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Synthesis, crystal structures and luminescent properties of two supramolecular assemblies containing $[Au(CN)_2]^-$ building block†

Wen Dong,[ab] Ya-Qiu Sun,[a] Bin Yu,[a] Hui-Bo Zhou,[a] Hai-Bin Song,[a] Zhan-Quan Liu,[a] Qing-Mei Wang,[a] Dai-Zheng Liao,*[a] Zong-Hui Jiang,[ac] Shi-Ping Yan[ad] and Peng Cheng[a]

[a] *Department of Chemistry, Nankai University, Tianjin, 300071 China*
[b] *Department of Chemistry, Guang Zhou University, Guang Zhou, 510405 China*
[c] *State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210093 China*
[d] *State Key Laboratory of Rare Earth Materials Chemistry and Applications, Peking University, Beijing, 100871 China*

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Two self-assembled supramolecular architectures $\{\{MnH_2O(Phen)_2[Au(CN)_2]\}[Au(CN)_2]\cdot 0.5C_2H_5OH\cdot 0.5H_2O\}_n$ (phen = 1, 10-phenanthroline) (**1**) and $[C_6H_{13}N_4][Au(CN)_2]\cdot H_2O$ ($C_6H_{13}N_4$ = 4-amide-3, 5-diethyl-1, 2, 4-triazole cation) (**2**) have been synthesized and structurally characterized. X-ray crystallography revealed a three-dimensional structure of **1** formed by the incorporation of coordinative linkage, aurophilic, hydrogen-bonding and π–π interactions. The 2D structure of **2** is formed by aurophilic and hydrogen-bonding interactions. Both the solid phases and aqueous solutions of **1** and **2** display interesting luminescence at room temperature.

Introduction

Recently, self-assembled supramolecular architectures have become an area of increasing interest due to their fascinating structures with potential applications in catalysis, host–guest chemistry, molecule-based magnets, optical materials, ion-exchange, gas absorption *etc.*[1–4] In general, hydrogen bonding interactions between moieties are the well-developed methods to increase structural dimensionality of supramolecular systems in the crystal engineering 'toolbox'.[5–8] On the other hand, the closed-shell intermolecular interactions between gold(I) ions, sometimes called aurophilicity, also play a key role in determining the supramolecular structure and increasing the supramolecular dimensionality.[9–12] This increase is important because high dimensionality systems often show useful magnetic, nonlinear optical, conducting, or zeolitic properties.[13–15] The supramolecular chemistry of Au(I) is replete with systems by virtue of the Au···Au interactions which are of equivalent strength to weak hydrogen bonds (*ca.* 7–11kca/mol).[16–21] The linear dicyanoaurate anion $[Au(CN)_2]^-$ is an ideal building block for the construction of multidimensional frameworks because it possesses the ability to link various central atoms and the Au(I) ions of dicyanoaurate groups can be involved in self-association through aurophilic interactions.[16,22,23] So far, several studies have shown that $[Au(CN)_2]^-$ can aggregate under a variety of conditions in both the solid state and in solution.[24–26] However, Schmidbaur and co-workers noted that anion aggregation occurred only in "very special cases" when they reviewed the available crystal structures of materials containing $[Au(CN)_2]^-$.[27] The conclusion seem to be disfavored by the aggregation of $[Au(CN)_2]^-$. In fact, the simple linear structure itself of $[Au(CN)_2]^-$ seems to encourage self-association through aurophilic interactions.[28] The aggregation of $[Au(CN)_2]^-$ anion show variations in their luminescence and the characteristic property in aqueous solution shows special importance in monitoring and probing biological processes associated with the luminescent material.[29–31] Using $[Au(CN)_2]^-$ anion and transition metal ions or primary and secondary amines as building blocks, new supramolecular assemblies with novel structural topologies and luminescence are expected to be obtained.[32–35] Here, we report the crystal structures, luminescent properties of two novel self-assembled supramolecular architectures formed by phen, the triazole cation and $[Au(CN)_2]^-$ anion building blocks.

