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Externally and Internally Functionalized Copper(II) β-Diketonate Molecular Squares

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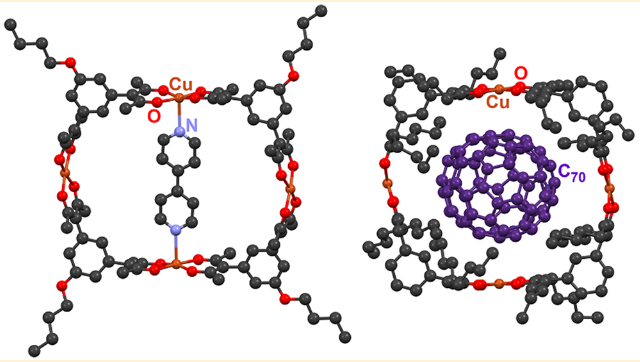
Ⓢ *Supporting Information*

ABSTRACT: Five functionalized bis(β-diketones) and their Cu(II) molecular squares are described. The new bis(β-diketones), *m*-pbhxH_2 (**3**), 5-MeO-*m*-pbaH_2 (**4**), 5-BuO-*m*-pbaH_2 (**5**), 2-MeO-*m*-pbaH_2 (**6**), and 2-MeO-*m*-pbprH_2 (**7**), were prepared by reaction of the corresponding aldehydes with phospholenes, as we previously reported for *m*-pbaH_2 (**1**) and *m*-pbprH_2 (**2**). Ligand **3** has long alkyl chains in its β-diketone moieties, while ligands **4**−**7** have alkoxy substituents on their aromatic rings. When treated with Cu^{2+}, the new bis(β-diketones) **3**, **4**, **5**, and **7** afford molecular squares, Cu_4(*m*-pbhx)$_4$ (**10**), Cu_4(5-MeO-*m*-pba)$_4$ (**11**), Cu_4(5-BuO-*m*-pba)$_4$ (**12**), and Cu_4(2-MeO-*m*-pbpr)$_4$ (**13**), respectively. Two of the new molecular squares, **10** and **12**, contain longer-chain substituents and are soluble in a wider range of organic solvents. The other squares, **11** and **13**, contain external and internal methoxy groups, respectively, and they show smaller changes in solubility. Single-crystal X-ray analyses are reported for three of the molecular squares without guest molecules, and for five adducts of the squares with σ- (polypyridine) and π-bonded (fullerene) guests. The Cu⋯Cu distances in the "empty" squares range from 14.047 to 14.904 Å; those in the adducts vary over a wider range depending on the guest molecule involved.



■ INTRODUCTION

Porous supramolecular metal−organic assemblies have attracted great attention in recent years because of their potential applications in areas such as catalysis, separation, gas storage, and host−guest chemistry.[1−10] Among the various assemblies known, molecular squares have been studied extensively. Many molecular squares have been constructed from linear 4,4′-bipyridine (4,4′-bpy) ligands and *cis*-protected square planar metal centers; octahedral metal centers and other ligands have been employed as well.[11−15] These square planar and octahedral metal centers provide the 90° corners needed for the squares. We have reported molecular squares prepared from Cu^{2+} and the bis(β-diketone) ligands *m*-pbaH_2 (**1**) and *m*-pbprH_2 (**2**);[16] see Figure 1. Our molecular squares are different from others that are commonly studied in two ways: (1) the ligands occupy the corners and the metals form the edges; and (2) the Cu metal centers are not protected and are coordinatively unsaturated, which means they can interact with guest molecules. The squares bind 4,4′-bpy and C_{60}; 4,4′-bpy is coordinated through its N atoms, while C_{60} is held through π−π interactions. Unfortunately, the squares are soluble only in a small number of solvents, which limits their usefulness.

One of our goals in the present work was to prepare Cu β-diketonate molecular squares that are soluble in a wider range of solvents. We pursued two routes toward molecular squares with improved solubility: modification of the alkyl groups in the β-diketone moieties of *m*-pbaH_2, and functionalization of the *m*-phenylene moieties. Herein, we describe the new bis(β-diketones) **3**−**7** (Figure 1) and their Cu(II) molecular squares.

For modification of the β-diketone alkyl groups, we considered commonly employed alternatives such as *t*-Bu (as in dipivaloylmethane, dpmH) and Ph (as in dibenzoylmethane, dbmH); see Figure 2. Indeed, in our earlier work with *m*-xbaH_2 and its complexes, we prepared such analogs, *m*-xbpH_2 and *m*-xbdH_2. However, we were unable to prepare metal complexes of either of these substituted bis(β-diketones).[17] Earlier investigators also noted that sterically hindered β-diketones react only weakly or not at all with metal ions such as Fe^{3+} and Cu^{2+}. For example, 3-propyl-2,4-pentanedione reacts readily with Fe^{3+} and Cu^{2+}, but 3-isopropyl-2,4-pentanedione does not;[18] the binding constants for β-diketones with Cu^{2+} are significantly smaller when the central C atom is substituted.[19,20] A general rule appears to be that if the 3 position in acetylacetone is substituted,[21] then branched substituents in the 1, 3, or 5 positions are likely to interfere with Cu^{2+} complexation. On the basis of this information, we chose *n*-pentyl groups for our experiments with longer-chain alkyl groups in the β-diketone moieties of *m*-pbaH_2.

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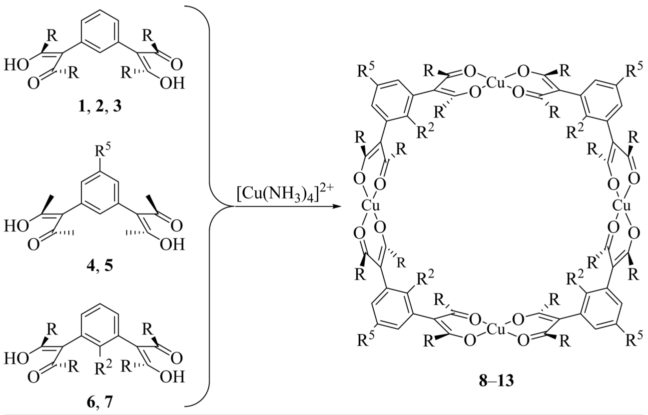


R	R^2	R^5	Bis(β-diketone) LH_2	Molecular square Cu_4L_4
CH_3	H	H	*m*-pbaH_2, **1**	Cu_4(*m*-pba)$_4$, **8** [16]
C_2H_5	H	H	*m*-pbprH_2, **2**	Cu_4(*m*-pbpr)$_4$, **9** [16]
C_5H_{11}	H	H	*m*-pbhxH_2, **3**	Cu_4(*m*-pbhx)$_4$, **10** (97%)
CH_3	H	OMe	5-MeO-*m*-pbaH_2, **4**	Cu_4(5-MeO-*m*-pba)$_4$, **11** (96%)
CH_3	H	OBu	5-BuO-*m*-pbaH_2, **5**	Cu_4(5-BuO-*m*-pba)$_4$, **12** (97%)
CH_3	OMe	H	2-MeO-*m*-pbaH_2, **6**	Insoluble product
C_2H_5	OMe	H	2-MeO-*m*-pbprH_2, **7**	Cu_4(2-MeO-*m*-pbpr)$_4$, **13** (60%)

Figure 1. Conversion of bis(*β*-diketones) (**1**−**7**) into molecular squares (**8**−**13**) by reaction with $[Cu(NH_3)_4]^{2+}$. The new substituted bis(*β*-diketones) **3**−**7**, and their molecular squares **10**−**13**, are reported here.

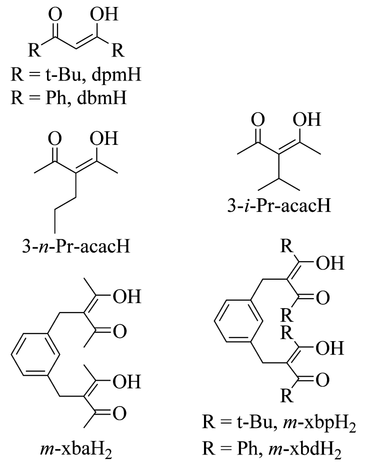


Figure 2. *β*-Diketones on the left generate metal complexes readily; those on the right do not, because of steric hindrance among their bulkier substituents.

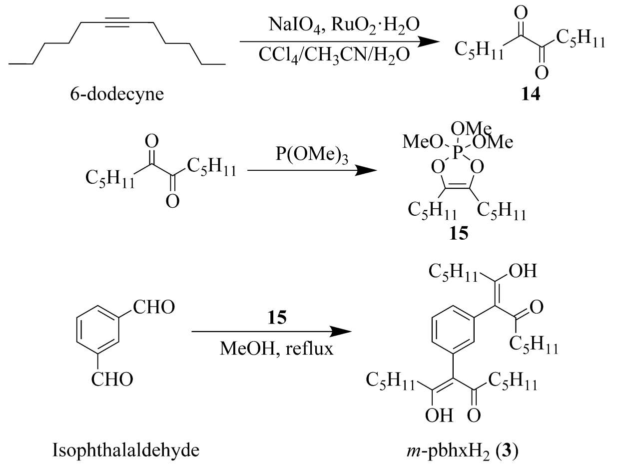
For functionalization of the *m*-phenylene moiety in *m*-pbaH_2, we introduced substituents in the 2- and 5-positions, leading to internally and externally functionalized squares, respectively. Yu and co-workers prepared a molecular square from a 5-substituted *m*-pbaH_2 ligand (R^5 = $PhCH_2O$ in Figure 1);[22] however, they discussed only its solutions in CH_2Cl_2. The preparation of 3-substituted *β*-diketones, and their use in supramolecular structures, has been reviewed by Ziessel et al.[21]

Adding functional groups to the 2-position in particular is attractive for two reasons: (1) if the substituents are large enough, steric factors may lead to formation of larger macrocycles such as molecular pentagons or hexagons, and (2) we could study the effects of changing the chemical environment inside the squares. Fujita and co-workers, for example, have reported coordination cages ("nanoballs") whose interiors are decorated with polyethylene glycol (PEG) or fluorocarbon substituents.[23,24]

■ RESULTS AND DISCUSSION

Ligands. *a. m-Phenylenebis(dihexanoylmethane), m-pbhxH$_2$ (3).* Our synthetic route for *m*-pbhxH_2 (the analog of *m*-pbaH_2 containing pentyl substituents) is shown in Scheme 1.

