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Exploring Intertrimer Cu···Cu Interactions and Further Phosphorescent Properties of Aryl Trimer Copper(I) Pyrazolates via Substituent Changing and External Pressure

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To explore the effect of intertrimer Cu···Cu interactions on the phosphorescent properties of trimeric copper(I) pyrazolates, three new complexes with identical core cluster structures and different substituents, $\{[3,5\text{-}(Me)_2\text{-}4\text{-}(Ph)Pz]Cu\}_3$ (MPC-P), $\{[3,5\text{-}(Me)_2\text{-}4\text{-}(1\text{-}Naph)Pz]Cu\}_3$ (MPC-N), and $\{[3,5\text{-}(Me)_2\text{-}4\text{-}(9\text{-}Anthr)Pz]Cu\}_3$ (MPC-A), were synthesized. The intertrimer Cu···Cu distances of the three complexes were obtained from X-ray crystallographic data or molecular dynamics simulations. The phosphorescent properties of the three complexes were investigated at various pressures. At ambient pressure, the emissions of the three complexes were dramatically different from each other. For MPC-P, the main emission band was identified as phosphorescence and MPC-N gave a predominant emission of fluorescence and a weak emission of phosphorescence. When the substitutent was replaced by an anthryl group in MPC-A, no phosphorescence was observed, except for a strong fluorescence band. The phosphorescence of the trimer copper(I) pyrazolates was assigned to the excited-state dimer/polymer $^*[Cu_3]_n$ with LMCT characteristics. Under higher external pressures, only phosphorescent intensities of MPC-P showed considerable enhancement at pressures up to 2 GPa. External pressure reduced the intertrimer Cu···Cu distances of MPC-P and enhanced the phosphorescence intensities, providing a direct evidence to support the assignment of phosphorescence.

Introduction

There has been considerable interest in polynuclear d^{10} metal (Cu(I), Ag(I), Au(I), Zn(II), Cd(II), Hg(II)) complexes, due to their intriguing structures and photoluminescent properties. Metal−metal and metal−ligand bonding natures were suggested to induce important or even unique photophysical/photochemical properties.[1−5] Among these complexes, polynuclear copper(I) complexes have attracted the most attention due to their low cost and special structures, from dinuclear to polynuclear species.[6−14] Recently, cyclic trimeric copper(I) complexes with pyrazolate ligands have

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been studied by several groups because of their significant applications in multiple fundamental areas.[15-20] Ehlert, Trotter, and co-workers reported the synthesis and X-ray crystal structures of $\{[3,5\text{-(Me)}_2\text{Pz}]\text{Cu}\}_3$ and $\{[3,4,5\text{-(Me)}_3\text{Pz}]\text{Cu}\}_3$.[15] A copper−nitropyrazole trimer was reported by Ardizzoia, Moret, and co-workers.[7] Omary, Dias, and co-workers have reported some trimeric copper(I) complexes with fluorinated pyrazolate ligands, such as $\{[3\text{-(CF}_3\text{)Pz}]\text{Cu}\}_3$, $\{[3\text{-(CF}_3\text{)-5-(Me)Pz}]\text{Cu}\}_3$, $\{[3\text{-(CF}_3\text{)-5-(Ph)Pz}]\text{Cu}\}_3$, and $\{[3,5\text{-(CF}_3\text{)}_2\text{Pz}]\text{Cu}\}_3$. For all of the cyclic trimeric copper(I) complexes, their structures were described as nine-membered Cu_3N_6 metallacycles in the center of the molecules, and their packing manners in crystal structures were greatly affected by the substituents of the ligands. In the fluorinated complexes, the Cu_3N_6 metallacycles gave rise to zigzag chains, whereas the nonfluorinated complexes ($\{[3,5\text{-(R)}_2\text{Pz}]\text{Cu}\}_3$, R = Me, i-Pr) tended to form dimers. In photophysical studies on the cyclic trimeric copper(I) complexes, their phosphorescent color and lifetime were found to be dramatically sensitive to the molecular status such as solvent, concentration, temperature, and rigidity of medium. For example, Dias et al. reported luminescence solvatochromism and concentration luminochromism of a series of trimeric copper(I) compounds and attributed this to a complex effect that related to the cuprophilic interactions.[16,17]

Up to now, Cu···Cu bonds as short as 2.35 Å have been well documented in other complexes,[21] and several theoretical studies were performed to explore the Cu···Cu interactions with longer distances.[21,22] However, reports of direct experimental evidence between the weak interactions and phosphorescence are rare. To investigate the effect of Cu···Cu interactions on the phosphorescent properties, a possible route was to modify the complex by various ligands with different volumes. Additionally, altering the pressure was another more direct choice to change the Cu···Cu interactions at the same temperature without molecular structural alteration.

In recent years, high pressure has been introduced to investigate the properties of luminescent materials.[23-26] It can alter the environment of molecules in a continuous and controlled way as a perturbing variable. When a sample is compressed by external pressure, the distance between adjacent molecules should be decreased, which directly enhances the intermolecular interactions and increases the possibilities of orbital overlapping. Although decreasing temperature also resulted in a volume decrease of the sample, the temperature effect on the electronic orbits involves a mixed dependence on both the temperature and the structure of the materials, while the pressure effect on the electronic orbits involves only the structure dependence.[27] The effects of pressure on the properties of photoelectric functional materials has been described previously. A pressure-induced red shift of the luminescence band in the nonstacked square-planar $[\text{Pt(SCN)}_4]^{2-}$ complex and pressure-induced luminescence enhancement of the $[\text{Pd(SCN)}_4]^{2-}$ complex were both reported.[28,29] Pressure could tune the molecular population with different conformations,[30a] and it was also utilized to distinguish different emission bands of luminescent materials with complicated luminescent species.[30b]