Experimental

Physical measurements

Elemental analyses were carried out using a Perkin-Elmer analyzer model 240. The IR spectra were recorded as KBr discs on a Shimadzu IR–408 infrared spectrophotometer in the 4000–600 cm^{-1} region. Conventional fluorescence excitation and emission spectra were recorded on a Perkin Elmer LS50B luminescence spectrophotometer.

X-Ray crystallography and structure solution

For two complexes, determination of the unit cell and data collection was performed on a Bruker Smart 1000 area detector using graphite monochromated MoKα radiation (λ = 0.71073 Å) at 293(2) K. The structure was solved by direct methods and successive Fourier difference syntheses (SHELXS-97) and refined by full–matrix least-squares procedure on F2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97).[36] Crystal data collection and refinement parameters are given in Table 1 for **1** and **2**.

CCDC reference numbers 226795 and 226796 for **1** and **2**, respectively. See http://www.rsc.org/suppdata/nj/b4/b403329a/ for crystallographic data in .cif or other electronic format.

Syntheses

$\{\{MnH_2O(Phen)_2[Au(CN)_2]\}[Au(CN)_2]\cdot 0.5C_2H_5OH\cdot 0.5H_2O\}_n$ (1). A solution of 39.6mg (0.2 mmol) of phen in 5 mL of ethanol was added dropwise to a solution of 36.2mg

† Electronic supplementary information (ESI) available: emission and excitation spectra. See http://www.rsc.org/suppdata/nj/b4/b403329a/

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Table 1 Summary of crystallographic data for complexes **1** and **2**

Complex	**1**	**2**
Formula	$C_{29}H_{22}Au_2MnN_8O_2$	$C_8H_5AuN_6O$
Fw	963.42	408.23
Crystal system	Triclinic	Monoclinic
Space group	P^{-1}	C2/m
M(Mo Kα) mm^{-1}	10.298	11.075
A/Å	10.514(3)	19.875(15)
B/Å	12.374(4)	6.493(5)
C/Å	12.384(4)	10.459(8)
α/°	109.481(5)	90.00
β/°	100.360(5)	100.427(11)
γ/°	91.607(5)	90.00
V/Å^3	1487.5(8)	1327.4(17)
Z	2	4
Total reflections	8643	3738
Observed reflections	6015	1468
R_{int}	0.0315	0.0553
$R1^a$ [$I>2\sigma(I)$]	0.0389	0.0617
$wR2^b$ [*all data*)]	0.0988	0.1670

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

(0.1 mmol) of $Mn(ClO_4)_2 \cdot 6H_2O$ in 15 mL of water under stirring. After the solution was stirred a few minutes, a solution of 59 mg (0.2 mmol) of potassium dicyanoaurate in 10 mL of water was further added dropwise. The reaction mixture was filtered. After a few days of slow evaporation of the solvent, red crystals of the product suitable for X-ray crystallography were formed. Yield: 40.6%. Anal. Found: C, 36.07; H, 2.65; N, 11.33%. Calcd for $C_{29}H_{22}Au_2MnN_8O_2$: C, 36.12; H, 2.28; N, 11.62%. IR spectrum (KBr, cm^{-1}): 3400br, 2158s(ν(CN), 2141m(ν(CN), 1660vs, 1610vs, 1450vs,1400vs.

$[C_6H_{13}N_4][Au(CN)_2]\cdot H_2O$ (2). A solution of 81.6mg (0.2 mmol) of 4-amide-3, 5-dtethyl-1, 2, 4-triazole in 5 mL of methanol was added dropwise to a 10 mL aqueous solution of 59 mg (0.2 mmol) of potassium dicyanoaurate under stirring. The reaction mixture was filtered. After a few days of slow evaporation of the solvent, the colorless crystals of **2** suitable for X-ray crystallography were obtained. Yield: 35.4%. Anal. Found: C, 23.28; H, 3.74; N, 20.61%. Calcd for $C_8H_{15}AuN_6O$: C, 23.52; H, 3.67; N, 20.58%. IR spectrum (KBr, cm^{-1}): 3420s, 2144s(ν(CN), 1650s, 1610vs, 1400vs 1150m.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handed in small quantities with care.

