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Reversible Luminescent Reaction of Amines with Copper(I) Cyanide

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Copper(I) cyanide exposed to various liquid or vapor-phase amines (L) at ambient temperature produces a variety of visible photoluminescence colors via reversible formation of amine
10 **adducts. The adducts show phase matches to authentic $(CuCN)L_n$, $n = 0.75–2.0$, produced by heating CuCN with liquid amine.**

One of the significant on-going challenges in chemistry is the specific and convenient detection of compounds of interest in
15 the environment.[1] Detection of volatile organic compounds (VOCs) via chemical "sniffing" requires an interaction between the VOC and a detector substrate, resulting in a measureable change. Crystal inclusion of VOCs into various d^8 and d^{10} metal complexes has been found to affect
20 intermetallic or other weak interactions, yielding visible color changes.[2] In contrast, direct and reversible VOC-metal bonding is very unusual.[3] Bonding of various nucleophiles to metal centers can serve to modulate substrate photophysics, leading to a wider variety of responses. Herein we report that
25 reversible surface bonding of amines to CuCN gives rise to a remarkable range of visible photoluminescent responses.

We have recently reported the structures and luminescence behavior of copper(I) cyanide networks with bridging diamine ligands.[4] Luminescence emission of CuCN-amine adducts
30 occurs in the visible region, representing a bathochromic shift from the 392 nm emission of CuCN. A DFT examination of $[Cu_n(CN)_{n+1}]^-$ polymeric chains (as models for the infinite chains found in CuCN) showed that the favored excitations are of π-symmetry, corresponding roughly to $d_{Cu}/\pi_{CN} \rightarrow$
35 pCu/π^*_{CN}.[5] Evidence was found for a low-energy triplet excited state with bent geometry at copper. Since bending at copper is an outcome of ligand coordination, this finding is consistent with the lower energy emission associated with CuCN-amine complexes compared to that of CuCN itself.[4a]
40 The observation that CuCN luminescence wavelength is modulated by various incoming ligands suggests that this system might provide the foundation for an amine vapor-sensing device.[1] We have now found that direct addition of amine (L) liquid or diffusion of amine vapor to solid CuCN at
45 room temperature produces a variety of visible colored luminescence responses (see Fig. 1, Pipd = piperidine, Cy = cyclohexyl, Morph = morpholine, Pipz = piperazine, Py = pyridine). While CuCN produces barely visible luminescence emission centered at 392 nm,[4a] CuCN samples exposed to
50 many liquid or vapor amines luminesce at wavelengths shifted well into the visible region.
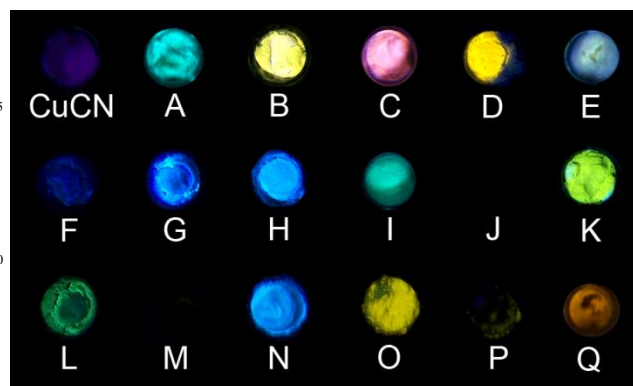
To probe the nature of the interaction between CuCN and

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Fig 1. Luminescence of CuCN + liquid L under 254 nm light
65 at room temperature. A: Pipd B: N-MePipd, C: N-Et-Pipd, D: N-MePyrrolidine, E: Me₂NCy, F: NEt₃, G: N-MeMorph, H: N-MePipz, I: N,N'-Me₂Pipz, J: Py, K: 2-MePy, L: 3-MePy, M: 4-MePy, N: 2-EtPy, O: 3-EtPy, P: 4-EtPy, Q: 4-ᵗBuPy.