Scheme 1. Synthesis of *m*-pbhxH$_2$ (3)



The *α*-diketone required for this route, dodecane-6,7-dione (**14**), has been prepared via a Grignard reaction.[25] We experimented with this method, but found the general method of Zibuck and Seebach[26] to be more convenient. Reaction of 6-dodecyne with $NaIO_4$ and a catalytic amount of $RuO_2 \cdot xH_2O$ in a $CCl_4/CH_3CN/H_2O$ solvent mixture gave yellow solid **14**. Treatment of **14** with trimethyl phosphite afforded 2,2,2-trimethoxy-4,5-dipentyl-1,3,2-dioxaphospholene (**15**), which reacted with isophthalaldehyde to yield *m*-pbhxH_2 (**3**), as a colorless oil after column chromatography.

b. 5-MeO-m-pbaH$_2$ (4), 5-BuO-m-pbaH$_2$ (5), 2-MeO-m-pbaH$_2$ (6), and 2-MeO-m-pbprH$_2$ (7). Scheme 2 shows the syntheses of these new bis(*β*-diketones).

Copper(II) Molecular Squares. Treatment of dichloromethane solutions of the *β*-diketones **3**, **4**, **5**, and **7** with aqueous $[Cu(NH_3)_4]^{2+}$ afforded green solutions, and upon evaporation of the solvent, the squares (**10**−**13**) were isolated as dark green powders in moderate to high yields (see Figure 1). These results are similar to those that we previously reported for the conversion of **1** and **2** into their molecular squares (**8** and **9**). Analogous experiments involving **6** yielded an insoluble dark green product. This may be a molecular square, but we were unable to characterize it further due to its lack of solubility.

Solubility. Table 1 shows the solubility of the molecular squares in various solvents. Squares **10** and **12** are soluble in nine organic solvents. We attribute the greater solubility of these two squares to the presence of long alkyl chains (pentyl) in the *β*-diketone moieties of **3** and the long alkoxy (butoxy) groups in the 5-position on the aromatic rings of **5**, respectively. Squares **11** and **13**, with methoxy groups in the 5- and 2-positions on the ligand aromatic rings, respectively, are soluble in about the same number of solvents as the unsubstituted square Cu_4(*m*-pba)$_4$,[16] though with a different range of polarities.

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Scheme 2. Syntheses of New Bis(β-diketones): (i) 4, (ii) 5, and (iii) 6 and 7

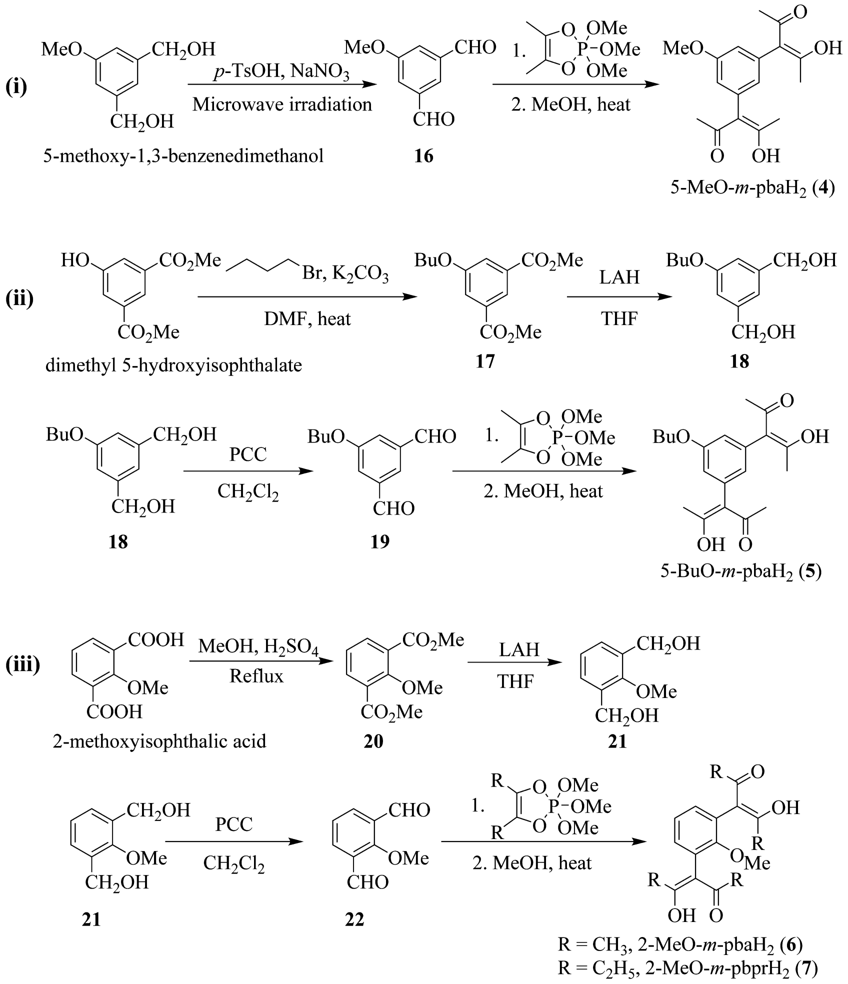

Table 1. Solubility of the Cu(II) Molecular Squares

solvent[a]	$Cu_4(m\text{-pba})_4$, **8**	$Cu_4(m\text{-pbpr})_4$, **9**	$Cu_4(m\text{-pbhx})_4$, **10**	$Cu_4(5\text{-MeO-}m\text{-pba})_4$, **11**	$Cu_4(5\text{-BuO-}m\text{-pba})_4$, **12**	$Cu_4(2\text{-MeO-}m\text{-pbpr})_4$, **13**
CH_2Cl_2	Y	Y	Y	Y	Y	Y
$CHCl_3$	Y	Y	Y	N	Y	Y
C_6H_6	N	N	Y	N	Y	N
Toluene	N	N	Y	N	Y	Y (hot)
CS_2	N	N	Y	N	Y	N
1,2-dichlorobenzene	N	N	Y	N	Y	N
chlorobenzene	N	N	Y	N	Y	N
THF	N	N	Y	Y	Y	N
bromobenzene	N	N	Y	N	Y	N

[a] All of the molecular squares are insoluble in methanol, acetone, acetonitrile, hexane, and diethyl ether.

Structures. $Cu_4(m\text{-pbhx})_4$ (**10**) crystallizes as a solvate with methanol (see Figure 3). The molecules have approximate inversion symmetry; two of the Cu atoms are square pyramidal, with apical CH_3OH, and the other two are square planar. The pyramidal distortion at Cu2 and Cu4 leads to a longer Cu···Cu distance than that between the four-coordinate Cu1 and Cu3. The apical Cu−O distances at Cu2 and Cu4 (2.262(4) and 2.263(3) Å) are similar to that reported by Clegg and coworkers for a Cu(II) β-diketonate with apical THF (2.342(1) Å).[27]

Compound **11**, $Cu_4(5\text{-MeO-}m\text{-pba})_4$, crystallizes as a coordination polymer (Figure 4), in which the external MeO groups are coordinated to Cu atoms in adjacent molecules. In these crystals, disordered water molecules are also bound on the inside of the squares (occupancy 0.5, for 2 water molecules per Cu_4 square), so that the overall coordination of the Cu atoms is approximately octahedral. The molecules of $Cu_4(5\text{-MeO-}m\text{-pba})_4$ have crystallographically imposed $4/m$ (C_{4h}) symmetry.

