Supporting information:

A semiconducting microporous framework of $Cd_6Ag_4(SPh)_{16}$ clusters interlinked using rigid and conjugated bipyridines**

Chao Xu, Niklas Hedin*, Hua-Tian Shi, Qian-Feng Zhang*

Table of contents in supporting information

General method

Preparation of $[Cd_6Ag_4(SPh)_{16}(DMF)_4]$ (1)

Preparation of $\{[Cd_6Ag_4(SPh)_{16}(bpe)_2]\}_n$ (2)

X-ray Crystallography

Table of crystal data, data collection and structure refinement parameters

Fig. S1 Energy-dispersive X-ray spectroscopy (EDS) of $Cd_6Ag_4(SPh)_{16}(DMF)_4$ and $\{[Cd_6Ag_4(SPh)_{16}](bpe)_2\}_n$.

Fig. S2 Three possible arrangement of inner Cd and Ag atoms in the cluster of $Cd_6Ag_4(SPh)_{16}(DMF)_4$.

Fig. S3 Comparision of expreimental and simulated powder X-ray diffraction (XRD)of $\{[Cd_6Ag_4(SPh)_{16}](bpe)_2\}_{n.}$

Fig. S4 Comparisons of powder X–ray diffraction patterns of standard hexagonal CdS, cubic Ag and hybrid crystals of CdS-Ag prepared from pyrolysis of $Cd_6Ag_4(SPh)_{16}(DMF)_4$.

Fig. S5 Infrared spectrum of $\{[Cd_6Ag_4(SPh)_{16}](bpe)_2\}_n$, $Cd_6Ag_4(SPh)_{16}(DMF)_4$ and *trans*-1,2-Bis(4-pyridyl)ethylene (bpe).

Fig. S6 Thermal gravimetric analysis (TGA) curve of $Cd_6Ag_4(SPh)_{16}(DMF)_4$ and $\{[Cd_6Ag_4(SPh)_{16}](bpe)_2\}_n$.

General method

The solvents were purified by conventional methods and degassed prior to use. $Cd(SPh)_2$ was prepared by the literature procedure.[1] PhSH, $AgNO_3$, and *trans*-1,2-bis(4-pyridyl)ethylene (bpe) were purchased from Sigma-Aldrich and used without further purification. All elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer. Thermal gravimetric analysis (TGA) data were recorded on a TGA-Perkin Elmer TGA 7 analyzer. Fourier transform infrared (FT-IR) spectra were recorded using a Varian 670-IR FT-IR spectrometer equipped with an attenuated total reflectance (ATR) accessory. UV/vis absorption and solid-state reflectance spectra were recorded on a Perkin Elmer Lambda 19 UV/VIS/NIR spectrometer. $BaSO_4$ as 100% reflectance references was used for the solid state reflectance spectra detecting. The fluorescent spectra were recorded on a Varian Cary Eclipse Fluorescence Spectrophotometer. Energy-dispersive X-ray spectroscopy (EDS) analysis was carried out on a JEOL JSM-7401F scanning electron microscope (SEM).CO_2 adsorption isotherm was recorded on a Micromeritics ASAP2020 analyzer; the sample was soaked in CH_2Cl_2 for 3 days and then degassed at 100°C under a condition of dynamic vacuum for 12 h before the measurement.

Preparation of $Cd_6Ag_4(SPh)_{16}(DMF)_4$ (1)

$AgNO_3$ (51 mg, 0.3 mmol) was added to a solution of $Cd(SPh)_2$ (198 mg, 0.6 mmol) in 5 mL DMF with stirring at room temperature. After the mixture stirred overnight, a small amount of white precipitate formed. The precipitate was removed by filtration to give a colorless filtrate. Colorless crystals of 1 were obtained from slow evaporation of the filtrate. Yield: 135 mg (56 % based on $Cd(SPh)_2$). Anal. Calcd. for $C_{108}H_{108}N_4O_4S_{16}Ag_4Cd_6$: C, 41.24; H, 3.46; N, 1.78. Found: C, 41.17; H, 3.54; N, 1.76. IR (cm^{-1}): ν (C–H) 3054 (m), ν (C=O) 1640 (s), ν (C–S) 685 (s).

