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Photophysical performance comparison between bulk Cu(I) complex and its electrospinning fibers: Synthesis and characterization



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ABSTRACT

In this report, a diamine ligand having an electron-pulling group in its conjugation plane was designed. A methyl group was connected with this diamine ligand, hoping to further increase its steric hindrance. Its Cu(I) complex was synthesized and characterized by NMR, single crystal analysis and photophysical analysis. There was a distorted tetrahedral coordination field in this Cu(I) complex. Its onset electronic transition owned a mixed character of metal-to-ligand-charge-transfer which suffered from bad geometric relaxation. To limit this geometric relaxation and improve emissive performance, this Cu(I) complex was odped into a polymer host through electrospinning technique. Photophysical comparison between solid state sample, solution sample and composite samples indicated that excited state geometric relaxation was effectively limited by polymer immobilization effect, resulting in improve emissive performance, such as emission blue shift, long emission decay lifetime and better photostability.

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1. Introduction

One-dimensional nanocomposite materials, such as nanorods, nanowires and nanofibers, have shown their wide application in optoelectronic and optical sensing systems and thus drawn much attention [1]. Among these samples, fibrous samples prepared by electrospinning have been usually proposed as supporting matrix for various optical dopants owing to their inexpensive preparation route, controllable morphology and good mechanical strength [2–8]. To satisfy various demands in practical application, a number of dopants and sensitizers have been doped into these electrospinning fibers to give composite fibrous samples [9–15].

Phosphorescent Cu(1) complexes with a general molecular formula of [Cu(N-N)(P-P)] have shown promising virtues and thus are usually applied as dopant in optical systems, including long emission decay lifetime, high emission quantum yield, promising photostability and low cost. Here N-N and P-P denote a diamine ligand and a phosphorous ligand, respectively [14–17]. Theoretical analysis on typical [Cu(N-N)(P-P)] complexes suggests that their occupied frontier molecular orbitals (FMOs) consist of metal d orbitals, while their unoccupied FMOs are essentially π^* orbitals of diamine ligands [18]. In this case, onset electronic transitions between occupied FMOs and unoccupied ones are assigned as a mixture of metal-to-ligand-charge-transfer (MLCT) and ligand-to-ligand-charge-transfer (LLCT). Such MLCT excited state is usually vulnerable to environment surrounding. Its structural relaxation is a major non-radiative decay path for [Cu(N—N)(P—P)] excited state, leading to decreased energy content and compromised emission quantum yield [18–20]. By introducing electron-pulling groups and large conjugation planes into diamine ligand, non-radiative decay probability of [Cu(N—N)(P—P)] emissive state can be decreased, which consequently improves its emissive performance [18–20].

Aiming at further improved photophysical performance from [Cu(N—N)(P—P)] complexes, such structural relaxation in MLCT excited state should be effectively limited. Some precursive methods include modifying ligands with steric hindrance groups, being doped into rigid supporting matrixes and being loaded into polymer frameworks [18–20].

Guided by above analysis, in this paper, a diamine ligand having an electron-pulling group in its conjugation plane is designed, as shown in Scheme 1. A methyl group is connected with this diamine ligand, hoping to increase its steric hindrance. Its Cu(I) complex is synthesized and doped into poly(vinylpyrrolidone) (PVP) fibers using

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Scheme 1. Design and synthesis strategy for our diamine ligand PYO, Cu(I) complex [Cu(PYO)(PPh₃)₂]BF₄ and electrospinning fibers ([Cu(PYO)(PPh₃)₂]BF₄/PVP).

electrospinning technique. Photophysical performance comparison between bulk Cu(I) complex and its electrospinning fibers is carried out. The correlation between structural relaxation in MLCT excited state and PVP framework is analyzed and discussed in detail.

