

Supporting Information

Electron Density of Delocalized Bonds Revisited: The Bond-Orbital Projection Algorithm

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S1 Computational protocol

S1.1 Geometry optimization

The neutral singlet *c*-P6[b6] nanoring ($C_{216}H_{108}N_{30}Zn_6$, 360 atoms) was used throughout the present study. The initial Cartesian coordinates were taken from the Supporting Information accompanying the study of global aromaticity in porphyrin nanorings by Rickhaus *et al.*[1] The structure was reoptimized with ORCA 6.1.1[2] using the ω B97M-V density functional developed by the Head-Gordon group [3] and the def2-SVP orbital basis set.[4] The RIJCOSX approximation was employed together with the corresponding def2-SVP/C auxiliary basis.[5] Molecular symmetry was exploited using the UseSym option, and the geometry optimization was terminated according to the ORCA LooseOpt convergence criteria. No additional user-defined geometric constraints were imposed.

The Cartesian coordinates included in the ORCA input reproduced in Section S3 correspond to the converged structure used in all subsequent calculations, rather than to the original literature geometry. The MINIX, def2-SVP, and def2-TZVPP density matrices were therefore generated as single-point calculations at one common, fixed molecular geometry.

S1.2 Density-matrix calculations

At the fixed optimized geometry, three independent spin-restricted Kohn–Sham single-point calculations were performed with ORCA 6 using the ω B97M-V density functional and the MINIX, def2-SVP, and def2-TZVPP orbital basis sets, respectively. [2–4, 6] All calculations corresponded to the neutral singlet state ($q = 0$, $2S + 1 = 1$).

The converged ω B97M-V/def2-SVP orbital file obtained from the geometry optimization was supplied through the ORCA MOrRead directive as the initial guess for each single-point calculation. Each self-consistent-field procedure was subsequently converged independently in its target orbital basis. The SlowConv and VeryTightSCF options were used throughout, molecular symmetry was retained with UseSym, and Coulomb and exchange contributions were evaluated using the RIJCOSX approximation. The auxiliary basis specifications were def2-SVP/C for the MINIX and def2-SVP calculations and def2-TZVPP/C for the def2-TZVPP calculation, as documented explicitly in the input files reproduced in Section S3.

The three converged one-particle density matrices constitute distinct parent electronic-structure descriptions of the same molecular geometry. No geometry relaxation was performed upon changing the orbital basis. Likewise, no orbital localization or modification of the Kohn–Sham occupations was applied before the EDDB analysis.

It is important to distinguish the parent orbital basis used to generate a density matrix from the atom-respecting working space used subsequently by BOP. For each of the three parent densities, RUNEDDB constructed the corresponding full NAO representation and its nested NMB and NVB subspaces. Thus, MINIX, def2-SVP, and def2-TZVPP determine the quality and dimension of the parent density-matrix representation, whereas NAO, NMB, and NVB define alternative hierarchical spaces in which the same density is analyzed.

S1.3 RUNEDDB analysis

All density-layer analyses were performed with RUNEDDB, compilation 2026–Jul–20. [7] For each parent density matrix, the program first generated a full natural atomic orbital representation using the current frozen-NMB NAO driver and then constructed the nested natural minimal basis and natural valence basis subspaces. The three working spaces were selected through the corresponding -b nao, -b nmb, and -b nvb options and are defined as

$$\begin{aligned}\mathcal{H}_{\text{NAO}} &= \mathcal{H}_{\text{Cor}} \oplus \mathcal{H}_{\text{Val}} \oplus \mathcal{H}_{\text{Ryd}}, \\ \mathcal{H}_{\text{NMB}} &= \mathcal{H}_{\text{Cor}} \oplus \mathcal{H}_{\text{Val}}, \\ \mathcal{H}_{\text{NVB}} &= \mathcal{H}_{\text{Val}}.\end{aligned}\tag{S1}$$

The same converged molecular density matrix was therefore analyzed in three progressively reduced, atom-respecting orbital spaces without any reoptimization of the parent Kohn–Sham orbitals.

For a given parent density matrix, the atom-pair connectivity mask was always generated from Wiberg-type bond orders evaluated in the full NAO representation. The resulting mask was subsequently retained unchanged when the BOP kernel was executed in the NAO, NMB, or NVB working space. Consequently, the hierarchical reduction modified only the dimensions of the local two- and three-center bond-order-orbital eigenproblems, whereas the analyzed atomic connectivity graph remained identical

within each MINIX, def2-SVP, or def2-TZVPP series.

Unless stated otherwise, the default connectivity and internal BOP thresholds of compilation 2026-Jul-20 were used. Global calculations were performed in the EDDB_G mode. The representation comparison reported in the main text therefore comprises nine independent BOP calculations:

$$\{\text{MINIX, def2-SVP, def2-TZVPP}\} \times \{\text{NAO, NMB, NVB}\}. \quad (\text{S2})$$

For each calculation, the final EDDB_G matrix was diagonalized to obtain the natural orbitals for bond delocalization (NOBDs) and their occupations. The π -resolved EDDB and BDF maps used for the representation comparison were reconstructed from the selected π -NOBD subspace according to the procedure described in the main text.[8]

The controlled NAO–NMB–NVB population analysis for the def2-TZVPP density was performed using the complete EDDB_G matrix, without any subsequent σ/π dissection. Atomic-orbital-resolved natural population analyses were generated separately for the NAO, NMB, and NVB calculations. These outputs were used to decompose the total population differences into core, valence, and Rydberg contributions and to compare the EDDB populations of the 1128 valence orbitals common to all three representations. Fragment-resolved calculations employed six nested cumulative fragments, F_1 – F_6 , constructed by successively adding one complete 60-atom porphyrin–linker spoke. The corresponding atom lists and exact RUNEDDB commands are reproduced in Section S4. After the occupied-space congruence projection, the final EDDB_F matrices and all auxiliary density matrices entering fragment-resolved real-space functions were restricted to the same atomic support.

S1.4 Real-space grids and visualization

All real-space density functions were exported by RUNEDDB as Gaussian cube files. For every set of functions compared directly, a single reference grid was generated from the corresponding full-NAO calculation. Its origin, lattice vectors, numbers of grid points, and voxel volume were then copied unchanged to the NMB and NVB calculations. No interpolation or resampling was applied. This procedure ensured a point-by-point correspondence between the density values obtained in the three hierarchical working spaces.

The π -resolved BDF maps shown in the main text and in Figs. S1–S9 were reconstructed from the selected π -NOBD subspaces according to

$$\text{BDF}_\pi(\mathbf{r}) = 2 \text{EDDB}_\pi(\mathbf{r}) - \text{ED}_\pi(\mathbf{r}). \quad (\text{S3})$$

[8] Within every comparison, the molecular geometry, camera orientation, surface isovalue, color convention, lighting, and rendering parameters were kept identical. Positive and negative BDF isosurfaces were rendered in turquoise and yellow, respectively. The exact isovalues used for the parent BDF maps are reported in the corresponding figure captions.

The hierarchical population analysis was based on the complete EDDB_G density, without a subsequent σ/π dissection. Differential density cubes were generated pointwise as

$$\begin{aligned} \Delta\rho_{\text{NAO} \rightarrow \text{NMB}}(\mathbf{r}) &= \rho_{\text{EDDB}_G}^{\text{NAO}}(\mathbf{r}) - \rho_{\text{EDDB}_G}^{\text{NMB}}(\mathbf{r}), \\ \Delta\rho_{\text{NMB} \rightarrow \text{NVB}}(\mathbf{r}) &= \rho_{\text{EDDB}_G}^{\text{NMB}}(\mathbf{r}) - \rho_{\text{EDDB}_G}^{\text{NVB}}(\mathbf{r}). \end{aligned} \quad (\text{S4})$$

Both differences were evaluated on the same cloned def2-TZVPP reference grid. Turquoise and yellow isosurfaces denote positive and negative differential EDDB density, respectively. The same differential-density isovalue was used in both panels so that their relative magnitudes could be assessed directly.

The integrated population represented by a differential cube was evaluated numerically as

$$\Delta N_{\text{grid}} = \Delta V \sum_{p=1}^{N_{\text{grid}}} \Delta\rho(\mathbf{r}_p), \quad (\text{S5})$$

where ΔV is the voxel volume. These grid integrals were compared with the corresponding trace differences of the EDDB matrices,

$$\Delta N_{\text{matrix}} = \text{Tr } \mathbf{D}_{\text{EDDB}}^X - \text{Tr } \mathbf{D}_{\text{EDDB}}^Y, \quad (\text{S6})$$

providing an independent consistency check on the cube generation and subtraction procedures. Complete integration logs are supplied as separate machine-readable files.

The fragment-resolved EDDB_F maps were generated using the same molecular orientation and rendering convention. For each cumulative fragment, the final EDDB_F matrix and the corresponding real-space density were restricted to the atom list defining that fragment. The isovalues used for Figs. S12–S17 are specified in their individual captions.

All molecular structures and density isosurfaces were visualized using Avogadro 2.0.0. The molecular orientation, camera position, surface isovalue, color convention, lighting, and other rendering parameters were kept unchanged within each directly compared series. Raster images were captured using the native macOS screenshot utility and subsequently cropped and adjusted for presentation in GIMP 3.2.4. The resulting images were assembled, annotated, and exported as vector-based figure layouts using Inkscape 1.4.4. These post-processing steps affected only the graphical presentation and did not modify the underlying cube-file data, isosurface definitions, or relative spatial dimensions of the rendered structures.

S2 High-resolution BDF and EDDB maps

This section presents full-page, high-resolution versions of the real-space maps shown in reduced form in the main text. All molecular structures and isosurfaces were rendered using Avogadro 2.0.0 with the application window maximized on a 4K display and with the default camera settings. The HTML colors #ffd16b and #00ffd4 were used for negative and positive function values, respectively. The images were subsequently prepared for publication as described in Section S1.4.

S2.1 Global π -BDF maps

Figures S1–S9 show the global π -BDF maps obtained for the three parent density matrices and the three hierarchical BOP working spaces. An isosurface value of 0.0150 a.u. was used throughout, allowing the spatial distributions to be compared directly.

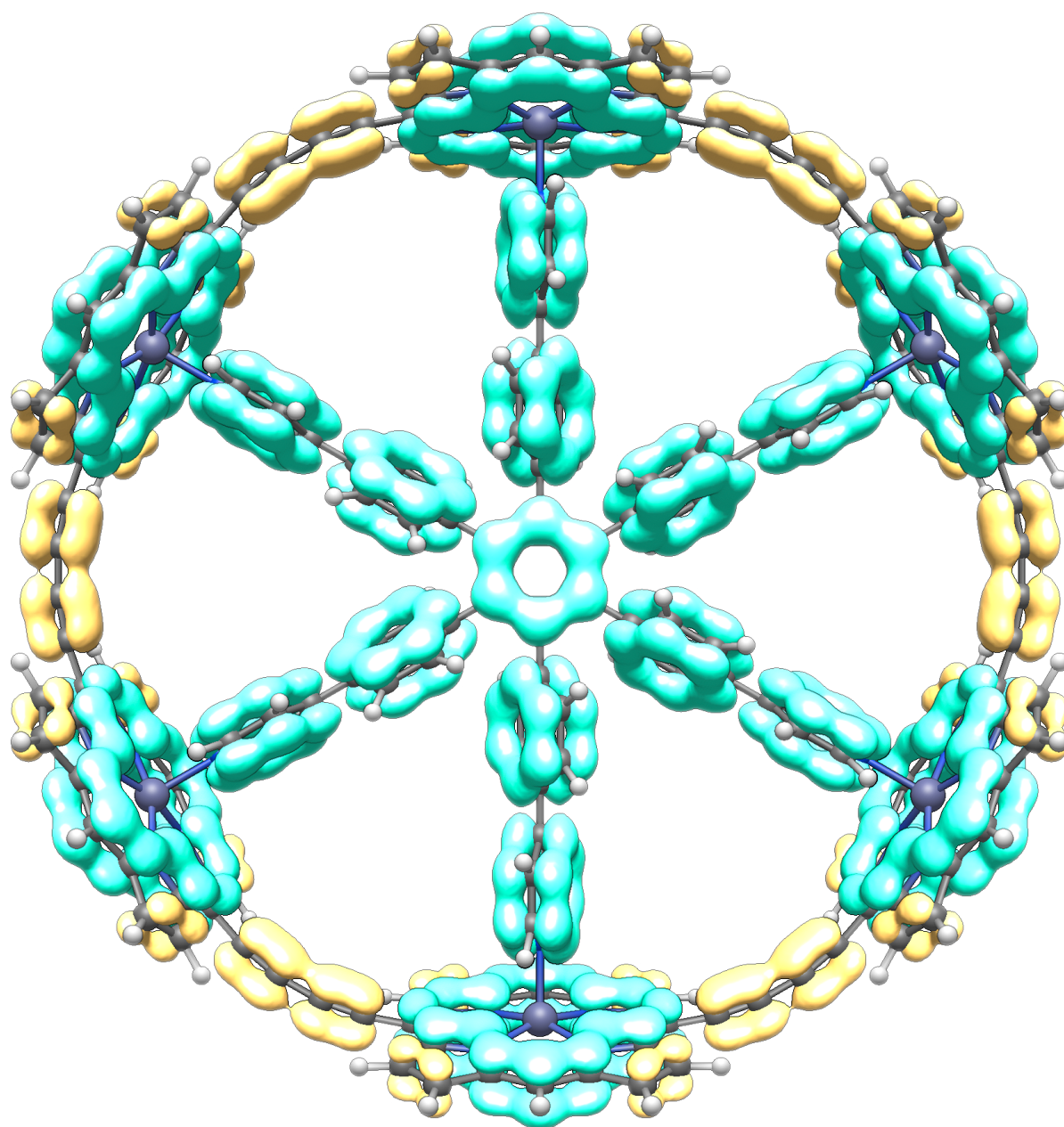


Figure S1. High-resolution global π -BDF map obtained from the ω B97M-V/MINIX parent density in the full NAO working space. Isosurfaces are shown at $|\text{BDF}_\pi(\mathbf{r})| = 0.0150$ a.u. Negative and positive values are rendered using the HTML colors #ffd16b and #00ffd4, respectively. The map was rendered in Avogadro 2.0.0 with the application window maximized on a 4K display and with the default camera settings.

