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Silver(I) N-Heterocyclic Carbenes with Long N-Alkyl Chains

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Silver(I) N-heterocyclic carbene complexes (Ag(I)−NHCs) with long N-alkyl side chains formulated as (a) ion pairs, (b) halide-bridged neutral complexes, and (c) disilver tetrahalide anion bridged tetranuclear complexes were obtained by the reaction of benzimidazolium and imidazolium halide salts with Ag_2O. Interestingly, when excess Ag_2O was used, Ag nanoparticles were formed along with Ag(I)−NHCs. Crystal structures of Ag(I)−NHC complexes including both long and short N-alkyl chains were determined. The diversity of the solid-state structures depended on the halide ions, chain length, carbene cores, and crystallization conditions. The Ag(I)−NHCs of long alkyl chains did not show liquid crystal properties but did so when mixed with their corresponding imidazolium salts. These organic−inorganic hybrids were good single-source precursors for silver nanomaterials.

Introduction

The first coordination compounds of N-heterocyclic carbenes (NHCs) with transition metals were explored from the pioneering work of Öfele and Wanzlick.[1] The isolation of stable NHC by Arduengo[2] provided information on their fundamental properties. The primary characteristic of NHCs is that they are strong σ-donor ligands, which can bind firmly to different metal ions with various oxidation states.[3] In addition, NHCs can be modified electronically and sterically. Consequently, numerous varieties of metal−NHCs have been encountered in the present organometallic chemistry.[4] The versatile steric and electronic properties of NHCs and their strong metal−NHC bonds have been considered as the major advantages in homogeneous catalysis.[5]

We have focused on the study of coinage metal−NHCs.[6] Our earlier reports addressed the synthesis and structural properties of Ag(I)−NHCs with *N*-methyl and ethyl substituents and their uses as effective carbene transfer agents to prepare many important transition-metal−NHC catalysts. Several other groups have advanced this technique by introducing both simple alkyl and functionalized N-substituents onto the NHCs.[7] The structural study of Ag(I)−NHCs offers an insight into the M−$C_{carbene}$ bond.[8] The potential use of Ag(I)−NHCs has also been realized as antimicrobial agents,[9] precursors for silver nanoparticles

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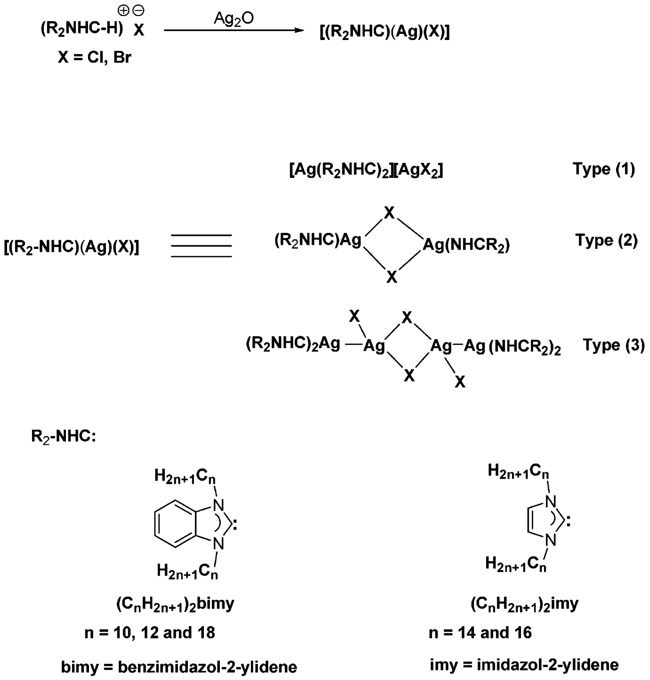
(AgNPs),[10] and efficient catalysts for a variety of organic transformations.[11]

We have also studied thermally stable liquid crystalline Pd(II)−NHCs and Au(I)−NHCs.[6g,12] Metal-containing liquid crystals (MLCs) have many interesting features. The presence of a metal ion in a mesogen can impart the resulting LC with structural, electronic, magnetic, photonic, and even catalytic properties.[13] Recently the preparation of nanostructured materials from MLCs has been reported.[14] We were therefore tempted to prepare Ag(I)−NHCs of long alkyl chains to investigate their liquid crystalline properties and their relevance to AgNP formation. The synthesis of AgNPs has received considerable attention because of their potential applications in antimicrobial[10,15] and anti-HIV-1 activity,[16] surface-enhanced Raman spectroscopy,[17] and catalysis.[18] Preliminary structural characterization of two N-long-chain Ag(I)−NHCs, $[Ag((C_{14}H_{29})_2\text{-imy})Br]_2$ and $\{[Ag((C_{14}H_{29})_2imy)_2][AgBr_2]\}_2$ (imy = imidazol-2-ylidene), were reported.[6c] In this paper we report the synthesis, characterization, and properties of Ag(I)−NHCs obtained from different benzimidazolium and imidazolium salts of long alkyl chains. Further in this study, we elucidate our findings that these organic−inorganic hybrids are good single-source precursors for AgNPs. The use of excess Ag_2O during the synthesis of Ag(I)−NHCs also resulted in the formation of AgNPs. A crystal structure study of short-chain Ag(I)−NHCs is also given for comparison.

Results and Discussion

Synthesis. Ag(I)−NHCs (including bimy and imy; bimy = benzimidazol-2-ylidene) were prepared by using the method described by us.[6b−d,7a] Reactions between Ag_2O and the benzimidazolium or imidazolium salts in CH_2Cl_2 with $n = 10$, 12, 14, 16, 18 were usually accomplished within ~12 h. Scheme 1 illustrates these reactions and the corresponding Ag(I)−NHC products. These Ag(I)−NHCs can be prepared with or without the exclusion of light. Ag(I)−NHCs were isolated as (a) ion pairs (type 1), (b) halide -bridged neutral complexes (type 2), and (c) $Ag_2X_4^{2-}$ anion bridged complexes (type 3), depending on the crystallization conditions.