The structure of $Cu_4(2\text{-MeO-}m\text{-pbpr})_4$ (**13**) is shown in Figure 5. In this crystal, the square has a puckered conformation, with crystallographically imposed $\bar{4}$ (S_4) symmetry. The internal methoxy groups alternately point toward opposite sides of the Cu_4 ring. Steric interactions between the methoxy groups and the nearby portions of the square may be strong enough to cause distortion away from the

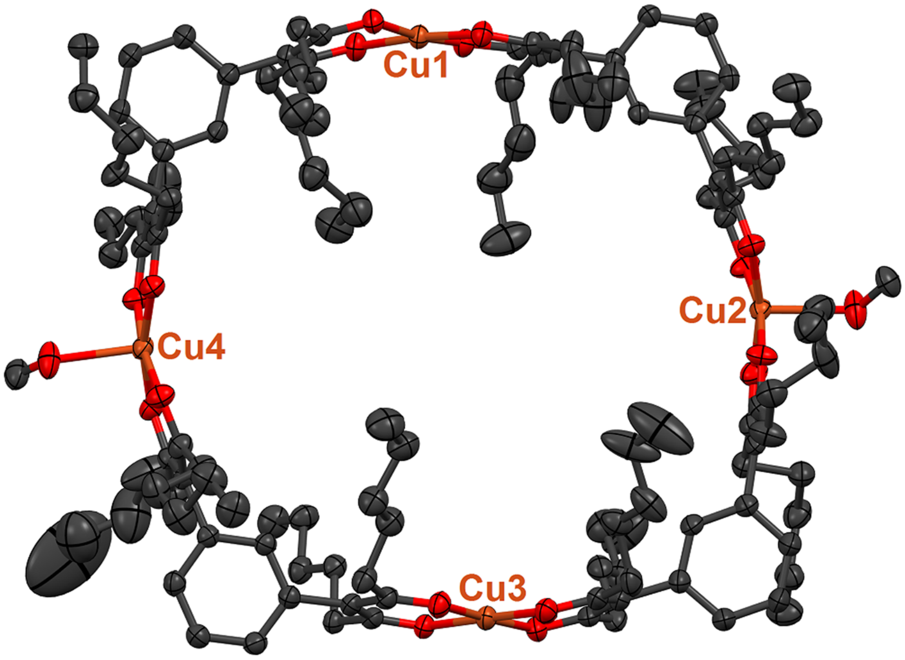

Figure 3. Crystal structure of $Cu_4(m\text{-pbhx})_4(CH_3OH)_2$, from **10**$(CH_3OH)_2 \cdot 12CHCl_3$, Cu1···Cu3 14.047(1) Å, Cu2···Cu4 14.904(1) Å. In this and all other crystal-structure illustrations, ellipsoids are at the 50% probability level, and hydrogen atoms and uncoordinated solvent molecules are omitted for clarity.

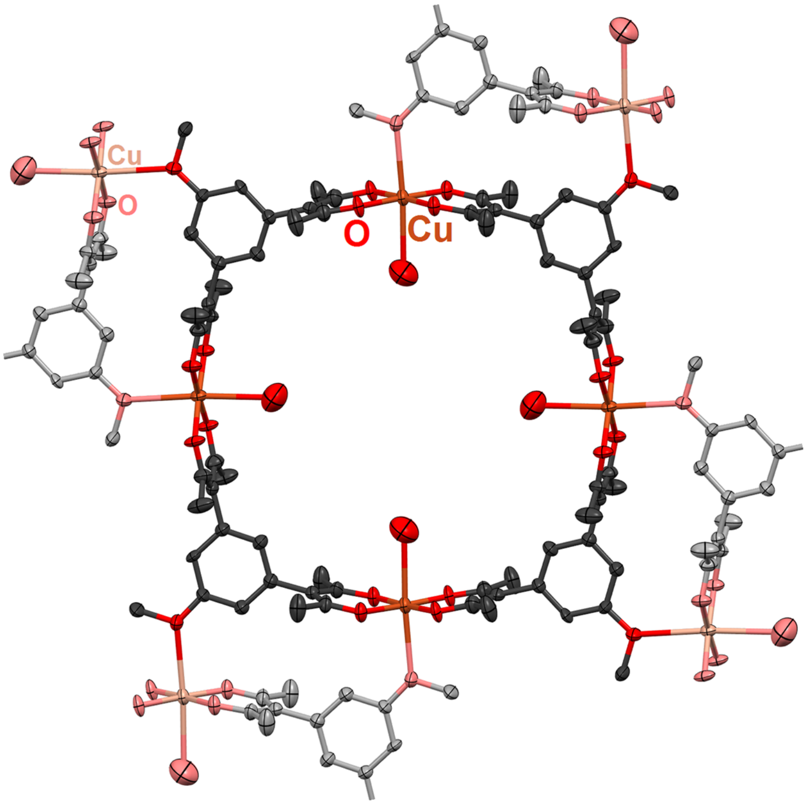

Figure 4. Structure of $[Cu_4(5\text{-MeO-}m\text{-pba})_4(H_2O)_2]$, from **11**$(H_2O)_2 \cdot 12CHCl_3 \cdot 8H_2O$, Cu···Cu 14.322(2) Å. Portions of adjacent molecules in the crystal are shown (with lighter coloring), to illustrate close Cu−O(methoxy) bonds (2.608(8) Å).

normally coplanar arrangement of aromatic rings and Cu atoms.

Host−Guest Chemistry of the Squares. *a. Adducts with Pyridine Derivatives.* Several of the new squares react with pyridine derivatives, forming adducts with internally coordinated guests. The reaction of $Cu_4(m\text{-pbhx})_4$ (**10**) with the guest molecules 1,2-bis(4-pyridyl)ethylene (bpe) and 1,2-bis(4-pyridyl)ethane (bpa) is confirmed by formation of the adducts $[Cu_4(m\text{-pbhx})_4(\mu\text{-bpe})(MeOH)_2]$ (**23**; Figure 6) and $[Cu_4(m\text{-pbhx})_4(\mu\text{-bpa})(MeOH)_2]$ (**24**; Supporting Information Figure

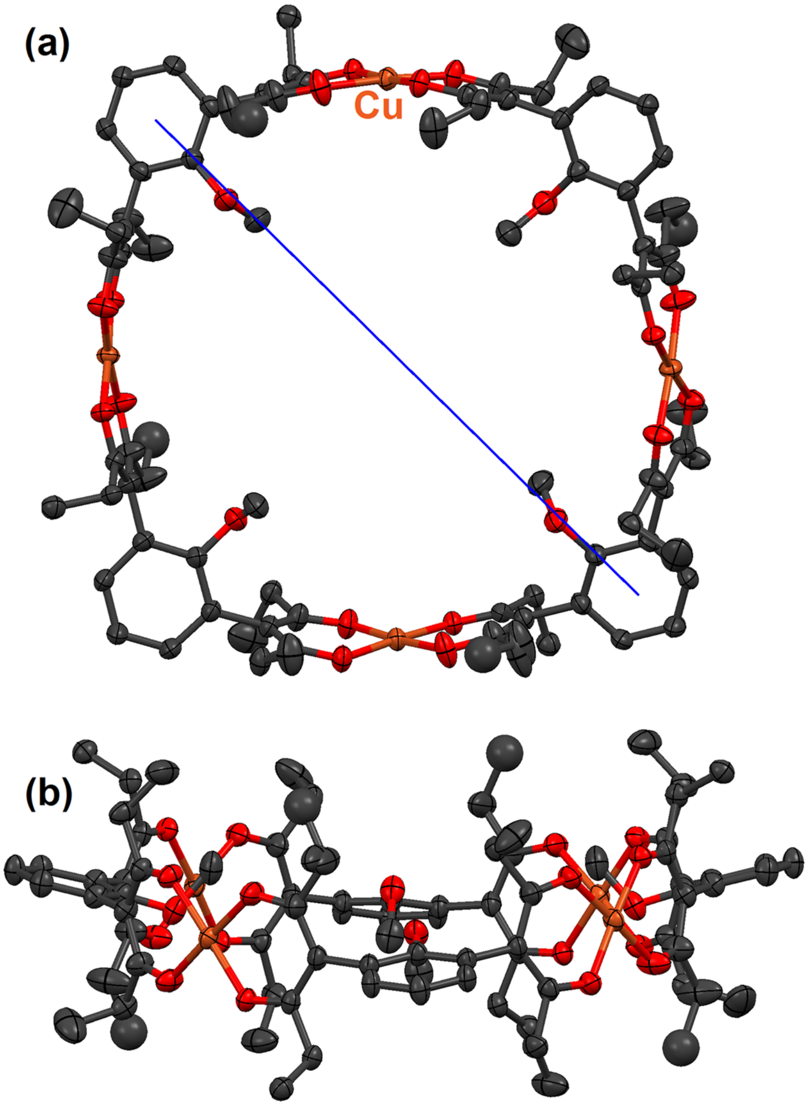

Figure 5. Crystal structure of Cu_4(2-MeO-*m*-pbpr)$_4$, from (**13**)·6.75CH_3CN, Cu···Cu′ 14.3862(5) Å. Minor components of disordered C atoms omitted for clarity. (a) Face view. (b) Edge view, approximately along the blue diagonal line in part a, showing puckering of the square. The CH_3O groups on the downward-facing aromatic rings also point downward, with corresponding upward displacements for the other two ligands.

S1). In both of these adducts, the Cu atoms bridged by the guest molecule are approximately 1 Å closer together than the unbridged Cu atoms. This indicates that the bpe and bpa guest molecules are slightly shorter (N···N′ 9.425(4) and 9.278(5) Å, respectively) than would be ideal for the Cu_4(*m*-pbhx)$_4$ host.

Cu_4(5-BuO-*m*-pba)$_4$ (**12**) reacts with 4,4′-bpy to produce adduct **25**, [Cu_4(5-BuO-*m*-pba)$_4$(*μ*-bpy)]. The structure of **25** (Figure 7) is similar to the one we previously reported for Cu_4(*m*-pba)$_4$(*μ*-bpy),[16] with the shorter 4,4′-bpy guest molecule leading to a greater difference in Cu···Cu distances (ca. 4 Å) than in the above bpe (**23**) and bpa (**24**) adducts.

In all three of these adducts, the unbridged Cu atoms have O atoms coordinated externally, either from solvent molecules (in **23** and **24**) or from an adjacent square (in **25**).This leads to outward-pointing square pyramidal coordination geometry, which also contributes to the larger unbridged Cu···Cu distances.

