Electronic Supplementary Information

Single-layer Polymeric Tetraoxa[8]circulene Modified by s-Metals: Toward Stable Spin Qubits and Novel Superconductors

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Table S1: The optimized Cartesian coordinates of the TOC#1-Li in the ground state calculated at the PBE level of theory. Lattice parameter *a*=*b*=8.416 Å.

Atom type	Coordinates (Angstroms)		
	X	Y	Z
C	8.34862703	4.88043266	0.00315573
C	7	9	8
C	8.34862703	3.40162581	0.00315573
C	7	9	8
C	3.40145752	8.34887934	0.00343057
C	8	9	6
C	4.88018035	8.34887934	0.00343057
C	6	9	6
C	3.42855626	2.42548892	0.00013660
C	4	4	1
C	4.85299734	5.85656956	0.00013660
C	8	4	1
C	5.85631725	3.42880857	0.00013660
C	2	7	1
C	2.42523636	4.85325016	0.00000000
C	1	2	0
C	4.85299734	2.42548892	0.00013660
C	8	4	1
C	3.42855626	5.85656956	0.00013660
C	4	4	1
O	2.42523636	3.42880857	0.00000000
O	1	7	0
O	5.85631725	4.85325016	0.00013660
O	2	2	1

Li	2.777685972	1.189138344	0.001646578
	5.503951912	7.092920144	0.001646578
	7.092667832	2.777938284	0.001371740
	1.188970052	5.504204224	0.001371740
	5.503951912	1.189222615	0.001646578
	2.777685972	7.092920144	0.001509159
	1.188885906	2.777854264	0.001371740
	7.092667832	5.504120454	0.001509159
	1.382699459	6.899190988	0.000822880
	6.898938174	1.382952022	0.000822880
	1.382699459	1.382867876	0.000822880
	6.898938174	6.899190988	0.000822880
	8.348879349	8.348879349	0.189244463

Table S2: The optimized Cartesian coordinates of the TOC#1-Na in the ground state calculated at the PBE level of theory. Lattice parameter *a*=*b*=8.429 Å.

Atom type	Coordinates (Angstroms)		
	X	Y	Z
C	0.001348656	4.953360645	0,027033031
C	0.001348656	3.473210744	0,026850129
C	3.475739391	8.427751559	0,027033031
C	4.955889293	8.427751559	0,027033031
C	3.505409924	2.499818223	0,000182902
C	4.926303166	5.926584355	0,000365259
C	5.929281813	3.502712466	0,000000000
C	2.502431276	4.923858924	0,000548161
C	4.926387571	2.499818223	0,000000000
C	3.505241364	5.926668761	0,000548161

O	2.502515430	3.502796871	0,000365259
O	5.929197408	4.923690113	0,000182902
O	2.856200476	1.262763487	0,017717547
Na	5.575428459	7.163639468	0,017899905
	7.166420829	2.853587424	0,017352287
	1.265292260	5.573068120	0,018082807
	5.575512362	1.262679207	0,017352287
	2.856031917	7.163807777	0,018082807
	1.265460820	2.853671829	0,017899905
	7.166336424	5.572899309	0,017717547
	1.469107857	6.959992180	0,028859330
	6.962436421	1.466663364	0,027945908
	1.469360697	1.466747644	0,028494070
	6.962268113	6.959739466	0,028494070
	0.000084291	8.429015631	0,950348705

Table S3: The optimized Cartesian coordinates of the TOC#1-Ca in the ground state calculated at the PBE level of theory. Lattice parameter *a*=*b*=8.457 Å.

