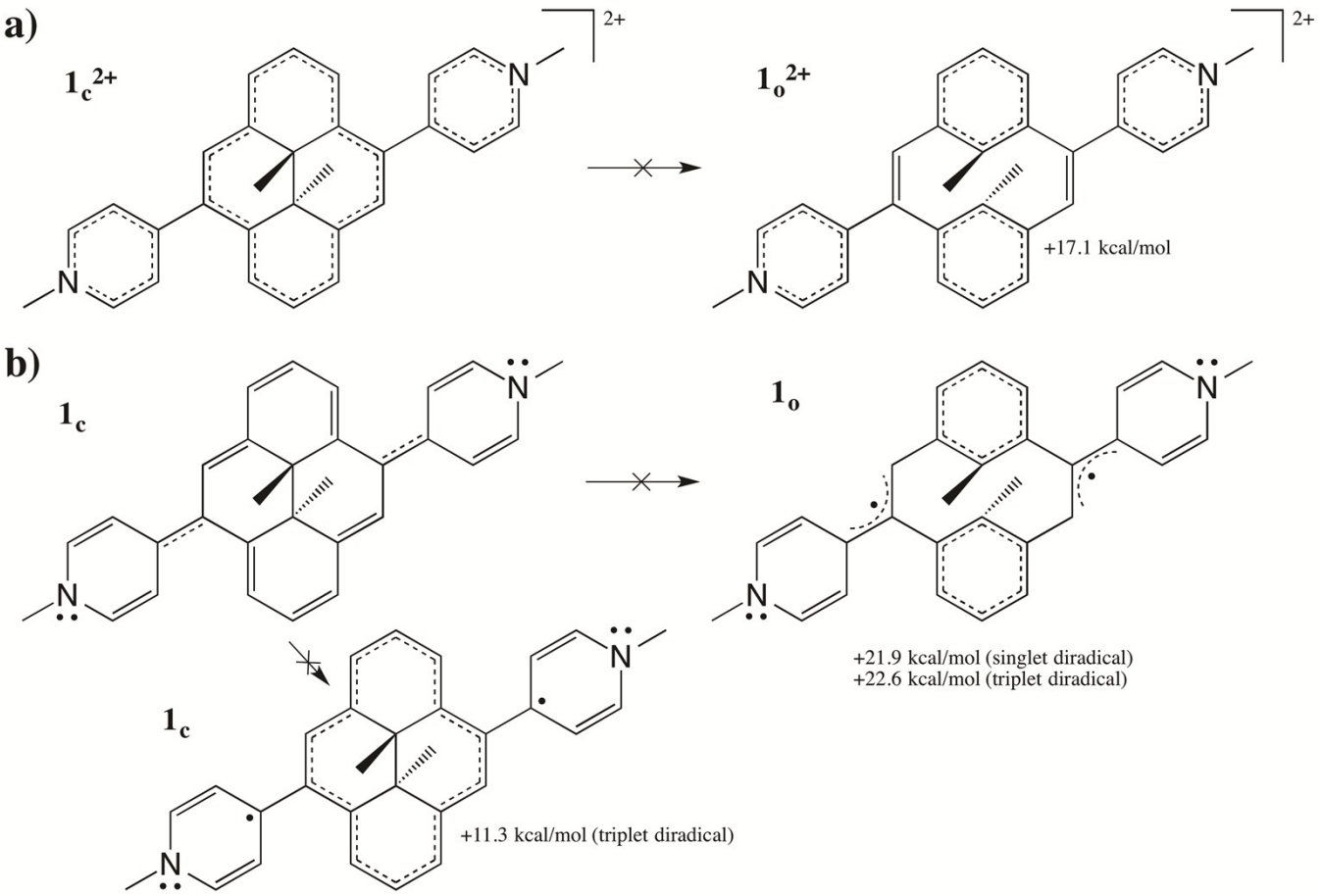

Figure S4. Main resonance structures derived from DFT calculations of a) $\mathbf{1_c^{2+}}$/$\mathbf{1_o^{2+}}$, and of b) $\mathbf{1_c}$/$\mathbf{1_o}$. Relative energies are given with respect to the closed-ring isomer ($\mathbf{1_c^{2+}}$ and $\mathbf{1_c}$).

