Blue to Red Fluorescent Emission Tuning of a Cadmium Coordination Polymer by Conjugated Ligands

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The hydrothermal hydrolysis reactions of $Cd(ClO_4)_2 \cdot (6H_2O)$ with 4-[2-(2-pyridyl)ethenyl]benzonitrile (2-PEBN) and 2-[2-(4-cyanophenyl)ethenyl]-8-quinolinol (2-CEQH) afforded two coordination polymers aquabis{4-[2-(2-pyridyl)-ethenyl]benzoate}cadmium(II) (**1**) and 2-[2-(4-carboxylatophenyl)ethenyl]-8-quinolinolate(pyridine)cadmium(II) (**2**), respectively. Complexes **1** and **2** display strong blue and red fluorescent emission, respectively. Both **1** and **2** have a 2-D grid framework containing a dimer as the corner unit. Crystal data for **1**: monoclinic, $P2_1/c$, a = 15.2411(2), b = 19.8651(2), c = 15.6929(1) Å, α = β = 90, γ = 96.961(1)°; for **2**: monoclinic, $P2_1/c$, a = 11.9219(1), b = 8.9515(1), c = 18.8204(1)Å, α = γ = 90.00, β = 104.372(1)°.

Introduction

Full-color electroluminescent displays require three color components — green, blue and red. Stable blue or red metal-organic coordination polymers useful in electroluminescent devices are still rare and challenging to prepare. However, organic polymers, such as poly(*p*-phenylene vinylene) and polythiophenes etc., permit color tuning through changes in their length, substitution, regioregularity, and degree of conjugation.[1] A common approach to control the emitted color of organic materials is to append fluorescent chromophores to a polymeric backbone or to blend dyes into inert polymeric matrices.[2] Similarly, the emission wavelength of most metal-organic complexes can be tuned or changed by adjusting the length or conjugation of ligand since fluorescent emission is mostly dominated by the coordinated ligand transition.[3,4] In addition, metal-organic fluorescent coordination polymers have many more advantages — such as high thermal stability, good mechanical properties and relatively high emitting intensity — over pure organic materials. These coordination polymers have thus attracted much attention recently.[5] The synthesis and rational design of suitable organic ligands is still a great challenge since the introduction of special physical properties can be achieved through conjugation of the ligand, combined with the crystal engineering strategy and hydro(solvo)thermal synthesis method.[6] Furthermore, 8-quinolinolate complexes of, for example, Al^{3+} and Be^{2+} and their derivatives have also attracted much attention due to their potential application for full-color, flat-panel displays.[7] To this end, the hydrolysis reactions of $Cd(ClO_4)_2 \cdot (6H_2O)$ with 4-[2-(2-pyridyl)ethenyl]benzonitrile (2-PEBN) and 2-[2-(4-cyanophenyl)ethenyl]-8-quinolinol (2-CEQH) under hydrothermal reaction conditions afford two different emitting color fluorescent coordination polymers, aquabis{4-[2-(2-pyridyl)ethenyl]benzoate}cadmium(II) (**1**) and 2-[2-(4-carboxylatophenyl)ethenyl]-8-quinolinolate(pyridine)cadmium(II) (**2**) (Scheme 1), respectively. Complexes **1** and **2** display strong blue and red fluorescent emission, respectively. Interestingly, both **1** and **2** have a 2-D grid framework containing a dimer as corner unit. To the best of our knowledge, **1** is the first example of a double-square grid while **2** also has an unusual herringbone-type network with a dimer as the connecting node. Herein we report their synthesis, solid-state structures and fluorescent properties.

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Results and Discussion

The coordination polymers **1** and **2** were prepared under hydrothermal reaction conditions from $Cd(ClO_4)_2 \cdot 6H_2O$

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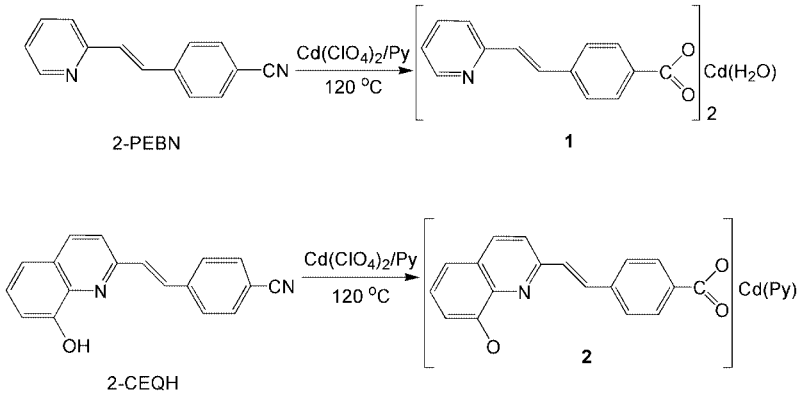