Taking into account the fact that the intramolecular Cu···Cu distances of these trimeric complexes had no apparent effects on their photophysical properties,[31] we expected that applying external pressure to adjust the intermolecular Cu···Cu distances could provide us a direct way to observe the connection between Cu···Cu intermolecular interactions and photophysical properties of these complexes. In this work, we prepared three trimeric copper(I) pyrazolates, $\{[3,5\text{-(Me)}_2\text{-4-(Ph)Pz}]\text{Cu}\}_3$ (MPC-P), $\{[3,5\text{-(Me)}_2\text{-4-(1-Naph)Pz}]\text{Cu}\}_3$ (MPC-N), and $\{[3,5\text{-(Me)}_2\text{-4-(9-Anthr)-Pz}]\text{Cu}\}_3$ (MPC-A), shown in Chart 1. Substituents with different volumes were used to tune the distance of intertrimer units, and the three trimeric complexes exhibited different luminescent behaviors. Both photophysical measurements and theoretical studies were carried out for comparison purposes. All the results suggested that the intertrimer Cu···Cu interactions affect the phosphorescent properties significantly. Additionally, we conducted in situ X-ray and luminescence experiments at pressures up to 3 GPa to explore the relation between intertrimer Cu···Cu distances and phosphorescent properties.

Experimental Section

Materials. MPC-P, MPC-N, and MPC-A were synthesized according to the routes described in Scheme S1 (see the Supporting Information) and characterized by ^{1}H NMR, ^{13}C NMR, elemental analysis, and MS or single-crystal X-ray diffraction. Similar to other trimeric complexes of Cu(I) and Ag(I),[4] MPC-P decomposed under ESI-MS and MALDI-TOF-MS conditions. Single-crystal X-ray diffraction was used to determine the molecular structure (see the Supporting Information). For MPC-N and MPC-A, MS data were obtained to characterize the structure of the complex. The crystal structures of these two

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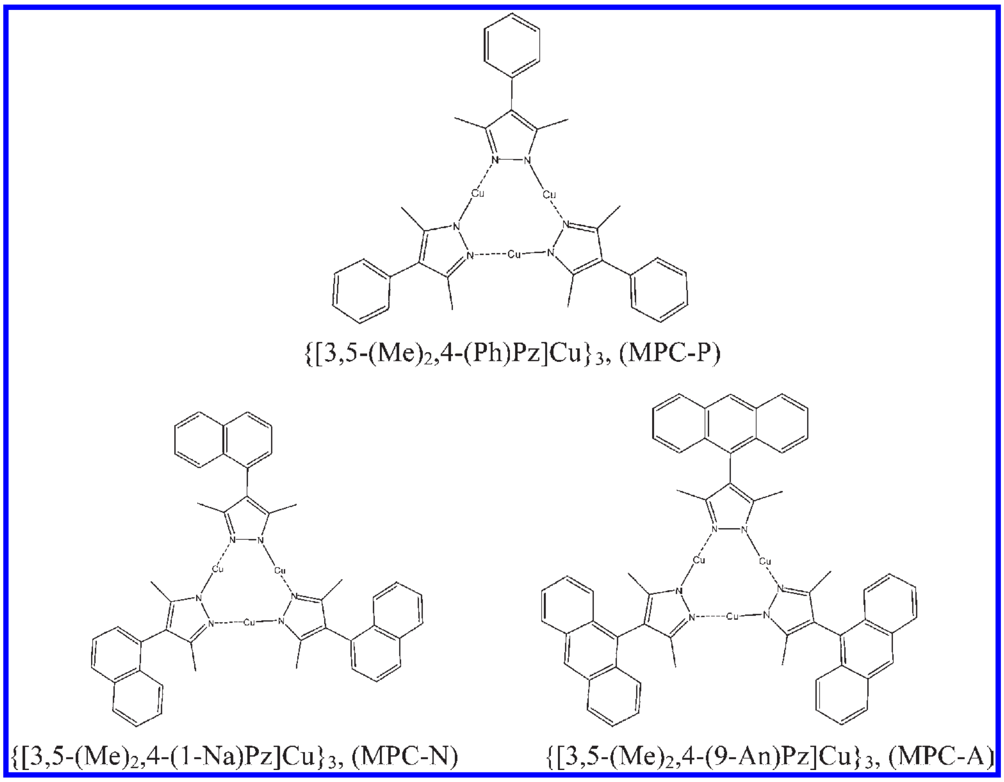
Chart 1. Structures of Three Trimeric Copper(I) Pyrazolates



complexes failed to be detected, since it was difficult to get reliable single crystals.

High-Pressure Experiments. The photophysical experiments were performed in a Merrill-Bassett diamond anvil cell (DAC). The stainless steel gasket had a hole 280 μm in diameter with a thickness of about 90 μm. The sample and a tiny ruby chip were placed in the hole, and light mineral oil (Aldrich 330779) was used as the pressure medium. The pressure was calibrated with a ruby fluorescence red shift. For the emission measurements, a DPSS laser (355 nm) and a BLN457-100 laser (457 nm) were used as the excitation sources. The luminescence spectra were dispersed with a 0.3 m spectrometer and a photomultiplier (PMT) coupled to a 32 bit microprocessor-based data acquisition and spectrometer controller module (NCL Electronics Interface, Acton-Research Corporation) and computer. Time-resolved fluorescence measurements were performed using a LifeSpec-ps fluorescence lifetime analytical spectrometer (Edinburgh Instruments) with modification for DAC. A 370 nm pulse diode laser (PDL 800-B, Pico Quant) and a 355 nm DPSS laser were used to excite the samples. The in situ angle dispersive X-ray diffraction experiments at high pressures were performed at the Beijing Synchrotron Radiation Facility (BSRF).

