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Synthesis, crystal structure and fluorescent property of two-dimensional Cu(I) coordination polymers with cyanide, thiocyanate and triazole bridges

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Abstract

Hydrothermal reaction of CuCN, $K_3[Fe(CN)_6]$ with 4-(6-amino-2-pyridyl)-1,2,4-triazole (apt) afforded a coordination polymer $[Cu_7(CN)_7(apt)_2]_n$ (**1**), while solvothermal reaction of CuSCN with apt in acetonitrile afforded a coordination polymer $[Cu_2(SCN)_2(apt)]_n$ (**2**). Complex **1** shows two-dimensional polymeric network with large hexagonal channels constructing by CuCN chains and tridentate apt ligands. Complex **2** shows two-dimensional polymeric framework assembled by ladder-like $[Cu(SCN)]_n$ chains and bidentate apt ligands, in which thiocyanate acts as a tridentate bridging ligand. Both polymers are thermal stable and strong fluorescent in the solid state.
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1. Introduction

The design, synthesis and crystal engineering of coordination polymers continue to be a quite active research field because of their intriguing structural motifs and potential applications as functional materials [1–3]. The diversity in the structures of coordination polymers was attributed to the selection of metal centers and organic bridging ligands as well as synthetic methods. Recently, there has been a growing interest in copper cyanide coordination polymers incorporating organodiimine and N-heterocycle as co-ligands [4–6]. Cu(I) ion is in favor of trigonal or tetrahedral coordination in the presence of cyanide and aromatic N-donor ligands gives the possibility of promoting the formation of metal-organic frameworks because of the strong coordinating nature of these ligands and their ability to act as connectors between different copper centers [7].

Analogous to cyanide, thiocyanate is a linear anion and a potential worthy bridging ligand in constructing coordination polymer. A few transition metal thiocyanate-containing coordination polymers have been reported which show interesting structural diversity and properties [8–11]. We report herein two interesting Cu(I) coordination polymers formulated as $[Cu_7(CN)_7(apt)_2]_n$ (**1**) and $[Cu_2(SCN)_2(apt)]_n$ (**2**), wherein an aminopyridyl-1,2,4-triazole (apt) is used as connector between Cu(I)-cyanide and Cu(I)-thiocyanate polymeric chains, which is different with previous monodentate or chelating N-donor groups used as co-ligands in preparing copper cyanide coordination polymers.

2. Experimental

2.1. Materials and measurements

All chemicals were of reagent grade and used as received without further purification. Apt was prepared as literature

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method [12]. C, H and N analyses were performed on a Vario EL III elemental analyzer. Infrared spectra were recorded with a Nicolet A370 FT-IR spectrometer in KBr pellets in the 4000–400 cm^{-1} region. TG-DSC analyses were completed on a Netzsch STA 449C thermal analyzer at a heating rate of 10 °C min^{-1} in air. Fluorescent spectra were recorded on a Shimadzu RF-5301 spectrophotometer.

2.2. Synthesis

[Cu$_7$(CN)$_7$(apt)$_2$]$_n$ (1): A mixture of CuCN (0.5 mmol), K$_3$[Fe(CN)$_6$] (0.5 mmol), apt (0.5 mmol), and water (10 mL) was sealed in a 15 mL Teflon-lined stainless-steel reactor, which was heated at 180 °C for 24 h under autogenous pressure. Upon cooling to room temperature at a rate of 10 °C h^{-1}, colorless block crystals suitable for X-ray structure study were obtained in 65% yield based on Cu. Anal. Found: C, 26.57; H, 1.50; N, 24.82. Calc. for C$_{21}$H$_{14}$Cu$_7$N$_{17}$: C, 26.51; H, 1.48; N, 25.03. IR (KBr, cm^{-1}): 3330 (m), 3129 (m), 2118 (s), 1617 (m), 1572 (w), 1531 (s), 1459 (s), 1246 (m), 786 (m), 718 (w).

