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A series of dinuclear cuprous iodide complexes chelated with 1,2-bis(diphenylphosphino)benzene derivatives: structural, photophysical and thermal properties<sup>†</sup>

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Three new bisphosphine ligands, 4-phenyl-1,2-bis(diphenylphosphino)benzene (Ph-dppb), 4-pyrrolyl-1,2-bis(diphenylphosphino)benzene (OMe-dppb), were synthesized to coordinate with cuprous iodide (Cul), and compared with 1,2-bis(diphenylphosphino)benzene (dppb). Single crystal X-ray diffraction and elemental analysis experiments indicate that three binuclear Cul complexes with formulae of [Cu( $\mu_2$ -I)Ph-dppb]<sub>2</sub>, [Cu( $\mu_2$ -I)Pr-dppb]<sub>2</sub>, and [Cu( $\mu_2$ -I)OMe-dppb]<sub>2</sub> were obtained, which are the same as the reference complex [Cu( $\mu_2$ -I)dppb]<sub>2</sub>. The three complexes showed a maximum emission band ( $\lambda_{max}$ ) in the range of 484–535 nm which varies in the electron effect of the substituted groups (*i.e.* methoxy, pyrrolyl, phenyl) on [Cu( $\mu_2$ -I)dppb]<sub>2</sub>, and in high photoluminescence quantum yield (PLQY) from 53 to 90% in the solid state. Furthermore, the complexes [Cu( $\mu_2$ -I)Ph-dppb]<sub>2</sub> and [Cu( $\mu_2$ -I)Pr-dppb]<sub>2</sub> exhibited a thermal decomposition temperature exceeding 380 °C. The high PLQY and excellent thermal stability of these Cul complexes imply their great potential application as efficient emitters in organic light-emitting diodes (OLEDs).

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### Introduction

Luminescent transition metal complexes are widely studied because of their potential use in organic light emitting diodes (OLEDs). Noble metal such as Ir(III), Pt(III), or Os(II)-based complexes can generate light from both triplet and singlet excitons in OLEDs, allowing the internal quantum efficiency (IQE) of such a device to approach 100%.<sup>1-6</sup> As they are relatively inexpensive, abundant and environment-friendly luminophores, Cu(I) complexes have been investigated widely. After the pioneering work of McMillin, Eisenberg and Ford,<sup>7-9</sup> it is well known that most Cu(I) complexes frequently feature metalto-ligand charge-transfer (MLCT) transition bands in the spectrum which can be associated with a transformation between Cu(I) in the ground state and Cu(II) in the excited state.

Systematic studies on mononuclear  $[Cu(N^N)_2]^+$  complexes, where N^N stands for a chelating bisimine ligand, have shown that the substituent effects of typical bisimine ligands, such as phenanthroline derivatives at 2,9-positions on the MLCT luminescence intensity can be explained by restraining the structural distortion from the tetrahedral to the flattened structure in the excited state.<sup>10,11</sup> The major nonradiative process for the MLCT excited state is attributed to the structural distortion, so the inhibition of diversification could increase the photoluminescence quantum yield (PLQY) of Cu(1) complexes. Thereafter, attention has been paid to  $[Cu(N^N)(P^P)]^+$ ,  $[Cu(P^N)(P^P)]^+$ , and  $[Cu(P^P)_2]^+$ complexes, where P^N and P^P denote an amidophosphine and bisphosphine ligand, respectively.<sup>12-14</sup> These complexes exhibited greatly enhanced emission intensity because the P atom introduces rigid and bulky groups, which prevents structural distortion and results in less nonradiative transition. By modifying the chemical and electronic structure of the N^N, P^N, or P^P type ligand, the emission properties of these complexes have been tuned, with emission colour varying from blue to red and PLQY up to unit,13,14 which shows great potential application as efficient emitter in OLEDs.

Besides the mononuclear Cu(i) complexes, there have also been several reports on dinuclear Cu(i) complexes.<sup>15–21</sup>

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 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available: X-ray crystallographic files in CIF format are all available. CIFs have also been deposited at the Cambridge Crystallographic Database Centre. CCDC 1456957, 1443647, and 1443643 for [Cu(µ<sub>2</sub>-I)Ph-dppb]<sub>2</sub>, [Cu(µ<sub>2</sub>-I)Pr-dppb]<sub>2</sub>, and [Cu(µ<sub>2</sub>-I)OMe-dppb]<sub>2</sub>, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ce02533h

Among which the one with chelation between CuI and 1,2bis(diphenylphosphino)benzene (dppb), named as  $[Cu(\mu_2 - \mu_2)]$ I)dppb]<sub>2</sub>, is appealing.<sup>17</sup> The compound showed not only high PLOY up to 80% in the solid state but also good thermal stability that can be processed in OLEDs using a traditional vacuum thermal deposition technique. Recently, we have demonstrated that high efficiency nondoped OLEDs can be achieved with a neat  $[Cu(\mu_2-I)dppb]_2$  film as the emissive layer, eliminating the need for a host matrix and making the device fabrication more simplified.<sup>22</sup> The device showed green emission and a maximum external quantum efficiency (EQE) of 8.3%, which is comparable to that of the doped OLEDs with triplet exciton confinement architecture in the literature.<sup>23</sup> Consequently, it would be interesting to tune the emission colour of this type of Cu(1) complex, hence to make high efficiency non-doped OLEDs with various emission colours.