Preparation of $\{[Cd_6Ag_4(SPh)_{16}](bpe)_2\}_n$ (2)

To a colorless solution of **1** (97 mg, 0.03 mmol) in 3 mL DMF was added *trans-1,*2-bis(4-pyridyl)ethylene (18 mg, 0.1 mmol) with stirring. A yellow mixture was obtained after stirring overnight and then filtered. The yellow filtrate was evaporated at room temperature. Large yellow crystals of **2** were obtained after one week. Yield: 72 mg (65 % based on **1**). Anal. Calcd. for $C_{122}H_{100}N_4S_{16}Ag_4Cd_6$: C, 45.21; H, 3.11; N, 1.73. Found: C, 45.02; H, 3.24; N, 1.72. IR (cm^{-1}): ν (C–H) 3055 (m), ν (C=C) 1603 (s), ν (C–S) 684 (s).

[1] I. G. Dance, R. G. Garbutt, D. C. Carig, M. L. Scudder, *Inorg. Chem*. **1987**, *26*, 4057-4064.

Photocatalysis measurement

The photocatalytic activities of **1** and **2** were evaluated by testing their behavior of degradation of Rhodamine B (RhB) aqueous solution under visible light illumination. A 500 W Xenon lamp was used as a light source. Typically, 20 mg of the catalyst and 10 mL of RhB aqueous solution (4.18 M, 20 mg/L) was mixed in a 20 mL glass vessel. The mixture was stirred for 1 h in dark to afford a homogeneous phase before the analysis. Then the vessel was irradiated by the light, a recycling water bath was used to keep the reaction temperature. At different intervals of 30 min, 60 min, 90 min, 120 min, 180 min, 1 mL of the mixture was withdrawn from the mother solution and the dispersed powder was removed by centrifugation. The concentration of RhB in the sample solution was analyzed by UV/vis spectroscopy.

X-ray Crystallography

Suitable single crystals of clusters **1** (0.07× 0.10× 0.34 mm) and **2** (0.22× 0.40× 0.41 mm) were selected and mounted on a Bruker SMART Apex 2K CCD diffractometer with graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å) at 296 K. Data were measured using ω scans of 0.5° per frame, such that a hemisphere was collected. Cell parameters were retrieved using SMART software and refined using SAINT [2] on all observed reflections. Data reduction was performed with SAINT software which corrects for Lorentz polarization and decay. Absorption corrections were applied using SADABS.[3] Structure was solved by direct methods using SHELXS[4,5] and refined by least squares on F^2 (SHELXL). Cadmium, silver and sulfur atoms were described anisotropically. All carbon, nitrogen and oxygen were refined isotropically for **1** and **2**. In **1**, the largest peak in the final difference map had a height of 1.115 e Å^{-3} and is in the vicinity of cadmium atom. **2** include disordered solvent molecules of DMF. We employed PLATON/SQUEEZE [6] to remove the electron density of disordered solvent molecules and calculate approximately solvent accessible void space in the unit cell. Hydrogen atoms were placed in idealized positions and refined employing a riding model with thermal parameters 1.2× or 1.5× those of the bonded carbon atoms.

[2] Bruker Analytical X-ray Instruments Inc. SMART and SAINT+ for Windows NT (Version 6.02a), Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA (**1998**).

[3] G. M. Sheldrick. SADABS, University of Göttingen, Germany (**1996**).

[4] G. M. Sheldrick. SHELXTL Software Reference Manual (Version 5.1), Bruker AXS Inc., Madison, Wisconsin, USA (**1997**).

[5] G.M. Sheldrick. *Acta Crystallogr.*, **2008**, *A64*, 112-122.

