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Article

Tetranuclear Copper(I) Iodide Complexes of Chelating Bis(1-benzyl-1*H*-1,2,3-triazole) Ligands: Structural Characterization and Solid State Photoluminescence

Gerald F. Manbeck, William W. Brennessel, Christopher M. Evans, and Richard Eisenberg*

Department of Chemistry, University of Rochester, Rochester, New York 14627

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A series of tetranuclear $Cu_4I_4(\mathbf{L_n})_2$ clusters (**1**−**3**) supported by the chelating 4,4′-(4,5-di***X***-1,2-phenylene)bis-(1-benzyl-1*H*-1,2,3-triazole) ligands (**L1**, *X* = H; **L2**, *X* = CH_3; **L3**, *X* = F) have been prepared. Crystal structure determinations have shown that the clusters adopt a distorted "step-type" geometry in which the triazole ligands exhibit both chelating and bridging coordination modes to Cu(I) ions. When **L3** was employed in a 3:2 CuI/**L3** ratio, a crystalline product, **4**, was obtained. Product **4** is actually a 1:1 cocrystallization of the tetranuclear cluster **3** (denoted **4a**) and the dinuclear $Cu_2I_2(\mathbf{L3})_2$ complex (**4b**). X-ray structures of **1**, **2**, and **4** show the presence of close Cu$\cdots$Cu contacts in the tetranuclear and dinuclear forms. ^{1}H NMR experiments indicate that rapid exchange occurs in these systems. All clusters are brightly luminescent in the solid state at 77 K and at room temperature with λ_{max} = 495−524 nm. Emission intensity decays fit a single exponential with lifetimes on the order of 10 to 35 microseconds at room temperature and 90 to 140 microseconds at 77 K. The origin of emission is tentatively assigned as a metal-to-ligand phenylene π^* charge transfer.

Introduction

Recent production of marketable flat panel displays based on organic light-emitting diodes (OLED′s) and electroluminescence[1,2] has led to a surge in research directed toward improvement of device efficiency, durability, and flexibility.[3−12] Typically, the emission in these devices arises from a luminophore doped in a polymer matrix. As a consequence of spin statistics,[13,14] quantum efficiencies of devices containing transition metal complexes as the luminophores are often better than those employing organic dyes. In electroluminescent devices, only 25% of the excitons generated are of singlet multiplicity and 75% are triplets. While organic emitters utilize the singlet excitons for light emission, they are unable to use the triplet excitons in a similar way, thereby restricting their overall quantum efficiencies. On the other hand, metal complex luminophores exhibit emission from triplet excitons, and are also able to promote rapid intersystem crossing to convert singlet excitons into emissive triplet excited states. This means that the *potential* overall efficiency of metal complex luminophores is substantially higher than that of organic emitters.

Of metal complex luminophores that are triplet emitters, iridium(III) *tris*-cyclometalated systems have enjoyed particular attention and success[15−27] because of their thermal stability and their photo- and electroluminescence properties.

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*To whom correspondence should be addressed. E-mail: eisenberg@chem.rochester.edu.

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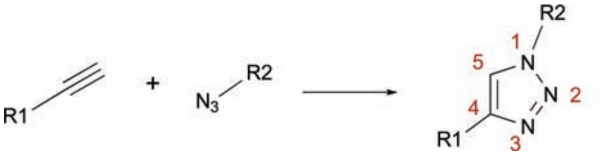
Unfortunately, iridium, as well as platinum which also forms luminescent cyclometalated complexes, are relatively rare and costly, so that an impetus exists to find suitable emitters based on less expensive metals. In this context, the luminescent properties of copper(I) complexes have driven recent interest, and a limited number of OLED devices containing such emitters have been studied.[28−38] For the preparation of devices by chemical vapor deposition (CVD), other factors regarding potential dopant emitters must also be considered, most notably, their thermal stability and sublimability. While many Cu(I) complexes are photoluminescent, they generally do not satisfy the last criterion for CVD device preparation because they are cationic or highly aggregated, making them unsublimable.

In 2005, Harkins and Peters reported a neutral dinuclear Cu(I) complex that exhibited an impressive phosphorescence quantum yield and excited state lifetime.[39] The complex was also found to be sublimable and thermally stable, leading to its incorporation in an OLED device with an external quantum efficiency of 16%.[40] Related mononuclear complexes show similar photophysical properties.[41] On the basis of these results, the synthesis and study of new Cu(I) complexes that possess charge neutrality for sublimability, thermal stability for CVD, and bright photoluminescence become even more compelling.

While the majority of emissive Cu(I) complexes studied contain nitrogen-heterocycle ligands,[31,42−47] one type of heterocycle which has not been investigated thoroughly as a ligand is the 1,4-disubstituted-1,2,3-triazole. In fact, the literature is nearly void of isolated copper(I) complexes of the 1,2,3-triazole, although Fokin and others have shown that chelating polytriazoles are viable ligands for accelerating by increasing the yield and decreasing the reaction time in triazole synthesis, presumably by stabilizing intermediates of the active Cu(I) catalyst.[48] The closest example of an isolated complex is a tetranuclear $L_4Cu_4Br_4$ complex where L = 1,2,3-triazole-1,5-α-quinoline.[49] The ligand was obtained by the Cu(II)-promoted oxidation of quinoline-2-carbaldehyde hydrazone, and the copper(I) complex was isolated *in situ* as a tetranuclear step-type cluster that exhibited solid state emission with λ_{max}=400 nm.

While an impressive number of papers have dealt with triazole synthesis,[50] their use in constructing complicated architectures,[51,52] and triazoles as links between molecular components such as porphyrins and fullerenes,[53] there are a limited number of reported transition metal complexes of 1,4-disubstituted triazoles. The virtues of making 1,4-disubstituted-1,2,3-triazoles by Sharpless "click" chemistry (eq 1)[54] and their relative stability once formed provide a strong case for increased study of triazole coordination chemistry. To date, palladium(II) and platinum(II) complexes have been prepared with monodentate 1,2,3-triazoles[55] and chelating phosphine-triazole ligands.[56] Ruthenium(II) complexes with 2-triazolo-pyridine ligands have been prepared for comparison of the electronic properties of a chelating triazole to 2,2′-bipyridyl.[57,58] The complex $[ReCl(CO)_3(Bn\text{-}pyta)]$ (Bn-pyta = 1-benzyl-4-(2-pyridyl)-1,2,3-triazole) exhibits a blue shift in its electronic spectrum relative to that of $[ReCl(CO)_3(bpy)]$,[59] consistent with a higher lowest unoccupied molecular orbital (LUMO) energy for the pyta complex.