Scheme 1

and 2-PEBN or 2-CEQH respectively. In these two reactions, the cyano groups were hydrolyzed into carboxylates to give 4-[2-(2-pyridyl)ethenyl]benzoate (2-PEBA) in **1** and 2-[2-(4-carboxylatephenyl)ethenyl]-8-quinolinolate (2-CEQA) in **2**. The presence of the carboxylates was confirmed by the presence of two very strong peaks at 1600 and 1380 cm^{-1} for **1** and 1582 and 1405 cm^{-1} for **2** in the IR spectra. No peak around 2100 cm^{-1} was found, suggesting that the cyano groups are no longer present in **1** and **2**. TGA analysis showed an onset temperature for **1** at 300 °C with a weight loss of 1.77%; **1** decomposes beyond 350 °C. This weight loss at 300 °C corresponds to the removal of one water molecule per formula unit (calcd. 1.58%) in **1**. An onset temperature of 280 °C was observed for **2**.

The two-dimensional polymeric structures of **1** and **2** were revealed by X-ray single-crystal diffraction. The local coordination environment around the Cd center in **1** can best be described as a slightly distorted octahedron (Figure 1) in which each Cd center coordinates to two N atoms, one O atom from the bridging water and three O atoms from three different 2-PEBA ligands. Thus there are two kinds of 2-PEBA ligands, with one acting as a tridentate spacer to link three Cd centers and the other as a bidentate spacer to bridge two Cd centers, resulting in the formation of a 2-D rectangular grid network (Figure 2a). A simplified network representation (Figure 2b) clearly shows that each net shares eight 2-PEBA ligands as a rhombic side and four dimers as a connecting node. Thus, **1** can be considered as a double-rectangular grid network with a dimer as connecting node. To the best of our knowledge, **1** is the first such network example in supramolecular motifs.[8,9]

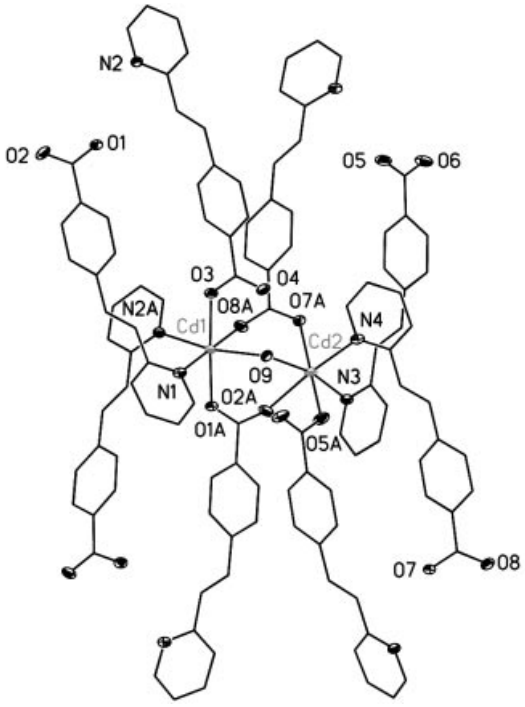

Figure 1. The asymmetric unit representation of **1** showing the local geometry around the Cd center; key bond lengths (Å): Cd1−O1A 2.213(2), Cd1−O3 2.253(2), Cd1−O8A 2.356(2), Cd1−O9 2.420(2), Cd1−N1 2.465(3), Cd1−N2A, 2.375(3), Cd2−O2A 2.389(3), Cd1−O5A 2.226(3), Cd1−O7A 2.211(2), Cd1−O9 2.413(2), Cd1−N3 2.374(3), Cd2−N4 2.461(3)

