Triplet Acetylenes as Synthetic Equivalents of 1,2-Bicarbenes, Part II: New Supramolecular Scaffolds from Photochemical Cycloaddition of Diarylacetylenes to 1,4-Cyclohexadienes

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Abstract: 1,5-Diaryl substituted homoquadricyclanes which are readily available through cascade photocycloaddition of diarylacetylenes to 1,4-cyclohexadienes are useful supramolecular scaffolds with an angle of about 60° formed by the two aromatic rings defining a hydrophobic cavity. These structural features of pyridinyl homoquadricyclanes were applied to the design of composite organic/inorganic materials with topologies depending on the ratio of ligand to metal. The crystal structure of complex **1** (**L1**/$AgNO_3$ in a 1:1 ratio) shows an alternating ligand–metal polymer in which each of the silver ions in its linear coordination geometry is shared between two **L1** molecules. A small change in the crystallization method yields a supramolecular rhomboid (complex **2**, **L1**/$AgNO_3$ 3:2 ratio) which has two ligands that occupy opposite corners of the rhomboid and two silver atoms occupy the other two corners. Connection of the rhomboids units through a third molecule forms unique "beads on a string" polymeric chains. In complex **2**, the silver ions adopt a distorted tetrahedral geometry with the nitrate anion occupying one of the vertices of the tetrahedron. The crystal packing of the chain of rhomboids generates cavities which are filled with disordered solvent molecules. Non-symmetrical homoquadricyclane **L3** coordinates with silver only through the nitrogen of the pyridine ring but not through the nitrogen of the tetrafluoropyridine ring in which the electron density of the nitrogen lone-pair is very low. The substituents on the polycyclic moiety of the homoquadricyclane cause restricted rotation of the pyridine rings which suggests that the flexibility of such systems can be fine-tuned to create a family of supramolecular scaffolds of controlled rigidity.

Keywords: coordination polymers · homoquadricyclanes · restricted rotation · self-assembly · silver

Introduction

Recently, we reported an efficient method to prepare 1,5-diaryl substituted tetracyclo[3.3.0.0^{2,8}.0^{4,6}]octanes (homoquadricyclanes) by means of photocycloaddition of diaryl acetylenes, in which at least one of the aryl groups is either a pyridine or a pyrazine, to 1,4-cyclohexadiene (Scheme 1).[1] Mechanistic and photophysical studies showed that this photocycloaddition proceeds through an electrophilic triplet state which is efficiently formed due to enhanced intersystem crossing (ISC) between $^1\pi,\pi^*$ and $^3n\,\pi^*$ states. Although this convenient one-pot transformation involves the cascade formation of four σ bonds, it often proceeds in high quantum and chemical yields. From a practical perspective, this process is interesting because "capping" the triple bond with the polycyclic framework orients the terminal aryl (4-pyridyl, 4-tetrafluoropyridyl, phenyl etc.) groups in an almost perfect 60° angle. It was suggested recently that this structural feature renders such molecules potentially useful ligands in coordination chemistry and offers promising supramolecular building blocks.[2]

In this context, it is interesting to quote a recent paper by Stang and co-workers: "The relative dearth of triangles synthesized to-date can be explained by the difficulty in finding

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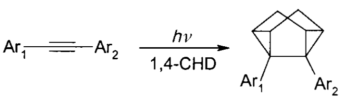


Scheme 1. One-pot synthesis of 1,5-diaryl homoquadricyclane.

the appropriate corner unit … there exist no single-center complex that possesses a 60° angle between coordinated ligands."[3] Intrigued by these comments, we decided to investigate the supramolecular chemistry of 1,5-(4,4′-dipyridyl) homoquadricyclane **L1** which has potential to serve as a corner unit for such supramolecular triangles or rhomboids[4] and provides other examples of V-shape textons that exhibit interesting solid state packing motifs.[5] Several groups have adopted a tactic for the synthesis of molecular triangles which uses a suitable ligand as the corner units and metal coordination acts as the linker between these ligands.[6]

Here we report the synthesis and characterization of a family of organometallic coordination polymers based on pyridine-metal interaction. Silver(I) is frequently used as the metal in crystal engineering because the flexibility of its coordination sphere can produce a large array of coordination architectures.[7] The ability to modify the ligand-to-metal ratio, the counterions and noncovalent interactions reflects this flexibility.[8] Different types of spacers (e.g. rigid, semi-rigid and flexible) were utilized in the construction of coordination polymers and supramolecular complexes with potential application in crystal engineering.