Square **11**, Cu_4(5-MeO-*m*-pba)$_4$, also changed color from green to blue on treatment with pyridine derivatives, which indicates that similar host−guest chemistry is occurring. However, we could not obtain the products in analytically pure or crystalline form, so they were not studied further. In contrast, square **13**, Cu_4(2-MeO-*m*-pbpr)$_4$, with internal methoxy groups, remained green in solution even in the presence of large excesses of potential guest molecules, and no adducts could be isolated. This suggests that **13** has a much lower affinity for guests than the other Cu molecular squares we have studied. We attribute this low guest affinity to steric interference from its internal OCH_3 groups.

*b. Adduct with C_{60} (**26**).* Treatment of square **10** with C_{60} produced Cu_4(*m*-pbhx)$_4$(*μ*-C_{60}) (**26**), whose crystal structure is shown in Figure 8. This structure is similar to that of our previously reported Cu-square-fullerene adduct, i.e., Cu_4(*m*-pbpr)$_4$(*μ*-C_{60}),[16] except for the longer *β*-diketone alkyl groups in the present structure. In both structures, several of the *β*-diketone alkyl groups are oriented inward, toward the face of the C_{60} guest. Multiple weak interactions between the alkyl groups and the guest are likely to provide some stabilization for the adducts, in addition to *π* interactions between the fullerene and unsaturated portions of the host.

The longer pentyl groups in Cu_4(*m*-pbhx)$_4$(*μ*-C_{60}) (**26**) could lead to guest−host attractions that are stronger than

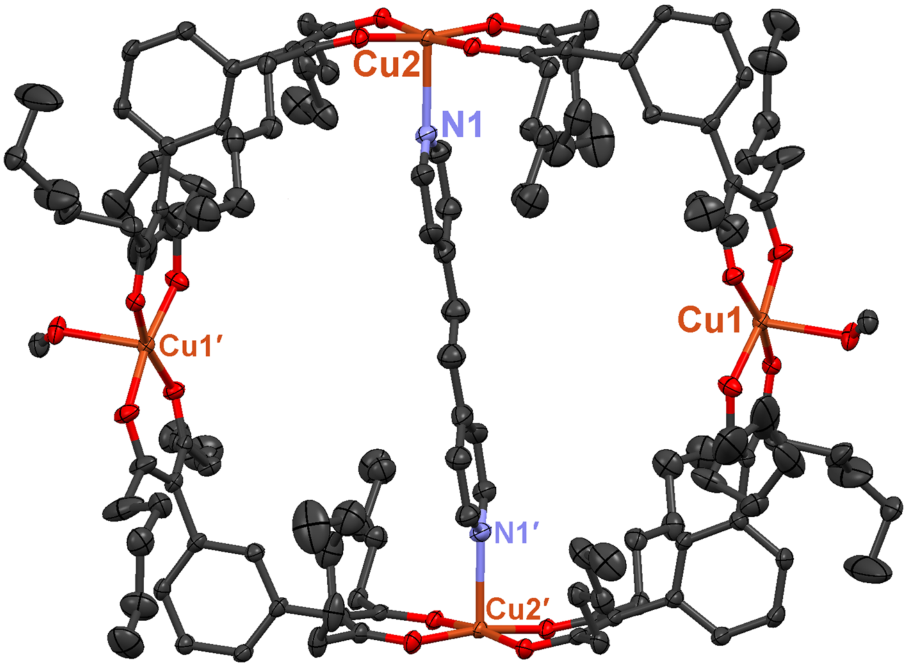

Figure 6. Crystal structure of Cu_4(*m*-pbhx)$_4$(*μ*-bpe)$(CH_3OH)_2$, from (**23**)$(CH_3OH)_2$·$10CHCl_3$. Cu1···Cu1′ 14.667(1) Å, Cu2···Cu2′ 13.9893(8) Å.

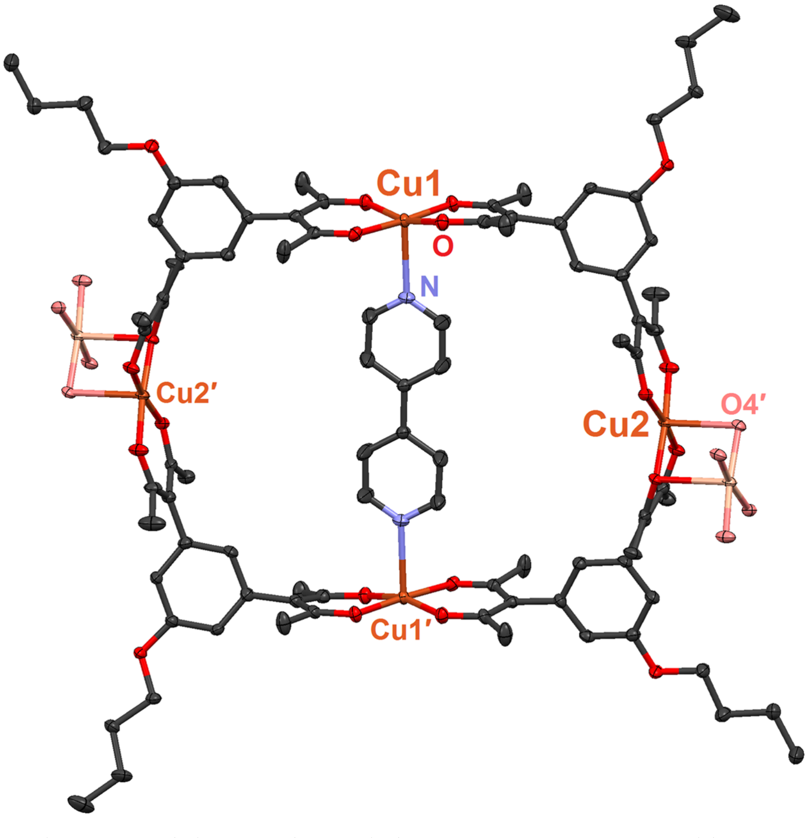

Figure 7. Crystal structure of Cu_4(5-BuO-*m*-pba)$_4$(*μ*-4,4′-bpy), from (**25**)·$16CHCl_3$; Cu1···Cu1′ 11.9537(7), Cu2···Cu2′ 15.9851(9) Å. Portions of adjacent molecules in the crystal are shown (with lighter coloring), to illustrate close Cu2···O4′ contacts (2.491(2) Å).

those in the previously described adduct Cu_4(*m*-pbpr)$_4$(*μ*-C_{60}).[16] However, it should be noted that, in both the present structures and the previous one, not all of the alkyl groups are directed inward. Molecular modeling of these adducts indicates that there is not enough room around the Cu square to accommodate all 16 *β*-diketonate alkyl groups (R in Figure 1) pointing inward, even with the smaller ethyl groups of Cu_4(*m*-pbpr)$_4$ (**9**). A recently reported hemicarceplex containing six $-OC_{10}H_{20}O-$ bridging groups is an effective host for C_{60}, also relying on multiple alkyl···fullerene interactions.[28]

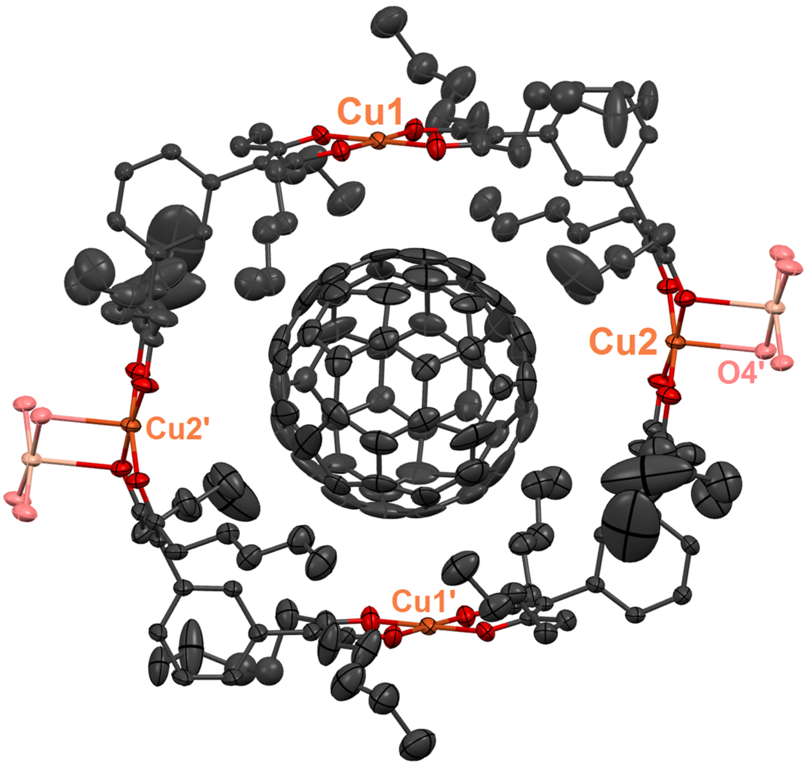

Figure 8. Crystal structure of $[Cu_4(m\text{-pbhx})_4(\mu\text{-}C_{60})]$, from (**26**)·$4C_6H_4Cl_2$: Cu1···Cu1′ 13.4326(9) Å; Cu2···Cu2′ 15.146(1) Å. The C_{60} molecule makes short contacts with Cu1 and neighboring atoms (minimum Cu1···C 3.40 Å) and with some of the alkyl C atoms (minimum C···C 3.57 Å). The $Cu_4(m\text{-pbhx})_4$ host makes short contacts with adjacent molecules: Cu2···O4′ 2.460(3) Å.