2. Experimental details

2.1. General information

Design strategy and synthesis route for our diamine ligand 2-(pyridin-2-yl)-5-(p-tolyl)-1,3,4-oxadiazole (PYO), Cu(I) complex [Cu(PYO)(PPh₃)₂]BF₄ and electrospinning fibers ([Cu(PYO)(PPh₃)₂]BF₄/ PVP) are shown in Scheme 1. Related chemicals, including polymer PVP (K30), NaN₃, Cu(BF₄)₂, Cu powder, ZnCl₂, triphenylphosphane and picolinonitrile, were commercially provided by Shanghai Chemical Co. (China) and used with no further purifications. Organic solvents, including CH₂Cl₂, CHCl₃, MeCN and *N*,*N*'-dimethylformamide (DMF), were bought from Tianjin Chemical Co. (China) and purified before use with standard procedures. Solvent water was deionized before use.

A Varian INOVA 300 spectrometer and a Agilent 1100 MS spectrometer (COMPACT) were responsible for data collection of NMR and mass spectra. Elemental analysis was performed on a Carlo Erba 1106 elemental analyzer. A Siemens P4 single-crystal X-ray diffractometer equipped with a Smart CCD-1000 detector was applied to collect single crystal data, using graphite-monochromated Mo Kα radiation at 298 K. All H atoms were calculated. A HP 8453 UV-Vis-NIR diode array spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer were used to take UV-Vis absorption and emission spectra. A two-channel TEKTRONIX TDS-3052 oscilloscope was responsible for emission decay lifetime analysis, using pulsed YAG laser (355 nm) as excitation source. A Hitachi S-4800 microscope and a Nikon TE2000-U fluorescence microscopy were applied to take scanning electron microscopy (SEM) and fluorescence microscopy pictures. Density functional theory (DFT) calculation was finished with GAMESS at RB3LYP/SBKJC level in vacuum using single crystal structure as initial geometry. Graphical plotting for FMOs was generated by wxMacmolplt software package with contour value of 0.025.

2.2. Synthesis of diamine ligand PYO

2-(2H-tetrazol-5-yl)-pyridine (TP) was firstly synthesized following a literature procedure [15]. A mixture of picolinonitrile (5 mmol) and

NaN₃ (10 mmol) in DMF (20 mL) was stirred at room temperature for 30 min. During this time, ZnCl₂ (1 g) was slowly added. The final solution was stirred at room temperature for 1 h and then at 80 °C for another 10 h under N₂ protection. Plenty of crushed ice was added. Crude product was purified on a silica gel column (*n*-hexane:CH₂Cl₂ = 50:1). ¹H NMR (300 MHz, CDCl₃): δ 7.72 (1H, m), 8.07 (1H, m), 8.23 (1H, d, *J* = 6.0), 8.76 (1H, m). Anal. Calcd for C₆H₅N₅: C, 48.98; H, 3.43; N, 47.60. Found: C, 48.84, H, 3.53; N, 47.50. MS *m*/*z*: [m + 1]⁺ calc. for C₆H₅N₅, 147.0; found, 148.3.

Then TP (5 mmol), 4-methyl-benzoyl chloride (6 mmol) and pyridine (20 mL) were mixed together and heated at 120 °C for 2 days under N₂ protection. After cooling, this mixture was dispersed with cold water. Crude product was purified on a silica gel column (*n*-hexane:CH₂Cl₂ = 50:1). ¹H NMR (CDCl₃): δ 2.49 (3H, s), 7.37 (2H, d, J = 6.0), 7.51 (1H, t), 7.95 (1H, t), 8.14 (2H, d, J = 6.0), 8.33 (1H, d, J = 3.6). Anal. Calcd. For C₁₄H₁₁N₃O: C, 70.87; H, 4.67; N, 17.71. Found: C, 70.99; H, 4.74; N, 17.61. MS *m*/*z*: [m + 1]⁺ calc. for C₁₄H₁₁N₃O, 239.1; found, 240.3.