Scheme 1



For the benzimidazolium salts of chloride, recrystallization of the crude product from CH_2Cl_2/hexane gave chloride-bridged neutral Ag(I)−NHC complexes (type 2). Under similar experimental conditions, the bromide salts produced ion-pair complexes (type 1). For the imidazolium salts, in accordance with our previous report,[6c] the reaction of long-chain imidazolium bromides with Ag_2O afforded a product with an empirical formula of [Ag(NHC)Br]. When this compound was crystallized from acetone, a type 2 complex was obtained. However, upon crystallization from CH_2Cl_2/hexane, a type 3 complex was isolated. In a similar way, the use of chloride salts ($n = 14$, 16, 18) produced type 2 chloride-bridged neutral Ag(I)−NHCs upon crystallization from acetone.

It is interesting to note that when excess molar ratios of Ag_2O to benzimidazolium or imidazolium salts ([Ag]/[salt] > 1) were used to synthesize Ag(I)−NHCs, AgNPs were always formed. This was also true for short-chain benzimidazolium and imidazolium halides. The yellow AgNPs can be removed by activated carbon. A more detailed discussion will be presented in later sections.

X-ray Crystallography. Molecular structures of five long-chain Ag(I)−NHCs, $[Ag((C_{18}H_{37})_2bimy)Cl]$, $[Ag((C_{10}H_{23})_2\text{-}bimy)_2][AgBr_2]$, $[Ag((C_{14}H_{29})_2imy)Br]$, $\{[Ag((C_{14}H_{29})_2imy)_2]\text{-}[AgBr_2]\}_2$, and $[Ag((C_{14}H_{29})_2imy)Cl]$, in the solid state have been determined by an X-ray crystal study. Two new short-chain Ag(I)−NHCs, $[Ag(Me_2bimy)_2][AgBr_2]$ and $[Ag(Et_2imy)\text{-}Cl]$, are also reported for comparison. The first four long-chain Ag(I)−NHCs and the two short-chain Ag(I)−NHCs were recrystallized from CH_2Cl_2/hexane. The long-chain Ag(I)−NHC $[Ag((C_{14}H_{29})_2imy)Cl]$ was recrystallized from acetone. Except

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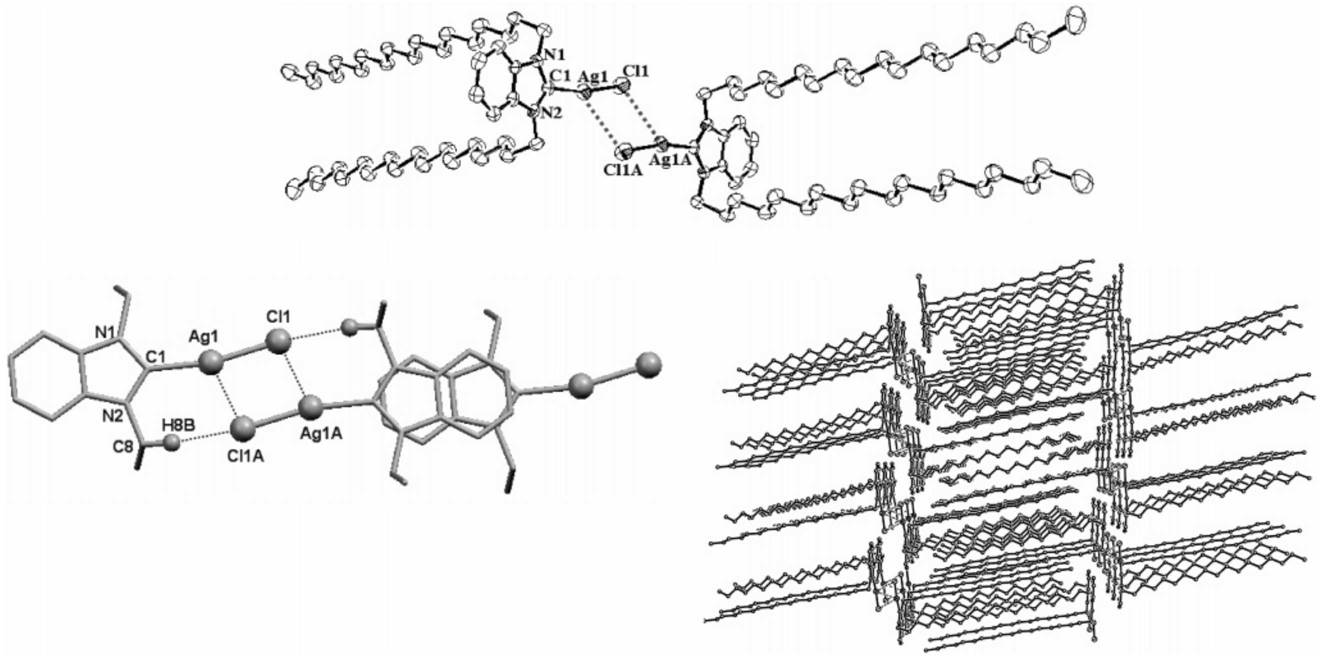

Figure 1. (a, top) ORTEP diagram of [Ag(($C_{18}H_{37}$)$_2$bimy)Cl], with 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Ag(1)−C(1), 2.086(3); Ag(1)−Cl(1), 2.3452(13); Ag(1)−Cl(1A), 3.205; C(1)−N(1), 1.353(4); C(1)−N(2), 1.364(4); C(1)−Ag(1)−Cl(1), 168.00(11). (b, bottom left) Intermolecular CH⋯Cl hydrogen bonding and ring $\pi-\pi$ interactions in [Ag(($C_{18}H_{37}$)$_2$bimy)Cl]. (c, bottom right) Packing diagram of [Ag(($C_{18}H_{37}$)$_2$bimy)Cl].