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the amines, CuCN suspensions in various neat amines were heated at 70 °C.‡ In most cases the CuCN did not dissolve in the amine, transforming directly to the solid $(CuCN)L_n$ complex. Thermogravimetry (TGA) of the $(CuCN)L_n$ products
75 revealed clean, quantitative loss of amine between 25 and 250 °C, depending on amine volatility. The following complexes were prepared: L = Py ($n = 2$, **1a**; 0.8, **1b**), 2-MePy ($n = 1.5$, **2a**; 1, **2b**), 3-MePy ($n = 1.5$, **3a**; 1, **3b**), 4-MePy ($n = 1.5$, **4**), 2-EtPy ($n = 1$, **5**), 3-EtPy ($n = 1.5$, **6a**; 1, **6b**), 4-EtPy ($n = 1$,
80 **7**), 4-ᵗBuPy ($n = 1.5$, **8**), Pipd ($n = 1.25$, **9**), N-MePipd ($n = 1$, **10**), N-EtPipd ($n = 0.75$, **11**), MeMorph ($n = 1$, **12**), and Me₂NCy ($n = 1$, **13**). For those amines that yielded more than one product (**1a/b**, **2a/b**, **3a/b**, **6a/b**) the more amine-rich species was produced directly, and overnight vacuum
85 treatment converted it cleanly to the less amine-rich species. These conversions are also evident in the TGA traces (see ESI†). Thus in Fig. 2, trace A (**2a**), reflects the conversion:
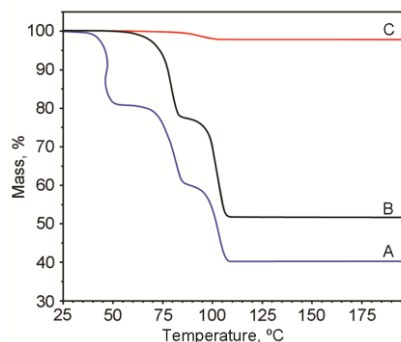

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100 **Fig 2.** TGA traces, A: **2a**, B: **2b**, C: CuCN + 2-MePy vapor.

2a → 2b → (CuCN)₂(2-MePy) → CuCN. Trace B (**2b**) shows reactions identical to steps 2 and 3 of trace A.

In several cases, X-ray structure determinations were carried out on crystals formed during the neat reactions. All of the new CuCN-amine X-ray structures (**2b**, **6a**, **8**, **9**, **12**, and **13**, see Fig. 3), as well as those already known (**1a**, **2a**, **4**, and (CuCN)L, L = NHEt₂, NEt₃, quinoline, 3- and 4-acetylPy, and 2,4,6-collidene),[6] reveal CuCN chains decorated with 1–2 amine ligands per Cu site. In N-MeMorph complex **12**, additional long Cu···O (2.537(3) Å) interactions were found, linking the chains into sheets. In the CuCN chains cyano C/N atom positions are disordered in most cases. The cyano–Cu–cyano angles and Cu–amine bond lengths are relatively large (128.6–154.2°, 2.04–2.25 Å for 3-coordinate Cu and 120.7–139.5°, 2.09–2.26 Å for 4-coordinate Cu). The latter observations are suggestive of relatively weak Cu–amine bonding. In each (CuCN)Lₙ structure, all amine molecules are bonded to copper, with one exception. Complex **8** proved to be (CuCN)(4-ᵗBuPy)•1/2(4-ᵗBuPy), having a half molecule of free 4-ᵗBuPy in the asymmetric unit. Powder diffraction patterns for neat-reaction bulk products **1a**, **2a**, **4**, **8**, **9**, **12**, and **13** showed good agreement to those calculated from the corresponding X-ray structures (see ESI†), while those of **2b** and **6a** did not, possibly reflecting polymorphism.
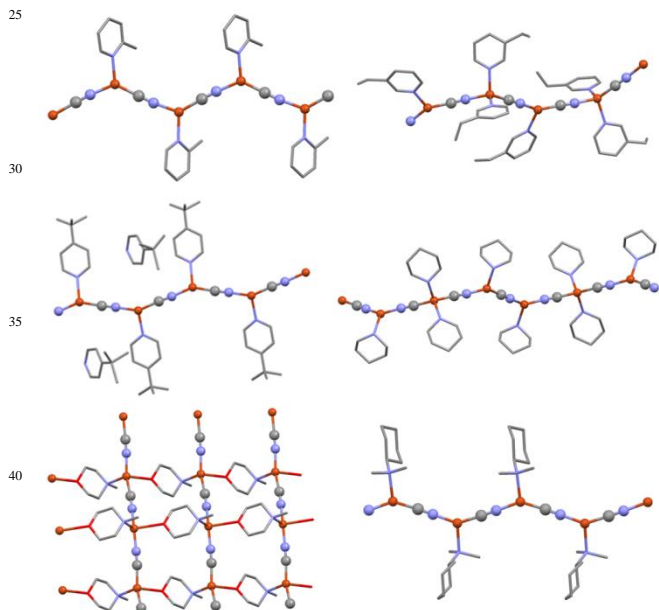