2.3. Synthesis of [Cu(PYO)(PPh₃)₂]BF₄

[Cu(CH₃CN)₄]BF₄ was firstly prepared in MeCN solution with Cu(BF₄)₂ and Cu powder as starting chemicals [19]. [Cu(PYO)(PPh₃)₂]BF₄ was synthesized following a literature procedure [19]. A mixture of [Cu(CH₃CN)₄]BF₄ (2 mmol), PPh₃ (4 mmol) in CH₂Cl₂ (10 mL) was stirred at room temperature for 30 min. Then PYO (2 mmol) was added. The resulting solution was stirred at room temperature for another 30 min. Solvent was extracted by thermal evaporation. Crude product was purified by recrystallization from tetrahydrofuran/ether. ¹H NMR: δ 2.42 (3H, s), 7.25 (19H, m), 7.29 (5H, m), 7.41 (8H, m), 7.66, (1H, t), 8.09 (2H, d, *J* = 6.0), 8.27 (2H, t), 8.36 (1H, t). Anal. Calcd. for C₅₀H₄₁BCuF₄N₃OP₂: C, 65.84; H, 4.53; N, 4.61. Found: C, 65.77; H, 4.40; N, 4.52. MS *m*/*z*: [m]⁺ calc. For C₅₀H₄₁BCuF₄N₃OP₂, 911.2; found, 911.5.

2.4. Construction of composite fibers [Cu(PYO)(PPh₃)₂]BF₄/PVP

Composite fibers $[Cu(PYO)(PPh_3)_2]BF_4/PVP$ were constructed by doping $[Cu(PYO)(PPh_3)_2]BF_4$ into PVP polymer through electrospinning technique [14]. First, PVP host was stirred and dissolved in DMF (5 mL, 20 wt%). After this solution become transparent, $[Cu(PYO)(PPh_3)_2]BF_4$ was weighted and added into this PVP solution. This solution was then transferred into a glass syringe (5 mL) with a plastic needle



Fig. 1. A. Single crystal structure of $[Cu(PYO)(PPh_3)_2]BF_4$. B. Inner-molecular π stacking of $[Cu(PYO)(PPh_3)_2]BF_4$.

(inner diameter = 0.6 mm). A copper wire was inserted into this glass syringe and connected with the anode terminal of a high-voltage generator. A piece of Al foil was connected to grounding electrode and placed under this glass syringe, working as collecting board with tip-to-target distance of 25 cm and driving voltage of 18 kV.

3. Results and discussion

3.1. Single crystal structure of [Cu(PYO)(PPh₃)₂]BF₄

Single crystal structure of $[Cu(PYO)(PPh_3)_2]BF_4$ is demonstrated in Fig. 1A. A representative tetrahedral coordination field is observed for each Cu center which is coordinated by two PYO N atoms and two PPh₃ P atoms. An electron-pulling oxadiazole ring is connected to a pyridine ring and a methylbenzene ring through σ bonds, showing a large conjugation plane of steric hindrance in PYO ligand which may slow down non-radiative decay of $[Cu(PYO)(PPh_3)_2]BF_4$ excited state and consequently increase its emissive performance. Face-to-face π - π attraction between PYO conjugation plane and PPh₃ phenyl rings allows a more organized geometry in [Cu(PYO)(PPh₃)₂]BF₄. It is observed that one of PPh₃ phenyl rings aligns nearly parallel to PYO plane with face-to-face distance of 3.396 Å and intersection angle of only 0.88°, respectively. Similar cases have been reported for [Cu(N—N)(P—P)] complexes having large conjugation planes in their ligands [19,20]. This

Table 1

Selected structural parameters of [Cu(PYO)(PPh₃)₂]BF₄.

Bond length	Å	Bond angle	ō
Cu-N(2)	2.129	N(2)CuN(3)	78.57
Cu-N(3)	2.177	N(2)— Cu — $P(1)$	123.41
Cu-P(1)	2.230	N(3)-Cu-P(1)	112.67
Cu-P(2)	2.274	N(2)—Cu—P(2)	98.57
		N(3)-Cu-P(2)	99.49
		P(1)CuP(2)	130.41

highly organized array has been found as a rigid structure and positive to restrict geometric relaxation in excited state [19]. Despite of the above mentioned inner-molecular π stacking, there is, however, no inter-molecular π stacking in [Cu(PYO)(PPh_3)_2]BF₄ crystal, as shown in Fig. 1B. This should be attributed to the free rotation of PPh₃ phenyl rings.