Based on Hartree–Fock calculation on  $[Cu(\mu_2-I)dppb]_{2,}^{17}$ the electron density in the highest occupied molecular orbital (HOMO) is distributed over the copper and iodine atoms, while that in the lowest unoccupied molecular orbital (LUMO) is localized on the dppb ligands. Theoretically, the emission colour of this type of complex could be tuned by attaching electron-rich or electron-poor groups on the dppb ligand. Herein, three dinuclear Cu(I) complexes,  $[Cu(\mu_2-I)Ph$  $dppb]_2$ ,  $[Cu(\mu_2-I)Pr-dppb]_2$ , and  $[Cu(\mu_2-I)OMe-dppb]_2$ , which are derived from  $[Cu(\mu_2-I)dppb]_2$  by attaching a phenyl, pyrrolyl, or methoxy group on the dppb ligand were designed and synthesized (Scheme 1). The structures, photophysical and thermal properties of these complexes are discussed.

### Experimental

### Instruments and measurements

The <sup>1</sup>H NMR and <sup>31</sup>P NMR spectra were recorded using a Bruker-400 MHz and 162 MHz spectrometer, respectively. Chemical shift data for each signal were reported in ppm units with CD<sub>3</sub>OD or CD<sub>2</sub>Cl<sub>2</sub> as reference, where  $\delta$ (CD<sub>3</sub>OD) and  $\delta$ (CD<sub>2</sub>Cl<sub>2</sub>) are 3.31 and 5.21, respectively. Elemental analyses (C, H, and N) were carried out with an elemental analyser vario MICRO cube from Elementar Co. The mass spectra were obtained using a Bruker Apex IV Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. The UV-vis spectra were recorded on a Shimadzu UV-3100. The photoluminescence spectra were recorded on an Edinburgh FLS980 fluorescence spectrometer and corrected for detector re-



 $\label{eq:scheme1} \begin{array}{l} \mbox{Synthetic route and molecular structure of } [Cu(\mu_2-l)dppb]_2, \\ [Cu(\mu_2-l)Ph-dppb]_2, \ [Cu(\mu_2-l)Pr-dppb]_2, \ and \ [Cu(\mu_2-l)OMe-dppb]_2. \end{array}$ 

sponse. Quantum yield measurements were conducted using a Hamamatsu C9920 system equipped with a xenon lamp, calibrated integrating sphere and model C10027 photonic multichannel analyser. Thermal gravimetric analysis was undertaken on a Q600SDT instrument unit at a heating rate of 5 °C min<sup>-1</sup> from room temperature to 600 °C under N<sub>2</sub>. The glass transition temperature was determined from the third heating scan.

#### X-ray crystallography

Suitable single crystals for X-ray measurement were collected by thermal sublimation or by a diffusion method with dichloromethane and pentane as the solvents described in the following section. The crystals were mounted on a glass fiber with Paratone-N oil. X-ray diffraction data were determined using an Agilent diffractometer with graphitemonochromated Mo  $K_{\alpha}$  radiation, and structures were solved by direct methods with standard Fourier techniques with the help of AXS software package.

### Synthesis

**Potassium diphenylphosphine (KPPh<sub>2</sub>).** KPPh<sub>2</sub> was prepared by adding a THF solution (20 mL) of chlorodiphenyl phosphine (5.50 g, 25 mmol) to drossy potassium metal (1.95 g, 50 mmol) in THF (60 mL) dropwise under N<sub>2</sub> at room temperature, and the resulting mixture was stirred and heated to reflux for 12 h. The solution of KPPh<sub>2</sub> in THF was brownish red, ultimately.

1,2-Bis(diphenylphosphino)benzene (dppb). dppb was synthesized in a way similar to the reported procedure.<sup>24</sup> To a solution of KPPh<sub>2</sub> (25 mmol) in THF (80 mL) was added slowly a solution of 1,2-difluorobenzene (1.25 g, 11 mmol) in toluene (50 mL). The mixture was refluxed for 28 h and then allowed to cool down to room temperature. A crude product was obtained by removal of the solvent, which was recrystallized in toluene to get 3.01 g of white solid (yield: 60%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.24–7.14 (m, 14H), 7.14–7.05 (m, 8H), 6.99–6.92 (m, 2H). MS: *m*/z 447.1 (M<sup>+</sup>, 100).