Table 1. Crystallographic Data for Ag(I)−NHC Complexes

	[Ag(($C_{18}H_{37}$)$_2$bimy)Cl]	[Ag(($C_{10}H_{21}$)$_2$bimy)$_2$][AgBr$_2$]	[Ag(($C_{14}H_{29}$)$_2$imy)Cl]$_2$	[Ag((Et$_2$-imy)Cl)]$_2$
formula	$C_{43}H_{78}AgClN_2$	$C_{54}H_{92}Ag_2Br_2N_4$	$C_{62}H_{120}Ag_2Cl_2N_4$	$C_{14}H_{24}Ag_2Cl_2N_4$
fw	766.39	1172.86	1208.26	535.01
cryst syst	triclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	*Pbcn*
a, Å	8.938(4)	18.390(2)	22.210(4)	9.029(2)
b, Å	9.254(3)	17.0750(17)	16.383(3)	15.9640(10)
c, Å	26.623(7)	18.536(4)	9.2619(18)	14.5600(10)
α, deg	84.03(3)	90.00	90.00	90.00
β, deg	86.14(4)	98.827(12)	99.055(4)	90.00
γ, deg	86.40(3)	90.00	90.00	90.00
V, Å	2181.7(14)	5751.5(16)	3328.1(11)	2098.7(5)
Z	2	4	2	4
D_{calcd}, Mg/m^3	1.167	1.355	1.206	1.693
T, K	293(2)	298(2)	294(2)	293(2)
μ, mm^{-1}	0.552	2.106	0.706	2.121
F(000)	828	2432	1296	1056
cryst size, mm	0.50 × 0.40 × 0.30	0.60 × 0.40 × 0.20	0.60 × 0.40 × 0.30	0.40 × 0.30 × 0.24
θ_{min}, θ_{max}, deg	2.22, 25.00	1.63, 25.00	1.55, 25.00	2.55, 24.98
no. of rflns collected	7553	9969	5849	1850
no. of indep rflns	5379	3973	4820	1411
no. of refined params	424	539	534	100
goodness of fit (F^2)	1.029	1.032	1.061	1.029
R1/wR2 ($I > 2\sigma(I)$)	0.0470/0.0976	0.0750/0.1496	0.0294/0.0773	0.0540/0.1330
R1/wR2 (all data)	0.0808/0.1103	0.2121/0.1961	0.0388/0.0812	0.0684/0.1455

for [Ag(Me$_2$-bimy)$_2$][AgBr$_2$], crystal data and details of the structure determination for the other five compounds are presented in Table 1.

[Ag($C_{18}H_{37}$)$_2$bimy)Cl]. A structural analysis (Figure 1a) showed that two neutral [Ag(($C_{18}H_{37}$)$_2$bimy)Cl] molecules (type 2) appeared to associate via intermolecular Ag⋯Cl interactions (∼3.2 Å)[19] to form a rodlike dimer. This pairwise association exhibited a nearly square Ag_2Cl_2 arrangement, in which the Ag(1)−Cl(1)−Ag(1A) and Cl(1)−Ag(1)−Cl(1A) bond angles were 92.14 and 87.86° respectively. In each quasi-linear molecule the Ag−C(1) and Ag−Cl(1) distances were normal (see the figure caption).[6b−d,20] The two N-alkyl chains on a bimy ring were extended perpendicularly to the bimy ring plane in the same direction. In a pair, two alkyl chains were pointing oppositely the other two. No Ag⋯Ag interactions were observed. In addition to the intermolecular Ag⋯Cl interactions, symmetrical C(8)H(8B)⋯Cl(Ag) interactions (2.78 Å) with a

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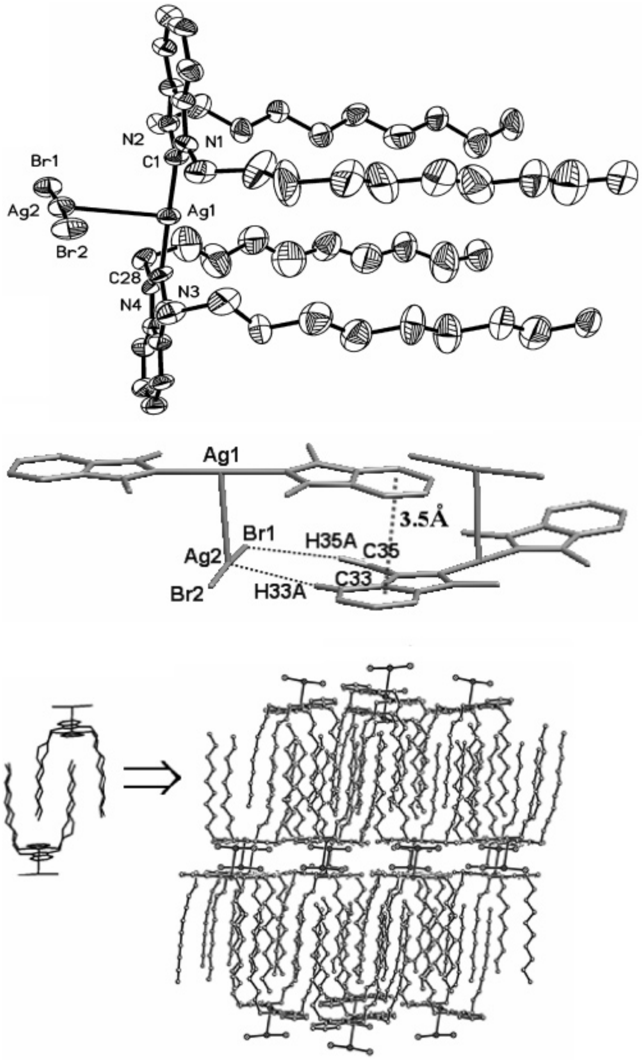

Figure 2. (a, top) ORTEP diagram of [Ag(($C_{10}H_{21}$)$_2$bimy)$_2$]-[$AgBr_2$], with 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Ag(1)−Ag(2), 2.9470(14); Ag(1)−C(1), 2.090(10); Ag(1)−C(28), 2.086(9); Ag(2)−Br(1), 2.4393(15); Ag(2)−Br(2), 2.4386(15); C(1)−N(1), 1.366(11); C(1)−N(2), 1.345(11); C(28)−N(3), 1.359(11); C(28)−N(4), 1.331(11); C(1)−Ag(1)−C(28), 179.1(4); Br(1)−Ag(2)−Br(2), 175.44(7); C(1)−Ag(1)−Ag(2), 87.2(3). (b, middle) Secondary interactions in [Ag(($C_{10}H_{21}$)$_2$bimy)$_2$][$AgBr_2$]. (c, bottom) Packing diagram of [Ag(($C_{10}H_{21}$)$_2$bimy)$_2$][$AgBr_2$] (left, two ion pairs; right, bulk).

CH···Cl angle of ∼160° gave rise to a pseudo-rectangular geometry (Figure 1b).[21] Further, weak bimy ring $\pi-\pi$ interactions (∼3.6 Å) between neighboring pairs were observed (Figure 1b).[22] The packing pattern formed a monolayer structure with alternating interdigitated alkyl chains and Ag_2(bimy)$_2Cl_2$ cores (Figure 1c).