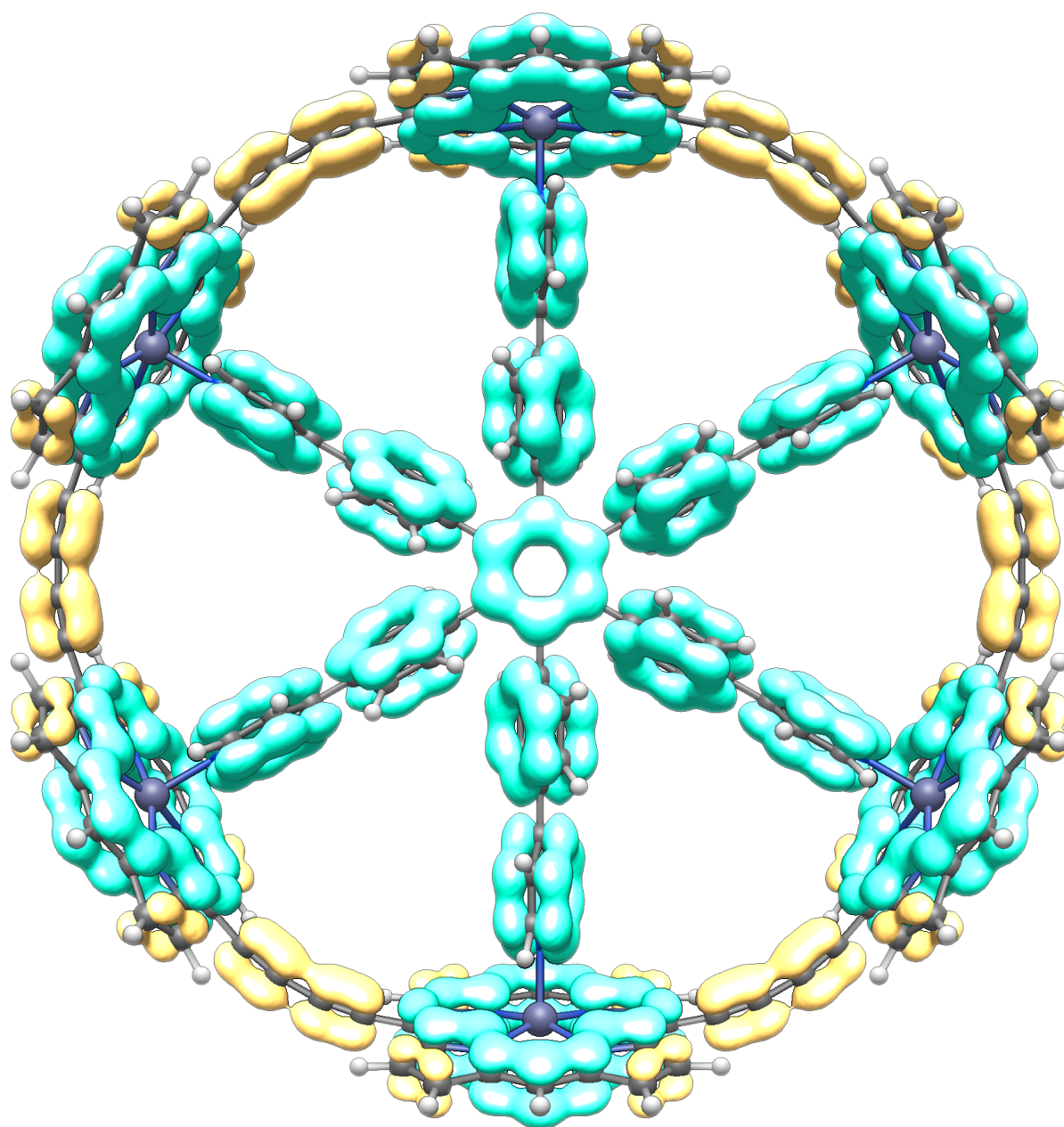


Figure S2. High-resolution global π -BDF map obtained from the ω B97M-V/MINIX parent density in the NMB working space. Isosurfaces are shown at $|\text{BDF}_{\pi}(\mathbf{r})| = 0.0150$ a.u. Negative and positive values are rendered using the HTML colors #ffd16b and #00ffd4, respectively. The map was rendered in Avogadro 2.0.0 with the application window maximized on a 4K display and with the default camera settings.

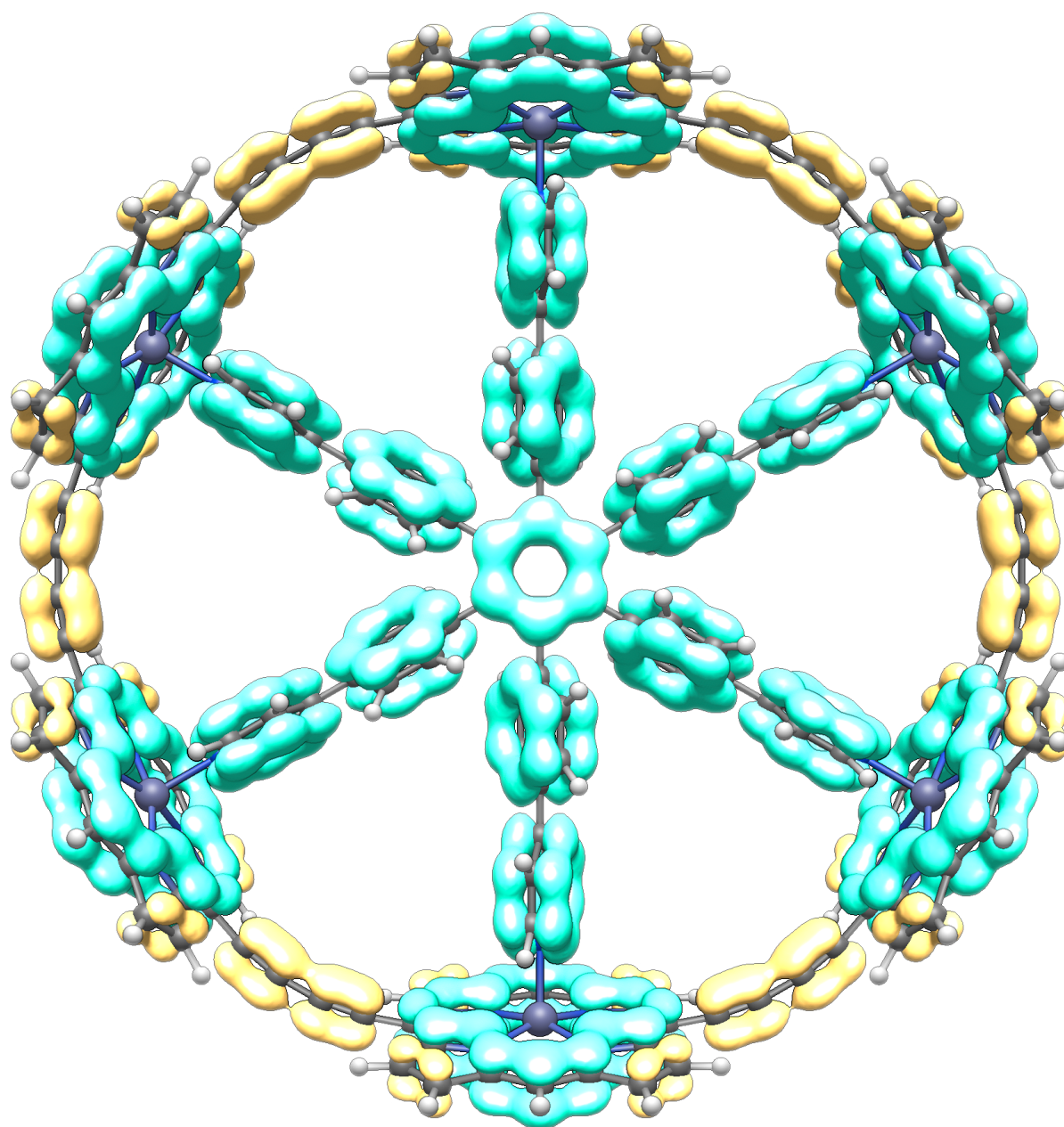


Figure S3. High-resolution global π -BDF map obtained from the ω B97M-V/MINIX parent density in the NVB working space. Isosurfaces are shown at $|\text{BDF}_{\pi}(\mathbf{r})| = 0.0150$ a.u. Negative and positive values are rendered using the HTML colors #ffd16b and #00ffd4, respectively. The map was rendered in Avogadro 2.0.0 with the application window maximized on a 4K display and with the default camera settings.

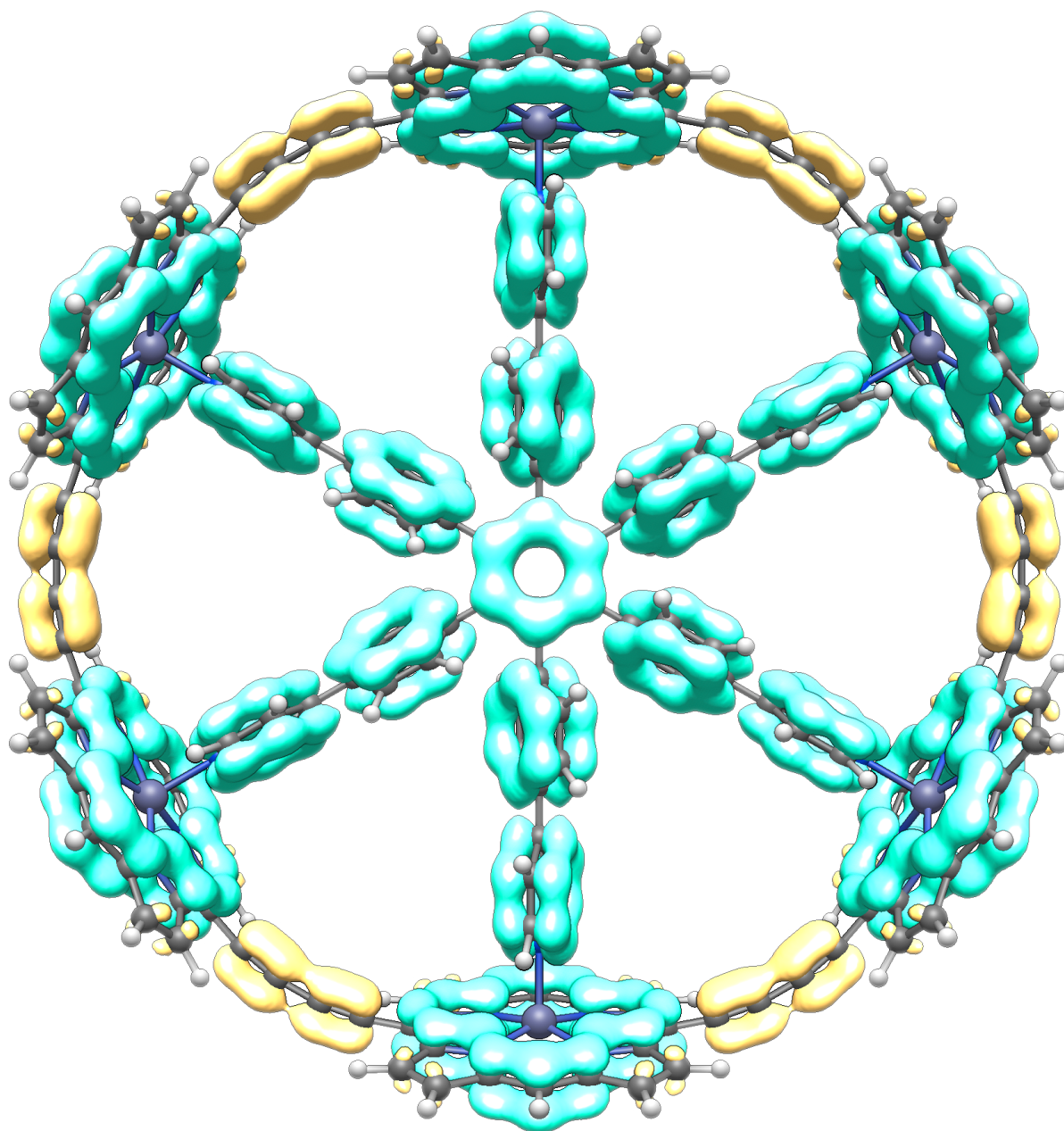


Figure S4. High-resolution global π -BDF map obtained from the ω B97M-V/def2-SVP parent density in the full NAO working space. Isosurfaces are shown at $|\text{BDF}_{\pi}(\mathbf{r})| = 0.0150$ a.u. Negative and positive values are rendered using the HTML colors #ffd16b and #00ffd4, respectively. The map was rendered in Avogadro 2.0.0 with the application window maximized on a 4K display and with the default camera settings.