3,4-Difluorobiphenyl (S1). To a round-bottom flask was added phenylboronic acid (2.70 g, 22 mmol), sodium carbonate (4.40 g, 41.5 mmol), 4-bromo-1,2-difluorobenzene (4.01 g, 20.7 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.40 g, 0.4 mmol), ethanol (100 mL) and water (50 mL), and the mixture was stirred at 80 °C for 16 h. After cooling to room temperature, the mixture was extracted by using DCM (3 × 50 mL). The organic phase was washed with NaCl solution, dried over MgSO<sub>4</sub>, filtered and removed off the solvent under reduced pressure. The crude product was purified by column chromatography to obtain 3.61 g of white solid (yield: 95%). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD):  $\delta$  (ppm) 7.58 (m, 2H), 7.52 (m, 1H), 7.42 (m, 3H), 7.34 (m, 2H). MS: *m/z* 191.1 (M<sup>+</sup>, 100).

**4-Phenyl-1,2-bis(diphenylphosphino) benzene (Ph-dppb).** Ph-dppb was prepared as a white solid in 30% yield by using the same synthesis and work up procedure to dppb, where S1 (2.09 g, 11 mmol) was used to substitute 1,2-difluorobenzene. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD):  $\delta$  (ppm) 7.275 (m, 28H). MS: *m*/*z* 523.2 (M<sup>+</sup>, 100).

1-(3,4-Difluorophenyl)-1*H*-pyrrole (S2). To a 100 mL roundbottom flask was added acetic acid (1.4 mL), 1,2dichloroethane (37.2 mL), water (22.4 mL), 3,4-difluoroaniline (2.58 g, 20 mmol), and 2,5-bis(methyloxy)tetrahydrofuran (2.77 g, 21 mmol). After overnight stirring at room temperature under N<sub>2</sub>, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 30 mL). The organic phase was washed with NaCl solution, dried over MgSO<sub>4</sub>, filtered and distilled off the solvent under a reduced pressure. The crude product was purified by column chromatography to get 2.80 g of product (yield: 77%). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD):  $\delta$  (ppm) 7.46 (m, 1H), 7.30 (m, 2H), 7.15 (t, 2H), 6.28 (t, 2H). MS: *m/z* 180.0 (M<sup>+</sup>, 100).

4-pyrrolyl-1,2-bis(diphenylphosphino)benzene (Pr-dppb). Pr-dppb was prepared as a white solid in 43% yield by using the same synthesis and work up procedure to dppb, where S2 (1.97 g, 11 mmol) was used to substitute 1,2-difluorobenzene. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD):  $\delta$  (ppm) 7.310 (m, 20H), 7.055 (m, 2H), 6.950 (m, 1H), 6.795 (t, 2H), 6.180 (t, 2H). MS: *m/z* 511.2 (M<sup>+</sup>, 100).

1,2-Bis(diphenylphosphino)-4,5-dimethoxybenzene (OMe-dppb). OMe-dppb was prepared with a different method to that of dppb.<sup>25</sup> A solution of 1,2-dibromo-4,5-dimethoxybenzene (1.48 g, 5 mmol) in 50 mL of Et<sub>2</sub>O/THF (1:1) was cooled to -100 °C, and a solution of n-BuLi (2.5 M in hexane, 4.2 mL, 10.5 mmol) was added dropwise. The pale brown reaction mixture was stirred at -100 °C for 45 min, after which a solution of chlorodiphenyl phosphine (2.32 g, 10.5 mmol, in 10 mL of THF) was slowly added. The temperature of the reaction flask was maintained at -100 °C during the addition. The reaction mixture was further stirred at -100 °C for 2 h and was then allowed to warm to room temperature overnight. The white product (0.63 g, yield: 25%) was obtained by concentrating the solution under vacuum and recrystallizing the precipitate in toluene. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD):  $\delta$  (ppm) 7.255 (m, 20H), 6.575 (m, 2H), 3.590 (s, 6H). MS: m/z506.1 (M<sup>+</sup>, 100).

### Cu(I) complexes

The four dinuclear Cu(i) complexes were prepared according to the following general procedure: the same equivalent of CuI and dppb series ligand in a moderate amount of toluene was stirred for 5 h at room temperature to form a pale-yellow precipitate. After concentrating the solution, the precipitation was filtered off, and washed with ether. Except for the complex [Cu( $\mu_2$ -I)OMe-dppb]<sub>2</sub> which was purified by recrystallization in DCM/ethanol due to a poor thermal stability, the other three complexes were purified by thermal gradient sublimation around 300 °C with a base pressure of 10<sup>-4</sup> Pa.

