Mononuclear Metallacyclic Silver(I) Complexes of Third Generation Bis(1-pyrazolyl)methane Ligands

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Supporting Information

The metallocycles described in the full paper are further organized into higher dimensional structures by a variety of non-covalent interactions, including π—π interactions, X—H•••π interactions (X = O, N, C), and C—H•••F interactions.

The supramolecular structure of metallocycles synthesized with the para-linked ligands, **{Ag[*p*-$C_6H_4(CH_2OCH_2CH(pz)_2)_2$]}$BF_4$·0.5($(CH_3)_2CO$) (1a), {Ag[*p*-$C_6H_4(CH_2OCH_2CH(pz)_2)_2$]}$BF_4$ (1b), {Ag[*p*-$C_6H_4(CH_2OCH_2CH(pz)_2)_2$]}$BF_4$ (1c), {Ag[*p*-$C_6H_4(CH_2OCH_2CH(pz)_2)_2$]}$PF_6$·($CH_3CN$) (2b), {Ag[*p*-$C_6H_4(CH_2OCH_2CH(pz)_2)_2$]}$SO_3CF_3$·($(CH_3)_2CO$) (3a),** and **{Ag[*p*-$C_6H_4(CH_2OCH_2CH(pz)_2)_2$]}$SO_3CF_3$·0.5($CH_3CN$) (3b)**, have several commonalities clearly present. Compounds crystallized from acetonitrile, **1b, 1c, 2b** and **3b**, have the

most similar organizational features. All of the silver metallacycles in these compounds form dimers via π—π interaction between two pyrazolyl rings; a representative example is shown in Figure S1 for metallacycles containing Ag(1) in **1b**.

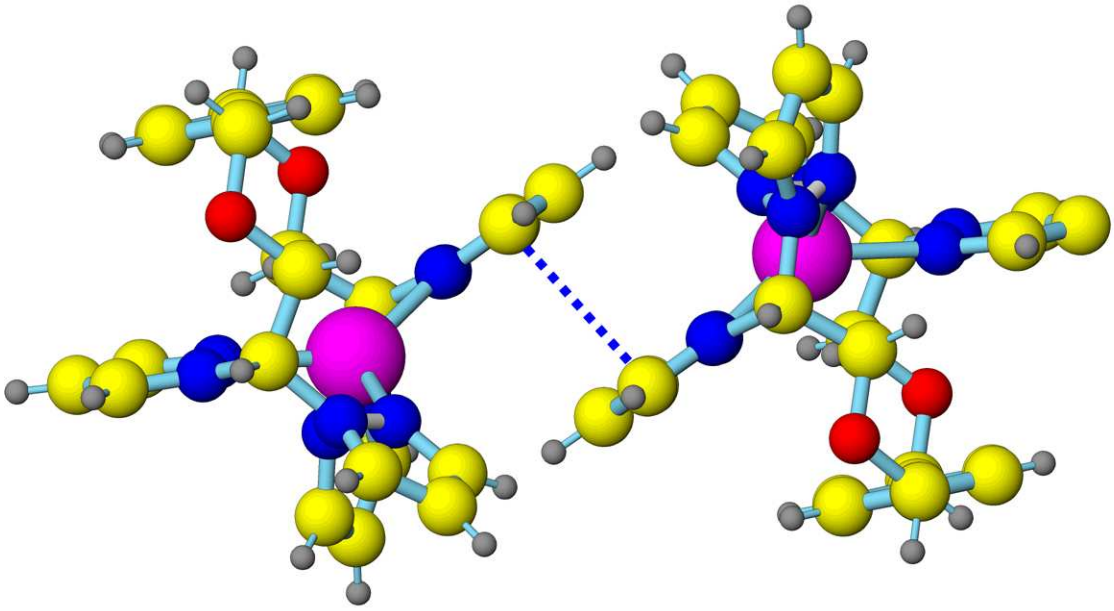

Figure S1. Two metallacyclic cations containing Ag(1) in **1b** held together into dimers by a π—π interaction, represented by the blue dashes.

The metallacycles in **1c** and **2b**, and those containing Ag(1) in **1b** and **3b** are held together into dimers only by this π—π interaction between pyrazolyl rings. The rings are parallel to each other and oriented head to tail, with a perpendicular distance of 3.27Å, 3.42Å, 3.28Å, and 3.29Å for each, respectively. The rings are slightly slipped and therefore, have a centroid—centroid distance of 3.38Å in **1c,** 3.55Å in **2b**, 3.43Å in **1b**, and 3.47Å in **3b**.

In compounds **1b** and **3b**, the metallacycles containing Ag(2) also from dimers held together by the π—π interaction described above, but in addition the interaction is supported by two cooperative C—H•••π interactions (Figure S2 shows **3b**). This motif of

cooperative non-covalent interactions between four pyrazolyl rings, which we have encountered previously, has been termed "quadruple pyrazolyl embrace".[19] As shown, the quadruple pyrazolyl embrace organizes four pyrazolyl rings, two pyrazolyl rings of one metallacycle and two pyrazolyl rings of a different metallacycle, through head-to-tail π—π and C—H•••π interactions. The rings in **1b** have a perpendicular distance of 3.33Å and a centroid—centroid distance of 3.41Å and in **3b** a perpendicular distance of 3.35Å and a centroid—centroid distance of 3.52Å. A C—H group from each of the two rings involved in the π—π interaction point into the π—cloud of a pyrazolyl ring, which is depicted in Figure S2 by the red dots. The H•••centroid distance is 3.00Å and the C—H•••centroid angle is 140° in **1b** and the H•••centroid distance is 2.87Å and the C—H•••centroid angle is 148° in **3b**.