Table 1 shows selected structural parameters of [Cu(PYO)(PPh₃)₂]BF₄. Similar to literature cases, this tetrahedral coordination field is slightly distorted owing to its heterogeneous ligands, including N-based PYO and P-based PPh₃ [18]. Its two Cu—P bonds are different from each other but still comparable to literature values (~2.27 Å) [15,18]. The two Cu—N bonds are much longer than literature values (~2.08 Å), suggesting that coordination affinity of PYO N atoms is decreased by its electron-pulling effect [15,18]. It seems that coordination affinity of the N atom in pyridine ring, N(3), is even weaker than that of the N atom in oxadiazole ring, N(2). This result can be explained by the fact that there



Fig. 2. SEM images of our composite samples (a, 7 wt%; b, 9 wt%; c, 11 wt%; d, 13 wt%) and fluorescence microscopy image of 13 wt% doped sample (e).

are a short conjugation chain and electron-donating N and O atoms in oxadiazole ring, which increases N(2)'s coordination affinity.

N—Cu—N bite angle of $[Cu(PYO)(PPh_3)_2]BF_4$ is comparable to literature values [15,18]. While, its P—Cu—P bite angle is larger than literature values (~120°), suggesting that PPh_3 ligand is distorting itself to satisfy inner-molecular π stacking. For most bond angles listed in Table 1, they are close to but not exactly equal to 109°, indicating a structural distortion in $[Cu(PYO)(PPh_3)_2]BF_4$ triggered by its heterogeneous ligands. Such structural distortion should be restricted since it increases non-radiative decay probability and decreases energy content of MLCT excited state [14,19,20]. With the help of inner-molecular π stacking and the large steric hindrance of conjugation plane in PYO ligand, structural relaxation in $[Cu(PYO)(PPh_3)_2]BF_4$ may be effectively restricted, showing promising emissive performance. Electronic structure of $[Cu(PYO)(PPh_3)_2]BF_4$ is analyzed through its DFT calculation, which confirms its MLCT/LLCT excitation nature. See Supporting Information for a detailed explanation.

3.2. Morphology analysis on [Cu(PYO)(PPh₃)₂]BF₄/PVP composite fibers

Although the electron-pulling oxadiazole and its steric hindrance in PYO ligand may improve $[Cu(PYO)(PPh_3)_2]BF_4$ emissive performance by restricting its structural relaxation, we still have to figure out another way to further restrict its structural relaxation. In this effort, $[Cu(PYO)(PPh_3)_2]BF_4$ is immobilized in a polymer matrix through electrospinning technique, hoping to minimize its structural relaxation through polymer rigid framework. Owing to its virtues of controllable morphology, proper mechanical strength and compatibility with various dopants, PVP is here selected as supporting matrix [14]. Aiming at a full comparison between bulk sample and PVP-based fibrous samples, various doping levels are tried, including 7 wt%, 9 wt%, 11 wt% and 13 wt%, respectively.

These PVP-based fibrous samples and their morphology are firstly evaluated through their SEM images, as shown in Fig. 2. For all samples, their fibers are randomly distributed on substrates with smooth surface and uniform morphology. There are no branch structures or knots in these fibers. They align cross each other, resulting in a porous structure with its surface-area-to-volume ratio two orders of magnitude higher than those of bulk materials [14]. Since there are no heterogeneous interface or phase separation, it is tentatively concluded that [Cu(PYO)(PPh₃)₂]BF₄ molecules have been successfully and uniformly doped into PVP matrix with good compatibility with it. Mean diameters of these composite fibers are determined as $\sim 0.9 \,\mu\text{m}$ and similar to each other. Dopant concentration variation has slim effect on sample diameter or morphology, which should be explained by the low doping concentrations in PVP matrix. Fig. 2 gives a fluorescence microscopy image of a representative sample (13 wt% doped). Under Hg lamp excitation, homogeneous green emission comes out from all fibers, further confirming that [Cu(PYO)(PPh₃)₂]BF₄ molecules have been uniformly distributed in PVP matrix with no phase separation or condensed aggregation.