(1)

In light of the scope and functional group tolerance of 1,4-disubstituted-1,2,3-triazole synthesis, as well as the tunability of their electronic and steric properties, we undertook a study of Cu(I) 1,2,3-triazolate complexes that would permit the synthesis of new luminescent neutral complexes. It was hypothesized that a chelating bis-triazole ligand with geometry rigidly defined by a phenylene backbone would possess a π^* orbital of appropriate energy for charge transfer from

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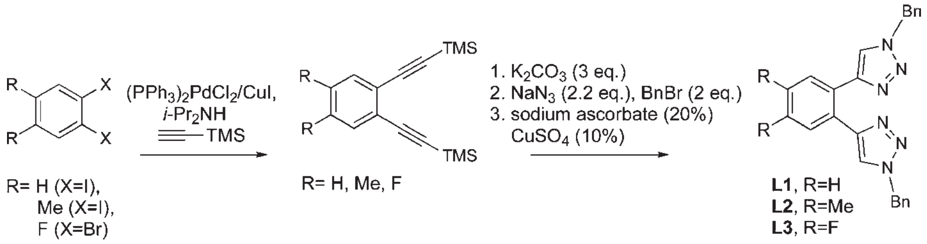
Scheme 1



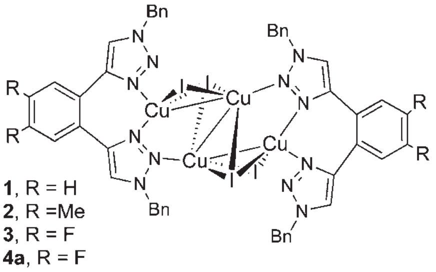
filled metal d-orbitals, while having the rigidity to suppress excited state distortions that commonly enhance non-radiative relaxation in Cu(I) complexes.[42,47,60−62]

Results and Discussion

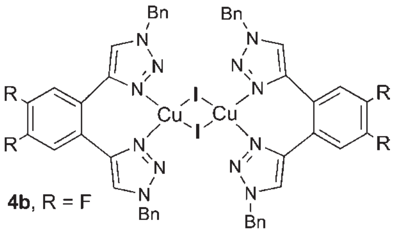
Synthesis. Ligands **L1**−**L3** were synthesized via the "click" reaction of 4,5-disubstituted-1,2-bis(trimethylsilylethynyl)arenes that were in turn obtained from Sonogoshira coupling of trimethylsilylacetylene and the corresponding *o*-dihaloarenes (Scheme 1). For R = F, the commonly used catalyst system of $PdCl_2(PPh_3)_2$ and CuI was sufficiently active to work successfully with the 1,2-dibromoarene but for R = H or CH_3, it was necessary to use the corresponding 1,2-diiodoarenes for the coupling chemistry. For triazole synthesis via click chemistry, the procedure reported by Fletcher[58] in which alkyne deprotection, alkyl azide formation, and cycloaddition are carried out in a single reaction vessel was preferred, although isolation of the free alkynes prior to cyclization worked with equal success. Ligands were obtained in satisfactory yields and purified without employing column chromatography.

For initial exploration of the coordination chemistry of the ligands, 1 equiv of **L1** was stirred in acetonitrile with CuI. After 3 h, addition of diethyl ether resulted in precipitation of a fine white powder, to which a few drops of acetonitrile were added to redissolve the precipitate. Upon standing for 1−2 days, block crystals formed that were identified by X-ray crystallography and microanalysis as the tetranuclear cluster, Cu_4I_4(**L1**)$_2$ (**1**). With the 1:1 metal-to-ligand ratio, a 1:1 Cu/**L1** dinuclear complex with halide bridges and a planar rhombic core had been anticipated with each Cu(I) ion tetrahedrally coordinated by the two bridging halides and the chelating bis(triazole) ligand. This type of coordination had been obtained before with chelating ligands such as diphosphines[35,63−67] and N-heterocycles such as pyridine derivatives[68−70] or phenanthroline,[71,72] and has been seen for related complexes containing monodentate phosphines and N-heteroaromatic ligands as well.[73] However, despite these precedents and the 1:1 Cu/**L1** stoichiometry used in these reactions, only the tetranuclear cluster **1** was obtained.

Subsequently, **2** and **3** were prepared without the use of excess ligand, that is, CuI/**L** ratios of 2:1 were employed. In the synthesis of **3** using the 2:1 metal-to-ligand ratio, two different crystalline products were obtained. The first was the analogous tetranuclear cluster **3**, which was the major product, but a second crystalline form, identified as **4**, was also present in small amounts. This form was found to be a 1:1 cocrystallization of the tetranuclear cluster **3** (denoted as **4a**) and the initially anticipated 1:1 dinuclear Cu_2I_2(**L2**)$_2$ compound (**4b**).



1, R = H
2, R =Me
3, R = F
4a, R = F



4b, R = F

The relative amounts of crystalline **3** and **4** are discernible under UV irradiation with a hand-held lamp (365 nm) as **3** is a green emitter and **4** exhibits bright blue emission. The crystals were large enough to separate **3** and **4** manually by pipet. In **4**, the empirical ratio of CuI to **L3** is 3:2, but the exclusive synthesis of this crystalline form using this particular metal-to-ligand ratio resulted only in mixtures of **3** and **4**. Ultimately, crystals of **4** were obtained

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Table 1. Summary of Crystallographic Data

	1	**L3**	**3**	**4**·2Et$_2$O
formula	$C_{48}H_{40}Cu_4I_4N_{12}$	$C_{24}H_{18}F_2N_6$	$C_{48}H_{36}Cu_4F_4I_4N_{12}$	$C_{104}H_{92}Cu_6F_8I_6N_{24}O_2$
fw	1546.68	428.44	1618.65	3004.66
T (K)	100.0(1)	100.0(1)	100.0(1)	100.0(1)
cryst syst	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.4633(7)	5.4883(7)	9.1964(6)	14.0558(7)
b (Å)	11.0674(8)	18.914(2)	11.7435(8)	14.4281(7)
c (Å)	12.2561(9)	19.122(2)	12.9597(8)	15.4527(8)
α (deg)	90.175(2)	90	114.113(1)	70.249(1)
β (deg)	108.660(1)	91.535(2)	91.823(1)	88.674(1)
γ (deg)	100.074(1)	90	101.446(1)	65.815(1)
V(Å^3)	1195.0(2)	1984.3(4)	1242.1(1)	2666.2(2)
Z	1	4	1	1
ρ_{calcd} (g cm^{-3})	2.149	1.434	2.164	1.871
μ (mm^{-1})	4.389	0.102	4.239	2.988
no. reflns collected	26582	31774	28875	62064
no. unique reflns	10825	8603	11823	25335
R_{int}	0.0395	0.0565	0.0472	0.0596
no. of obsd reflns	7836	5700	8428	16179
no. of params	307	361	325	696
GOF on F^2	0.973	1.031	0.956	0.992
R1 [$I > 2\sigma(I)$]	0.0388	0.0524	0.0382	0.0449
wR2	0.0821	0.1278	0.0711	0.0813

Table 2. Selected Bond Lengths (Angstroms) and Angles (Degrees)