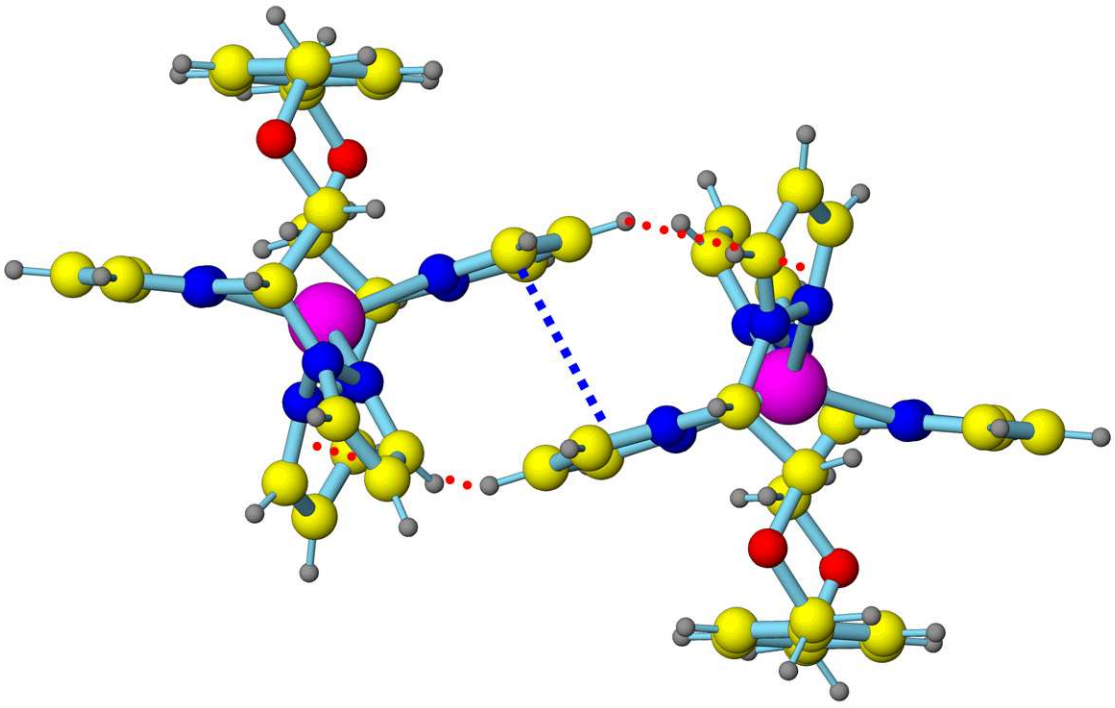

Figure S2. The "quadruple pyrazolyl embrace" formed by two metallacycles containing Ag(2) in **3b**. The blue dashes represents the π—π interaction and the red dots represent the C—H•••π interactions.

The dimers in **1b** and **3b** containing Ag(2) are further organized into ribbons by a π—π interaction between a pyrazolyl ring and the central—arene ring. Figure S3 shows the dimers held together by π—π interactions, depicted in green, to form a ribbon in **3b**. The dihedral angle between the pyrazolyl ring and the arene ring is 5° and the perpendicular distance is 3.52Å. The centroid—centroid distance is 3.76Å.