3.3. Photophysical comparison between bulk $[Cu(PYO)(PPh_3)_2]BF_4$ and $[Cu(PYO)(PPh_3)_2]BF_4/PVP$

3.3.1. UV-Vis absorption and solid state diffuse reflection spectra

UV–Vis absorption (abs.) spectra of pure PVP, $[Cu(PYO)(PPh_3)_2]BF_4$ (in CH₂Cl₂, 2 μ M) and the four composite samples are shown in Fig. 3. In solution, $[Cu(PYO)(PPh_3)_2]BF_4$ has two strong absorption bands, peaking at 233 nm and 270 nm, respectively. There is still a broad absorption band ranging from 350 nm to 450 nm. The first strong absorption band is quite similar to PPh_3 absorption and thus attributed to $\pi \to \pi^*$ absorption of PPh_3, as shown by Fig. 3 inset. The second strong absorption band is considered as an absorption conduct of PPh_3 and PYO ligands. This assignment is consistent with their LLCT nature, as suggested by above DFT calculation result. The weak band, however, is



Fig. 3. Solid state diffuse reflection spectrum (ref.) of bulk $[Cu(PYO)(PPh_3)_2]BF_4$, UV-Vis absorption (abs.) spectra of pure PVP, $[Cu(PYO)(PPh_3)_2]BF_4$ (in CH_2Cl_2 , 2 μ M) and the four composite samples. Inset: UV-Vis absorption spectra of PYO and PPh₃ in CH_2Cl_2 (2 μ M).

a new one and different from absorption spectra of PPh₃ and TP ligands. It is tentatively attributed to electronic absorption of MLCT, as suggested by above DFT calculation result. This MLCT transition energy and corresponding absorption edge (450 nm) are found much higher than those of other [Cu(N—N)(P—P)] complexes. We attribute its causation to the electron-pulling effect of PYO ligand and its short conjugation chain [18–20].

As for PVP, there are three $\pi \to \pi^*$ absorption bands peaking at 260 nm, 300 nm and 350 nm, respectively. These bands are traced in all absorption spectra of our composite samples, with no obvious spectral shift. There is a broad absorption band ranging from 350 nm to 490 nm in each composite absorption spectrum, which can be attributed to MLCT absorption of [Cu(PYO)(PPh₃)₂]BF₄ dopant. This MLT band is found enhanced in PVP composite samples, compared to that of $[Cu(PYO)(PPh_3)_2]BF_4$ in CH₂Cl₂ solution, along with a slight red shift. This result confirms that [Cu(PYO)(PPh₃)₂]BF₄ MLCT excited state is vulnerable to surrounding environment, which is consistent with literature reports [19,20]. Despite of their different absorption intensity values, absorption wavelength and band shape of our composite samples are similar to those of [Cu(PYO)(PPh₃)₂]BF₄ in CH₂Cl₂ solution, without any new absorption bands. We thus come to a conclusion that [Cu(PYO)(PPh₃)₂]BF₄ dopant is simply immobilized in PVP framework, with its excited state well protected by PVP framework. There is no strong interaction between dopant molecules and PVP matrix.

Since bulk $[Cu(PYO)(PPh_3)_2]BF_4$ sample is too thick for light penetration, we here use its solid state diffuse reflection (ref.) spectrum to replace its absorption spectrum. This reflection spectrum has two low reflection regions peaking at 283 nm and 427 nm, respectively, ending at 458 nm. These two regions are consistent with the strong absorption bands of $[Cu(PYO)(PPh_3)_2]BF_4$ in CH_2Cl_2 solution and composite samples. The slight red shift in this reflection spectrum, compared to absorption spectrum of $[Cu(PYO)(PPh_3)_2]BF_4$ in CH_2Cl_2 solution, should be attributed to solid state aggregation. In this case, it is further confirmed that PVP matrix only immobilizes and protects $[Cu(PYO)(PPh_3)_2]BF_4$ molecules, without changing its electronic transition.

