

### Electronic Supplementary Information

## Syntheses, structures and theoretical investigations of [Au<sub>10</sub>S<sub>2</sub>(PPh<sub>2</sub>)<sub>2</sub>(dppma2)<sub>4</sub>(dppma3)]·[Au<sub>6</sub>S<sub>2</sub>(dppma2)<sub>2</sub>(dppma3)]

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## 1. Synthesis details

### 1.1 Materials and reagents

The ligand 2,3-bis(diphenylphosphino)maleic anhydride (dppma)<sup>[1]</sup>, the binuclear gold(I) chloride precursors, [(AuCl)<sub>2</sub>(dppma)],<sup>[2]</sup> and S(SiMe<sub>3</sub>)<sub>2</sub><sup>[3]</sup> were synthesized according to literature procedures. All solvents were purified and distilled in a nitrogen atmosphere using standard procedures prior to use.

### 1.2 Synthesis of **1**

To a suspension of [(AuCl)<sub>2</sub>(dppma)] (158 mg, 0.17 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) with a drop of water S(SiMe<sub>3</sub>)<sub>2</sub> (0.042 ml, 0.20 mmol) was added. The reaction mixture immediately turned dark and was stirred for one hour at room temperature. Layering *n*-heptane onto the solution gave three kinds of crystalline products (yields given with respect to Au): yellow needle-like [Au<sub>5</sub>(PPh<sub>2</sub>)<sub>3</sub>(dppma<sub>2</sub>)<sub>2</sub>] (about 40% yield) and red cube-like [Au<sub>24</sub>(PPh<sub>2</sub>)<sub>4</sub>S<sub>6</sub>(dppma<sub>2</sub>)<sub>8</sub>] (about 35% yield) beside a very small amount (ca. 8 mg, about 5% yield) of dark-orange, needle-like crystals of [Au<sub>10</sub>S<sub>2</sub>(PPh<sub>2</sub>)<sub>2</sub>(dppma<sub>2</sub>)<sub>4</sub>(dppma<sub>3</sub>)]·[Au<sub>6</sub>S<sub>2</sub>(dppma<sub>2</sub>)<sub>2</sub>(dppma<sub>3</sub>)] (**1**).

## 2. Details of the X-ray diffraction measurements, structure solutions and refinements

*Crystal structure determination.* The X-ray diffraction data of **1** were collected at 150 K on a STOE StadiVari diffractometer with a Pilatus300K detector using a Mo GeniX 3D HF micro focus X-ray source ( $\lambda = 0.71073 \text{ \AA}$ ). The structure was solved by direct methods; full-matrix least-squares refinement on  $F^2$  was done by using the program packages SHELX<sup>[4]</sup> and OLEX2.<sup>[5]</sup> H atoms were added on idealized positions. The crystallographic data for compound **1** are summarized in Table S1.

**Table S1.** Crystallographic data for **1**

CCDC Depository number	1046523
Formula weight	7246.05
Temperature/K	150.15
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	15.4644(3)
b/Å	25.0982(5)
c/Å	27.0905(4)
$\alpha$ /°	92.1940(10)
$\beta$ /°	91.0980(10)
$\gamma$ /°	93.1300(10)
Volume/Å <sup>3</sup>	10488.8(3)
Z	2
$\rho_{\text{calc}}/\text{gcm}^{-3}$	2.294
$\mu/\text{mm}^{-1}$	11.596
F(000)	6740.0
Crystal size/mm <sup>3</sup>	0.25 × 0.14 × 0.08
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\Theta$ range for data collection/°	3.01 to 52.2
Index ranges	$-19 \leq h \leq 18, -30 \leq k \leq 31, -33 \leq l \leq 31$
Reflections collected	79203
Independent reflections	40454 [ $R_{\text{int}} = 0.0653, R_{\text{sigma}} = 0.0644$ ]
Data/restraints/parameters	40454/13/2266
Goodness-of-fit on F <sup>2</sup>	0.976
Final R indexes [ $I > 2\sigma(I)$ ]	$R_1 = 0.0634, wR_2 = 0.1669$
Final R indexes [all data]	$R_1 = 0.0779, wR_2 = 0.1770$
Largest diff. peak/hole / e Å <sup>-3</sup>	4.41/-3.99

### 3. Density functional theory (DFT) calculations

#### 3.1 General procedure

Before the quantum chemical investigations could be performed properly, the complex had to be transformed to point group  $C_2$ . Symmetrization was realized by employment of the DIAMOND 3 software<sup>[6]</sup> (to delete one half of the molecule) and addition of the missing half within the DEFINE routine of the program system TURBOMOLE V6.5.<sup>[7]</sup>

Then three single runs of TURBOMOLE's RIDFT program<sup>[8]</sup> were performed with the specifications shown below to obtain an initial guess of the wave function.

The next step was the actual geometry optimization with TURBOMOLE V6.5 using the RIDFT program with the functional B97-D<sup>[9]</sup> (grid size m3). Dispersion correction was performed via Grimme's DFT-D3<sup>[10]</sup> with BJ-damping.<sup>[11]</sup> The used basis sets were of the quality def2-TZVP (Triple-Zeta Valence Plus Polarization)<sup>[12]</sup> with an effective core potential at the Au atoms (au def-ecp).<sup>[13]</sup>

For further investigations Mulliken,<sup>[14]</sup> NPA,<sup>[15]</sup> and PABOON<sup>[16]</sup> analyses, as well as a Boys localization of the molecular orbitals,<sup>[17]</sup> were performed as implemented in TURBOMOLE V6.5.

The bond lengths and angles after the calculations were analyzed with the program Molden.<sup>[18]</sup> The molecular structure was illustrated by employment of DIAMOND 3; pictures of the MOs and LMOs were realized with gOpenMol 3.00 (contour values:  $\pm 0.033$  a.u.).<sup>[19]</sup>

### ***3.2 Intramolecular Au-P and Au-S bond lengths and the respective angles***

The following tables show the calculated bond lengths and angles in comparison to the experimentally obtained values. Due to the calculation in  $C_2$  symmetry opposing bond lengths and angles become equivalent.