Atom type	Coordinates (Angstroms)		
	X	Y	Z
C	0.000000000	4.967362413	1.645031187
C	0.000000000	3.489906874	1.645031187
C	3.489822188	0.000084571	1.645031187
C	4.967277727	0.000084571	1.645031187
C	3.516377503	2.507868342	1.672980069
C	4.940806846	5.949400692	1.672980069
C	5.949316007	3.516377503	1.672980069
C	2.507783908	4.940806846	1.672980069

C	4.940806846	2.507868342	1.672980069
C	3.516377503	5.949400692	1.672980069
C	2.507783908	3.516377503	1.672980069
O	5.949316007	4.940806846	1.672980069
O	2.863827666	1.265182140	1.656785535
O	5.593356682	7.192002208	1.656785535
O	7.191917522	2.863827666	1.656785535
Ca	1.265182140	5.593356682	1.656785535
	5.593356682	1.265182140	1.656785535
	2.863827666	7.192002208	1.656785535
	1.265182140	2.863827666	1.656785535
	7.191917522	5.593356682	1.656785535
	1.460794858	6.996389490	1.655740877
	6.996389490	1.460794858	1.655740877
	1.460794858	1.460794858	1.655740877
	6.996389490	6.996389490	1.655740877
	0.000084571	0.000084571	0.000000000

Table S4: The optimized Cartesian coordinates of the TOC#2-Li in the ground state calculated at the PBE level of theory. Lattice parameter *a*=*b*=9.762 Å.

Atom type	Coordinates (Angstroms)		
	X	Y	Z
C	0.731526871	5.607884446	0.000000000
C	9.029973270	4.153615913	0.000000000
C	4.153615913	0.731526871	0.000000000
C	5.607884446	9.029973270	0.000000000
C	9.029973270	5.607884446	0.000000000
C	0.731526871	4.153615913	0.000000000

C	5.607884446	0.731526871	0.000000000
C	4.153615913	9.029973270	0.000000000
C	4.173041496	3.164971119	0.000000000
C	5.588458862	6.596528948	0.000000000
C	6.596528948	4.173041496	0.000000000
C	3.164971119	5.588458862	0.000000000
O	5.588458862	3.164971119	0.000000000
O	4.173041496	6.596528948	0.000000000
Li	3.164971119	4.173041496	0.000000000
	6.596528948	5.588458862	0.000000000
	3.481634257	1.914815945	0.000000000
	6.279865811	7.846684268	0.000000000
	7.846684268	3.481634257	0.000000000
	1.914815945	6.279865811	0.000000000
	6.279865811	1.914815945	0.000000000
	3.481634257	7.846684268	0.000000000
	1.914815945	3.481634257	0.000000000
	7.846684268	6.279865811	0.000000000
	2.094427537	7.667073112	0.000000000
	7.667073112	2.094427537	0.000000000
	2.094427537	2.094427537	0.000000000
	7.667073112	7.667073112	0.000000000
	0.000000000	0.000000000	0.000000000

Table S5: The optimized Cartesian coordinates of the TOC#2-Na in the ground state calculated at the PBE level of theory. Lattice parameter *a*=*b*=9.765 Å.

Atom type	Coordinates (Angstroms)		
	X	Y	Z

C	0.732089506	5.609561579	0.000000000
C	9.033009946	4.155538238	0.000000000
C	4.155538238	0.732089506	0.000000000
C	5.609561579	9.033009946	0.000000000
C	9.033009946	5.609561579	0.000000000
C	0.732089506	4.155538238	0.000000000
C	5.609561579	0.732089506	0.000000000
C	4.155538238	9.033009946	0.000000000
C	4.174970693	3.166821689	0.000000000
C	5.590128833	6.598277836	0.000000000
C	6.598277836	4.174970693	0.000000000
C	3.166821689	5.590128833	0.000000000
O	5.590128833	3.166821689	0.000000000
O	4.174970693	6.598277836	0.000000000
Na	3.166821689	4.174970693	0.000000000
	6.598277836	5.590128833	0.000000000
	3.483992136	1.916596122	0.000000000
	6.281107389	7.848503549	0.000000000
	7.848503549	3.483992136	0.000000000
	1.916596122	6.281107389	0.000000000
	6.281107389	1.916596122	0.000000000
	3.483992136	7.848503549	0.000000000
	1.916596122	3.483992136	0.000000000
	7.848503549	6.281107389	0.000000000
	2.096957406	7.668142265	0.000000000
	7.668142265	2.096957406	0.000000000

	5	6	0
	2.096957406	2.096957406	0.000000000
	7.668142265	7.668142265	0.000000000
	0.000000000	0.000000000	0.002416456

Table S6: The optimized Cartesian coordinates of the TOC#2-Ca in the ground state calculated at the PBE level of theory. Lattice parameter *a*=*b*=9.748 Å.