Results and discussion

Compounds **1** and **2** were synthesized by the following reactions:

$$\text{Phen} + Mn(ClO_4)_2 \cdot 6H_20 + K[Au(CN)_2] + C_2H_5OH + H_2O \rightarrow \{\{MnH_2O(Phen)_2[Au(CN)_2]\}[Au(CN)_2] \cdot 0.5C_2H_5OH \cdot 0.5 \cdot H_2O\}_n. \quad (1)$$

$$C_6H_{13}N_4 + K[Au(CN)_2] + H_2O \rightarrow [C_6H_{13}N_4][Au(CN)_2] \cdot H_2O \quad (2)$$

Crystal structures

$\{\{MnH_2O(Phen)_2[Au(CN)_2]\}[Au(CN)_2]\cdot 0.5C_2H_5OH\cdot 0.5.H_2O\}_n$. X-Ray crystallography shows that **1** is made up of a three-dimensional network constructed by the incorporation of

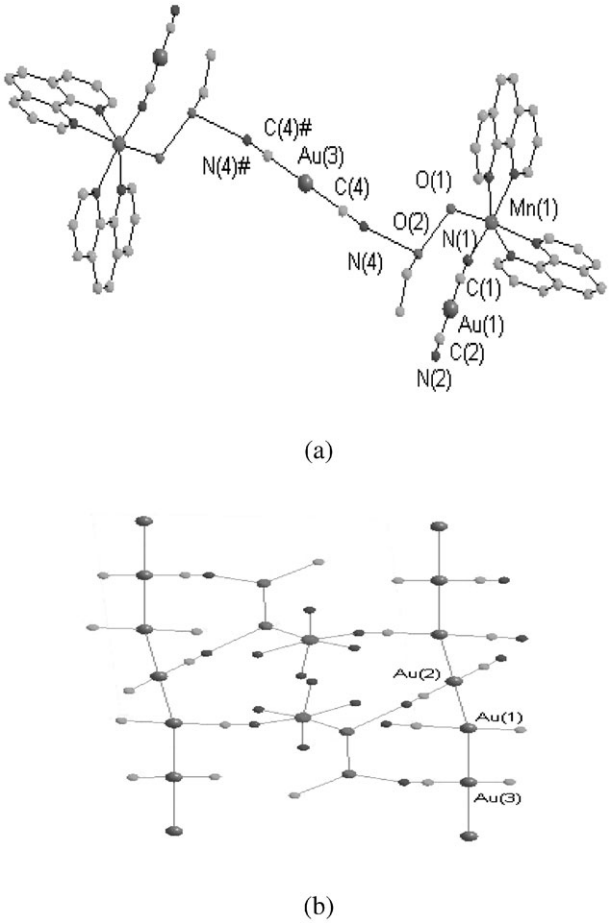

Fig. 1 (a) The atomic labeling of 1. (b) The 1D Au···Au liner chain $[Au(CN)_2]_n^{n-}$. Hydrogen atoms are omitted for clarity.

coordinative linkage, aurophilic, hydrogen-bonding and π–π interactions. Fig. 1 shows the atomic labeling scheme of **1**. The selected bond lengths and angles are listed in Table 2. In **1** each Mn atom is six-coordinated, with a distorted octahedron geometry by means of four nitrogen atoms of two phen ligands and a nitrile nitrogen atom from a $[Au(CN)_2]^-$ anion and an oxygen atom of a H_2O molecule. The $[Au(CN)_2]^-$ anions act as monodentate ligands or free anions. The bond angles are C(1)–