Computational Details. The ground-state geometries of MPC-P, MPC-N, and MPC-A were optimized with the Kohn−Sham (KS) density functional theory (DFT) using Becke's three-parameter hybrid functional with the Lee−Yang−Parr fit for the correlation functional (B3LYP). Then the optimization geometries were used as initial conformations for the thermostatic atom-centered density-matrix propagation (ADMP) simulations, which were performed at 300 K with time step 0.2 fs. Single-point calculations of the dimer MPC-P was run at the single-crystal geometries. All of the above calculations employed an all-electron 6-31G(d) basis set for carbon, hydrogen, and nitrogen atoms and a valence-electron LanL2DZ basis set for the copper atom. An effective core potential (Lanl2DZ) was also used on the copper atom. All calculations described here were carried out using the GAUSSIAN suite of programs.[32]

Results and Discussion

UV/Vis and Emission Measurements. UV−vis absorption spectra of the three copper(I) complexes recorded at room temperature in degassed chloroform are shown in Figure 1a. There were no absorption peaks at wavelengths longer than 250 nm for MPC-P. MPC-N exhibited an absorption peak at about 290 nm similar to the absorption of naphthalene, but without fine structures. For MPC-A, both the shape and location of the absorption band were almost the same as those of anthracene, implying that little conjugation between anthryl and the pyrazolyl ring existed. Figure 1b shows a photoluminescence spectrum of the three complexes at room temperature in degassed chloroform. It was obvious that no credible emissions were observed, except MPC-A,

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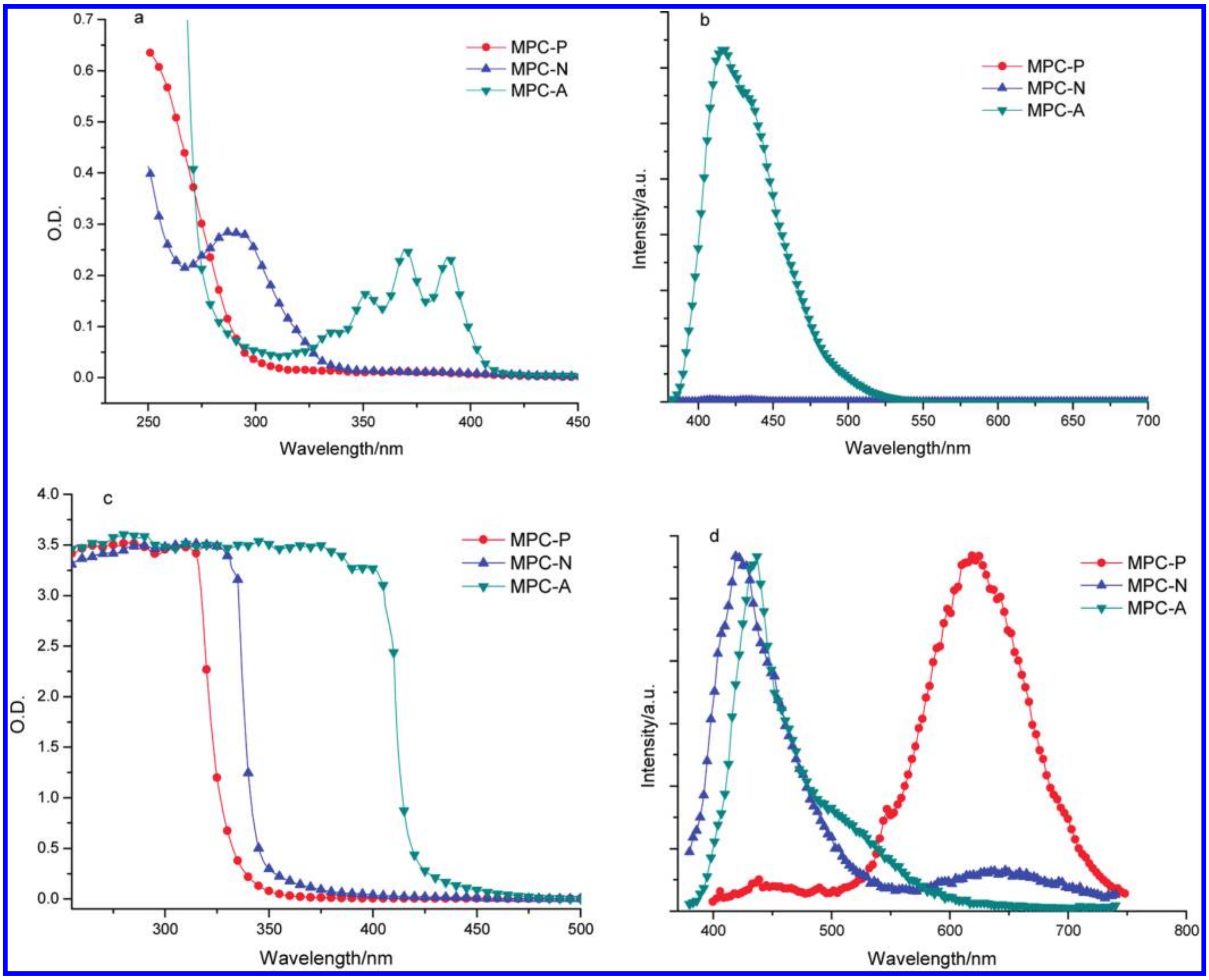

Figure 1. Absorption and luminescence spectra of MPC-P, MPC-N, and MPC-A in solution and as powders.

which presented bright blue fluorescence with a maximum at 420 nm.