Atom type	Coordinates (Angstroms)		
	X	Y	Z
C	0.728880396	5.601080502	0.000000000
C	9.019419494	4.147219097	0.000000000
C	4.147219097	0.728880396	0.000000000
C	5.601080502	9.019419494	0.000000000
C	9.019419494	5.601080502	0.000000000
C	0.728880396	4.147219097	0.000000000
C	5.601080502	0.728880396	0.000000000
C	4.147219097	9.019419494	0.000000000
C	4.166520795	3.159813951	0.000000000
C	5.581778804	6.588485647	0.000000000
C	6.588485647	4.166520795	0.000000000
C	3.159813951	5.581778804	0.000000000
O	5.581778804	3.159813951	0.000000000
O	4.166520795	6.588485647	0.000000000
Ca	3.159813951	4.166520795	0.000000000
	6.588485647	5.581778804	0.000000000
	3.477998258	1.910081851	0.000000000
	6.270301340	7.838217603	0.000000000
	7.838217603	3.477998258	0.000000000
	1.910081851	6.270301340	0.000000000

	1 6.27030134 0 3.47799825 8 1.91008185 1 7.83821760 3 2.08740338 6 7.66089635 8 2.08740338 6 7.66089635 8 0.00000000 0	0 1.91008185 1 7.83821760 3 3.47799825 8 6.27030134 0 7.66089635 8 2.08740338 6 2.08740338 6 7.66089635 8 0.00000000 0	0 0.00000000 0 0.00000000 0 0.00000000 0 0.00000000 0 0.00000000 0 0.00000000 0 0.00000000 0 0.00000000 0

Figure S1. Band structure of the Ca-tetraoxa[8]circulene porous sheet (TOC#1-Ca) with Ca 4s and 3p contributions coloured in red and blue colors and the sum of all C and O orbital contributions is coloured green. The circle's radius is proportional to the spectral weight. For better visualization the radii of the red and bluer circles are multiplied by 0.02, the radius of green circles are multiplied by 0.005. The Fermi level corresponds to 0 eV.

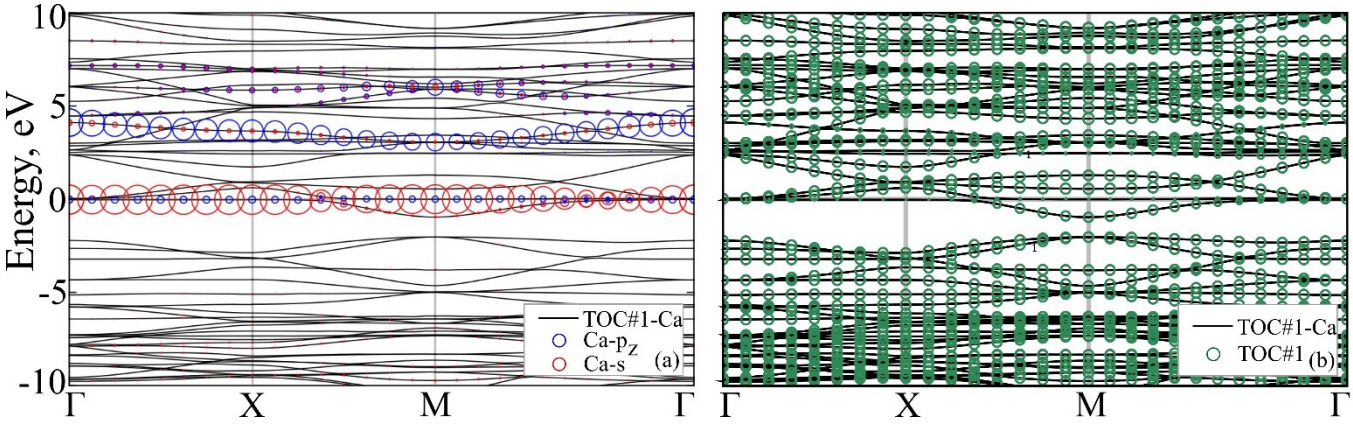


Figure S2. Partial density of states (PDOS) of the Ca-tetraoxa[8]circulene porous sheet (TOC#1-Ca). The Fermi level corresponds to 0 eV.