[6] A. L. Spek, *Acta Cryst.,* **2009**, *D65*, 148-155

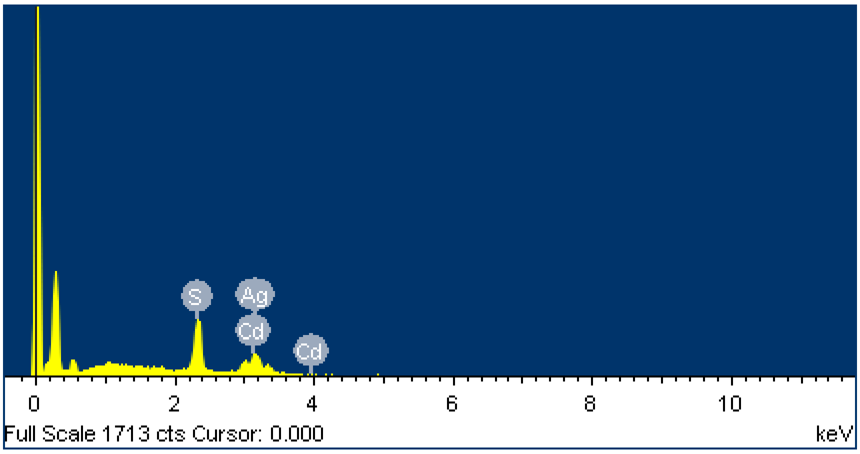
Table S1. Crystal data, data collection and structure refinement parameters

compound	**1**	**2**
empirical formula	$C_{108}H_{108}N_4O_4S_{16}Ag_4Cd_6$	$C_{65.63}H_{63.13}O_{1.88}N_{3.88}S_8Ag_2Cd_3$
formula weight	3144.82	1745.49
crystal system	monoclinic	tetragonal
space group	$P2_1/c$	$I4_1/a$
unit cell dimension, Å / °	a = 20.4501(4), α = 90.00	a = 18.3203(2), α = 90.00
	b = 16.8939(3), β = 97.659(1)	b = 18.3203(2), β = 90.00
	c = 36.0972(8), γ = 90.00	c = 45.4431(11), γ = 120.00
volume, Å^3	12359.7(4)	15252.2(4)
Z	4	8
density (calculated), Mg · m^{-3}	1.690	1.520
absorption coefficient, mm^{-1}	1.947	1.586
F(000)	6192	6920
crystal size, mm	0.07× 0.10× 0.34	0.22 × 0.40× 0.41
crystal color	Colorless	Yellow
temperature, K	296(2)	296(2)
wavelength (Mo Kα), Å	0.71073	0.71073
scan type	ω	ω
reflections collected	103188	44353
independent reflections	21734 (R_{int} = 10.38%)	6539 (R_{int} = 7.69%)
observed reflections	9051 ($I > 2.0\sigma(I)$)	2880 ($I > 2.0\sigma(I)$)
data/restraints/parameters	21734/1139/1287	6539/286/327
weight scheme ϖ[a]	$1/[\sigma^2(F_o)^2 + 0.0512P^2 + 0.2528P]$	$1/[\sigma^2(F_o)^2 + 0.0320P^2 + 44.2200P]$
goodness-of-fit on F^2	0.936	1.045
final R* indices [$I>2\sigma(I)$] [b,c]	$R1$= 0.0681, w$R2$= 0.1661	$R1$= 0.0551, w$R2$= 0.1421
R indices (all data)	$R1$= 0.1614, w$R2$= 0.2002	$R1$= 0.1149, w$R2$= 0.1570
largest diff. peak and hole, e·Å^{-3}	1.115 and –1.269	0.754 and –0.457

[a] $P = (F_o^2 + 2F_c^2)/3$.

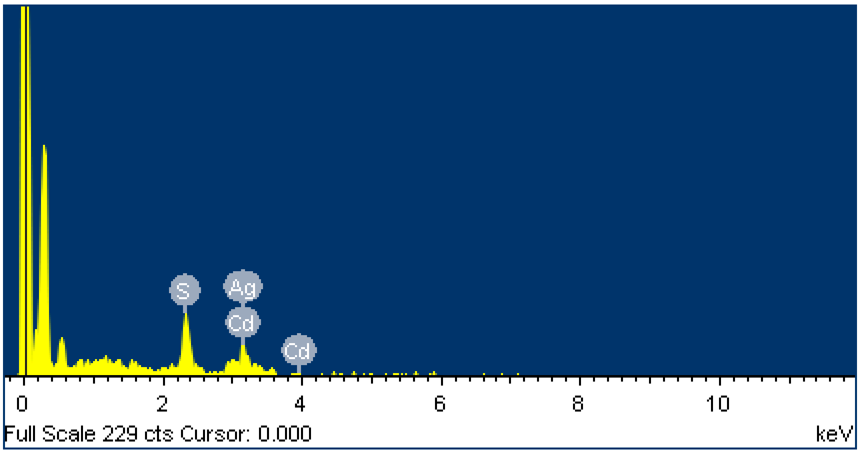
[b] $R1 = ||F_o| - |F_c||/|F_o|$.