Results and Discussion

Photocycloadditions of 4,4′-bispyridyl acetylene,[9] bis-tetrafluoropyridyl acetylene and 4-pyridyl tetrafluoropyridyl acetylene to 1,4-cyclohexadiene (1,4-CHD) afford 1,5-diaryl homoquadricyclanes **L1**, **L2** and **L3** in 45, 48 and 80 % isolated yields, respectively.[10] The structures of **L1**, **L2** and **L3** were determined using spectroscopic techniques and confirmed by single crystal X-ray analysis.

The first useful structural feature of **L1** is the high (C_{2v}) symmetry of the molecule—a generally useful property in supramolecular chemistry (Figure 1). The two pyridine rings form a diverging cavity with an angle of 63.2°. The distance between the two nitrogens is 6.049 Å and the dihedral angle formed by the C1(Ar)-C6(Hq)-C7(Hq)-C1(Ar′) carbon bonds is 0°.

The torsional angle between the two pyridyl rings in homoquadricyclane **L2** is 1.1° (Figure 2a). Despite this slight distortion, the angle between the two electron deficient TFP rings flanking the cavity is essentially unchanged (62.9°). A similar situation is observed in the case of unsymmetric 1,5-diaryl homoquadricyclane **L3**, Figure 2b, where the angle formed by the two aryl rings of different acceptor abilities (TFP and 4-Py) is 63.3°. The distance between the two pyridyl nitrogens is 6.023 Å and the dihedral angle is 2.64°. Comparison of selected distances, angles and torsional angles of ligands **L1**, **L2** and **L3** in Table 1 suggests that the main geometrical features of the scaffold remain nearly intact in these structural modifications.

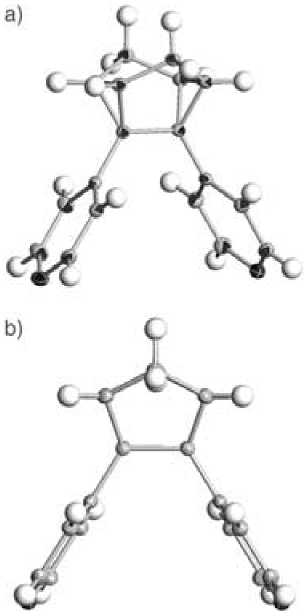


Figure 1. ORTEP representations of geometry of **L1** [di-4,4′-[7,6-tetracyclo[3.2.1.0^{2,7}.0^{4,6}]octyl]-pyridine] (a) and a side view showing molecular symmetry and the angle between the planes of the two pyridine rings (b).

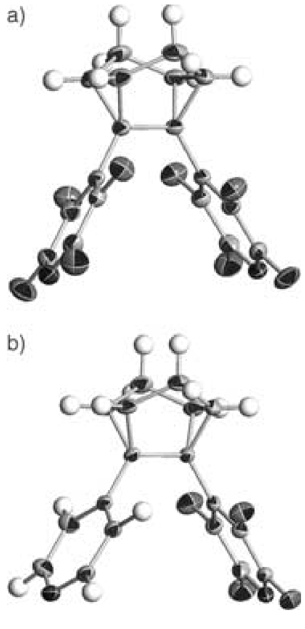
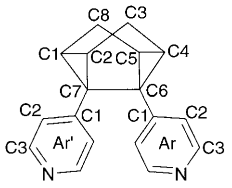


Figure 2. ORTEP representations of a) **L2** [Di-4,4′-[7,6-tetracyclo[3.2.1.0^{2,7}.0^{4,6}]octyl]-2,3,5,6-tetrafluoropyridine] and b) **L3** [4-[7-(2,3,5,6-tetrafluoropyridin-4-yl)-tetracyclo [3.2.1.0^{2,7}.0^{4,6}]oct-6-yl]-pyridine].

Symmetry, shape and electronic properties of the hydrophobic cavity control packing of the diaryl homoquadricyclanes (Figure 3) in the crystals. In **L1**, the cavity formed by

Table 1. Selected distances [Å] and angles [°] for homo-quadricyclanes **L1**, **L2** and **L3** and for complexes **1**, **2** and **3**.



