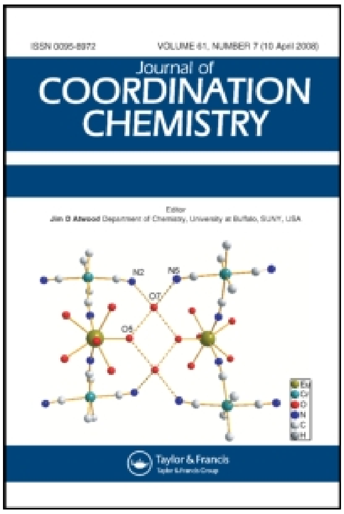

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# The influence of the carbon double bond on the structure and photophysical properties of copper(I) coordination polymers

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# The influence of the carbon double bond on the structure and photophysical properties of copper(I) coordination polymers

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The reaction of $[Cu(CH_3CN)_4]BF_4$, pyridine-2-carbaldehyde azine, triphenylphosphine, and diimine ligands derived from 4,4′-bipyridine and/or *trans*-1,2-*bis*(4-pyridyl)ethylene gave two copper(I) coordination polymers, $[Cu_2(\mu\text{-paa})(\mu\text{-bp})(PPh_3)_2]_n(BF_4)_{2n}$ (**1**) and $[Cu_2(\mu\text{-paa})(\mu\text{-tbpe})(PPh_3)_2]_n(BF_4)_{2n}$ (**2**). Despite **1** and **2** differing only by a double bond, they have significantly different photophysical and structural properties. Crystallographic studies show that **2** is a porous solid while **1** is not porous. The two polymers are photoluminescent as solids at room temperature, but the emission peaks of **2** are obviously red-shift. Moreover, different from **1**, **2** has a good emission centered at 510 nm in $CH_3CN$ solution. The double bond in the diimine ligand plays an important role in these two copper(I) coordination polymers.

*Keywords*: Copper(I) coordination polymers; Aromatic diimine; Carbon double bond; Photophysical properties; Crystal structures

## 1. Introduction

Coordination polymers have marvelous structures and applications for nonlinear optic materials [1–4], electrical materials [5–7], magnetic materials [8–11], and the materials used for separation and/or catalysis [12–15]. Coordinate polymers with interesting structures emerge unceasingly and understanding of coordination polymers is emerging [16–19]. In this article, we synthesized two new copper(I) coordination polymers: $[Cu_2(\mu\text{-paa})(\mu\text{-bp})(PPh_3)_2]_n(BF_4)_{2n}$ (**1**) and $[Cu_2(\mu\text{-paa})(\mu\text{-tbpe})(PPh_3)_2]_n(BF_4)_{2n}$ (**2**) using $[Cu(CH_3CN)_4]BF_4$, pyridine-2-carbaldehyde azine (paa), triphenylphosphine ($PPh_3$) and diimine ligands derived from 4,4′-bipyridine (bp) and/or *trans*-1,2-*bis*(4-pyridyl)ethylene (tbpe) at room temperature. These polymers are similar with only one carbon double bond difference; however, they have different structures and photophysical properties.

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## 2. Experimental

Ligand paa and the precursor complex $Cu(CH_3CN)_4BF_4$ were prepared and purified following literature procedure [20, 21]. The bp (Acros, 98%) and tbpe (Aldrich, 97%) were obtained commercially. Acetonitrile, methylene dichloride, and methanol used for photochemical studies were purified by standard methods [22]. All other chemicals and solvents were of A. R. grade and used as received. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 analyzer. Electronic spectra were recorded on a HITACHI U-3010 spectrophotometer and emission spectra on a HITACHI F-4500 fluorescence spectrophotometer. All syntheses were carried out under nitrogen.

### 2.1. *Synthesis of {trans-[$Cu_2(PPh_3)_2$(μ-paa)(μ-4′,4-bipyridine)]}$_n(BF_4)_{2n}$ (1)*

To a stirred solution of paa (0.29 mmol, 0.0600 g) in methylene dichloride, $Cu(CH_3CN)_4BF_4$ (0.57 mmol, 0.1796 g) was added. The mixture was stirred at room temperature for 12 h and then bp (0.29 mmol, 0.0446 g) was added and stirred for another 72 h at room temperature. Ultimately, $PPh_3$ (0.57 mmol, 0.1496 g) was added and stirred eight additional hours. The mixture was filtered and the filter residue was dissolved in 20 mL acetonitrile. Crystals were grown by diffusion of diethyl ether vapor into the acetonitrile solution of product. Yield: 56%. Anal. Calcd for $(C_{58}H_{48}N_6P_2Cu_2B_2F_8)_n$ (powder): C, 58.44; H, 4.03; N, 7.05. Found: C, 58.57; H, 4.10; N, 6.96.