**Table S2.** Comparison of experimentally found *versus* calculated Au-P bond lengths within the two types of cluster subunits.

	Crystal Structure / Å	Calculated Structure / Å
[Au <sub>10</sub> S <sub>2</sub> (PPh <sub>2</sub> ) <sub>2</sub> (dppma2) <sub>4</sub> (dppma3)] subunit		
Au(1)–P(2)	2.276(3)	2.307
Au(6)–P(7)	2.285(3)	
Au(2)–P(1)	2.279(3)	2.299
Au(7)–P(6)	2.279(3)	
Au(3)–P(4)	2.258(3)	2.269
Au(8)–P(5)	2.253(3)	
Au(4)–P(3)	2.276(3)	2.292
Au(9)–P(8)	2.274(4)	
Au(5)–P(2)	2.290(3)	2.308
Au(10)–P(7)	2.285(3)	
[Au <sub>6</sub> S <sub>4</sub> (dppma2) <sub>2</sub> (dppma3)] subunit		
Au(12)–P(11)	2.284(3)	2.302
Au(16)–P(12)	2.274(3)	
Au(13)–P(9)	2.278(3)	2.299
Au(15)–P(10)	2.281(3)	

**Table S3.** Comparison of experimentally found *versus* calculated Au–S bond lengths within the two types of cluster subunits.

	Crystal Structure / Å	Calculated Structure / Å
[Au <sub>10</sub> S <sub>2</sub> (PPh <sub>2</sub> ) <sub>2</sub> (dppma2) <sub>4</sub> (dppma3)] subunits		
Au(1)–S(1)	2.324(3)	2.371
Au(6)–S(5)	2.339(4)	
Au(2)–S(3)	2.335(3)	2.378
Au(7)–S(4)	2.339(3)	
Au(3)–S(3)	2.322(3)	2.361
Au(8)–S(4)	2.318(3)	
Au(4)–S(3)	2.331(3)	2.356
Au(9)–S(4)	2.317(3)	
Au(5)–S(2)	2.312(3)	2.354
Au(10)–S(6)	2.305(3)	
[Au <sub>6</sub> S <sub>4</sub> (dppma2) <sub>2</sub> (dppma3)] subunit		

Au(11)–S(7)	2.283(3)	
Au(14)–S(8)	2.282(3)	2.308
Au(11)–S(9)	2.308(3)	
Au(14)–S(10)	2.304(3)	2.338
Au(12)–S(9)	2.328(3)	
Au(16)–S(10)	2.313(3)	2.356
Au(13)–S(9)	2.335(3)	
Au(15)–S(10)	2.336(3)	2.375

**Table S4.** Comparison of experimentally found *versus* calculated S–Au–P and S–Au–S angles within the two types of cluster subunits.

	Crystal Structure / °	Calculated Structure / °
[Au <sub>10</sub> S <sub>2</sub> (PPh <sub>2</sub> ) <sub>2</sub> (dppma <sub>2</sub> ) <sub>4</sub> (dppma <sub>3</sub> )] subunits		
S(1)–Au(1)–P(2)	170.4(1)	
S(5)–Au(6)–P(7)	166.1(1)	168.8
S(3)–Au(2)–P(1)	173.7(1)	
S(4)–Au(7)–P(6)	172.5(1)	177.2
S(3)–Au(3)–P(4)	170.1(1)	
S(4)–Au(8)–P(5)	168.5(1)	164.6
S(3)–Au(4)–P(3)	170.5(1)	
S(4)–Au(9)–P(8)	175.2(1)	176.7
S(2)–Au(5)–P(2)	176.1(1)	
S(6)–Au(10)–P(7)	173.6(1)	175.5
[Au <sub>6</sub> S <sub>4</sub> (dppma <sub>2</sub> ) <sub>2</sub> (dppma <sub>3</sub> )] subunit		
S(9)–Au(12)–P(11)	162.5(1)	
S(10)–Au(16)–P(12)	167.3(1)	167.4
S(9)–Au(13)–P(9)	171.6(1)	
S(10)–Au(15)–P(10)	170.2(1)	172.8
S(7)–Au(11)–S(9)	171.2(1)	
S(8)–Au(14)–S(10)	170.1(1)	170.9

### 3.3 Calculated Au-Au distances

Table S5 shows the calculated and the experimentally obtained Au...Au distances. Due to the calculation in  $C_2$  symmetry opposing gold-gold distances become equivalent.

See also Table S6 for an investigation of possible aurophilic interactions.

**Table S5.** Comparison of experimentally found *versus* calculated Au...Au distances within the two types of cluster subunits.

	Crystal Structure / Å	Calculated Structure / Å
[Au <sub>10</sub> S <sub>2</sub> (PPh <sub>2</sub> ) <sub>2</sub> (dppma2) <sub>4</sub> (dppma3)] subunit		
Au(1)...Au(2)	2.912(1)	2.965
Au(6)...Au(7)	2.891(1)	
Au(2)...Au(3)	3.124(1)	3.124
Au(7)...Au(8)	3.047(1)	
Au(3)...Au(4)	3.389(1)	3.361
Au(8)...Au(9)	3.403(1)	
Au(4)...Au(5)	2.978(1)	3.011
Au(9)...Au(10)	2.957(1)	
[Au <sub>6</sub> S <sub>4</sub> (dppma2) <sub>2</sub> (dppma3)] subunit		
Au(11)...Au(13)	3.195(1)	3.339
Au(14)...Au(15)	3.188(1)	
Au(11)...Au(15)	2.983(1)	3.081
Au(13)...Au(14)	2.971(1)	
Au(12)...Au(15)	3.154(1)	3.348
Au(13)...Au(16)	3.338(1)	
Au(12)...Au(13)	3.753(1)	3.802
Au(15)...Au(16)	3.690(1)	
Au(11)...Au(14)	3.352(1)	3.502
Au(12)...Au(16)	3.175(1)	3.210
Au(13)...Au(15)	4.376(1)	4.582

### 3.4 Investigation of possible aurophilic interactions

A population analysis based on occupation numbers (PABOON)<sup>T11</sup> was performed to investigate possible Au(I)⋯Au(I) interactions. Since the calculated shared electron numbers (SEN) do not correlate with the observed gold-gold distances, we don't assume the existence of aurophilic interactions within the two complex subunits (see Table S6). Due to the calculation in *C*<sub>2</sub> symmetry opposing gold-gold distances and the corresponding SEN become equivalent.