Table 2 Selected bond distances (Å) and bond angles (deg) of **1**

Au(1)–C(1)	1.994(10)	Au(2)–Au(1)–Au(3)	157.180(16)
Au(1)–C(2)	2.006(10)	C(3)#1–Au(2)–C(3)	180.000(1)
Au(1)–Au(2)	3.1086(9)	Au(1)–Au(2)–Au(1)#1	180.000(13)
Au(1)–Au(3)	3.2084(10)	C(4)–Au(3)–C(4)#2	180.0(7)
Au(2)–C(3)#1	2.004(12)	Au(1)-Au(3)-Au(1)#2	180.0
Au(2)–C(3)	2.004(12)	O(1)–Mn(1)–N(1)	94.4(3)
Au(2)–Au(1)#1	3.1086(9)	O(1)–Mn(1)–N(8)	95.9(3)
Au(3)–C(4)	1.995(15)	N(1)–Mn(1)–N(8)	95.7(3)
Au(3)–C(4)#2	1.995(15)	O(1)–Mn(1)–N(5)	94.3(2)
Au(3)–Au(1)#2	3.2084(10)	N(1)–Mn(1)–N(5)	104.4(3)
Mn(1)–O(1)	2.147(6)	N(8)–Mn(1)–N(5)	156.7(3)
Mn(1)–N(1)	2.193(8)	O(1)–Mn(1)–N(6)	167.8(3)
Mn(1)–N(8)	2.241(7)	N(1)–Mn(1)–N(6)	89.1(3)
Mn(1)–N(5)	2.261(7)	N(8)–Mn(1)–N(6)	95.3(3)
Mn(1)–N(6)	2.272(7)	N(5)–Mn(1)–N(6)	73.6(3)
Mn(1)–N(7)	2.337(7)	O(1)–Mn(1)–N(7)	86.4(2)
C(1)–Au(1)–C(2)	178.6(4)	N(1)–Mn(1)–N(7)	168.3(3)
C(1)–Au(1)–Au(2)	89.5(2)	N(8)–Mn(1)–N(7)	72.7(3)
C(2)–Au(1)–Au(2)	90.0(3)	N(5)–Mn(1)–N(7)	87.2(2)
		N(6)–Mn(1)–N(7)	92.5(2)

Symmetry transformations used to generate equivalent atoms: #1 − x, −y + 2, −z + 1 #2 −x, −y + 2, −z.

Table 3 The Au···Au distances of **1** and other similar complexes

Complexes	Structure	Au···Au [Å]
1	1D	3.1086, 3.2084
$[Ni(en)_2Au(CN)_2][Au(CN)_2]$[34]	2D	3.2620(10)
$[Cu(en)_2Au(CN)_2][Au(CN)_2]$[12]	2D	3.1405(2)
Cu(dien) $[Au(CN)_2]_2$[12]	1D	3.35
$Co(DMF)_2$ $[Au(CN)_2]_2$[11]	2D	3.1949(10)
$Mn(H_2O)_2[Au(CN)_2]_2$[35]	2D	3.17
$KFeAu(CN)_2]_3$[35]	3D	3.421

Au(1)–C(2) = 178.6(3)° and C(3)–Au(2)–C(3A) = 180.0°, respectively. The former for the monodentate ligand $[Au(CN)_2]^-$ anion slightly deviate from 180.0°. A 1D liner chain $[Au(CN)_2]_n^{n-}$ is formed by a self-association of $[Au(CN)_2]^-$ anions. The adjacent monocoordinated and the noncoordinated dicyanoaurate anions have a nearly staggered orientation with a torsion angle of 85°. The torsion angle is slightly smaller than that of similar complex $Ni(en)_2Au(CN)_2][Au(CN)_2]$ (90°).[34] Because of these aurophilic interactions dicyanoaurate anions form a metal chain that can be viewed as a pseudometal wire. The Au···Au distances of 3.1086(9) Å and 3.2084(10) Å are much shorter than the sum of the van der Waals radii of Au (3.60 Å), indicating the existence of Au···Au interactions. Comparing the Au···Au distances of this complex with those of similar complexes, the results are listed in Table 3. The Au···Au distance is slightly shorter than those of similar complexes. The different Au···Au distances in these complexes may be relative to the different cationic building blocks, the different topological structure and the different hydrogen–bonding network. Oxygen atoms of water molecule and ethanol molecules are disorder. The 50% occupancies were decided on thermal parameter. H atoms were initially located in a difference Fourier map. The ethyl H atoms were the constrained to an ideal geometry, with C–H distances of 0.96 Å and Viso(H) = 1.5eq (C), but each group was allowed to rotate freely about its C–C bond. The nitrile nitrogen atoms of the uncoordinated $[Au(CN)_2]^-$ anions and oxygen atoms of water and ethanol molecules are all involved in hydrogen bonding interactions. The N···O distance from the uncoordinated $[Au(CN)_2]^-$ anion and the coordinated water molecule is 2.822 Å and the O···N distance from the ethanol molecule and uncoordinated $[Au(CN)_2]^-$ anion is 2.762 Å. The O···O distance is 2.644 Å. Furthermore; the distances between atoms of the two parallel phen molecules are 3.56–3.60 Å, which indicates π–π interactions between parallel aryl rings. The result of incorporation of coordinative linkage, aurophilic, hydrogen-bonding and π–π interactions results in an elaborate three-dimensional network (Fig. 2), in which the aurophilicity plays an important role.