### 2.2. *Synthesis of {trans-[$Cu(PPh_3)_2$(μ-paa)(μ-trans-1,2-bis(4-pyridyl)ethylene)]$(BF_4)_2$}$_n$ (2)*

The procedure was similar to that for **1**, except tbpe (0.29 mmol, 0.0521 g) was used in place of bp. Yield: 49%. Anal. Calcd for $(C_{60}H_{50}N_6P_2Cu_2B_2F_8)_n$ (powder): C, 59.16; H, 4.11; N, 6.90. Found: C, 59.11; H, 4.18; N, 6.92.

### 2.3. *X-ray structure determination*

Crystals of **1** and **2** suitable for X-ray structure analysis were grown from $CH_3CN$ by slow diffusion of diethyl ether over several days. The diffraction data were collected at room temperature with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) on a Rigaku R-AXIS RAPID IP X-ray diffractometer. An absorption correction was applied by correction of symmetry-equivalent reflections using the ABSCOR program. The structure was solved by direct methods using the SHELXS 97 program and refined by full-matrix least-squares on $F^2$ using SHELXL 97 software [23]. The hydrogen atoms were added using ideal geometries with a fixed C–H bond distance. The $BF_4^-$ anion is disordered over two positions with occupancies of 56/44 and 54/46 for the B/B′ pair in **1** and **2**, respectively. All atoms in $BF_4^-$ were refined isotropically and the isotropic displacement parameter was restrained to be equal. The B–F bond lengths were restrained to 1.37(1) Å. The relevant crystallographic data as well as selected bond distances and angles for polymers **1** and **2** are listed in tables 1 and 2, respectively.

Table 1. Summary of X-ray crystallographic data for **1** and **2**.

| | **1** | **2** |
|---|---|---|
| Formula | $C_{58}H_{48}B_2Cu_2F_8N_6P_2$ | $C_{30}H_{25}BcuF_4N_3P$ |
| Fw | 1191.66 | 608.85 |
| Space group | $P2(1)/n$ | $P\bar{1}$ |
| Crystal system | Monoclinic | Triclinic |
| Unit cell dimensions (Å, °) | | |
| $a$ | 10.450(4) | 10.196(5) |
| $b$ | 14.027(5) | 10.710(6) |
| $c$ | 18.950(6) | 13.590(7) |
| $\alpha$ | 90 | 82.447(12) |
| $\beta$ | 100.459(5) | 84.181(12) |
| $\gamma$ | 90 | 84.620(13) |
| $V$ (Å$^3$) | 2731.7(16) | 1458.8(14) |
| $Z$ | 2 | 2 |
| $T$ (K) | 293(2) | 293(2) |
| $\rho_{calcd}$ (g cm$^{-3}$) | 1.449 | 1.386 |
| $\theta$ range (°) | 2.19–26.38 | 2.30–25.00 |
| $\mu$ (mm$^{-1}$) | 0.909 | 0.853 |
| Observed data | 5582 | 4985 |
| No. of parameters | 349 | 407 |
| $R_1$$^{a}$ | 0.0602 | 0.0763 |
| $wR_2$$^{a}$ | 0.1328 | 0.1732 |
| Max, min peaks (e Å$^{-3}$) | 0.807 and −0.587 | 0.800 and −1.168 |

$^{a}I > 2\sigma(I)$. $R_1 = \Sigma||F_o| - |F_c|\Sigma|F_o|$. $wR_2 = \{\sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]\}^{1/2}$.