**Table S6.** Calculated Au⋯Au distances within the two types of cluster subunits and the corresponding SEN values.

	Calculated Structure / Å	SEN
[Au <sub>10</sub> S <sub>2</sub> (PPh <sub>2</sub> ) <sub>2</sub> (dppma2) <sub>4</sub> (dppma3)] subunit		
Au(1)⋯Au(2)	2.965	0.22
Au(6)⋯Au(7)		
Au(2)⋯Au(3)	3.124	0.49
Au(7)⋯Au(8)		
Au(3)⋯Au(4)	3.361	0.23
Au(8)⋯Au(9)		
Au(4)⋯Au(5)	3.011	0.09
Au(9)⋯Au(10)		
[Au <sub>6</sub> S <sub>4</sub> (dppma2) <sub>2</sub> (dppma3)] subunit		
Au(11)⋯Au(13)	3.339	0.46
Au(14)⋯Au(15)		
Au(11)⋯Au(15)	3.081	0.56
Au(13)⋯Au(14)		
Au(12)⋯Au(15)	3.348	0.27
Au(13)⋯Au(16)		
Au(12)⋯Au(13)	3.802	0.35
Au(15)⋯Au(16)		
Au(11)⋯Au(14)	3.502	0.36
Au(12)⋯Au(16)	3.210	0.30
Au(13)⋯Au(15)	4.582	0.53



### 3.5 Intermolecular distances and interactions

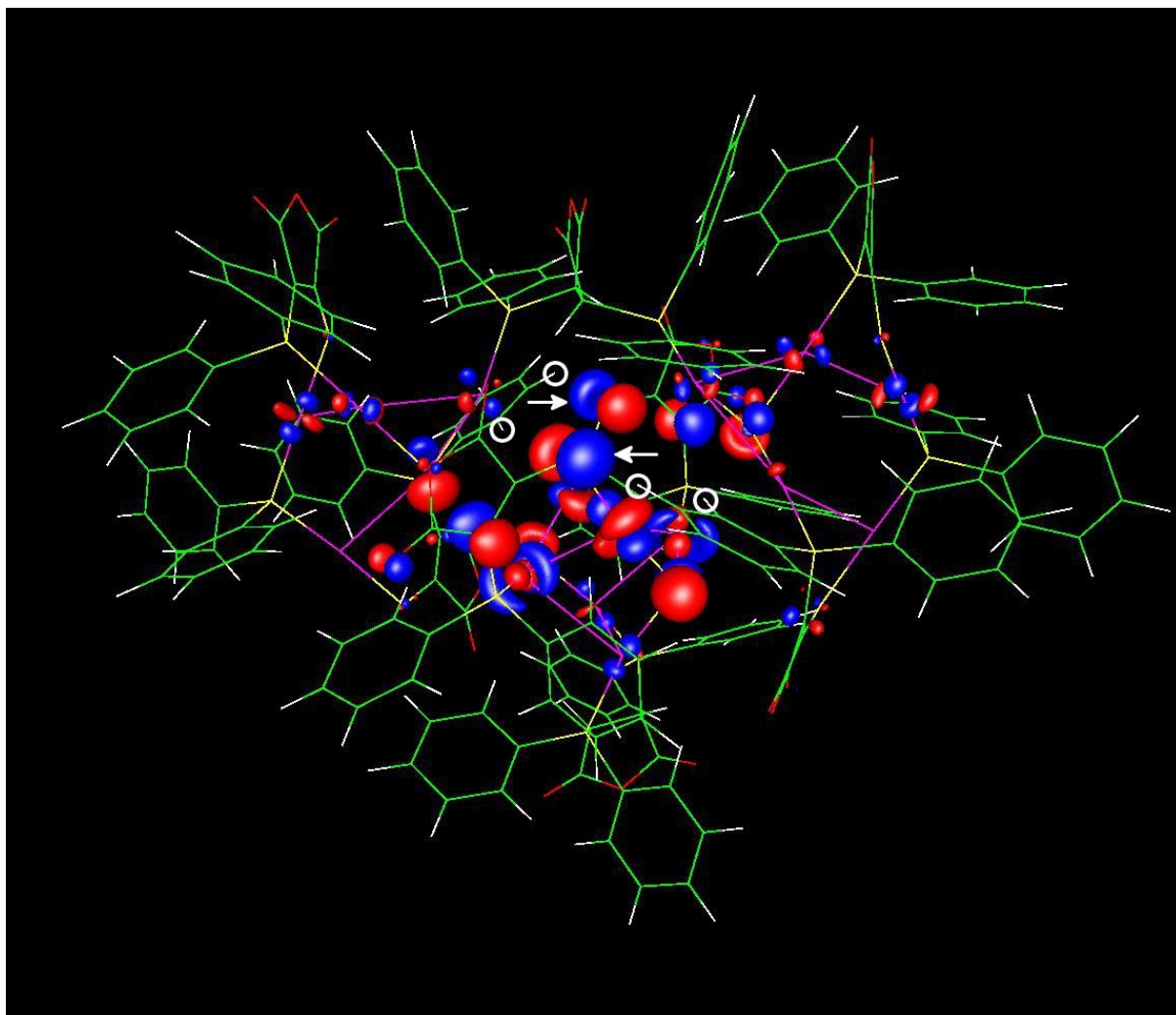
Table S7 shows the intermolecular Au $\cdots$ S distances as well as the intermolecular hydrogen bonds. Due to the calculation in  $C_2$  symmetry opposing distances become equivalent.