Like **1**, the local coordination geometry around each Cd center in **2** can also be described as a slightly distorted octahedron (Figure 3), in which each Cd center coordinates to two O atoms from a chelating, bridging 2-CEQA ligand and to two O atoms from the chelating carboxylate group of a different 2-CEQA ligand; the coordination sphere is completed by two N atoms, one from the chelating, bridging quinolinolate and one from pyridine. Thus, each 2-CEQA ligand acts as a pentadentate spacer to bridge three Cd centers, resulting in the formation of a 2-D rectangular grid network (Figure 4a). A simplified network representation of **2** (Figure 4b) clearly demonstrates that each rectangular grid shares four 2-CEQA ligands as a rhombic side and four dimers as connecting node resulting in the formation of a 2-D herringbone-type network. The structural feature in **2** is unusual as most supramolecular motifs with a herringbone net contain only one metal center as the connecting node.[8,9]

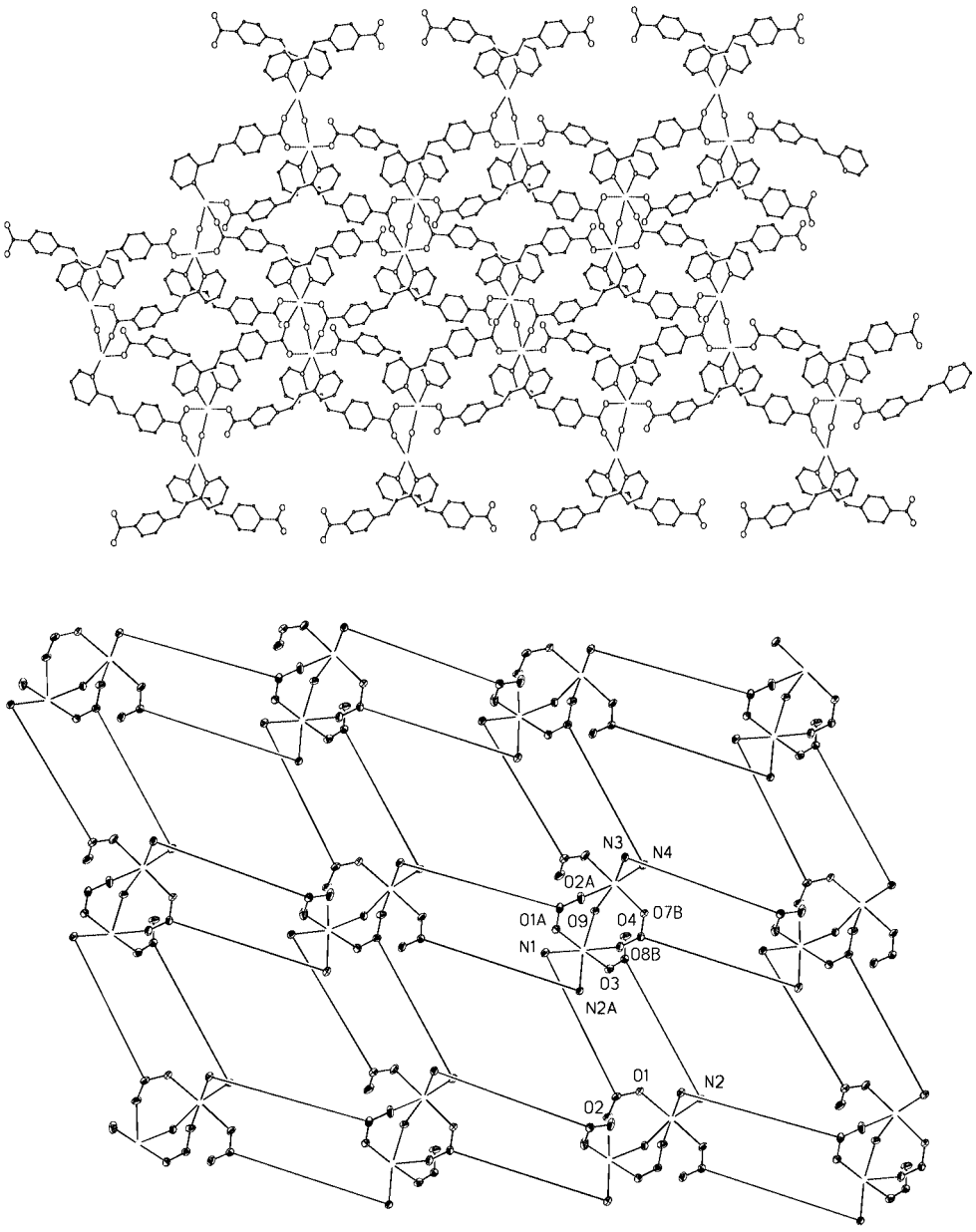

Figure 2. (a) 2-D grid network representation of **1**; (b) a simplified network representation of **1** in which the straight line is the 4-[2-(2-pyridyl)ethenyl]benzene group