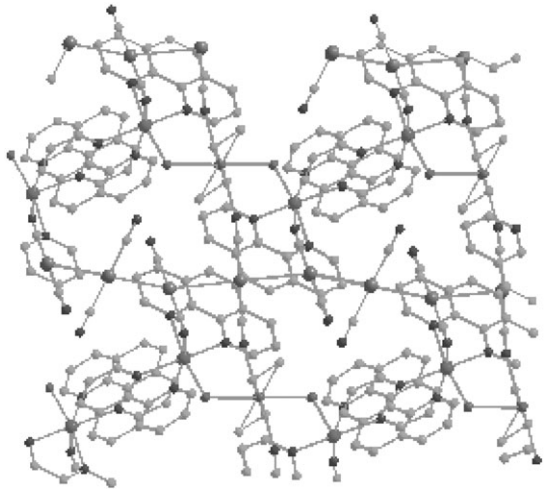

Fig. 2 The 3D scheme of 1. Hydrogen atoms are omitted for clarity.

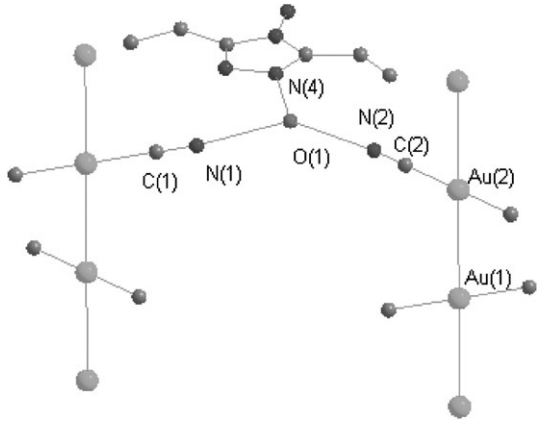

Fig. 3 The atomic labeling scheme of 2. Hydrogen atoms are omitted for clarity.

$[C_6H_{13}N_4][Au(CN)_2]\cdot H_2O$ (2). The atomic labeling scheme of **2** is shown in Fig. 3. The selected bond lengths and angles are listed in Table 4. X-ray crystallography reveals a 2D structure formed by aurophilic and hydrogen-bonding interactions. The bond angle Au···Au···Au is 180°. The Au(1)–Au(2) distance is 3.247(2) Å, much shorter than the sum of the van der Waals radii of Au (3.60 Å), indicating the existence of Au···Au interactions. Comparing the Au···Au distance of this complex with those of similar complexes, the results are listed in Table 5. The different aurophilic behaviors of the dicyanoaurate anions in these complexes may be relative to the different cationic building blocks and the hydrogen–bonding network. Adjacent $[Au(CN)_2]^-$ anions have a nearly staggered orientation with a torsion angle of 63.3°. The torsion angle is slightly smaller than that of similar complex $[C_5H_{10}NH_2][Au(CN)_2]$ (64.8°). $C_6H_{13}N_4$ cations and H_2O molecules are situated between the chains of $[Au(CN)_2]_n^{n-}$ chains. The H_2O molecules are hydrogen bonded to the $C_6H_{13}N_4$ cations and $[Au(CN)_2]^-$ anion with the O(1)···N(2) of 2.781 Å, O(1)···N(4) of 2.664 Å and N(1)···O(1) of 2.812 Å, resulting in an elaborate 2D structure (Fig. 4).