**Table S7.** Comparison of experimentally found *versus* calculated distances between the two subunits of the complex.

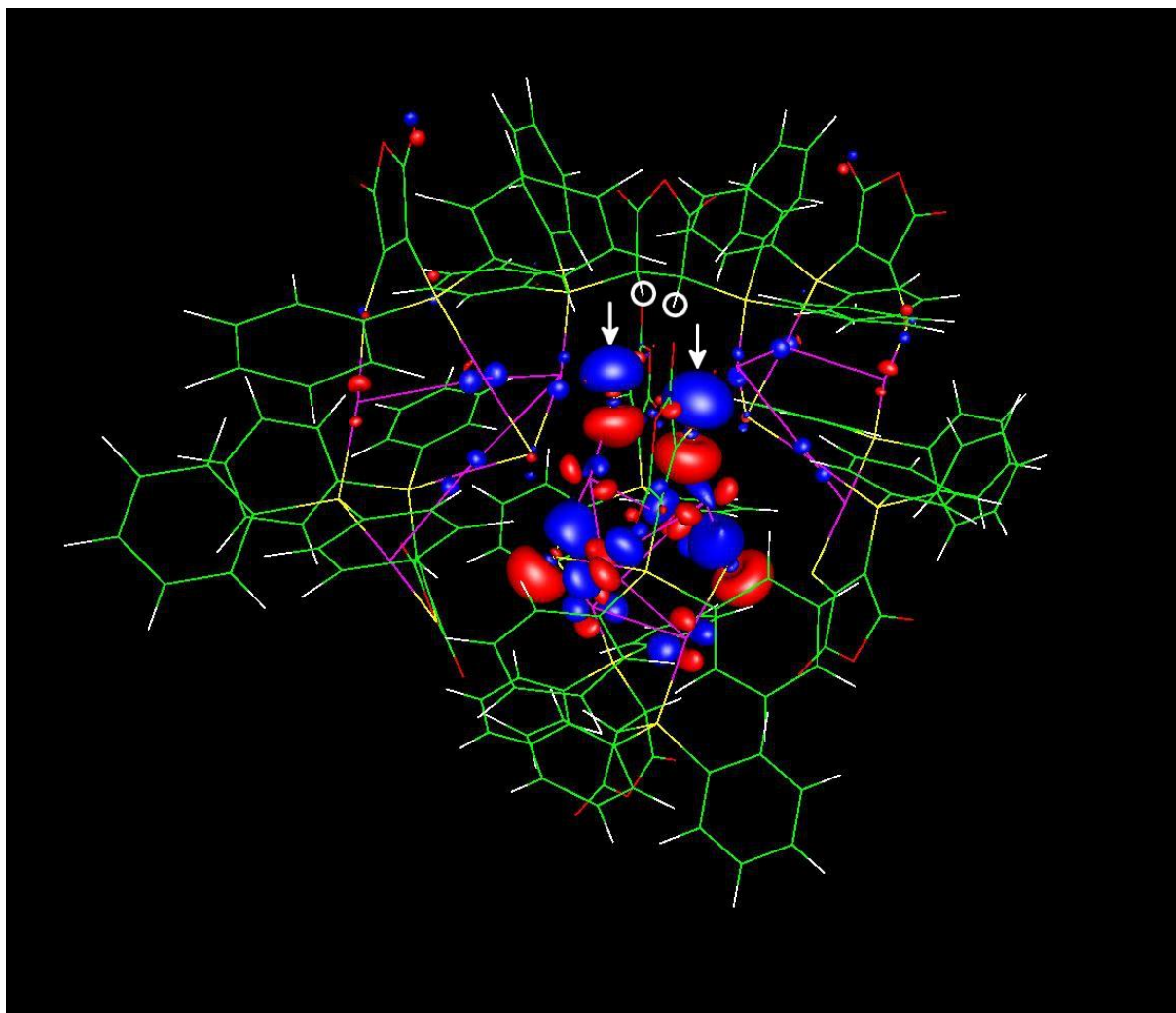
	Crystal Structure / Å	Calculated Structure / Å
Postulated dipole-dipole interactions		
Au(3) $\cdots$ S(8)	3.597(1)	3.400
Au(8) $\cdots$ S(7)	3.474(1)	
S(3) $\cdots$ Au(11)	4.558(1)	4.514
S(4) $\cdots$ Au(14)	4.589(1)	
Au(4) $\cdots$ S(9)	4.143(1)	3.733
Au(9) $\cdots$ S(10)	4.037(1)	
Hydrogen bonds		
O(16) $\cdots$ H(57)	2.477(1)	2.494
O(19) $\cdots$ H(60)	2.412(1)	
O(6) $\cdots$ H(138)	2.787(1)	2.958
O(15) $\cdots$ H(118)	3.254(1)	
O(6) $\cdots$ H(124)	3.000(1)	2.629
O(15) $\cdots$ H(144)	2.439(1)	
S(7) $\cdots$ H(57)	2.892(1)	3.015
S(8) $\cdots$ H(60)	2.968(1)	
S(7) $\cdots$ H(43)	3.867(1)	3.115
S(8) $\cdots$ H(115)	3.547(1)	
S(7) $\cdots$ H(44)	3.832(1)	3.290
S(8) $\cdots$ H(116)	3.464(1)	

The canonical MOs (Figures S1–S4) and the localized molecular orbitals (LMOs; Figures S5–S8) clearly show that their respective orientations fit well in case of the postulated hydrogen bonds but not in case of the Au $\cdots$ S dipole-dipole interactions.