In our previous report of the binding of C_{60} to $Cu_4(m\text{-pbpr})_4$ (**9**),[16] we were unable to study the reaction in detail, because the host and guest are not readily soluble in the same solvents. However, the new host $Cu_4(m\text{-pbhx})_4$ (**10**) is soluble in several solvents that are also good solvents for fullerenes. Among the good solvents for $Cu_4(m\text{-pbhx})_4$ (**10**), 1,2-dichlorobenzene is the best solvent for fullerenes,[29,30] and toluene is also commonly used for fullerene binding studies. Thus, we used these two solvents for our experiments.

Host−guest reactions are often studied by electronic absorption spectroscopy. Often, the guest molecules do not absorb in the region of interest, so the changes in the spectrum of the host on binding guest molecules are easy to observe. However, in the present case, both $Cu_4(m\text{-pbhx})_4$ (**10**) and C_{60} are colored, and the absorption of C_{60} is more intense than that of the Cu square. Thus, in these experiments, we used a fixed concentration of fullerene, and varied the concentration of the Cu square. Figure 9 shows a series of absorption spectra of 0.17 mM C_{60} in 1,2-$C_6H_4Cl_2$, with increasing concentrations of $Cu_4(m\text{-pbhx})_4$ (**10**). Analysis of these spectra with the global analysis program SPECFIT/32 gives a binding constant of 5400 ± 800 M^{-1}. Experiments in toluene solution gave a binding constant about 6 times as large (see Table 2); binding of C_{60} and C_{70} to hosts is usually stronger in toluene than in 1,2-$C_6H_4Cl_2$, because toluene solvates fullerenes more weakly.[31−34] The new binding constants are larger than those we previously observed for σ-donating guests such as dabco and pyrazine with the binuclear host $Cu_2(nba)_2$.[35] Still, they are significantly smaller than values reported (>10^5 M^{-1}) for binding of C_{60} to other macrocyclic polynuclear metal complexes.[36−38]

*c. Adduct with C_{70} (**27**).* In our previous work with $Cu_4(m\text{-pba})_4$ and $Cu_4(m\text{-pbpr})_4$,[16] we observed color changes that suggested C_{70} is also capable of binding as a guest. However, we were unable to isolate either of the C_{70} adducts. These reactions, like those with C_{60}, were complicated by the lack of a common solvent for host and guest. We now report that 1,2-dichlorobenzene solutions of $Cu_4(m\text{-pbhx})_4$ (**10**) and C_{70} react

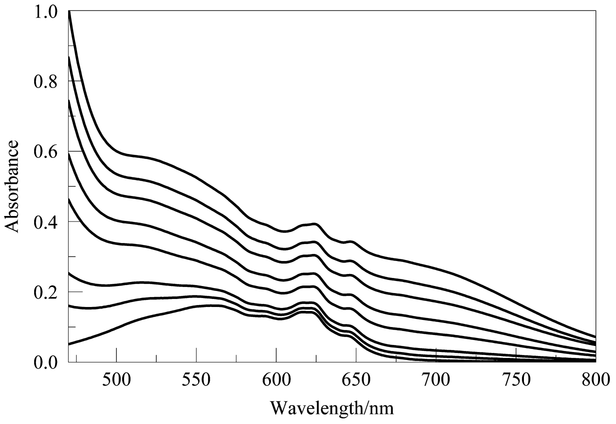

Figure 9. Portions of the electronic absorption spectra of solutions of $Cu_4(m\text{-pbhx})_4$ and C_{60} in 1,2-dichlorobenzene. All solutions contain 0.167 mM C_{60}. Concentrations of added $Cu_4(m\text{-pbhx})_4$ increase in order from the bottom spectrum upward: 0, 0.0922, 0.184, 0.461, 0.738, 1.01, 1.29, and 1.57 mM.

Table 2. Binding Constants for the Reaction of $Cu_4(m\text{-pbhx})_4$ (10) with Fullerene Guests

solvent	guest = C_{60}	guest = C_{70}
1,2-dichlorobenzene	5.4 ± 0.8 × 10^3	3.5 ± 0.8 × 10^4
toluene	3.4 ± 0.7 × 10^4	7 ± 3 × 10^5

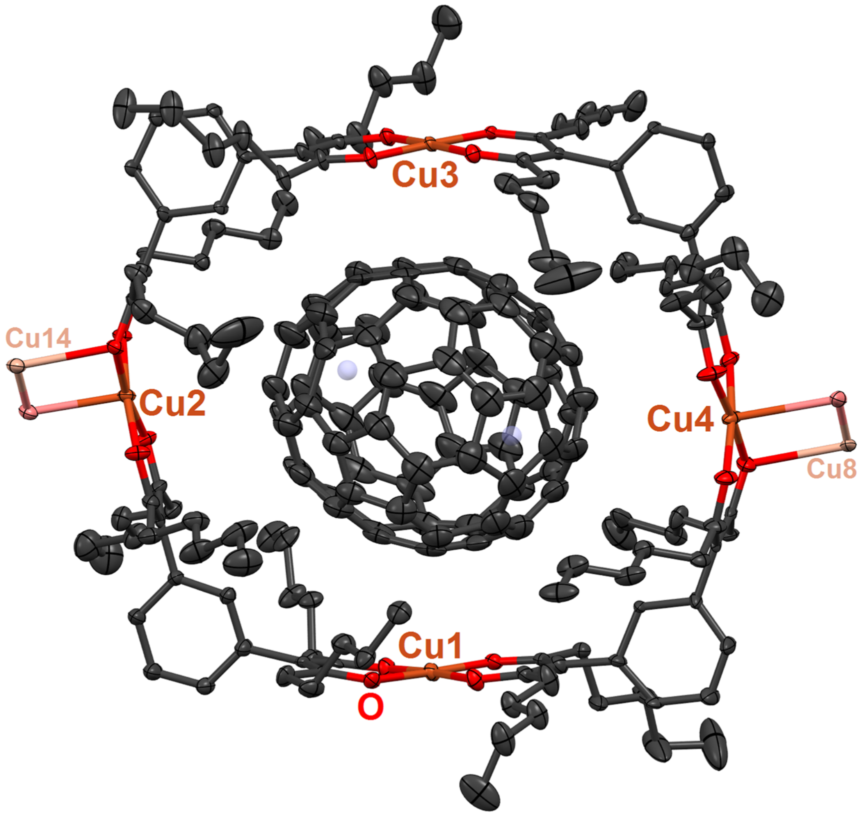

Figure 10. Crystal structure of [Cu_4(*m*-pbhx)$_4$(μ-C_{70})], from (**27**)·3.25$C_6H_4Cl_2$. Only one of the four molecules in the asymmetric unit is shown. The (approximate) 5-fold axis of the C_{70} guest is shown by the two lavender balls (centroids of 5-membered rings). Cu1···Cu3 13.315(3), Cu2···Cu4 15.260(3) Å; short contacts with adjacent molecules are shown in lighter colors. For an illustration of all four [Cu_4(*m*-pbhx)$_4$(μ-C_{70})] molecules in the asymmetric unit, see the Supporting Information.

readily. The structure of the resulting adduct (**27**) is shown in Figure 10.

Crystals of Cu_4(*m*-pbhx)$_4$(μ-C_{70}) (**27**) contain four crystallographically independent molecules in the asymmetric unit. This gave us an opportunity to investigate whether the C_{70} guest has a similar orientation in each molecule. Whereas C_{60} is approximately spherical, C_{70} has the approximate shape of a prolate spheroid, slightly longer than C_{60} but with the same diameter. It appeared from the structures of our C_{60} adducts as if the size of C_{60} is well-matched with the internal cavity of the host molecule, Cu_4(*m*-pbhx)$_4$ (Figure 8) or Cu_4(*m*-pbpr)$_4$.[16] If the hosts have the ideal cavity size for C_{60}, then they should also be ideal for the equatorial diameter of C_{70}. If this is true, then C_{70} should bind to our molecular squares in a preferred orientation, with its 5-fold symmetry axis parallel to the 4-fold axis of the Cu_4 host. This is sometimes called the "lying" orientation of a C_{70} guest; see schematic illustration in Figure 11a ($\theta = 0°$).

The preferred orientation of C_{70} guest molecules in ring-shaped [*n*]CPP hosts (CPP = cycloparaphenylene, with *n* = number of *p*-phenylene moieties in the ring) has been studied experimentally and computationally. Yamago and co-workers determined the crystal structure of the C_{70} adducts of two CPPs.[39] When bound in a 10-ring host ([10]CPP), the C_{70} guest prefers the "lying" orientation, i.e., with its 5-fold axis parallel to the principal axis of the CPP ring (Figure 11a, $\theta = 0°$). In the next larger host, [11]CPP, on the other hand, the C_{70} symmetry axis is perpendicular to the CPP axis (i.e., in the plane of the ring); this is the "standing" orientation (Figure 11c, $\theta = 90°$). A recent computational study by Zhao et al. supports a thermodynamic preference for these orientations, and suggests that the next larger host, [12]CPP, prefers an intermediate "half-lying" orientation of C_{70} (Figure 11b).[40]

If our Cu molecular squares are considered to be ring-shaped hosts, their interactions with fullerenes may be similar to those of CPPs. In the crystal structure of Cu_4(*m*-pbhx)$_4$(μ-C_{70}) (**27**), molecules A, B, C, and D (see Figure 10 and Supporting Information Figure S2) in the asymmetric unit are all in the "half-lying" orientation, with angles θ of 50.2°, 33.6°, 50.2°, and 50.0°, respectively. According to the logic of Zhao et al., this suggests that our Cu_4 host is slightly too large for optimal interaction with C_{70}. Thus, a host that is slightly smaller than Cu_4(*m*-pbhx)$_4$ might be a better match for guests such as C_{60} and C_{70}, with correspondingly higher binding constants.