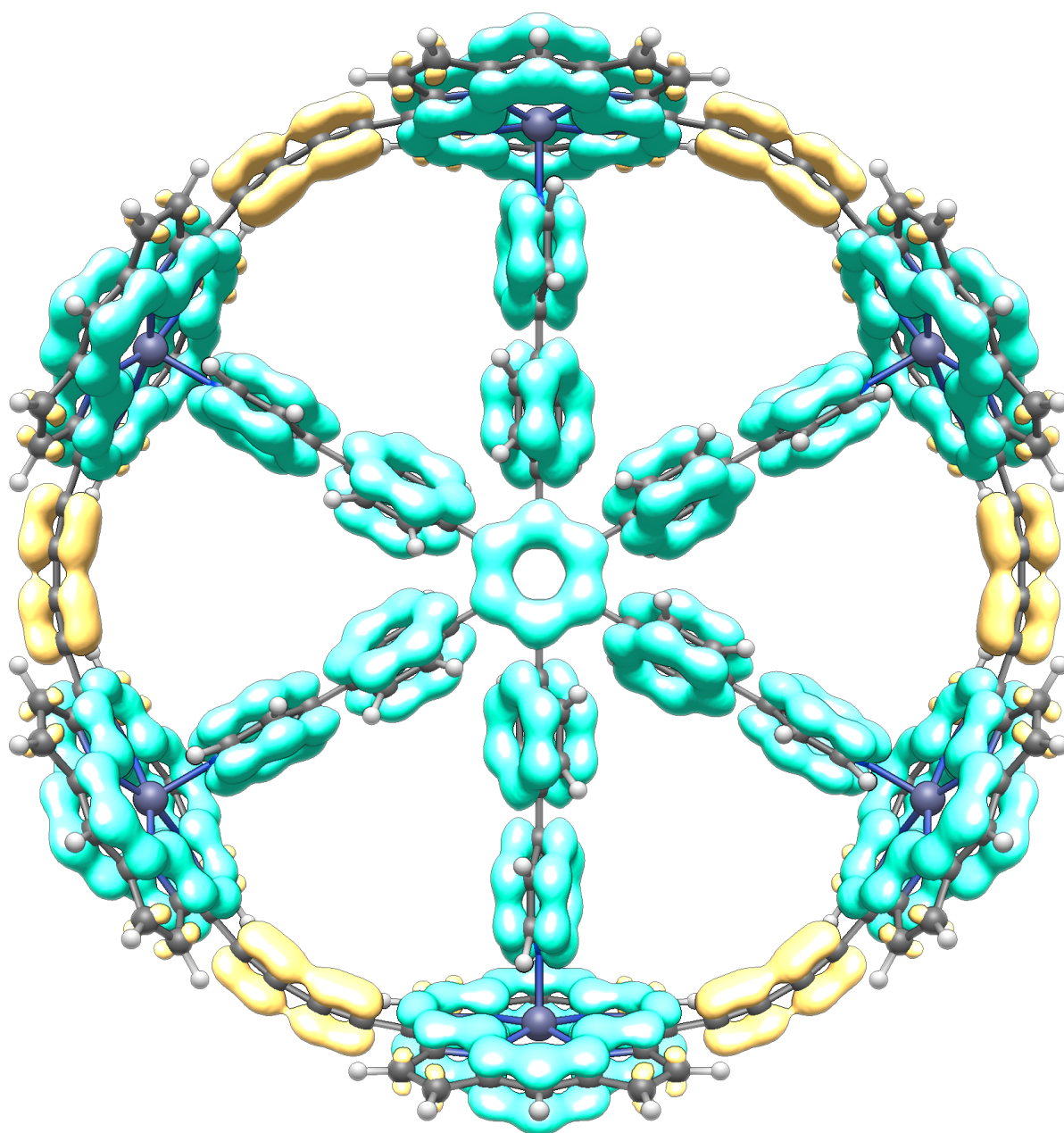


Figure S5. High-resolution global π -BDF map obtained from the ω B97M-V/def2-SVP parent density in the NMB working space. Isosurfaces are shown at $|\text{BDF}_{\pi}(\mathbf{r})| = 0.0150$ a.u. Negative and positive values are rendered using the HTML colors #ffd16b and #00ffd4, respectively. The map was rendered in Avogadro 2.0.0 with the application window maximized on a 4K display and with the default camera settings.

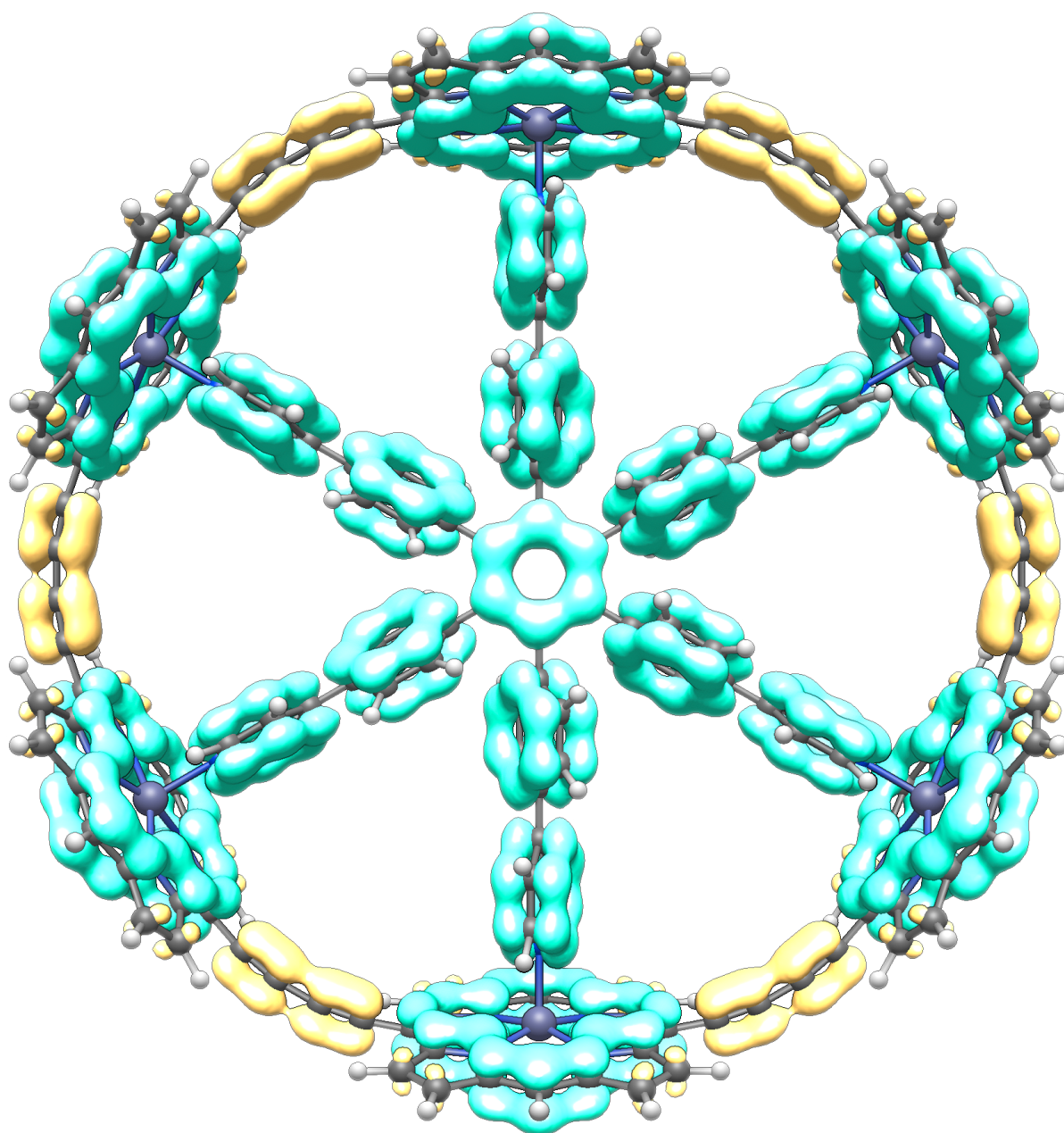


Figure S6. High-resolution global π -BDF map obtained from the ω B97M-V/def2-SVP parent density in the NVB working space. Isosurfaces are shown at $|\text{BDF}_{\pi}(\mathbf{r})| = 0.0150$ a.u. Negative and positive values are rendered using the HTML colors #ffd16b and #00ffd4, respectively. The map was rendered in Avogadro 2.0.0 with the application window maximized on a 4K display and with the default camera settings.

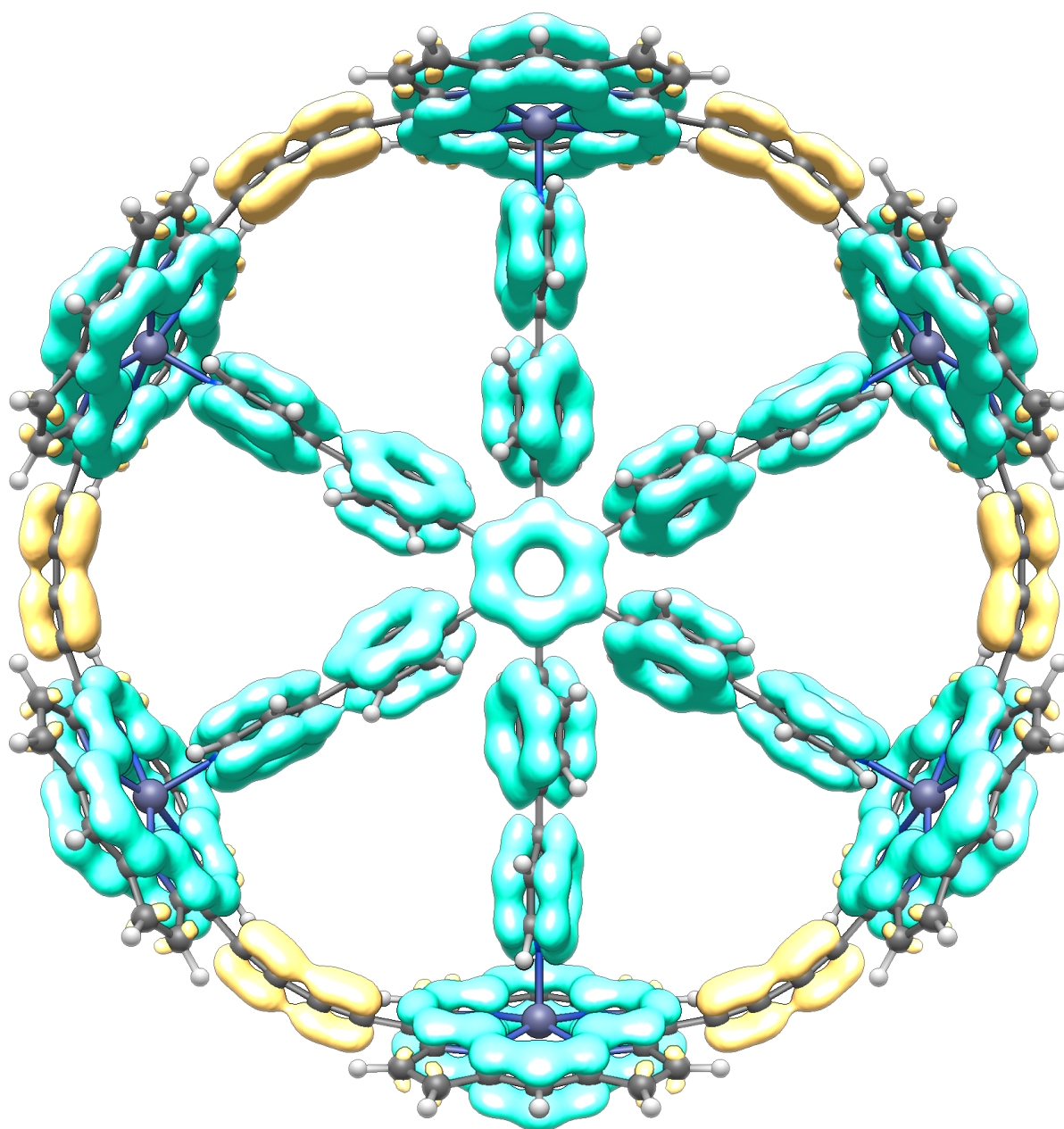


Figure S7. High-resolution global π -BDF map obtained from the ω B97M-V/def2-TZVPP parent density in the full NAO working space. Isosurfaces are shown at $|\text{BDF}_{\pi}(\mathbf{r})| = 0.0150$ a.u. Negative and positive values are rendered using the HTML colors #ffd16b and #00ffd4, respectively. The map was rendered in Avogadro 2.0.0 with the application window maximized on a 4K display and with the default camera settings.