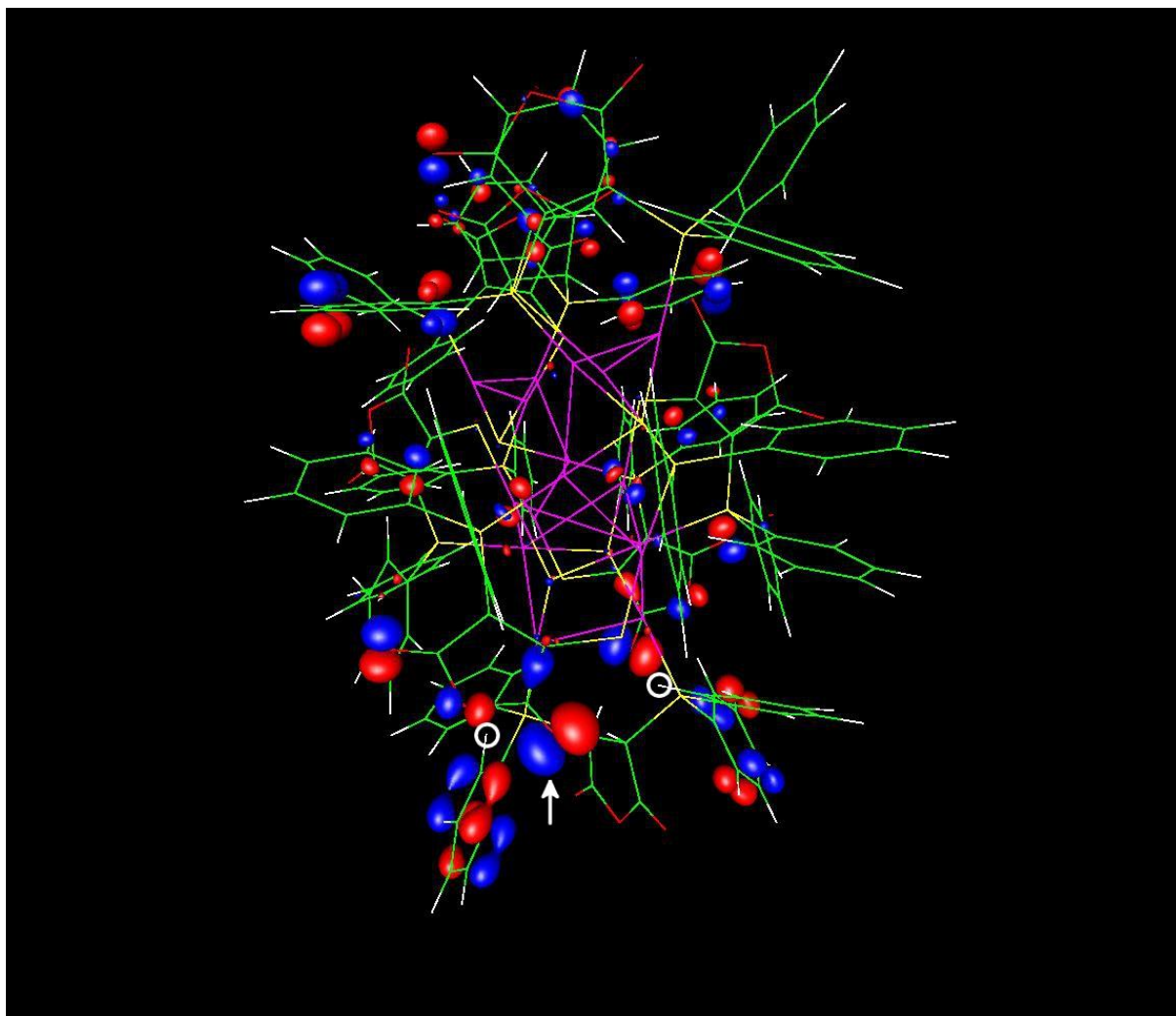
The H atoms, which are involved in the hydrogen bonds, are encircled. The corresponding canonical MOs and the LMOs are marked with an arrow. In all of the following figures the contour values of the orbitals are  $\pm 0.033$  a.u.



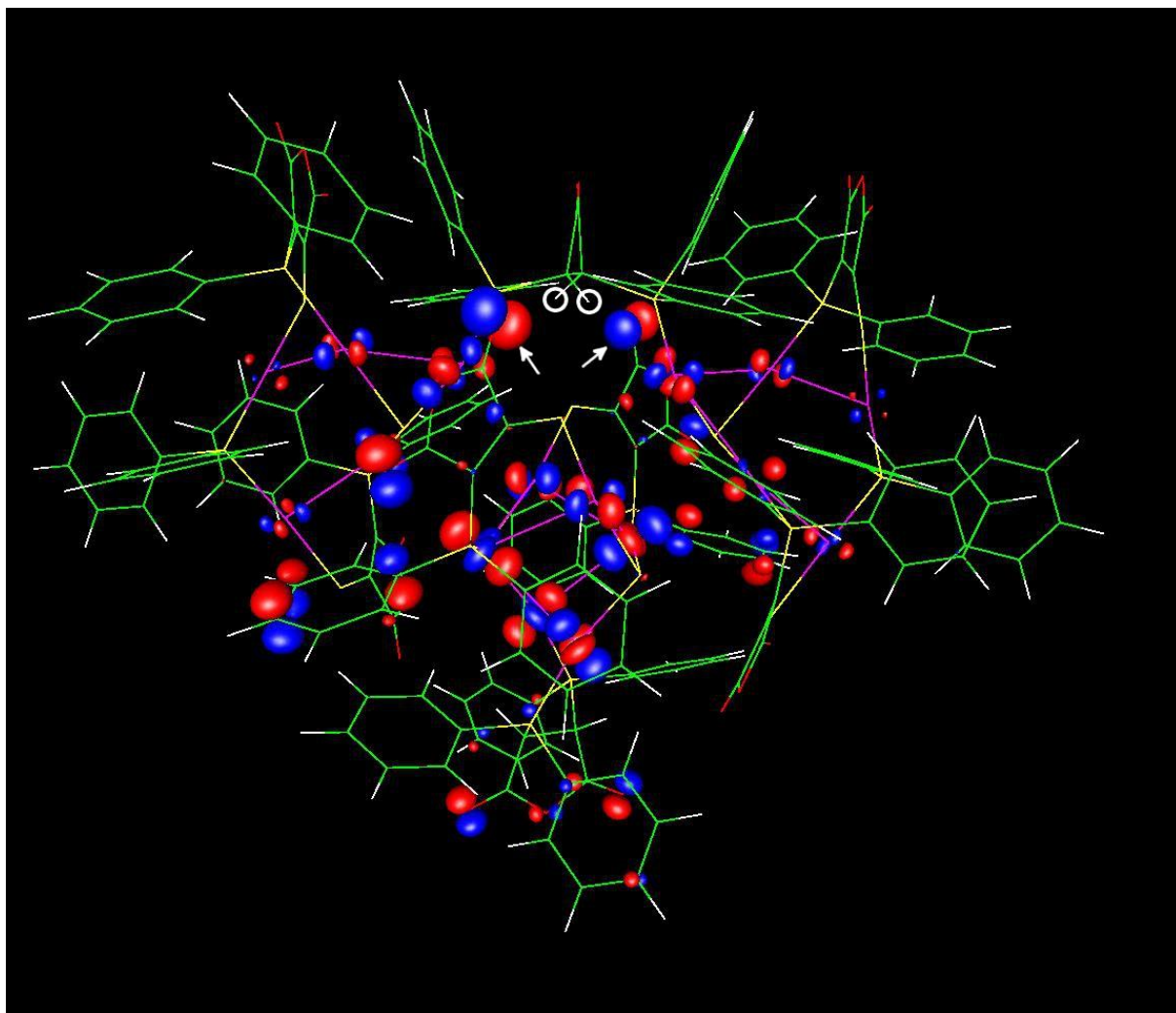
**Figure S1.** HOMO-3, -5.275 eV.