[c] $wR2 = [w(|F_o^2| - |F_c^2|)^2/w|F_o^2|^2]^{1/2}$.



Element	Weight%	Atomic%
S K	31.01	60.81
Ag L	25.83	15.05
Cd L	43.16	24.14
Totals	100.00	

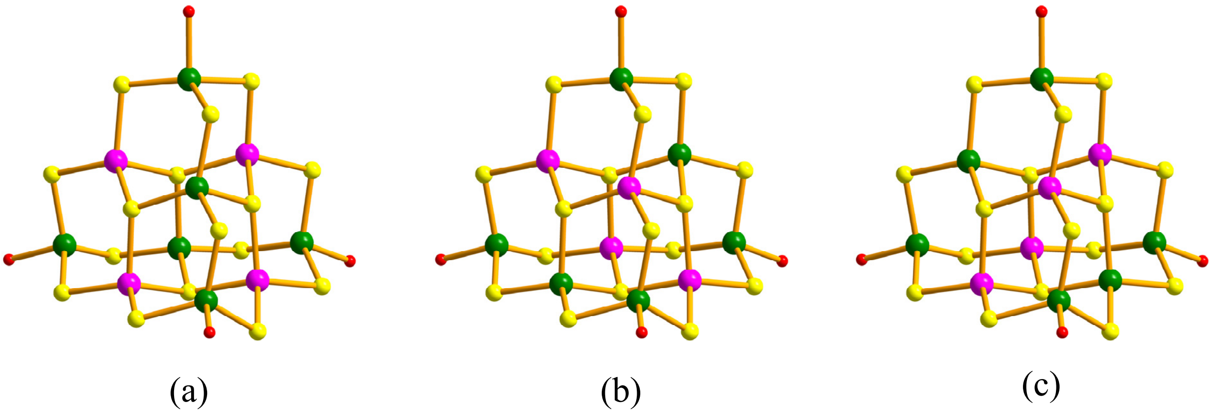
(a)



Element	Weight%	Atomic%
S K	30.54	60.29
Ag L	25.22	14.80
Cd L	44.24	24.91
Totals	100.00	

(b)

Fig. S1 Energy-dispersive X-ray spectroscopy (EDS) of $Cd_6Ag_4(SPh)_{16}(DMF)_4$ (a) and $\{[Cd_6Ag_4(SPh)_{16}](bpe)_2\}_n$ (b).



(a) (b) (c)

Fig. S2 Three possible arrangement of inner Cd and Ag atoms in the cluster of $Cd_6Ag_4(SPh)_{16}(DMF)_4$, each μ3-SPh group connected with one Cd and two Ag to a bond valence of 1. (Green, Cd; pink, Ag; yellow, SPh^-; red, oxygen from DMF molecule)