[Cu(µ<sub>2</sub>-I)dppb]<sub>2</sub>. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.44–7.31 (m, 4H), 7.29 (q, *J* = 5.9, 5.3 Hz, 20H), 7.24 (t, *J* = 7.6 Hz, 8H), 7.12 (t, *J* = 7.5 Hz, 16H). (1H). <sup>31</sup>P NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  −22.74 (brs, *W*<sub>1/2</sub> = 188 Hz). Anal. calcd. for C<sub>60</sub>H<sub>48</sub>Cu<sub>2</sub>I<sub>2</sub>P<sub>4</sub>, C, 56.57; H, 3.80%. Found: C, 56.77; H, 3.79%.

[Cu(µ<sub>2</sub>-I)Ph-dppb]<sub>2</sub>. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.49 (d, J = 8.0 Hz, 2H), 7.42–7.34 (m, 2H), 7.34–7.17 (m, 28H), 7.12 (t, J = 7.5 Hz, 8H), 7.01 (t, J = 7.6 Hz, 16H). <sup>31</sup>P NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  −19.70 to −26.80 (m). Anal. calcd. for C<sub>72</sub>H<sub>56</sub>Cu<sub>2</sub>I<sub>2</sub>P<sub>4</sub>, C, 60.64; H, 3.96%. Found: C, 60.65; H, 3.99%.

[Cu(µ<sub>2</sub>-I)Pr-dppb]<sub>2</sub>. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.39 (dd, J = 8.3, 2.2 Hz, 2H), 7.35–7.19 (m, 28H), 7.11 (t, J = 6.9 Hz, 16H), 6.95–6.82 (t, J = 2.2 Hz, 4H), 6.37–6.12 (t, J = 2.2 Hz, 4H). <sup>31</sup>P NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  −23.31 (q, J = 200.3,  $W_{1/2}$ = 197.1 Hz). Anal. calcd. for C<sub>68</sub>H<sub>54</sub>Cu<sub>2</sub>I<sub>2</sub>N<sub>2</sub>P<sub>4</sub>, C, 58.17; H, 3.88; N, 1.99%. Found: C, 58.16; H, 3.88; N, 2.00%.

[Cu( $\mu_2$ -I)OMe-dppb]<sub>2</sub>. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.31– 7.18 (m, 24H), 7.01 (t, J = 7.5 Hz, 16H), 6.60 (t, J = 4.6 Hz, 4H), 3.46 (s, 12H). <sup>31</sup>P NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -21.97 (brs,  $W_{1/2}$  = 162 Hz). Anal. calcd. for C<sub>65</sub>H<sub>56</sub>Cu<sub>2</sub>I<sub>2</sub>O<sub>4</sub>P<sub>4</sub>, C, 55.53; H, 4.01%. Found: C, 55.48; H, 4.19%.

### Results and discussion

### Synthesis and structures

The dppb series ligands used in this study were prepared from coupled reactions of potassium diphenylphosphine and 1,2-difluorobenzene derivatives, or chlorodiphenyl phosphine and methoxy substituted 1,2-dibromobenzene with the aid of n-BuLi, in a mixed solvent under N2 atmosphere. According to the work of Ford,<sup>26</sup> CuI complexes exhibit various coordination motifs depending on the chemical structure of the coordinating ligand as well as the molar ratio of the ligand and CuI. Choosing the stoichiometry with a molar ratio of 1:1:2 results in a  $[Cu(\mu_2-I)]_2L_4$  (where L stands for a ligand) form with an isolated rhombohedron Cu<sub>2</sub>I<sub>2</sub> core. Consequently, three new dinuclear Cu(I) iodide complexes  $[Cu(\mu_2-I)Ph$ dppb]<sub>2</sub>, [Cu(µ<sub>2</sub>-I)Pr-dppb]<sub>2</sub>, [Cu(µ<sub>2</sub>-I)OMe-dppb]<sub>2</sub>, and a reference complex  $[Cu(\mu_2-I)dppb]_2$  were prepared by the reaction of CuI with one equivalent of dppb series ligands in toluene at room temperature, and purified by recrystallization or vacuum thermal gradient sublimation according to their thermal stability. The characterization of intermediates, ligands, and complexes were established on the basis of <sup>1</sup>H/<sup>31</sup>P NMR, ESI mass spectra, or elemental analysis, which is shown in the experimental section. The three complexes  $[Cu(\mu_2-I)Ph$  $dppb]_2$ ,  $[Cu(\mu_2-I)Pr-dppb]_2$ , and  $[Cu(\mu_2-I)OMe-dppb]_2$  were further characterized by X-ray diffraction for comparison with the reference complex  $[Cu(\mu_2-I)dppb]_2$ , where the single crystals of  $[Cu(\mu_2-I)Ph-dppb]_2$  and  $[Cu(\mu_2-I)OMe-dppb]_2$  were obtained by a diffusion method with dichloromethane and pentane as the solvents, while that of  $[Cu(\mu_2-I)Pr-dppb]_2$  was formed during vacuum thermal sublimation.