**Figure S2.** HOMO-23, -5.991 eV.

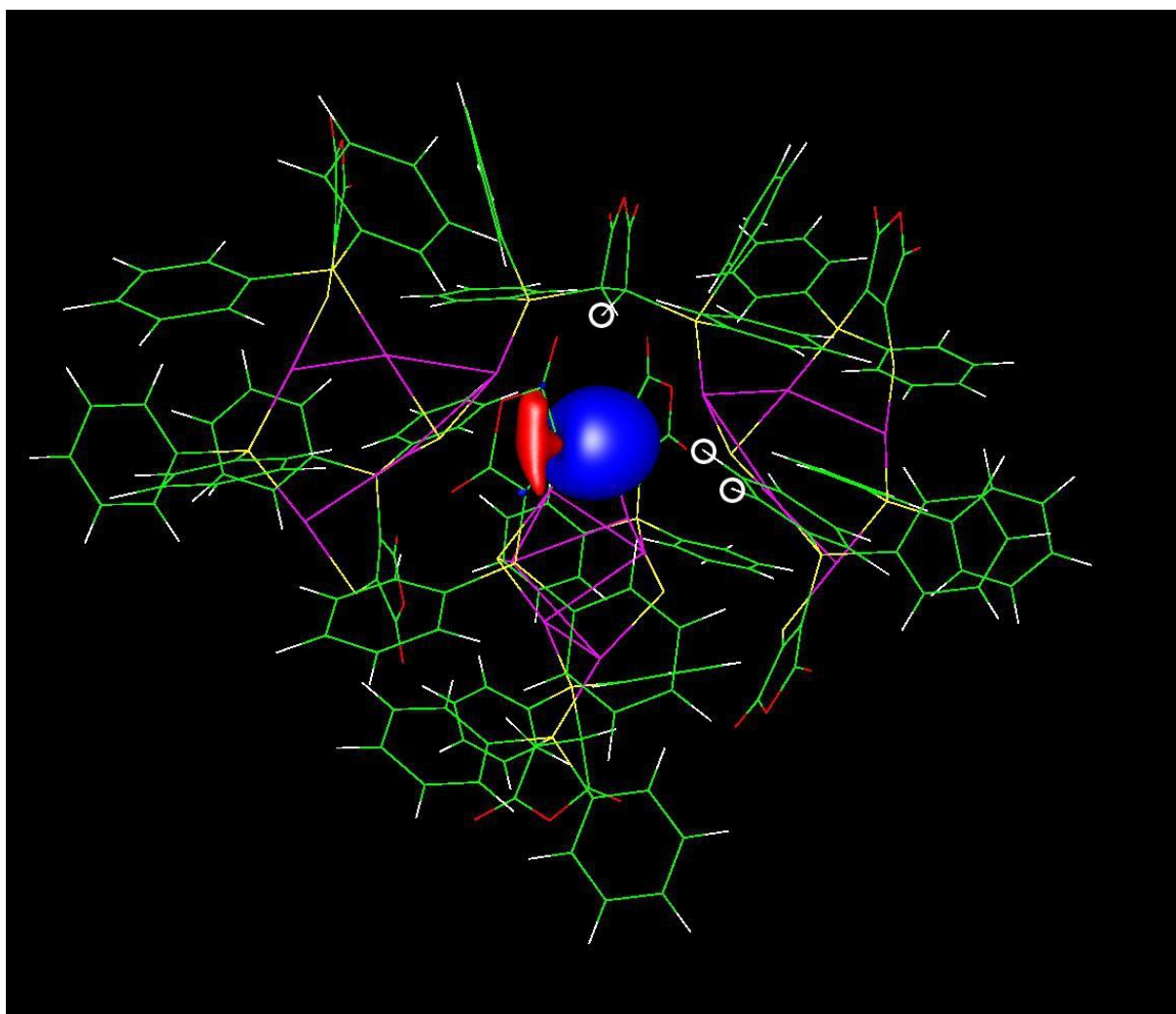


**Figure S3.** HOMO-59, -6.571 eV. The hydrogen bonds on the opposite side of the complex are omitted for clarity.

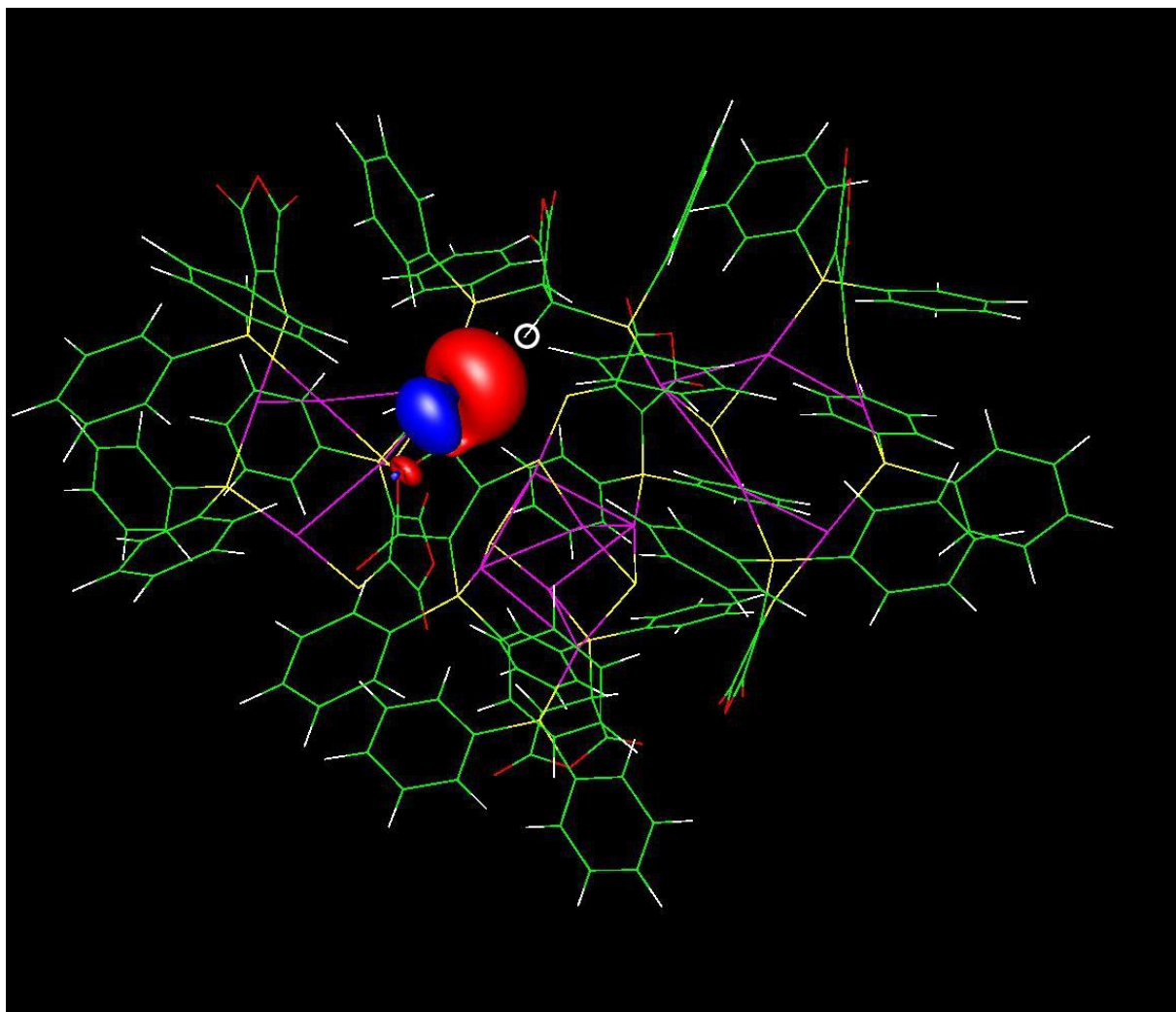


**Figure S4.** HOMO-81, -6.871 eV.

For reasons of clarity Figures 5–8 only show one of two possible LMOs. Due to the calculation in  $C_2$  symmetry they both become equivalent.