A molecular square "nanobarrel" has been prepared from four nickel-porphyrin units by Osuka et al.,[41] and the structure of its C_{60} adduct was determined. The binding constant between C_{60} and this Ni_4 host is 5.3×10^5 M^{-1} in toluene, about 15 times as large as that with our Cu_4(*m*-pbhx)$_4$ host. And yet the crystal structure of the Osuka Ni_4–C_{60} adduct shows that the fullerene guest is not fully inserted into its host. This may be because the Ni···Ni distances in the host are slightly too short for the optimum interaction with C_{60}. Thus, the best metal–metal distance in a molecular square for forming a C_{60} adduct may be somewhere between those in the "nanobarrel" (13.7 Å) and those we have observed in the present study (average 14.25 Å).

We also determined the equilibrium constants for the binding of C_{70} to Cu_4(*m*-pbhx)$_4$ from UV–vis spectra; see Table 2. The values obtained were substantially larger than

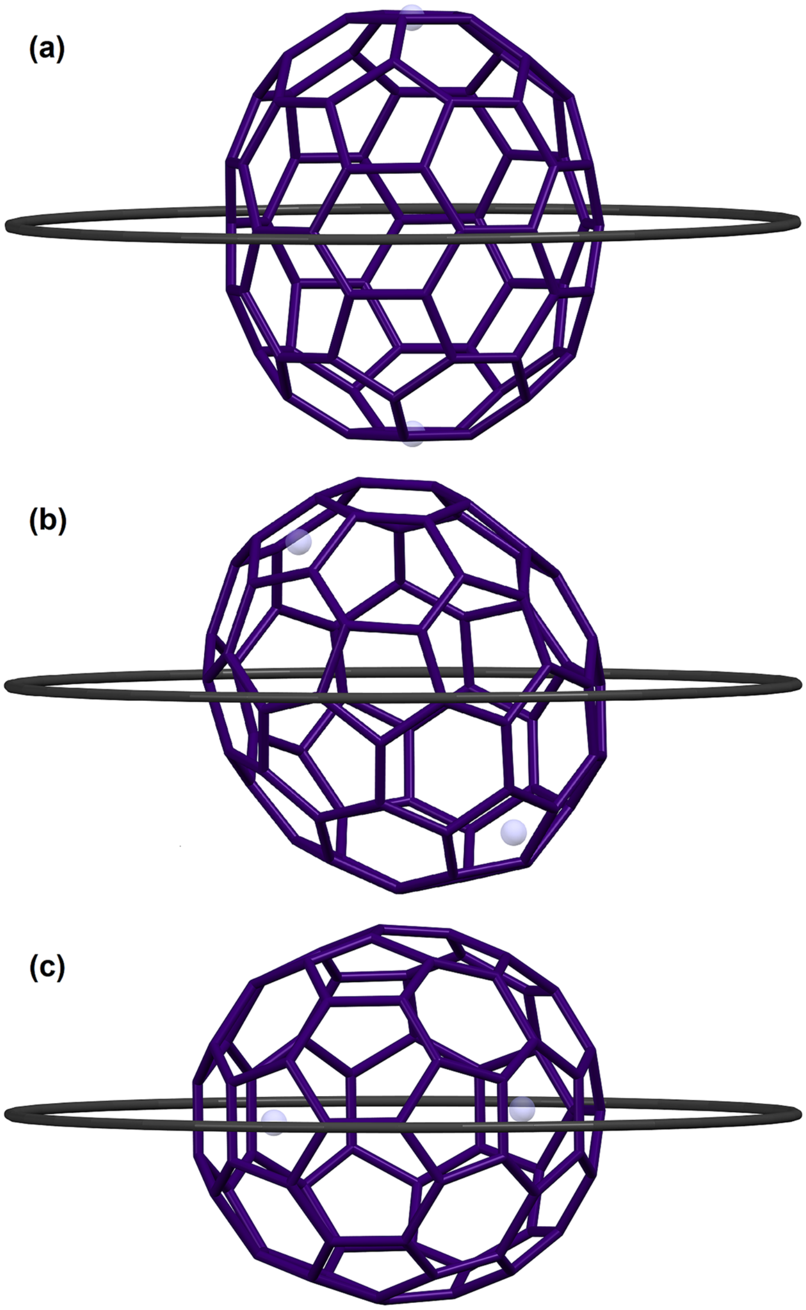

Figure 11. Three possible orientations of a C_{70} guest molecule (purple) in a ring-shaped host (black). In each diagram, the centroids of the two opposite C_5 rings of the C_{70} guest (coincident with its 5-fold symmetry axis) are marked by small lavender spheres. (a) "Lying" orientation, with the C_{70} and ring axes coincident, defined as $\theta = 0°$. (b) "Half-lying" orientation, with $0° < \theta < 90°$ ($\theta \approx 54°$ shown). (c) "Standing" orientation, with the C_{70} and ring axes perpendicular ($\theta = 90°$).

those for C_{60}, in both 1,2-dichlorobenzene and toluene. Other metal-based hosts also tend to show higher affinities for C_{70} than for C_{60}.[37,38] Calculated spectra for Cu_4(*m*-pbhx)$_4$(μ-C_{60}) and Cu_4(*m*-pbhx)$_4$(μ-C_{70}) derived from this analysis are included in Supporting Information.

■ CONCLUSION

Externally and internally substituted Cu(II) molecular squares have been prepared from appropriate derivatives of the bis(β-diketone) *m*-pbaH_2. Substituted squares exhibit modified solubility, with longer substituents (OC_4H_9, C_5H_{11}) leading to solubility in a variety of common organic solvents. The solubility of the molecular square changes only slightly when an internal substituent (2-OCH_3) is introduced. All but one of the new squares react with guest molecules such as 1,2-bis(4-pyridyl)ethylene (bpe) (σ) and C_{60} and C_{70} (π). The structure of the C_{70} adduct suggests that it may be possible to build a molecular square that binds fullerenes more strongly than Cu_4(*m*-pbhx)$_4$ does. We observed no reaction between the internally substituted molecular square, Cu_4(2-MeO-*m*-pbpr)$_4$ (**13**), and potential guest molecules. This is likely due to steric interference. In order to permit both internal substitution and guest binding, the hosts will need to be made larger. We are now preparing bis(β-diketones) with longer bridging groups so as to allow for both functions.

■ EXPERIMENTAL SECTION

General Considerations. Reagents were used as received, from Sigma-Aldrich (except for 6-dodecyne, which was obtained from GFS Chemicals, and fullerenes, from MER Corporation). Silica gel (Sorbent Technologies, 230−450 mesh) was used for column chromatography. Dry solvents were obtained from a commercial solvent purification system. Mass spectra were taken with Agilent 6210 (ESI) and Varian Saturn 2200 GC/MS, and UV−vis spectra with an Aviv 14DS instrument. Binding constants were calculated from UV−vis spectra (25.5 °C) by using the global-analysis program SPECFIT/32 (Spectrum Software Associates). Elemental analyses were performed by M-H-W Laboratories (Phoenix, AZ). NMR spectra were recorded on Bruker 250 or 400 MHz spectrometers with $CDCl_3$ as solvent. Microwave reactions were performed using a CEM MARS microwave oven. The phospholenes 2,2,2-trimethoxy-4,5-dimethyl-[42] and 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene[16] were prepared by literature methods.

Precursors and β-Diketones: Dodecane-6,7-dione (14). This compound was prepared following the reported procedure for making other α-diketones.[26] 6-Dodecyne (5.0 g, 30.0 mmol) was added to $CCl_4/CH_3CN/H_2O$ (2:2:3 v/v; 140 mL) and the mixture stirred for 10 min at room temperature. To this mixture was added solid $NaIO_4$ (25.72 g, 120.0 mmol), and stirring continued vigorously at room temperature until the solid dissolved, giving two colorless phases. Then $RuO_2{\cdot}xH_2O$ (0.088 g, 0.66 mmol) was added; immediately, the mixture turned black. Ten minutes later, the color of the mixture changed to dark green, and a white solid precipitated out. As stirring continued, the mixture gradually changed to lighter green and finally to yellow. After 12 h, CH_2Cl_2 (50 mL) was added, and the mixture was separated into two phases; the organic phase was dried over Na_2SO_4, filtered, and evaporated to yield a yellow solid. Column chromatography (hexane−ethyl acetate, 70:30 v/v) gave a yellow solid, 3.57 g (60%). ^{1}H NMR confirmed the identity of the product.[25]

2,2,2-Trimethoxy-4,5-dipentyl-1,3,2-dioxaphospholene (15). Trimethyl phosphite (2.06 g, 16.6 mmol) was cooled to 0 °C. Dodecane-6,7-dione (**14**; 3.0 g, 15 mmol) dissolved in dry CH_2Cl_2 (20 mL) was added dropwise and the reaction mixture allowed to warm to room temperature under nitrogen; stirring was continued for 24 h. Completion of the reaction was indicated by the disappearance of the yellow color. The crude product was isolated as an oil by evaporation of solvent; its ^{1}H NMR spectrum indicated that it was sufficiently pure for use in the next step. ^{1}H NMR: δ 3.59 (d, 9H, OCH_3), 2.17 (t, 4H), 1.51 (q, 4H), 1.34−1.26 (m, 8H), 0.89 (t, 6H)).

