Alkyl Pyridinium Iodocuprate(I) Clusters: Structural Types and Charge Transfer Behavior

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ABSTRACT: The reaction of copper(I) iodide (CuI) and N-alkyl pyridinium (RPy+) salts yields pyridinium iodocuprate(I) salts. Crystal structures of iodocuprate ions coupled with RPy+ include \([\text{Cu}_3\text{I}_5^{2-}]_n\) (R = H), \([\text{Cu}_3\text{I}_5^{2-}]_n\) (R = Me), \([\text{Cu}_4\text{I}_7^{2-}]_n\) (R = Et), \([\text{Cu}_4\text{I}_7^{2-}]_n\) (R = Pr), and \([\text{Cu}_5\text{I}_7^{2-}]_n\) (R = Bu, Pr, Hx). The \([\text{N}-\text{Bu}-3\text{-PyX}]^+\) ions were typically paired with the 1-D chain \([\text{Cu}_3\text{I}_4^{2-}]_n\). Diffuse reflectance spectroscopy performed on the \([\text{N}-\text{Bu}-3\text{-PyX}]^+\) iodocuprate salts revealed that increasing the electron withdrawing capacity of the \([\text{N}-\text{Bu}-3\text{-PyX}]^+\) system reduced the absorption edge of the iodocuprate salt. Variable temperature emission spectra of several \([\text{N}-\text{Bu}-3\text{-PyX}]^+\) compounds revealed two emission peaks, one consistent with a cluster-centered halide to metal charge transfer and the other consistent with an intermolecular mixed halide/metal charge transfer to the organic cation. The emission intensity and emission wavelength of the mixed halide/metal to cation charge transfer depends on the organic cation substitution.

INTRODUCTION

Anionic metal halide clusters show remarkable structural diversity and are of interest for their electronic and photophysical properties. 1 We are interested in the clusters of copper(I) because of its variable coordination number, relative softness, and photoemissive behavior. 2 Similarly, iodide possesses a large electron sphere which exhibits both softness and coordinative flexibility, having been shown to bridge 2–8 Cu(I) centers or acting as a terminal ligand. Thus, iodocuprate(I) clusters, \([\text{Cu}_3\text{I}_4^{2-}]^{n-}\), show great structural diversity and have been prepared with various organic cations. The secondary building units (SBUs) associated with these iodocuprates span the range from zero- (molecular) to one-, two-, and three-dimensional clusters. Because of their relative ease of formation, iodocuprates are very well represented in the literature. 3 Iodocuprates may be network or molecular, with cluster size varying tremendously, ranging from \([\text{Cu}_3\text{I}_4^{2-}]\) up to \([\text{Cu}_6\text{I}_6^{2-}]^{20-}\).

In order to prepare a tetraalkylammonium iodocuprate, the organic salt is first prepared from a tertiary amine and an alkyl iodide, reaction 1. Next, this salt is reacted with copper(I) iodide according to reaction 2. However, under solventothermal conditions, combined use of a tertiary amine, an alcohol, and iodide source with CuI can directly give an iodocuprate salt as shown in reaction 3. 4–6

\[
\text{R}_3\text{N} + \text{RI} \rightarrow \text{R}_4\text{NI} \quad (1)
\]

\[
\text{R}_3\text{NI} + \text{CuI} \rightarrow \text{R}_4\text{NI}[\text{CuI}]_2 \quad (2)
\]

\[
\text{R}_3\text{N} + \text{ROH} + \text{KI} + \text{CuI} \rightarrow \text{R}_4\text{NI}[\text{CuI}]_2 \quad (3)
\]

It should be noted that the products, which are given the simplified formula \(\text{R}_3\text{NI}[\text{CuI}]_2\) above, are anything but simple or predictable. In fact, the two-coordinate CuI\(^{2+}\) ion is quite rare, occurring instead as larger iodocuprate clusters or networks. Moreover, despite a large number of known examples, it remains almost impossible to predict the stoichiometry of the particular iodocuprate formed under any given circumstances. A single published study has probed the relationship between cation volume and resulting anion cluster size. 7 The authors used tetraalkylammonium cations with varying alkyl chain length. They found that longer chain cations, such as tetra-\(n\)-hexylammonium, tend to produce larger iodocuprate clusters, such as \([\text{Cu}_3\text{I}_4^{2-}]^{3-}\) and \([\text{Cu}_4\text{I}_7^{2-}]^{3-}\). These authors noted that crystallization does not guarantee production of the lowest energy anion and that anion transformations can take place even in samples stored at low temperature. Our results below suggest a similar behavior.

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Although arylinium salts derived from pyridine,\textsuperscript{5} cyanopyridine,\textsuperscript{11} quinoline,\textsuperscript{12} 4,4′-bipyridine,\textsuperscript{11} bis-(isoquinoline),\textsuperscript{13} and other aromatics\textsuperscript{5,14} have been reported for iodocuprates; nevertheless, no systematic study of their anion structures or photophysical behavior upon systematic variation of arylinium cations has been undertaken. Photoluminescence behavior has been noted for iodocuprates having both aliphatic and aromatic cations.\textsuperscript{5,8,4,14b} In the former case, this must necessarily be the result of anion cluster-centered and/or internal Cu(I) transitions. The question then is whether pyridinium iodocuprates also show cation involvement through charge transfer. In the present study, we set out to see (1) what effect N-alkyl chain length would exert on iodocuprate cluster size and (2) whether luminescence changes resulting from pyridinium ring substitution by donor and acceptor groups would offer evidence of charge transfer between the iodocuprate anion and the aromatic cation. To carry out these studies, we chose the two sets of cations shown in Chart 1. Varying the R group = H, confirmation of previous observations.\textsuperscript{8} The bulk and crystallized products showed different formulations for compounds 5, 7, and 10. Nevertheless, Table 1 reveals a strong preference for \( y = 2.5 \), that is, \((\text{pyridinium})_2[\text{Cu}_3\text{I}_7]\). This value was found as often as all the others combined.