The ORTEP diagrams of  $[Cu(\mu_2-I)Ph-dppb]_2$ ,  $[Cu(\mu_2-I)Pr-dppb]_2$ , and  $[Cu(\mu_2-I)OMe-dppb]_2$  are displayed in Fig. 1. Detailed crystal parameters and structure refinements of the three complexes are summarized in Table 1. The comparison on key parameters, *i.e.* Cu–Cu, Cu–P, Cu–I distances, I–Cu–I, Cu–I–Cu, and P–Cu–P angles among  $[Cu(\mu_2-I)Ph-dppb]_2$ ,  $[Cu(\mu_2-I)Pr-dppb]_2$ ,  $Cu(\mu_2-I)OMe-dppb]_2$ , and  $[Cu(\mu_2-I)dppb]_2$ 



**Fig. 1** ORTEP drawings of  $[Cu(\mu_2-I)Ph-dppb]_2$  (top),  $[Cu(\mu_2-I)Pr-dppb]_2$  (middle), and  $[Cu(\mu_2-I)OMe-dppb]_2$  (bottom), respectively, with ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

are listed in Table 2. In all complexes, two Cu(I) ions are bridged by two µ2-I ions to form a dinuclear structure with a four-membered Cu<sub>2</sub>I<sub>2</sub> ring and coordinated by two bidentate P^P ligands additionally; each Cu(1) ion is in a distorted tetrahedral geometry. The Cu-Cu distances are 2.904(3), 2.7745(7), 2.8317(10), and 2.8238(11) Å for [Cu(µ<sub>2</sub>-I)Ph-dppb]<sub>2</sub>,  $[Cu(\mu_2-I)Pr-dppb]_2$ ,  $[Cu(\mu_2-I)OMe-dppb]_2$ , and  $[Cu(\mu_2-I)dppb]_2$ , respectively. Except  $[Cu(\mu_2-I)Ph-dppb]_2$ , all the three complexes have a Cu-Cu distance shorter than those found in dinuclear complexes with isolated P and N ligands (2.872-3.303 Å),<sup>18</sup> but longer than those found in dinuclear complexes with P^N type ligands (2.51-2.63 Å).<sup>27,28</sup> Among the four complexes, it is found that the complex  $[Cu(\mu_2-I)Pr-dppb]_2$  showed a Cu-Cu distance a little shorter than that in the reference complex  $[Cu(\mu_2-I)dppb]_2$ , while the other two complexes showed a Cu–Cu distance longer than that in  $[Cu(\mu_2-I)dppb]_2$ . This phenomenon was also observed when comparing Cu-P distances among the four complexes. The dihedral angle between the Cu(1)–I(1)–Cu(2) and Cu(1)–I(2)–Cu(2) faces are 158.22°, 154.57°, 156.98°, and 156.20° for  $[Cu(\mu_2-I)Ph-dppb]_2$ ,  $[Cu(\mu_2-I)Pr-dppb]_2$ ,  $[Cu(\mu_2-I)OMe-dppb]_2$  and  $[Cu(\mu_2-I)dppb]_2$ , respectively. The crystallography study indicates that a compact structure was obtained by attaching a pyrrolyl group on the dppb ligand.

#### Photophysical properties

Fig. 2 shows the UV-vis absorption spectra of  $[Cu(\mu_2-I)Ph-dppb]_2$ ,  $[Cu(\mu_2-I)Pr-dppb]_2$ ,  $[Cu(\mu_2-I)OMe-dppb]_2$  and  $[Cu(\mu_2-I)dppb]_2$  in CH<sub>2</sub>Cl<sub>2</sub> solution  $(10^{-5} \text{ M})$  at room temperature. These complexes showed intense absorption bands at 260–290 nm, which are assigned to the  $\pi$ - $\pi$ \* transition of the bisphosphine ligand (Fig. S1†). All the complexes showed broad shoulders around 330 nm and weak ones around 390 nm. These absorption shoulders can be attributed to the electronic transition of the Cu(I) chromophore.<sup>17</sup>

As anticipated, the band gap  $(E_g)$  of this type of complexes changed as an electron-rich or electron-poor group was attached on the dppb ligand. For example, the complex  $[Cu(\mu_2-I)OMe-dppb]_2$  having two electron-donating methoxy groups showed the maximum  $E_g$  of 3.13 eV (396 nm), while the complex  $[Cu(\mu_2-I)Ph-dppb]_2$  having a phenyl group showed the minimum  $E_g$  of 2.84 eV (437 nm). This is consistent with the Hartree–Fock calculation on  $[Cu(\mu_2-I)dppb]_2$ : the electron density in the HOMO is distributed over the copper and iodine atoms, while that in the LUMO is localized on the dppb ligands. Attaching an electron-rich or electron-poor group on the ligand results in a lower or higher LUMO energy level and consequently enlarged or decreased  $E_g$ , respectively.