[Cu$_2$(SCN)$_2$(apt)]$_n$ (2): A mixture of CuSCN (0.5 mmol), apt (0.5 mmol), and acetonitrile (5 mL) was sealed in a 15 mL Teflon-lined stainless-steel reactor, which was heated at 140 °C for 72 h under autogenous pressure. Upon cooling to room temperature at a rate of 10 °C h^{-1}, yellow rod-like crystals suitable for X-ray structure study were obtained in 40% yield based on Cu. Anal. Found: C, 27.05; H, 1.76; N, 24.11. Calc. for C$_9$H$_7$Cu$_2$N$_7$S$_2$: C, 26.73; H, 1.74; N, 24.23. IR (KBr, cm^{-1}): 3422 (m), 3311 (m), 3319 (m), 2138 (s), 2119 (s), 1620 (s), 1570 (w), 1529 (s), 1451 (s), 1247 (m), 788 (m), 615 (w).

2.3. Crystal structure determination

Single crystal X-ray diffraction measurements for complexes 1 and 2 were carried out on a Bruker Smart Apex-II CCD diffractometer with graphite monochromatic Mo Kα radiation (λ = 0.71073 Å) using both φ and ω-scan modes at 273(2) K. Data reductions were made with SAINT package. Absorption corrections were performed using SADABS program. The structures were solved by direct method with SHELXS-97 program and refined on F^2 by full-matrix least squares techniques with SHELXL-97 program [13]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were treated by mixture of independent and constrained refinement. The crystal data and structure refinement results are summarized in Table 1. The selected bond lengths and angles are given in Table 2.

3. Results and discussion

3.1. Description of crystal structures

X–ray structure analysis revealed that complex 1 assumes a two-dimensional polymeric network constructing by CuCN chains and tridentate apt ligands. As shown in Fig. 1, the molecular structure of [Cu$_7$(CN)$_7$(apt)$_2$]$_n$ is central symmetric, and the center locates at Cu(4) atom. Each asymmetric structure unit contains four crystallographically independent copper(I) atoms. Cu(1) atom

Table 1
Crystallographic data and structure refinement for 1 and 2

	Complex 1	Complex 2
Empirical formula	C$_{21}$H$_{14}$Cu$_7$N$_{17}$	C$_9$H$_7$Cu$_2$N$_7$S$_2$
Formula weight	951.27	404.42
Crystal system	Triclinic	Monoclinic
Space group	P1	P2$_1$
a (Å)	8.2529(11)	5.7255(9)
b (Å)	9.7052(13)	12.1360(19)
c (Å)	10.3996(14)	9.3084(14)
α (°)	67.298(2)	90
β (°)	69.518(2)	94.792(2)
γ (°)	79.187(2)	90
V (Å^3)	718.52(17)	644.53(17)
Z	1	2
Dc (Mg m^{-3})	2.198	2.084
Absorption coefficient (mm^{-1})	5.129	3.621
F(000)	463	400
Crystal size (mm^3)	0.40 × 0.30 × 0.10	0.40 × 0.30 × 0.30
Measured reflections	3727	3360
Independent reflections	2501 [R_{int} = 0.0405]	2168 [R_{int} = 0.0170]
Data/restraints/parameters	2501/0/210	2168/1/181
Goodness-of fit on F^2	1.093	1.092
R [$I > 2\sigma(I)$]	R_1 = 0.0526, wR_2 = 0.1474	R_1 = 0.0242, wR_2 = 0.0515
R (all data)	R_1 = 0.0594, wR_2 = 0.1523	R_1 = 0.0272, wR_2 = 0.0531
Largest diff. peak and hole	0.772 and −1.043 e Å^{-3}	0.236 and −0.241 e Å^{-3}

Table 2
Selected bond lengths (Å) and angles (°) for **1** and **2**

Complex **1**

Cu(1)–N(1) 2.052(4)	Cu(2)–N(9) 1.905(5)
Cu(1)–N(2) 2.007(4)	Cu(2)–C(9) 1.905(5)
Cu(1)–N(5) 2.434(5)	Cu(3)–N(7) 1.865(6)
Cu(1)–N(6) 1.909(7)	Cu(3)–C(8) 1.834(5)
Cu(2)–N(8) 1.945(6)	Cu(4)–C(10) 1.842(5)
N(1)–Cu(1)–N(2) 104.76(16)	N(5)–Cu(1)–N(6) 108.5(2)
N(1)–Cu(1)–N(6) 117.2(2)	C(9)–Cu(2)–N(9) 120.1(2)
N(2)–Cu(1)–N(6) 130.4(2)	C(9)–Cu(2)–N(8) 123.0(2)
N(5)–Cu(1)–N(2) 93.32(16)	C(8)–Cu(3)–N(7) 177.1(3)