**X-ray Crystallography.** Crystals of the complexes are readily grown from acetonitrile or acetone solution with ethyl ether diffusion. Structures were solved for all complexes herein, except 2, 3, and 6. Complexes 2 and 3 are known structures, and unit cell determinations were sufficient to confirm matches to the known structure in both cases.\textsuperscript{4,5,10} In the case of 6, serious disorder rendered full structure solution nearly impossible, but nevertheless, clearly revealed a Cu\(_5\)I\(_7\) cluster similar to the others seen herein and in agreement with elemental analysis results. The structure solution data and selected structural parameters for all compounds are presented in Tables 2 and 3, respectively.

The X-ray crystal structure of the parent pyridinium iodocuprate(I), \((\text{HPy})_3[\text{Cu}_3\text{I}_6]\) 1, is shown in Figures 1, S13, and S14. The novel and unique structure consists of isolated HPy\(^+\) cations and chain iodocuprate anions. Both the cations and the anions sit on a mirror plane in the monoclinic P2\(_1\)/m structure. This plane bisects the pyridinium cation through the nitrogen and para-carbon atoms. The C\(_4\)-symmetric Cu\(_3\)I\(_6\) iodocuprate SBUs are also bisected by this plane, resulting in only two crystallographically independent Cu atoms and five such I atoms. The cluster is built on a triangular tricopper center with three Cu···Cu interactions of 2.7103(9) and 2.7315(11) Å. These are shorter than the 2.8 Å van der Waals sum for copper, but are larger than the metallic copper value of 2.65 Å. Three \( \mu_2\)-bridging and one \( \mu_5\)-bridging iodide over-gird the Cu\(_3\) triangle. Another iodide (I5) is terminal. The clusters share an iodide (I5) which lies on the screw axis and has an unusual linear coordination. This \( \mu_2\)-bridging causes the clusters to link into a chain with the formula Cu\(_3\)I\(_6\)\( \ldots \). Ignoring the Cu···Cu interactions, the Cu geometry is nearly tetrahedral, with I–Cu–I bond angles of 103.63(3)–113.92(2)°. There are only a few known iodocuprates with the Cu\(_3\)I\(_6\)\( \ldots \) formulation. These include closed \textsuperscript{6} and open \textsuperscript{9} nonnetworked I-bridged Cu\(_3\) clusters and a chain consisting of Cu corner-sharing Cu\(_3\) SBUs.\textsuperscript{30} A previous synthesis of pyridinium iodocuprate(I) in refluxing acetone produced a very different product with the remarkable formula \((\text{HPy})_{24}[\text{Cu}_{36}\text{I}_{65}]\).
Table 2. Crystal and Structure Refinement Data

| 1       | 3      | 5          | 7          |
|---------|--------|------------|------------|
| CCDC deposit no. | 1859229 | 1859226 | 1859225 | 1859224 |
| color and habit | yellow block | yellow needle | yellow needle | yellow blade |
| size, mm | 0.07 × 0.05 × 0.03 | 0.45 × 0.03 × 0.02 | 0.32 × 0.08 × 0.06 | 0.39 × 0.09 × 0.06 |
| formula | C₆H₁₂Cu₄I₆N₃ | C₆H₁₂Cu₄I₆N₃ | C₆H₁₂Cu₄I₆N₃ | C₆H₁₂Cu₄I₆N₃ |
| formula weight | 1192.34 | 1681.86 | 2956.84 | 3110.11 |
| space group | P₂₁₋₁/m | P₂₁₋₁̅ | P₂₁₋₁̅ | C₂₋₁/c |
| a, Å | 8.8040(4) | 13.9901(10) | 10.4550(3) | 33.6214(15) |
| b, Å | 14.0866(7) | 10.8190(8) | 26.2454(8) | 10.7706(5) |
| c, Å | 11.5559(6) | 24.0532(17) | 23.8540(7) | 25.1921(12) |
| α, deg | 90 | 90 | 90 | 90 |
| β, deg | 111.2960(10) | 99.2430(10) | 97.093(2) | 124.6180(10) |
| γ, deg | 90 | 90 | 90 | 90 |
| volume, Å³ | 1335.28(11) | 3593.4(4) | 6495.3(3) | 7507.5(6) |
| Z | 2444 | 2444 | 2444 | 2444 |
| ρ calc, g cm⁻³ | 2.966 | 3.019 | 3.024 | 2.752 |
| F₀₀₀ | 1068 | 3016 | 5328 | 5672 |
| μ (Mo Kα), mm⁻¹ | 9.311 | 10.375 | 55.946 | 8.562 |
| temp., K | 100 | 100 | 100 | 100 |
| residuals: aR; R | 0.0225; 0.0478 | 0.0356; 0.0886 | 0.0336; 0.0892 | 0.0342; 0.0937 |
| goodness of fit | 1.042 | 1.151 | 1.007 | 1.038 |
| peak and hole, e Å⁻³ | 1.772, −2.857 | 1.392, −1.243 | 1.308, −1.208 | 2.333, −1.385 |