Fig. 3 shows the photoluminescence spectra of the four complexes in the solid state as microcrystallites (Fig. S2<sup>+</sup>) at room temperature. The maximum emission peaks  $(\lambda_{max})$  for  $[Cu(\mu_2-I)Ph-dppb]_2$ ,  $[Cu(\mu_2-I)Pr-dppb]_2$ ,  $[Cu(\mu_2-I)OMe-dppb]_2$ , and  $[Cu(\mu_2-I)dppb]_2$  are at 535, 528, 484, and 512 nm, respectively, which is consistent with the order of their band gap. Obviously, the luminescent excited state is affected by the electronic properties of the substituted group (i.e. methoxy, pyrrolyl, or phenyl) on the centered-benzene. The complex  $[Cu(\mu_2-I)Ph-dppb]_2$  modified by a phenyl group, which expands the  $\pi$ -conjugation of the ligand hence to decrease the LUMO energy of the complex, showed a low transition energy with the most red-shifted  $\lambda_{max}$ . While the complex [Cu( $\mu_2$ -I)OMe-dppb]<sub>2</sub> showed a significant blue-shifted  $\lambda_{max}$  since two electron-donating methoxy groups were attached on the centered-benzene. Interestingly, the complex  $[Cu(\mu_2-I)Pr$ dppb]<sub>2</sub> having an electron-donating pyrrolyl group showed a slightly red-shifted  $\lambda_{max}$ , which may be due to an enhanced electron-conjugation of the ligand. All the complexes have excited state lifetimes on the microsecond scale, implying that these emissions may arise from triplet excited states (Table 3).

As the temperature is decreased to 77 K, all of the complexes showed a similar emission spectrum to that observed at room temperature and less than 15 nm shifted maximum CrystEngComm

Table 1	Summary of X-ray	data collection a	and refinement	of [Cu(µ2-I)Ph-	·dppb] <sub>2</sub> , [Cι	u(μ <sub>2</sub> -I)Pr-dppb] <sub>2</sub> ,	and [Cu(µ2-I)C	)Me-dppb] <sub>2</sub>
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	$[Cu(\mu_2-I)Ph-dppb]_2$	$[Cu(\mu_2\text{-}I)Pr\text{-}dppb]_2$	$[Cu(\mu_2-I)OMe-dppb]_2$
Formula	$C_{72}H_{56}Cu_2I_2P_4$	$C_{68}H_{54}Cu_2I_2N_2P_4$	$C_{64}H_{56}Cu_2I_2O_4P_4$
Mw	1510.85	1404.00	1648.63
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	C121	$Par{1}$	C12/c1
a (Å)	24.271(2)	13.6302(6)	19.5414(11)
b (Å)	14.1584(14)	13.8186(5)	14.5730(6)
c (Å)	9.6410(9)	18.0831(7)	26.9535(14)
$\alpha(\circ)$	90	110.055(3)	90.00
β(Θ)	98.970(9)	104.744(3)	113.268(7)
y (°)	90	97.913(3)	90.00
Volume (Å <sup>3</sup> )	3272.5(5)	2997.7(2)	7051.5(6)
Z	2	2	4
T (K)	180.01(10)	100.1(2)	180.01(10)
$D_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.533	1.5553	1.553
F(000)	1508	1400.9	3288
$\theta$ range (°)	2.927-25.022	3.2040-28.4070	3.17-26.02
Index range	$-27 \le h \le 28$	$-15 \le h \le 18$	$-17 \le h \le 24$
8	$-14 \le k \le 17$	$-17 \leq k \leq 12$	$-14 \le k \le 17$
	$-16 \le l \le 16$	$-22 \le l \le 22$	$-33 \le l \le 33$
GOF on $F^2$	1.034	1.074	1.023
$R\left[I>2\sigma(I)\right]$	0.0558	0.0367	0.0429
R (all data)	0.0828	0.0598	0.0681

 $\label{eq:comparison} \textbf{Table 2} \quad \textbf{The comparison on key structure parameters of } [Cu(\mu_2-l)Ph-dppb]_2, \\ [Cu(\mu_2-l)Pr-dppb]_2, \\ [Cu(\mu_2-l)OMe-dppb]_2, and \\ [Cu(\mu_2-l)dppb]_2, \\ [Cu(\mu_2-l)Ph-dppb]_2, \\ [Cu(\mu_2-l)Ph-$ 