Complex **2**

Cu(1)–S(1) 2.4279(11)	Cu(2)–S(1) 2.8068(11)
Cu(1)–S(2) 2.6236(11)	Cu(2)–S(2) 2.3378(11)
Cu(1)–N(4) 1.982(3)	Cu(2)–N(5) 1.970(3)
Cu(1)–N(6) 1.906(3)	Cu(2)–N(7) 1.907(3)
Cu(1)–S(1)–Cu(2) 69.53(3)	Cu(1)–S(2)–Cu(2) 74.19(3)
S(1)–Cu(1)–S(2) 109.74(4)	S(2)–Cu(2)–S(1) 106.55(4)
N(6)–Cu(1)–N(4) 143.76(13)	N(7)–Cu(2)–N(5) 134.66(13)
N(6)–Cu(1)–S(1) 103.88(9)	N(7)–Cu(2)–S(2) 105.97(9)

adopts a distorted trigonal-pyramidal geometry, coordinated by four N atoms from two triazoles, one amino group and one cyanide group. The basal plane is constructed by the coordination of N(1), N(2) and N(6). The bond lengths of Cu(1)–N(1), Cu(1)–N(2) and Cu(1)–N(6) are 2.052(4), 2.007(4), 1.909(7) Å, respectively, while the bond angles of N(1)–Cu(1)–N(2), N(1)–Cu(1)–N(6) and N(2)–Cu(1)–N(6) are 104.76(16), 117.2(2), 130.4(2)°, respectively. The amino N(5) atom occupies the axial position with the Cu(1)–N(5) bond distance of 2.434(5) Å and the N(5)–Cu(1)–N(1) bond angle of 93.38(18)°. This bond distance is significantly longer than those of other three Cu–N bonds, indicating a weak coordination behavior between amino group of apt and Cu(1) atom. Cu(2) atom is planar trigonally coordinated by three cyanide bridges. The bond angles of C(9)–Cu(2)–N(9), C(9)–Cu(2)–N(8) and N(9)–Cu(2)–N(8) are 120.1(2), 123.0(2), 116.6(2)°, respectively. Cu(3) and Cu(4) atoms are typically two-coordinated by bridging cyanide groups in linear fashion. Bond angles C(8)–Cu(3)–N(7) and C10–Cu(4)–C(10A) are 177.1(3), 179.998(1)°, respectively.