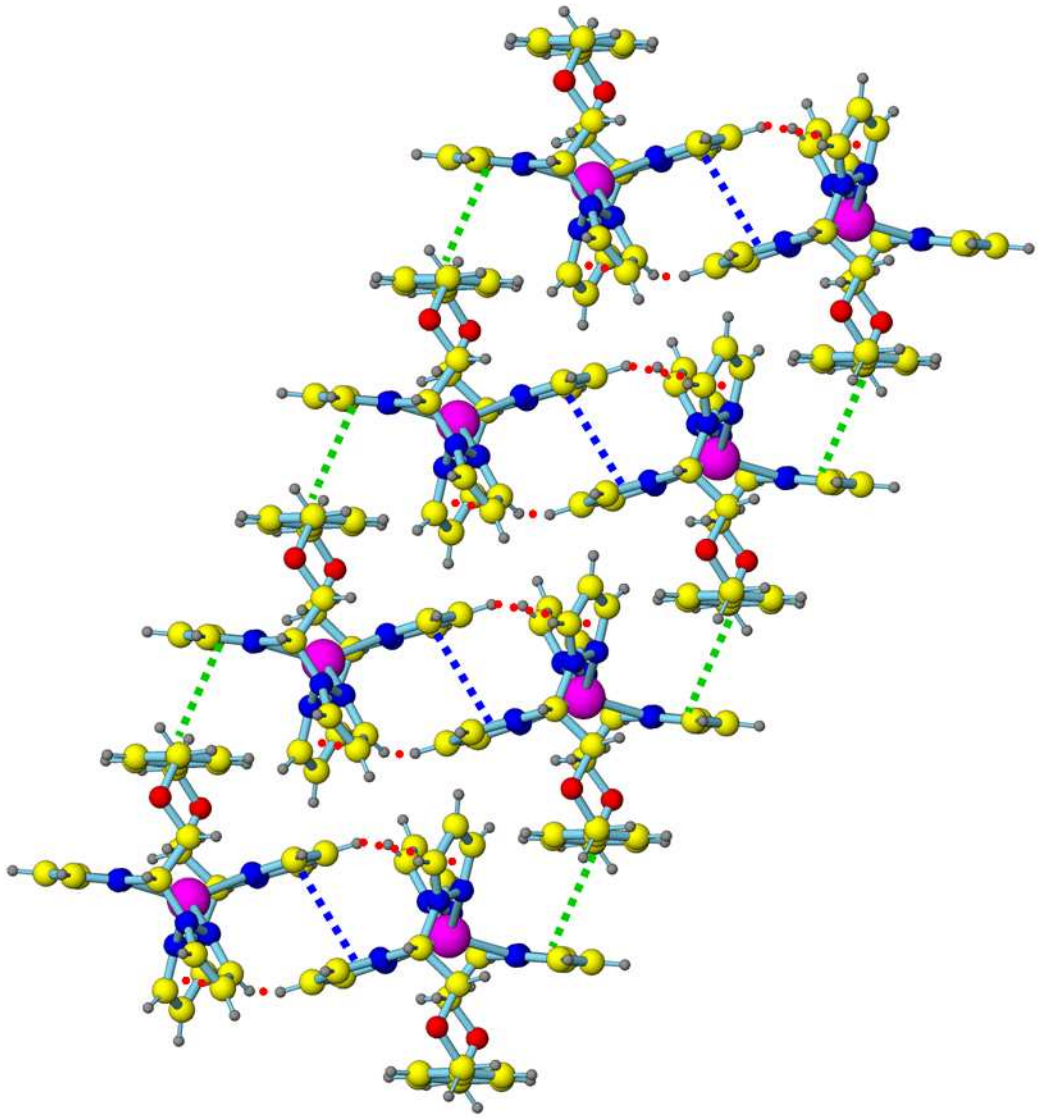

Figure S3. Strands of metallacylic Ag(2) dimers of **3b** held together by π—π interactions between arene and pyrazolyl rings, denoted by the green dashes. Blue dashes indicate π—π interactions between two pyrazolyl rings and red dots indicate C—H•••π interactions.

As mentioned, **1b** also forms ribbons like the one depicted in Figure S3. The arene ring and pyrazolyl ring are not perfectly parallel, with a dihedral angle of 6°. The perpendicular distance between the two centroids is 3.49Å and the centroid—centroid

distance is 3.89Å. In addition to the π—π interactions between the pyrazolyl rings and the central—arene rings, a C—H•••π interaction is also present, shown in Figure S4 as a black dotted line. A C—H group of the central arene ring points into the π—cloud of a pyrazolyl ring. The H•••centroid distance is 2.89Å and the C—H•••centroid angle is 139°.