	L1	**L2**	**L3**	**1**	**2**		**3**
					L1 (corner)	**L1** (linker)	
angles [°]							
Ar–Ar′	63.2	62.9	63.3	65.7	71.8	69.6	65.4
C1(Ar)-C6(Hq)-C1(Ar′) average	121.2	120.8	120.9	123.1	126.7	121.9	121.1
torsion angles [°]							
C1(Ar)-C6(Hq)-C7(Hq)-C1(Ar′)	0	1.14	2.64	5.8	4.5	11.6	4.20
C2(Ar)-C1(Ar)-C6(Hq)-C7(Hq)	85.3	103.9	101.2	119.7	162.4	126.9	103.5
C2(Ar)-C1(Ar)-C6(Hq)-C7(Hq)	85.3	75.6	94.1	58.2	82.9	58.1	70.2
distances [Å]							
π–π Ar1–Ar2	3.373	3.338	3.621	–	–	–	–
N(Ar)–N(Ar′)	6.049	5.987	6.023	6.193	6.539	6.416	6.151
H at C1 (Hq1)–N(Ar2)	2.619	–	2.575	–	–	–	–
H at C3 (Hq1)–F at C1 (Ar2)	–	2.572	2.599	–	–	–	–
F at C2 (Ar1)–F at C3 (Ar12)	–	2.755	–	–	–	–	–
N(Ar1)–C1(Ar2)	–	3.063	–	–	–	–	–

the pyridyl rings accommodates C–H bonds from the polycyclic homoquadricyclane moiety, possibly due to weak CH-π interactions of the aromatic moieties and the homoquadricyclane C–H bonds.[11] **L1** also shows π–π stackings of parallel pyridyl rings in an offset fashion with a distance of about 3.373 Å.[12] Interestingly, the pyridine rings are twisted inward by about 5°, thus opening up the cavity from one side.

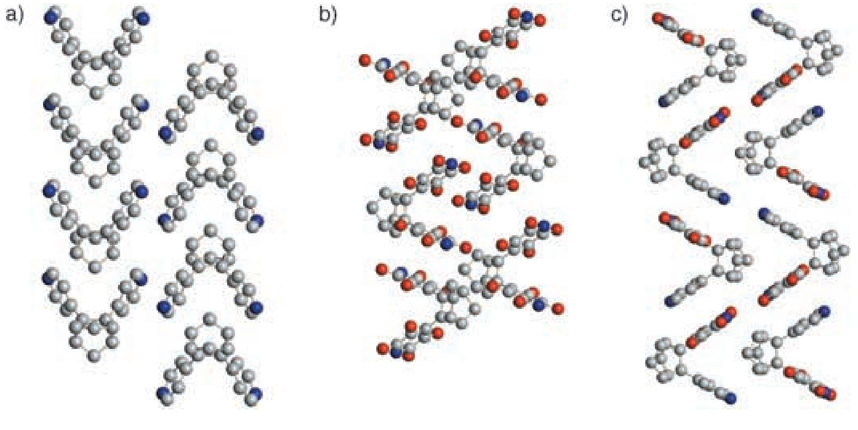


Figure 3. Crystal packing of homoquadricyclanes a) **L1**, b) **L2** and c) **L3**.

By contrast, the electron deficient cavity of bis-TFP ligand **L2** is occupied by the edge of another TFP molecule. This is due to the stabilizing interaction between the electron deficient π system and the lone pairs of the fluorine atoms that supplement the π–π interactions in providing intermolecular forces in the solid state. The most regular and well-defined packing is in the mixed Py-TFP ligand **L3** which is controlled by face-to-face stacking interactions between the electron acceptor TFP and the electron donor Py rings, see Figure 3.[13] Finally, hydrogen bond interactions between aromatic hydrogens of 4-Py rings and fluorine atoms provides additional stabilization to the crystal network (see also Figure 4).[14]

Homoquadricyclanes **L1** and **L3** readily form silver complexes when mixed with $AgNO_3$. Details of their X-ray analyses are presented in Table 2.[15] Interestingly, **L1** produces different $AgNO_3$ complexes at different **L1**:$AgNO_3$ ratios, see below. When a THF solution of **L1** is layered on top of a CH_3CN solution of $AgNO_3$ in a 1:1 ratio, slow diffusion affords X-ray quality single crystals of a 1:1 complex.[16]