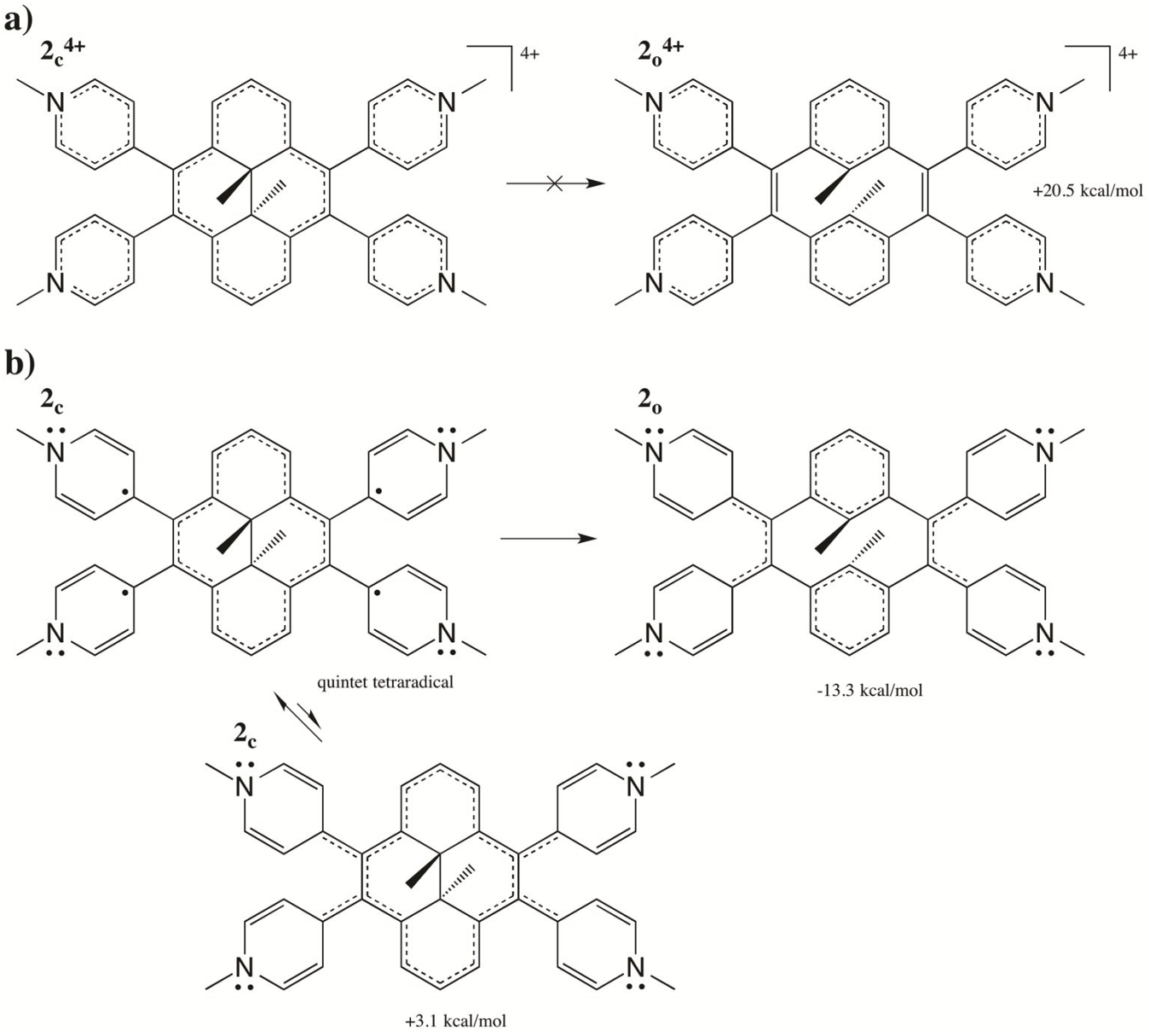

Figure S5. Main resonance structures derived from DFT calculations of a) $\mathbf{2_c^{4+}}/\mathbf{2_o^{4+}}$, and of b) $\mathbf{2_c}/\mathbf{2_o}$. Relative energies are given with respect to the closed-ring isomer ($\mathbf{2_c^{4+}}$ and $\mathbf{2_c}$).