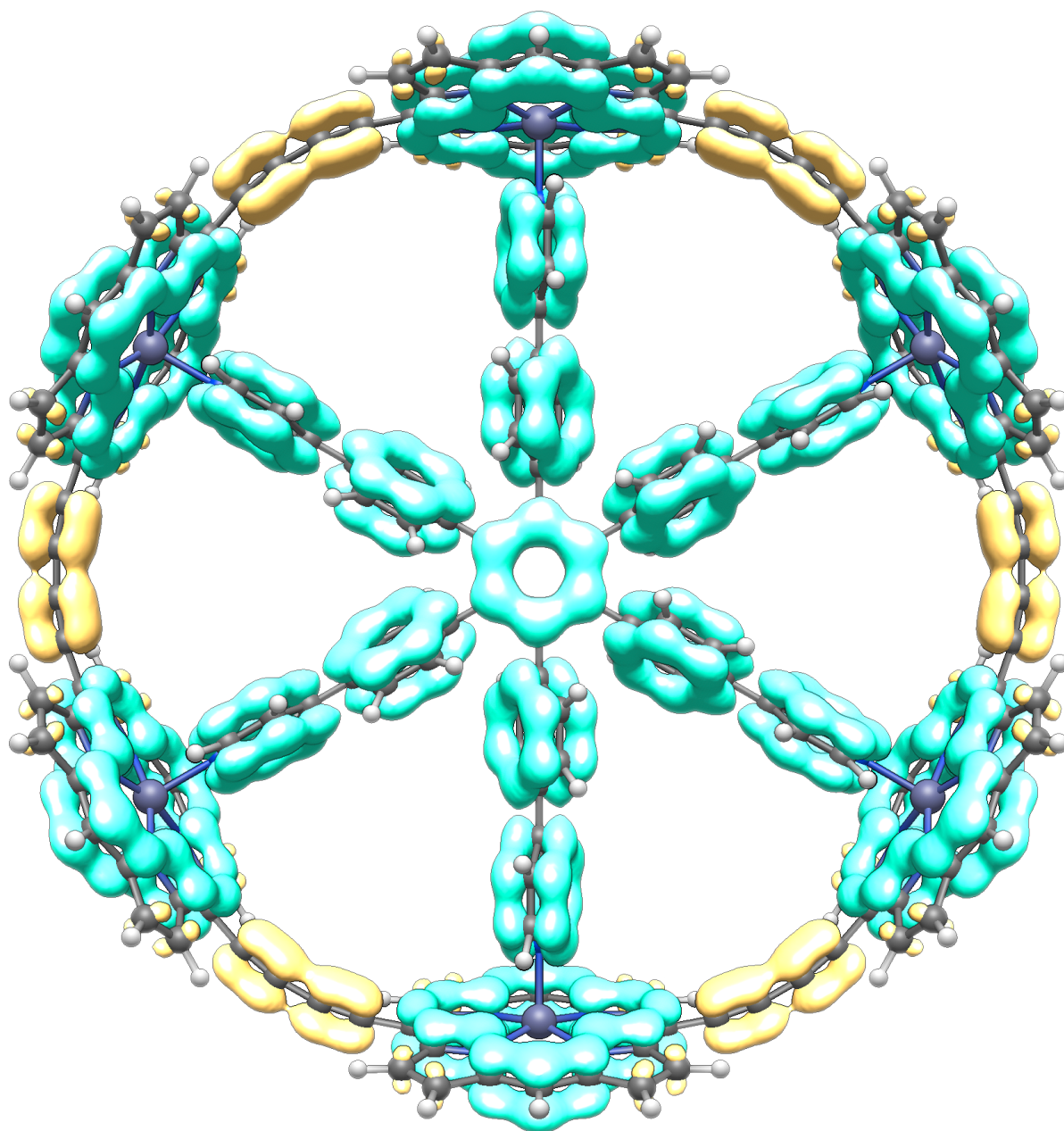


Figure S8. High-resolution global π -BDF map obtained from the ω B97M-V/def2-TZVPP parent density in the NMB working space. Isosurfaces are shown at $|\text{BDF}_{\pi}(\mathbf{r})| = 0.0150$ a.u. Negative and positive values are rendered using the HTML colors #ffd16b and #00ffd4, respectively. The map was rendered in Avogadro 2.0.0 with the application window maximized on a 4K display and with the default camera settings.

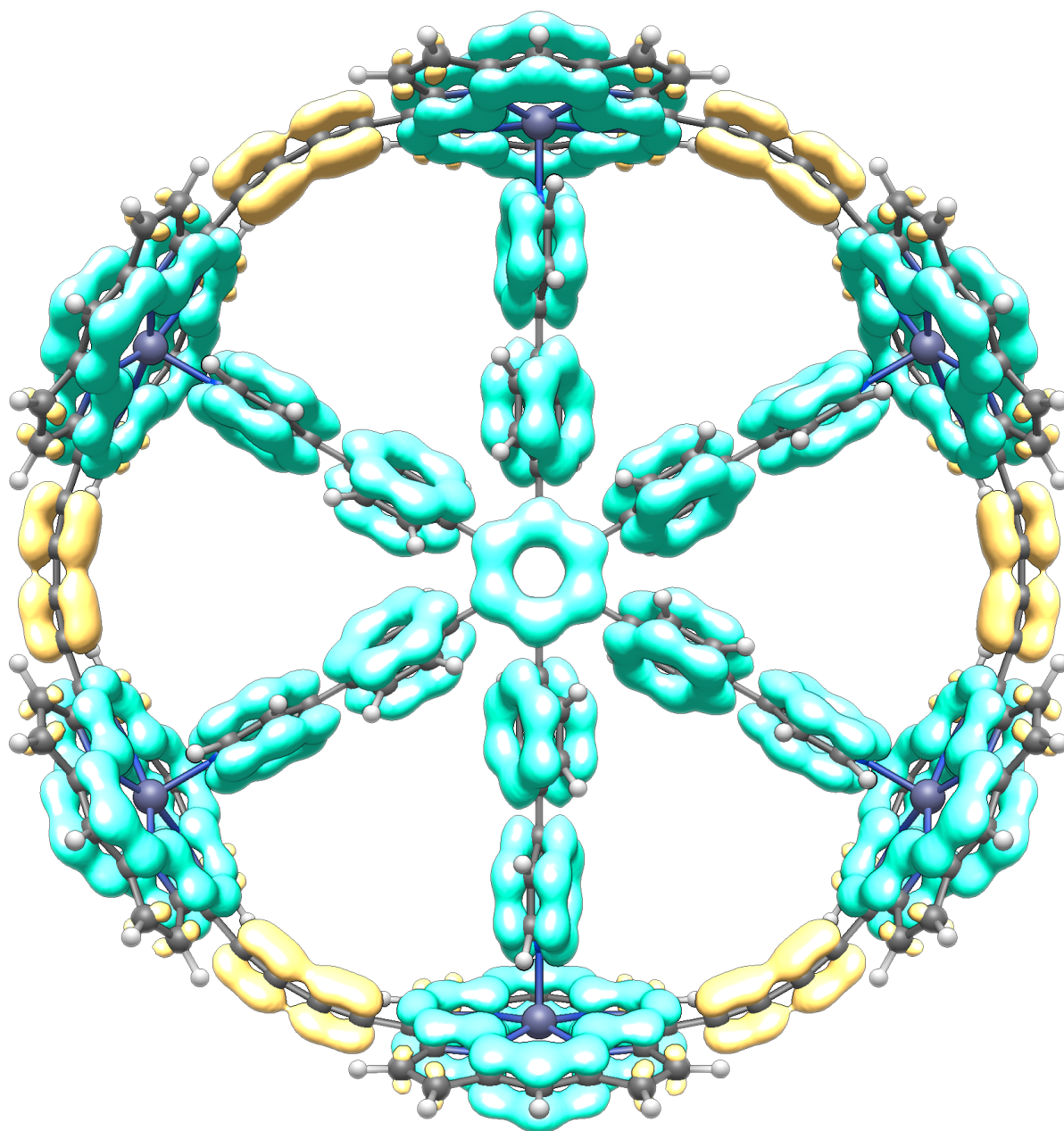


Figure S9. High-resolution global π -BDF map obtained from the ω B97M-V/def2-TZVPP parent density in the NVB working space. Isosurfaces are shown at $|\text{BDF}_{\pi}(\mathbf{r})| = 0.0150$ a.u. Negative and positive values are rendered using the HTML colors #ff416b and #00ff44, respectively. The map was rendered in Avogadro 2.0.0 with the application window maximized on a 4K display and with the default camera settings.

S2.2 Differential EDDB_G maps

Figures S10 and S11 present the complete differential EDDB_G densities associated with the hierarchical reduction of the def2-TZVPP analysis space. Both maps were evaluated on the same cloned real-space grid and are shown using the common isosurface value of 0.0015 a.u.

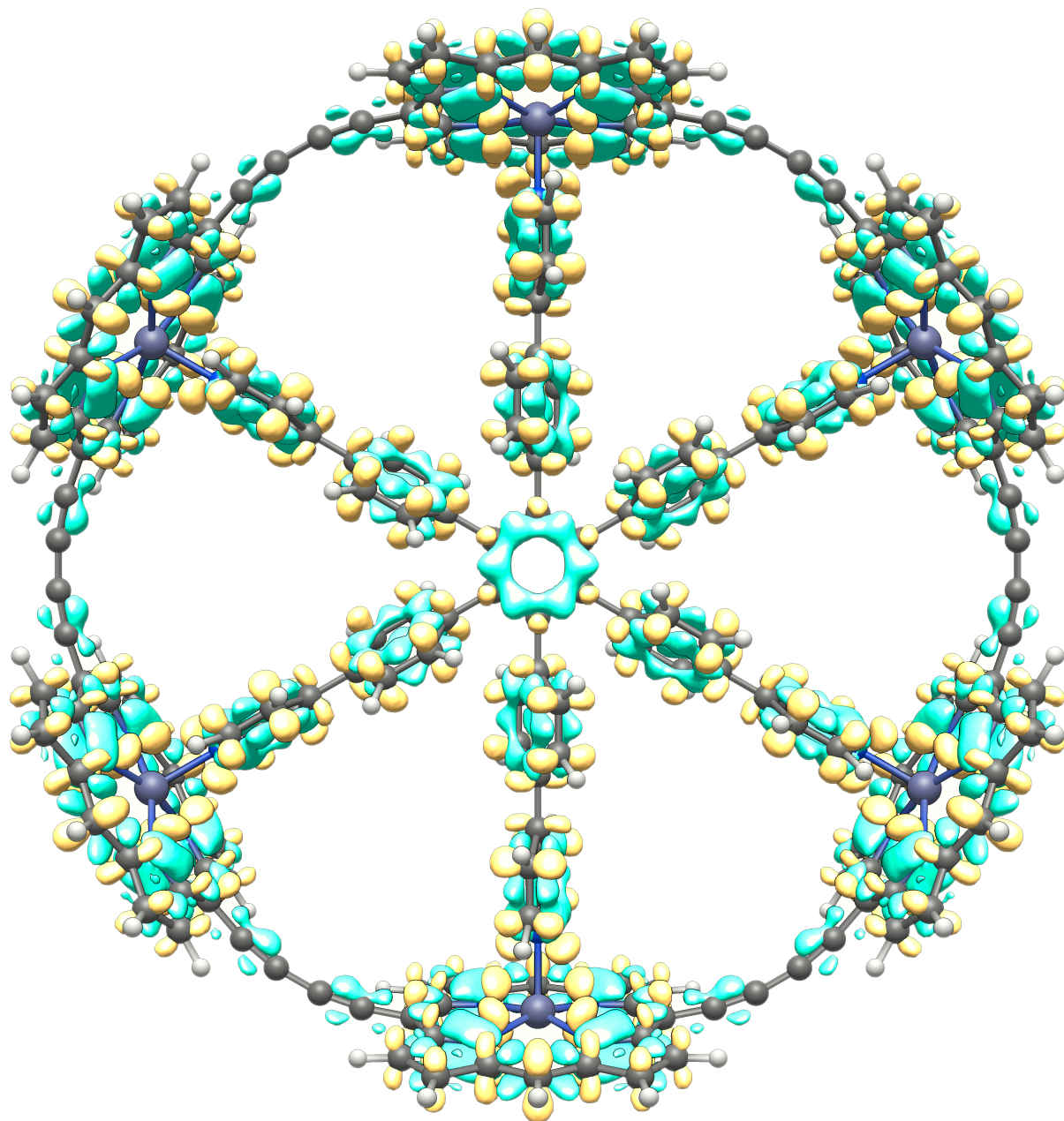


Figure S10. High-resolution differential EDDB_G map, $\rho_{\text{EDDB}_G}^{\text{NAO}}(\mathbf{r}) - \rho_{\text{EDDB}_G}^{\text{NMB}}(\mathbf{r})$, obtained from the ω B97M-V/def2-TZVPP parent density. The map represents the effect of removing the Rydberg complement while retaining the NAO-derived atom-pair connectivity mask. Isosurfaces are shown at an absolute value of 0.0015 a.u. Negative and positive differential-density values are rendered using the HTML colors #ff416b and #00ff44, respectively. The map was rendered in Avogadro 2.0.0 with the application window maximized on a 4K display and with the default camera settings.