The luminescent properties

Both the solid phases and the aqueous solutions of **1** and **2** are all luminescent at room temperature. Fig. 5 shows the emission

Table 4 Selected bond distances (Å) and bond angles (deg) of **2**

Au(1)–C(1)#1	1.957(18)	C(2)–N(2)	1.16(2)
Au(1)–C(1)	1.957(18)	C(3)–N(3)	1.31(2)
Au(1)–Au(2)	3.247(2)	C(1)#1–Au(1)–C(1)	180.0(12)
Au(1)–Au(2)#2	3.247(2)	C(1)#1–Au(1)–Au(2)	90.0
Au(2)–C(2)#3	1.957(18)	C(1)–Au(1)–Au(2)	90.0
Au(2)–C(2)	1.957(18)	Au(2)–Au(1)–Au(2)#2	180.0
Au(2)–Au(1)#4	3.247(2)	C(1)#1–Au(1)–Au(2)#2	90.0
C(1)–N(1)	1.12(2)	C(1)–Au(1)–Au(2)#2	90.0

Symmetry transformations used to generate equivalent atoms: #1 −x + 1, −y, −z #2 x, y − 1, z #3 −x + 1, −y + 1, −z #4 x, y + 1, z.

Table 5 The Au···Au distances of **1** and other similar complexes

Complexes	Structures	Au···Au [Å]
2	1D	3.247
$[C_5H_{10}NH_2][Au(CN)_2]$[31]	1D	3.0969(3)
$[C_4H_8NH_2][Au(CN)_2]$[31]	1D	3.0795(4)
$[Ph_2NNH_3]$ $[Au(CN)_2]\cdot H_2O$[31]	1D	3.0866(4)
$[(C_6H_8N_3)_6][Au(CN)_2]_4(NO_3)_2\cdot 2H_2O$[24]	dimer	3.271(4), 3.492(5)

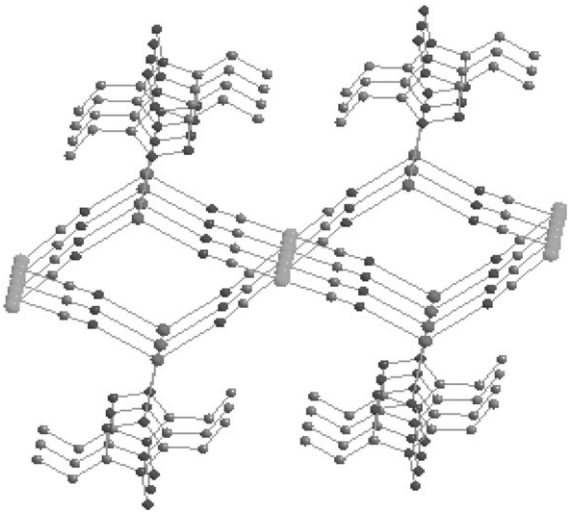

Fig. 4 The 2D structure of 2. Hydrogen atoms are omitted for clarity.

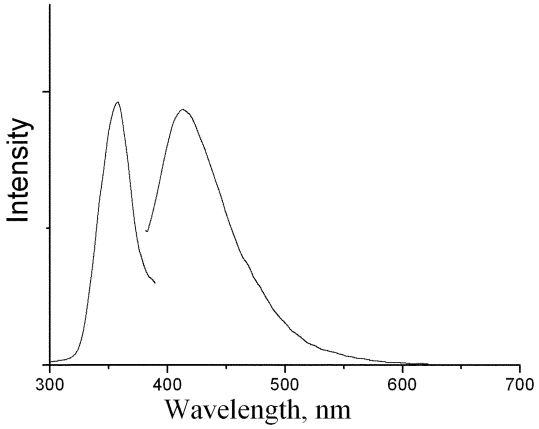

Fig. 6 The emission (right) and excitation (left, 358 nm) spectra in aqueous for 1.