X-ray analysis shows that silver cations are shared between two pyridine moieties from two different homoquadricyclane molecules which pack in infinite zigzag layers (Figure 5). The structure of **1** shows the coordination sphere of Ag to be almost linear with a **L1**-Ag-**L1** angle of 171.26°. The average Ag–N distance is 2.149 Å indicating strong coordination between the pyridyl nitrogen and the silver cation. Although, NO_3^- is usually a relatively strong coordinating anion,[17] it interacts rather weakly with Ag^+ in this system where the shortest Ag–O distance in complex **1** is only 2.902 Å. The NO_3^- positions itself perpendicularly to the **L1**-Ag-**L1** plane, thus providing pseudo-square planar geometry at Ag^+ (Ag-O-N 96.6°). The nitrate counterions complete the "salt" inorganic layers which are sandwiched between the hydrophobic organic layers of silver complexes. Furthermore, the nitrate ions bridge the adjacent Ag–**L1** chains through two of their oxygen atoms. The packing of this interesting composite material which combines two potentially tunable and interchangeable organic and inorganic moieties is shown in Figures 5 and 6. Silver cations and nitrate anions alternate through the packing layers forming polar rods which are separated by organic relatively nonpolar "pipes".

A slight change in the crystallization conditions (slow diffusion of ligand and inorganic salt through a U-tube) leads to formation of a different complex, **2**, with the **L1**/$AgNO_3$

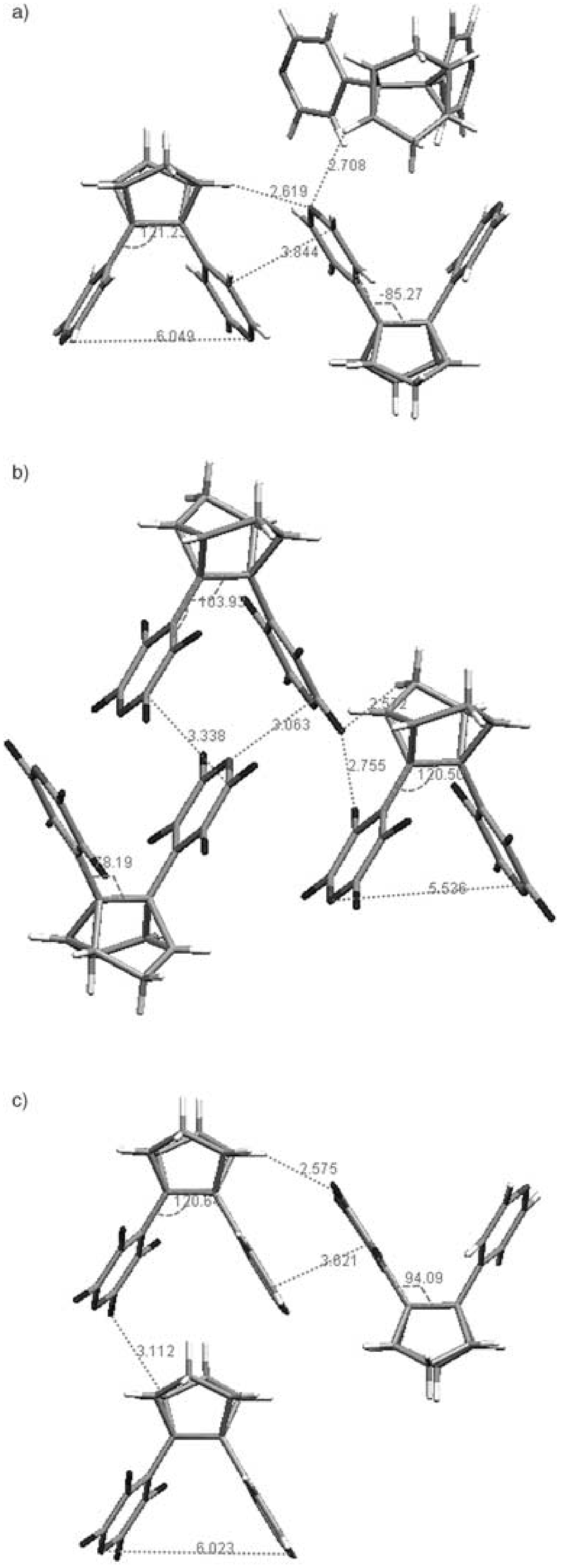


Figure 4. Distances, angles and torsion angles of homoquadricyclanes a) **L1**, b) **L2** and c) **L3**.