Figure 1c shows the absorption spectra of the three complexes as powders at room temperature. Saturated absorption spectra were observed for all three complexes, which shifted to longer wavelength with increasing conjugation of the end substituents. Normalized luminescence spectra of the three complexes in powder at ambient pressure are shown in Figure 1d. It could be seen that the luminescence spectra of the three complexes could be identified as two series according to different substituents: phenyl, naphthyl, and anthryl. The predominant emission of MPC-P located above 600 nm, in contrast to that of MPC-A in the blue region, suggested that luminescence of the two series originated from excited states with different characteristics. MPC-P exhibited one broad unstructured emission band located at 620 nm together with a small emission band with a maximum at 440 nm. According to the lifetime measurements (shown in Table 1), they were due to phosphorescence and fluorescence, respectively. The lifetime of the phosphorescence implied that the orbits of the copper atom deeply involved in the transition $T_1 \rightarrow S_0$ and the phenyl substituent had only a slight effect on the conjugation system of the Cu_3N_6 metallacycles. The emission of MPC-N exhibited two bands with maxima at 638 and 420 nm, which were phosphorescence and fluorescence for their luminescent lifetimes. For MPC-A, a significant difference from the first two complexes was no phosphorescence in its luminescence spectrum. Both the main emission band locatied at 430 nm and the shoulder band at 530 nm were identified as fluorescence.

Table 1. Decay Data of the Emission of Three Trimeric Copper(I) Pyrazolates

MPC-P		MPC-N		MPC-A	
measd wavelength (nm)	lifetime	measd wavelength (nm)	lifetime	measd wavelength (nm)	lifetime
440	2.0 ns	420	4.0 ns	430	3.7 ns
		480	3.8 ns	476	3.8 ns
630	18.2 μs	640	2.3 μs	540	3.2 ns

As described above, absorption and luminescence spectra of the complexes showed great differences between the powder and solution states. The divergences of absorption spectra were not surprising in terms of the presence of solvation and packing effect of the molecules. The powder

Table 2. Calculated and Experimental Structural Parameters of MPC-P, MPC-N, and MPC-A

	intratrimer Cu···Cu dist (Å)	aryl−pyrazolyl bond length (Å)	aryl−pyrazolyl dihedral angle (deg)
MPC-P	3.29 (calcd), 3.27 (exptl)	1.48 (calcd) 1.50 (exptl)	47 (calcd), 46 (exptl av)
MPC-N	3.29 (calcd)	1.49 (calcd)	75 (calcd)
MPC-A	3.29 (calcd)	1.50 (calcd)	88 (calcd)

absorbance could be considered as that of the solution with unlimited high concentration. However, the presence of phosphorescence only in the powder form could not be simply assumed as the result of a common concentration effect, since the luminescence intensities of organic coordination compounds in the solid state generally decreased greatly in comparison with those in dilute solution.

Assignment of Phosphorescence. In general, for solid-state compounds, random packing without special interactions and ordered arrays between molecules are the main kinds of packing modes. The molecular system with random packing could be considered as a solution with unlimited high concentration. In contrast to dilute solution, random packing severely decreases intermolecular distances and thus more or less impedes the intramolecular vibration and rotation. Therefore, one consequence of the random packing is to reduce the nonradiative internal conversion decay process of the excited state. Another impact caused by the random mode is the great increase of short-range interactions, such as energy transfer (ET) with high-order multipole interactions or energy emigration (EM).[33] Usually, ET and EM are the main factors controlling the emission of organic coordination compounds and the luminescence intensity of solid-state compounds is generally lower than that in solution. However, for some compounds, such as the so-called AIEE compounds,[34] the reduction of the nonradiative decay process of the excited state is the predominant factor and the emission of AIEE compounds in the solid state is enhanced by the packing of molecules. As for the ordered array mode, one or more special interactions, such as hydrogen bonding, $\pi-\pi$ interactions, van der Waals interactions, coordination, and charge-transfer interactions, could be present between the adjacent molecules.

To investigate the contribution of random packing on the phosphorescence of trimeric copper(I) pyrazolates, the three complexes were monodispersed in PMMA films (concentration 1.0×10^{-3} mol kg^{-1}). The free volume of PMMA was small enough to partially hinder the phenyl rotation, and the higher excitation energy of the polymer compared to that of the trimers decreased greatly the possibility of ET and EM processes; thus, the polymer was suitable to simulate this pure hindrance effect.[35] The luminescence spectra of the complexes are shown in Figure S1 (Supporting Information). It was similar to the case in chloroform solutions, and no phosphorescence was observed for all three complexes in PMMA. Therefore, the phosphorescence observed only in the powder form actually indicates that the molecules of the trimer in the solid were not involved in random packing, and some special interactions between the trimer molecules should be present. Additionally, the significant dissimilarity of phosphorescent properties implied that the interactions in these three complexes might present great differences.

The $\pi-\pi$ stacking interactions between aromatic units, especially for those nonfused rings such as phenyl and pyrazolyl, were very small. These weak interactions would have only a slight contribution to the packing process of the trimers with heavy atoms. Therefore, another possible existing interaction, the so-called "cuprophilic interaction", had to be considered. Cuprophilic interaction is the attractive force between closed-shell d^{10} copper(I) atoms but is not a commonly accepted concept due to its weakness,[36] which was estimated by calculations as being up to 17−25 kJ mol^{-1} per Cu···Cu pair.[37] Since a cuprophilic interaction is expected to depend on the inverse sixth power of the distance, its interaction range is limited to about 2.5−3.8 Å between the two Cu atoms. Therefore, a cuprophilic interaction, present or not in the three complexes, could be dependent on their substituent volume. To explore the substituent volume effect, theoretical studies on the molecular geometries and molecular conformation dynamics were carried out.