The most important feature in the structures of **1** and **2** is that both have a 2-D condensed polymeric structure; this unique structure perhaps leads to significant enhancement of the fluorescent intensities, which are approximately two to three times larger than those of free 2-PEBA and 2-CEQA. These enhancements are perhaps a result of coordination of those ligands to Cd^{II}, which increases the ligands' conformational rigidity, thereby reducing the non-radiative decay of the intraligand $^1(\pi\text{-}\pi^*)$ excited state. Similar enhancement of the intraligand fluorescence has also been reported for $[Zn(terpyridine)_2]^{2+}$ and $[Zn(L)_2(OAc)_2]$ (L = *N*,*N*′-bisbenzyl-2,7-diamino-1,8-naphthyridine) [10] as well as $Zn(Norf)_2{\cdot}4(H_2O)$ (Norf = norfloxacin).[3] The solid-state diffuse reflectance UV/Vis spectra of **1** and **2** show two intense bands at 381 and 239 nm for **1** and 337 and 220 nm for **2**, which are assigned to intraligand π-π* transitions of 2-PEBA (388 and 246 nm) and 2-CEQA (338 and 215 nm). These bands match well with those in the excitation spectra of **1**, **2** and the free ligands (λ_{max} = 391 nm for 2-PEBA and λ_{max} = 348 nm for 2-CEQA). The emissions of **1** [λ_{max} = 418 nm, τ (lifetime) = 1.8 ns, Φ_{em} (quantum efficiency) ≈ 0.34; the short lifetime suggests that luminescence should be assigned to fluorescence] and **2** (λ_{max} = 600 nm, τ = 1.9 ns, Φ_{em} ≈ 0.46; Figure 5), are

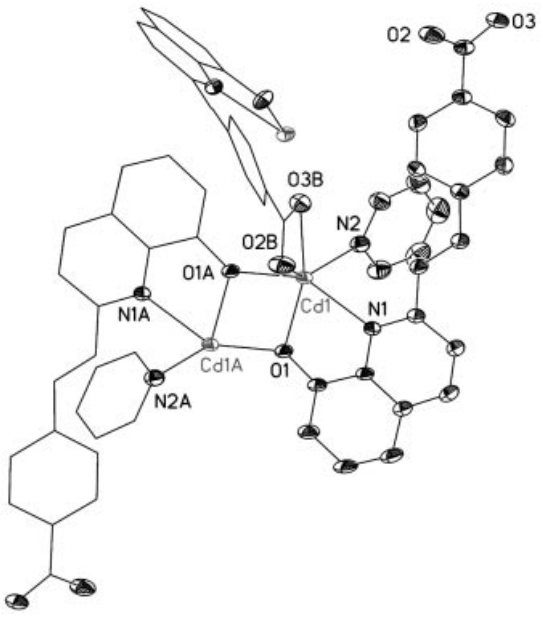

Figure 3. The asymmetric unit representation of **2** showing the local geometry around the Cd center; key bond lengths (Å): Cd1−O1 2.253(2), Cd1−O2B 2.369(3), Cd1−O3B 2.356(3), Cd1−N1 2.317(3), Cd1−N2 2.367(3)

Table 1. Crystal data and structure refinement for **1** and **2**

	1	**2**
Empirical formula	$C_{56}H_{40}N_4O_9Cd_2$	$C_{23}H_{16}N_2O_3Cd$
Mol. wt.	1137.72	480.78
T (K)	293(2)	293(2)
Crystal system	monoclinic	monoclinic
Space group	*P*21/*c*	*P*21/*c*
a, Å	15.2411(2)	11.9219(1)
b, Å	19.865(2)	8.9515(1)
c, Å	15.6929(1)	18.8204(1)
α, Deg	90.00	90.00
β, Deg	96.961(1)	104.372(1)
γ, Deg	90.00	90.00
V, Å^3	4716.25(8)	1945.64(3)
Z	4	4
ρ (cald), g/cm^3	1.602	1.641
μ (Mo-K_α), cm^{-1}	9.67	11.490
F(000)	2288	960
GOF	0.946	0.944
*R*1, *wR*2 [$I > 2\sigma(I)$][a]	0.0449, 0.0970	0.0426, 0.1004
(all data)	0.0790, 0.1062	0.0566, 0.1058