In structure of **1**, all cyanide groups play μ_2-bridge. The structure can be described as that both $Cu_3(CN)_3$ pieces are linked to central Cu(4) atom through a cyanide group to form a $Cu_7(CN)_7$ unit, which is further polymerized to form $[Cu_7(CN)_7]_n$ zigzag chain. These $[Cu_7(CN)_7]_n$ chains
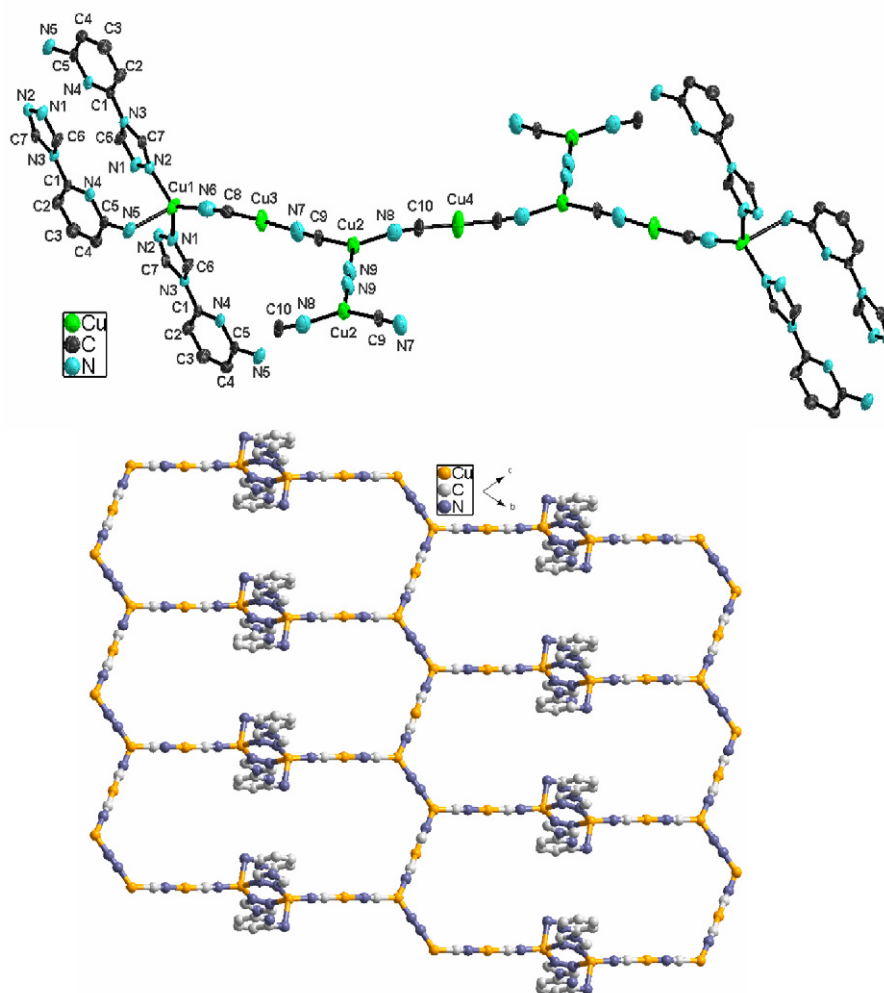

Fig. 1. Views of asymmetric structural unit and 2D polymeric network of **1**.

are connected by apt via its two triazole nitrogen atoms N(1) and N(2), leading to the formation of a 2D polymeric network with large hexagonal channels. In previous reports, monodentate and chelating N-donor ligands were frequently used as co-ligands in preparing copper cyanide coordination polymers. Such designs often led to the formation of one-dimensional chains [14,15]. The complex **1** is exampled that 2D or 3D copper cyanide coordination polymers can be expected when multidentate bridging ligand is selected as co-ligand.

The complex **2** exhibits two-dimensional polymeric structure as shown in Fig. 2. The asymmetric structure unit consists of two crystallographically independent copper(I) atoms, one apt, and two thiocyanate ligands. Both copper(I) atoms adopt distorted tetrahedral geometry, coordinated by one nitrogen atom and two bridging sulfur atoms from three μ_3-thiocyanate groups, and one nitrogen atom from the triazole group of apt. The bond lengths of Cu(1)–S(1) and Cu(1)–S(2) are 2.4279(11), 2.6236(11) Å, while those of Cu(2)–S(1) and Cu(2)–S(2) are 2.8068(11), 2.3378(11) Å, respectively. Cu(1) and Cu(2) atoms are linked by two bridging S atoms to form a Cu_2S_2 dimmer. The bond angles of Cu(1)–S(1)–Cu(2) and Cu(1)–S(2)–Cu(2) are 69.53(3), 74.19(3)°, while S(1)–Cu(1)–S(2) and S(1)–Cu(2)–S(2) are 109.74(4), 106.55(4)°, respectively. Such Cu_2S_2 dimmers are further linked by linear thiocyanate groups to form ladder-like $[Cu(SCN)]_n$ chains. The bond lengths of Cu(1)–N(6) and Cu(2)–N(7) are 1.906(3), 1.907(3) Å, respectively. Generally, thiocyanate acts as counter anion or monodentate ligand in metal complexes [16]. Thiocyanate acting as tridentate ligand is rarely observed and only found in copper(I) complexes [8,9].

On the other hand, apt acts as bidentate ligand in complex **2**. Amino nitrogen atom of apt is uncoordinated, which is different with the structure of complex **1**. The triazole group of apt binds to two copper(I) centers between two adjacent $[Cu(SCN)]_n$ ladder-like chains, which extends the structure to a two-dimensional polymeric framework. Such structure is rare in previous reports. Using apt as ligand, only tetranuclear Ag(I) complex is prepared and structurally characterized to date [17].