The important structural parameters of the three complexes are given in Table 2 and compared with the experimental data, if they exist. The calculated results prove that the central Cu_3N_6 metallacycles are close to D_{3h} symmetry and the nine atoms in the metallacycles are coplanar. It is obvious that the structures of metallacycles in the three complexes are almost the same and are not dependent on changes in the substituents. The intramolecular Cu···Cu distances in the three complexes were calculated as 3.29 Å, which is close to those in other known Cu_3N_6 metallacycles (3.17−3.21 Å).[16a] In the molecules of MPC-P, MPC-N, and MPC-A, the bond lengths between the aryl and pyrazolyl rings are 1.48, 1.49, and 1.50 Å, respectively. They are close to the lengths of the common C−C bond, implying that there is less conjugation between the aryl and pyrazolyl rings. Moreover, the values of the dihedral angle between the aryl and pyrazolyl rings are calculated as 47, 75, and 88° for MPC-P, MPC-N, and MPC-A, respectively. The results are in line with the expected results for various sizes of aryl groups. The different dihedral angles would induce various repulsion forces among the paired trimers, supporting our strategy that tuning the intertrimer Cu···Cu distances by changing the substituent on the pyrazolyl ring was feasible. It is worth noting that all calculated values given in Table 2 are in good agreement with the experimental data (available for MPC-P),

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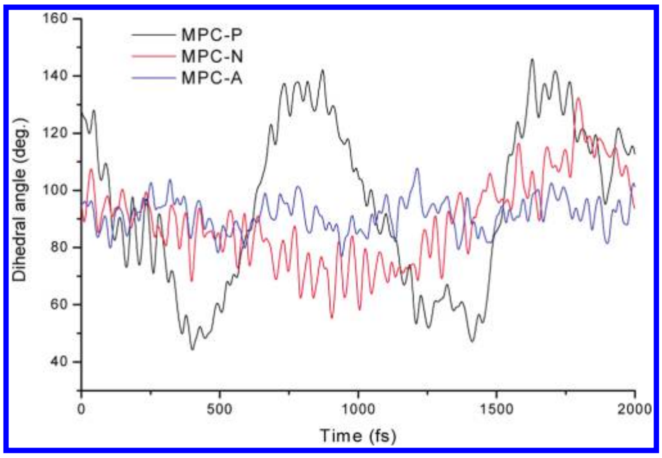

Figure 2. Three dihedral angles between aryl and pyrazolyl rings in MPC-P, MPC-N, and MPC-A as a function of time.

which suggests that the chosen computational level is able to give a reliable description for the structures of the three complexes.

It is well-known that the molecular packing was a thermostatic dynamic process in which the molecular geometry changed more or less with time. Therefore, the thermostatic MD simulation was particularly helpful to understand the substituent effects on the packing process in the real systems. The ADMP approach combined with the ab initio method, the same as the approach used in geometry optimizing, was used to simulate the dynamics of the three complexes, and the kinetic energies of these systems were kept constant in the thermostatic simulations.[38] The MD results showed that the structures with substituents of the three complexes omitted were extremely similar to each other. Nevertheless, the kinetic behaviors of dihedral angles between the aryl and pyrazolyl rings showed great divergences. Figure 2 predicted the dihedral angles as a function of time. It was obviously obtained that the main fluctuation range of Φ in MPC-A was about 25°, which was the smallest among the three dihedral angles, and its mean value was close to 90°. This was not surprising, due to the great repulsion between anthryl and the two methyl groups located on the pyrazolyl ring. With regard to the other two dihedral angles, however, both of them were apparently fluctuating, and the swing scopes were as high as 80 and 100° in MPC-N and MPC-P, respectively. The minimum values of the three dihedral angles were less than those in optimized geometries, suggesting that in the packing process the two trimers had small probabilities to be closer than that in thermodynamic stable state for existing of internal kinetic energy, which were proven partially by the MPC-P geometry in a single crystal. On the basis of the simulation results, the contributions of cuprophilic interaction in the packing process of trimers could be evaluated.

As mentioned above, the interaction of the Cu$\cdots$Cu pair was about 17−25 kJ mol^{-1}. Two pairs would have a value higher than 35 kJ mol^{-1}, which was enough to have significant effects on the assembly of most organic coordination molecules. Coincidentally, X-ray diffraction revealed that MPC-P molecules were constructed as a zigzag chain where adjacent trimers connected with each other just through two Cu$\cdots$Cu pairs. In the chain structure, each two adjacent molecules were arranged in a "chair" conformation (as shown in Figure 3). The short intertrimer Cu$\cdots$Cu distances of ~3.58 Å (average value) for MPC-P, smaller than those of {[3-(CF$_3$), 5-(Me)Pz]Cu}$_3$ and {[3,5-(CF$_3$)$_2$Pz]Cu}$_3$,[16a] suggested a domination of intermolecular cuprophilic interaction over chain organization. On the other hand, the Cu$\cdots$Cu distance of MPC-P was remarkably longer than that of {[3,5-(Me)$_2$Pz]Cu}$_3$,[15a] suggesting a repulsion among the phenyls in the paired copper(I) trimers and a weaker cuprophilic interaction. However, for MPC-N and MPC-A, since it was hard to obtain the ideal single crystals for crystal analysis, molecular modeling on the basis of molecular mechanic calculations using the Hyperchem 7.0 package was applied.[39] For the bulky naphthyl groups, the MPC-N molecules were not able to possess an energy-favored zigzag chainlike stacking. As shown in Figure 3, when two molecules were forced to assemble as a dimer with chair conformation, the intermolecular Cu$\cdots$Cu distances would arrive at a minimum value of about 4.1 Å when the naphthyl groups of two molecules were situated in opposite directions. The distance implied a weak intermolecular cuprophilic interaction. However, the outward naphthyls would hinder the third trimer coming close to the dimer. The possible minimal distance between the dimer and the third trimer was calculated as long as 6.4 Å, as shown in Figure 3. Therefore, cuprophilic interactions were likely to be present only in the dimer and they made no contribution to the interdimer attractive forces. With regard to MPC-A, the large repulsion between intertrimer anthryl groups resulted in a long intermolecular Cu$\cdots$Cu distance of 6.5 Å, indicating that there was still no cuprophilic interaction and the corresponding crystal could not be formed.