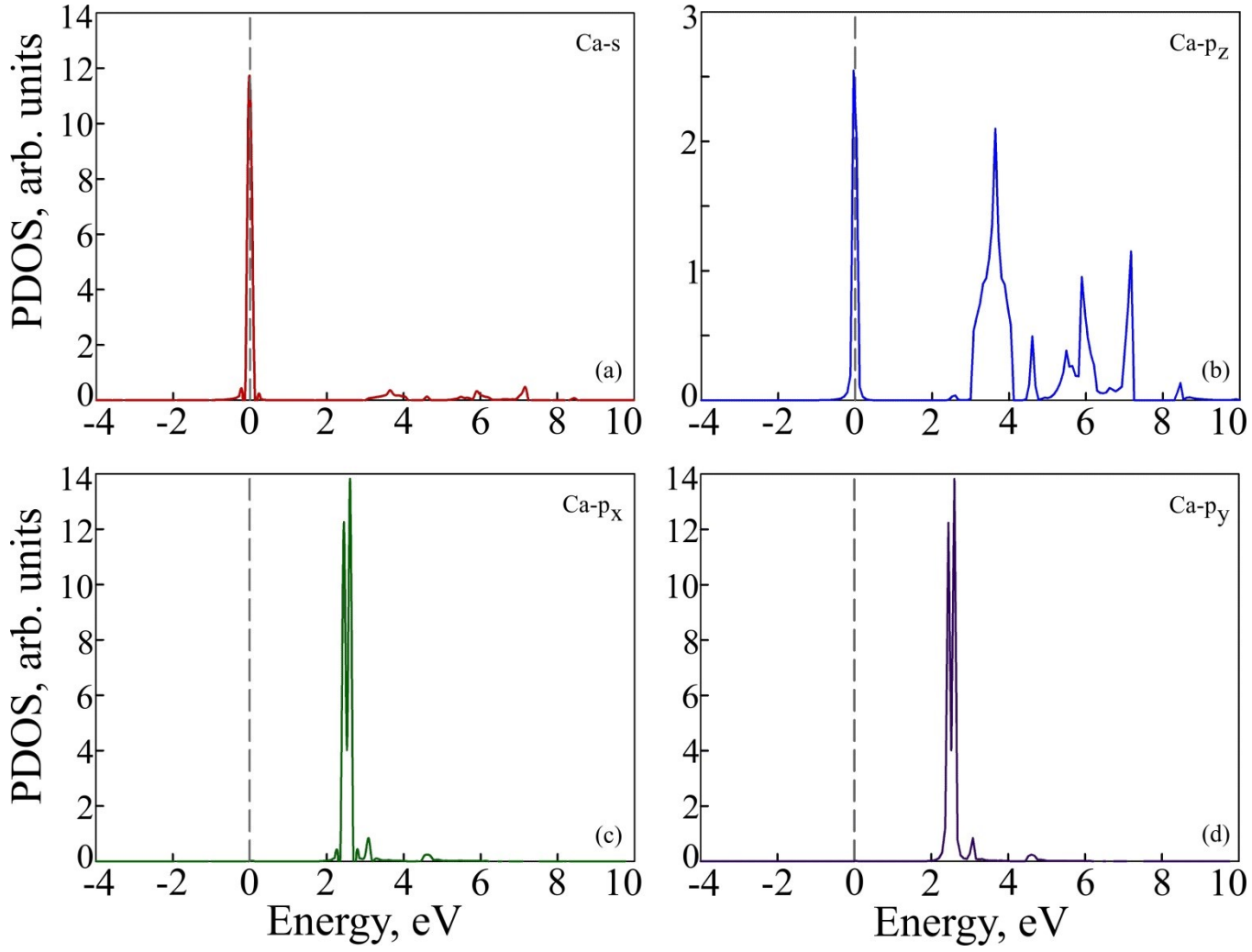


Figure S3. Total density of states (TDOS) of the Ca-tetraoxa[8]circulene porous sheet (TOC#1-Ca), calculated using plane-wave (VASP[1] and Quantum Espresso[2,3]) and linear combination of pseudoatomic orbital[4] (OpenMX[5]) based codes. The Fermi level corresponds to 0 eV. All calculations were carried out within the Perdew–Burke–Ernzerhof generalized gradient approximation (PBE)[6] with the Grimme's D3 empirical dispersion correction[7,8]. The criteria for the total energy minimization and interatomic forces were set to $1 \cdot 10^{-7}$ Hartree and $1 \cdot 10^{-5}$ Hartree/Borh, respectively. The cutoff energy was equal to 40 Ry. The pseudo-atomic orbital basis set *s3p3d2* for *Ca*, *s3p2* for *Na* and *Li*, *s2p2d2* for *C*, *s2p2d2f1* for *O* with cutoff radii 9.0 a.u. for *Ca* and *Na*, 8.0 a.u. for *Li*, 5.0 a.u. for *C* and *O* were used in OpenMX. We used the pseudopotentials C.pbe-n-kjpaw_psl.1.0.0.UPF, O.pbe-n-kjpaw_psl.1.0.0.UPF and Ca.pbe-spn-kjpaw_psl.1.0.0.UPF from http://www.quantum-espresso.org in Quantum Espresso and norm-conserving pseudopotentials[9–13] in OpenMX. The first Brillouin zone was sampled on a grid of 10×10×1 k-points generated according to the Monkhorst-Pack method[14]. We applied vacuum region of at least 15 Å along the z-direction to avoid interactions between neighboring images in periodic boundary conditions.