[Ag(($C_{10}H_{21}$)$_2$bimy)$_2$][$AgBr_2$]. The molecular structure in Figure 2a shows that this Ag(I)−NHC crystallized as an ion pair (type 1). The linear cations and anions were held together perpendicularly by Ag···Ag attractions of 2.947(14) Å.[23] The bond distances around the core were normal (see the figure caption). The two bimy carbene rings were almost coplanar. The four N-alkyl chains were stretched perpendicularly to the bimy rings in the same direction, and thus the cations adopted the shape of a four-legged stool. The disorder in the N-alkyl side chain did not influence the coordination around the Ag(I) ion.

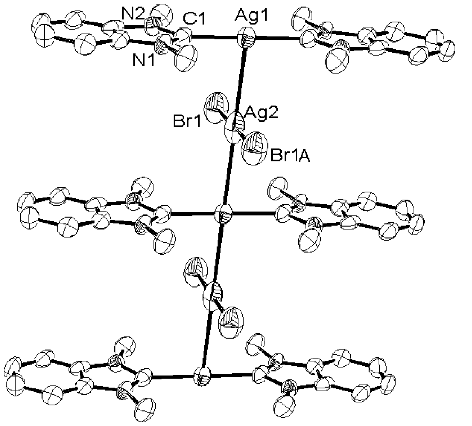

Figure 3. Packing diagram of [Ag(Me_2-bimy)$_2$][$AgBr_2$].

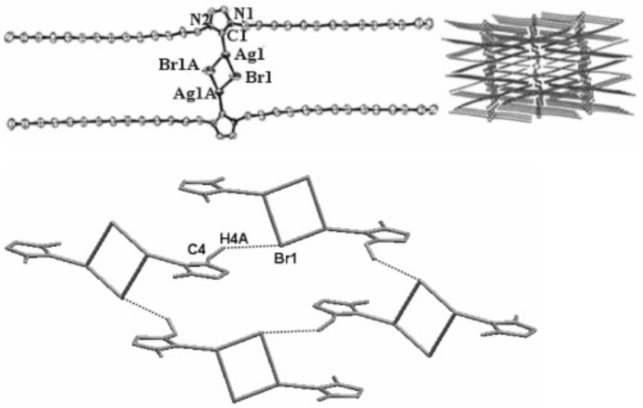

Figure 4. (a, top) ORTEP view of the molecular structure (left) and packing diagram (right) of [Ag(($C_{14}H_{29}$)$_2$imy)Br]. (b, bottom) Hydrogen bonding in [Ag(($C_{14}H_{29}$)$_2$imy)Br].

Ring $\pi-\pi$ interactions (∼3.5 Å) between oppositely oriented ion pairs were observed (Figure 2b). Short contact distances of CH···Br (∼3 Å, ∼158°) and Ag···H (∼2.82 Å, ∼138°), which were less than the sum of the van der Waals radii, were also observed between the ion pairs (Figure 2b). The N-alkyl chains were interdigitated to form a bilayer structure (Figure 2c). This kind of aggregation was compared with that of ion-pair complexes with short alkyl chains, [Ag(Me_2bimy)$_2$][$AgBr_2$] and [Ag(Et_2-bimy)$_2$][$AgBr_2$]. The crystal structure analysis of [Ag(Me_2bimy)$_2$][$AgBr_2$], which is also reported for the first time in this work, shows the formation of a linear polymer via Ag···Ag interactions because of the small methyl groups (Figure 3) (see also ESI). Although the poor quality of the crystal yielded a relatively high *R* value, nevertheless, the skeletal arrangement was correct, whereas in the case of the previously reported [Ag(Et_2-bimy)$_2$][$AgBr_2$], simple ion-pair interactions were observed.[6b]

[Ag(($C_{14}H_{29}$)$_2$imy)Br] and {[Ag(($C_{14}H_{29}$)$_2$imy)$_2$][$AgBr_2$]}$_2$. Crystal structures of these two bromide compounds were provided in our previous communication.[6c] [Ag(($C_{14}H_{29}$)$_2$imy)-

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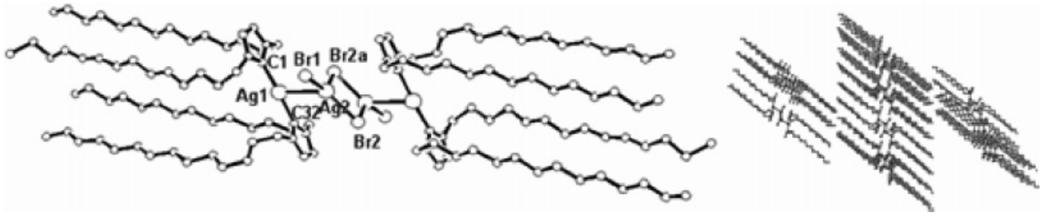

Figure 5. ORTEP view of the molecular structure (left) and packing diagram (right) of $\{[Ag((C_{14}H_{29})_2imy)_2][AgBr_2]\}_2$.

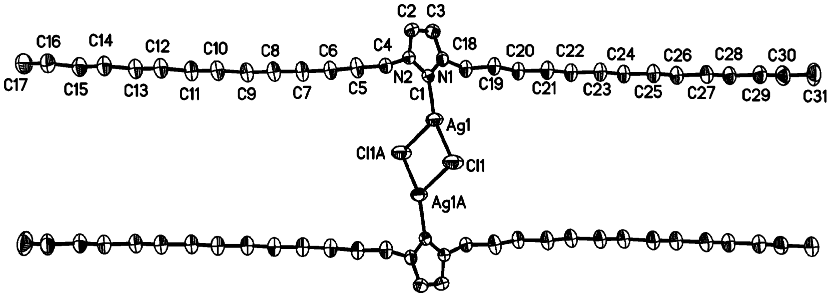

Figure 6. ORTEP diagram of $[Ag((C_{14}H_{29})_2imy)Cl]$, giving 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Ag(1)−C(1), 2.087(2); Ag(1)−Cl(1), 2.3824(8); Ag(1)−Cl(1A), 2.8845(8); C(1)−N(1), 1.349(3); C(1)−N(2), 1.353(3); Ag(1)−Cl(1)−Ag(1A), 87.64(2).