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

| | | | |
|---|---|---|---|
| Polymer **1** | | | |
| Cu(1)–N(1) | 2.096(3) | Cu(1)–N(2) | 2.181(3) |
| Cu(1)–P(1) | 2.2128(13) | N(2)–N(2)#1 | 1.405(6) |
| N(1)–C(6) | 1.338(5) | N(1)–C(2) | 1.357(5) |
| N(2)–C(1) | 1.274(5) | C(1)–C(2) | 1.450(5) |
| C(9)–C(9)#2 | 1.483(8) | | |
| N(3)–Cu(1)–N(1) | 103.90(14) | N(3)–Cu(1)–N(2) | 111.73(13) |
| N(1)–Cu(1)–N(2) | 77.25(12) | N(3)–Cu(1)–P(1) | 127.42(11) |
| N(1)–Cu(1)–P(1) | 118.68(10) | N(2)–Cu(1)–P(1) | 106.79(9) |
| Polymer **2** | | | |
| Cu(1)–N(3) | 2.024(6) | Cu(1)–N(1) | 2.052(6) |
| Cu(1)–N(2) | 2.118(5) | Cu(1)–P(1) | 2.182(2) |
| N(1)–C(1) | 1.314(9) | N(1)–C(5) | 1.347(8) |
| N(2)–C(6) | 1.267(8) | N(2)–N(2)#1 | 1.396(10) |
| N(3)–C(11) | 1.296(9) | N(3)–C(7) | 1.336(10) |
| C(12)–C(12)#2 | 1.09(2) | | |
| N(3)–Cu(1)–N(1) | 104.0(2) | N(3)–Cu(1)–N(2) | 112.4(2) |
| N(1)–Cu(1)–N(2) | 78.7(2) | N(3)–Cu(1)–P(1) | 112.28(17) |
| N(1)–Cu(1)–P(1) | 128.12(17) | N(2)–Cu(1)–P(1) | 117.03(15) |

## 3. Results and discussion

The ligand paa has four nitrogen donors that can be used to coordinate to metal, offering several possible mononucleating and dinucleating coordination modes. In our experiments, $Cu(CH_3CN)_4BF_4$ to paa was 2 : 1 to form binuclear copper(I) complexes.

Then, residual $CH_3CN$ was displaced by $PPh_3$, bp or tbpe to produce **1** or **2**. The identities were confirmed by elemental analyses and crystal structures. $CH_3CN$ is weaker in coordination to copper(I) than $PPh_3$, bp, and tbpe. Different stoichiometric ratio of paa to bp (or tbpe) can form various polymers (such as net structure, etc.).

An ORTEP view of **1** is depicted in figure 1 and the packing arrangement is shown in figure 2. Table 2 gives selected bond lengths and angles. Polymer **1** is a zig-zag infinite chain with copper(I) bridged by paa and bp alternately. Each copper(I) is a distorted tetrahedron as inferred from the smaller N(1)–Cu(1)–N(2) angle [77.25(12)°] and bigger N(3)–Cu(1)–P(1) angle [127.42(11)°]. The copper(I) to pyridyl nitrogen distances Cu(1)–N(3) [2.021(3) Å] and Cu(1)–N(1) [2.096(3) Å] are slightly less than the copper diazine bond length Cu(1)–N(2) [2.181(3) Å]. C(2), C(3), C(4), C(5), C(6), N(1), and C(1) are approximately coplanar [torsion angles C(1)–C(2)–N(1)–C(6) (179.8(4)°), C(1)–C(2)–C(3)–C(4) (−178.6(4)°), N(1)–C(6)–C(5)–C(4) (0.9(7)°)]. Cu(1) and N(2) are slightly out of this plane [the distance of Cu(2) or N(2) to the plane is 0.19(2) Å or 0.17(1) Å, respectively].

Polymer **2** is also a zig-zag infinite chain with copper(I) bridged by paa and tbpe. Its ORTEP drawing is shown in figure 3 and the packing arrangement is shown in figure 4. Selected bond lengths and angles are given in table 2. Same as polymer **1**, the geometry of each copper is a distorted tetrahedral [angle N(1)–Cu(1)–N(2) = 78.7(2)°, N(1)–Cu(1)–P(1) = 128.12(17)°]. Bond lengths Cu–N (range 2.024(6)–2.118(5) Å) and Cu–P (2.182(2) Å) are very near to that of **1**. The sum of the angles at N(2) is 359.4(15)°,