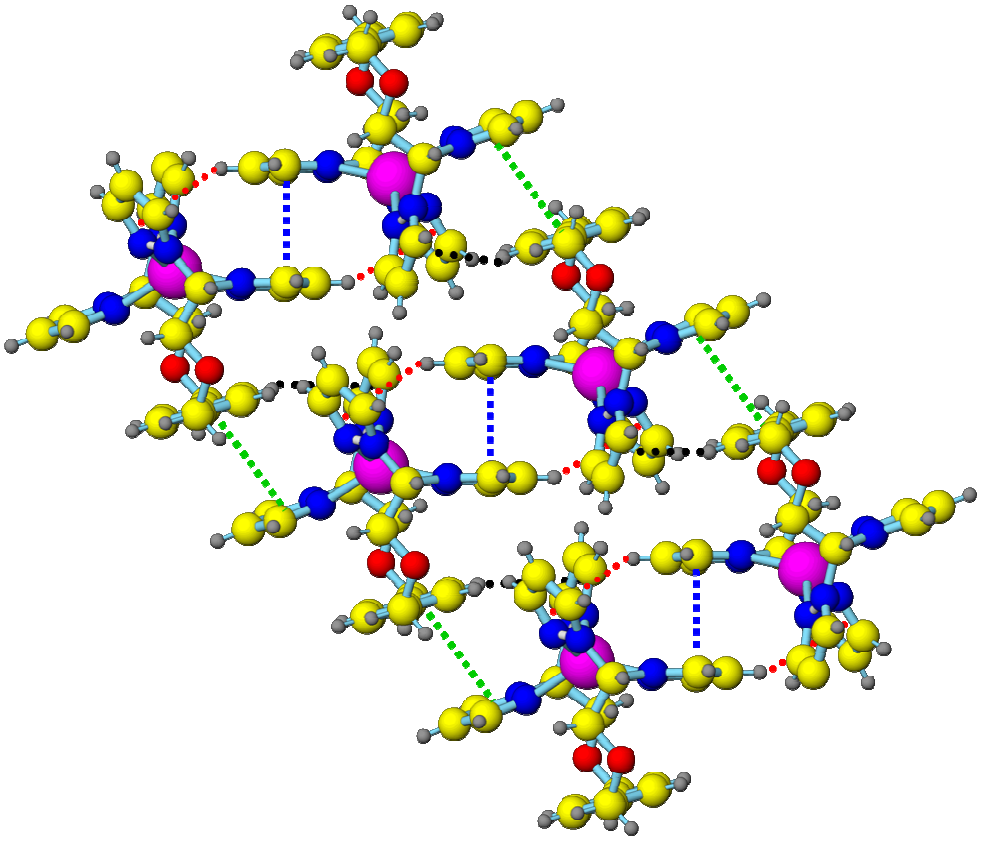

Figure S4. Strand formed by dimers containing Ag(2) in **1b**. The blue dashes and red dots show the π—π interaction C—H•••π interactions, respectively, that form the dimer. The green dashes and black dots indicate the π—π interaction C—H•••π interactions, respectively, that form the strand.

The non-covalent organization of the other two compounds containing $\mathbf{L_p}$ that were crystallized from acetone, **1a** and **3a**, are noticeably different from the structures crystallized from acetonitrile and from each other. The metallacycles of **1a** are held together in highly organized strands by three types of C—H•••π interactions. The metallacycles containing Ag(1) are connected into dimers through a cooperative set of C—H•••π interactions, which occur between the C—H in a pyrazolyl ring from one metallacyle containing Ag(1) to the π—cloud of a pyrazolyl ring in a different metallacycle containing Ag(1) to form a dimer (shown in blue in Figure S5). The H•••centroid distance is 2.89Å (C-centroid distance = 3.78 Å), and the corresponding C—H•••centroid angle is 156°.

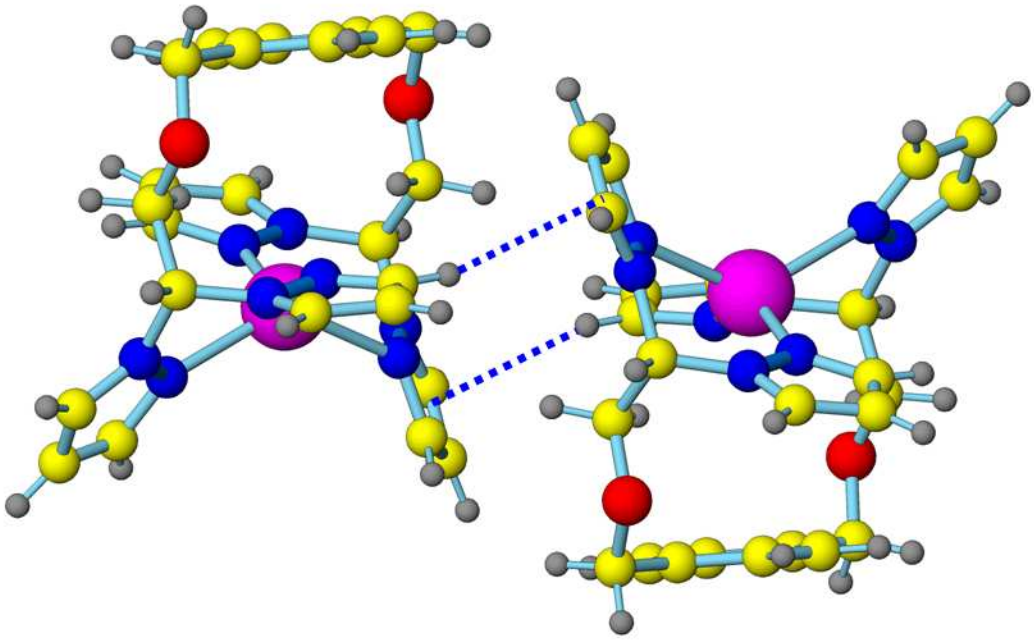

Figure S5. Cationic metallacycles in **1a**, showing the C—H•••π interactions between the two metallacycles containg Ag(1) in blue.

Another dimer is formed that links metallacycles containing Ag(2) by similar set of cooperative C—H•••π interactions (shown in green in Figure S6). Again, the C—H group in a pyrazolyl ring of one metallacyle containing Ag(2) points into the π—cloud of a different metallacycle containing Ag(2). The H•••centroid distance is 2.67Å (C-centroid distance = 3.46 Å), and the corresponding C—H•••centroid angle is 141°. The two different set of dimer are then linked together in strands by a single C—H•••π interaction, as pictured in red in Figure S6. The C—H group from a pyrazolyl ring in the metallacycle containing Ag(2) points into the pyrazolyl ring from the metallacycle containing Ag(1). The H•••centroid distance is 2.71Å (C-centroid distance = 3.59 Å), and the corresponding C—H•••centroid angle is 148°.