Br] adopted a type 2 structure (Figure 4a). The long alkyl chains stretched along the imy ring (one up one down) but were perpendicular to the Ag_2Br_2 square plane. As a result, a distorted H-shaped geometry, different from that of $[Ag((C_{18}H_{37})_2bimy)Cl]$, was observed (Figure 4a). Upon crystal packing, the bridging bromides and $N-C^{\alpha}-H$ protons formed C−H⋯Br bonds (2.995 Å, 145.77°), which linked four dimeric units to form a hydrogen-bonded ring (Figure 4b).

In the type 3 tetranuclear complex $\{[Ag((C_{14}H_{29})_2imy)_2][AgBr_2]\}_2$, the $[Ag_2Br_4]^{2-}$ anion was intercalated between two $[Ag((C_{14}H_{29})_2imy)_2]^+$ cations with weak Ag(cation)⋯Ag(anion) interactions (~3.0 Å) (Figure 5a). The alkyl chains on the imy ring of a cation stretched toward the same direction, and the cations came into view as a four-legged stool similar to that of $[Ag((C_{10}H_{23})_2bimy)_2]^+$ (Figure 5). The packing diagram shows a layered structure with Ag_4Br_4 cores and noninterdigitated alkyl chains (Figure 5). In this state, both the bridging and terminal bromides of $Ag_2Br_4^{2-}$ formed intermolecular Br⋯H(C) hydrogen bonds (~2.95 Å, 129°; ~3 Å, 155°) with the imy ring hydrogens. Notably, the previously reported short-chain Ag(I)−NHC $[Ag(Me_2imy)_2][AgBr_2]$ was a linear polymer composed of alternating cations and anions with an Ag⋯Ag distance of ~3.2 Å.[6d]

$[Ag((C_{14}H_{29})_2imy)Cl]$. The geometrical arrangement and the stacking pattern of $[Ag((C_{14}H_{29})_2imy)Cl]$ resembled those of the type 2 dinuclear bromo compound (an iso structure). Only an ORTEP diagram (Figure 6) is provided. The CH⋯Cl hydrogen-bonding criteria (~2.81 Å, ~142°) appeared as linkers between adjacent molecules, and this event mimicked the CH⋯Br hydrogen bonding in $[Ag((C_{14}H_{29})_2bimy)Br]$.

The crystal structure of a short-chain chloro Ag(I)−NHC, $[Ag(Et_2imy)Cl]$, was also analyzed in this work to compare the influence of chain length on the solid-state structures. The molecules of $[Ag(Et_2imy)Cl]$ were stacked pairwise through Ag⋯Ag interactions (Figure 7). On the other hand, the previously reported $[Ag(Me_2imy)_2][AgCl_2]$[6d] was a linear polymer composed of alternating cations and anions aggregated through Ag⋯Ag interactions.

This result revealed that long-chain Ag(I)−NHCs tended to self-assemble to form a variety of lamellar frameworks. The long alkyl chain also prevented extended Ag⋯Ag interactions; rather, chain−chain and several other secondary interactions took part in the construction and stabilization of the assemblies.

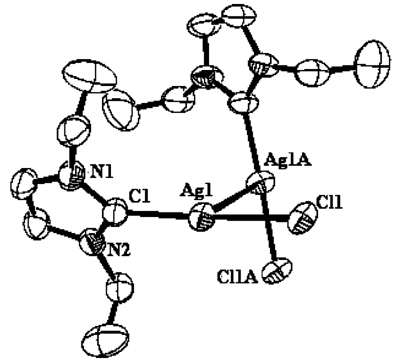

Figure 7. ORTEP diagram of $[Ag(Et_2\text{-}imy)Cl]$, with 30% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Ag(1)−Ag(1A), 3.0553(10); Ag(1)−C(1), 2.064(5); Ag(1)−Cl(1), 2.3237(14); C(1)−N(1), 1.367(8); C(1)−N(2), 1.341(7); C(1)−Ag(1)−Cl(1), 175.12(16).

Thermal Properties of Ag(I)−NHCs. To investigate the phase transition properties of these Ag(I)−NHCs, differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) techniques were employed. The phase transition temperatures of these long-chain Ag(I)−NHCs are given in Table 2. These Ag(I)−NHCs were nonmesomorphic, possibly due to the insufficient core−core interactions. The mp values of the bimy-based Ag(I)−NHCs were higher than those of imy, presumably due to the $\pi-\pi$ interactions occurring in the former. The enthalpies of melting were found to increase upon increasing the chain length, an indication of increased hydrophobic chain−chain interactions.

Previously we have shown that the Ag(I) complexes of 1-alkylimidazoles complexes exhibited liquid crystalline properties with $[NO_3]^-$, $[BF_4]^-$, and $[PF_6]^-$ counterions.[24] In a similar approach, efforts to isolate the Ag(I)−NHCs with an $[NO_3]^-$ counteranion led to the decomposition of carbene and produced imidazolium salts. The $[BF_4]^-$ and $[PF_6]^-$ compounds isolated were stable but were not liquid crystals. The lack of liquid

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Table 2. Phase-Transition Temperatures of Ag(I)−NHCs by DSC at a Rate of 10 °C min^{-1} [b]

$[Ag((C_nH_{2n+1})_2bimy)Cl]$

$n = 12$ $Cr \xrightarrow{116.7(68.1)} I$; $n = 18$, $Cr \xrightarrow{119.4(85.2)} I$

$[Ag(C_nH_{2n+1})_2bimy)_2][AgBr_2]$

$n = 10$ $Cr \xrightarrow{118.3(83.9)} I$; $n = 18$, $Cr \xrightarrow{118.8(176.4)} I$

$[Ag((C_nH_{2n+1})_2imy)X]$

$n = 14$, $X = Br$, $Cr \xrightarrow{82.6(73.5)} I$; $X = Cl$, $Cr \xrightarrow{70.4(81.4)} I$

$n = 16$, $X = Cl$, $Cr \xrightarrow{76.8(64.8)} I$

$\{[Ag(C_{14}H_{29})_2imy)_2][AgBr_2]\}_2$

$Cr \xrightarrow{83.8(147.2)} I$

$[(C_{16}H_{33})_2Imy\text{-}H)]Cl$

$Cr \xrightarrow{69.4(43.3)} SmA \xrightarrow{165.0(4.1)} I$ (See Ref. 25)

$[(C_{16}H_{33})_2Imy\text{-}H)]Cl/[Ag(C_{16}H_{33})_2imy)Cl]$

$Cr \xrightarrow{62.4(15.1)} SmA \xrightarrow{110.0^{a}} I$

[a] Data from POM. [b] ΔH values in kJ mol^{-1} are given in parentheses.