3.2. Thermal stability and fluorescent properties

Thermal analyses for complexes **1** and **2** were performed in the temperature range of 20–800 °C. As shown in Fig. 3, the complexes **1** and **2** are stable up to 250 °C without weight-loss. Complex **1** decomposed rapidly near 300 °C with 5.70% weight-loss, and then decomposed continuously to 800 °C with 36.89% weight-loss. The final residue is CuO (found: 57.41%, calc.: 58.53%). Complex **2** showed an endothermic maximum at 255.7 °C without weight-loss indicated a phase transfer process happened. This phenomenon is also observed in $[Cu_3(CN)_3(phen)]_n$ complex [5]. In the temperature range of 270–800 °C, complex **2** decomposed successively with the final 56.01% residue left, which may be a mixture of CuO and $CuSO_4$ [18].

In the solid state, complexes **1** and **2** show strong fluorescent emission bands centered at 387 and 525 nm, respectively, under photoexcitation of 356 nm (Fig. 4). Generally, metal-to-ligand charge transfer (MLCT) is the most common assignment for the fluorescent emission of copper(I) cyanide complexes [6]. The fluorescent emission of complex **1** is assigned to metal-to-ligand charge transfer where the electron is transferred from Cu(I) ion to π^* orbital of cyanide group [19]. The emission band of complex **2** is obviously different with the one of complex **1**. This phenomenon is observed in several copper(I) thiocyanate coordination polymers such as $[Cu_2(SCN)_2(dmpz)]_n$ (582 nm) and $[Cu_2(SCN)_2(dps)]_n$ (538 nm), and the most possible assignment for these emissions originates from ligand-to-metal charge transfer (LMCT) [8,9].
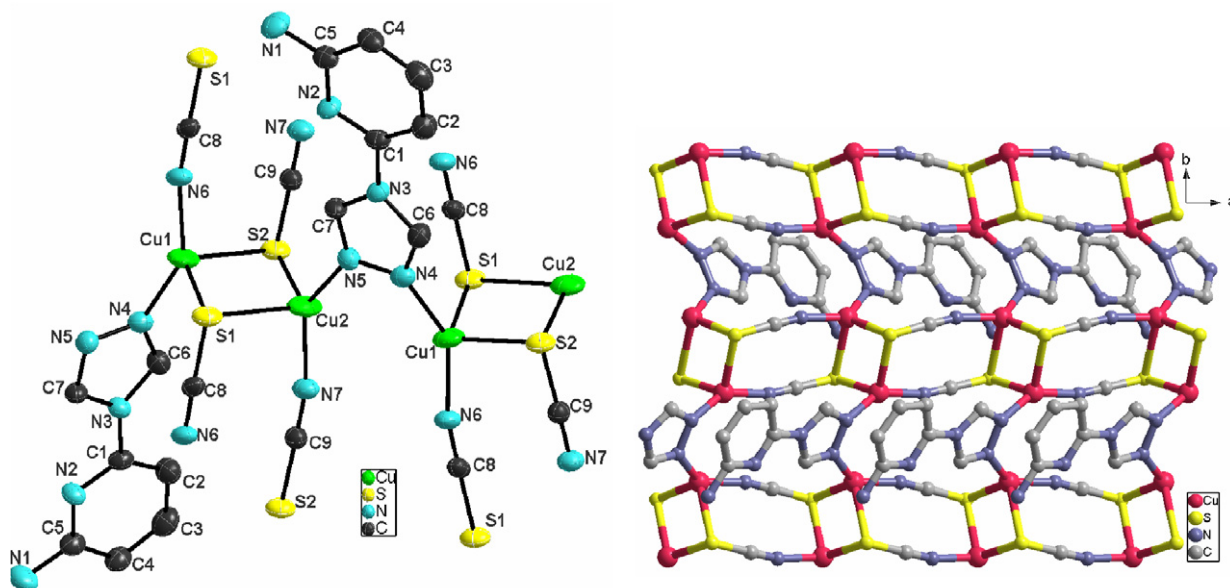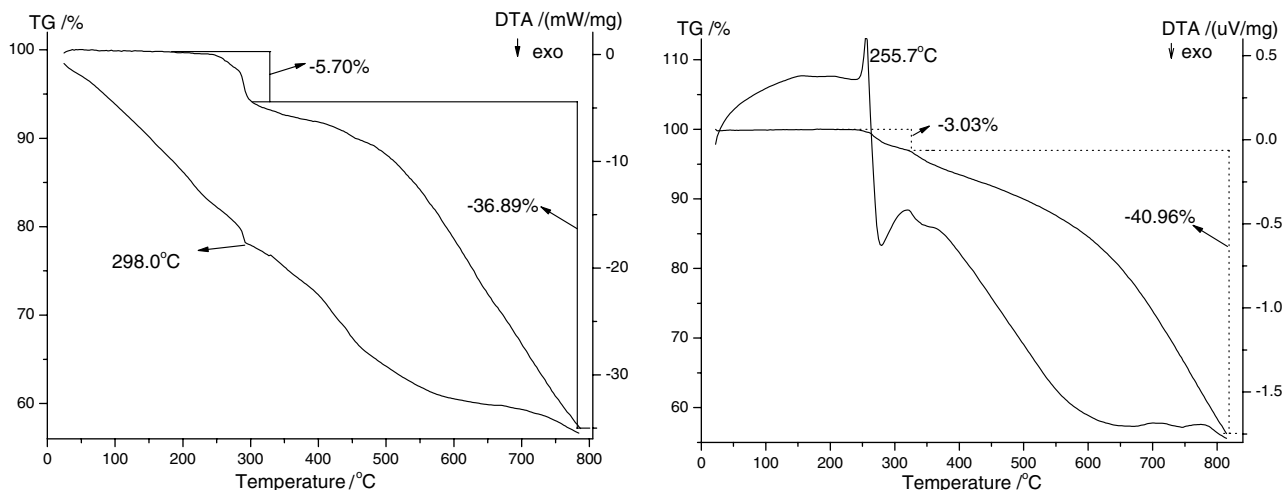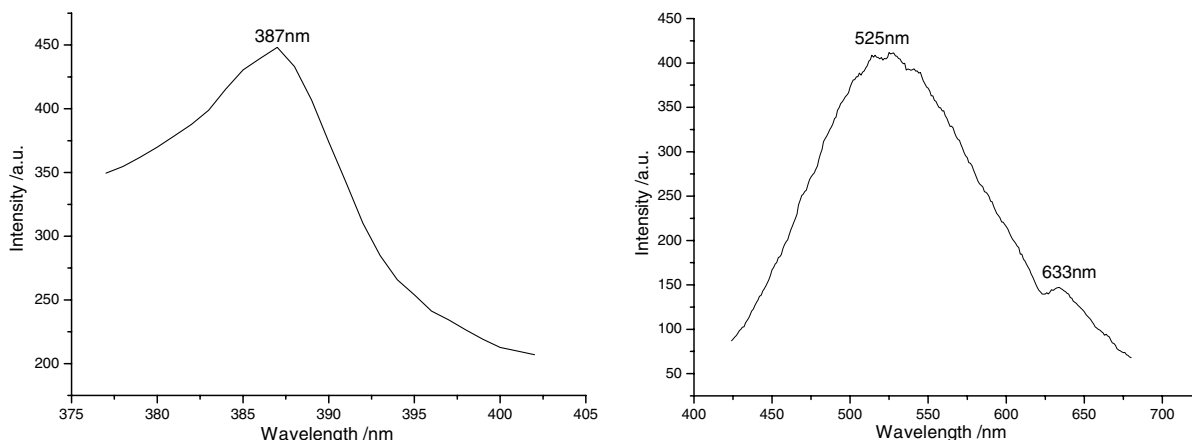

Fig. 2. Views of asymmetric structural unit and 2D polymeric network of **2**.

Fig. 3. Thermal analysis curves of **1** and **2**.

Fig. 4. Fluorescent emission spectra of **1** (left) and **2** (right).

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC-619857 for complex **1** and CCDC-636040 for complex **2**. Copies of the data can be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2IEZ, UK. E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

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