Additionally, frontier molecular orbitals of dimers of three trimers were calculated on single-crystal geometry (MPC-P) or optimized structures (MPC-N, MPC-P). Figure 4 shows the calculated results for the MPC-P dimer. It was obvious that the highest occupied molecular orbital (HOMO) largely preserved the electronic structure of the ligand (3,5-dimethyl-4-phenylpyrazole) with a few contributions from the copper atoms, while the lowest two unoccupied molecular orbitals (LUMO and LUMO+1) contained more copper contributions. The results suggested that the lowest energy transitions of the MPC-P dimer had some LMCT characteristics.[40] It is worthwhile to note that a significant difference could be observed in the virtual orbitals of the dimers in comparison to the occupied orbital. In the former case, the intermolecular orbital overlapping resulted from the same phase of the orbital increase, which indicated the existence of intermolecular Cu−Cu interactions, especially in the excited-state dimer. As for MPC-N and MPC-A, no apparent orbital overlapping was observed.

Therefore, it was rational to conclude that the solid MPC-P could be considered as the inorganic−organic hybrid coordination polymer [Cu$_3$]$_n$ constructed with Cu$_3$

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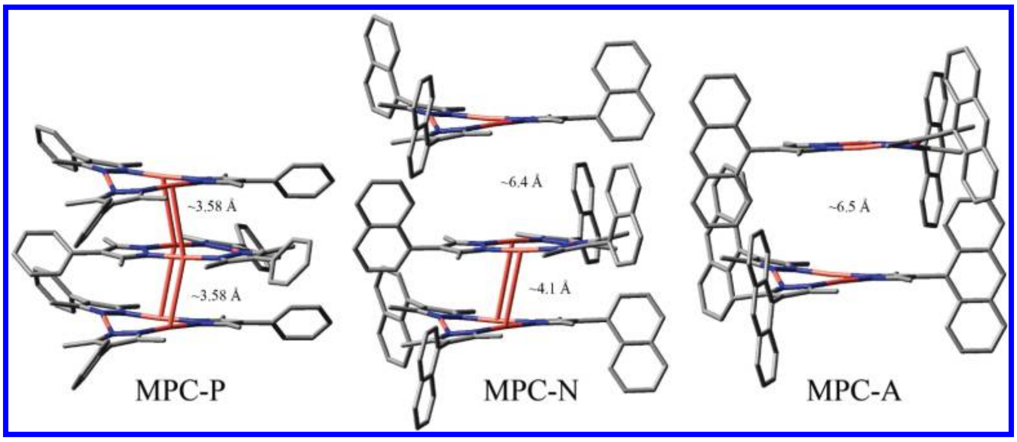

Figure 3. Perspective drawings of MPC-P, MPC-N, and MPC-A, showing the actual packing for MPC-P and calculated assembly of MPC-N and MPC-A, along with intertrimer cuprophilic interactions.

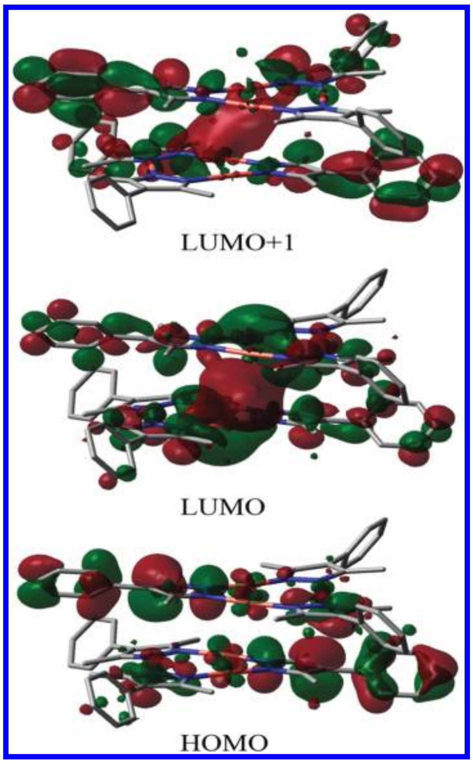

Figure 4. Contours of the frontier orbitals for the MPC-P dimer with single-crystal geometry.

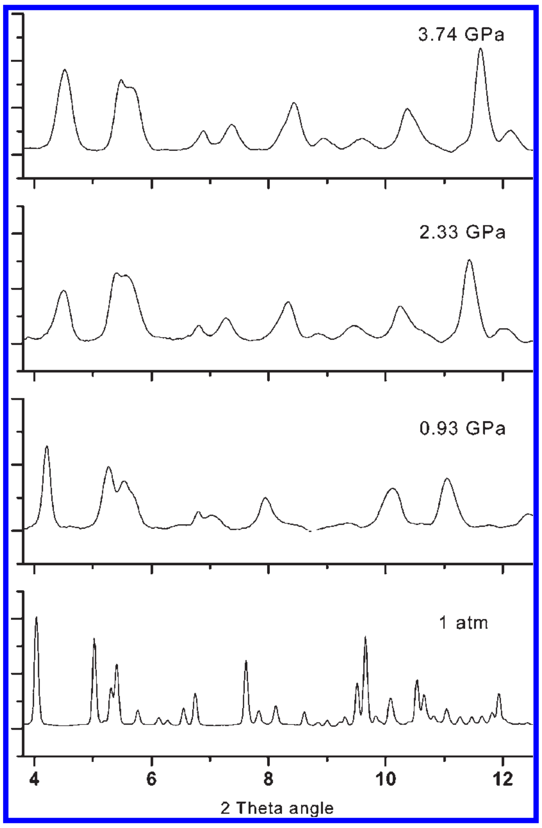

Figure 5. In situ angle dispersive X-ray diffraction experiments of MPC-P at different pressures (λ 0.6199 Å).