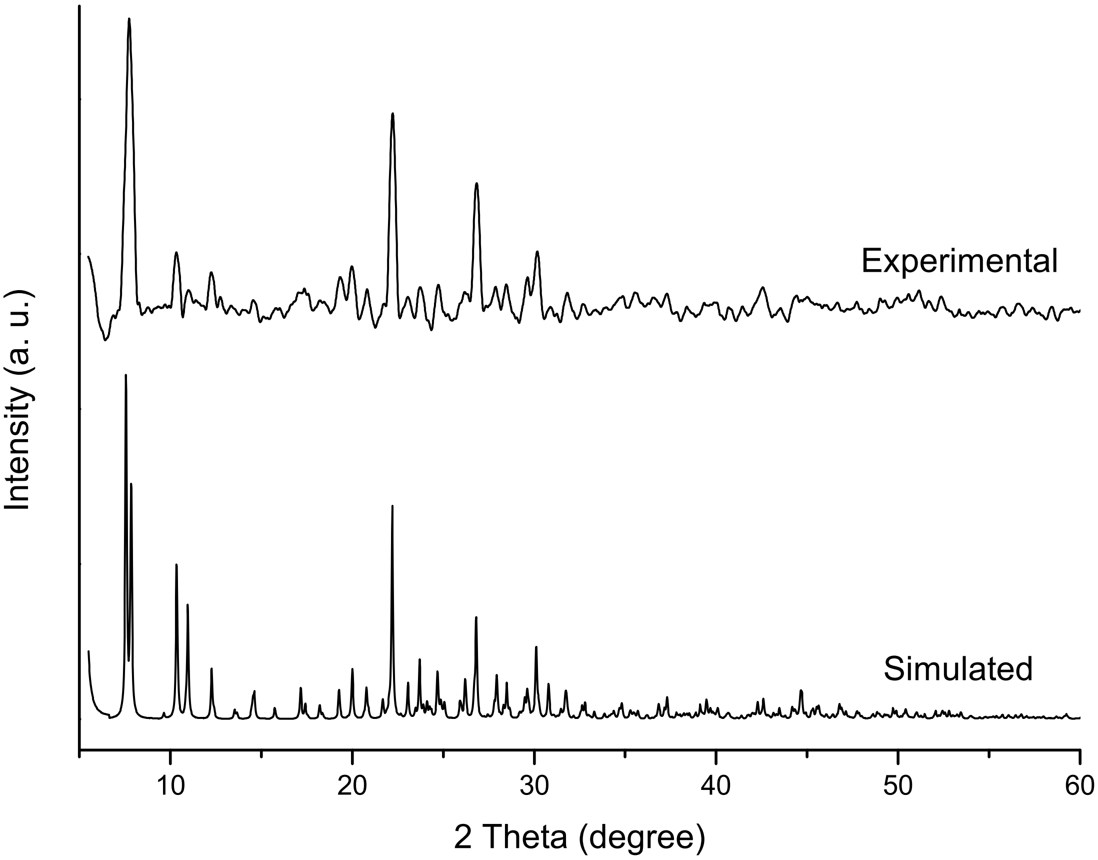


Fig. S3 Comparision of expreimental and simulated powder X-ray diffraction of $\{[Cd_6Ag_4(SPh)_{16}](bpe)_2\}_n$.