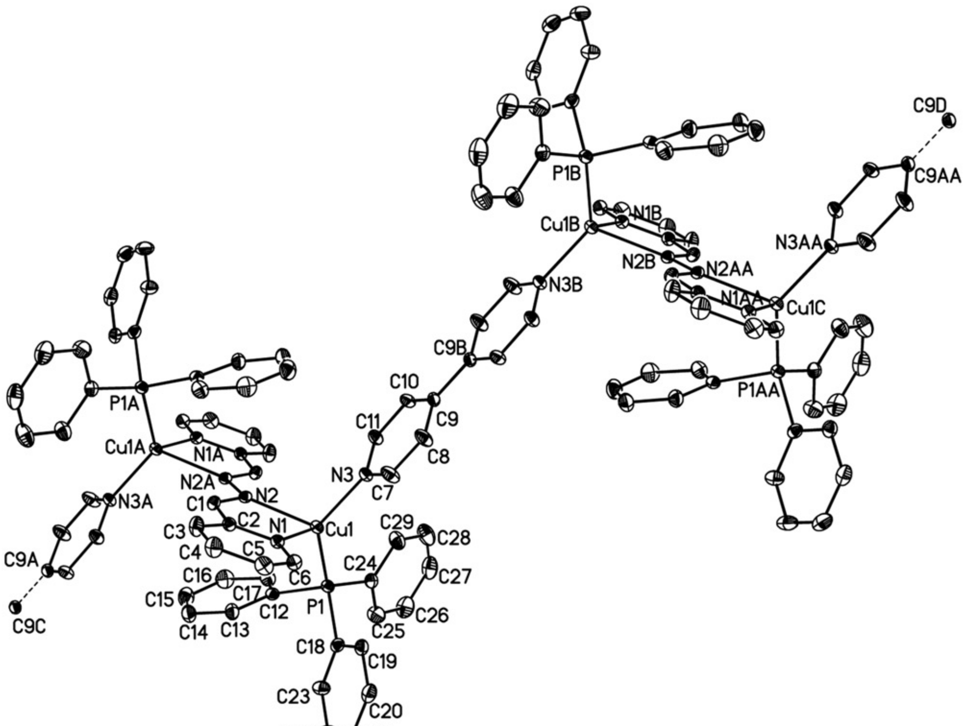

Figure 1. Molecular structure of **1** (ellipsoids shown at 30% probability level).

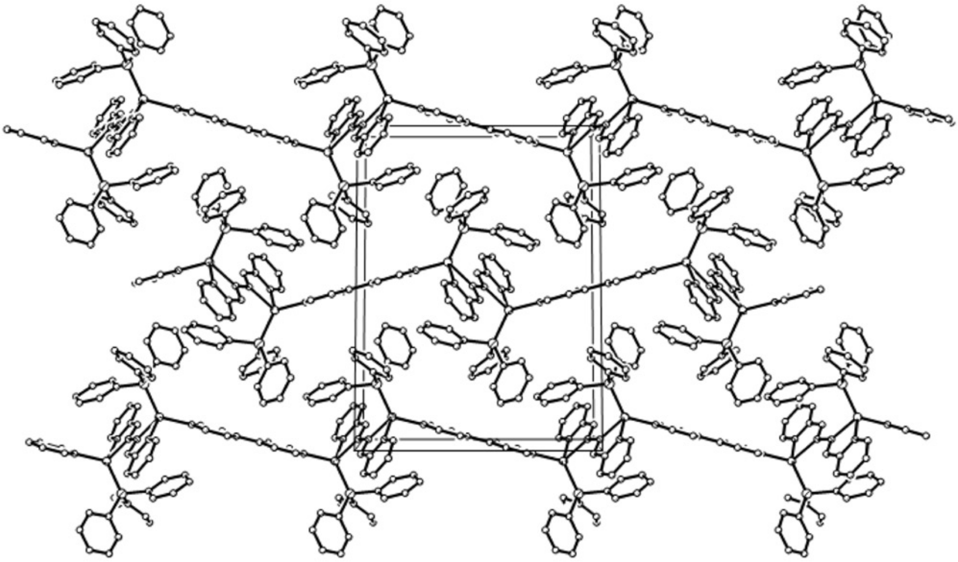

Figure 2. Crystal packing for **1**.