Table 3. In Situ Angle Dispersive X-ray Diffraction Data of MPC-P at Different Pressures

pressure (GPa)	0	0.93	2.33	3.74
2θ angle (deg)	5.018	5.252	5.392	5.470
$d_{(010)}$ (Å)	7.080	6.765	6.590	6.496
theor inter $d_{(\mathrm{Cu}\cdots\mathrm{Cu})}$ (Å)	3.494−3.671	3.339−3.508	3.252−3.417	3.206−3.368

units or $[\mathrm{Cu}_3]_m$ ($1 < m < n/2$) oligomers, but MPC-N could only be as an accumulation of $[\mathrm{Cu}_3]_2$ rather than $[\mathrm{Cu}_3]_n$. As for MPC-A, it was only aggregates of $[\mathrm{Cu}_3]_1$. Obviously, the observed and simulated aggregation fashions (whether cuprophilic interaction existed or not) correlated well with different phosphorescent behaviors of the three complexes, suggesting that the room-temperature phosphorescence originated from the excited-state dimer $^*[\mathrm{Cu}_3]_2$ (MPC-N, MPC-P) or polymer $^*[\mathrm{Cu}_3]_n$ (MPC-P) with cuprophilic interaction.

Pressure-Dependent Luminescence. The above results revealed that the size of the substituents on the pyrazolyl ring provided an effective tool to tune the emissions of the trimers through adjusting intermolecular distances.[41] However, due to the fact that the volume of the substituent was a fixed value and could not be adjusted continuously, only a few fixed values of intertrimer distance were obtained. In order to deeply understand the effect of varying intertrimer Cu···Cu interactions on the

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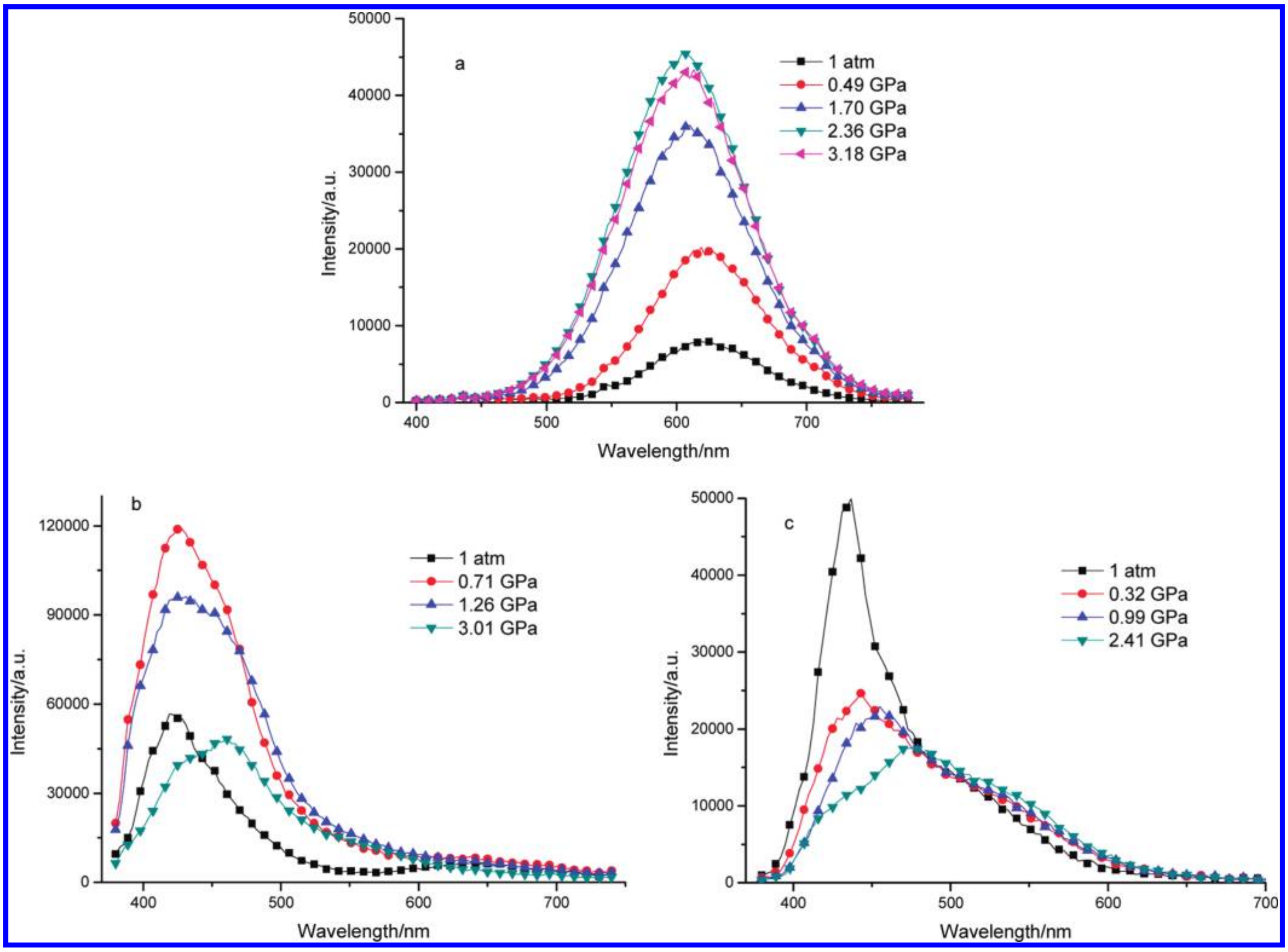

Figure 6. Pressure-dependent luminescence spectra of the complexes of (a) MPC-P, (b) MPC-N, and (c) MPC-A.

luminescent properties of the trimer copper(I) pyrazolates, high pressure was introduced to change continuously the distance between two adjacent molecules. Furthermore, considering the fact that pressure from 1 atm to 6 GPa could induce a large change in intermolecular distance but had only a slight effect on intramolecular change for organic compounds,[42] it was reasonable to apply pressure (< 5 GPa) to explore the association between intertrimer Cu···Cu interactions and phosphorescent properties.