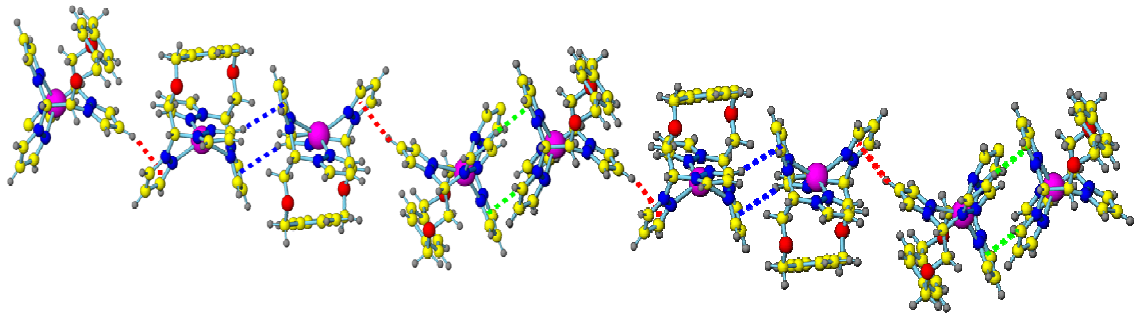

Figure S6. Cationic metallacycle strands of **1a** held together by C—H•••π interactions. Red dashes indicate C—H•••π interactions between metallacycles containing Ag(1) and Ag(2). Blue dashes indicate C—H•••π interactions between metallacycles containing Ag(1). Green dots indicate C—H•••π interactions between metallacycles containing Ag(2).

In contrast to all the compounds mentioned thus far, the metallacycles in **3a** do not have any direct non-covalent interactions between the rings of the metallacycles. Instead, the metallacycles are linked into dimers by acetone molecules. One cationic unit

associates with an acetone molecule though a C—H•••π interaction, shown in red in Figure S7. The hydrogen on a methyl group of the acetone points toward the π-cloud of one of the pyrazolyl rings in the metallacycle. The H•••centroid distance is 2.76Å and the C—H•••centroid angle is 145°. Two cationic metallacycles and acetone molecules are held into dimers by weak hydrogen interactions between the C—H group of a pyrazolyl ring and the oxygen atom in acetone (shown in blue in Figure S7). The H•••O distance is 2.38Å and the C—H•••O angle is 164°.

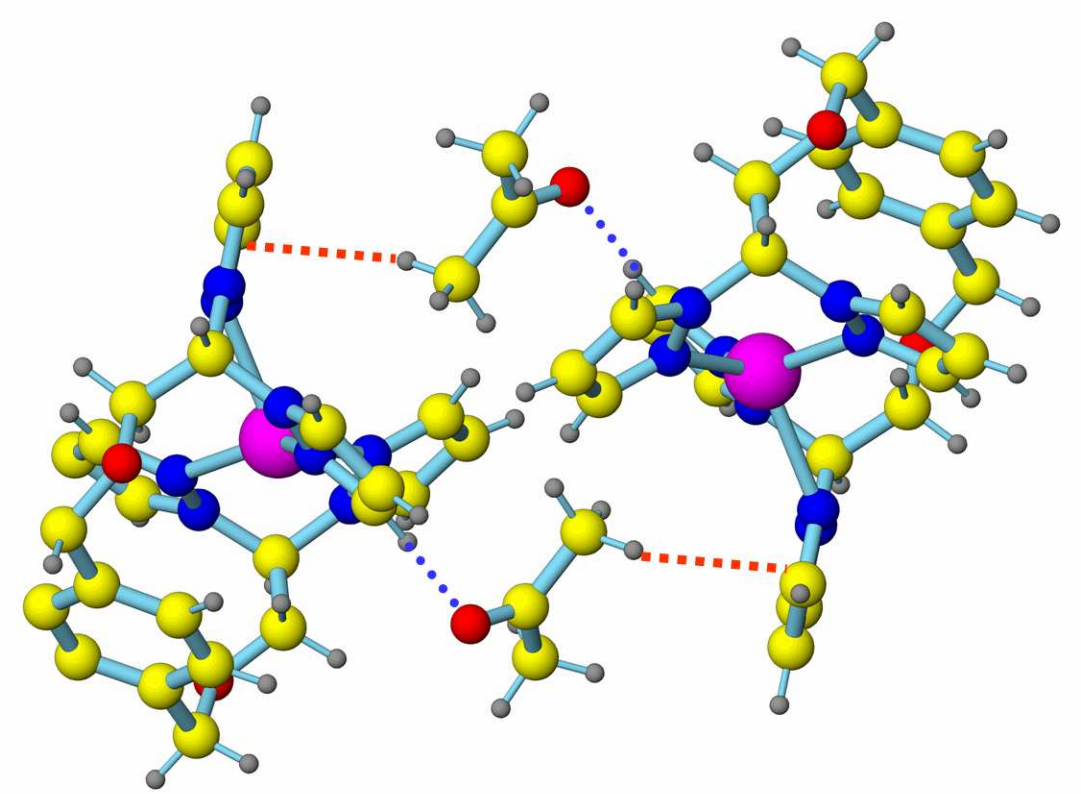

Figure S7. Two cationic metallacycles and two acetone molecules in **3a** held together by C—H•••π interactions (red) and weak hydrogen interactions (blue).