3.3.2. Emission spectra

Emission (em.) spectra of $[Cu(PYO)(PPh_3)_2]BF_4$ (in CH_2Cl_2 , 2 μ M), bulk $[Cu(PYO)(PPh_3)_2]BF_4$ and the four composite samples are shown in Fig. 4. In solution, $[Cu(PYO)(PPh_3)_2]BF_4$ shows a broad and weak emission band peaking at 580 nm with FWHM of 76 nm, where FWHM means full width at half maximum. There are no vibronic



Fig. 4. Emission spectra ($\lambda_{ex} = 355 \text{ nm}$) of [Cu(PYO)(PPh_3)_2]BF_4 in CH_2Cl_2 (2 μ M), bulk [Cu(PYO)(PPh_3)_2]BF_4 and the four composite samples.

progressions, which means that its emissive center owns a charge transfer character. This finding is consistent with its MLCT electronic nature. There is a large Stokes shift (130 nm) between absorption edge (450 nm) and emission peak (580 nm), suggesting that $[Cu(PYO)(PPh_3)_2]BF_4$ excited state suffers from bad geometric relaxation in CH₂Cl₂ solution which is attributed to solvent molecule attack and limited PYO steric hindrance. In bulk state, $[Cu(PYO)(PPh_3)_2]BF_4$ emission peaking at 552 nm is obviously enhanced with FWHM of 98 nm. Its Stokes shift between absorption edge (458 nm) and emission peak (552 nm) is 94 nm. This decreased Stokes shift value, along with its emission blue shift, suggests that the geometric relaxation of $[Cu(PYO)(PPh_3)_2]BF_4$ in bulk state is weaker than that in CH₂Cl₂ solution, owing to its inner-molecular π stacking [19,20]. Its effect, however, is limited owing to the limited steric hindrance of PYO ligand.

In PVP matrix, [Cu(PYO)(PPh₃)₂]BF₄ shows a Gauss-liked emission band peaking 505 nm which is clearly blue shifted compared to emission spectra of [Cu(PYO)(PPh₃)₂]BF₄ in CH₂Cl₂ solution and in solid state. Composite emission intensity generally increases with increasing dopant concentration. FWHM values are found as 80 nm for the 7 wt% doped sample, 78 nm for the 9 wt% doped sample, 80 nm for the 11 wt% doped sample and 81 nm for the 13 wt% doped sample, respectively. Clearly, these values are smaller than those of [Cu(PYO)(PPh₃)₂]BF₄ in CH₂Cl₂ solution and in solid state. These decreased FWHM values are consistent the highly ordered arrangement in our composite samples. Stokes shift of our composite samples between absorption edge (490 nm) and emission peak (505 nm) is only 15 nm. It is not usual to see a green emission with small Stokes shift from a Cu(I) complex with N/P ligands, and we are giving an explanation as follows. According to a literature report, the geometric relaxation of MLCT excited state in [Cu(N—N)(P—P)] complexes acts as a major energy loss and non-radiative decay path [18-20]. After being doped into PVP matrix, dopant molecules are dispersed and immobilized in polymer framework with their geometric relaxation greatly limited. Corresponding energy loss is thus decreased, with minimal Stokes shift between absorption edge and emission peak. Emission quantum yields (Φ) of these samples are listed in Table 2. After a systematical comparison between [Cu(PYO)(PPh_3)_2]BF₄ in CH₂Cl₂ solution, in solid state and in PVP matrix, it is found that PVP immobilization limits MLCT geometric relaxation the most effectively due to its rigid framework. In the meanwhile, [Cu(PYO)(PPh_3)_2]BF₄ excited state is effectively restricted, showing small FWHM values of [Cu(PYO)(PPh_3)_2]BF₄/PVP samples.