***m*-Phenylenebis(dihexanoylmethane), *m*-pbhxH_2 (3).** This procedure is similar to those previously reported for *o*-, *m*-, and *p*-phenylenebis(acetylacetone) (*o*-, *m*-, and *p*-pbaH_2).[16,43] Isophthalaldehyde (0.60 g, 4.47 mmol) was dissolved in dry CH_2Cl_2 (20 mL), followed by addition of 2,2,2-trimethoxy-4,5-dipentyl-1,3,2-dioxaphospholene (**15**; 2.88 g, 8.94 mmol). The mixture was stirred at room temperature under nitrogen and the reaction monitored by ^{1}H NMR. Reaction was judged to be complete when the isophthalaldehyde CHO peak (10.1 ppm) had disappeared (ca. 12 h). Then, methanol (30 mL) was added and the mixture refluxed for 3 h; solvent was removed to yield a light-brown oily product. Column chromatography (hexane−ethyl acetate, 7:3 v/v) yielded a colorless oil, 1.00 g (45%). GC/MS: m/z 498 [M]. ^{1}H NMR: δ 16.81 (s, 2H), 7.42 (t, 1H), 7.14 (d, 2H), 7.00 (s, 1H), 2.10 (t, 8H), 1.52 (quintet, 8H), 1.25−1.12 (m, 16H), 0.82 (t, 12H). ^{13}C NMR: δ 193.7, 137.4, 134.7, 130.8, 129.4, 114.5, 36.8, 31.7, 25.4, 22.5, 14.0.

5-Methoxyisophthalaldehyde (16). 5-Methoxy-1,3-benzenedimethanol (0.502 g, 2.98 mmol), *p*-toluenesulfonic acid (2.29 g, 12.0 mmol), and $NaNO_3$ (0.523 g, 6.15 mmol) were placed in a microwave reaction vessel and CH_3CN (2 mL) added. Then the solvent was evaporated and the vessel was placed in the microwave. The mixture was heated for a total of 6 min, via 30-s intervals separated by approximately 10 s of cooling time.[44] After cooling, the solid was taken up in a mixture of CH_2Cl_2 and water and the organic phase separated, dried over Na_2SO_4, and evaporated to yield a yellow solid, 0.470 g (96%). ^{1}H NMR: δ 10.06 (s, 2H, CHO); 7.97 (s, 1H); 7.66 (s, 2H); 3.94 (s, 3H, OCH_3).

5-Methoxy-*m*-phenylenebis(acetylacetone), 5-MeO-*m*-pbaH_2 (4). Compound **4** was prepared using the same procedure as **3**. 5-Methoxyisophthalaldehyde (**16**) (0.30 g, 1.8 mmol) and 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene (0.76 g, 3.6 mmol) were mixed together. After the reaction was complete, the crude material was purified by column chromatography (ethyl acetate−hexane, 1:5 v/v) to obtain a white solid, 0.19 g (34%). ^{1}H NMR: δ 16.6 (s, 2H); 6.71 (s, 2H); 6.62 (s, 1H), 3.84 (s, 3H, $OC\mathit{H}_3$), 1.92 (s, 12H). ^{13}C NMR: δ 190.5, 160.1, 138.7, 126.1, 115.6, 114.6, 55.2, 23.9. Anal. Calcd for $C_{17}H_{20}O_5$ (M = 304.34): C 67.09, H 6.62. Found: C 66.13, H 6.93. Although this material is somewhat impure, as judged by microanalysis, we saw no evidence for impurities in its NMR or mass spectra (m/z 305 [M + H]).

Dimethyl 5-Butoxyisophthalate (17). Dimethyl 5-hydroxyisophthalate (4.50 g, 21.4 mmol), powdered K_2CO_3 (7.40 g, 53.6 mmol), and 1-bromobutane (3 mL, 27.6 mmol) were placed in a round-bottom flask. Then, the flask was flushed with N_2 for about 10 min, and dry DMF (50 mL) was added to the flask via syringe. The reaction mixture was heated to ca. 80 °C for 7 h, with stirring and under nitrogen. It was allowed to cool to room temperature and extracted with ethyl acetate and water; the organic phase was dried over Na_2SO_4 and evaporated. The tan solid residue was purified by column chromatography (ethyl acetate−hexane, 1:4 v/v) to yield a white solid, 3.13 g (62%). GC/MS: m/z 265.9 $[M]^+$. ^{1}H NMR: δ 8.25 (s, 1H), 7.74 (s, 2H), 4.04 (t, 2H, $OC\mathit{H}_2CH_2CH_2CH_3$), 3.94 (s, 6H, $CO_2C\mathit{H}_3$); 1.79 (quintet, 2H, $OCH_2C\mathit{H}_2CH_2CH_3$); 1.51 (sextet, 2H, $OCH_2CH_2C\mathit{H}_2CH_3$); 1.00 (t, 3H, $O(CH_2)_3C\mathit{H}_3$)).

5-Butoxy-1,3-benzenedimethanol (18). Compound **18** was prepared according to a procedure developed by Hayama et al. for forming 5-methoxybenzenebis(methanol-α,α-d_2) from dimethyl 5-methoxyisophthalate and lithium aluminum deuteride.[45] Dry THF (30 mL) was added to a three neck round-bottom flask with an addition funnel under N_2. Then, 5.0 mL (10 mmol) of lithium aluminum hydride (2 M in THF) was added via syringe. Into this solution was added dropwise dimethyl 5-butoxyisophthalate (**17**; 1.097 g, 4.12 mmol) in dry THF (20 mL). The mixture was allowed to stir for 22 h at room temperature. It was then cooled to 0 °C and 16 mL of 1 M H_2SO_4(aq) was added slowly, followed by water (30 mL) and ethyl acetate (100 mL). The organic layer was separated and washed with 100 mL of saturated NaCl, dried over Na_2SO_4, and evaporated to give a light yellow solid, 0.690 g (80%). ^{1}H NMR: δ 6.93 (s, 1H), 6.85 (s, 2H), 4.66 (s, 4H, $C\mathit{H}_2OH$); 3.98 (t, 2H, $OC\mathit{H}_2CH_2C_2H_5$), 1.77 (m, 2H, $OCH_2C\mathit{H}_2CH_2CH_3$); 1.48 (m, 2H, $OCH_2CH_2C\mathit{H}_2CH_3$), 0.97 (t, 3H, $O(CH_2)_3C\mathit{H}_3$). ESI-MS: m/z 193.12 [M − OH]. Anal. Calcd for $C_{12}H_{18}O_3$ (M = 210.27): C 68.54, H 8.63. Found: C 67.33, H 8.06. The microanalysis indicated that the product is not quite pure, and some small impurity peaks were observed in the ^{1}H NMR spectrum. However, it was used successfully to prepare pure **19** (see below).

5-Butoxyisophthalaldehyde (19). Compound **19** was prepared according to a procedure developed by Bennani et al. to convert 5-*tert*-butyl-1,3-benzenedimethanol to 5-*tert*-butylisophthalaldehyde.[46] Pyridinium chlorochromate (PCC; 1.54 g, 7.15 mmol) and 3 g of Celite were added to a 250 mL flask equipped with an addition funnel under N_2. Then, about 10 mL of dry CH_2Cl_2 was added, and the mixture was vigorously stirred. A solution of 5-butoxy-1,3-benzenedimethanol (**18**; 0.520 g, 2.47 mmol) in CH_2Cl_2 (10 mL) was added dropwise into the mixture. Stirring was continued for 3 h, and the material was filtered through a short pad of silica gel using CH_2Cl_2 and ethyl acetate. Volatiles were removed *in vacuo*, leaving a yellow liquid, 0.420 g (82%). ^{1}H NMR: δ 9.97 (s, 2H, C*H*O), 7.86 (s, 1H), 7.56 (s, 2H), 4.00 (t, 2H, $OC\mathit{H}_2CH_2C_2H_5$), 1.74 (quintet, 2H, $OCH_2C\mathit{H}_2CH_2CH_3$), 1.42 (sextet, 2H, $OCH_2CH_2C\mathit{H}_2CH_3$), 0.91 (t, 3H, $O(CH_2)_3C\mathit{H}_3$). ^{13}C NMR: δ 190.82, 160.19, 138.15, 123.74, 119.71, 68.41, 30.84, 18.98, 13.60. ESI-MS: m/z 207.1 [M + H]. Anal. Calcd for $C_{12}H_{14}O_3$ (M = 206.24): C 69.88, H 6.84. Found: C 69.80, H 6.66.

5-Butoxy-*m*-phenylenebis(acetylacetone), 5-BuO-*m*-pbaH_2 (5). This compound was prepared using the same procedure as for compound **3**. 5-Butoxyisophthalaldehyde (0.40 g, 1.9 mmol) was treated with 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene (0.81 g, 3.8 mmol). After the reaction was complete, the crude product was purified by column chromatography (ethyl acetate–hexane, 1:2 v/v) which yielded a yellow-brown solid, 0.29 g, (44%). ^{1}H NMR: δ 16.6 (s, 2H), 6.70 (s, 2H), 6.60 (s, 1H), 3.97 (t, 2H, $OCH_2CH_2C_2H_5$), 1.92 (s, 12H, CH_3); 1.80 (m, 2H, $OCH_2CH_2CH_2CH_3$), 1.53 (m, 2H, $OCH_2CH_2CH_2CH_3$), 1.00 (t, 3H, $O(CH_2)_3CH_3$). ^{13}C NMR: δ 190.76, 190.55, 163.86, 138.62, 125.90, 116.15, 114.70, 67.79, 31.01, 26.06, 19.07, 13.71. GC/MS: *m/z* 347 [M + H].