| 8       | 9      | 10        | 11        |
|---------|--------|-----------|-----------|
| CCDC deposit no. | 1859227 | 1859232 | 1859230 | 1859228 |
| color and habit | orange blade | yellow block | yellow blade | red prism |
| size, mm | 0.34 × 0.11 × 0.05 | 0.34 × 0.21 × 0.13 | 0.59 × 0.15 × 0.02 | 0.38 × 0.08 × 0.06 |
| formula | C₂₆H₂₁₂Cu₆I₇N₃ | C₂₆H₂₁₂Br₂Cu₆I₇N₃ | C₂₆H₂₁₂Cu₆I₇N₃ | C₂₆H₂₁₂Cu₆I₇N₃ |
| formula weight | 1588.36 | 1677.28 | 1349.33 | 1569.50 |
| space group | P₂₁₋₁/c | P₂₁₋₁̅ | P₂₁₋₁̅ | P₂₁₋₁̅ |
| a, Å | 14.4604(10) | 28.346(3) | 9.1888(4) | 14.1523(14) |
| b, Å | 10.8225(7) | 11.4404(12) | 11.3217(5) | 10.6793(11) |
| c, Å | 25.1937(17) | 24.058(2) | 16.2778(7) | 25.264(3) |
| α, deg | 90 | 90 | 73.5910(10) | 90 |
| β, deg | 106.1940(10) | 106.029(2) | 73.5910(10) | 106.029(2) |
| γ, deg | 90 | 90 | 87.9980(10) | 90 |
| volume, Å³ | 3786.3(4) | 7498.6(13) | 1585.08(12) | 3688.5(7) |
| Z | 8 | 8 | 8 | 8 |
| ρ calc, g cm⁻³ | 2.766 | 2.971 | 2.827 | 2.826 |
| F₀₀₀ | 2880 | 6048 | 1212 | 2848 |
| μ (Mo Kα), mm⁻¹ | 8.628 | 10.702 | 8.821 | 8.717 |
| temp., K | 200 | 100 | 100 | 100 |
| residuals: aR; R | 0.0224, 0.0684 | 0.0248, 0.0517 | 0.0148, 0.0371 | 0.0024, 0.0526 |
| goodness of fit | 1.042 | 1.151 | 1.007 | 1.038 |
| peak and hole, e Å⁻³ | 0.825, −0.889 | 0.834, −0.617 | 0.696, −0.711 | 0.755, −0.660 |

CCDC deposit no. | 1859231 |
| color and habit | orange needle |
| size, mm | 0.42 × 0.03 × 0.02 |
| formula | C₂₆H₁₅₁₂Cu₆I₇N₂₅O₂ |
| formula weight | 1559.00 |
| space group | C₂₋₁/c |
| a, Å | 36.7069(9) |
| b, Å | 10.6697(3) |
| c, Å | 24.9824(6) |
| α, deg | 90 |
| β, deg | 129.1920(10) |
| γ, deg | 90 |
| volume, Å³ | 7583.2(3) |
| Z | 8 |
| ρ calc, g cm⁻³ | 2.731 |
| F₀₀₀ | 5672 |
sheets. These consist of triangular Cu$_3$(μ$_2$-I)$_2$ units that are linked by pairs of sheet-forming μ$_3$-I at each copper producing D$_3$h-symmetric Cu$_4$I$_6$ SBUs. At 2.97 Å, Cu···Cu distances within the Cu$_3$ triangles are much longer than those in 1 and cannot be considered bonding. The cations lie between these sheets, with four C–H···I hydrogen bonds linking them to the anionic layers and forming a 3-D network.

N-Propylpyridinium iodocuprate 4 was revealed by X-ray crystallography to have the formulation (PrPy)$_2$[Cu$_6$I$_8$].MeCN (see Figures 3 and S15–S17). The anionic network consists of Cu$_7$I$_{10}$ SBU clusters in which all copper atoms are tetrahedral. The SBUs are bridged together by edge-sharing Cu$_2$I$_2$ rhombs, forming an extended 2-D honeycomb network. Eight of the iodides in the SBU are μ$_3$-bridging and one each is μ$_2$- and μ$_4$-bridging. There is a continuous series of close Cu···Cu interactions along the backbone of the cluster (Figure S15). The shortest of these are Cu1···Cu2A = 2.485(2) and Cu2A···Cu5A = 2.485(2) and are thus shorter than the metallic bonding distance for copper, although it should be noted that Cu2A and Cu5A are both the major sites for Cu in two-site disorder. The pore size in the network is 12.0 × 6.7 Å. One of the cations and the solvent MeCN sit in the pores, while the other MeCN molecule lies between the roughly planar anionic sheets. Four C–H···I interactions with the anionic network are increased. The anion in 2 consists of a series of rippled Cu$_4$I$_6$ partial ladder SBUs composed of and linked together by edge-sharing Cu$_2$I$_2$ rhombs. Iodide centers are μ$_2$- and μ$_4$-bridging. All copper centers are nearly tetrahedral. Hydrogen-bonding interactions (C–H···I) to MePy$^+$ cations cross-link the ladders to form sheets. In 3, the iodocuprate itself forms infinite planar...
the Cu atoms are tetrahedral and there are three \( \mu_2^- \), two \( \mu_3^- \), and two \( \mu_4^- \)-iodides. As is common with iodocuprates, the SBUs are linked together via Cu2I2 rhombs, and as is the case with \( \mathbf{3} \), Cu⋯Cu interactions follow the chains of fused Cu2I2 rhombs (Figure S18). The Cu5I7 SBU is relatively common. It occurs either as a molecular anion in which a Cu5 pentagon is capped with two \( \mu_3^- \)-iodides and stellated with five additional \( \mu_2^- \)-iodides\(^{21}\) or as an opened up and slightly rearranged version of this cluster seen for \( \mathbf{5} \). In \( \mathbf{5} \) and related networks, two of the Cu atoms have migrated toward the inside of the cluster, allowing a pair of outer Cu−I to share edges and thus producing the polymer seen here, which we will call a ribbon-cluster.\(^{3e,12,22}\)

The anionic ribbon-clusters in \( \mathbf{5} \) form zigzag threads that propagate through the structure. The grooves in the zigzag are occupied by cations, enabling significant cation−anion C−H⋯I interactions. In the case of \( \mathbf{5} \), each cation showed at least one such interaction with the anion chains. Moreover, the Cu5I7 ribbon-cluster motif was also identified for larger N-alkyl pyridiniums. Therefore, we decided to use a series of substituted N-butyl pyridinium iodocuprates in the second part of the study hoping to produce analogous Cu5I7 SBUs for consistency as we compared photophysical behavior (see below).