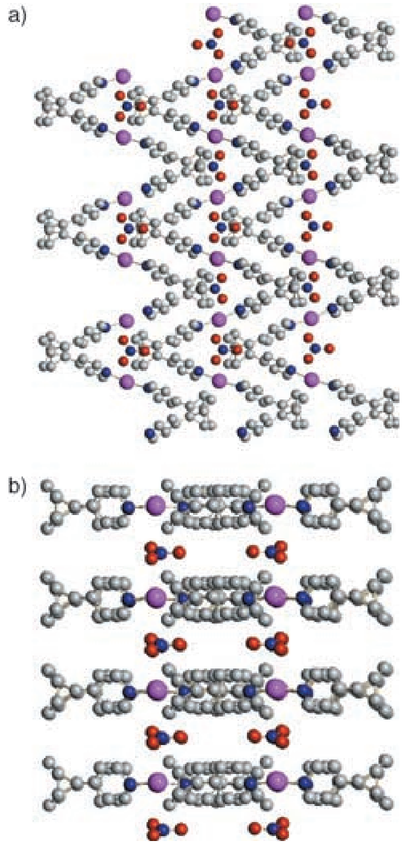


Figure 5. Alternating layers of organic and inorganic molecules in the crystal structure of complex **1** (1:1 ratio **L1**:$AgNO_3$).

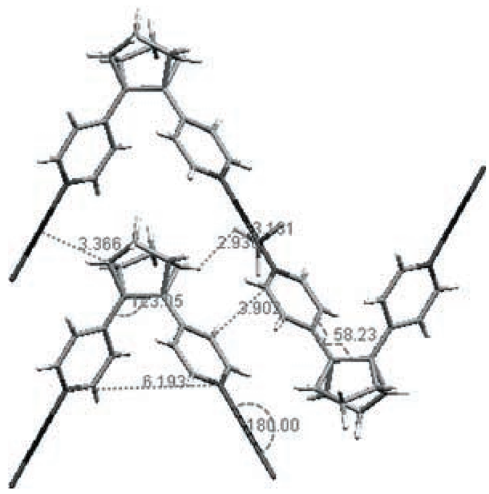


Figure 6. Distances, angles and torsion angles of complex **1**.

3:2 ratio (Figure 7). X-ray analysis of this complex also indicates presence of disordered $CHCl_3$ molecules. Thermal gravimetric analysis (TGA) suggests that there are two molecules of chloroform per each $(\mathbf{L1})_3/(AgNO_3)_2$ unit, see below. In this complex, two pyridine moieties are assembled into rhomboids by coordination with two Ag^+ ions. Each of the two Ag^+ ions which occupy two opposite corners of the

Table 2. Details of X-ray crystallographic analysis of homoquadricyclanes **L1**, **L2** and **L3** and the corresponding silver nitrate complexes **1**, **2** and **3**.

	L1	**L2**	**L3**	**1**	**2**	**3**
empirical formula	$C_{18}H_{16}N_2$	$C_{18}H_8F_8N_2$	$C_{18}H_{12}F_4N_2$	$C_{18}H_{16}AgN_3O_3$	$C_{27}H_{24}AgN_4O_3$	$C_{36}H_{24}AgF_8N_5O_3$
M [g mol^{-1}]	260.33	404.26	332.30	430.21	560.37	834.47
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	orthorhombic	triclinic	monoclinic	monoclinic	orthorhombic	monoclinic
space group	*Pnma*	$P\bar{1}$	*P*2(1)/*n*	*P*2/*c*	*Pccn*	*P*2(1)/*n*
a [Å]	11.3748(9)	8.0015(7)	7.7667(6)	9.6811(6)	34.8648(17)	6.7893(4)
b [Å]	15.1163(12)	8.1970(7)	14.8121(12)	8.1066(5)	10.9050(5)	7.6743(5)
c [Å]	7.6120(6)	11.9516(10)	12.6730(10)	12.6643(9)	15.1589(7)	31.3763(18)
α [°]	90	85.903(2)	90	90	90	90
β [°]	90	81.555(2)	99.8570(10)	121.3020(10)	90	93.5760(10)
γ [°]	90	75.332(2)	90	90	90	90
V [Å^3]	1308.84(18)	749.63(11)	1436.4	849.23(10)	5763.4(5)	1631.62(17)
Z	4	2	4	2	8	2
ρ_{calcd} [g cm^{-3}]	1.321	1.791	1.537	1.682	1.292	1.699
$\mu(Mo_{K\alpha})$ [mm^{-1}]	0.078	0.177	0.128	1.209	0.730	0.711
T [K]	100(2)	173(2)	173(2)	173(2)	173(2)	100(2)
F[000]	552	404	680	432	2280	836
reflns measured	16961	10295	19245	11302	7186	21.666
independent reflns	1697	3696	3557	2109	7186	4051
ratio min/max	0.8090	0.8490	0.8474	0.8591	0.8768	0.8819
$R1$ [$I > 2\sigma(I)$]	0.0568	0.0581	0.0670	0.0905	0.0948	0.0513
$wR2$	0.1448	0.1405	0.1805	0.1514	0.2302	0.1055