Weak hydrogen bonds between the metallacycles, the counterions and solvent from crystallization (if present) further organize **1c, 2b,** and **3b** into higher dimensional

structures. The dimers of **1c** are held together in a 3-D network by weak H•••F interactions between the BF_4^- anions and the metallacycles. The dimers of **2b** are held together into 2-D sheets by three types of weak hydrogen bonds. The first type is a C—H•••N interaction between one of the methyne hydrogens in the ligand and the nitrogen of the acetonitrile; the distance is 2.38Å and has a C—H•••N angle of 165°. The second type is a C—H•••O interaction between the CH on the methyl group of the acetonitrile and one of the oxygens found in the ligand; this interaction has a distance of 2.45Å and a C—H•••O angle of 136°. The third type is three C—H•••F interactions. The shortest distance is 2.43Å and has a CH•••F angle of 130°, the next distance is 2.51 and has a C—H•••F angle of 155° and the longest distance is 2.51Å with a C—H•••F angle of 138°. In **3b** the dimers containing Ag(1) and the strands containing Ag(2) are held together in a 3-D network through weak hydrogen bonding between C—H units in the ligands and the oxygen atoms in both independent triflate anions. The shortest bond distance is 2.24Å and has a C—H•••O angle of 158°. The longest bond distance is 2.56Å and has a C—H•••O angle of 155°. Several of these hydrogen bonds are almost linear with angles of 177°, 173° and 171° (bond distances are 2.53Å, 2.34Å, and 2.47Å, respectively). The interactions between the metallacycles and the counterions of **1a**, **1b**, and **3a** could not be investigated due to disorder in the anion.

Non-covalent C—H•••π interactions also organize the metallacyles formed from the meta-linked ligand into ribbons **{Ag[*m*-C_6H_4($CH_2OCH_2CH(pz)_2)_2$]}BF_4 (4b)** and **{Ag[*m*-C_6H_4($CH_2OCH_2CH(pz)_2)_2$]}PF_6· 0.5(CH_3CN) (5b)**. In **4b t**he metallacycles containing Ag(1) are held together in dimers by a cooperative set of C—H•••π interactions, indicated by the red dots in Figure S8. A C—H group in the central arene

ring points into the π-cloud of a pyrazolyl ring. The H•••π distance is 2.57Å and the C—H•••centroid angle is 153°. These dimers are further organized into ribbons by another set of cooperative C—H•••π interactions, indicated by the blue dots in Figure S8. The H•••π distance is 2.88Å and the C—H•••centroid angle is 145°. The metallacycles containing Ag(2) cannot be analyzed due to a disorder present in the ligand.

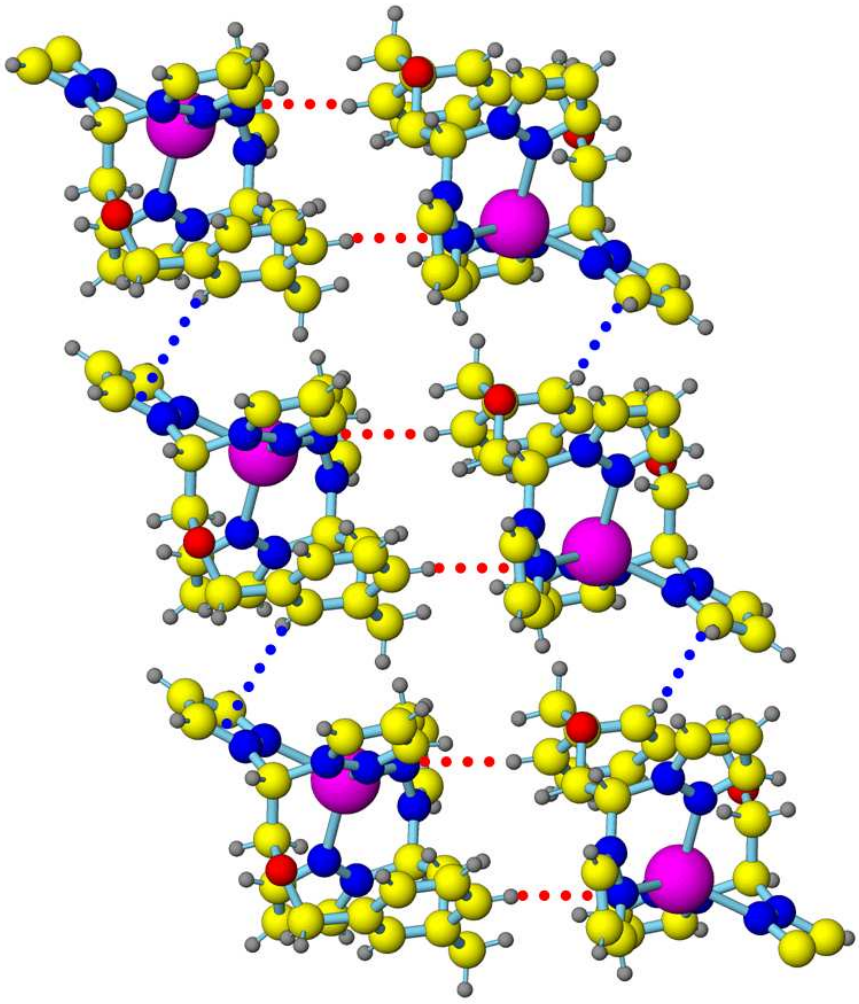

Figure S8. Dimers of metallacycles containing Ag(1) of **4b** are held together by C—H •••π interactions, shown in red, and these dimers are held together in strands by C—H•••π interactions, shown in blue.