Crystals of N-pentyl pyridinium (PnPy) and N-hexyl pyridinium (HxPy) iodocuprate(I) compounds \( \mathbf{6} \) and \( \mathbf{7} \) were also examined by X-ray diffraction. The former was highly disordered and a final structure was not readily achieved. Nevertheless, both structures showed ribbon-clusters containing the Cu5I7 SBU, proving to be \((\text{PnPy})_2\{\text{Cu}_5\text{I}_7\}\) (6) and \((\text{HxPy})_2\{\text{Cu}_5\text{I}_7\}\cdot 1/2\text{MeCN} \ (7\), see Figures 5, S21, and S22), respectively. The ribbon-cluster anions in these complexes are essentially identical to that in \( \mathbf{5} \), the only significant difference being that the anion repeat unit (and SBU) in \( \mathbf{5} \), Cu10I144−, is twice as long as that seen in \( \mathbf{6} \) and \( \mathbf{7} \), Cu5I72−. Compound \( \mathbf{7} \) showed minor disorder in both crystallographically independent cations. The cations in \( \mathbf{7} \) both showed C−H⋯I interactions with the anions, in particular, for cations that were located in the grooves of the zigzag ribbon-clusters.
For further comparison, polyhedral diagrams of the iodocuprate(I) anions for 1−5 are collected together in Figure 6. Shared in common between all of the structures is the tetrahedral coordination of Cu(I) and its tendency to engage in corner-, edge-, and/or face-sharing with other tetrahedra. Examining network dimensionality as a function of N-alkyl pyridinium chain length reveals interesting behavior. All the iodocuprate anions reported herein, except that of 10, formed extended networks. There was no consistent motif for the anions associated with the shorter alkyl chains for RPy+, R = H (1), Me (2), Et (3), and Pr (4). These produced corner- and edge-sharing chains (1), edge-sharing ribbons (2), corner- and edge-sharing sheets (3), and corner-, edge-, and face-sharing 2-D honeycombs (4). In contrast, isostructural ribbon-cluster networks were found for each of the larger N-alkyl pyridiniums (R = Bu, Pn, and Hx). These networks are constructed of Cu4I2 SBU’s that result from edge- and face-sharing of tetrahedra. Thus, sufficiently large cation size seems to exert a common, and therefore predictable, influence on anion formation.

After studying the effect of alkyl chain length on pyridinium iodocuprate structures, we turned our attention to producing a series of ring-substituted N-butyl pyridinium iodocuprates 8−12. Given that longer pyridinium alkyl chain complexes 5−7 all produced the Cu4I2 SBU, we anticipated that the structures of N-butyl pyridinium cations with small substituents at the 3-position of the pyridinium ring would prove analogous to the parent complex 5. If this were the case, the effects of iodocuprate cluster size, arrangement, and stoichiometry could be factored out during analysis of the photophysical properties of complexes 8−12.

Substituted N-butyl pyridinium iodide salts [N-Bu-3-PyX]I (X = Cl, Br, I, CN, OMe) were prepared, reacted with CuI, and crystallized as described above. This resulted in [N-Bu-3-PyX]2{Cu5I7}·nMeCN crystal structures for all but one of the complexes: 8: X = Cl, n = 1; 9: X = Br, n = 1; 11: X = CN, n = 1; 12: X = OMe, n = 0.5 (see Figures 7, and S23−S31). The crystal structures of chloro and cyano complexes 8 and 11 were isomorphic. The bromo complex 9 showed a unit cell that was isomorphic to that of 8 and 11, except with a doubled a-axis cell edge and doubled formula. This formula doubling was akin to that of the parent N-butyl pyridinium complex 5. Thus, following upon the example of 5, all of the ring-substituted analogs, except that of the iodopyridinium complex 10, showed a ribbon-cluster iodocuprate structure with extensive C−H···I interactions. Multiple Cu···Cu interactions of <2.8 Å were also

Figure 5. X-ray structures of 7. Anion SBU emphasized by ball and stick.

Figure 6. X-ray structures of 1−5. Anions only are shown using polyhedral rendering. Anions of 6 and 7 are similar to that of 5.

Figure 7. X-ray structures of 8 (top) and 10 (bottom). Anion SBU emphasized by ball and stick.
found. In contrast to the non-ring-substituted complex 5, iodocuprate salts 8, 9, 11, and 12 all contained acetonitrile solvent, and 9 and 12 showed some positional disorder.

Among the ring-substituted N-butyl pyridinium iodocuprates, only the 3-iodo complex 10 was found to have a different formulation: [N-Bu-3-Py][CuI] (Figures 7, S27, and S28). Two CuI$_2$ SBU groups are dimerized to form a molecular dimer CuI$_{10}^{4-}$ anion in 10. Interestingly, formation of the CuI$_{10}^{4-}$ units into chains appears to be disrupted by the insertion of cations between them. Cation–anion C−H···I interactions are found at one end of the inserted cations, and a short 1−I (3.56 Å) between the cation and anion is seen at the other end. Of the five crystallographically unique iodide centers in the 10 anion, two each are μ$_2$- and μ$_3$-bridging and the remaining iodide (14) is terminal. Related CuI$_{10}^{4-}$ anions have previously been reported, but in contrast to that in 10, these previous clusters are centered by a Cu$_2$(μ$_2$-I)$_6$ while 10 shows only Cu$_2$I$_2$ rhombs. A copper atom (Cu3A) in 10 is 3-coordinate, the only non-four-coordinate Cu center in the current study.