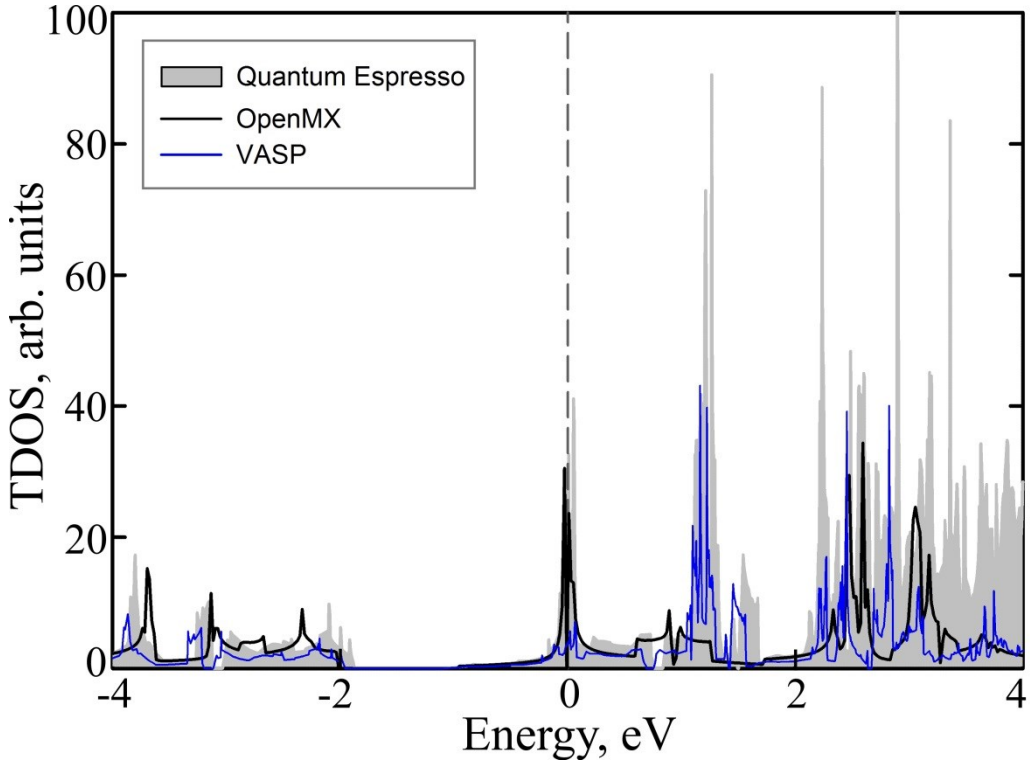


Figure S4. Spatial distribution of electron density in Me-tetraoxa[8]circulene organometallic porous sheets (TOC-Me, where Me = Li, Na and Ca) with two types of fusing between tetraoxa[8]circulene moieties. Isosurface level is 0.1 Bohr radius.