	1	**3**	**4a**	**4b**
Cu1−Cu2A	2.6311(5)	2.6443(5)	2.7034(5)	2.5303(7) [Cu3−Cu3A]
Cu2−Cu2A	2.7465(8)	2.7403(7)	2.6857(8)	
Cu1−I1	2.7711(4)	2.7286(4)	2.6131(4)	2.6272(4) [Cu3−I3]
Cu1−I2A	2.5564(2)	2.5746(4)	2.5968(5)	2.6091(4) [Cu3−I3A]
Cu2−I1	2.6723(4)	2.6449(4)	2.6331(5)	
Cu2−I1A	2.7148(5)	2.6929(4)	2.7520(5)	
Cu2−I2	2.5883(5)	2.5891(4)	2.6112(5)	
Cu1−N1 (chelate)	2.040(3)	2.037(2)	2.028(3)	2.053(2) [Cu3−N7]
Cu1−N4 (chelate)	2.046(2)	2.070(2)	2.057(3)	2.042(3) [Cu3−N10]
Cu2−N5 (bridge)	2.083(2)	2.079(2)	2.083(3)	
N1−Cu1−N4	90.2(1)	90.94(9)	92.2(1)	92.1(1) [N7−Cu3−N10]
I2A−Cu1-Cu2A	59.84(1)	59.47(1)	58.99(1)	57.79(1)[Cu3−I3−Cu3A]
Cu2−I1−Cu1	75.37(1)	75.37(1)	80.73(1)	107.50(7) [N7−Cu3−I3A)]
Cu2−I1−Cu2A	61.30(2)	61.77(1)	59.78(2)	
Cu1−I1−Cu2A	57.31(1)	58.38(1)	60.10(1)	
Cu2A−Cu2-Cu1A	76.45(2)	75.18(2)	78.71(2)	
N5−Cu2−I2	120.89(7)	120.95(6)	125.03(7)	

as the sole product by seeding an ether/acetonitrile solution of CuI and **L3** in a 3:2 ratio with a few crystals of **4** which had been collected previously. It was not possible to isolate the binuclear compound **4b** as a separate entity despite several attempts to do so, including the use of excess ligand. A reaction carried out with a 1:5 CuI to **L3** ratio yielded only mixtures of **3** and **4**. In addition, if during the reactions of **L** with CuI, a small volume of acetonitrile was employed, a white precipitate formed after 1−2 h regardless of the CuI/**L** ratio used. This precipitate was found to exhibit blue emission, but its identity could not be established by X-ray crystallography or NMR spectroscopy. The ^{1}H NMR spectrum of this precipitate showed broadened resonances suggesting the presence of mixtures or coordination polymers. Dissolution of the precipitate in acetonitrile followed by addition of ether until saturation resulted in crystallization of the tetranuclear compounds **1**−**3**.

All complexes are stable to air for extended periods of time in the solid state, and for several days in solution. Analogues with CuBr or CuCl were not prepared successfully as rapid oxidation to Cu(II) was observed even under an inert atmosphere.

In an attempt to prepare mixed ligand complexes of the formulation CuI(**L3**)L′, 1 equiv of PPh_3 was added to **3**. In a separate experiment, CuI, **L3**, and PPh_3 were combined in equimolar amounts in MeCN to achieve the same product. However, both experiments resulted in the formation of $[PPh_3CuI]_4$. No mixed species such as $[Cu_4I_4(\mathbf{L_2})(PPh_3)_2]$ or [CuI(**L3**)(PPh_3)] were obtained. Likewise, mixed ligand species incorporating 2,9-dimethylphenanthroline could not be obtained. Upon addition of this ligand to an acetonitrile solution of **3**, rapid precipitation of [CuI(2,9-Me$_2$-phen)]$_2$ occurred.

X-ray Crystallography. Crystals of **1**−**4** were grown from saturated acetonitrile/diethyl ether solutions (~1:5 v/v) that were covered and left to stand for 1−2 days at room temperature. Unit cell, data collection and structure refinement parameters for all structures reported here are provided in Table 1 (see Supporting Information for the cif file containing all crystal and refinement information as well as all metrical parameters). Selected bond lengths and angles are given in Table 2. Complexes **1**, **3**, **4a**, and **4b**

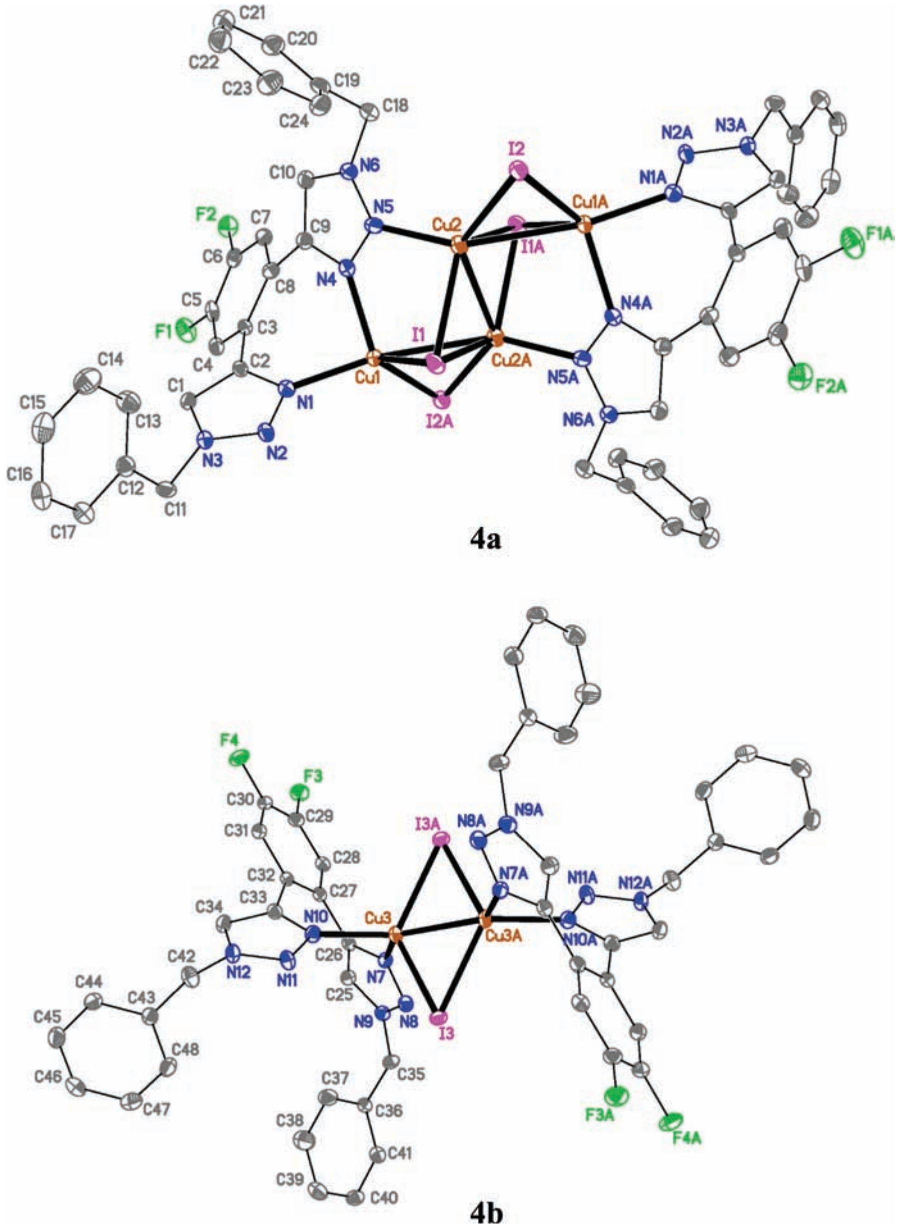

Figure 1. ORTEP drawings of **4** with **4a** and **4b** shown separately. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

each lie on a crystallographic inversion center with symmetry related atoms in Table 2 and the structural figures denoted by "A".