Comparing the cation–anion interactions in compounds 8−12, it is noteworthy that all six species show multiple hydrogen-bonds of the type C−H···I. In each case except 10, these interactions cross-link the zigzag iodocuprate ribbon-clusters to form a 2-D sheet. For 10, the chains are disrupted into dimers, although they still lie roughly in threaded clusters to form a 2-D sheet. For 11, the interactions cross-link the zigzag iodocuprate ribbon-clusters to form a 2-D sheet. For 12, the interactions cross-link the zigzag iodocuprate ribbon-clusters to form a 2-D sheet. For 12, the interactions cross-link the zigzag iodocuprate ribbon-clusters to form a 2-D sheet.

**Diffuse Reflectance Spectroscopy.** In order to conform to the structures established above, all samples were recrystallized before spectroscopic measurements were carried out. The N-butyl pyridinium complexes 5 and 8−12 were investigated spectrophotoscopically. The colors of these salts vary, from light yellow for 5 to dark red for 11, suggesting that the band gap of these salts is dependent upon the organic cation. Therefore, UV−visible diffuse reflectance spectroscopy (DRS) measurements were performed on solid samples. The results are displayed in Figure 8.

All compounds showed strong absorption in the visible region, with absorption falling sharply between 450 and 550 nm. Generally speaking, the absorption edge shifts to lower energies with increasing electron-withdrawing character of the pyridinium substituent/aryl group, with the optical band gap increasing for N-butyl 3-X-pyridinium complexes in the order: X = CN (1.58 eV), OMe (1.75 eV), Br (1.89 eV), CI (1.94 eV), I (2.01 eV), and H (2.29 eV). A number of related copper(I) halide compounds have been reported to undergo a mixed halide-metal to ligand charge transfer (XMLCT) transition with strong absorption bands between 300 and 500 nm.

Electronic transitions in iodocuprates can originate from an intermolecular halide-metal to cation charge transfer XMCCT or a cluster-centered halide-metal charge transfer (XMCT). In the case of an XMCT, absorption should be independent of cation substitution, a result that is not consistent with the observed DRS spectra. For XMCT, pyridinium stabilization by an electron-withdrawing substituent, such as cyano, would be expected to decrease the energy difference between the iodocuprate cluster and pyridinium orbital energy levels. The weak electron-withdrawing ability of the halide substituents will do little to stabilize the N-butyl pyridinium ring. With this in mind, we directly observe a reduction of the absorption edge with increased stabilization of the N-butyl pyridinium cation in 5 and 8−12 via an increase in substituent electron withdrawing capacity. Given that an intermolecular charge transfer for these salts is similar to an XMLCT, and that we observe a clear shift in absorption edge that varies with cation substitution, it follows that absorption within this region is the result of an XMCT.

**Luminescence Spectroscopy.** Variable temperature photoluminescence spectra for complexes 5, 8, 9, 10, and 12 were collected to evaluate the effects the various pyridinium cation substituents had on the photophysical properties. Compounds 10 and 11 showed no emission between ambient temperature and 78 K. Among the luminescent complexes, we observed a clear relationship between the emission properties and the withdrawing capabilities of the pyridinium ring, indicating that the luminescence of these compounds can be tuned via careful selection of the substituent. The luminescence spectra are shown in Figure 9 and summarized in Table 4.

Under UV excitation at room temperature, only complex 5 emits weakly in the visible range. Upon cooling to 78 K, all four complexes become very bright emitters when irradiated with UV light. Emission bands for all complexes are very broad between 500 and 700 nm with correspondingly broad excitation bands. The emission bands are composed of two distinct features: (1) a maximum peak between 540 and 558 nm and (2) a lower energy shoulder between 570 and 600 nm. The emission energy of the shoulder closely follows the trend seen in the DRS spectra. Because the iodocuprate clusters are identical among the four complexes, it follows that the observed emission shoulder is likely the result of an XMCT from the iodocuprate cluster to the pyridinium cation. Evidence of charge transfer can also be seen in the excitation spectra of 8 and 9 which contain sharp peaks between 450 and 500 nm. These sharp peaks are uncharacteristic of halo- and pseudohalocuprate complexes, for which excitation spectra are typically smooth and broad. The maximum
emission peak energy is independent of the choice of cation and is relatively unchanged between complexes. Thus, we assign the remaining maximum emission band to an XMCT within the iodocuprate cluster.

It is interesting to point out that the relative intensity of the shoulder in comparison with the maximum emission intensity is dependent on the electron-withdrawing ability of the pyridinium substituent where the ratio of the emission $I_{\text{max}}/I_{\text{shoulder}}$ for $X = \text{H, Br, Cl, OMe}$ is 1.37, 1.11, 1.28, and 1.10, respectively, further supporting our assignment. In order to compare the DRS and luminescence behavior of the N-butyl pyridinium salts to the electronic demand of the cation ring substituents, the absorption edge energy values and emission wavelengths for the studied complexes were plotted against the $\sigma$ Hammett parameter for the meta ring position (Figure 10). Hammett parameters are linear free-energy relationships based on ionization constants for various benzoic acid derivatives. They have proved to be a very valuable measure of electron donation and withdrawal behavior for aromatic ring substituents. Because the amount of data is very limited, the trends in Figure 10 must be treated with great care, especially the spectroscopic data for which two of the six compounds studied did not reveal luminescence emission. Nevertheless, it is apparent that the halogens, methoxy, and cyano substituents, all of which have positive (electron withdrawing) Hammett parameters, show reduced absorption edge energy and longer emission wavelengths than the nonsubstituted N-butyl pyridinium cation. These trends support electron withdrawal stabilization of the acceptor cation, lessening the energy gap both for absorption and emission. The methoxy substituent (complex 12) appears to deviate greatly from the trend line in both measures, suggesting a possible resonance effect in this case. It becomes clear that strategic synthetic considerations for this class of complexes are able to produce desired photophysical properties such as emission energy and charge transfer efficiency. On the basis of our observations, this