3.3.3. Excited state decay lifetimes

Excited state decay lifetimes of $[Cu(PYO)(PPh_3)_2]BF_4$ (in CH₂Cl₂, 2 μ M), bulk $[Cu(PYO)(PPh_3)_2]BF_4$ and the four composite samples are shown in Fig. 5. All samples follow biexponential decay pattern with mean decay lifetimes of 1.26 μ s for $[Cu(PYO)(PPh_3)_2]BF_4$ solution, 106.0 μ s for bulk $[Cu(PYO)(PPh_3)_2]BF_4$, 156.1 μ s for the 7 wt% doped sample, 168.6 μ s for the 9 wt% doped sample, 175.9 μ s for the 11 wt% doped sample and 150.5 μ s for the 13 wt% doped sample, respectively. Their detailed fitting parameters are listed in Table 2. Phosphorescent nature of these samples are thus confirmed by their long-lived emissive components [19–22]. Taking the above DFT calculation result into account, their emissive state can be assigned as ³(MLCT&LLCT), which is consistent with literature cases [19–20].

In CH₂Cl₂ solution, [Cu(PYO)(PPh₃)₂]BF₄ shows the shortest lifetime of only 1.26 µs. This observation is consistent with our above conclusion that it suffers from bad geometric relaxation and solvent molecule attack, owing to the limited steric hindrance of PYO ligand. In solid state, solvent effect is eliminated, [Cu(PYO)(PPh₃)₂]BF₄ lifetime is greatly increased to 106.0 µs. Clearly, the highly ordered arrangement in solid state [Cu(PYO)(PPh₃)₂]BF₄ forms a rigid environment. With its geometric relaxation restricted, [Cu(PYO)(PPh₃)₂]BF₄ lifetime is obviously increased. After being immobilized in PVP matrix, its geometric relaxation is further depressed by polymer framework, showing an even longer lifetime than that of solid state [Cu(PYO)(PPh₃)₂]BF₄. Taking above emission spectrum analysis into account, we come to a conclusion that MLCT geometric relaxation in [Cu(PYO)(PPh₃)₂]BF₄ excited state can be effectively restricted by PVP framework.

There is an interesting fact worthy of more explanation words. Composite sample lifetime firstly increases from 156.1 µs (7 wt%) to 175.9 µs (11 wt%). Then composite sample lifetime is decreased to 150.5 µs at doping concentration of 13%. There seems an optimal doping concentration (11 wt%) for our composite samples, which can be explained as follows. It is assumed that there are two or more factors that affect excited state decay lifetime: (1) PVP immobilization effect which is positive for lifetime and (2) self-quenching/absorption between dopant molecules which is negative for lifetime. If doping concentration is quite low, self-quenching/absorption between dopant molecules can be ignored. PVP immobilization effect is increased with increasing doping concentration, with composite sample lifetime gradually increased. On the other hand, if dopant molecules are more than enough, PVP immobilization effect gets to its ceiling, self-quenching/absorption tends to dominate composite samples, compromising lifetime. There should be both strong PVP immobilization effect and limited self-quenching/absorption in the optimal composite sample, showing its longest excited state decay lifetime.

Table 2

Fitting parameters of $[Cu(PYO)(PPh_3)_2]BF_4$ in CH_2Cl_2 (2 μ M), bulk $[Cu(PYO)(PPh_3)_2]BF_4$ and the four composite samples. $y = A_1 * exp(-x/t_1) + A_2 * exp(-x/t_2) + y_0, \tau = (A_1t_1^2 + A_2t_2^2) / (A_1t_1 + A_2t_2)$.

Sample	Φ	A ₁	t ₁ (s)	A ₂	t ₂ (s)	R ²	τ(s)
Solution	0.089	0.3111	1.12674E-7	0.46272	1.32709E-6	0.999	1.26
Bulk	0.55	0.38843	1.13131E-5	0.25775	1.19502E-4	0.996	106.0
7 wt%	0.40	0.48915	1.14853E-5	0.28594	1.72553E-4	0.993	156.1
9 wt%	0.52	0.42806	1.45892E-5	0.31326	1.85179E-4	0.992	168.6
11 wt%	0.60	0.47067	1.59409E-5	0.37050	1.9267E - 4	0.994	175.9
13 wt%	0.58	0.37931	1.55636E-5	0.21727	1.71843E-4	0.996	150.5



Fig. 5. Excited state decay lifetimes of [Cu(PYO)(PPh₃)₂]BF₄ (in CH₂Cl₂, 2 µM), bulk $[Cu(PYO)(PPh_3)_2]BF_4$ and the four composite samples ($\lambda_{ex} = 355$ nm).

