Electronic Supplementary Information (ESI)

Novel 2D coordination network built from hexacopper(I)-iodide clusters and cagelike aminophosphine blocks for reversible "turn-on" sensing of aniline

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[d] *†Electronic Supplementary Information (ESI) available: Additional emission spectra, sensing experiment pictures, and additional experimental data. See DOI: 10.1039/x0xx00000x*

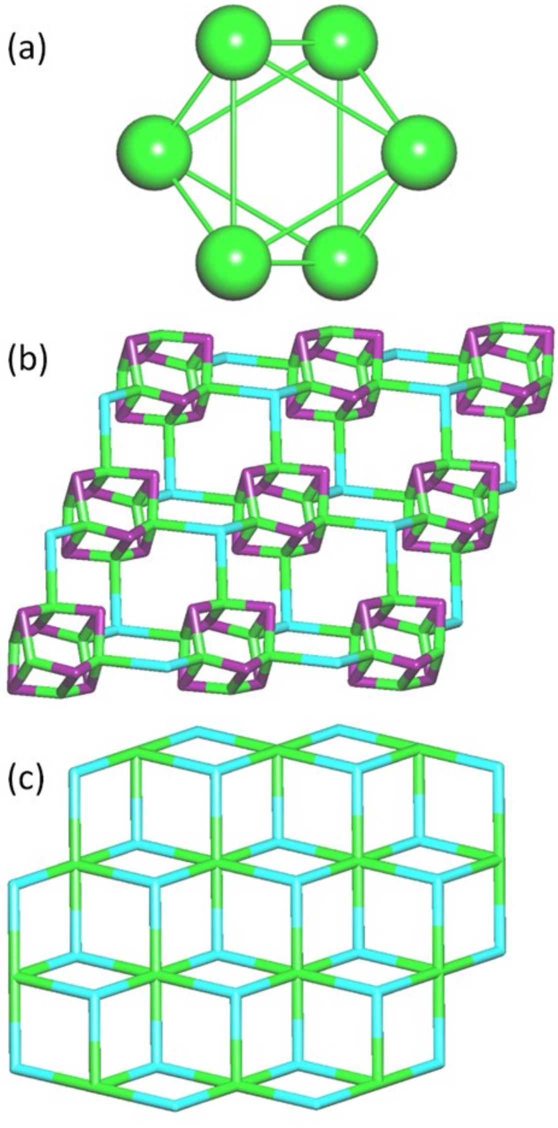

Figure S1. Topological fragments of **1**. (a) Simplified graph representation of the $[Cu_6(\mu_3\text{-}I)_6]$ SBU showing a uninodal 4-connected motif with the **4M6-1** topology. (b) Underlying trinodal 3,3,4-connected 2D net with the unique topology and point symbol of $(4^2.6.8^3)_3(4^2.6)^3(8^3)$. (c) Further simplified binodal 3,6-connected net with the **kgd** topology obtained after treating the $[Cu_6(\mu_3\text{-}I)_6]$ units as cluster nodes. Further details: (b, c) rotated views along the c axis; color codes: centroids of Cu or $[Cu_6(\mu_3\text{-}I)_6]$ nodes (green), μ_3-I nodes (purple), centroids of μ_3-PTA=O nodes (cyan).

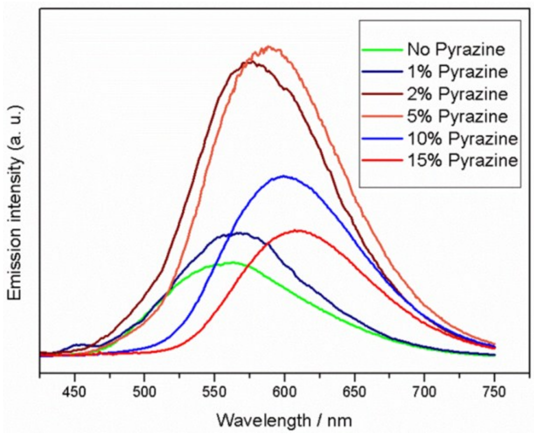

Figure S2. Emission spectra of the acetonitrile solution of **1** (5×10^{-4} M) at 77 K upon addition of various amounts of pyrazine (0–15 vol.%). λ_{ex} =300 nm.