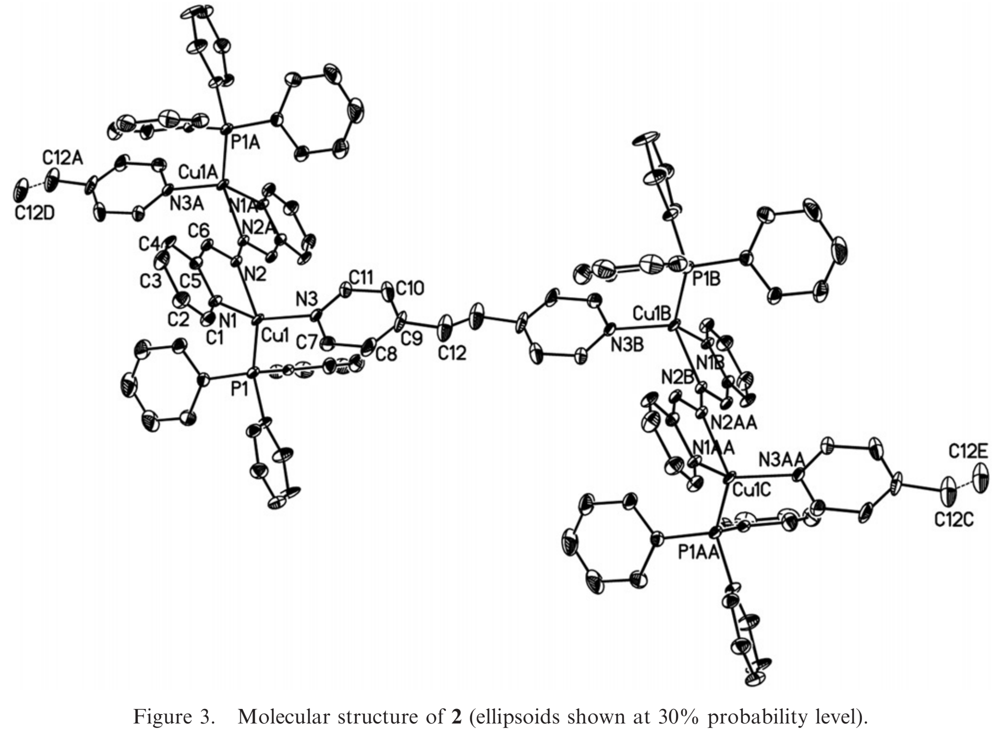

Figure 3. Molecular structure of **2** (ellipsoids shown at 30% probability level).

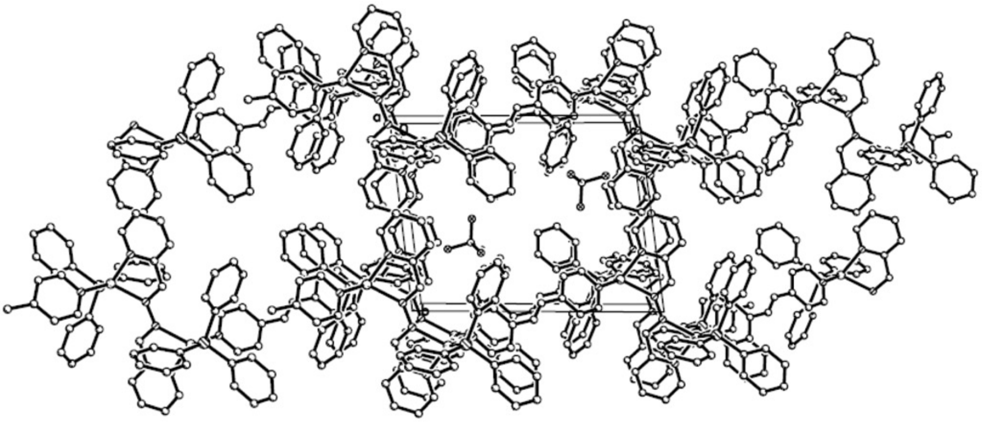

Figure 4. Crystal packing for **2**.