	$[Cu(\mu_2\text{-}I)Ph\text{-}dppb]_2$	$[Cu(\mu_2-I)Pr-dppb]_2$	$[Cu(\mu_2-I)OMe-dppb]_2$	$[Cu(\mu_2-I)dppb]_2$
Cu1-Cu2	2.904(3)	2.7745(7)	2.8317(10)	2.8238(11)
Cu1-I1	2.6039(17)	2.6540(5)	2.6578(6)	2.6786(10)
Cu1-I2	2.6558(18)	2.6044(6)	2.6086(6)	2.6197(9)
Cu1-P1	2.291(4)	2.2793(11)	2.2875(12)	2.281(2)
Cu1-P2	2.283(4)	2.2772(10)	2.2805(12)	2.277(3)
Cu2-I1	2.6039(17)	2.6042(6)	2.6578(6)	2.5710(10)
Cu2–I2	2.6044(6)	2.6275(5)	2.6086(6)	2.6504(10)
Cu2-P3	2.291(4)	2.2716(11)	2.2875(12)	2.273(2)
Cu2-P4	2.283(4)	2.2564(10)	2.2805(12)	2.267(2)
P1-Cu1-P2	86.03(14)	87.38(4)	86.85(4)	89.31(8)
P1-Cu1-I1	114.40(11)	110.10(3)	118.43(3)	104.27(6)
I1-Cu1-I2	109.94(6)	111.325(19)	111.43(2)	110.08(3)
I2-Cu1-P2	105.19(11)	121.09(3)	107.50(3)	119.49(6)
P3-Cu2-P4	86.03(14)	90.67(4)	86.85(4)	86.97(8)
P3-Cu2-I1	123.47	121.44(3)	121.00(4)	118.19(7)
I1-Cu2-I2	109.94(6)	112.186(19)	111.43(2)	112.53(3)
I2-Cu2-P4	115.96(11)	112.04(3)	108.99(4)	109.64(6)



Fig. 2 The UV-vis spectra of complexes  $[Cu(\mu_2-I)Ph-dppb]_2$ ,  $[Cu(\mu_2-I)Pr-dppb]_2$ ,  $[Cu(\mu_2-I)OMe-dppb]_2$ , and  $[Cu(\mu_2-I)dppb]_2$  in CH\_2Cl<sub>2</sub> solution (10<sup>-5</sup> M) at room temperature.

emission wavelength. Obvious bathochromic shifts were observed in  $[Cu(\mu_2-I)Pr-dppb]_2$  and  $[Cu(\mu_2-I)OMe-dppb]_2$ . This phenomenon may be attributed to the suppression of thermally activated delayed fluorescence (TADF) and is usually accompanied by a marked increase in emission lifetime.<sup>29</sup> As expected, the decay lifetimes of these complexes increased dramatically from less than 5 µs at room temperature to more than 100 µs at 77 K. Based on the aforementioned photophysical study, as well as previous work in the literature,<sup>10,17</sup> excited states of these complexes can be explained by the assumption that the singlet and triplet metal/halide to ligand charge transfer (MLCT/XLCT) excited states are in thermal equilibrium.

All the four complexes showed strong emission in the solid state at room temperature with high PLQYs of 0.72, 0.90, 0.53, and 0.80 for  $[Cu(\mu_2-I)Ph-dppb]_2$ ,  $[Cu(\mu_2-I)Pr-dppb]_2$ ,



Fig. 3 PL spectra of complexes  $[Cu(\mu_2-I)Ph-dppb]_2$ ,  $[Cu(\mu_2-I)Pr-dppb]_2$ ,  $[Cu(\mu_2-I)OMe-dppb]_2$ , and  $[Cu(\mu_2-I)dppb]_2$  in solid state at room temperature.

 $[Cu(\mu_2-I)OMe-dppb]_2$ , and  $[Cu(\mu_2-I)dppb]_2$ , respectively. The high PLQY may arise from the bulky bisphosphine ligand, which can tightly wrap the Cu center and effectively suppress the flattening distortion of the Cu(1) complex in the excited state, leading to less non-radiative transition and hence high PLQY. To correlate the PLQY and molecular structure, we analyzed the single crystal data of the four complexes thoroughly, and found that the PLQY may depend on the Cu-Cu distance, i.e. the compact degree of the copper center. For example, the Cu–Cu distances in  $[Cu(\mu_2-I)Pr-dppb]_2$ ,  $[Cu(\mu_2-I)Pr-dppb]_2$ I)dppb]<sub>2</sub>, and  $[Cu(\mu_2-I)Ph-dppb]_2$  are 2.7745(7) 2.8238(11) and 2.904(3) respectively, which is in a reverse order with respect to their PLQYs. Though the complex  $[Cu(\mu_2-I)OMe-dppb]_2$  is out of the line, this may be attributed to a different purification method, i.e. recrystallization, in which it is more difficult to eliminate the negative effect of impurity and solvent as compared with thermal gradient sublimation.