Dimethyl 2-Methoxyisophthalate (20). 2-Methoxyisophthalic acid (3.00 g, 15 mmol) was dissolved in MeOH (20 mL) and 0.5 mL of conc H_2SO_4, and the mixture was refluxed for ca. 16 h. The mixture was neutralized with NH_3(aq), and the solvent was removed under reduced pressure to give a yellowish-white solid. This was taken up in CH_2Cl_2 (100 mL) and the solution washed with water, 0.5 M Na_2CO_3, and brine (50 mL). The organic phase was dried over Na_2SO_4 and evaporated to yield a colorless oil (3.02 g, 88%). ^{1}H NMR: δ 7.32 (d, 2H), 7.18 (t, 1H), 3.92 (s, 3H, OCH_3), 3.91 (s, 6H, CO_2CH_3).

2-Methoxy-1,3-benzenedimethanol (21). This procedure is similar to one recently reported by Ay and co-workers.[47] Lithium aluminum hydride ($LiAlH_4$) (1.84 g, 48 mmol) was suspended in dry THF (40 mL). Into this suspension a solution of **20** (3.03 g, 13.5 mmol) in THF (20 mL) was added dropwise under N_2. The mixture was stirred at room temperature for 24 h, and then cooled to 0 °C, and an aqueous solution of 1 M H_2SO_4 (47 mL) was added slowly, followed by ethyl acetate (100 mL). The organic layer was washed with brine, dried over Na_2SO_4, and evaporated to give a white solid (1.96 g, 86%). GC/MS: *m/z* 168. ^{1}H NMR: δ 7.33 (d, 2H), 7.15 (t, 1H), 4.75 (s, 4H, CH_2OH); 3.87 (s, 3H, OCH_3).

2-Methoxyisophthalaldehyde (22). Compound **21** (1.00 g, 5.9 mmol) was dissolved in CH_2Cl_2 (30 mL) and added all at once to a mixture of PCC (3.83 g, 17.8 mmol) and Celite (8 g) suspended in CH_2Cl_2 (30 mL). The mixture was stirred vigorously for 4 h, and then filtered over a short pad of silica gel, followed by a rinse with CH_2Cl_2/ethyl acetate (1:1 v/v). Solvent was removed *in vacuo* to yield a white solid (0.95 g, 97%). The ^{1}H NMR spectrum of the product matches that reported for the authentic compound.[48]

2-Methoxy-*m*-phenylenebis(acetylacetone), 2-MeO-*m*-pbaH$_2$ (6). This compound was prepared in the same manner as compound **3**. 2-Methoxyisophthalaldehyde (**22**; 0.40 g, 2.4 mmol) and 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene (1.02 g, 4.8 mmol) were mixed together. After the reaction was complete, the crude product was purified by column chromatography (ethyl acetate–hexane, 1:4 v/v), yielding a white solid, 0.33 g (45%). ^{1}H NMR: δ 16.76 (s, 2H), 7.27–7.16 (m, 3H), 3.47 (s, 3H), 1.94 (s, 12H). Anal. Calcd for $C_{17}H_{20}O_5$ (M = 304.34): C 67.09; H 6.62. Found: C 67.31; H 6.75.

2-Methoxy-*m*-phenylenebis(dipropionylmethane), 2-MeO-*m*-pbprH$_2$ (7). This compound was prepared following the same procedure as described for **3**. Compound **22** (0.40 g, 2.4 mmol) and 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene (1.15 g, 4.8 mmol) were combined together. Column chromatography of the crude product (ethyl acetate–hexane, 1:4 v/v) afforded a colorless oil (0.26 g, 30%). ^{1}H NMR: δ 16.84 (s, 2H), 7.17–7.10 (m, 3H), 3.46 (s, 3H), 2.17 (q, 8H), 1.07 (t, 12H).

Syntheses of Copper Molecular Squares: [Cu$_4$(*m*-pbhx)$_4$] (10). The procedure described here was followed for all four squares, **10**–**13**. Aqueous $CuSO_4\cdot 5H_2O$ (0.401 g, 1.6 mmol, in 30 mL H_2O) was converted to $[Cu(NH_3)_4]^{2+}$ by treatment with conc NH_3(aq). A solution of *m*-pbhxH$_2$ (**3**) (0.8 g, 1.6 mmol) in CH_2Cl_2 (40 mL) was added, and stirring continued for 4 h; the green organic phase was dried over Na_2SO_4 and the solvent removed to yield a dark green powder, 0.87 g (97%). ESI-MS: *m/z* 2238.15 [M + H]. Anal. Calcd for $C_{128}H_{192}Cu_4O_{16}$ (M = 2241.07): C 68.60, H 8.64. Found: C 68.42, H 8.51. Crystals for X-ray analysis were grown by layering methanol on a chloroform solution. Anal. Calcd for $C_{130}H_{200}Cu_4O_{18}$ ([Cu$_4$(*m*-pbhx)$_4$]·2CH$_3$OH, M = 2305.15): C 67.73, H 8.75. Found: C 68.00, H 8.64.

[Cu$_4$(5-MeO-*m*-pba)$_4$] (11). $CuSO_4\cdot 5H_2O$ (0.18 g, 0.72 mmol); **4** (0.219 g, 0.72 mmol). Yield: 0.24 g of dark green powder (96%). ESI-MS: *m/z* 1461.18 [M + H]. Blue crystals suitable for X-ray analysis were grown by layering $CHCl_3$ onto a solution of the compound in a CH_3OH–CH_2Cl_2 mixture. Anal. Calcd for $C_{68}H_{76}Cu_4O_{22}$ ([Cu$_4$(5-MeO-*m*-pba)$_4$]·2H$_2$O, M = 1499.50): C 54.47, H 5.11. Found: C 54.54, H 5.61.

[Cu$_4$(5-BuO-*m*-pba)$_4$] (12). $CuSO_4\cdot 5H_2O$ (0.18 g, 0.72 mmol); **5** (0.250 g, 0.72 mmol). Yield: 0.28 g of an olive green powder (97%). ESI-MS: *m/z* 1629.32 [M + H]. Anal. Calcd for $C_{80}H_{96}Cu_4O_{20}\cdot 2H_2O$ (M = 1667.82): C 57.61, H 6.04. Found: C 57.88, H 6.41.

[Cu$_4$(2-MeO-*m*-pbpr)$_4$] (13). $CuSO_4\cdot 5H_2O$ (0.138 g, 0.55 mmol); **7** (0.20 g, 0.55 mmol). Yield: 0.14 g of a dark green powder (60%). ESI-MS: *m/z* 1685.45 $[M + H]^+$. Anal. Calcd for $C_{84}H_{104}Cu_4O_{20}$ (M = 1687.90): C 59.77, H 6.21. Found, C 59.64, H 6.24. Crystals suitable for X-ray analysis were grown from a solution in hot toluene by layering with acetonitrile.

Adducts with Guest Molecules: [Cu$_4$(*m*-pbhx)$_4$(μ-bpe)(MeOH)$_2$]·10CHCl$_3$ (23). Molecular square **10** (0.020 g, 0.008 mmol) was dissolved in chloroform (2 mL); this was layered with 1,2-bis(4-pyridyl)ethylene (bpe) (0.006 g, 0.03 mmol) in methanol (3 mL). After 10 days, blue block-shaped crystals had formed. Anal. Calcd for $C_{143}H_{211}Cl_3Cu_4N_2O_{18}$ ([Cu$_4$(*m*-pbhx)$_4$(μ-bpe)(MeOH)$_2$]·CHCl$_3$, M = 2606.75): C 65.89, H 8.16, N 1.07. Found: C 66.16, H 8.20, N 0.80.

[Cu$_4$(*m*-pbhx)$_4$(μ-bpa)(MeOH)$_2$] (24). This adduct was prepared using the same procedure as for **23** above except that 1,2-bis(4-pyridyl)ethane (bpa) was used in place of bpe. After 7 days, blue crystals had formed.

[Cu$_4$(5-BuO-*m*-pba)$_4$(μ-4,4′-bpy)] (25). A solution of square **12** (0.015 g, 0.009 mmol) in chloroform (2 mL) was layered with 4,4′-bpy (0.0057 g, 0.036 mmol) in methanol (3 mL). Blue crystals formed after several days.

[Cu$_4$(*m*-pbhx)$_4$(μ-C$_{60}$)] (26). A solution of square **10** (0.015 g, 0.006 mmol) and C_{60} (0.005 g, 0.006 mmol) in 1,2-dichlorobenzene (2 mL) was layered with acetonitrile (3 mL) and left at −20 °C. After 4 days, dark brown crystals had formed.

[Cu$_4$(*m*-pbhx)$_4$(μ-C$_{70}$)] (27). The same procedure was followed as with the C_{60} adduct (**26**), except that C_{70} was used instead. Dark brown crystals formed over a period of 7 days.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Illustrations of the crystal structure of Cu$_4$(*m*-pbhx)$_4$(μ-bpa)(CH$_3$OH)$_2$ (**24**), and of the orientations of all four C_{70} guest molecules in [Cu$_4$(*m*-pbhx)$_4$(μ-C$_{70}$)] (**27**); spectral data for Cu$_4$(*m*-pbhx)$_4$(μ-C$_{60}$) and Cu$_4$(*m*-pbhx)$_4$(μ-C$_{70}$); and X-ray crystallographic data for **10**, **11**, **13**, **23**, **24**, **25**, **26**, and **27**, as summary table and in CIF format. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00792.

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Notes

The authors declare no competing financial interest.

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