### Table 4. Summary of 78 K Luminescence Parameters for 5, 8, 9, and 12

| complex | excitation $\lambda_{\text{max}}$ (nm) | emission $\lambda_{\text{max}}$ (nm) | emission $\lambda_{\text{shoulder}}$ (nm) |
|---------|-----------------|-----------------|-----------------|
| 5       | 400             | 546             | 570             |
| 8       | 468             | 556             | 590             |
| 9       | 400             | 558             | 588             |
| 12      | 400             | 540             | 600             |

Figure 9. Luminescence spectra of 5, 8, 9, and 12 between 78 and 298 K (dashed line excitation, solid lines emission).

Figure 10. Hammett plots of absorption edge and emission shoulder wavelength (at 78 K) for N-Bu-3-PyX$^+$ iodocuprates $X = \text{H (5), Cl (8), Br (9), I (10), CN (11), and OMe (12).}$
tunability is directly related to the electron-withdrawing or -donating ability of the cation substituent.

**CONCLUSIONS**

The results presented herein show that a diverse range of iodocuprate(I) clusters is produced with N-alkyl pyridinium cations. In several cases, crystal structure formulations did not match those of the bulk products. Crystallization of pyridinium and N-alkyl pyridinium ions (RPy+; R = H, Me, Et, and Pr) produced polymeric Cu4I10− ions. Hydrogen-bonding-like interactions between C–H (and N–H for pyridinium) and iodide create longer range networks and potentially offer pathways for charge transfer in these salts.

The 3-substituted N-butyl pyridinium iodocuprates all show fairly distinct optical band gap behavior in the diffuse reflectance spectra. Electron-withdrawing substituents lower this band gap energy with the trend: H > I > Cl > Br > OMe. The spectroscopic results in tandem with the structural studies support the fact that the photophysical properties of these materials can be tuned through selection of the cation substituent.

**METHODS**

**General.** All reagents were purchased from Aldrich or Acros. Acetone was dried by distilling from Drierite. Other reagents and solvents were used as received. Proton NMR spectra were collected in 5 mm o.d. NMR tubes on a Varian Mercury 400 VX NMR spectrometer operating in the pulse Fourier transform mode. Chemical shifts were measured with respect to internal solvent. All J_HH coupling constants are reported in hertz. NMR spectra of pyridinium iodide salts are shown in Figures S1–S12 (electronic Supporting Information).

Diffuse reflectance spectra were collected on solid samples at 298 K. The light source was a Micropac PH-2000 deuterium and halogen light source coupled with an Ocean Optics USB4000 detector. Scattered light was collected with a fiber optic cable. Spectra were referenced with MgSO4. Data were processed using SpectraSuite 1.4.2.09. Steady-state luminescence spectra were collected with a QuantaMaster-1046 photoluminescence spectrometer from Photon Technology International. This device uses a 75 W xenon arc lamp combined with two excitation monochromators and one emission monochromator to adjust the bandwidth of light hitting the sample and detector, respectively. Signal intensity was measured using a photomultiplier tube. The samples were mounted on a copper plate using nonemitting copper dust-high vacuum grease. Low-temperature scans were run on this system coupled to a Janis ST-4 100 optical cryostat. Liquid nitrogen was used as a coolant.

**Pyridinium Iodide Syntheses.** [HPy][I]. Hydroiodic acid (0.762 g, 5.96 mmol) and pyridine (0.475 g, 6.00 mmol) were combined and heated with stirring for 12 h in a sealed tube at 100 °C, producing a brown oil. Upon trituration with Et2O, a light gray powder was produced. This powder was collected via decantation and dried overnight under vacuum: 0.597 g, 2.88 mmol, 48.4%. 1H NMR (DMSO-d6, 25 °C): δ 9.82 (dd, J = 4.7, 1.6, 2H), 8.56 (tt, J = 7.9, 1.6, 1H), 8.04 (dq, J = 4.3, 1.2, 2H).

**[MePy][I].** Methyl iodide (2.035 g, 14.3 mmol) and pyridine (1.13 g, 14.3 mmol) were combined and heated with stirring for 12 h in a sealed tube at 100 °C, producing a tan solid which was collected via decantation: 2.164 g, 9.79 mmol, 68.5%. 1H NMR (DMSO-d6, 25 °C): δ 8.99 (dd, J = 5.5, 2H), 8.60 (t, J = 7.9, 1H), 8.14 (t, J = 7.1, 2H), 4.36 (s, 3H).

**[EtPy][I].** Ethyl iodide (1.551 g, 9.94 mmol) and pyridine (0.786 g, 9.94 mmol) were combined and heated with stirring for 12 h in a sealed tube at 115 °C, producing a brown oil. Upon trituration with Et2O, a light brown powder was produced: 1.620 g, 6.89 mmol, 69.3%. 1H NMR (acetone-d6, 25 °C): δ 9.67 (d, J = 5.9, 2H), 8.67 (d, J = 7.4, 1H), 8.29 (t, J = 7.0, 2H), 5.00 (q, J = 7.6, 2H), 1.73 (t, J = 7.4, 3H).

**[PrPy][I].** n-Propyl iodide (1.461 g, 8.59 mmol) and pyridine (0.680 g, 8.60 mmol) were combined and heated with stirring for 12 h in a sealed tube at 115 °C, producing a light brown oil which was collected via decantation: 1.503 g, 6.03 mmol, 70.2%. 1H NMR (acetone-d6, 25 °C): δ 9.10 (d, J = 5.5, 2H), 8.79 (tt, J = 7.4, 1.2, 1H), 8.30 (t, J = 7.0, 2H), 4.96 (t, J = 7.4, 2H), 2.15 (m, 2H), 1.02 (t, J = 7.4, 3H).