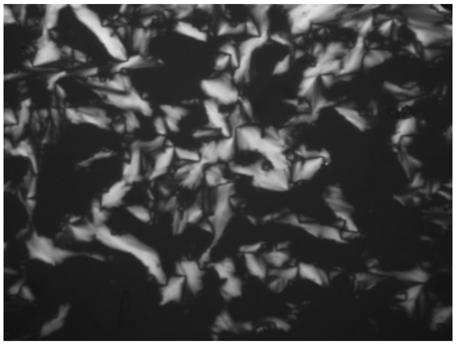

Figure 8. Texture of $[(C_{16}H_{33})_2imy\text{-}H]Cl/[Ag((C_{16}H_{33})_2imy)Cl]$ (1:1) observed from POM.

crystal behavior could be due to the anionic size being too large to allow the cations to undergo ordered motion.

However, these Ag(I)−NHCs showed liquid crystal properties when they were mixed with the corresponding imidazolium salts. A mixture with a 1:1 molar ratio of $[(C_{16}H_{33})_2imy\text{-}H][Cl]$ to $[Ag((C_{16}H_{33})_2imy)Cl]_2$ showed that the phase transition from solid crystal to fluidic mesophase occurred at 62.4 °C, while that from mesophase to isotropic liquid occurred at 110.0 °C. The fluidic mesophase exhibited a fan-shaped texture with some dark domains (Figure 8). These dark domains, also known as homeotropic domains, were caused by rodlike molecules aligned perpendicularly to the glass substrate, such that no light could be passed under POM. An SmA mesophase, in which rodlike mesogens have an averaged director perpendicular to the layered surface, was therefore assigned. This mixture had lower melting and clearing temperatures compared to those of $[(C_{16}H_{33})_2imy\text{-}H)][Cl]$.

Silver Nanomaterials. Although the Ag(I)−NHCs reported in this work did not exhibit liquid crystalline properties, these special types of organic−inorganic hybrids were good single-source precursors to produce silver nanomaterials. Several methods have been prescribed for the synthesis of metal nanoparticles (NPs) in the presence of templates and capping agents.[26] The use of metal complexes as single-source precursors to produce NPs has also been reported.[27,28] The diversity in metal−ligand interaction and the type of molecular assemblies in some complexes were found to provide a suitable environment to form nanostructured materials. Ag(I) complexes with long-chain amines and other ligands have already been reported to be good precursors to produce spherical AgNPs.[28] The use of Ag(I)−NHC complexes to form AgNPs was reported by Youngs' group.[10]

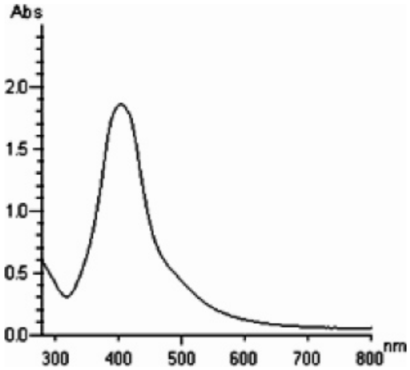

Figure 9. UV−visible spectrum of AgNPs obtained by chemical reduction.

Recently imidazolium-based ionic liquids (ILs) have been employed as solvents and stabilizers for the formation of metal NPs.[29] The nature of these stabilized NPs has been studied; while the structured imidazolium ILs can stabilize the NPs formed in situ, NHC ligands[30] and metal−NHC complexes[31] have also

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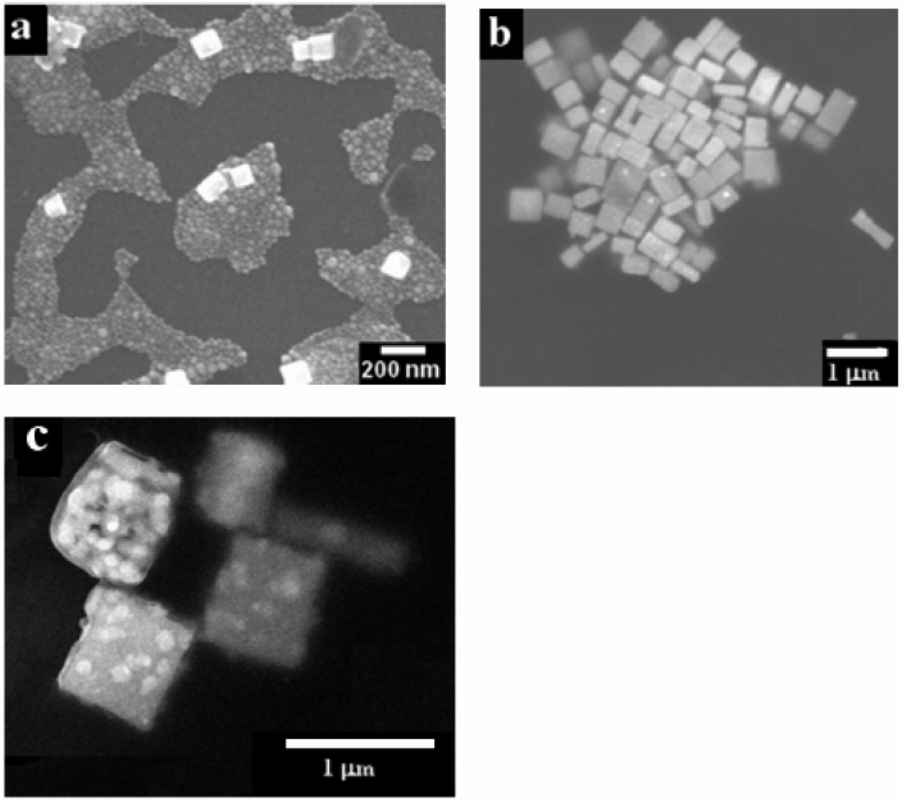

Figure 10. SEM images of AgNPs.

been proposed to serve as stabilizers for the NPs of Ir, Au, and Pt. Our Ag(I) complexes composed of NHCs of long alkyl chains should be excellent candidates to form AgNPs. Apart from being Ag(I)−NHCs, the long-chain NHCs may provide additional chain−chain interactions to function as templating and stabilizing agents either as NHCs or imidazolium salts upon reduction by $NaBH_4$. The long-chain Ag(I)−NHC complexes may also allow AgNPs to be prepared and stabilized in organic solvents.