3.3.4. Photostability under continuous radiation

Based on our above analysis, it is confirmed that [Cu(PYO)(PPh₃)₂]BF₄ dopant molecules have been immobilized and well protected in PVP matrix. Their geometric relaxation in excited state is effectively restricted. With this perfect protection from PVP framework, we assume that photostability of our dopant may be improved as well in our composite samples. Emission intensity monitoring under continuous radiation is performed on [Cu(PYO)(PPh₃)₂]BF₄ (in CH_2Cl_2 , 2 μ M), bulk $[Cu(PYO)(PPh_3)_2]BF_4$ and the four composite samples to confirm this hypothesis. It is observed in Fig. 6 that $[Cu(PYO)(PPh_3)_2]BF_4$ has the lowest photostability in solid state. Only 60% of its initial emission intensity is recovered after 40 min of continuous radiation. Photo-induced oxidization and deconstruction during this time should be responsible for this emission intensity decrease. In CH₂Cl₂ solution, photostability of [Cu(PYO)(PPh₃)₂]BF₄ is greatly improved. This is because dopant molecules are dispersed in solution and thus protected by solvent molecules. After being immobilized in PVP matrix, [Cu(PYO)(PPh₃)₂]BF₄ shows an even better photostability, which can be explained as follows. In composite samples, all $[Cu(PYO)(PPh_3)_2]BF_4$ molecules are dispersed in PVP framework which offers a protective environment for them. This framework may absorb excitation energy first and then transfer its energy to dopant molecules, resulting in an indirect energy transfer mechanism. Since there is no direct exposure to excitation light, it is thus rational to see their greatly improved photostability of our composite samples.

In addition, it is found that photostability of our composite samples is decreased by increasing doping concentration, which can be explained by the increasing aggregation between dopant molecules. Never the less, photostability of our composite samples is obviously improved compared to that in solid state and in CH₂Cl₂ solution. We then come to a conclusion that PVP is a good supporting matrix for [Cu(PYO)(PPh₃)₂]BF₄ dopant, offering a rigid and protective environment which restricts MLCT geometric relaxation effectively.

4. Conclusion

To sum up, this paper synthesized a diamine ligand having an electron-pulling group in its conjugation plane. A methyl group was connected to this diamine ligand, hoping to further increase its steric hindrance. Geometric structure and electronic nature of corresponding Cu(I) complex were discussed based on its single crystal. It was found that this Cu(I) complex took a distorted tetrahedral coordination field. Its onset electronic transition had a mixed character of MLCT which suffered from bad geometric relaxation. To restrict this geometric relaxation and improve emissive performance, [Cu(PYO)(PPh₃)₂]BF₄ was



Fig. 6. Emission intensity monitoring under continuous radiation is performed on [Cu(PYO)(PPh₃)₂]BF₄ (in CH₂Cl₂, 2 µM), bulk [Cu(PYO)(PPh₃)₂]BF₄ and the four composite samples ($\lambda_{ex} = 355 \text{ nm}$).

doped into PVP fibers through electrospinning technique. Detailed analvsis and comparison between solid state sample, solution sample and composite samples suggested that MLCT geometric relaxation was effectively restricted by PVP immobilization effect. With its geometric relaxation greatly limited, emissive performance of [Cu(PYO)(PPh₃)₂]BF₄ was obviously improved, including emission blue shift, long emission decay lifetime and better photostability. MLCT geometric relaxation is widely existed in transition metal complexes. In most cases, this geometric relaxation compromises their emissive centers more or less. Polymer immobilization effect can effectively limit such geometric relaxation. Thus, it is reasonable to assume that similar polymer immobilization effect should be found for other composite samples. This finding should be helpful for later design of one dimensional nanostructures for photoelectronic applications.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.saa.2016.06.017.

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