Complexes **1**, **3**, and **4a** adopt the same distorted step-type structure with minor differences in bond lengths and angles. The structures of the two complexes in **4** are shown in Figure 1. In the tetranuclear complexes **1**, **3**, and **4a**, there are two types of Cu(I) ions present. In each Cu_4I_4 cluster, Cu1 ions are coordinated by N1 and N4 of the triazole rings of a chelating triazole ligand and by two bridging iodide ligands, whereas the Cu2 ions are coordinated by three μ_2-I ligands and N5 of a *bridging* triazole moiety. To accommodate the Cu1 ions of the cluster, the triazole rings of each ligand are significantly twisted out of plane of the phenylene backbone. The structure contains two different types of iodide ligands: two that are doubly bridging (μ_2) and two that are triply bridging (μ_3). The short copper−copper distances between Cu1 and Cu2 and between the two Cu2 atoms (2.6311(5)−2.7034(5) Å and 2.6857(8)−2.7465(8) Å, respectively) in the structures of **1**, **3**, and **4a**, indicate some positive or attractive interaction between these closed shell d^{10} metal ions. As imposed crystallographically, atoms defining the central step, Cu2, Cu2A, I1, and I1A, all reside in the same plane, while the outer Cu_2I_2 units are folded along the Cu1−Cu2A and Cu1A−Cu2 axes. An extended network connected by π-stacking is observed in the structure of **4** (Figure 2). The phenylene rings of adjacent **4a** units overlap with an interplanar distance of 3.390 Å, and a second π-stacking arrangement exists between the triazole rings of **4b** and the benzyl rings of **4a** at 3.464 Å.

The dinuclear compound **4b** contains the planar Cu_2I_2 rhombic core that was originally expected and is very similar in geometry to the central Cu_2I_2 portion of **1**, **3**, and **4a**. The Cu···Cu distance of 2.5303(7) Å (compared to 2.6857(8) Å in **4a**) is among the shortest in planar dinuclear $Cu_2(\mu_2\text{-I})$ compounds such as those supported

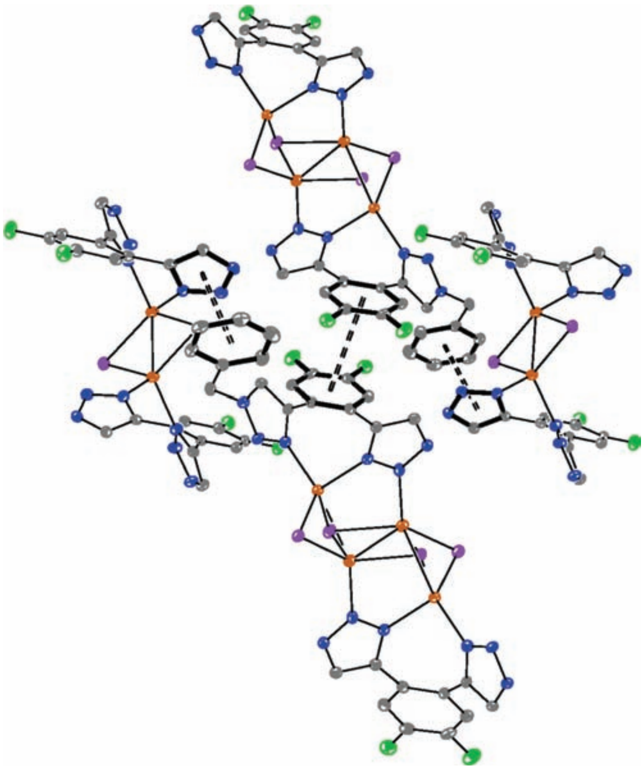

Figure 2. Packing diagram for **4** indicating π-stacking interactions between adjacent phenylene rings of **4b** and between **4b** benzyl rings and **4a** triazole rings.

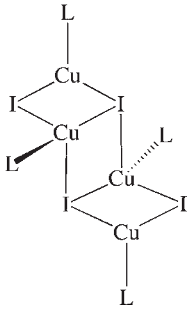

Figure 3. Typical step-type cluster arrangement for complexes formulated as $(CuI\mathbf{L})_4$ or $Cu_4I_4\mathbf{L}_2$ where $\mathbf{L}$ = monodentate ligand.

by bulky pyridine ligands (2.557 Å),[74] benzimidazoles (2.546 Å),[75] 2-benzoyl pyridines (2.587 Å),[70] imidazolyl pyridines (2.592 Å),[76] phenanthroline (2.609 Å),[71] and others.[77−79] Separations shorter than 2.530 Å in planar Cu_2I_2 are observed only for dinuclear compounds with bridging ligands such as diphosphino carbenes (2.356 Å).[80]

The step-type arrangement (Figure 3) in cuprous iodide cluster chemistry is often obtained in discrete complexes with monodentate,[81,82] bidentate,[83,84] or tridentate[85−91] ligands. The latter case is limited to a few examples, most of which contain NSN bis(pyridyl) thioether ligands. The structures of **1**, **3**, and **4a** are rare examples of Cu_4I_4 step clusters with tridentate ligands. Uniquely in this series of compounds, adjacent atoms of the triazole rings (N4 and N5) form part of the donor set. Close metal−metal distances are accompanied by a folding of the outer Cu_2I_2 units of the clusters. The $Cu\cdots Cu$ distances in **1**, **3**, and **4a** are comparable to those reported in other distorted step clusters (2.655−2.778 Å),[85,86,88,89] although examples with two unique close metal−metal contacts are more rare.[83,87,90] Generally, metal−metal distances in step-type clusters are greater than the sum of of the van der Waals radii (2.8 Å).

NMR Studies. The ^{1}H NMR spectra of **1**−**4** in CD_3CN at 25 °C are characterized by resonances similar to those of the respective free ligands. For **3** the ^{1}H NMR spectrum exhibits a sharp benzyl CH_2 singlet, multiplets from the benzyl aromatic protons, an A_2B_2 pattern characteristic of the phenylene backbone protons, and a singlet from the CH protons of the triazole rings. In light of the absence of ligand symmetry in the crystal structure of **3**, the observation of only a single set of ligand resonances in the ^{1}H NMR spectra of these compounds was unexpected and suggestive of fluxional behavior or rapid exchange between the free ligand and the complex. Disregarding slight changes in chemical shift upon coordination, the only observable difference in proton signals was a slight broadening of the triazole CH resonance in the clusters (2.5 Hz fwhm vs 1.5 Hz). Similar observations were also made for **1** and **2**.