and excitation spectra of crystal sample of **1**. The emission spectrum obtained with excitation at 251 nm exhibits five peak bands with the maxima of 325, 336, 438, 467 and 512 nm. Comparing to the luminescence of the solid pattern of $Mn(phen)_3(ClO_4)_2$, the complex $Mn(phen)_3(ClO_4)_2$ do not show the emission spectra when it is excited with the same wavelength of 251 nm. However when $Mn(phen)_3(ClO_4)_2$ is excited with wavelength of 319 nm, it exhibits two peak bands with the maxima of 399, 454 nm (seeing the supporting information). This luminescence of the solid phase of **1** may be attributed to supramolecular nature, in which the Au···Au interactions are crucial.[28] Fig. 6 shows the emission and excitation spectra of **1** in the aqueous solution with the concentration of 10^{-2} mol·l^{-1}. The emission maxima is obtained at 424 nm with excitation at 358 nm. Changing the excitation wavelength to 252 nm, the emission maxima is obtained at 414 nm (seeing the supporting information). The results are slightly different with that of $K[Au(CN)_2]$ in aqueous solution (0.03M, $\lambda_{exc} = 290$ nm, the maxima at 430 nm) reported by H. H. Patterson.[30] The corresponding emission maxima are slightly affected with the excitation wavelength. However the aqueous solution of $Mn(phen)_3(ClO_4)_2$ did not showed the emission spectra when it was excited with the same wavelength of 358 nm and 252 nm. This luminescence of **1** in aqueous solution may be also attributed to the Au···Au interactions.

Comparing to the emission spectra of the solid phase of **1** at the excited wavelength (251 nm), the profile of the emission maxima in aqueous solution have changed, which indicate that the oligomers of $[Au(CN)_2]^-$ species in aqueous solution is different to that of the solid phase. In aqueous solutions the polymers may break in some part of oligomers and new oligomers $[Au(CN)_2]_n^{n-}$ may be formed by weak aurophilic attraction.[34] In general, the higher-energy bands (shorter excited wavelength) should be assigned to the smallest oligomers $[Au(CN)_2]_n^n$, while the lower-energy bands correspond to larger oligomers in solution.[30] The luminescence of **1** should be attributed to the following factors: the first is excited state interactions in oligomeric forms of $[Au(CN)_2]^-$ anion.[27] The oligomeric forms of $[Au(CN)_2]^-$ anion allow the overlap of the occupied gold 5d orbitals to produce filled bands of orbitals and the overlap of the empty gold 6p orbitals to produce corresponding bands of unoccupied orbitals. When elections are excited from the filled 5d bands to the empty 6p bands, the reverse process related to excited electrons from the 6p bands back to the 5d band results from emission.[34] The second may be ligand to metal charge transfer (LMCT), or/and metal to ligand charge transfer (MLET), or/and ligand to ligand charge transfer (LLCT), *etc*.[37] Because the effects of the ligand, solvent, concentration and uncertain oligomers $[Au(CN)_2]_n^{n-}$, the exact assign of the emission bands is very difficult.

Fig. 7 shows the emission and excitation spectra of crystal sample of **2**. The emission spectrum obtained with excitation wavelength at 393 nm exhibits several bands with the maxima of 459 nm. Changing the higher-energy excitation wavelength at 319 nm, the emission maxima is also obtained at 459 nm (Fig. 8). The main emission maxima at 459 nm is not affected with the excitation wavelength and the profile of two emission spectra are similar to each other. In aqueous solution, both the emission maxima and the excitation maxima of **2** have changed comparing to the luminescence of the solid pattern (Fig. 9). In

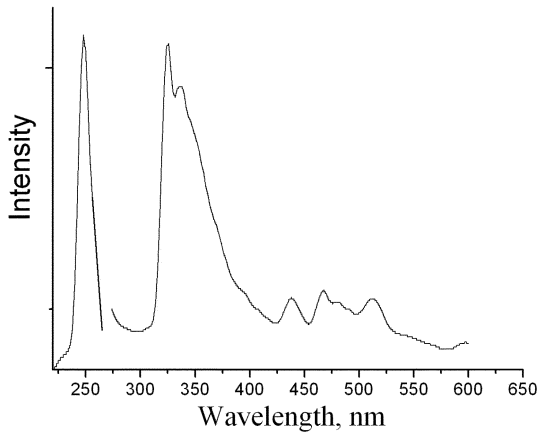

Fig. 5 The emission (right) and excitation (left, 251 nm) spectra of the solid pattern of 1.