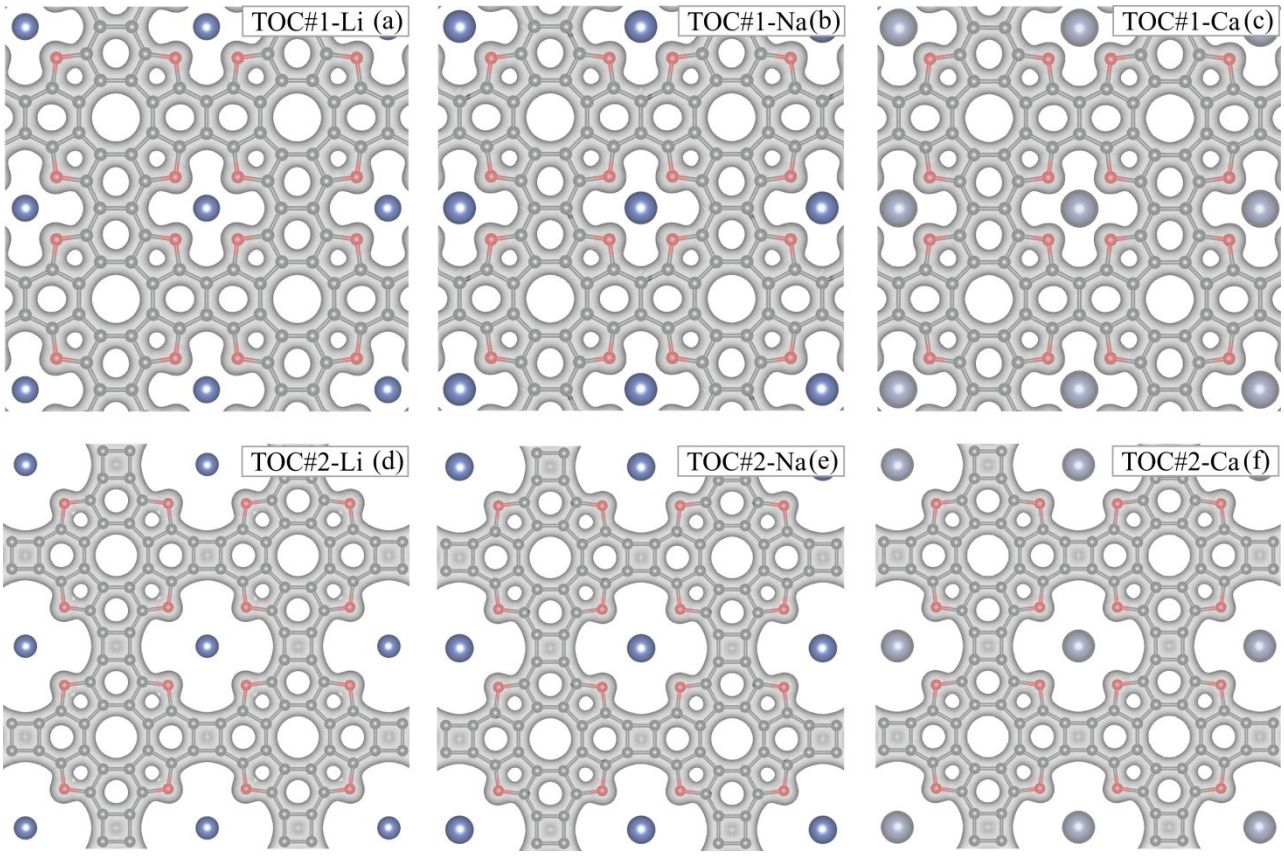


Figure S5. Charge density difference induced by the interaction between the TOC#1 porous sheet and Ca atoms. Top and bottom views of TOC#1-Ca are presented at (a) and (b) figures, respectively. Difference charge density is calculated as the difference in charge densities between TOC#1-Ca and superposition of charge densities of free-standing