Fig 3. X-ray structures of **2b**, **6a**, **8**, **9**, **12**, and **13**. Copper and cyano atoms shown as spheres. Amine ligands shown as wireframe. Orange = Cu, grey = C, blue = N, red = O. Hydrogen atoms omitted.

Importantly, the luminescence behavior of these authentic (CuCN)Lₙ samples was found to be analogous in color to that observed in amine-exposed CuCN (see Fig. 1 above and S1, ESI†). X-ray powder patterns were collected for samples of CuCN that were exposed to amine vapor or liquid at ambient temperature. Fig. 4 shows the resulting patterns for CuCN exposed to Py vapor (A), CuCN (B), and (CuCN)₅Py₄ (**1b**, C). It can readily be seen that CuCN exposed to Py shows traces
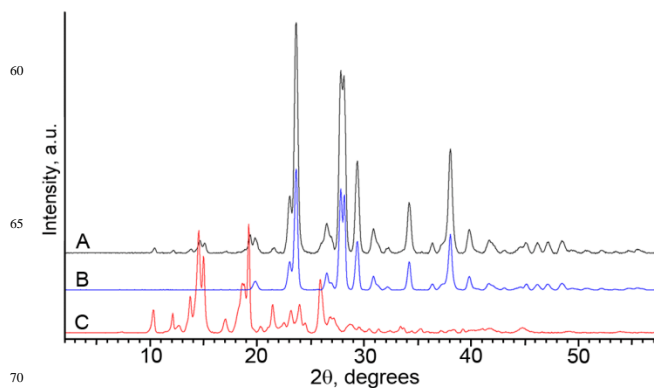

Fig 4. X-ray powder traces, A: CuCN + Py vapor, B: CuCN, C: **1b**.

of the **1b** phase, while remaining mostly CuCN. Under these mild conditions, it seems reasonable to infer that **1b** is formed through partial surface reaction of amine with the CuCN particles whose bulk remains unaffected. TGA further reveals that the amine-exposed CuCN samples indeed lose amine at the same temperature as do the authentic (CuCN)Lₙ compounds. Thus, as illustrated in Fig. 2 above, while (CuCN)Lₙ samples show volatilization of 40–60% of their mass (A and B), the amine-exposed samples lose less than 3% (C). Finally, it is noteworthy that the liquid- or vapor-exposed samples quickly lose their visible luminescence when placed under vacuum, in stark contrast to the authentic (CuCN)Lₙ compounds which only partially lose amine over a period of weeks under vacuum (although **1a**, **2a**, **3a** and **6a** transform over a few hours to **1b**, **2b**, **3b** and **6b**, see above). The overall behavior of the CuCN-amine system is summarized in Scheme 1. The top pathway describes the essentially irreversible formation of authentic (CuCN)Lₙ via the reaction of CuCN in neat heated amine. The bottom pathway traces the reversible surface formation of CuCN-amine adducts through ambient temperature exposure of CuCN to amine liquid or vapor.