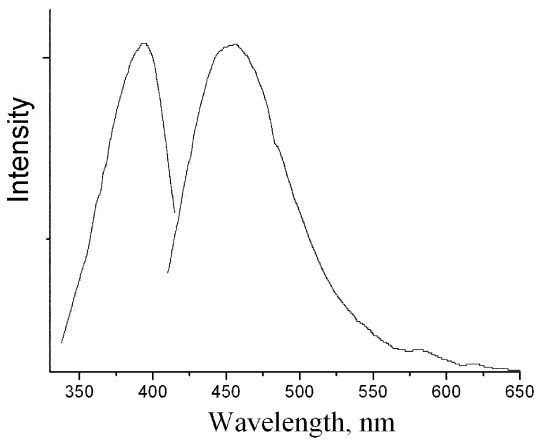

Fig. 7 The emission (right) and excitation (left, 393 nm) spectra of the solid pattern of 2.

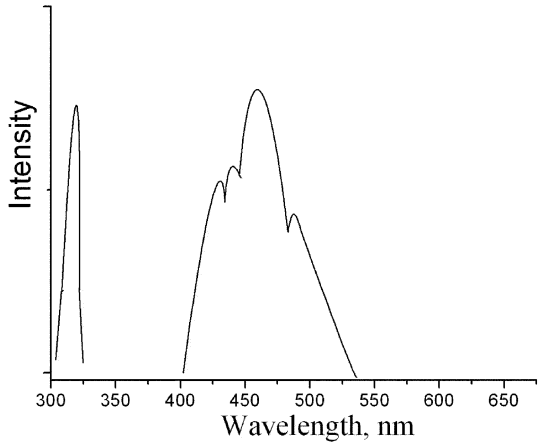

Fig. 8 The emission (right) and excitation (left, 319 nm) spectra of the solid pattern of 2.

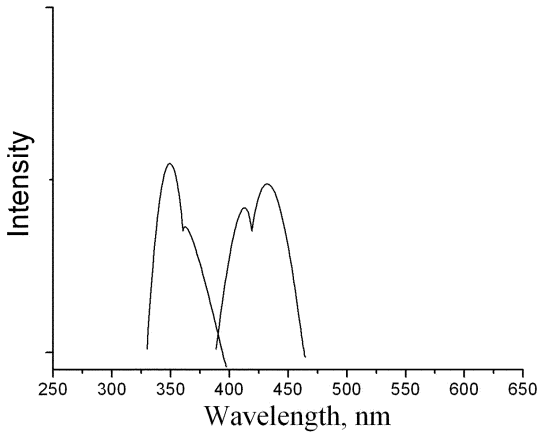

Fig. 9 The emission (right) and excitation (left, 347 nm) spectra of 2 in aqueous solution.

aqueous solution, the emission spectrum obtained with excitation at 347 nm exhibits several bands with the maxima of 414, 432 and 447 nm. The luminescence of **2** should be also mainly attributed to the presence of aurophilic interactions.[29,34]

Conclusions

Two supramolecular assemblies **1** and **2** have been synthesized from $[Au(CN)_2]^-$ building block and structurally characterized. The 3D structure of **1** is formed by the incorporation of coordinative linkage, aurophilic, hydrogen-bonding and π–π interactions. The 2D structure of **2** are formed by aurophilic and hydrogen-bonding interactions. Both the solid phases and aqueous solutions of **1** and **2** display interesting luminescence at room temperature. In one word, when the dicyanoaurate anion is used as a building block, the supramolecular assemblies possessing different structures with interesting luminescent properties are expected to be obtained.

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