The metallacycles of **5b** are organized by two types of C—H•••π interactions into ribbons containing both Ag(1) and Ag(2). The metallacycles containing Ag(1) are held together by C—H•••π interactions between a C—H group in the central arene ring and the π cloud of a pyrazolyl ring, depicted in Figure S9 by the red dots. The H•••centroid distance is 2.89Å and the C—H•••centroid angle is 146°. Each metallacycle containing Ag(1) coordinates to a metallacycle containing Ag(2) through a C—H•••π interaction, shown in blue in Figure S9. The H•••centroid distance is 2.76Å and the C—H•••centroid angle is 164°. Strangely, the metallacycles containing Ag(2) have no strong non-covalent interactions between them to further support the ribbon structure formed by the metallacycles containing Ag(1).

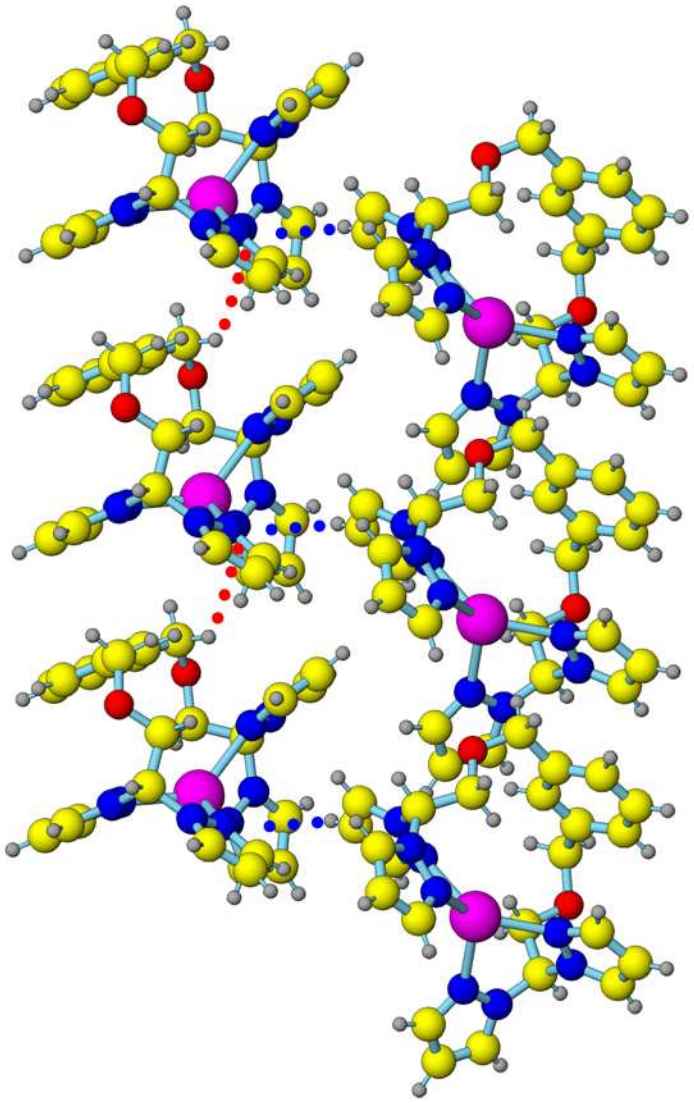

Figure S9. Metallacycles containing Ag(1) and Ag(2) of **5b** held together by C—H•••π interactions. Red dots indicate C—H•••π interactions between metallacycles containing Ag(1) and blue dots indicate C—H•••π interactions between metallacycles containing Ag(1) and Ag(2).

In **{Ag[*m*-$C_6H_4(CH_2OCH_2CH(pz)_2)_2$]}$PF_6$·$((CH_3)_2CO)$ (5a)**, the metallacycles are organized into ribbons by both C—H•••π and π—π interactions. Two different ribbons are formed; one contains metallacyles that have only Ag(1), while the other is comprised

of metallacycles containing only Ag(2). The structures for both contain two very similar π—π interactions. The first type is an intramolecular π—π interaction between a pyrazolyl ring and the arene ring from the same ligand (shown in red for Ag(1) in Figure S10). The rings are slightly tilted from being perfectly parallel to each other by 4°. The shortest perpendicular distance between the rings is 3.65Å, and the rings are slightly slipped, so the centroid—centroid distance is 4.33Å. The second π—π interaction is between metallacycles involving the same two rings involved in the intramolecular interactions that organizes the metallacyles into chains (shown in blue in Figure S10). The shortest perpendicular distance between the rings is 3.63Å and the centroid—centroid distance is 3.97Å. These chains for Ag(1) are organized into dimeric strands by a cooperative set of C—H•••π interactions between the C—H group of a pyrazolyl ring and the π—cloud of a second pyrazolyl ring, shown in green in Figure S10. The H•••centroid distance is 2.86Å and the C—H•••centroid angle is 148°. The dimeric strands of Ag(2) are also organized by cooperative set of C—H•••π interactions, but in this case the C—H donor group comes from the central arene.