Scheme 1
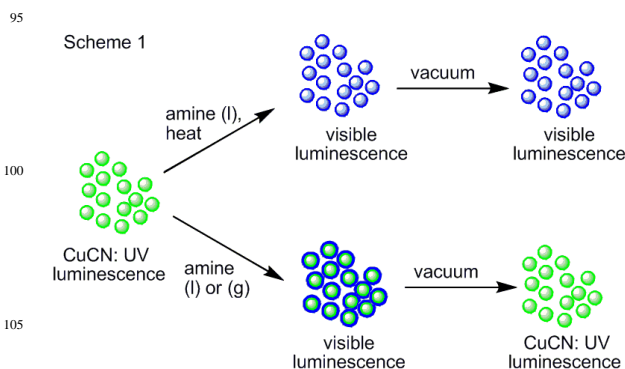
The aromatic amine complexes of CuCN luminesce upon either long (365 nm) or short (254 nm) wavelength excitation, while the aliphatic amine adducts luminesce only upon short wavelength excitation. Initial studies of (CuCN)Lₙ photophysics reveal high energy (HE) blue emission, often accompanied by a less intense low energy (LE) band. For example, two CuCN complexes have been found with 2-MePy: yellow-emitting **2a** and blue-emitting **2b** (Note that evidence of both the yellow and blue emission is evident in

Fig. 1K.) In Fig. 5 the 77 K emission spectra of **2a** show both HE and LE bands, but **2b** exhibits only a HE band. Preliminary studies show emission lifetimes in the microsecond range and quantum yields in the range of 0.5. Importantly, with regard to the luminescence sensor potential of CuCN for amines, we note the diverse emission colors for the CuCN-adducts of chemically similar amines: compare *e.g.* Pipd (Fig. 1A, blue-green), N-MePipd (Fig. 1B, yellow), and N-EtPipd (Fig. 1C, pink) or Py (Fig. 1J, dark), 2-MePy (Fig. 1K, blue/yellow), 3-MePy (Fig. 1L, green), 4-MePy (Fig. 1M, dark), 2-EtPy (Fig. 1N, blue), 3-EtPy (Fig. 1O, yellow), 4-EtPy (Fig. 1P, dark), and 4-^{t}BuPy (Fig. 1Q, orange).
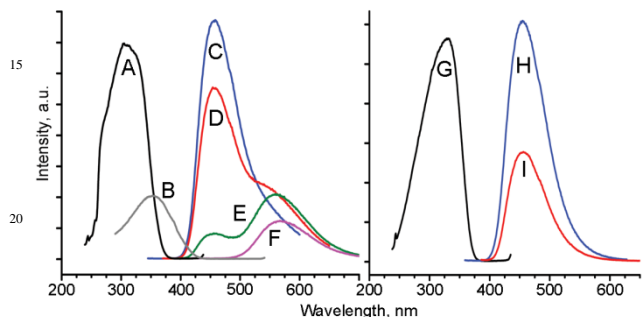

Fig 5. Luminescence spectra (77 K) of **2a**, A–B: excitation (emission λ = 458, 561 nm, respectively), C–F: emission (excitation λ = 315, 340, 365, 420 nm, respectively) and **2b**, G: excitation (emission λ = 452 nm), H–I: emission (excitation λ = 329, 356 nm, respectively).

In conclusion, we report unique and remarkable ligand-dependent luminescence behavior upon the fully-reversible reaction of a number of amines with CuCN. The ligand-induced CuCN emission shift from the UV into the visible region offers the potential for a sniffing detection system for amines or other nucleophilic VOCs. Emission color differences resulting from very similar amines are noted in some cases, offering the potential for independent monitoring of multiple chemically related analytes.