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

neither MLCT (metal-to-ligand charge transfer) nor LMCT (ligand-to-metal charge transfer) in nature, and can be tentatively assigned to the intraligand fluorescent emission since a similar weak emission (2-PEBA for $\lambda_{max} = 420$ nm, $\tau = 1.0$ ns, $\Phi_{em} \approx 0.11$) and (2-CEQA for $\lambda_{max} = 604$ nm, $\tau = 1.0$ ns, $\Phi_{em} \approx 0.16$) is also observed for the free ligands. Thus, the emitting color of a Cd coordination polymer can be tuned by ligand conjugation. Due to the low solubility of compounds **1** and **2** in common solvents such as water, ethanol, benzene, chloroform, ethyl acetate, acetone and acetonitrile, a film can be prepared by the spin-coating method.

In conclusion, through tuning of ligand length and conjugation, complexes **1** and **2** display a strong fluorescent emission at different wavelengths, and may be used as excellent advanced materials for blue- or red-light-emitting diode devices. These polymeric structures show high thermal stability and their low solubility in most common solvents means that they could be used in LED devices.

Experimental Section

Synthesis of Cd(2-PEB)$_2$·(H$_2$O) (1): Hydrothermal treatment of $Cd(ClO_4)_2 \cdot 6H_2O$ (1.0 mmol), PEBN (2.0 mmol), pyridine (0.6 mL) and water (0.6 mL) for 2 days at 120 °C yielded pale-yellow, crystalline blocks of **1** with only one pure phase. The yield of **1** was about (0.313 g) 55% based on PEBN. $C_{56}H_{40}Cd_2N_4O_9$ (1137.8): calcd. C 59.07, H 3.52, N 4.92; found C, 59.07, H 3.45, N 5.03. IR (KBr): $\tilde{\nu} = 3400$ cm^{-1} (br., w), 3008 (w), 1600 (s), 1551 (m), 1480 (m), 1420 (w), 1380 (s), 1180 (w), 1160 (m), 1010 (w), 960 (m), 850 (w), 793 (m), 742 (w), 700 (w), 681 (w), 640 (w), 532 (w), 434 (w).

Synthesis of Cd(2-CEQA)(Py) (2): The procedure with 2-CEQB was similar to that for **1**. Yellow block crystals (one phase) of **2** were harvested in 0.312 g (65%) yield based on 2-CEQB. $C_{23}H_{16}CdN_2O_3$ (480.8): calcd. C 57.41, H 3.33, N 5.82; found C, 57.60, H 3.42, N 5.90. IR (KBr): $\tilde{\nu} = 3424$ cm^{-1} (br., w), 1583 (s), 1532 (s), 1504 (w), 1445 (s), 1405 (s), 1371 (sh, w), 1278 (w), 1101 (m), 1035 (w), 1010 (w), 958(w), 833 (w), 779 (w), 739 (w), 703 (w), 616 (w), 417 (w).