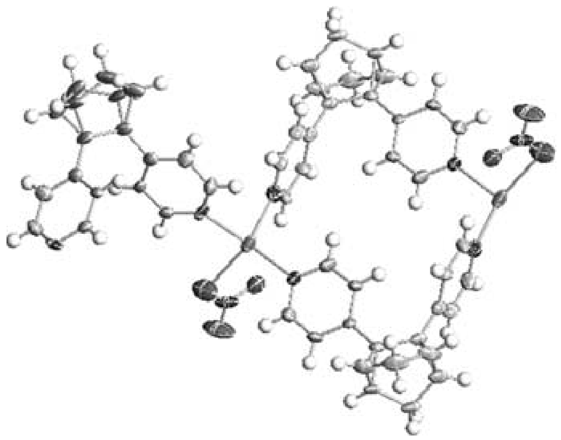


Figure 7. View of the basic trimeric unit $[Ag_2(L1)_3(NO_3)_2(CHCl_3)_2]$ of complex **2**.

rhomboid (Ag–Ag 11.544 Å), is also coordinated with an oxygen atom of a nitrate anion and with the third bis-Py ligand that bridges it to an analogous adjacent $(bis\text{-}Py)_2$–$(AgNO_3)_2$ unit. As a result, the silver cation adopts a distorted tetrahedral coordination sphere where each Ag cation coordinates with pyridyl nitrogens belonging to three different **L1** molecules and an oxygen atom from the NO_3^- anion (Ag–O 2.537 Å) (Figure 8a). All three Ag–N distances (Ag–N(1) 2.311 Å, Ag–N(2) 2.350 Å, Ag–N(3) 2.260 Å) are significantly longer than in the linear complex 1:1, see above. The distance between the parallel pyridine rings which form the four sides of the rhomboid are 8.013 and 7.452 Å. The chains of interconnected rhomboids pack in a highly porous structure with large cavities that are also rhomboid (Figure 8b). The density of **2**, Table 2, which is less than in other complexes and ligands indicates its unusual porous crystal architecture. These large voids are occupied by disordered solvent molecules to sustain the structure. The dimensions of the cavities are as follows: the diagonal distances (from one corner to the opposite one) are 14.92 and 14.70 Å and distances from one edge of the rhomboid to the opposite one are 10.46 and 8.09 Å. In both complexes **1** and **2** the geometry of the homoquadricyclane **L1** is altered from the geometry of the free ligand as shown in Table 1.

Figure 9 compares the TGA plots for complexes **1** and **2**. As a reference point, we have also included data for **L1** alone. **L1** sublimes almost completely at 500 °C. In contrast, complexes **1** and **2** show only 40 and 75 % loss of weight at 500 °C, respectively. The remaining weight is consistent with the amount of silver nitrate present in the complexes. Most interestingly, the thermal analysis for complex **2** (the dotted line in Figure 9) shows a shoulder between 190 and 200 °C which is absent for both **L1** and complex **1**. This 18 % loss is consistent with loss of two molecules of $CHCl_3$ from the silver rhomboid. The TGA data suggest that the 1:1 complex **1** may also contain an acetonitrile molecule.[18]