Notes and references

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† Electronic Supplementary Information (ESI) available: [(1) synthetic details, yields, and analyses (2) crystal structure determination tables. (3) TGA traces for all (CuCN)L$_n$ compounds, (4) experimental and calculated X-ray powder patterns for all (CuCN)L$_n$. (5) X-ray Powder Patterns for CuCN + L experiments. (6) luminescence photograph and spectra for authentic (CuCN)L$_n$.]. See DOI: XX.XXXX/XXXXXXX

‡ *Representative Synthesis:* **1a**. Copper(I) cyanide (0.150 g, 1.67 mmol) was suspended in about 5 mL Py in a sealed tube under Ar. The mixture was heated to 70 °C in an oil bath overnight without stirring. After cooling, the suspended solid was collected by means of filtration, washed with diethyl ether, and then air dried for 15 min. A yellow powder was isolated (0.393 g, 1.59 mmol, 94.7%). See ESI for additional synthesis and analytical data. *General Method for Vapor Diffusion Reactions.* 80 mg CuCN powder or pressed pellet (prepared using an IR press) in a 10 mL beaker was placed in a small jar containing about 1-2 mL of liquid amine. After a few min. the CuCN luminescence reflected formation of the surface CuCN-amine phase.

§ *Crystal Data:* All crystals from neat reactions, data collection: T = 100(2) K (except **8**), λ = 1.54178 Å. **2b**: C$_7$H$_7$CuN$_2$, *M* 182.69, monoclinic, *P*2$_1$/c, *a* 10.0593(2), *b* 8.7276(1), *c* 8.9901(2) Å, β 108.709(1)°, V 747.57(2) Å^3, Z 4, 7274 refl., 1273 independ., R$_{int}$ = 0.0362, R1 = 0.0276 (*I* > 2σ(I)), w*R*2 = 0.0791 (all data), CCDC 743728. **6a**: C$_{23}$H$_{27}$Cu$_2$N$_5$, *M* 500.58, orthorhombic, *P*2$_1$2$_1$2$_1$, *a* 8.6557(2), *b* 16.5520(4), *c* 17.2948(4) Å, V 2477.8(1) Å^3, Z 4, 26626 refl., 4362 independ., R$_{int}$ = 0.0362, R1 = 0.0217 (*I* > 2σ(I)), w*R*2 = 0.0574 (all data), Flack = 0.00(2), CCDC 743729. **8**: C$_{29}$H$_{39}$Cu$_2$N$_5$, *M* 584.73, orthorhombic, *F*dd2, *a* 14.9500(2), *b* 35.3082(4), *c* 11.6471(1) Å, V 6148.0(1) Å^3, Z 8, T = 296(2) K, 16270 refl., 2594 independ., R$_{int}$ = 0.0307, R1 = 0.0311 (*I* > 2σ(I)), w*R*2 = 0.0934 (all data), Flack = 0.02(5), CCDC 743727. **9**: C$_{23}$H$_{44}$Cu$_3$N$_7$, *M* 609.27, monoclinic, *C*2/c, *a* 26.3331(2), *b* 5.2292(1), *c* 23.7064(2) Å, β 122.6785(3)°, V 2747.68(6) Å^3, Z 4, 14544 refl., 2413 independ., R$_{int}$ = 0.0294, R1 = 0.0212 (*I* > 2σ(I)), w*R*2 = 0.0594 (all data), CCDC 743724. **12**: C$_6$H$_{11}$CuN$_2$O, *M* 190.71, orthorhombic, *A*ma2, *a* 9.7119(2), *b* 12.2714(3), *c* 6.2836(2) Å, V 748.87(3) Å^3, Z 4, 3902 refl., 661 independ., R$_{int}$ = 0.0379, R1 = 0.0175 (*I* > 2σ(I)), w*R*2 = 0.0406 (all data), Flack = 0.03(4), CCDC 743726. **13**: C$_9$H$_{17}$CuN$_2$, *M* 216.79, orthorhombic, *P*2$_1$2$_1$2$_1$, *a* 6.3145(1), *b* 9.3450(1), *c* 17.4458(3) Å, V 1029.46(3) Å^3, Z 4, 10747 refl., 1814 independ., R$_{int}$ = 0.0285, R1 = 0.0164 (*I* > 2σ(I)), w*R*2 = 0.0440 (all data), Flack = 0.53(2), CCDC 743725. For crystallographic data in CIF or other electronic format, see DOI: XX.XXXX/XXXXXXX Programs: Bruker SMART Apex II and SAINT+ control and integration software,[7] Bruker SHELXTL and WinGX for structure refinement and graphics.[8]

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