#### Thermal properties

To evaluate whether and how these complexes could be utilized in OLEDs, the four complexes were investigated by thermo gravimetric analysis (TGA, Fig. 4a) and differential scanning calorimetry (DSC, Fig. 4b). TGA measurement reveals high decomposition temperature values ( $T_d$ , corresponding to 5% weight loss) of 388, 396, and 387 °C for [Cu( $\mu_2$ -I)dppb]<sub>2</sub>, [Cu( $\mu_2$ -I)Ph-dppb]<sub>2</sub>, and [Cu( $\mu_2$ -I)Pr-dppb]<sub>2</sub>, respectively, which are higher than 373 °C for 4,4'-*N*,*N*'dicarbazole-biphenyl (CBP, a widely used host material in



Fig. 4 (a) TGA and (b) DSC thermograms of  $[Cu(\mu_2-I)dppb]_2$ ,  $[Cu(\mu_2-I)Ph-dppb]_2$ ,  $[Cu(\mu_2-I)Pr-dppb]_2$ , and  $[Cu(\mu_2-I)OMe-dppb]_2$  recorded at a heating rate of 5 °C min<sup>-1</sup>.

OLEDs).<sup>30</sup> While the complex  $[Cu(\mu_2-I)OMe-dppb]_2$  showed a decomposition temperature of 174 °C during TGA measurement, which is a disadvantage since this compound emits an efficient and nice blue emission in solid state. During the DSC measurement, it is found that the glass-transition temperatures  $(T_g)$  are 177.1 and 178.5 °C for  $[Cu(\mu_2-I)Ph-dppb]_2$ and  $[Cu(\mu_2-I)Pr-dppb]_2$ , respectively, while that for  $[Cu(\mu_2-I)Pr-dppb]_2$ I)OMe-dppb]<sub>2</sub> was not measured due to its poor thermostability. As for the reference complex  $[Cu(\mu_2-I)dppb]_2$ , no  $T_g$  was observed even at the third ramp heating, which arises from an easy crystallization property that can be observed in the heat flow curve. Such good thermal properties provide advantages for  $[Cu(\mu_2-I)Ph-dppb]_2$  and  $[Cu(\mu_2-I)Pr-dppb]_2$  to be processed in OLEDs using a traditional vacuum thermal deposition technique, as well as may guarantee the stability of the corresponding OLEDs, since it has been reported that the

Table 3 Photophysical and thermal properties of $[Cu(\mu_2-I)Ph-dppb]_2$ , $[Cu(\mu_2-I)Pr-dppb]_2$ , $[Cu(\mu_2-I)OMe-dppb]_2$ , and $[Cu(\mu_2-I)dppb]_2$					
	$[Cu(\mu_2\text{-}I)Ph\text{-}dppb]_2$	[Cu(µ2-I)Pr-dppb]2	[Cu(µ2-I)OMe-dppb]2	[Cu(µ <sub>2</sub> -I)dppb] <sub>2</sub>	
PLQY (%)	72	90	53	80	
$\lambda_{\rm max}$ (nm, 298 K)	535	528	484	512	
$\lambda_{\rm max}$ (nm, 77 K)	536	534	496	507	
Lifetime (µs, 298 K)	3.6/6.7	3.2/1.0	2.6/1.0	4.1/1.7	
Lifetime (µs, 77 K)	191.6	145.8	42.0/101.1	165.74	
$E_{g}$ (eV)	2.84	2.91	3.13	3.01	
$T_{\rm d}$ (°C)	396	387	174	388	
$T_{g}(^{\circ}C)$	177.1	178.5	—	—	

temperature inside an actual OLED can be higher than 86  $^{\circ}\text{C.}^{^{31}}$ 

# Conclusions

Based on 1,2-bis(diphenylphosphino)benzene (dppb), three P^P-type ligands with a methoxy, pyrrolyl, or phenyl group attached on the central benzene ring were designed and synthesized for coordination with CuI. Consequently, three dinuclear Cu(I) complexes with formulae of  $[Cu(\mu_2-I)Ph$ dppb]<sub>2</sub>, [Cu( $\mu_2$ -I)Pr-dppb]<sub>2</sub>, and [Cu( $\mu_2$ -I)OMe-dppb]<sub>2</sub> were obtained and characterized by single crystal X-ray diffraction. Photophysical property comparison of the three complexes and a reference complex  $[Cu(\mu_2-I)dppb]_2$  indicates that all complexes exhibited strong emission in the solid state with maximum PLQY up to 90%, as well as the emission color of this type of complex could be tuned by attaching an electronrich or electron-poor group to the dppb ligand, which arises from a varied LUMO with unchanged HOMO energy levels. Through thermo gravimetric analysis, it is found that complexes  $[Cu(\mu_2-I)Ph-dppb]_2$  and  $[Cu(\mu_2-I)Pr-dppb]_2$  showed excellent thermal stability that can be processed in OLEDs using a traditional vacuum thermal deposition technique. Application of the two complexes in high efficiency non-doped OLEDs is in progress.

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