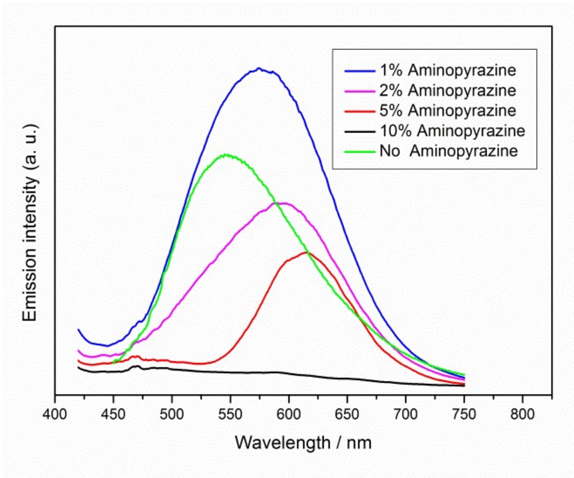

Figure S3. Emission spectra of the acetonitrile solution of **1** (5×10^{-4}M) at 77 K upon addition of various amounts of 2-aminopyrazine (0–15 vol.%). λ_{ex} = 300 nm.

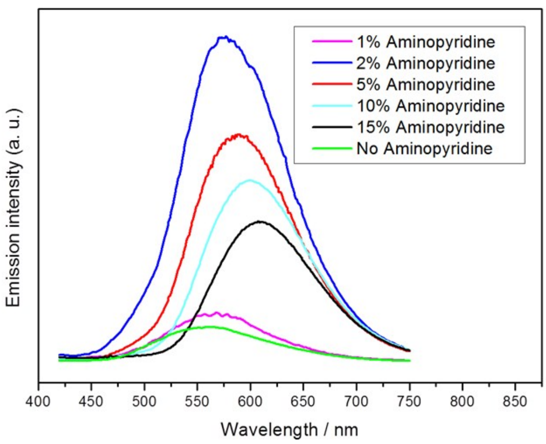

Figure S4. Emission spectra of the acetonitrile solution of **1** (5×10^{-4} M) at 77 K upon addition of various amounts of 2-aminopyridine (0–15 vol.%). λ_{ex} = 300 nm.

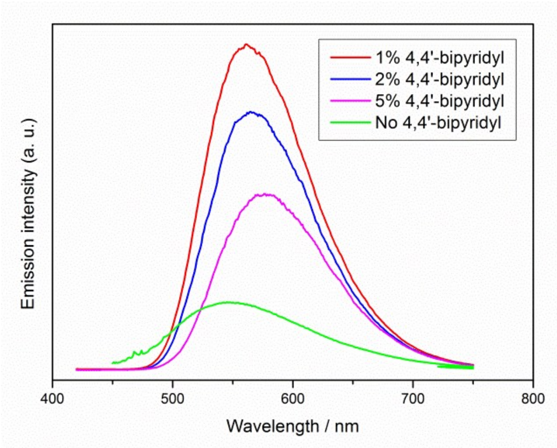

Figure S5. Emission spectra of the acetonitrile solution of **1** (5×10^{-4} M) at 77 K upon addition of various amounts of 4,4'-bipyridyl (0–5 vol.%). λ_{ex} = 300 nm.

Sensing experiment and preparation of 0.26 and 0.065 ppb aniline in vapor phase

A 0.1 M solution of aniline in dry MeCN was used for all luminescence measurements and sensing experiments. The atmosphere of gaseous aniline (0.26–0.065 ppb) was prepared by heating an appropriate amount of aniline solution in a sealed quartz beaker (150 mL). The aniline vapor concentrations ware calculated according to the following equation[S1]:

$$C = \frac{\omega \rho V}{V_0}$$

C: aniline concentration in ppb, ω: mass fraction of aniline solution, ρ: density of aniline solution (g/cm^3), V: volume of aniline solution (μL), V_0: system volume (L).