Variable temperature proton NMR spectra of **3** in CD_3CN from −35 °C to + 65 °C are shown in Figure 4 and Supporting Information, Figure S1 (the former has spectra at three representative temperatures while the latter contains the full experiment). The sample was first cooled in 10 °C increments, then warmed to 65 °C, and finally cooled back to room temperature. Throughout the entire range of temperatures, only a single set of resonances was observed, with the most notable change in the spectra being the chemical shift of the triazole signal varying from 7.70 ppm at −35 °C to 7.53 ppm at 65 °C. A slight decrease in line width was also observed at −35 °C. Upon returning to room temperature after heating, the spectrum was identical to that prior to heating.

To probe further the possibility of dynamic solution behavior, 1 equiv of **L3** was added to a CD_3CN solution of complex **3**, and the mixture was cooled to −35 °C. ^{1}H NMR spectra of the solutions containing **L3** + **3**, **L3**, and **3** at room temperature and −35 °C are shown in Figure 5.

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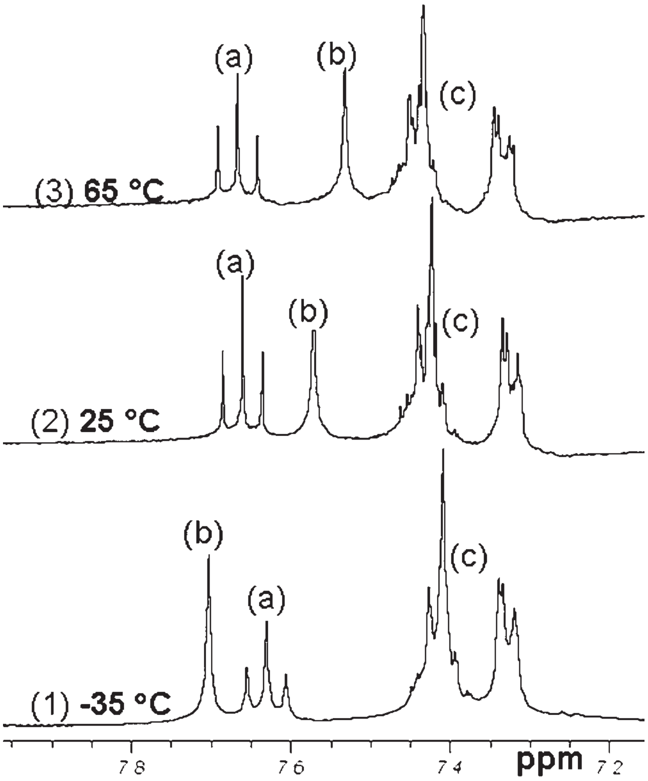


Figure 4. Variable temperature ^{1}H NMR of $Cu_4I_4(\mathbf{L3})_2$ in CD_3CN from −35 to + 65 °C. (a) phenylene C−H, (b) triazole C−H (c) aromatic benzyl C−H.

The complete set of spectra is presented in the Supporting Information, Figure S2. The triazole CH resonance of free **L3** (spectrum 5) is sharper than that of the complex (spectrum 4) at a lower chemical shift. Resonances for the mixture of **L3** and **3** (spectrum 2) are nearly identical to those of complex **3**. Upon cooling of the sample to −35 °C, only one set of resonances was observed (spectrum 1). The only significant change is the shift in triazole CH resonance to higher frequency as was observed upon cooling **3** without added **L3**. Addition of a second equivalent of **L3** to the mixture at room temperature (spectrum 3) resulted in additional line broadening compared to spectrum 2 with a slight upfield shift in the triazole CH resonance.

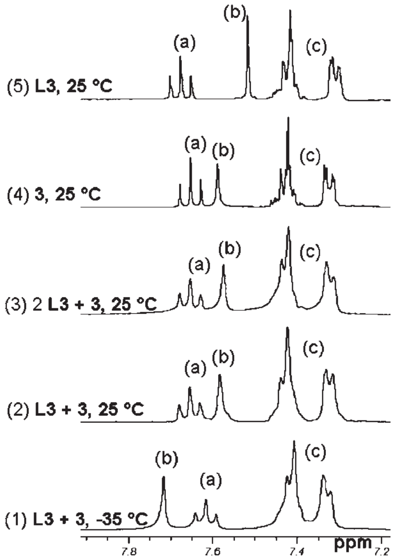
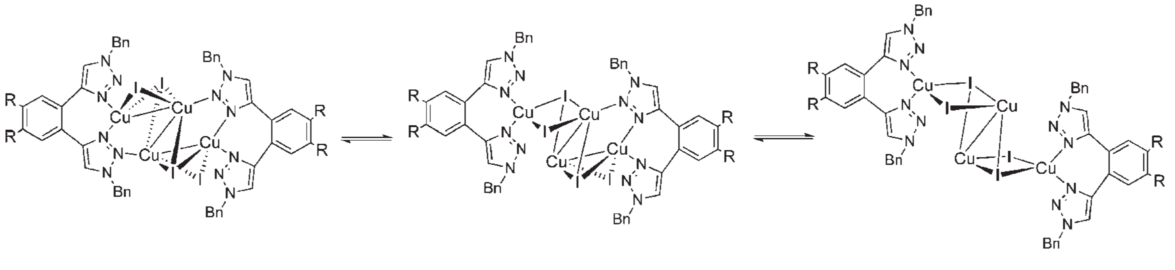


Figure 5. ^{1}H NMR spectra of **3** + 1 equiv of **L3** in CD_3CN from −35 to +25 °C. (a) Phenylene C−H, (b) triazole C−H, (c) benzyl C−H.

The combined results of these variable temperature NMR studies indicate that exchange occurs at a rate rapid on the NMR time scale. In the first experiment, only a single set of resonances is present at low temperature. This suggests that in solution rapid exchange occurs even at −35 °C so that the inequivalent triazoles of each ligand in the solid state structure are completely averaged. A possible mechanism of exchange to rationalize the observed equilibration is loss of N5 bridging coordination to leave Cu2 trigonally coordinated by three bridging iodides in solution (eq 2). In this manner, triazole equivalence is achieved yielding a single set of resonances on the NMR time scale. In the second experiment, in which ^{1}H NMR spectra were measured of **3** + **L3**, the absence of free **L3** resonances further supports the notion of intermolecular exchange occurring rapidly in this series of compounds. As additional evidence for rapid interconversion of several species, the ^{1}H NMR spectrum of **4** is nearly identical to that of **3**. Only one set of resonances is observed, and **4a** and **4b** are not seen separately. Thus, once dissolved, the tetranuclear clusters likely exist as a mixture of $Cu_4I_4L_2$, $Cu_2I_2L_2$, and free **L** that are undergoing rapid exchange. Rapid exchange has been examined in other tetranuclear Cu_4I_4 clusters as well.[87]



(2)

Emission Spectroscopy. Solid state photophysical data for **1**−**4** and solution emission maxima for **L1**−**L3** are summarized in Table 3. Complexes **1**−**4** are not emissive in solution, but their solid state luminescence appears bright. The emission spectra for **1**−**4** at room temperature (Figure 6) are independent of excitation wavelength. Emission maxima at 298 K range from 495 (**2** and **4**) to 524 (**1**). At 77 K, there is a slight red shift (5−20 nm) in emission (Supporting Information, Figure S3) and for **1**−**3**, the same order of emission energy is observed.