**[BuPy][I].** n-Butyl iodide (1.92 g, 10.4 mmol) and pyridine (0.825 g, 10.4 mmol) were combined and heated with stirring for 12 h at 100 °C, producing a dark brown oil which was collected via decantation: 1.78 g, 6.67 mmol, 65.1%. 1H NMR (acetone-d6, 25 °C): δ 9.94 (dd, J = 6.3, 2H), 8.56 (dd, J = 8.5, 1.1, 1H), 8.29 (t, J = 7.1, 2H), 4.99 (t, J = 7.4, 2H), 2.10 (m, 2H), 1.46 (m, 4H), 0.96 (t, J = 7.4, 3H).

**[PnPy][I].** n-Pentyl iodide (1.55 g, 7.83 mmol) and pyridine (0.610 g, 7.71 mmol) were combined and heated with stirring for 12 h at 100 °C, producing a dark brown oil which was collected via decantation: 1.12 g, 4.04 mmol, 52.4%. 1H NMR (CDCl3, 25 °C): δ 9.37 (d, J = 5.1, 2H), 8.70 (dd, J = 7.8, 1.1, 1H), 8.16 (t, J = 7.3, 2H), 4.97 (t, J = 7.7, 2H), 2.06 (m, 2H), 1.40 (m, 4H), 0.89 (t, J = 7.0, 3H).

**[HxPy][I].** n-Hexyl iodide (1.50 g, 7.07 mmol) and pyridine (0.559 g, 7.07 mmol) were combined and heated with stirring for 12 h at 100 °C, producing a dark brown oil which was collected via decantation: 1.43 g, 4.91 mmol, 69.5%. 1H NMR (acetone-d6, 25 °C): δ 9.51 (d, J = 5.6, 2H), 8.78 (tt, J = 7.8, 1.6, 1H), 8.29 (t, J = 7.4, 2H), 4.98 (t, J = 7.7, 2H), 2.13 (p, J = 7.8, 2H), 1.43 (m, 2H), 1.32 (m, 4H), 0.86 (t, J = 7.1, 3H).

**[N-Bu3-PyBr][I].** n-Butyl iodide (2.02 g, 11.0 mmol) and 3-chloropyridine (1.12 g, 10.9 mmol) were combined and heated with stirring for 12 h at 100 °C, producing a brown oil. Upon trituration with Et3O, a yellow powder was produced.
This powder was collected via decantation and dried overnight under vacuum: 1.53 g, 4.47 mmol, 70.6%. 1H NMR (DMSO-d$_6$, 25 °C): δ 9.53 (s, 1H), 9.14 (d, j = 5.9, 1H), 8.87 (qdd, j = 5.3, 1.1, 1H), 8.35 (sds, j = 6.1, 2.3, 1H), 4.58 (t, j = 7.6, 2H), 1.98 (m, 2H), 1.29 (6, j = 7.4, 2H), 0.99 (t, j = 7.0, 3H).

[N-Bu-3-Py][I]. n-Butyl iodide (1.48 g, 8.04 mmol) and 3-iodopyridine (0.074 g, 0.361 mmol) were combined and heated with stirring for 12 h at 100 °C, producing a brown oil. The yellow powder. This suspension was stirred for 30 min, at which time the powder was collected via decantation, washed with Et$_2$O, and dried overnight under vacuum: 0.382 g, 1.33 mmol, 79.4%. 1H NMR (acetone-6,2 J = 7.5, 2H), 1.89 (5, J = 7.4, 2H), 1.28 (6, j = 7.4, 2H), 0.90 (t, j = 7.2, 3H).

[N-Bu-3-PyCN][I]. n-Butyl iodide (0.308 g, 1.67 mmol) and 3-cyanopyridine (0.175 g, 1.50 mmol) were combined and heated with stirring for 12 h at 100 °C, producing an oily brown solid. Upon trituration with Et$_2$O, a yellow powder was formed. This suspension was stirred for 30 min, after which time the powder was collected via decantation and dried overnight under vacuum: 0.370 g, 0.615 mmol, 82.0%. Anal. Calcd for C$_6$H$_8$Cu$_2$I$_3$N: C, 11.97; H, 1.34; N, 2.33. Found: C, 11.35; H, 1.16; N, 3.53.

(MePy)[Cu$_2$I$_3$] (2). [MePy]I (0.331 g, 1.50 mmol) was dissolved in 20 mL dry acetonitrile under Ar to form a yellow solution. CuI (0.376 g, 1.97 mmol) was added to the solution, forming a yellow suspension. This suspension was stirred for 30 min, after which the powder was collected via centrifugation, washed with Et$_2$O, and dried overnight under vacuum: 0.423 g, 0.355 mmol, 54.0%. Anal. Calcd for C$_{16}$H$_{24}$Cu$_6$I$_8$N$_2$: C, 11.76; H, 1.43; N, 1.75. Found: C, 15.40; H, 1.81; N, 1.71.

Mechanism of Iodocuprate(I) Syntheses. (HxPy)$_2${Cu$_6$I$_8$N$_2$} (1). Py (0.156 g, 1.97 mmol) and HI (0.200 g, 1.05 mmol) was dissolved in 20 mL EtOH to form a yellow solution. CuI (0.376 g, 1.33 mmol) was added to the solution, forming a yellow suspension. This suspension was stirred for 30 min, at which time the powder was collected via centrifugation, washed with Et$_2$O, and dried overnight under vacuum: 0.299 g, 0.207 mmol, 72.6%. Anal. Calcd for (N-Bu-3-PyBr)$_2${Cu$_4$I$_6$}C$_{18}$H$_{26}$Br$_2$Cu$_4$I$_6$N$_2$: C, 13.97; H, 1.69; N, 1.81. Found: C, 13.90; H, 1.55; N, 1.77.