In this work, in situ angle dispersive X-ray diffraction was introduced to investigate the Cu···Cu distance as a function of the pressure. In situ X-ray diffraction (XRD) measurement, using synchrotron radiation, is a very important method for determining the effect of pressure on crystal structure.[43] The angle dispersive X-ray diffraction spectra of MPC-P and of MPC-N and MPC-A at different pressures are shown in Figure 5 and Figure S2 (Supporting Information), respectively. It is worth noting that no phase transition was observed during the entire process of increasing the pressure, and the detected XRD pattern after the release of high pressure was the same as that at 1 atm. Upon an increase in pressure, all diffraction peaks shifted in the direction of greater θ angle with a decrease in intensity. This suggests that all interplanar spacing of the three complexes decreased with increasing pressure. Additionally, at high pressure, all three samples became partially amorphous, as shown by the fact that some diffraction peaks dropped a great deal and became broader. X-ray crystallographic data showed that molecules of MPC-P packed as zigzag chains along the axial direction of (010). Changes in the interplanar spacing $d_{(010)}$ with pressures were measured and are given in Table 3. Additionally, because no phase transition was observed, the intermolecular Cu···Cu distances and interplanar spacing $d_{(010)}$ were supposed to decrease in parallel with increasing pressure. The estimated values of intermolecular Cu···Cu distances are also given in Table 3. For MPC-N and MPC-A, without crystallographic data, the pressure-dependent intermolecular distances were estimated by averageshifts of diffraction peaks. It could be seen that in the whole measuring range the intertrimer Cu···Cu distance of MPC-P gradually decreased from 3.494−3.671 Å to 3.206−3.368 Å with a maximum contraction of about 8.1%. Nevertheless, the maximum contractions were calculated as 5.0% from 4.1 Å to 3.9 Å for MPC-N and 4.9% from 6.5 Å to 6.2 Å for MPC-A, respectively. The changes in the intertrimer Cu···Cu distances consequently resulted in the variations of the luminescence spectra.

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Figure 6 shows the pressure-dependent luminescence spectra of the three complexes. With an increase in pressure, the phosphorescence intensity of MPC-P increased dramatically, about 6-fold at 2.36 GPa, in comparison with that under ambient conditions. It is known that external pressure generally results in decreased emission for luminescent organic compounds, and only a few compounds have been explored for their pressure-induced emission enhancement, possibly due to their complexity.[28] In this case, the reduced intertrimer Cu···Cu distances resulted in more intense cuprophilic interactions, favoring the form of dimers or polymers ($[Cu_3]_n$). Additionally, the pressure-induced tighter packing organization of dimers/polymers of trimers resulted in a decrease in difference between the triplet geometry and the lowest singlet excited state geometry, which would promote the possibility of intersystem crossing. Moreover, recent computational results suggested that the intertrimer Cu···Cu distance causes a great contraction (23%) in the triplet emissive state.[37b] Thus, the compression process promotes the population of the triplet state, resulting in greater phosphorescence quantum efficiency. Furthermore, pressure inhibited the rotation in the molecule and then retarded the nonradiative decay, which would also enhance the phosphorescence. However, in contrast to the case for MPC-P, the phosphorescence intensity of MPC-N at 638 nm exhibited a slight pressure dependence, where its intensity diversification was only about 15% over the entire measured pressure range. As mentioned above, the in situ XRD measurements for MPC-N suggested that the intertrimer Cu···Cu distances changed slightly (from 4.1 Å to 3.9 Å) with increasing pressure. However, either 4.1 Å or 3.9 Å is a relatively large distance, implying weak cuprophilic interaction and further low phosphorescence intensity. With regard to MPC-A, no phosphorescence was observed because distances of 6.5 and 6.2 Å were too large to allow intertrimer Cu···Cu interactions. The results of the pressure-dependent luminescence spectra further suggested that the phosphorescence originated from the dimer $*[Cu_3]_2$ for MPC-N and MPC-P or the polymer $*[Cu_3]_n$ for MPC-P.

Conclusions

Although there have been a great number of reports about the photoluminescent behavior of solid copper(I) complexes, there have been relatively few focusing on cuprophilic interactions and phosphorescence. The novel luminescent copper(I) pyrazolates MPC-P, MPC-N, and MPC-A presented different emissive behaviors, suggesting that tuning the intertrimer Cu···Cu interactions and further emission properties through the choice of pyrazolate substituents was judicious and feasible. External pressure was introduced to reduce the distance between two adjacent molecules, revealing profound effects on the cuprophilic interactions and phosphorescent behaviors. The results in this work gave a novel route to understand the relationship between the intermolecular Cu···Cu distance and phosphorescent properties of copper(I) complexes. It was unambiguous that intermolecular Cu···Cu interactions played the most important role in the photophysical properties of the trimer copper(I) pyrazolates.

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Supporting Information Available: Figures, text, and tables giving luminescence spectra of the three complexes in PMMA, the angle dispersive X-ray diffraction spectra of MPC-N and MPC-A at different pressures, and synthesis and characterization conditions and a CIF file giving X-ray crystallographic data at 293 K for MPC-P. This material is available free of charge via the Internet at http://pubs.acs.org.