Equally interesting is the possibility of changing the symmetry and coordinating properties of the homoquadricyclane ligands. Not surprisingly, homoquadricyclane **L2** does not react with silver nitrate due to the low donor ability of the TFP nitrogen atoms. However, cocrystallization of Py-TFP homoquadricyclane **L3** with $AgNO_3$ resulted in formation of complex **3** in a **L3**/$AgNO_3$ 2:1 ratio. In complex **3**, only nitrogen in the stronger donor Py moiety participates in coordination with the silver ions. Similar to complex **1**, the silver ions in **3** adopt a square planar geometry (**L3**-Ag-**L3** 180.0° and Ag–N 2.159 Å) where each Ag coordinates with two **L3** molecules and two nitrate oxygens. As a result, the layers of $AgNO_3$ are separated by thicker "organic walls" (Figure 10). Disordered nitrate anions bridge two Ag ions (Ag–O (NO_3^-) 2.594 Å) providing communication between the layers which form a stair-like network.

The data in Table 1 suggest that the homoquadricyclane framework possesses significant flexibility to accommodate geometric requirements in respective complexes. Remarkably, this flexibility can be readily fine-tuned by substituent effects. We found that rather subtle modifications in the ho-

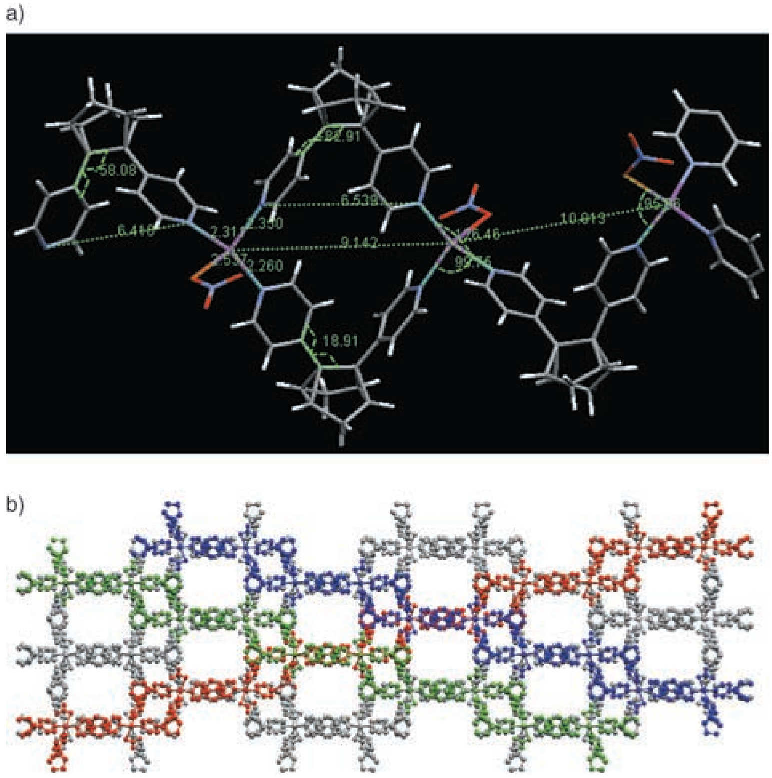


Figure 8. a) Distances, angles and torsion angles of the basic unit in complex **2**. b) "Beads on a string" packing of supramolecular rhomboids in complex **2**. Different colors show three different strings forming the cavities. Hydrogens are omitted for clarity.

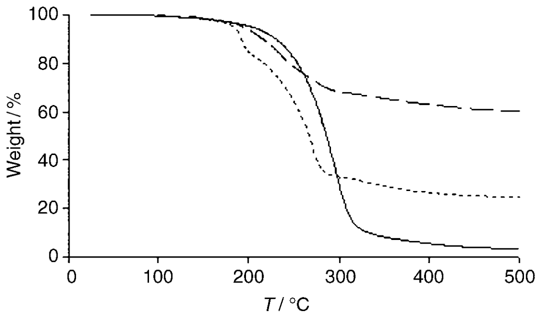


Figure 9. TGA plots for **L1** (solid line) and complexes **1** (dashed line) and **2** (dotted line). Complex **2** shows a shoulder where the weight loss is 18 %, corresponding to two $CHCl_3$ molecules in complex **2**.

moquadricyclane skeleton may fine-tune the shape and conformational properties of the cavity flanked by the two aryl groups. This sensitivity makes substituted diaryl homoquadricyclanes interesting scaffolds for molecular recognition. Interestingly, the ^{19}F NMR of TFP moiety in dimethoxy-homoquadricyclanes **L4** (readily produced by the reaction of the respective acetylenes with 1,5-dimethoxy-1,4-cyclohexadiene) displays four fluorine signals (Scheme 2).