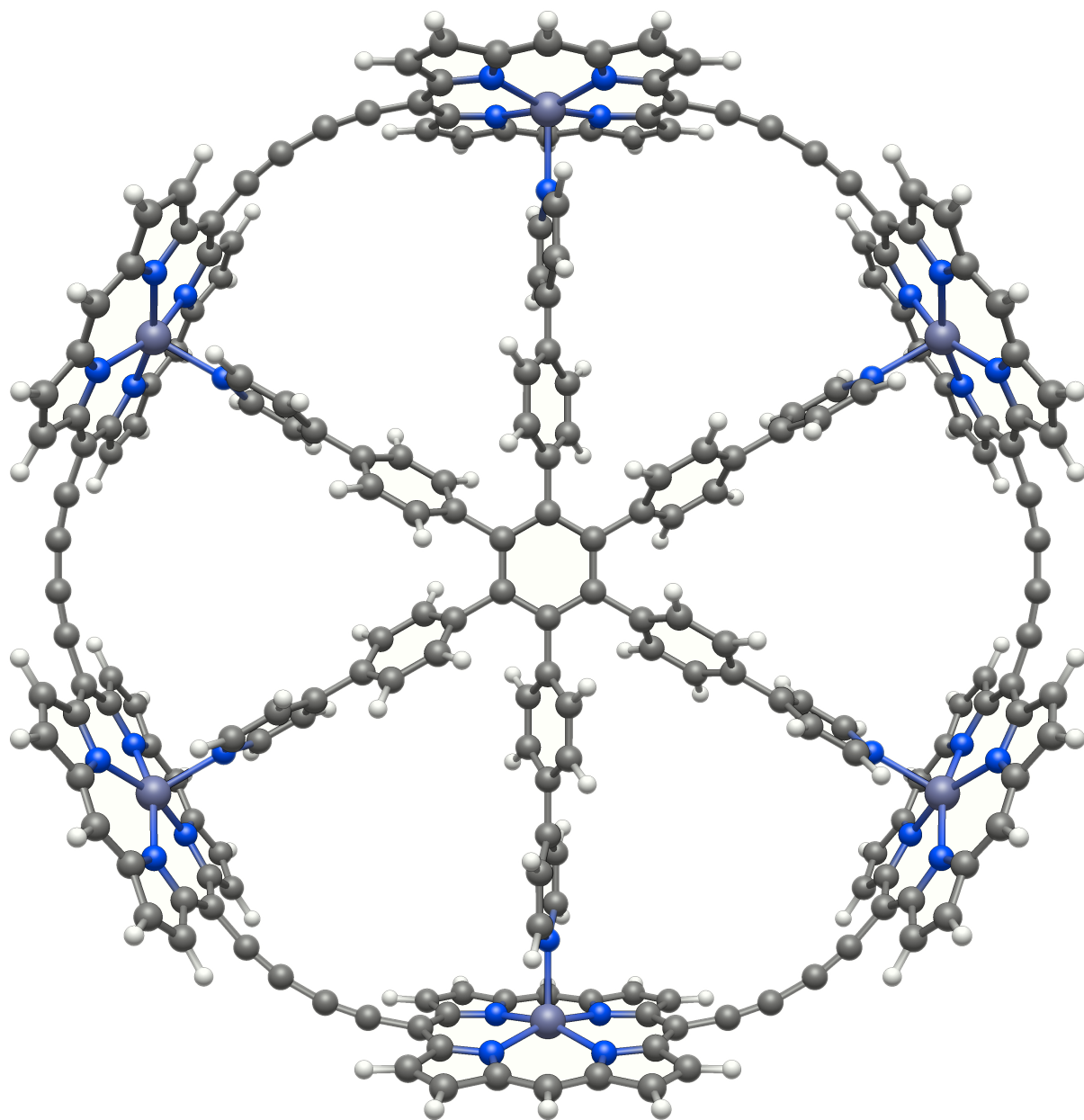


Figure S11. High-resolution differential EDDB_G map, $\rho_{\text{EDDB}_G}^{\text{NMB}}(\mathbf{r}) - \rho_{\text{EDDB}_G}^{\text{NVB}}(\mathbf{r})$, obtained from the ω B97M-V/def2-TZVPP parent density. The map represents the effect of removing the core space while retaining the NAO-derived atom-pair connectivity mask. Isosurfaces are shown at an absolute value of 0.0015 a.u. Negative and positive differential-density values are rendered using the HTML colors #ff416b and #00ff44, respectively. The map was rendered in Avogadro 2.0.0 with the application window maximized on a 4K display and with the default camera settings.

S2.3 Fragment-restricted EDDB_F maps

Figures S12–S17 show the complete EDDB_F densities obtained for the six nested cumulative fragments F_1 – F_6 . All maps are shown at an isosurface value of 0.0150 a.u. The exact atom lists, fragment definitions, and corresponding RUNEDDB commands are provided in Section S4.

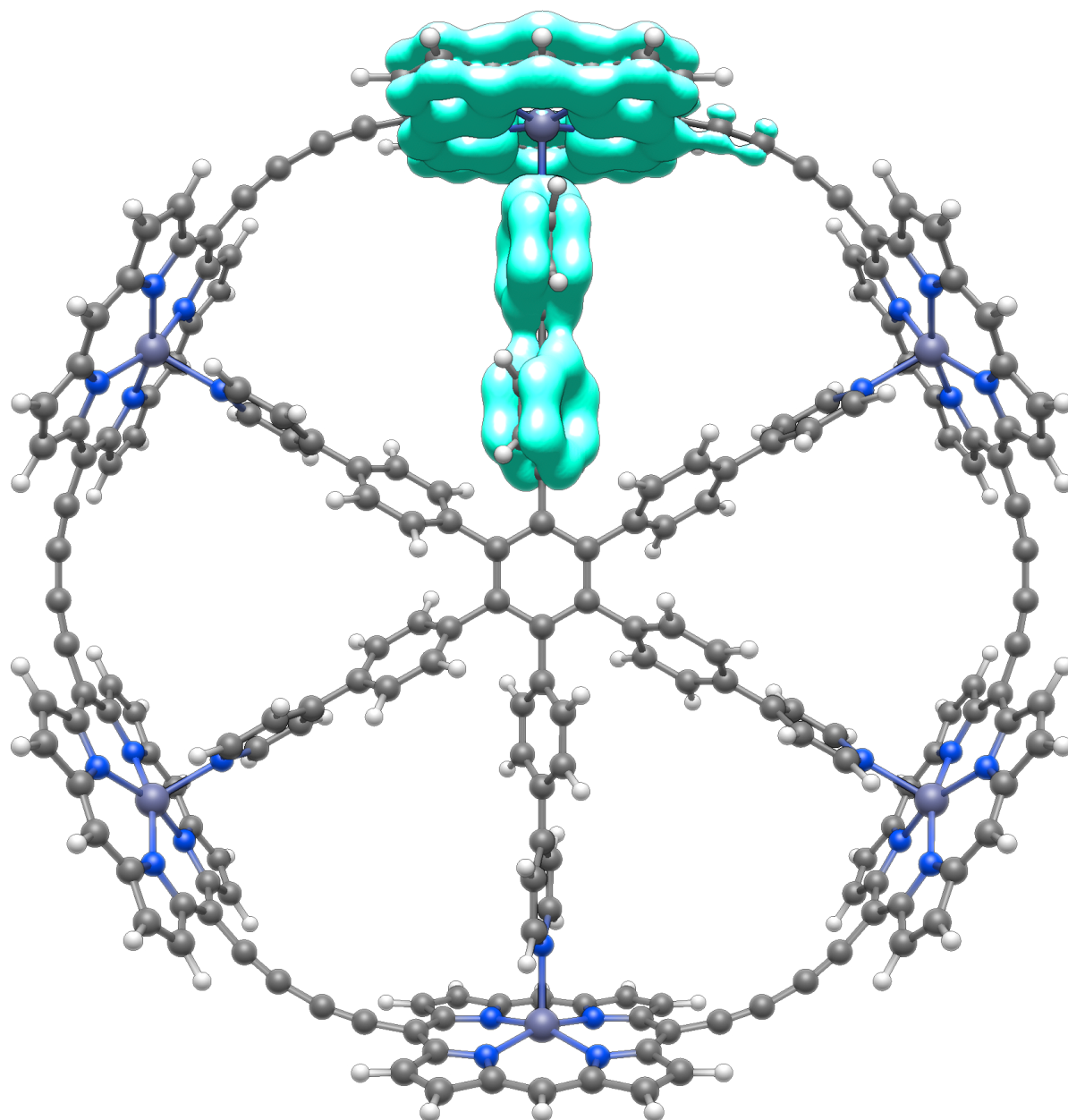


Figure S12. High-resolution EDDB_F map obtained for cumulative fragment F_1 of the *c*-P6[b6] nanoring using the $\omega\text{B97M-V/def2-TZVPP}$ parent density and the full NAO working space. Isosurfaces are shown at 0.0150 a.u. The common rendering convention assigns the HTML colors #ffd16b and #00ffa4 to negative and positive function values, respectively. The map was rendered in Avogadro 2.0.0 with the application window maximized on a 4K display and with the default camera settings. The complete definition of F_1 is given in Section S4.