The two individual ribbons formed by Ag(1) and Ag(2) are held together in sheets by weak C—H•••F interactions between the metallacycles and the PF_6^- counterion. Figure S11 shows the ribbons viewed down their long axes, connected through C—H•••F interactions, shown in orange. There are four different C—H•••F interactions with H•••F distances of 2.22Å, 2.22Å, 2.39Å, 2.39Å and corresponding C—H•••F angles of 170°, 175°, 146°, 150°.

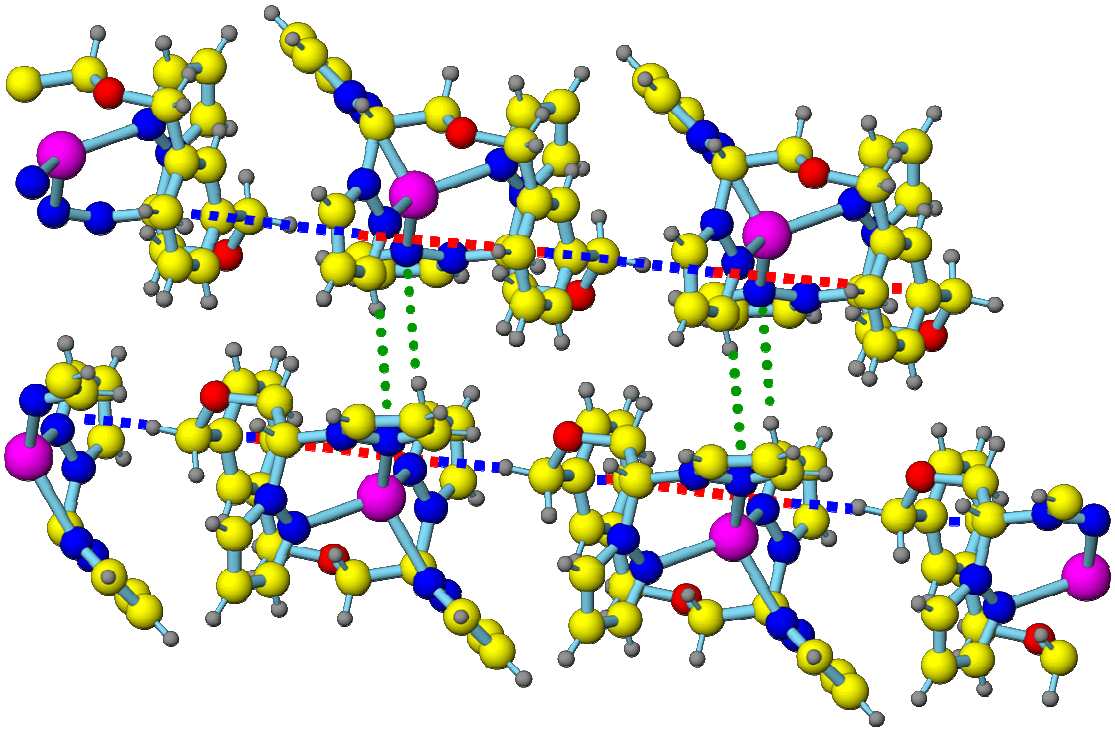

Figure S10. Dimeric strands of metallacycles containing Ag(1) formed in **5a**. Red dashes represent intramolecular π—π interactions. Blue dashes represent intermolecular π—π interactions. Green dots represent C—H•••π interactions.

Weak hydrogen bonds between the metallacycles, the counterions and solvent from crystallization (if present) further organize **5a** and **5b** into higher dimensional structures. The disorder in **4b** prevents further analysis of the interactions organizing the overall structure.

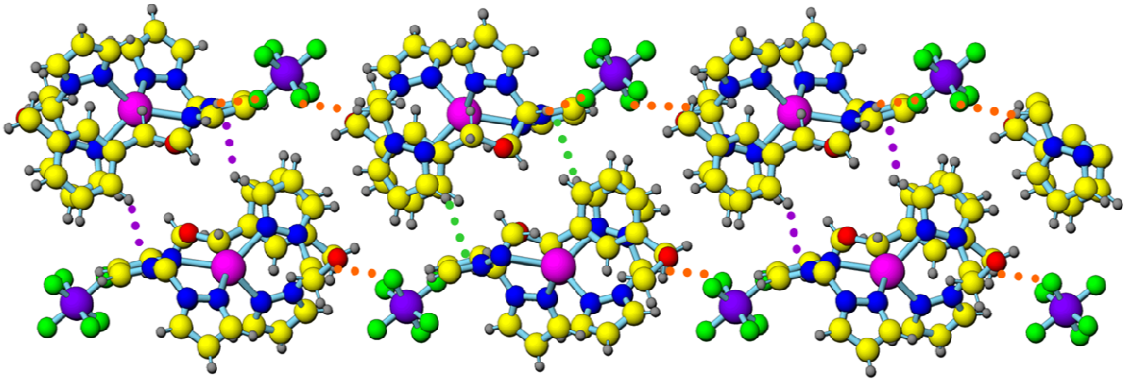

Figure S11. Sheets formed in **5a** of ribbons, viewed down the long axes, held together by weak C—H•••F interactions, shown in orange. Green dots represent C—H•••π interactions found in ribbons containing Ag(1) and purple dots represent C—H•••π interactions in ribbons containing Ag(2).