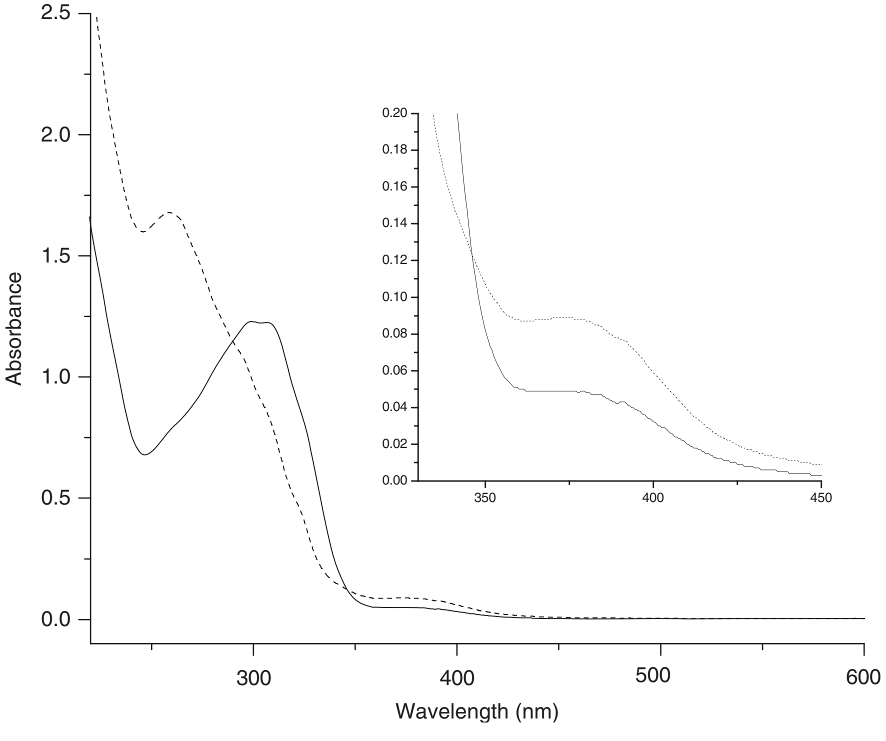

Figure 5. Electronic absorption spectra of {*trans*-[$Cu_2(pph_3)_2$(μ-Paa)(μ-4′4-bipyridine)]}$_n$($BF_4$)$_{2n}$ (**1**) (dash line) and {*trans*-[Cu($pph_3$)$_2$(μ-paa)(μ-*trans*-1,2-*bis*(4-pyridyl)ethylene)]($BF_4$)$_2$}$_n$ (**2**) (solid line) in $CH_3CN$ solution at room temperature. Inset: long wavelength region of the electronic absorption spectra of **1** and **2**.

indicating that there is no pyramidal distortion. Cu(1) and N(2) are slightly pulled out of the plane of the pyridine ring (C1C2C3C4C5N1) [the distance of Cu(2) or N(2) to the plane is 0.24(3) Å or 0.33(2) Å, respectively]. Polymers **1** and **2** differ only by one carbon double bond; however, there are many differences in the structures. C6 in **2** is slightly