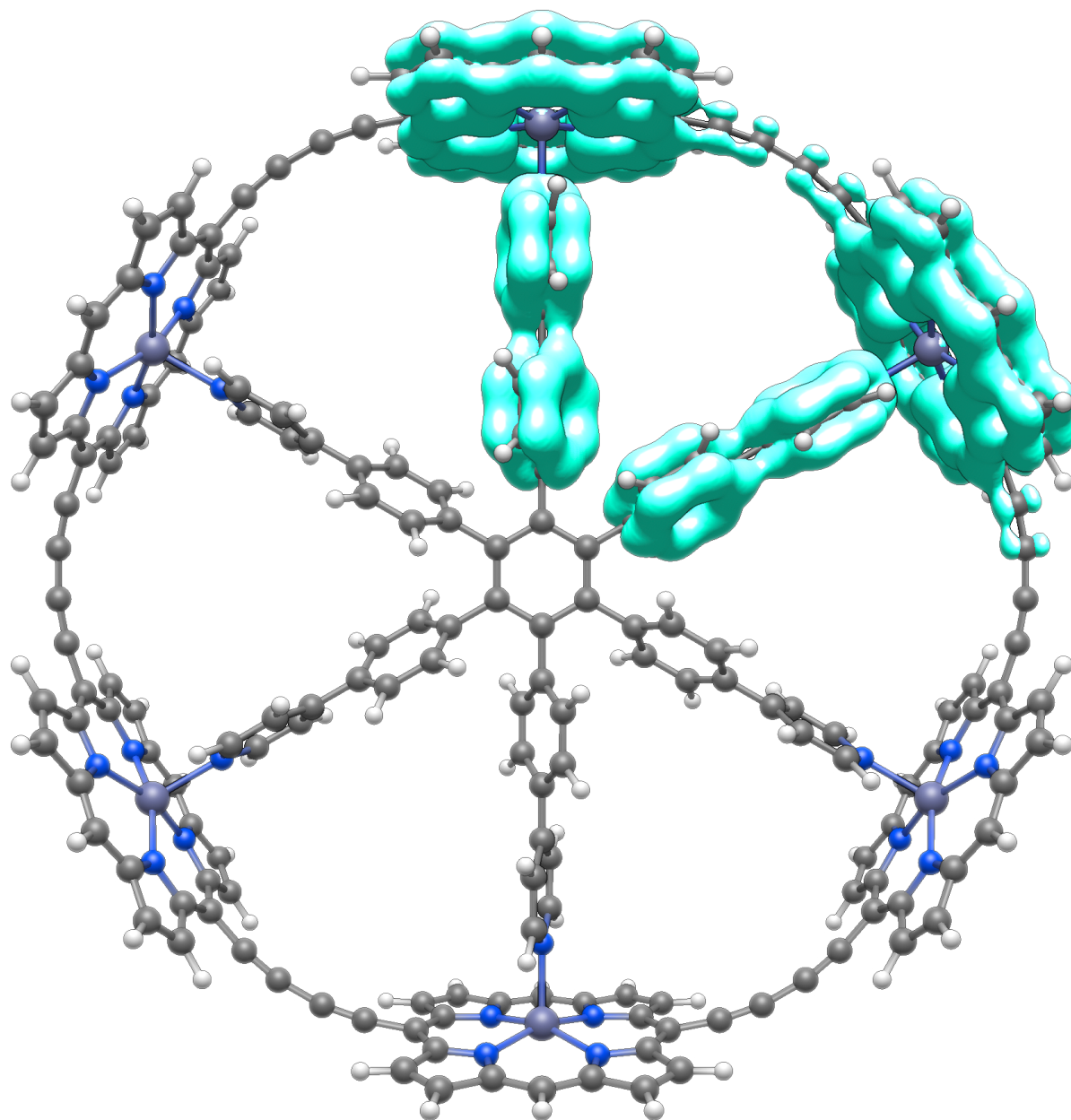


Figure S13. High-resolution EDDB_F map obtained for cumulative fragment F_2 of the *c*-P6[b6] nanoring using the $\omega\text{B97M-V/def2-TZVPP}$ parent density and the full NAO working space. Isosurfaces are shown at 0.0150 a.u. The common rendering convention assigns the HTML colors #ffd16b and #00ffd4 to negative and positive function values, respectively. The map was rendered in Avogadro 2.0.0 with the application window maximized on a 4K display and with the default camera settings. The complete definition of F_2 is given in Section S4.

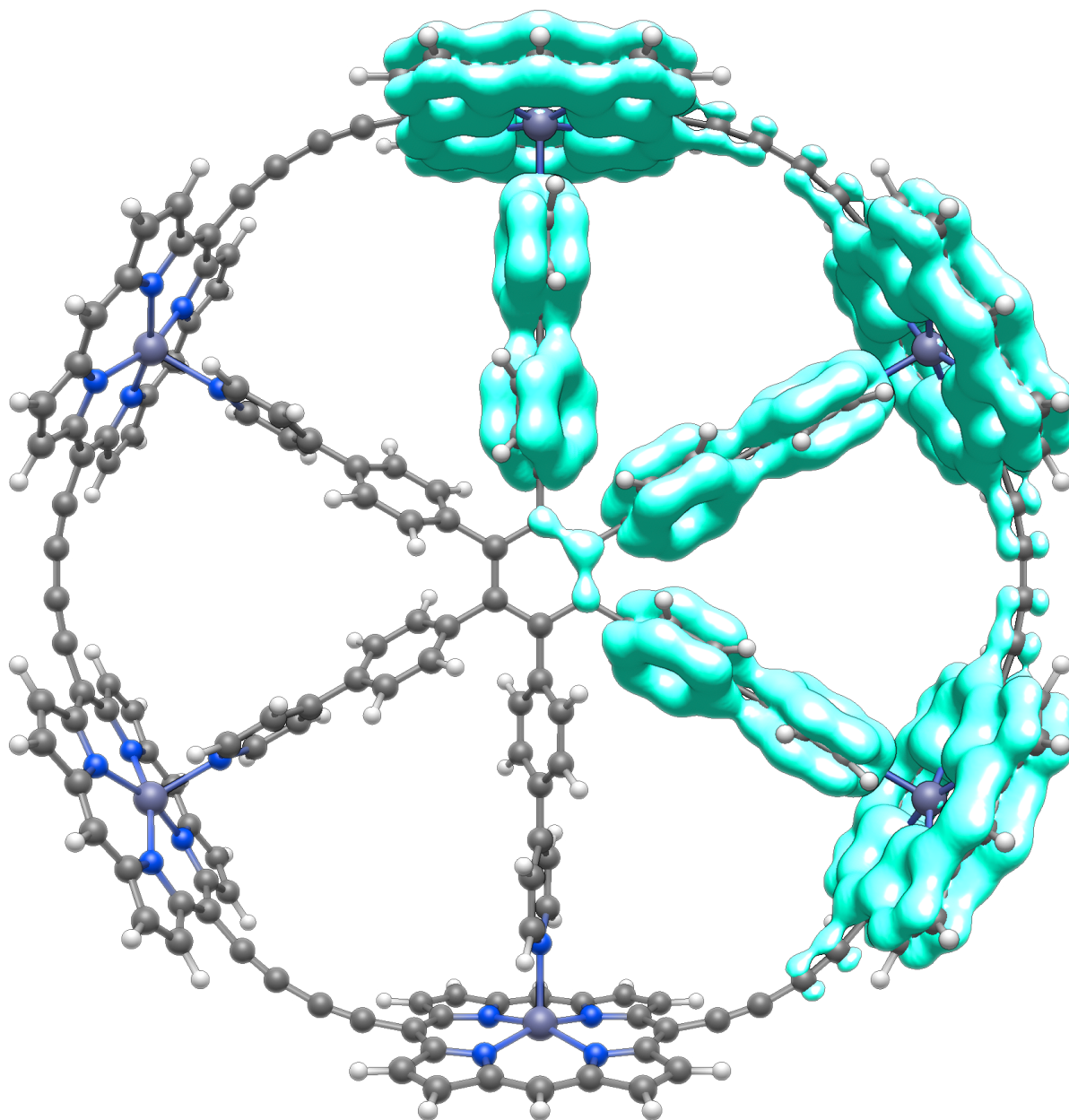


Figure S14. High-resolution EDDB_F map obtained for cumulative fragment F_3 of the *c*-P6[b6] nanoring using the $\omega\text{B97M-V/def2-TZVPP}$ parent density and the full NAO working space. Isosurfaces are shown at 0.0150 a.u. The common rendering convention assigns the HTML colors #ffd16b and #00ffd4 to negative and positive function values, respectively. The map was rendered in Avogadro 2.0.0 with the application window maximized on a 4K display and with the default camera settings. The complete definition of F_3 is given in Section S4.

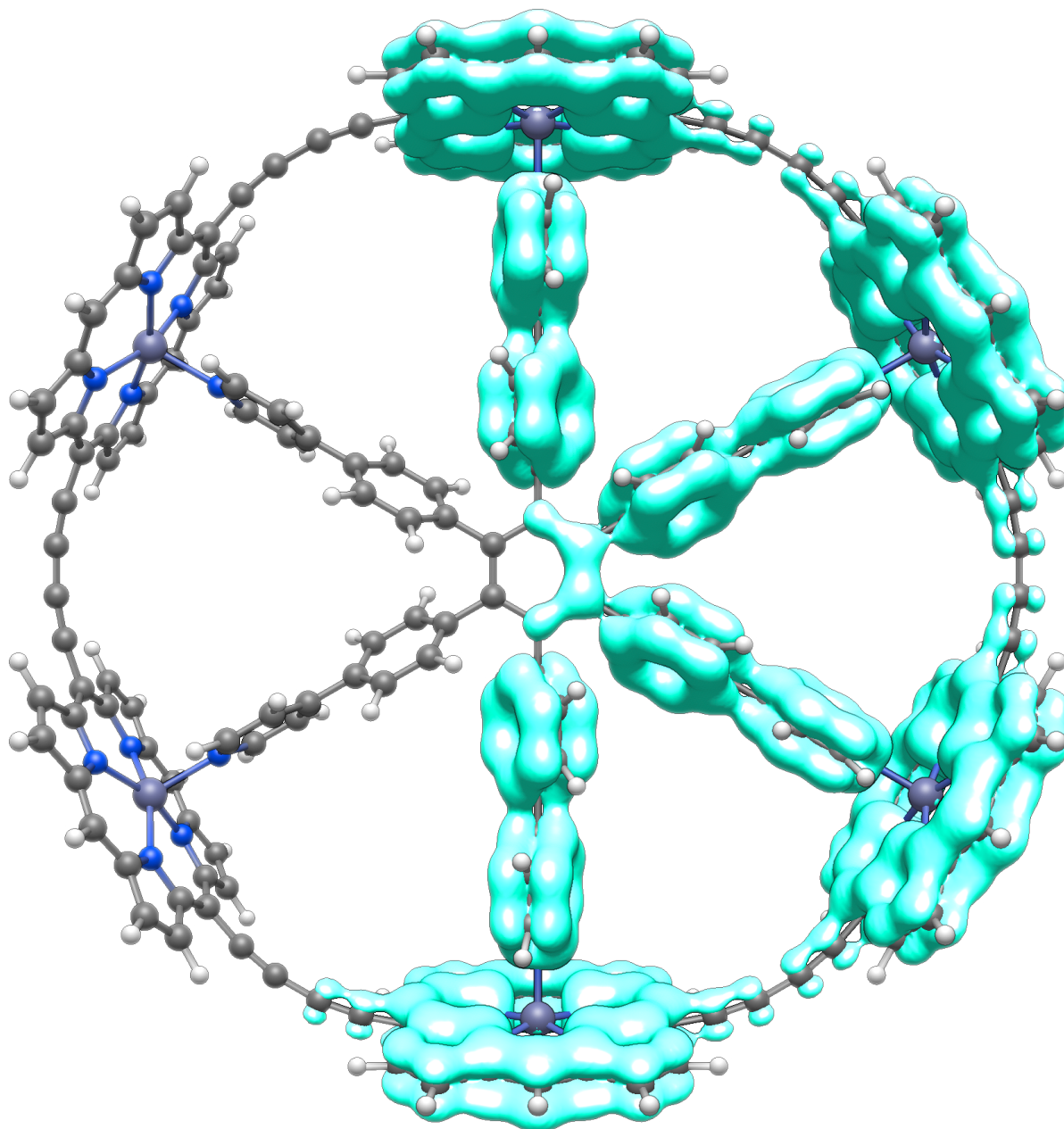


Figure S15. High-resolution EDDB_F map obtained for cumulative fragment F_4 of the *c*-P6[b6] nanoring using the ω B97M-V/def2-TZVPP parent density and the full NAO working space. Isosurfaces are shown at 0.0150 a.u. The common rendering convention assigns the HTML colors #ffd16b and #00ffd4 to negative and positive function values, respectively. The map was rendered in Avogadro 2.0.0 with the application window maximized on a 4K display and with the default camera settings. The complete definition of F_4 is given in Section S4.