7. Computed absorption spectra

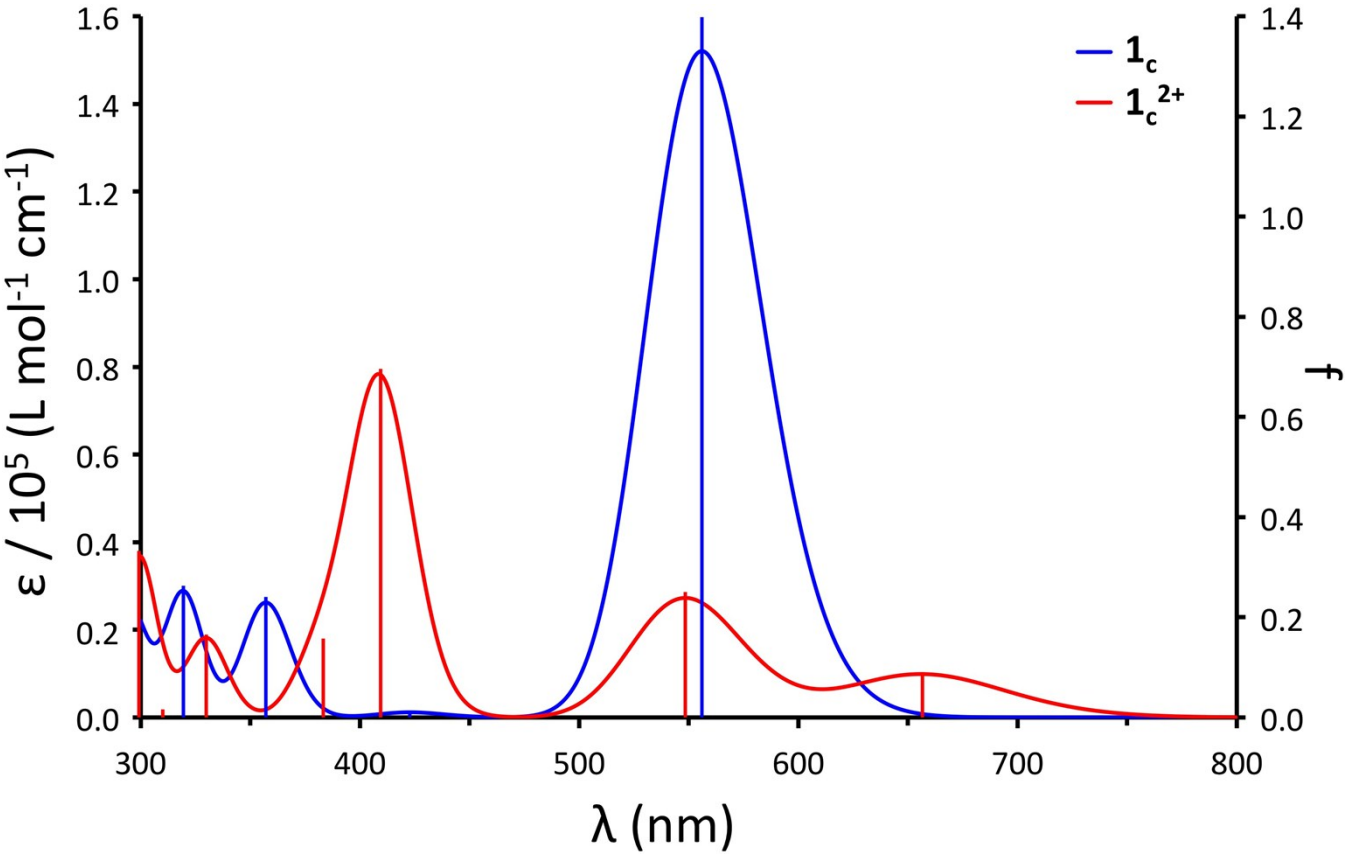

Figure S6. UV/Vis absorption spectra of $\mathbf{1_c^{2+}}$ and $\mathbf{1_c}$ computed at TD-DFT level in vacuo. Oscillator strengths (f) of each vertical transition are indicated. Gaussian functions of half-width at half-maximum of 1500 cm^{-1} have been used for spectral broadening and visualization purposes.