[N-Bu-3-PyCl][Cu$_2$I$_3$] (6). (N-Bu-3-PyMeO)I (0.352 g, 1.50 mmol) and HI (0.207 g, 1.09 mmol) was dissolved in 20 mL EtOH to form a gold powder. This suspension was stirred for 30 min, at which time the powder was collected via centrifugation, washed with Et$_2$O, and dried overnight under vacuum: 0.203 g, 0.243 mmol, 67.6%. Anal. Calcd for (N-Bu-3-PyCN)I (0.088 g, 0.482 mmol) was dissolved in 20 mL EtOH to form an orange powder. CuI (0.207 g, 1.09 mmol) was added to the solution, forming a yellow powder. This suspension was stirred for 30 min, at which time the powder was collected via centrifugation, washed with Et$_2$O, and dried overnight under vacuum: 0.192 g, 0.313 mmol, 86.3%. Anal. Calcd for (N-Bu-3-PyCl)$_2${Cu$_5$I$_7$}C$_{18}$H$_{26}$Cl$_2$Cu$_5$I$_7$N$_2$: C, 15.95; H, 2.14; N, 1.86. Found: C, 15.40; H, 1.81; N, 1.71.

[N-Bu-3-PyCl][Cu$_2$I$_3$]·MeCN (8). [N-Bu-3-PyCl]I (0.324 g, 1.09 mmol) was dissolved in 20 mL EtOH to form a dark orange solution. CuI (0.207 g, 1.09 mmol) was added to the solution, forming an orange powder. This suspension was stirred for 30 min, at which time the orange powder was collected via centrifugation, washed with Et$_2$O, and dried overnight under vacuum: 0.291 g, 0.207 mmol, 72.6%. Anal. Calcd for (N-Bu-3-PyBr)$_2${Cu$_5$I$_7$}C$_{18}$H$_{26}$Br$_2$Cu$_5$I$_7$N$_2$: C, 14.95; H, 1.81; N, 1.94. Found: C, 14.78; H, 1.65; N, 1.92.

[N-Bu-3-PyBr]$d$[Cu$_6$I$_8$]·2MeCN (9). [N-Bu-3-PyBr]I (0.390 g, 1.14 mmol) was dissolved in 20 mL EtOH to form an orange solution. CuI (0.217 g, 1.14 mmol) was added to the solution, forming a dark orange powder. This suspension was stirred for 30 min, at which time the orange powder was collected via centrifugation, washed with Et$_2$O, and dried overnight under vacuum: 0.299 g, 0.207 mmol, 72.6%. Anal. Calcd for (N-Bu-3-PyBr)$_2${Cu$_6$I$_8$}C$_{18}$H$_{26}$Br$_2$Cu$_6$I$_8$N$_2$: C, 13.97; H, 1.69; N, 1.81. Found: C, 13.90; H, 1.55; N, 1.77.

[N-Bu-3-PyBr]$d$[Cu$_6$I$_8$]·MeCN (11). [N-Bu-3-PyBr]I (0.139 g, 0.348 mmol) was dissolved in 20 mL EtOH to form a yellow solution. CuI (0.092 g, 0.483 mmol) was added to the solution, forming an orange powder. This suspension was stirred for 30
empirical absorption correction applied using SADABS. 16

vacuum: 0.125 g, 0.0818 mmol, 84.7%. Anal. Calcd for (N-Bu-3-PyOMe)2{Cu5I7}: C, 15.26; H, 1.49; N, 3.40. Found: C, 15.26; H, 1.49; N, 3.40.

This product proved to be subject to oil formation and could not be analyzed.

X-ray Crystallography. Crystals were grown via ethyl ether diffusion into a MeCN solution (acetone solution for 1) of the iodocuprate complex. Crystals were mounted on glass fibers. All measurements were made using graphite-monochromated Mo (1 – 6 and 11) or microfocus Cu (5 and 12) Kα radiation on a Bruker-AXS DUO three-circle diffractometer, equipped with an APEX II CCD detector. Initial space group determination was based on a matrix consisting of 36 or 121 frames. The data were reduced using SAINT+;17 and empirical absorption correction applied using SADABS.16 Structures were solved using intrinsic phasing. Least-squares refinement for all structures was carried out on SHELXTL.18

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ASSOCIATED CONTENT

Supporting Information

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1H NMR spectrum of [Hpy][I], 1H NMR spectrum of [MePy][I], 1H NMR spectrum of [EtPy][I], 1H NMR spectrum of [PrPy][I], 1H NMR spectrum of [BuPy][I], 1H NMR spectrum of [HxPy][I], 1H NMR spectrum of [Bu 3-PyCl][I], 1H NMR spectrum of [Bu 3-PyBr][I], 1H NMR spectrum of [Bu 3-PyCN][I], 1H NMR spectrum of [Bu 3-PyOMe][I], hydrogen bonding in 1, packing diagram for 1, Cu···Cu interactions in 4, hydrogen bonding in 4, packing diagram for 4, Cu···Cu interactions in 5, hydrogen bonding in 5, packing diagram for 5, hydrogen bonding in 7, packing diagram for 7, hydrogen bonding in 8, packing diagram for 8, hydrogen bonding in 9, packing diagram for 9, hydrogen bonding in 10, packing diagram for 10, hydrogen bonding in 11, packing diagram for 11, hydrogen bonding in 12, and packing diagram for 12 (PDF)

Crystallographic data for compound 1 ( CIF )

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Notes

The authors declare no competing financial interest.

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