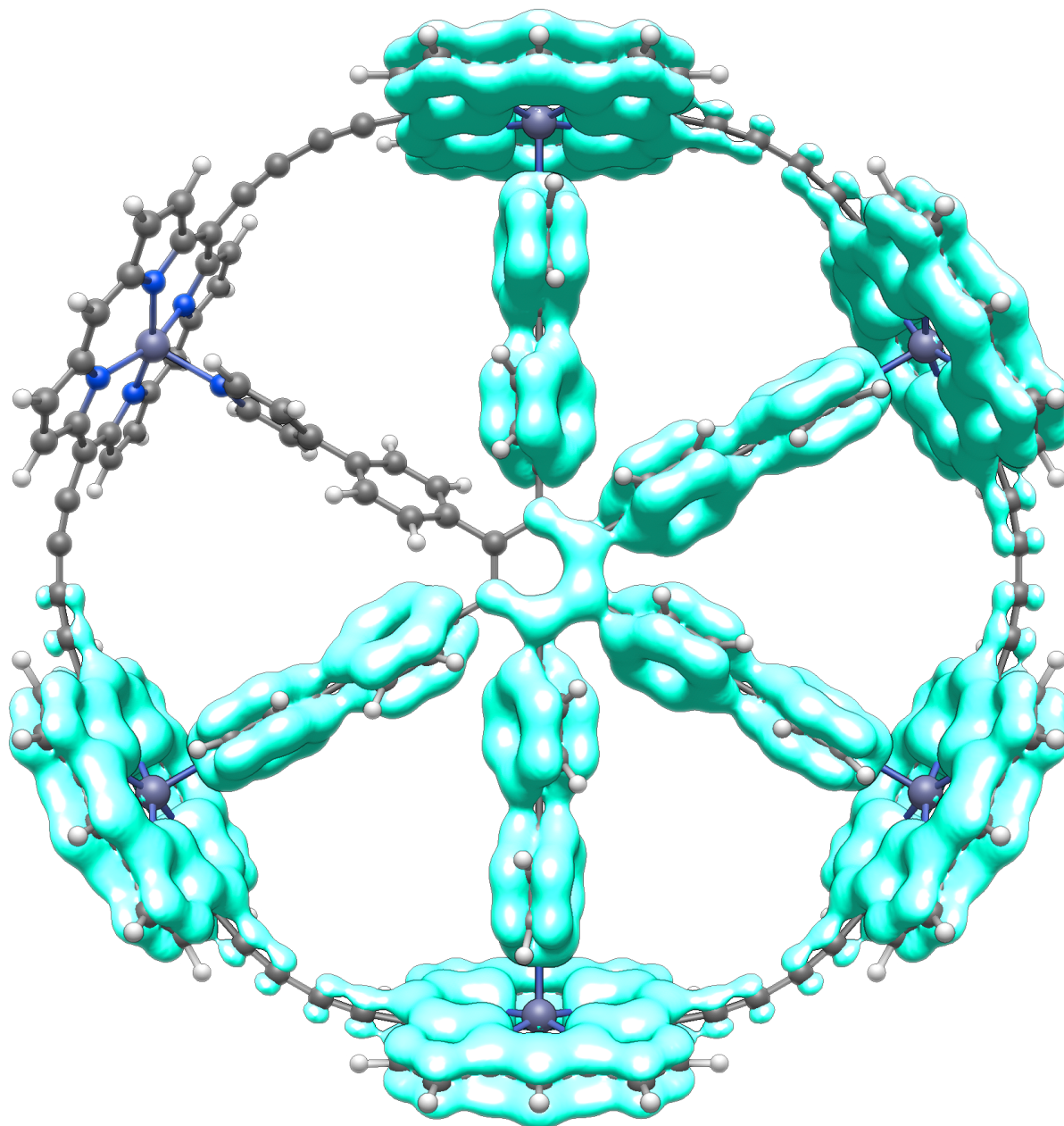


Figure S16. High-resolution EDDB_F map obtained for cumulative fragment F_5 of the *c*-P6[b6] nanoring using the $\omega\text{B97M-V/def2-TZVPP}$ parent density and the full NAO working space. Isosurfaces are shown at 0.0150 a.u. The common rendering convention assigns the HTML colors #ffd16b and #00ffd4 to negative and positive function values, respectively. The map was rendered in Avogadro 2.0.0 with the application window maximized on a 4K display and with the default camera settings. The complete definition of F_5 is given in Section S4.

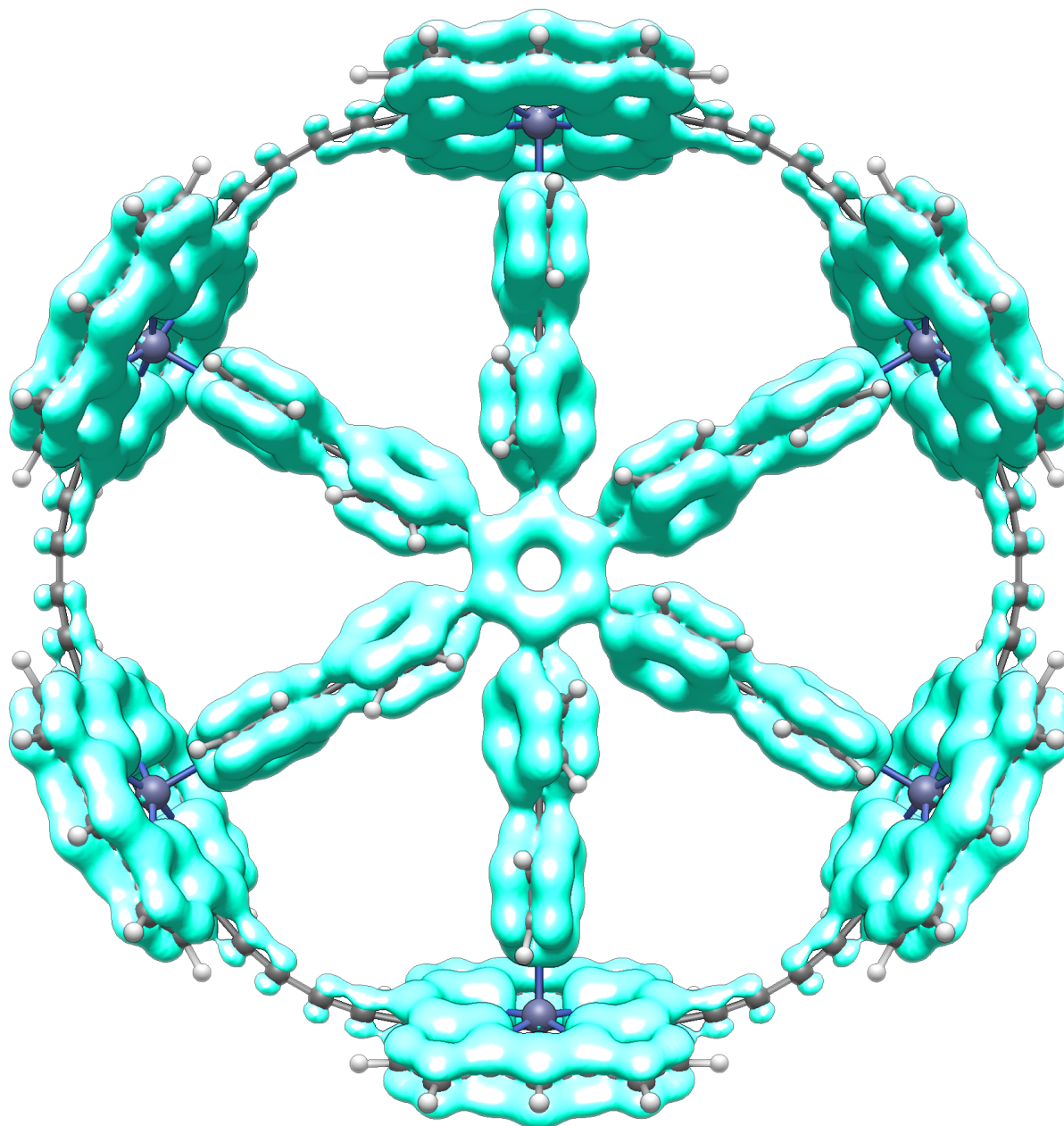


Figure S17. High-resolution EDDB_F map obtained for cumulative fragment F_6 , corresponding to the complete *c*-P6[b6] nanoring, using the $\omega\text{B97M-V/def2-TZVPP}$ parent density and the full NAO working space. Isosurfaces are shown at 0.0150 a.u. The common rendering convention assigns the HTML colors #ffd16b and #00ffd4 to negative and positive function values, respectively. The map was rendered in Avogadro 2.0.0 with the application window maximized on a 4K display and with the default camera settings. The complete definition of F_6 is given in Section S4.

S3 ORCA input files

c-p6[b6] (neutral, singlet, D₆ symmetry, optimized geometry)

geometry_def2-svp.inp

```
! wB97M-V RIJCOSX def2-SVP def2-SVP/C UseSym LooseOpt
* xyz 0 1
Zn      -0.000000000000000    12.23208119027527    -0.000000000000000
N       1.45104055374101    12.53707201549846    1.45252871488332
C       2.79134604061061    12.48074901682373    1.25853933320723
C       3.48341951058354    12.52667203416140    2.53152803630128
C       2.52117602510358    12.62449945752923    3.48882758817403
C       1.24800806399169    12.61983086091386    2.79985010132906
N      -1.45052061832370    12.54330971539373    1.45193961368140
C      -1.24701763006309    12.61963946844983    2.79862536822581
C      -2.52004205618451    12.62019154535765    3.48908686024566
C      -3.48234781099982    12.52335691158314    2.53254844457154
N      -1.45104055374101    12.53707201549846   -1.45252871488332
C      -2.79134604061061    12.48074901682373   -1.25853933320723
C      -3.48341951058354    12.52667203416140   -2.53152803630128
C      -2.52117602510358    12.62449945752923   -3.48882758817403
C      -1.24800806399169    12.61983086091386   -2.79985010132906
N       1.45052061832370    12.54330971539373   -1.45193961368140
C       1.24701763006309    12.61963946844983   -2.79862536822581
C       2.52004205618451    12.62019154535765   -3.48908686024566
C       3.48234781099982    12.52335691158314   -2.53254844457154
C       2.79013604343926    12.48250534363544   -1.25865307010810
C       3.42902861016449    12.40653868814696   -0.00052326871830
C       4.83007292163517    12.13767696892877   -0.00078200339287
C       5.97929236919118    11.73282040696546   -0.00199694064627
C      -4.83007292163517    12.13767696892877    0.00078200339287
C      -5.97929236919118    11.73282040696546    0.00199694064627
C       0.00004322041164    12.66055936661100    3.42399244919964
C      -0.00004322041164    12.66055936661100   -3.42399244919964
N     -10.13190257762613    7.52517398921038    1.45252871488332
C      -9.41297268652170    8.65775109033376    1.25853933320723
C      -9.10670645116810    9.28006580528440    2.53152803630128
C      -9.67254922773139    8.49565221391659    3.48882758817403
C     -10.30509008501840    7.39072211800157    2.79985010132906
N     -11.58808517022898    5.01546715351543    1.45193961368140
C     -11.55243718130984    5.22987078762321    2.79862536822581
C     -12.18942750699757    4.1276753341787    3.48908686024566
C     -12.58671913159034    3.24587678665259    2.53254844457154
N     -11.58294313136714    5.01189802628807   -1.45252871488332
C     -12.20431872713231    3.82299792648997   -1.25853933320723
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C	8.21782780220605	4.49937213189893	1.12799694198493
C	7.01761957902773	3.79763041168358	1.17341170091173
C	4.08093795441193	2.98822032649599	1.06935522472539
C	2.87279899832609	2.29467228477184	1.06670618629787
C	-0.21234333379880	-9.36653370658595	1.12799694198493
C	-0.21996537881153	-7.97625203537487	1.17341170091173
C	0.54740573764459	-5.02830610303683	1.06935522472539
C	0.55084499280945	-3.63525305490280	1.06670618629787
H	0.39062311095907	9.96388254810887	2.02780575516459
H	0.42021986142150	7.47188636309855	2.12002587358222
H	-0.42021986142150	7.47188636309855	-2.12002587358222
H	-0.39062311095907	9.96388254810887	-2.02780575516459
H	-0.99996709605164	5.56265185985118	1.90786685157808
H	-0.99684963346130	3.09706858732131	1.90658973674874
H	0.99684963346130	3.09706858732131	-1.90658973674874

H	0.99996709605164	5.56265185985118	-1.90786685157808
H	-8.43366385150717	5.32023081145030	2.02780575516459
H	-6.26073347392311	4.09986425671508	2.12002587358222
H	-6.68095333534462	3.37202210638348	-2.12002587358222
H	-8.82428696246624	4.64365173665857	-2.02780575516459
H	-5.31738137106570	1.91532902179631	1.90786685157808
H	-3.18056489061369	0.68523718732996	1.90658973674874
H	-2.18371525715239	2.41183139999134	-1.90658973674874
H	-4.31741427501406	3.64732283805487	-1.90786685157808
H	-8.82428696246624	-4.64365173665857	2.02780575516459
H	-6.68095333534462	-3.37202210638348	2.12002587358222
H	-6.26073347392311	-4.09986425671508	-2.12002587358222
H	-8.43366385150717	-5.32023081145030	-2.02780575516459
H	-4.31741427501406	-3.64732283805487	1.90786685157808
H	-2.18371525715239	-2.41183139999134	1.90658973674874
H	-3.18056489061369	-0.68523718732996	-1.90658973674874
H	-5.31738137106570	-1.91532902179631	-1.90786685157808
H	-0.99684963346130	-3.09706858732131	-1.90658973674874
H	-0.99996709605164	-5.56265185985118	-1.90786685157808
H	0.42021986142150	-7.47188636309855	-2.12002587358222
H	0.39062311095907	-9.96388254810887	-2.02780575516459
H	8.82428696246624	-4.64365173665857	-2.02780575516459
H	6.68095333534462	-3.37202210638348	-2.12002587358222
H	6.26073347392311	-4.09986425671508	2.12002587358222
H	8.43366385150717	-5.32023081145030	2.02780575516459
H	4.31741427501406	-3.64732283805487	-1.90786685157808
H	2.18371525715239	-2.41183139999134	-1.90658973674874
H	3.18056489061369	-0.68523718732996	1.90658973674874
H	5.31738137106570	-1.91532902179631	1.90786685157808
H	3.18056489061369	0.68523718732996	-1.90658973674874
H	5.31738137106570	1.91532902179631	-1.90786685157808
H	6.26073347392311	4.09986425671508	-2.12002587358222
H	8.43366385150717	5.32023081145030	-2.02780575516459
H	8.82428696246624	4.64365173665857	2.02780575516459
H	6.68095333534462	3.37202210638348	2.12002587358222
H	4.31741427501406	3.64732283805487	1.90786685157808
H	2.18371525715239	2.41183139999134	1.90658973674874
H	-0.39062311095907	-9.96388254810887	2.02780575516459
H	-0.42021986142150	-7.47188636309855	2.12002587358222
H	0.99996709605164	-5.56265185985118	1.90786685157808
H	0.99684963346130	-3.09706858732131	1.90658973674874
Zn	0.00000000000000	-12.23208119027527	-0.00000000000000
Zn	10.59329305193218	-6.11604059513763	-0.00000000000000
Zn	10.59329305193218	6.11604059513763	-0.00000000000000
*			

density_minix.inp