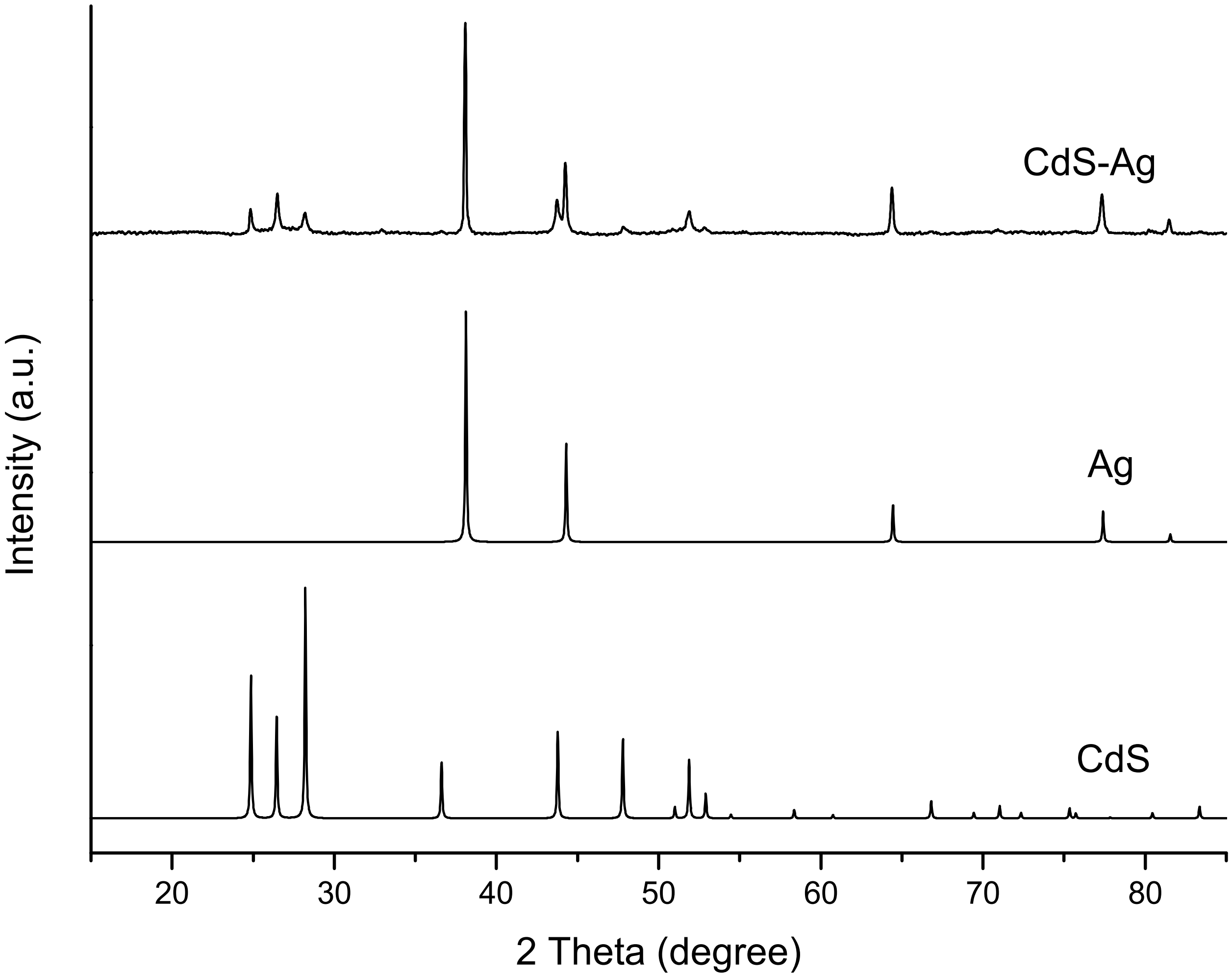


Fig. S4 Comparisons of powder X–ray diffraction patterns of standard hexagonal CdS, cubic Ag and hybrid crystals of CdS-Ag prepared from pyrolysis of $Cd_6Ag_4(SPh)_{16}(DMF)_4$.