Results showed that reduction of these Ag(I)−NHCs (n = 16, 18; Cl^- and Br^- salts) by $NaBH_4$ in a biphasic system gave AgNPs. The UV−visible spectrum (Figure 9) of these AgNPs showed a prominent band at ∼409 nm. This band was attributed to the plasmon resonance absorption of AgNPs and was size dependent.[32] SEM images exhibited spherical and rectangular morphologies (Figure 10). A high-magnification image showed that the latter was in fact formed by the assembly of Ag spherical particles presumably capped with imidazolium moieties (Figure 10c). Energy-dispersive X-ray spectroscopy (EDX) showed the presence of Ag metals (ESI). The ^{1}H NMR spectrum of the as-prepared solution obtained immediately after the reduction of Ag(I)−NHCs displayed signals corresponding to the imidazolium moiety. It has been reported that imidazolium ILs were noninnocent toward the metal sources (M^0 state).[33] Therefore, the AgNP solution prepared from Ag(I)−NHC was monitored for 2 months to observe the changes. To our surprise, the yellow color of the solution faded gradually. This phenomenon signifies the possible formation of Ag(I)−NHCs. Further studies will be required to understand the nature of this reaction.

As mentioned in the synthesis, when excess Ag_2O was used to react with *N*-methyl- or *N*-ethyl-substituted imidazolium halides ([Ag]/[salt] > 1) in CH_2Cl_2 with or without light, a yellow color developed in solution, and a silver mirror together with a brown powdery solid coated the reaction vessel. When the ratio of [Ag] to [salt] was ≤1.0, neither a yellow solution nor a silver mirror was observed. Similarly, when long-chain imidazolium halides were used to react with Ag_2O at ([Ag]/[salt] ≤ 1), no yellow solution developed. However, when excess Ag_2O (i.e., [Ag]/[salt] > 1) was used, a yellow solution was formed but not the silver mirror or the brown solid. The more Ag_2O was added, the faster the yellow solution formed. Although the yellow solution was formed with or without light, the presence of light enhanced the development of this yellow solution. Addition of excess Ag_2O to a preformed Ag(I)−NHC in CH_2Cl_2 also produced the yellow solution. The UV−vis spectrum of the yellow solution showed surface plasmon resonance (SPR) bands at ∼426 nm, suggesting the formation of AgNPs (see ESI). It appeared that long-chain imidazolium halides could stabilize AgNPs better than the short-chain imidazolium salts and that Ag(I)−NHCs were formed prior to the formation of AgNPs. Again, further studies are required to better understand the possible causes of this observation.

Conclusion

The present study revealed that the structural formulas and the packing patterns of Ag(I)−NHCs acquired in the solid state depended on the nature of halide ions, chain length, carbene cores, and the crystallization conditions applied. In general, the chloride salts favored the formation of neutral structures. In comparison to the chloride salts, the bromide salts of benzimi-

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dazolium or imidazolium displayed more propensity to form ionic Ag(I)−NHCs. The use of long-chain benzimidazolium or imidazolium ligands afforded self-assembled Ag(I)−NHCs. The lamellar structures of the long-chain Ag(I)−NHCs were different from those of the short-chain speices and appeared as special types of motifs in the crystal engineering. In addition to chain−chain interactions, both long-chain and short-chain Ag(I)−NHCs were stabilized by many secondary attraction forces such as extended hydrogen bonding and intermolecular Ag$\cdots$halide interactions. Extended Ag$\cdots$Ag interactions were possible only for the short-chain Ag(I)−NHCs but not the long-chain compounds; presumably, packings with better chain−chain interactions were more important than those with Ag$\cdots$Ag interactions. Due to the extended π-cloud system, the benzimidazolium core based Ag(I)−NHC can be stabilized additionally by ring $\pi-\pi$ interactions. The long-chain Ag(I)−NHCs alone were nonmesomorphic, possibly due to the core−core interactions being insufficient to hold the molecules in close proximity after melting. However, they exhibited liquid crystalline properties upon mixing with their corresponding imidazolium salts. More significantly, these special organic−inorganic hybrid structures were good precursors to synthesize AgNPs. It was also interesting to note that Ag_2O, when used in excess to prepare Ag(I)−NHCs, always produced AgNPs.

Experimental Section

Imidazolium and benzimidazolium salts were prepared according to the literature methods.[25] Elemental analysis was carried out by the Taiwan Instrumentation Center. ^1H NMR spectra were recorded on a Bruker AC-F300 spectrometer. Optical characterization was performed by using covered microscope slides on an Olympus BH-2 polarizing microscope equipped with a Mettler FP 82 hot stage and a Mettler FP 90 central processor. Transition temperatures and heats of fusion were determined at a scan rate of 10 °C/min by differential scanning calorimetry using a Perkin-Elmer DSC-7 calorimeter that was calibrated with indium and tin standards in conjunction with a Perkin-Elmer 7700 thermal analysis data station. UV−vis spectra were recorded on a Shimadzu UV-2101PC spectrophotometer. FE-SEM images of AgNP morphologies were collected on a scanning electron microscope (SEM, JMF-6500F. JEOL), with a drop of the sample over a carbon-coated copper grid.

Single-crystal X-ray data of [Ag(($C_{18}H_{37})_2$-bimy)Cl] were collected on a Bruker P4 diffractometer, those of [Ag(($C_{10}H_{22})_2$bimy)$_2$][$AgBr_2$] and [Ag(Et_2-imy)Cl] were collected on a Siemens P4 diffractometer, and those of [Ag(($C_{14}H_{29})_2$-imy)Cl] and [Ag(Me_2-bimy)$_2$][$AgBr_2$] were collected on a Bruker SMART APEX diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Except for [Ag(Me_2-bimy)$_2$][$AgBr_2$], crystal data and details of the structure determination for the other four compounds are presented in Table 1. The structures were solved using direct methods with absorption corrections. All the structures were solved and refined using SHELXL 97. All non-hydrogen atoms were refined anisotropically. In all cases, hydrogen atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms. There were some unreasonably large displacement parameters for some C atoms and short C−C distances on the aliphatic side chains in the structure of [Ag(($C_{10}H_{21})_2$bimy)$_2$][$AgBr_2$] due to the unsolved disorder problems.