```
% MOInp "./geometry_def2-svp.gbw"
! MORRead SlowConv VeryTightSCF wB97M-V RIJCOSX MINIX def2-SVP/C UseSym
* xyzfile 0 1 ./geometry_def2-svp.xyz
```

density_def2-svp.inp

```
% MOInp "./geometry_def2-svp.gbw"
! MORRead SlowConv VeryTightSCF wB97M-V RIJCOSX def2-SVP def2-SVP/C UseSym
* xyzfile 0 1 ./geometry_def2-svp.xyz
```

density_def2-tzvpp.inp

```
% MOInp "./geometry_def2-svp.gbw"
! MORRead SlowConv VeryTightSCF wB97M-V RIJCOSX def2-TZVPP def2-TZVPP/C UseSym
* xyzfile 0 1 ./geometry_def2-svp.xyz
```

S4 RUNEDDB commands and fragment definitions

S4.1 Preparing ORCA JSON files

```
#
orca_2json density_minix.gbw -json
#
orca_2json density_def2-svp.gbw -json
#
orca_2json density_def2-tzvpp.gbw -json
#
```

S4.2 Single-core π -BDF calculations

The commands listed below generate the complete set of results for the single-core calculations, including export of the BDF maps in Gaussian cube format. For practical benchmarking, however, single-core BOP timings and related numerical parameters should be obtained in separate runs without cube generation. The RUNEDDB module responsible for exporting EDDB and BDF real-space maps is strongly parallelized, and the `-export-cube` option should therefore be used with the largest practical number of available CPU cores (option `-n 0`). On a single core, cube generation may require substantially more wall time than the BOP calculation itself.

```
#
# FIGURE S1 - MINIX basis, NAO representation
#
runEDDB -i density_minix.json -v -n 1 -s 1:117,124:126,145:153 -b nao --export-cube bdf >& density_minix.BDF_G.NAO.out
mv density_minix.BDF_G.cube density_minix.BDF_G.NAO.cube
#
# FIGURE S2 - MINIX basis, NMB representation
#
runEDDB -i density_minix.json -v -n 1 -s 1:117,124:126,145:153 -b nmb --export-cube bdf >& density_minix.BDF_G.NMB.out
mv density_minix.BDF_G.cube density_minix.BDF_G.NMB.cube
#
# FIGURE S3 - MINIX basis, NVB representation
#
runEDDB -i density_minix.json -v -n 1 -s 1:117,124:126,145:153 -b nvb --export-cube bdf >& density_minix.BDF_G.NVB.out
mv density_minix.BDF_G.cube density_minix.BDF_G.NVB.cube
#
# FIGURE S4 - def2-SVP basis, NAO representation
#
runEDDB -i density_def2-svp.json -v -n 1 -s 1:129 -b nao --export-cube bdf >& density_def2-svp.BDF_G.NAO.out
mv density_def2-svp.BDF_G.cube density_def2-svp.BDF_G.NAO.cube
#
# FIGURE S5 - def2-SVP basis, NMB representation
#
runEDDB -i density_def2-svp.json -v -n 1 -s 1:129 -b nmb --export-cube bdf >& density_def2-svp.BDF_G.NMB.out
mv density_def2-svp.BDF_G.cube density_def2-svp.BDF_G.NMB.cube
#
# FIGURE S6 - def2-SVP basis, NVB representation
#
runEDDB -i density_def2-svp.json -v -n 1 -s 1:129 -b nvb --export-cube bdf >& density_def2-svp.BDF_G.NVB.out
mv density_def2-svp.BDF_G.cube density_def2-svp.BDF_G.NVB.cube
#
# FIGURE S7 - def2-TZVPP basis, NAO representation
#
runEDDB -i density_def2-tzvpp.json -v -n 1 -s 1:129 -b nao --export-cube bdf >& density_def2-tzvpp.BDF_G.NAO.out
mv density_def2-tzvpp.BDF_G.cube density_def2-tzvpp.BDF_G.NAO.cube
#
# FIGURE S8 - def2-TZVPP basis, NMB representation
#
runEDDB -i density_def2-tzvpp.json -v -n 1 -s 1:129 -b nmb --export-cube bdf >& density_def2-tzvpp.BDF_G.NMB.out
mv density_def2-tzvpp.BDF_G.cube density_def2-tzvpp.BDF_G.NMB.cube
#
# FIGURE S9 - def2-TZVPP basis, NVB representation
#
runEDDB -i density_def2-tzvpp.json -v -n 1 -s 1:129 -b nvb --export-cube bdf >& density_def2-tzvpp.BDF_G.NVB.out
mv density_def2-tzvpp.BDF_G.cube density_def2-tzvpp.BDF_G.NVB.cube
#
```

S4.3 Differential NAO→NMB→NVB EDDB_G calculations

```
#
# def2-TZVPP basis, EDDB_G(NMB), reference
#
```

```

runEDDB -i density_def2-tzvpp.json -v -n 0 -b nmb --export-cube eddb -c 200 --table npa,ao >& density_def2-tzvpp.
EDDB_G.NMBref.out
mv density_def2-tzvpp.EDDB_G.cube density_def2-tzvpp.EDDB_G.NMBref.cube
#
# FIGURE S10 - def2-TZVPP basis, EDDB_G(NAO) - EDDB_G(NMB)
#
runEDDB -i density_def2-tzvpp.json -v -n 0 -b nao --export-cube eddb -c 200 --cube-ref density_def2-tzvpp.EDDB_G.
NMBref.cube --table npa,ao >& density_def2-tzvpp.EDDB_G.NAO-NMB.out
mv density_def2-tzvpp.EDDB_G.cube density_def2-tzvpp.EDDB_G.NAO-NMB.cube
#
#
# def2-TZVPP basis, EDDB_G(NVB), reference
#
runEDDB -i density_def2-tzvpp.json -v -n 0 -b nvb --export-cube eddb -c 200 --table npa,ao >& density_def2-tzvpp.
EDDB_G.NVBref.out
mv density_def2-tzvpp.EDDB_G.cube density_def2-tzvpp.EDDB_G.NVBref.cube
#
# FIGURE S11 - def2-TZVPP basis, EDDB_G(NMB) - EDDB_G(NVB)
#
runEDDB -i density_def2-tzvpp.json -v -n 0 -b nmb --export-cube eddb -c 200 --cube-ref density_def2-tzvpp.EDDB_G.
NVBref.cube --table npa,ao >& density_def2-tzvpp.EDDB_G.NMB-NVB.out
mv density_def2-tzvpp.EDDB_G.cube density_def2-tzvpp.EDDB_G.NMB-NVB.cube
#

```

S4.4 OpenMP strong scaling of the EDDB_G(NAO) calculations

```

#
# FIGURE 4 - def2-TZVPP basis, EDDB_G(NAO), 1 core
#
runEDDB -i density_def2-tzvpp.json -v -n 1 -b nao >& density_def2-tzvpp.EDDB_G.NAO.01c.out
#
# FIGURE 4 - def2-TZVPP basis, EDDB_G(NAO), 2 core
#
runEDDB -i density_def2-tzvpp.json -v -n 2 -b nao >& density_def2-tzvpp.EDDB_G.NAO.02c.out
#
# FIGURE 4 - def2-TZVPP basis, EDDB_G(NAO), 4 core
#
runEDDB -i density_def2-tzvpp.json -v -n 4 -b nao >& density_def2-tzvpp.EDDB_G.NAO.04c.out
#
# FIGURE 4 - def2-TZVPP basis, EDDB_G(NAO), 8 core
#
runEDDB -i density_def2-tzvpp.json -v -n 8 -b nao >& density_def2-tzvpp.EDDB_G.NAO.08c.out
#
# FIGURE 4 - def2-TZVPP basis, EDDB_G(NAO), 16 core
#
runEDDB -i density_def2-tzvpp.json -v -n 16 -b nao >& density_def2-tzvpp.EDDB_G.NAO.16c.out
#
# FIGURE 4 - def2-TZVPP basis, EDDB_G(NAO), 32 core
#
runEDDB -i density_def2-tzvpp.json -v -n 32 -b nao >& density_def2-tzvpp.EDDB_G.NAO.32c.out
#
grep "BOP time:" density_def2-tzvpp.EDDB_G.NAO.*.out
#

```

S4.5 Cumulative fragment EDDB_F(NAO) calculations

```

#
# FIGURE S12 - def2-TZVPP basis, EDDB_F(NAO), Fragment -1-
#
runEDDB -i density_def2-tzvpp.json -v -n 4 -b nao --export-cube eddb -f
1:23,26:27,56:57,83,162,170:177,224:225,232:244,310:317 >& density_def2-tzvpp.EDDB_F1.NAO.out
mv density_def2-tzvpp.EDDB_F.cube density_def2-tzvpp.EDDB_F1.NAO.cube
#
# FIGURE S13 - def2-TZVPP basis, EDDB_F(NAO), Fragment -2-
#
runEDDB -i density_def2-tzvpp.json -v -n 4 -b nao --export-cube eddb -f
1:23,26:27,56:57,83,134:162,170:177,206:213,218:219,224:225,232:244,270,294:305,310:317,346:353,360 >&
density_def2-tzvpp.EDDB_F2.NAO.out
mv density_def2-tzvpp.EDDB_F.cube density_def2-tzvpp.EDDB_F2.NAO.cube
#
# FIGURE S14 - def2-TZVPP basis, EDDB_F(NAO), Fragment -3-
#
runEDDB -i density_def2-tzvpp.json -v -n 4 -b nao --export-cube eddb -f
1:23,26:27,56:57,83,110:166,170:177,200:215,218:219,224:227,232:244,270,281:305,310:317,338:353,359:360 >&
density_def2-tzvpp.EDDB_F3.NAO.out
mv density_def2-tzvpp.EDDB_F.cube density_def2-tzvpp.EDDB_F3.NAO.cube
#

```

```
# FIGURE S15 - def2-TZVPP basis, EDDB_F(NAO), Fragment -4-  
#  
runEDDB -i density_def2-tzvpp.json -v -n 4 -b nao --export-cube eddb -f  
1:23,26:27,56:57,82:83,86:177,194:221,224:227,232:244,270,272:317,334:360 >& density_def2-tzvpp.EDDB_F4.NAO.out  
mv density_def2-tzvpp.EDDB_F.cube density_def2-tzvpp.EDDB_F4.NAO.cube  
#  
# FIGURE S16 - def2-TZVPP basis, EDDB_F(NAO), Fragment -5-  
#  
runEDDB -i density_def2-tzvpp.json -v -n 4 -b nao --export-cube eddb -f  
1:23,26:27,51:52,56:177,186:227,231:244,258:317,326:360 >& density_def2-tzvpp.EDDB_F5.NAO.out  
mv density_def2-tzvpp.EDDB_F.cube density_def2-tzvpp.EDDB_F5.NAO.cube  
#  
# FIGURE S17 - def2-TZVPP basis, EDDB_F(NAO), Fragment -6-  
#  
runEDDB -i density_def2-tzvpp.json -v -n 4 -b nao --export-cube eddb -f 1:360 >& density_def2-tzvpp.EDDB_F6.NAO.out  
mv density_def2-tzvpp.EDDB_F.cube density_def2-tzvpp.EDDB_F6.NAO.cube  
#
```

S5 Computational resources

All calculations were performed using the supercomputer Helios available in the HPC infrastructure PLGrid (ACK Cyfronet AGH, grant no. PLG/2025/018981) and an in-house server with the following specification:

- Model: Supermicro Hyper A+ Server AS-2125HS-TNR.
- Operating system: Debian GNU/Linux x86_64.
- RAM: 24×64 GB DDR5-4800 MHz ECC REG.
- CPU: 2× AMD EPYC 9554 (Genoa), 64C/128T, 3.1 GHz, 256 MB L3.
- NVMe (system): Intel Optane DC P5800X 3.2 TB PCIe 4.0.
- NVMe (scratch): Micron 9400 MAX 12.8 TB PCIe 4.0.
- Network: Supermicro AIOM 2×10 GbE.

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