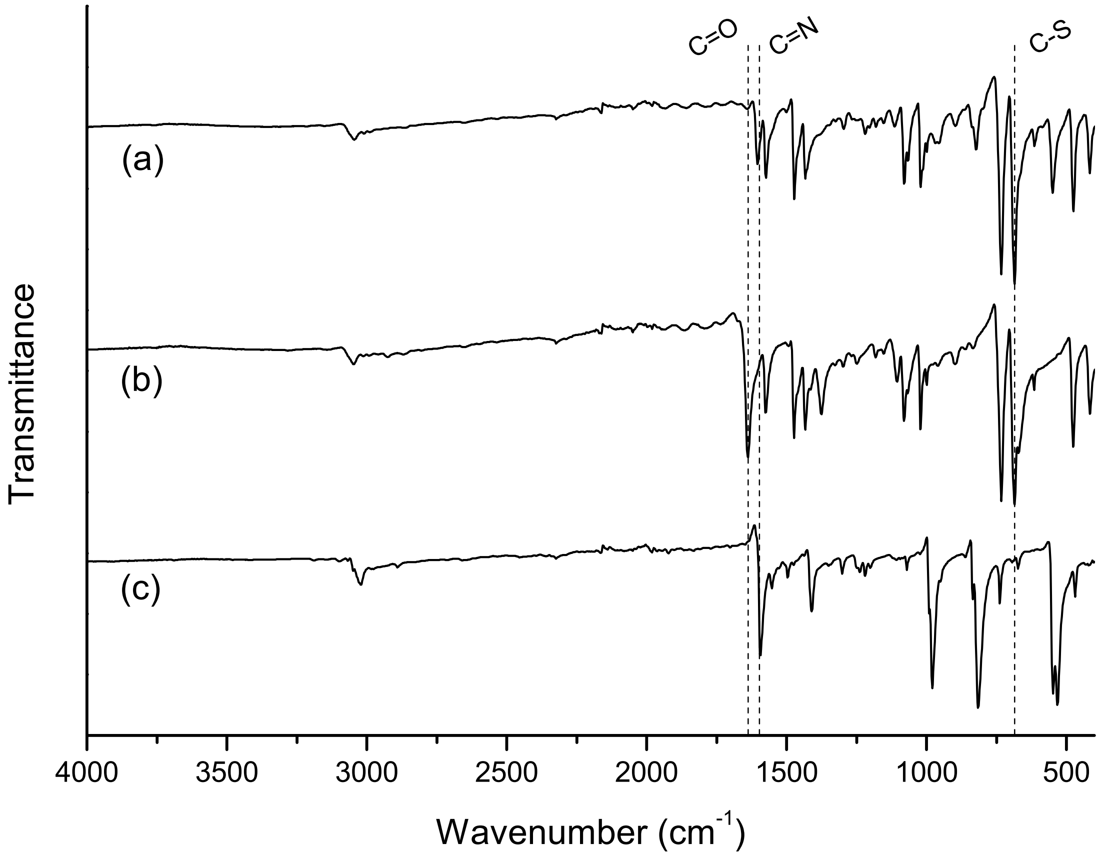


Fig. S5 Infrared (IR) spectrum of (a) $\{[Cd_6Ag_4(SPh)_{16}](bpe)_2\}_n$, (b) $Cd_6Ag_4(SPh)_{16}(DMF)_4$ and (c) *trans*-1,2-bis(4-pyridyl)ethylene (bpe).

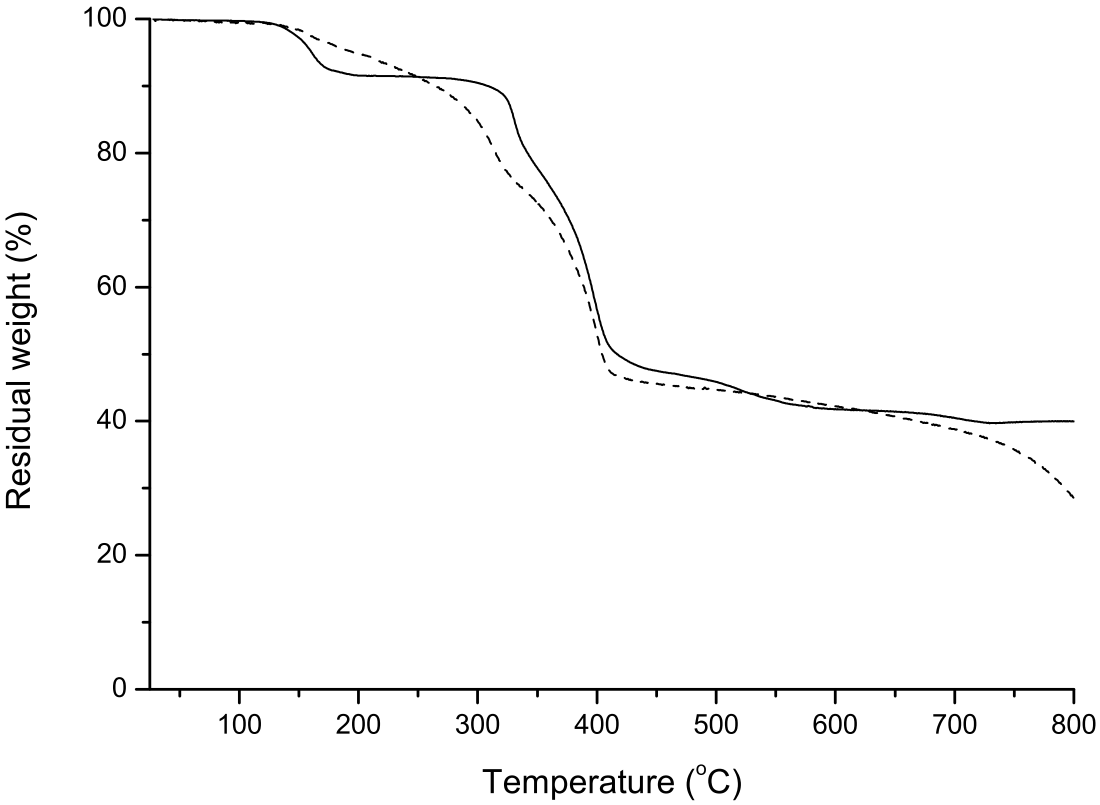


Fig. S6 Thermal gravimetric analysis (TGA) curve of $Cd_6Ag_4(SPh)_{16}(DMF)_4$ (solid line) and $\{[Cd_6Ag_4(SPh)_{16}](bpe)_2\}_n$ (dashed line).