[Ag(($C_{12}H_{25})_2$bimy)Cl]. Ag_2O (46.34 mg, 0.20 mmol) was added to a dichloromethane solution (30 mL) of [($C_{12}H_{24})_2$bimy-H]Cl (200 mg, 0.40 mmol). The reaction mixture was stirred for 12 h at room temperature. After the disappearance of the Ag_2O suspension, the resulting solution was concentrated to 10 mL and dried under vacuum. The white residue obtained was then recystallized from CH_2Cl_2/hexane to afford the white crystalline title compound. Notably, if an excess of Ag_2O (i.e., [Ag]/[salt] > 1) was used in the reaction, a yellow solution consisting of AgNPs developed. Removal of these AgNPs by activated carbon yielded the Ag(I)−NHC. ^1H NMR ($CDCl_3$): 7.42 and 7.47 (dd, ^3J = 6 Hz, ^4J = 3 Hz, 4H, CH), 4.37 (t, ^3J = 7 Hz, 4H, CH_2), 1.93 (m, 4H, CH_2), 1.23−1.32 (m, 36H, CH_2), 0.86 (t, ^3J = 7 Hz, 6H, CH_3) ppm. Anal. Calcd for $C_{31}H_{54}N_2AgCl$: C, 62.25; H, 9.10; N, 4.68. Found: C, 61.84; H, 9.14; N, 4.63.

The following compounds were prepared similarly.

[Ag(($C_{18}H_{37})_2$bimy)Cl]. This compound was recrystallized from CH_2Cl_2/hexane. ^1H NMR ($CDCl_3$): 7.47 and 7.42 (dd, ^3J = 6 Hz, ^4J = 3 Hz, 4H, CH), 4.37 (t, ^3J = 7 Hz, 4H, CH_2), 1.86 (m, 4H, CH_2), 1.18−1.32 (m, 60H, CH_2), 0.87 (t, ^3J = 7 Hz, 6H, CH_3) ppm. Anal. Calcd for $C_{86}H_{156}N_4Ag_2Br_2$: C, 63.83; H, 9.72; N, 3.46. Found: C, 64.12; H, 9.86; N, 3.40.

[Ag(($C_{10}H_{21})_2$bimy)$_2$][$AgBr_2$]. This compound was recrystallized from CH_2Cl_2/hexane. ^1H NMR ($CDCl_3$): 7.40 and 7.48 (dd, ^3J = 6 Hz, ^4J = 3 Hz, 8H, CH), 4.41 (t, ^3J = 7 Hz, 8H, CH_2), 1.90 (m, 8H, CH_2), 1.27−1.56 (m, 56H, CH_2), 0.87 (t, ^3J = 7 Hz, 12H, CH_3) ppm. Anal. Calcd for $C_{54}H_{92}N_4Ag_2Br_2$: C, 55.30; H, 7.91; N, 4.78. Found: C, 55.34; H, 8.00; N, 4.71.

[Ag($C_{18}H_{37})_2$bimy)$_2$][$AgBr_2$]. This compound was recrystallized from CH_2Cl_2/hexane. ^1H NMR ($CDCl_3$): 7.40 and 7.48 (dd, ^3J = 6 Hz, ^4J = 3 Hz, 8H, CH), 4.39 (t, ^3J = 7 Hz, 8H, CH_2), 1.90 (m, 8H, CH_2), 1.27−1.56 (m, 120H, CH_2), 0.87 (t, ^3J = 7 Hz, 12H, CH_3) ppm. Anal. Calcd for $C_{86}H_{156}N_4Ag_2Br_2$: C, 63.83; H, 9.72; N, 3.46. Found: C, 64.12; H, 9.86; N, 3.40.

[Ag(Me_2bimy)$_2$][$AgBr_2$]. This compound was also recrystallized from CH_2Cl_2/hexane. ^1H NMR ($CDCl_3$): 7.42 and 7.49 (m, 8H,-CH), 4.02 (s, 6H, CH_3), ppm. Anal.calcd. for $C_{18}H_{20}N_4Ag_2Br_2$: C,-32.37; H,3.02; N,8.39; found: C,32.38; H,2.88; N,8.38%.

[Ag(($C_{14}H_{29})_2$imy)Cl]. This compound was recrystallized from acetone. ^1H NMR ($CDCl_3$): 8.13(s, 2H, CH), 4.34 (t, ^3J = 7 Hz, 4H, CH_2), 1.78(m, 4H, CH_2), 1.27∼1.40 (m, 44H,CH_2), 0.88(t, ^3J = 7 Hz, 6H, CH_3) ppm.Anal.calcd. for $C_{31}H_{60}N_2AgCl$: C, 61.76; H, 10.04; N, 4.65; found: C, 61.57; H,10.03; N, 4.67%.

[Ag(($C_{16}H_{33})_2$imy)Cl]. This compound was recrystallized from CH_2Cl_2/hexane. ^1H NMR ($CDCl_3$): 6.95 (s, 2H, CH), 4.05 (t, ^3J = 7 Hz, 4H, CH_2), 1.56 (m, 4H, CH_2), 1.20−1.28 (m, 52H, CH_2), 0.87 (t, ^3J = 7 Hz, 6H, CH_3) ppm. Anal. Calcd for $C_{35}H_{68}N_2AgCl$: C, 63.67; H, 10.38; N, 4.24. Found: C, 63.23; H, 10.41; N, 4.20.

The short-chain Ag(I)−imy complex [Ag(Et_2imy)Cl] was also prepared similarly. Only crystal structure measurements were obtained. The data for [Ag($C_{14}H_{29})_2$imyBr] and {[Ag(($C_{14}H_{29})_2$-imy)$_2$][$AgBr_2$]}$_2$ are provided in ref 6c.

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Supporting Information Available: Details of the X-ray crystal data of five Ag(I)−NHCs as CIF files and figures giving an EDX profile of AgNPs, UV−vis spectra, and SEM images of AgNPs obtained during the synthesis of Ag(I)−NHCs. This material is available free of charge via the Internet at http://pubs.acs.org.

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