Table 3. Photophysical Data for Complexes **1**−**4** and Ligands **L1**−**L3**

	solution λ_{em}^{max}/nm	solid λ_{em}^{max}/ nm (298 K)^c	solid λ_{em}^{max}/ nm (77 K)^c	$\tau/\mu s$, 298 K^{d,e}	$\tau/\mu s$ 77 K^{d,e}
L1	370^{a,b}				
L2	342^{a,b}				
L3	355^{a,b}				
1		524	545	33	110
2		495	513	12	93
3		514	528	43	140
4		495	503	26	140

[a] Spectra obtained in 1.0×10^{-5} M MeCN at room temperature. [b] $\lambda_{ex} = 260$ nm. [c] $\lambda_{ex} = 365$ nm. [d] $\lambda_{ex} = 335$ nm. [e] Luminescence decay data are fit to a single exponential decay $y = y_0 + Ae^{(-t/\tau)}$.

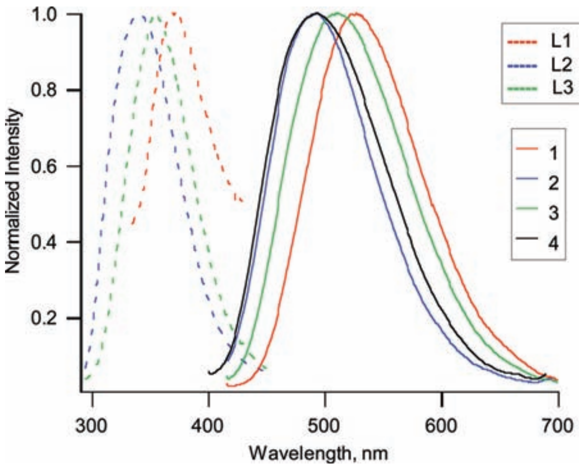


Figure 6. Normalized solid state emission spectra of **1**−**4** at 298 K ($\lambda_{exc} = 365$ nm) and solution emission of **L1**−**L3** (1×10^{-5} M in acetonitrile, $\lambda_{exc} = 260$ nm).

Emission bands at room temperature and 77 K are broad and featureless with large Stokes shifts of 5,900−9,200 cm^{-1} from the excitation maxima of 350−400 nm. Time-resolved emission traces can be fit to single exponential decay with lifetimes at 298 and 77 K of about 30 and 120 μs, respectively, suggestive of triplet state emissions.

The order of emission energy of the complexes in the solid state (**2** > **3** > **1**) follows that of the free ligands in solution (Figure 6). This trend does not correlate with any inductive or resonance parameters[92] that describe the effects of methyl or fluoro substitution of the ligand phenylene backbone. While ligand emission likely arises from a $\pi-\pi^*$ excited state, the nature of the excited state in **1**−**4** is more difficult to assign. Possibilities include ligand-based $^3(\pi-\pi^*)$, metal-to-ligand charge transfer ^{3}(MLCT), halogen-to-ligand charge transfer ^{3}(XLCT), cluster-centered ^{3}(CC), or an admixture of more than one of the above.

In several reported examples, the emissive properties of multinuclear Cu(I) complexes with short Cu···Cu distances are affected by metal−metal interactions;[91,93,94] however, short metal−metal distances do not necessarily influence the emission as the unoccupied Cu 4s and 4p orbitals can be higher in energy than π^* orbitals of the ligands.[93] Clusters **1**−**4** are the first examples of distorted step-type Cu_4I_4 clusters with tridentate ligands exhibiting bright photoluminescence. In tetranuclear $(CuIL)_4$ cubane complexes with short Cu···Cu contacts, dual emission is observed from ^{3}CC and ^{3}XLCT states.[94] For dinuclear complexes in which the emission has been assigned to an MLCT excited state, a slight blue shift is often observed at low temperatures.[85,87] The temperature dependence of emission in **1**−**3** most closely matches the behavior of the low energy ^{3}CC band in $Cu_4I_4(pyr)_4$ which red shifts from 580 nm at 298 K to 619 nm at 77 K with an increase in lifetime from 11 μs to 25.5 μs.[94] With these similarities in mind, it is tempting to assign the excited state of **1**−**3** as ^{3}(CC) modified by close Cu···Cu contacts; however, the ligand substitution effects (Me vs F vs H) are not consistent with this assignment. Twisting of the triazoles out of plane with the phenylene ring prevents influence of the 4,5-phenylene substitutions on electron density at the coordinated triazole via resonance effects. Also, the trends in emission are not consistent with an inductive field effect. Congruity between ligand solution emission trends and solid state cluster trends suggests involvement of the ligand π^* orbitals in the complex excited state, most likely as a component of the lowest unoccupied molecular orbital (LUMO). A metal-based or halogen-based highest occupied molecular orbital (HOMO) cannot be assigned definitively in the absence of stable CuBr or CuCl analogues since emission energies in dinuclear complexes can correlate well with the ligand field strength of the halogen.[35]

The problem becomes more difficult when comparing the emissions of **3** and **4**. Metal−metal distances in **3** and **4a** are similar, but shorter in **4b**. Since **4b** could not be isolated, its individual emission properties are unknown. A possible explanation for the blue shift from **3** to **4** is the combined effects of different Cu···Cu distances and aromatic intra-complex π-stacking in **4**. Assuming the LUMO of the complex is largely ligand-based, this π-stacking interaction can modify the energy level of the LUMO.

In summary, the following factors must be considered in assigning the nature of emission. There is a red shift and increase in lifetimes upon cooling which are similar to ^{3}(CC) emissions in tetranuclear cubane complexes. Ligand and complex emission follow the same trend in energy. A blue shift in emission occurs from **3** to **4** in which the phenylene ring of **4a** is involved in intra-complex π-stacking. Thus, without evidence for contribution of empty cluster-centered orbitals to the LUMO, the excited state in **1**−**4** is assigned as metal-to-ligand phenylene π^* charge transfer.

Conclusions

New 4,4′-(4,5-di*X*-1,2-phenylene)bis(1-benzyl-1*H*-1,2,3-triazole) ligands **L1**−**L3** have been prepared and their $Cu_4I_4L_2$ complexes **1**−**3** have been characterized. These are the first Cu(I) iodide complexes of chelating 1,2,3-triazoles. X-ray crystallographic studies have shown that the complexes adopt distorted "step-type" geometries in which the triazole ligands *chelate* through the N3 atom of the triazoles and *bridge* Cu(I) centers through coordination of both N2 and N3 of a

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given triazole. This N2 triazole coordination has not been observed before in 1,2,3-triazole coordination chemistry. In conjunction with the distorted step-geometry, short Cu···Cu contacts are present. Under certain synthetic conditions, crystals are obtained containing a 1:1 cocrystallization of tetranuclear $Cu_4I_4(\mathbf{L3})_2$ and binuclear $Cu_2I_2(\mathbf{L3})_2$. ^1H NMR experiments have been carried out to probe the solution dynamics of the complexes in view of the fact that ligand resonances are simpler than the solid state structures would predict. It is found that exchange occurs extremely rapidly, even at low temperatures. To our knowledge, these are the first examples of distorted Cu_4I_4 step-type clusters with tridentate ligands that exhibit solid state luminescence. All complexes are brightly emissive with trends in emission energy following those of the free ligands. Low temperature emission and lifetime data have been measured, and the data support an assignment of the excited state as MLCT Cu d to triazole π^*.