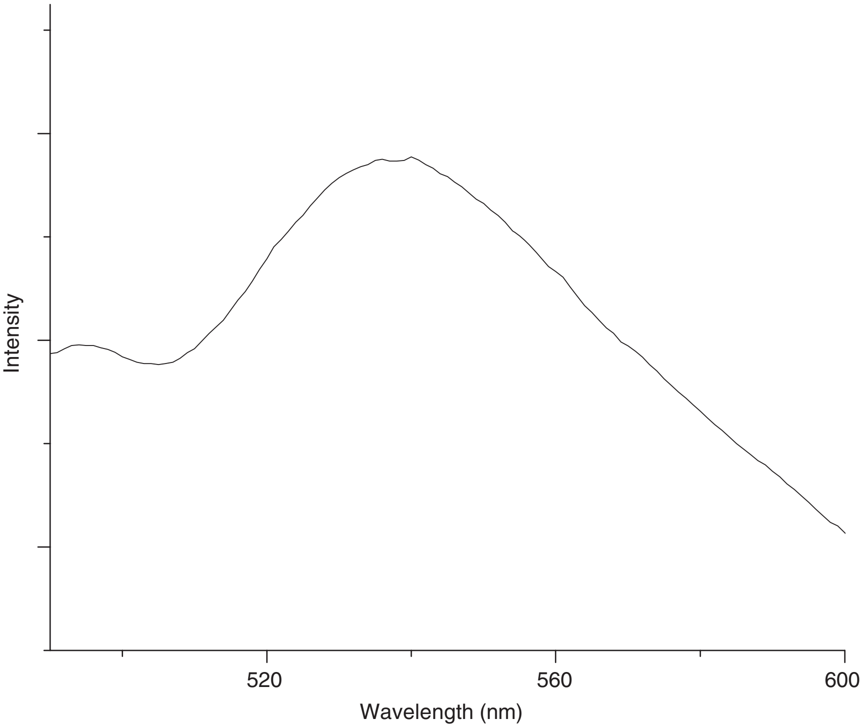

Figure 6. Room temperature solid-state emission spectrum of {*trans*-[$Cu_2(pph_3)_2$(μ-Paa)(μ-4′4-bipyridine)]}$_n(BF_4)_{2n}$ (**1**) upon excitation at 350 nm.

out of the plane of pyridine ring (C1C2C3C4C5N1) [the C6 to the plane: C1C2C3C4C5N1 distance is 0.10(3) Å]. The carbon double bond C(12) = C(12#1) is not coplanar with the pyridyl rings of both ends [the angle of the plane: C(9)C(10)C(11)N(3)C(7)C(8) and the plane: C(12)C(12#1)H(12) is 10.57°]. The packing arrangement shows that molecules in **2** overlay regularly. Through calculation of voids and their positions in the lattice by Platon, **2** is porous and solvent accessible areas were calculated to be *ca*. 20% of the total crystal volume. The cavities in **2** are occupied by $BF_4^-$ anions [24].

The two polymers display slight solubility in nonpolar solvents. The electronic absorption spectra of **1** and **2** in MeCN exhibit weak low-energy bands in the 330–600 nm region and intense high-energy bands in the 200–330 nm region (figure 5). The high-energy absorption peaks of **1** and **2** at 259 nm and 303 nm likely arise from a paa ligand-centered ($\pi \rightarrow \pi^*$) transition since these absorptions are similar to those of free paa. The absorption at 260 nm could arise from a phosphine ligand-centered ($\pi \rightarrow \pi^*$) or a bp ligand-centered ($\pi \rightarrow \pi^*$) transition. Absorption near 300 nm results from a tbpe ligand-centered ($\pi \rightarrow \pi^*$) transition; the free ligand also absorbs strongly in this region. The low-lying absorptions at 375 and 380 nm are tentatively assigned as a metal-perturbed [$\pi \rightarrow \pi^*$(paa)] IL or [d$\sigma^*$(Cu) $\rightarrow \pi^*$(paa)] MLCT transition [25, 26].

The two polymers are photoluminescent as solids at room temperature (figures 6 and 7). Because the ligands are not photoluminescent above 550 nm, emissions of **1** and **2** come from MLCT or metal-perturbed intraligand charge transfer [26]. In fluorescence spectra of **2**, a weak emission peak centered at 709 nm was attributed to