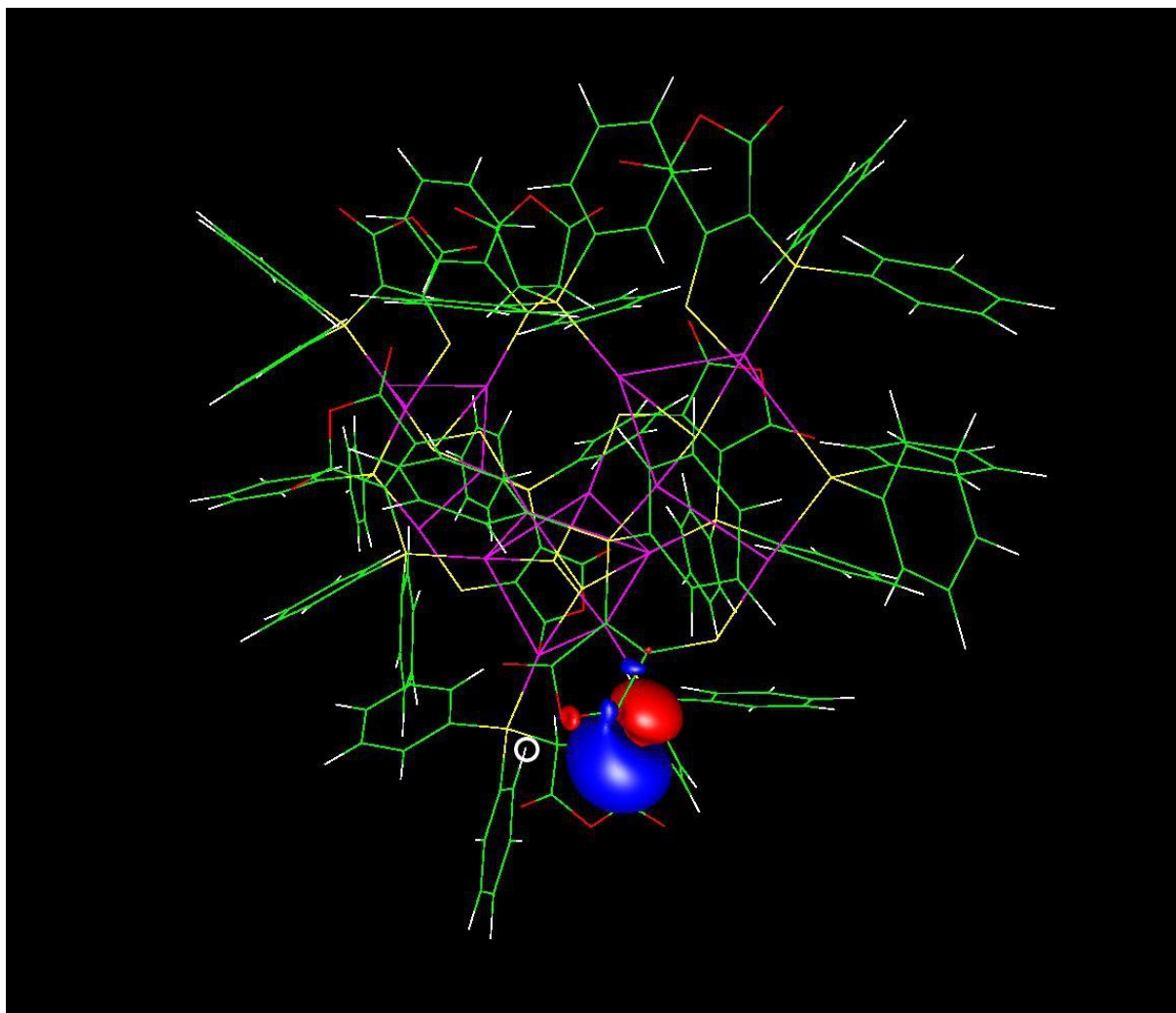


**Figure S5.** LMO 158



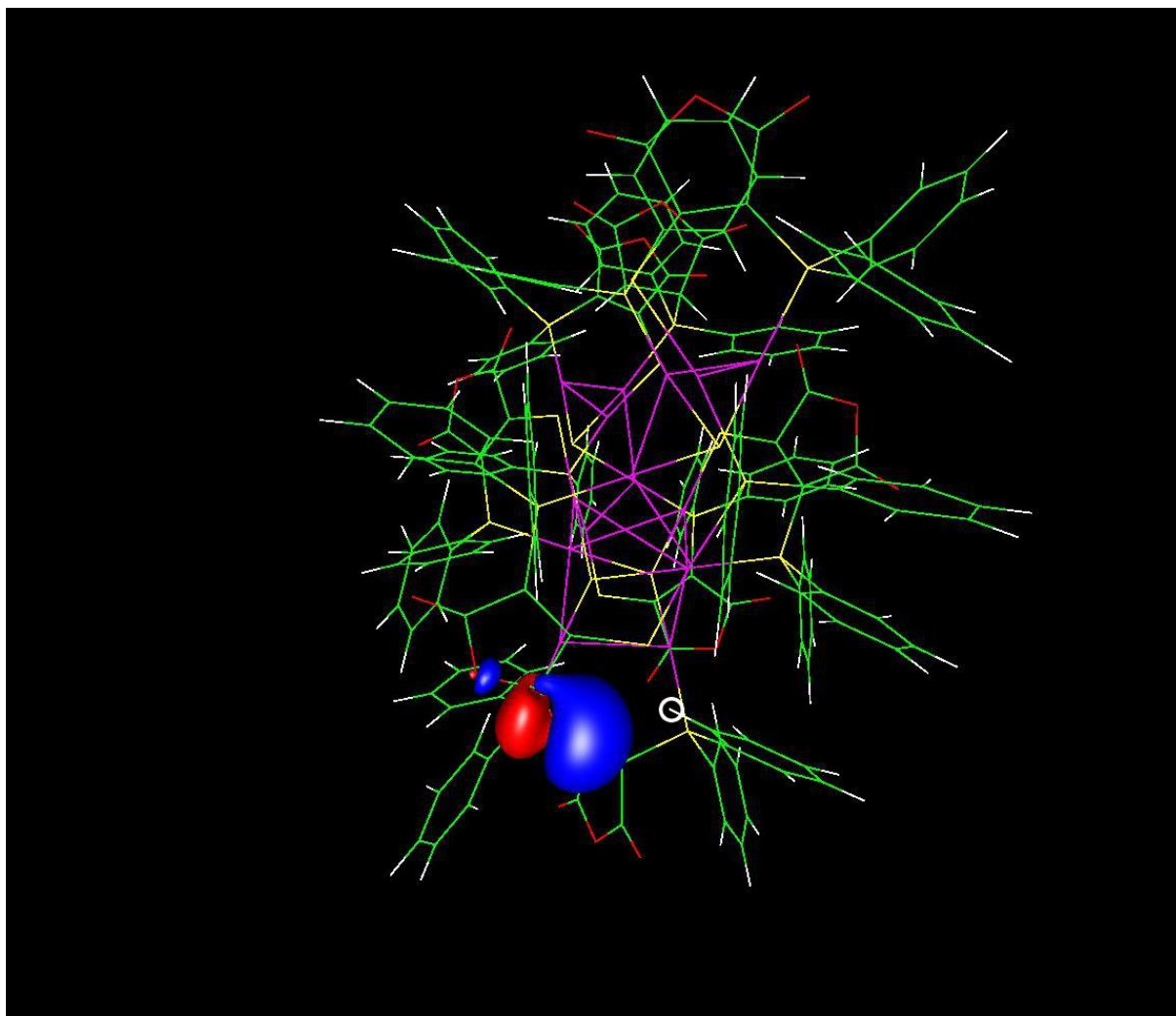
**Figure S6.** LMO 322





**Figure S7.** LMO 343





**Figure S8.** LMO 357

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