Experimental Section

General Procedures. NMR spectra were obtained using Bruker Avance 400 and 500 MHz spectrometers with ^1H NMR chemical shifts referenced to residual solvent peaks in $CDCl_3$ or CD_3CN. Mass spectra of organic compounds were measured on a Shimadzu 2010 series liquid chromatography mass spectrometer (LCMS) under atmospheric pressure chemical ionization (APCI). Steady-state excitation and emission spectra were measured using a Spex Fluoromax-P fluorometer with excitation and emission slits set for a 2 nm band-pass. Ligand emission spectra in acetonitrile were obtained at a concentration of 1×10^{-5} M. Solid state emission samples were prepared by packing a capillary tube with the emissive complex. For low temperature measurements, the capillary was held in a vacuum dewar flask filled with liquid nitrogen. Lifetime measurements were performed using a model LN203C nitrogen laser (Laser Photonics Inc.) with $\lambda = 337.1$ nm and a 0.1 nm spectral width pulsed at 1 pulse/second. Signals were detected by a silicon photodiode and photomultiplier tube (1P28 type) with a 2 ns rise time and viewed with a Hewlett-Packard 54510-B oscilloscope connected to a computer via a GPIB interface.

Sonogashira reactions and complex syntheses were carried out under standard Schlenk conditions. Diisopropyl amine and acetonitrile (HPLC grade) were degassed via sparging with N_2 for 20 min prior to use. Trimethylsilylacetylene, 1,2-diiodobenzene, and 1,2-dibromo-4,5-difluorobenzene were purchased from Oakwood Chemicals. 1,2-Diiodo-4,5-dimethylbenzene was prepared by literature methods from *o*-xylene.[95] Benzyl bromide and sodium azide were purchased from Aldrich Chemical Co. and used as received.

Crystal Structure Determinations. Each crystal was placed onto the tip of a glass fiber using Paratone and mounted on a Bruker SMART Platform diffractometer equipped with an APEX II CCD area detector. All data were collected at 100.0(1) K using MoKα radiation (graphite monochromator).[96] For each sample, a set of preliminary cell constants and an orientation matrix were determined from reflections harvested from three orthogonal wedges of reciprocal space. Full data collections were carried out with frame exposure times of 45−60 s at detector distances of 4 cm. Randomly oriented regions of reciprocal space were surveyed for each sample: four major sections of frames were collected with 0.50° steps in ω at four different φ settings and a detector position of −38° in 2θ. The intensity data were corrected for absorption,[97] and final cell constants were calculated from the *xyz* centroids of approximately 4000 strong reflections from the actual data collection after integration.[96]

Structures were solved using SIR97[98] and refined using SHELXL-97.[99] Space groups were determined based on systematic absences, intensity statistics, and Cambridge Structural Database frequencies.[100] Direct-methods solutions were calculated which provided most non-hydrogen atoms from the difference Fourier map. Full-matrix least-squares (on F^2)/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic thermal parameters.

Synthesis of 1,2-Diethynylbenzene. To a solution of *o*-diiodobenzene (2.74 g, 8.3 mmol) in N_2 purged diisopropylamine (50 mL) was added $PdCl_2(PPh_3)_2$ (0.29 g, 5%) and CuI (0.28 g, 17.5%) in one portion. The vessel was sealed with a septum, and trimethylsilylacetylene (2.87 mL, 2.5 equiv) was added dropwise via syringe. The reaction darkened with heavy precipitates and was stirred at 25 °C for 1 h and then at 80 °C for 20 h. Upon cooling, the amine salts were removed by filtration, and the solvent was evaporated. The dark residue was taken up in hexanes and filtered through a frit packed with a 3 in. plug of silica gel. The silica was washed with 300 mL of hexanes. Removal of the solvent using a rotary evaporator provided a yellow oil which was dissolved in 80 mL of degassed MeOH. KOH (20 mg in 2 mL H_2O) was added. After stirring for 2 h, the solvent was evaporated, and the residue was partitioned between ether (50 mL) and saturated NaCl (20 mL). The organic layer was dried ($MgSO_4$), filtered, and evaporated to provide the title compound. NMR data were in agreement with literature values.[101]

Synthesis of 1,2-Dimethyl-4,5-bis(trimethylsilyl)ethynyl benzene. To a solution of 1,2-diiodo-4,5-dimethyl benzene (6.00 g, 18 mmol) in N_2 purged diisopropylamine (125 mL) was added $PdCl_2(PPh_3)_2$ (0.63 g, 5%) and CuI (0.51 g, 15%) as solids in one portion. Trimethylsilylacetylene (5.47 mL, 2.5 equiv) was added via syringe. The mixture was sealed with a septum and stirred for 16 h at 60 °C, cooled, and filtered. After evaporation of the solvent, the residue was filtered through a plug of silica gel and eluted with 10:1 hexanes/ethylacetate. The solvent was evaporated to provide 4.27 g (80%) of the title compound. NMR data are in agreement with the literature.[102]

Synthesis of 1,2-Diethynyl-4,5-difluorobenzene. The same procedure used to prepare 1,2-diethynylbenzene was followed using 1,2-dibromo-4,5-difluorobenzene (1.00 g, 3.67 mmol), $PdCl_2(PPh_3)_2$ (0.13 g, 5%), and CuI (0.12 g, 17.5%). A yield of 67% yield was obtained after workup. Spectral data are in agreement with literature values.[103]

4,4′-(1,2-Phenylene)bis(1-benzyl-1*H*-1,2,3-triazole) (L1). To a stirred solution of 1,2-diethynylbenzene (1.13 g, 8.95 mmol) in 1:1 *t*-BuOH/H_2O (60 mL) were sequentially added NaN_3 (1.28 g, 19.69 mmol), benzyl bromide (2.12 mL, 17.9 mmol), sodium ascorbate (0.53 g, 2.68 mmol), and $CuSO_4$ (2.7 mL of a 0.5 M solution, 1.34 mmol). The reaction was stirred overnight at room temperature whereupon heavy precipitates formed. Water (50 mL) was added, and the mixture was heated until complete dissolution. Tan microcrystals (1.81 g, 52% yield) formed upon cooling. ^1H NMR ($CDCl_3$ 25 °C): δ 7.72−7.70 (m, 2H, Ar−H), 7.43−7.41 (m, 2H, Ar−H), 7.36−7.35 (m, 6H, Ar−H), 7.21

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(s, 2H, triazole), 7.22−7.19 (m, 4H, Ar−H), δ 5.40 (s, 4H, $-CH_2-$) CD_3CN: δ 7.70−7.68 (m, 2H, Ar−H), 7.47−7.45, (m, 4H, Ar−H, triazole), 7.39−7.33 (m, 6H, Ar−H), 7.26−7.25 (m, 4H, Ar−H), 5.45 (s, 4H, $-CH_2-$). MS (APCI positive) Calcd *m*/*z* 392.17, Found 393.15 $(M+H)^+$.