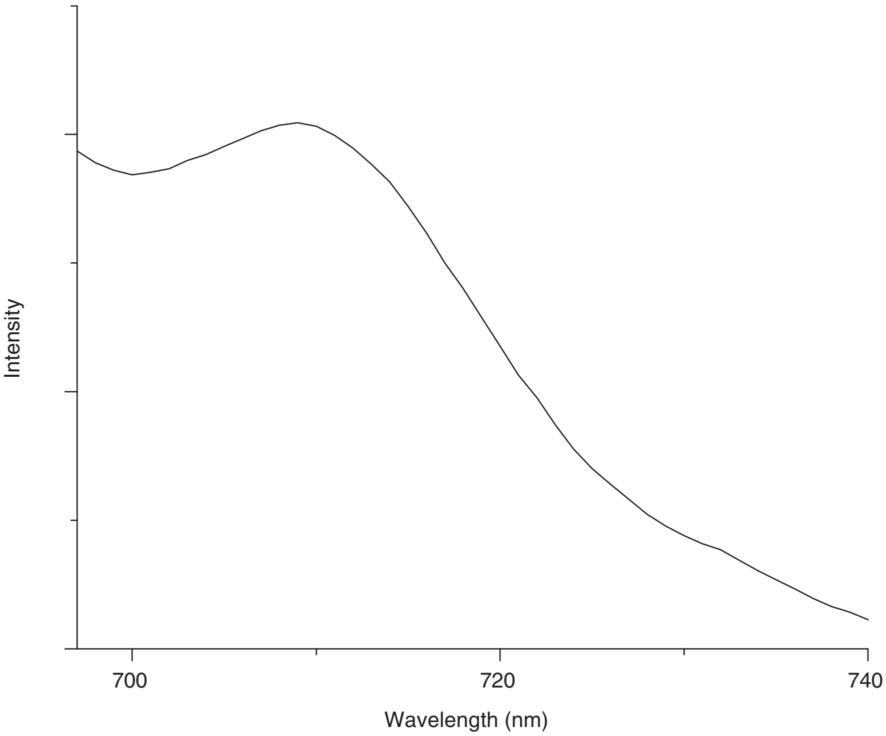

Figure 7. Room temperature solid-state emission spectrum of {*trans*-[Cu(pph$_3$)$_2$(μ-paa)(μ-*trans*-1,2-*bis*(4-pyridyl)ethylene)](BF$_4$)$_2$}$_n$ (**2**) upon excitation at 470 nm.

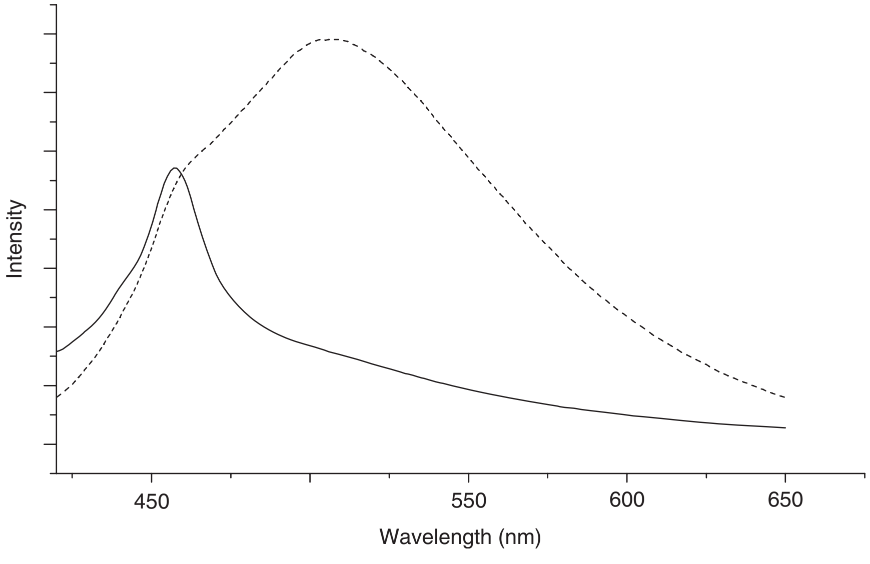

Figure 8. Room temperature emission spectra of {*trans*-[Cu(pph$_3$)$_2$(μ-paa)(μ-*trans*-1,2-*bis*(4-pyridyl)ethylene)](BF4)2}*n* (2) in CH$_3$CN solution (dash line) and the solution CH$_3$CN (solid line) upon excitation at 350 nm.

transfer of Z to E conformation of carbon double bond. Calculation for the *trans*- and *cis*-1,2-*bis*(4-pyridyl)ethylene (for simplifying) by Gaussian 03 software revealed that the energy difference of the *cis*-excited-state and the *trans*-ground-state is 2.01 eV. If emission came from electron transfer from the *cis*-excited-state to the *trans*-ground-state, the emission should be centered at 620 nm. The experimental value approximated the theoretical value. So the weak emission centered at 709 nm probably results from electron transfer from the *cis*-excited-state to the *trans*-ground-state.

In addition, different from **1**, **2** displayed a strong emission in $CH_3CN$ (shown in figure 8), indicating that the carbon double bond offered an avenue for electron transfer, benefiting intramolecular charge transfer facilitated by polar solution. Therefore, fluorescent emission in polar solution was enhanced by the carbon double bond.

## Supplementary material

Supplementary data for the polymers are available free of charge from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk), quoting the deposition number: CCDC-682956 and 682957 for **1** and **2**, respectively.

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