The structure of compound **L4** was elucidated based on the H1–C13 one-bond and long-range couplings, revealed by the gHMQC and gHMBC spectra.[19] The TFP moiety is silent in the gHMBC experiment, although it is accounted for in the F19 spectrum, which displayed four signals at δ −143.23, −138.36, −93.96 and −93.24. These four signals, together with the broadening of the signals of the bridgehead hydrogens in the ^{1}H NMR spectrum suggest restricted rotation of the TFP moiety.

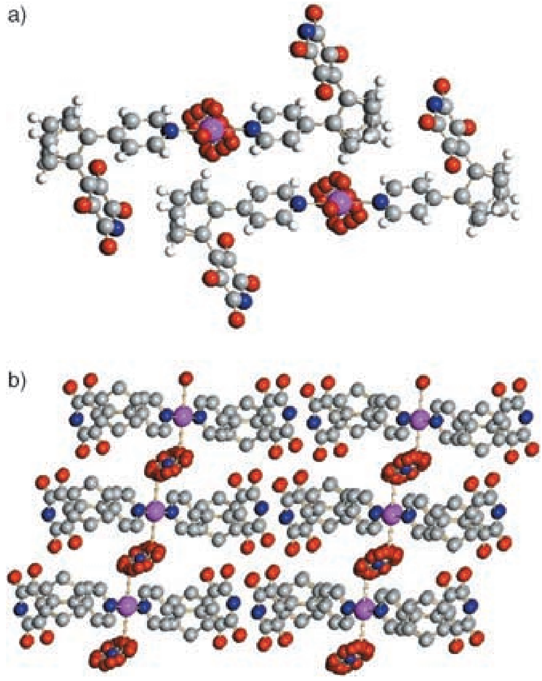
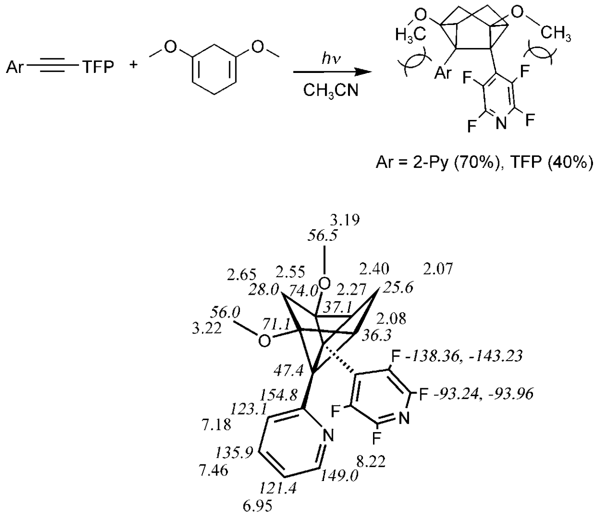


Figure 10. Thicker "walls" between the inorganic layers in the 2:1 (**L1**/$AgNO_3$) complex **3**.



Scheme 2. Photochemical reaction of acetylenes with 1,5-dimethoxy-1,4-cyclohexadiene and NMR chemical shifts assignments in the homoquadricyclane products.

Conclusion

Symmetry and geometry of bis-pyridinyl homoquadricyclane ligands renders them promising supramolecular scaffolds for preparation of self-assembling metal-coordination polymers and rhomboids. Reaction with silver nitrate produces metal-coordinate polymers in which the silver coordination sphere is sensitive to the ligand/metal ratio. Electronic properties and rigidities of the scaffolds can be modified by appropriate substitution. For example, homoquadricyclanes bearing substituents on their aliphatic polycyclic framework displayed restricted rotation of the aryl groups, thus indicating the possibility for controlling the rigidity of the hydrophobic cavity by such substituents.

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[15] CCDC-263937 (**L1**), -263938 (**L2**), -263939 (**L3**), -263940 (**1**), -263941 (**2**) and -263942 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif/.

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[18] DSC-TGA graphs and analysis are included into the SI section.

[19] Preparation and detailed spectroscopic characterization of dimethoxyhomoquadricyclane **L4** are included in the Supporting Information.

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