4,4′-(4,5-Dimethyl-1,2-phenylene)bis(1-benzyl-1*H*-1,2,3-triazole) (L2). A mixture of 1,2-dimethyl-4,5-bis(trimethylsilyl)-ethynyl benzene (0.40 g, 1.3 mmol) and K_3CO_3 (0.55 g 3 equiv.) was stirred in 10 mL 1:1 *t*-BuOH/H_2O for 15 min. Sequentially, sodium azide (0.19 g (2.2 equiv.), benzyl bromide (0.32 mL, 2.6 mmol), sodium ascorbate (0.005 g, 20%), and $CuSO_4$ (0.26 mL of a 0.5 M solution in water, 10%) were added. The mixture was stirred at 60 °C for 24 h, cooled, then diluted with water and a few drops of NH_4OH. The brown precipitate was collected, dissolved in hot EtOH, and filtered through a pad of Celite. Upon standing at −10 °C, **L2** crystallized as white needles (0.19 g, 34%) ^1H NMR ($CDCl_3$ 25 °C): δ 7.49 (s, 2H, Ar−H), 7.36−7.34 (m, 6H, Ar−H), 7.20−7.18 (m, 6H, Ar−H, triazole), 5.38 (s, 4H, $-CH_2-$), 2.30 (s, 6H, $-CH_3$). CD_3CN: δ 7.37 (s, 2H, Ar−H), 7.37 (s, 2H, triazole), 7.36−7.35 (m, 6H, Ar−H), 7.33−7.23 (m, 4H, Ar−H), 5.44 (s, 4H, $-CH_2-$), 2.31 (s, 6H, $-CH_3$). MS (APCI positive) Calcd *m*/*z* 420.20, Found 421.20 $(M+H)^+$.

4,4′-(4,5-Difluoro-1,2-phenylene)bis(1-benzyl-1*H*-1,2,3-triazole) (L3). To a stirred solution of 1,2-diethynyl-4,5-difluorobenzene (0.228 g, 1.4 mmol) in 1:1 *t*-BuOH/H_2O (8 mL) were sequentially added NaN_3 (0.20 g, 3.1 mmol), benzyl bromide (0.33 mL, 2.8 mmol), sodium ascorbate (0.056 g, 10%), and $CuSO_4$ (0.28 mL of a 0.5 M solution, 5%). The reaction was stirred 12 h at 60 °C. The mixture was cooled and triturated with dilute aqueous NH_4OH. After decanting the solution phase, the solid was dissolved in CH_2Cl_2 and filtered through a plug of silica gel eluting with a 1:1 mixture of hexanes/ethylacetate (300 mL). The volume was reduced to about 10 mL, and ether (25 mL) was added. After 30 min, a crop of white crystals formed. The crystals were collected by vacuum filtration and washed with cold ether to provide 0.15 g of **L3** in 42% yield. ^1H NMR ($CDCl_3$ 25 °C): δ 7.55 (t, 2H, Ar−H *J* = 9.53), 7.37−7.36 (m, 6H, Ar−H), 7.21−7.20 (m, 6H, Ar−H, triazole), 5.39 (s, 4H, $-CH_2-$). CD_3CN: δ 7.62 (t, 2H, Ar−H *J* = 9.93), 7.46 (s, 2H, triazole), 7.38−7.35 (m, 6H, Ar−H), 7.26−7.25 (m, 4H, Ar−H), 5.47 (s, 4H, $-CH_2-$). **MS** (APCI positive) Calcd *m*/*z* 428.16, Found 429.20 $(M+H)^+$.

General Procedure for Cluster Synthesis. A mixture of **L** and CuI (1:2 for **1**−**3** and 2:3 for **4**) was dissolved in acetonitrile and stirred for 3 h. Diethyl ether was added until a white precipitate began to form, after which a few drops of MeCN were added to prepare a saturated solution. After standing 12−24 h, the products were collected as block crystals.

Complex 1. The general procedure was followed using **L1** (38 mg, 97 μ-mol) and CuI (37 mg, 190 μ-mol). **1** crystallized as white blocks (62 mg, 83% yield). ^1H NMR (CD_3CN, 25 °C): δ 7.67−7.65 (m, 4H, Ar−H), 7.52 (s, 4H, triazole), 7.48−7.46, (m, 4H, Ar−H), 7.38−7.35 (m, 12H, Ar−H), 7.27−7.26 (m, 8H, Ar−H), 5.47 (s, 8H, $-CH_2-$). *Anal.* Calcd for $C_{48}H_{40}Cu_4I_4N_{12}$: C, 37.27; H, 2.61; N, 10.87. Found: C, 37.20; H, 2.27; N, 10.71.

Complex 2. The general procedure was followed using **L2** (38 mg, 90 μ-mol) and CuI (70 mg, 180 μ-mol). Block crystals were obtained (70 mg, 97%). ^1H NMR (CD_3CN, 25 °C): δ 7.64 (s, 4H, triazole), 7.41−7.29 (m, 24H, Ar−H), 5.49 (s, 8H, $-CH_2-$), 2.36 (s, 12H, $-CH_3$). *Anal.* Calcd for $C_{52}H_{48}Cu_4I_4N_{12}$: C, 38.97; H, 3.02; N, 10.49. Found: C, 38.98; H, 2.78; N, 10.36.

Complex 3. The general procedure was followed with **L3** (37 mg, 86 μ-mol) and CuI (33 mg, 173 μ-mol). Two subsequent crops of block crystals were collected for a total of 60 mg (86%). In a separate experiment, about 5% of the resultant crystals were identified as **4**. ^1H NMR (CD_3CN, 25 °C): δ 7.60 (t, 4H, Ar−H, *J* = 12.35), 7.53 (s, 4H, triazole), 7.39−7.35 (m, 12H, Ar−H), 7.27−7.26 (m, 8H, Ar−H), 5.47 (s, 8H, $-CH_2-$). *Anal.* Calcd for $C_{48}H_{36}Cu_4F_4I_4N_{12}$: C, 35.62; H, 2.24; N, 10.38. Found: C, 35.57; H, 1.95; N, 10.27.

Complex 4. The general procedure was used with **L3** (20 mg, 47 μ-mol) and CuI (13 mg, 70 μ-mol). The saturated solution was seeded with about 1 mg of **4** and left to stand at room temperature. After 2 days, additional compound **4** was collected as white microcrystals (22 mg, 66%). ^1H NMR (CD_3CN, 25 °C): δ7.60 (t, 8H, Ar−H, *J* = 12.4), 7.50 (s, 8H, triazole) 7.39−7.35 (m, 24H, Ar−H), 7.28−7.25 (m, 16H, Ar−H), 5.47 (s, 16H, $-CH_2-$). *Anal.* Calcd for $C_{96}H_{72}Cu_6F_8I_6N_{24}-2Et_2O$: C, 41.47; H, 3.09; N, 11.19. Found: C, 41.27; H, 2.84; N, 11.00.

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Supporting Information Available: Variable temperature ^1H NMR spectra, ligand and complex absorption spectra, solid state emission spectra at 77 K, luminescence decay traces at 298 and 77 K, crystallographic data in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.