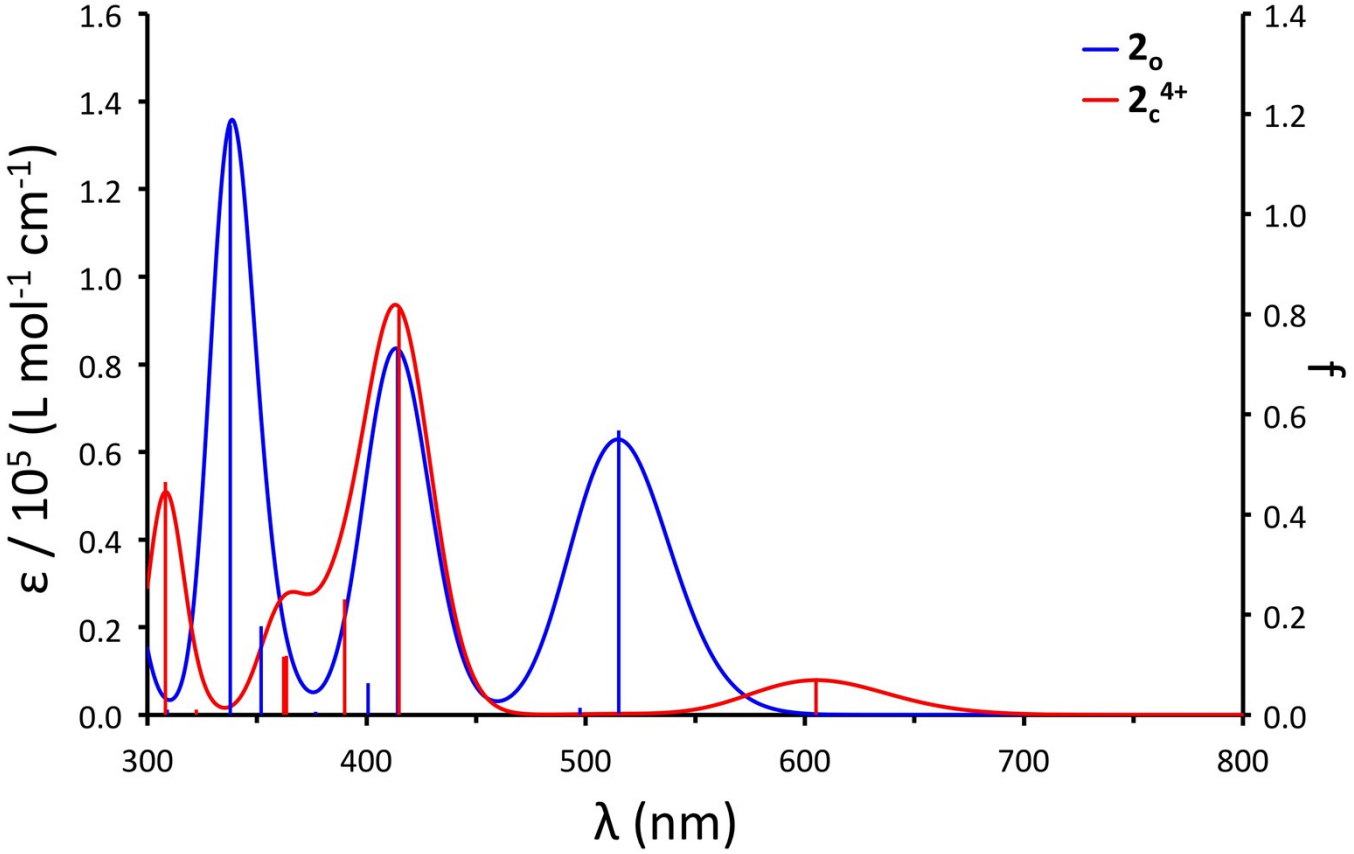

Figure S7. UV/Vis absorption spectra of $\mathbf{2_c}^{4+}$ and $\mathbf{2_o}$ computed at TD-DFT level in vacuo. Oscillator strengths (f) of each vertical transition are indicated. Gaussian functions of half-width at half-maximum of 1500 cm^{-1} have been used for spectral broadening and visualization purposes.

1.3 Thermodynamic data

Key Kinetic parameters corresponding to the thermal conversion process from the opened form to the closed forms were estimated by UV-Visible spectroscopy measurements conducted at different temperatures.

A $1 \cdot 10^{-5}$ M solution in CH_3CN was irradiated with visible light ($\lambda \geq 630$) to afford opened form in quantitative yield, the evolution of the absorption at λ_{max} was monitored over time at different temperatures (308K, 318K and 328K). The conversion of the UV-Vis data to a concentration was done using Lambert Beer law (1) were **A** is the absorption, **ε** is the molar absorptivity, **b** is the path length and **c** is the concentration. The total concentration ($\mathbf{c}_{total}$) is obtained in the initial scan (before irradiation) and corresponds to completely closed compound.

$$\mathbf{A=\varepsilon bc} \qquad (1)$$

$$\mathbf{A}= \boldsymbol{\varepsilon}_{DHP}\mathbf{bc}_{DHP} + \boldsymbol{\varepsilon}_{CPD}\mathbf{bc}_{CPD} \qquad (2)$$

$$\mathbf{c}_{total}=\mathbf{c}_{DHP} + \mathbf{c}_{CPD} \qquad (3)$$

and $\chi_{CPD}=(\mathbf{c}_{CPD}/\mathbf{c}_{total})$ (4)

Table S2. Rate constant (k), half-life time ($t_{1/2}$), and activation energy (E_a) for the thermal relaxation of $1c^{2+}$ and $2c^{4+}$

	T [K]	**k [10^{-5} s^{-1}]**	**t1/2 [h]**	**Ea [kcalmol^{-1}]**
$1c^{2+}$	**308**	2.00 ± 0.08	9.6	23 ± 1
	318	7.81 ± 0.04	2.5	
	328	23.3 ± 0.3	0.8	
$2c^{4+}$	**308**	3.67 ± 0.10	5.2	19±1
	318	7.50 ± 0.07	2.5	
	328	19.3 ± 0.4	1.0	