fragments, located at the same positions as in the organometallic sheet. Blue and yellow colors represent electron-deficient and electron-excess areas, respectively. Isosurface level is $5.0 \cdot 10^{-5}$ Bohr radius.

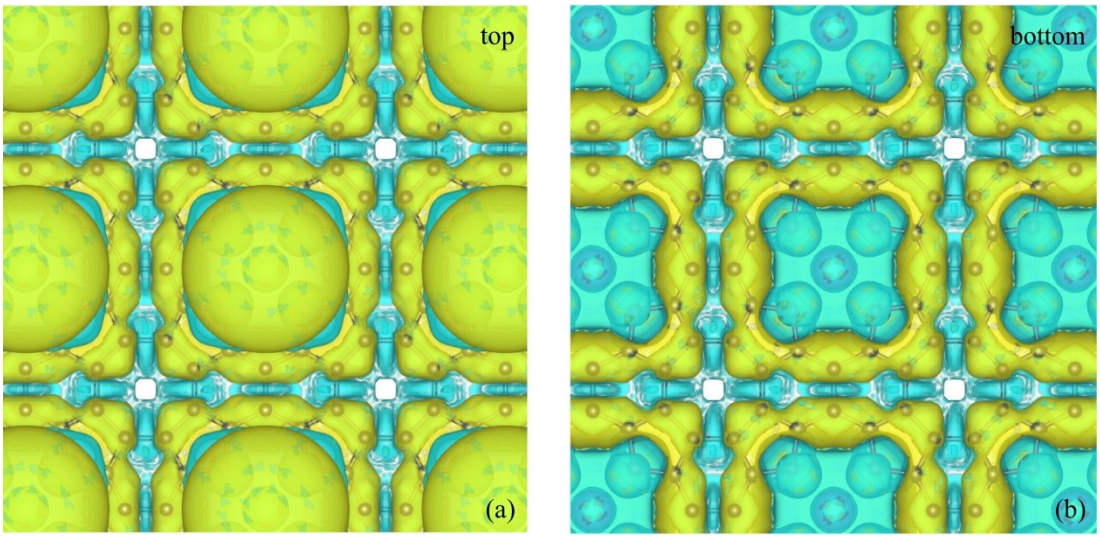
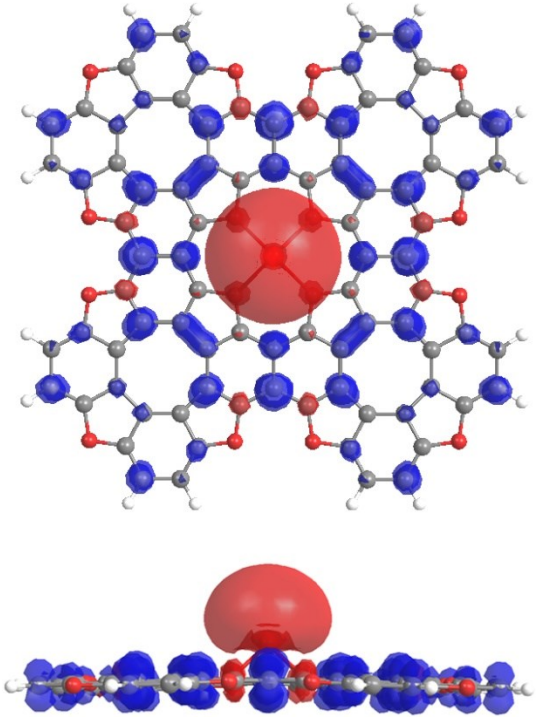


Figure S6. Spin density map of TOC#1-Ca.



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