S1. C-W. Zhao, J-P. Ma, Q-K. Liu, X-R Wang, Y. Liu, J. Yang,J.-S. Yang, Y-B. Dong, *Chem Commun.* 2016, **52**, 5238.

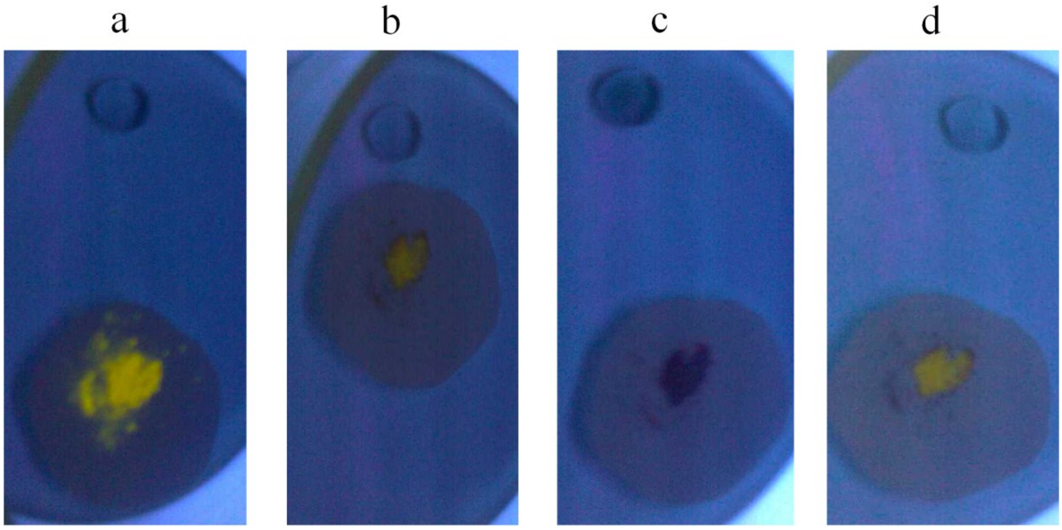

Figure S6. Time-dependent evolution of the photographic images of **1** (5×10^{-4} M) exposed to the aniline solution (5 μL) at room temperature under UV lamp: (a) 0 min, (b) 5 min, (c) 14 min, and (d) during slow evaporation of aniline in air after sensing experiment.

Table S1. Luminescence lifetimes of **1** at 77 K before and after addition of aniline (λ_{ex} = 300 nm).[a]

	1	**1** with aniline[b]
τ_1	7.95 (52.28)	5.31 (43.12)
τ_2	18.58 (42.38	16.22 (49.56)
τ_3	56.08 (5.34)	41.83 (7.32)

[a] In parentheses the percentage contribution of the lifetime to the total emission is indicated.

[b] 0.1 M aniline solution in MeCN, 5×10^{-4} M solution of **1** in MeCN.

Table S2. Crystal Data.

	1
empirical formula	$C_6H_{12}Cu_3I_3N_3OP$
fw	744.48
temp (K)	123(2)
λ(Å)	1.54184 Å
cryst syst	Monoclinic
space group	C2/m
a (Å)	16.9600(9)
b (Å)	9.8296(5)
c (Å)	9.9981(9)
β (°)	101.847(7)
V (Å^3)	1631.29(19)
Z	4
ρ_{calc} (Mg/m^3)	3.031
μ(Kα) (mm^{-1})	49.963
No. reflns.	7592
Unique reflns.	1802
GOOF (F^2)	1.050
R_{int}	0.0729
R1[a] ($I \geq 2\sigma$)	0.0814
wR2[b] ($I \geq 2\sigma$)	0.2130

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.