X-ray Crystallographic Determinations of 1 and 2: Data were collected at room temperature from epoxy-coated crystals mounted on a glass fiber. All measurements were made on a CCD Smart diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were applied in each case. The relevant crystallographic data are presented in Table 1. The structure was solved by direct methods using the program SHELXTL (Sheldrick, 1997).[11] All the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedure. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The final difference Fourier map was found to be featureless. CCDC-167840 (**1**) and CCDC-167841 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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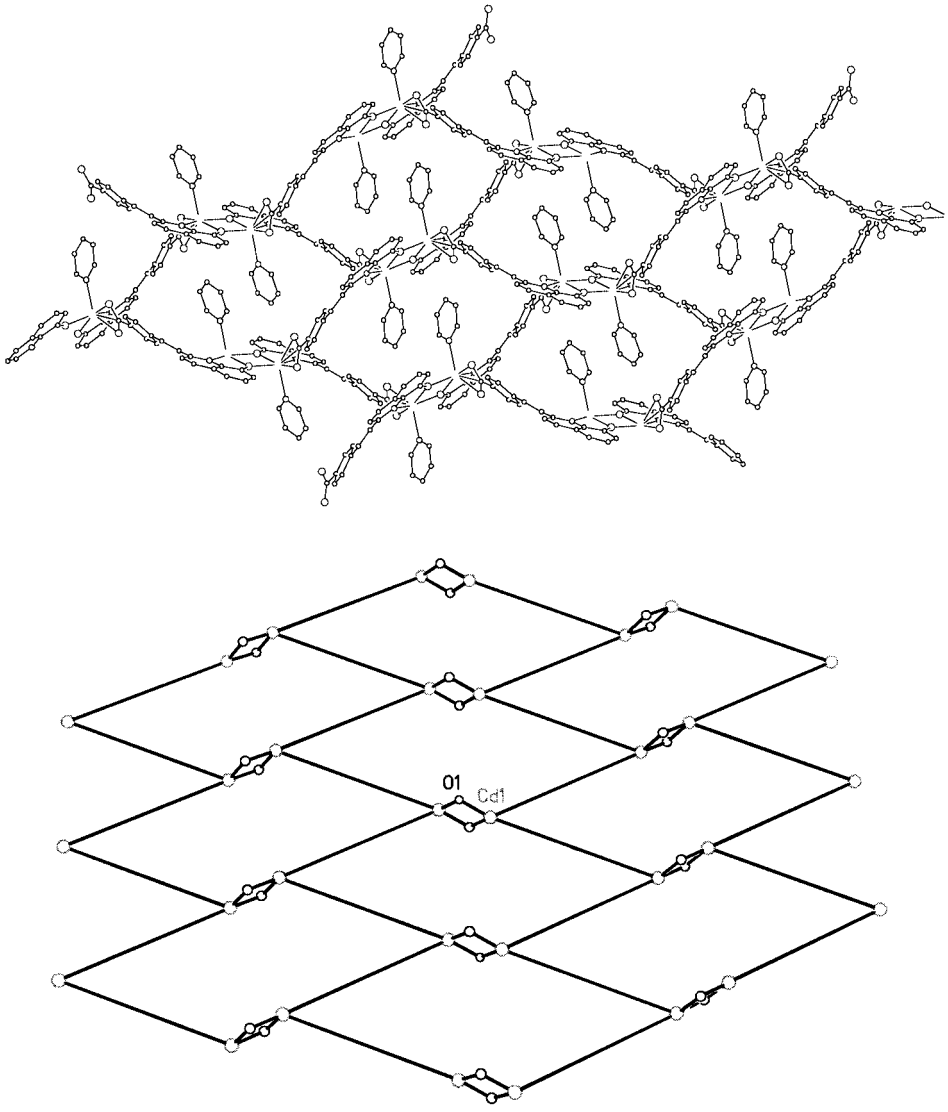

Figure 4. (a) 2-D grid network representation of **2**; (b) a simplified network representation of **1** in which the straight line is the 2-[2-(4-carboxylatephenyl)ethenyl]quinoline group

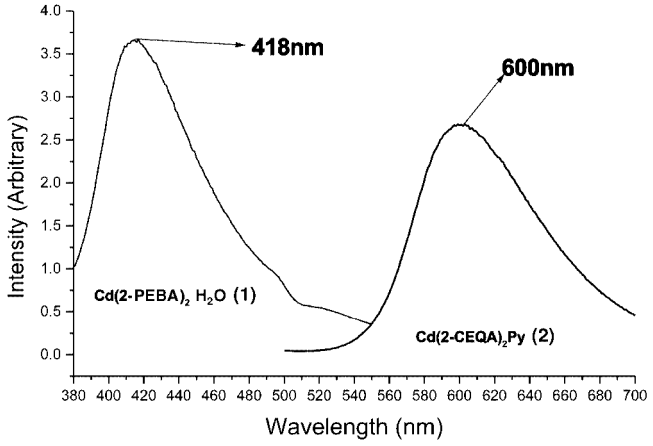

Figure 5. Fluorescence spectra of **1** and **2** in the solid state at room temperature

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